Pergamon

Geochimica et Cosmochimica Acta, Vol. 64, No. 6, pp. 1029–1041, 2000

0016-7037/00 $20.00 + .00

PII S0016-7037(99)00361-0

Dissolved and particulate carbohydrates in contrasting marine sediments

D. J. BURDIGE,[1,*] A. SKOOG,[2] and K. GARDNER[1]

[1]Department of Ocean, Earth and Atmospheric Sciences, Old Dominion University, Norfolk, VA 23529-0276 USA
[2]Department of Marine Sciences, The University of Connecticut, Groton, CT 06340-6097 USA

(*Received April* 5, 1999; *accepted in revised form September* 13, 1999)

Abstract—Dissolved and particulate carbohydrates were examined in contrasting Chesapeake Bay (estuarine) and mid-Atlantic shelf/slope break (continental margin) sediments. Particulate carbohydrates (PCHOs) represented ~5–9% of the total sediment particulate organic carbon (POC), and PCHO remineralization appeared to be a similar fraction of total sediment carbon oxidation (or C_{ox}). When these results are compared with results from other coastal sediments and a pelagic turbidite, PCHO remineralization (as a percentage of C_{ox}) did not vary by more than a factor of ~2–3 over a 3–4 order of magnitude range in C_{ox} values. The causes of this are not well understood, but may be related to specific effects associated with the remineralization of highly altered organic matter mixtures under aerobic conditions. Dissolved carbohydrates (DCHOs) in these sediment pore waters ranged from ~30 to 400 μM, increased with depth in a manner similar to total DOC, and represented ~10 to 55% of pore water DOC. In Chesapeake Bay sediments this percentage decreased with sediment depth, while in these continental margin sediments it was constant (upper 30 cm). Of the DCHOs in these pore waters ~30 to 50% could be identified as individual aldoses (monomeric neutral sugars), and total aldose yields (individual aldoses as a percentage of total DOC) were higher in these continental margin sediment pore waters (>9%) than they were in the estuarine sediment pore waters (<5%). A comparison of DCHO and PCHO concentrations in these sediments indicates that their concentrations are uncoupled, and that pore water DCHO concentrations are primarily controlled by sediment remineralization processes. Pore water DCHOs appeared to be preferentially found in the high molecular weight (HMW) DOC pool, and likely occur as some of the initial HMW intermediates produced and consumed during sediment POC remineralization. These results also support past suggestions about the differing controls on carbon remineralization processes in continental margin versus estuarine sediments.

1. INTRODUCTION

Carbohydrates are some of the major biochemicals produced by marine organisms, and also represent a significant component of the pools of non-living dissolved and particulate organic matter in the water column (Mopper et al., 1980; Benner et al., 1992; Pakulski and Benner, 1994; McCarthy et al., 1996; Borch and Kirchman, 1997; Skoog and Benner, 1998). In marine sediments, particulate carbohydrates (PCHOs) have been shown to account for 10–20% of the total sediment particulate organic carbon (POC), and a similar percentage of the sediment POC undergoing remineralization (Hamilton and Hedges, 1988; Cowie and Hedges, 1992; Cowie et al., 1992; Cowie et al., 1995; Martens et al., 1992).

In contrast, little is known about dissolved carbohydrate (DCHO) concentrations and cycling in marine sediment pore waters (Lyons et al., 1979; Boschker et al., 1995; Arnosti and Holmer, 1999). A better understanding of the cycling of DCHOs in sediment pore waters is important for several reasons. The extracellular degradation of macromolecular POC to a range of dissolved organic carbon (DOC) intermediates is an important part of sediment carbon remineralization (Henrichs, 1992; Burdige and Gardner, 1998), and dissolved carbohydrates are known to be produced and consumed as intermediates during remineralization (Arnosti et al., 1994; Boschker et al., 1995; Arnosti and Holmer, 1999). However, many of the details of these sediment remineralization reactions are not well understood. At the same time, several models for sediment carbon preservation suggest that pore water DOC compounds may play a role in this process (Nissenbaum et al., 1971; Tissot and Welte, 1978; Krom and Westrich, 1981; Hedges, 1988; Mayer, 1994a; Mayer, 1994b; Hedges and Kiel, 1995). Furthermore, despite the biological lability of carbohydrates, some fraction of the chemically-recognizable carbohydrates deposited in marine sediments escape remineralization and are "preserved" on time scales of years to decades (in coastal sediments; see references above), to >100 kyr (in the oxidized portion of pelagic turbidites; Cowie et al., 1995), to >1 million y (e.g., in pelagic sediments at sediment depths greater than 100 m; Whelan and Emeis, 1992; also see discussions in Sinneghe Damsté et al., 1998). Thus a better understanding of pore water carbohydrate cycling in sediments may also help understand carbohydrate (as well as total carbon) preservation in sediments.

In this manuscript we present the results of studies of dissolved and particulate carbohydrates in contrasting estuarine and continental margin marine sediments. With these results we are able to examine on several different levels the role of carbohydrates in sediment organic matter remineralization and preservation with varying biogeochemical conditions.

* Author to whom correspondence should be addressed (dburdige@odu.edu).

Table 1. Site characteristics.

Station*	Water depth (m)	Bottom water salinity (psu)**	Sfc. Sediment POC (mg C/gdw)	Avg. PCHO (% of POC)	C_{OX}*** (mol C/m^2/yr)
Chesapeake Bay					
N3	10	<0.1–10	~20–40[a]	8.3 ± 1.9	0.8 ± 0.4
M3	15	10–20	>30[b]	9.2 ± 1.8	7.2 ± 0.7
S3	12	20–30	~5[b]	6.2 ± 0.7	4.4 ± 1.0
Average for all Chesapeake Bay stations				7.8 ± 2.0	
Mid-Atlantic shelf/slope break					
WC4	390	35	~20[c]	4.9 ± 0.8	1.7 ± 1.1
WC7	775	35	~20[c]	5.5 ± 0.6	0.7 ± 0.3
AI	740	35	~12[c]	4.9 ± 0.6	0.9 ± 0.3
Average for all shelf/slope break stations				5.1 ± 0.7	

* See map in Burdige and Gardner (1998) for station locations.

** For the Chesapeake Bay sites, these are general seasonal ranges.

*** Depth-integrated sediment carbon oxidation rates. Values for stations S3 and M3 are based on integrated annual averages of measured ΣCO_2 benthic fluxes made during temporal studies at these sites (time period 3/95–10/96; data in Burdige and Zheng, 1998). The value at sta. WC4 is based on a combination of ΣCO_2 benthic flux measurements (made in 7/94 and 8/97) and modeling of ΣCO_2 pore water profiles (collected in 7/94, 7/95, 8/96 and 8/97), using procedures described in Burdige and Homstead (1994). The values at sta. N3, WC7 and AI were also determined by modeling pore water ΣCO_2 profiles (sta. WC7 and AI cores collected on the four dates listed above for sta. WC4).

[a] From Burdige et al. (1995). Also see Fig. 1

[b] From Burdige and Homstead (1994). Also see Fig. 1.

[c] See Figure 1.

2. MATERIALS AND METHODS

2.1. Field Sites

Studies were carried out at three contrasting estuarine sites in Chesapeake Bay, and three sites along the shelf/slope break of the mid-Atlantic continental margin, approx. 100 miles southeast of the mouth of Delaware Bay (see map in Burdige and Gardner, 1998). Geochemical characteristics of these sediments are summarized below and in Table 1; they are also described in more detail in previous publications (Burdige and Homstead, 1994; Ferdelman, 1994; Burdige et al., 1995; Cowan and Boynton, 1996; Skrabal et al., 1997; Burdige and Gardner, 1998; Burdige and Zheng, 1998; Marvin-DiPasquale and Capone, 1998).

The sediments at sta. M3 in the mid-Chesapeake Bay are fine-grained, sulfidic sediments where sulfate reduction dominates organic matter remineralization. During most of the year bioturbation is virtually absent in these sediments, although a few bivalve spat and small polychaete worms inhabit the upper ~5 cm of sediment in the early spring (Kemp et al., 1990). The sediments at sta. S3 in the southern Bay are silty sands, and are bioturbated and bioirrigated by large tube worms and other benthic macrofauna (Schaffner, 1990). The sediments at sta. N3 in the northern Bay are clay dominated and iron-rich, and contain a diverse community of mixed polychaetes and bivalves. Organic matter in the surface sediments at sta. N3 appears to be largely terrestrially-derived, based on carbon isotope values (J. Cornwell unpub. data cited in Marvin-DiPasquale and Capone, 1998).

The sediments on the mid-Atlantic shelf/slope break (stations WC4, WC7 and AI) are grey/green silty clays, and based on radiochemical measurements some bioturbation ($D_B \sim 1.5$–5 cm^2/y) occurs in the upper 20–30 cm of these sediments (Ferdelman, 1994). Pore water profiles suggest that both sub-oxic and anoxic organic matter remineralization processes occur in these sediments.

2.2. Sample Collection

All sediments were collected by box core and sub-cored for further analysis. Sub-cores were processed under an inert (N_2) atmosphere and pore waters extracted by centrifugation at all stations except Chesapeake Bay sta. S3. At this station pore waters were obtained from sub-cores using a modified pressurized core barrel technique (Jahnke, 1988), to avoid artifacts associated with the collection of pore water dissolved organic matter samples via centrifugation from heavily bioturbated sediments (Martin and McCorkle, 1993; Burdige and Gardner, 1998; Alperin et al., 1999). Both pore water collection techniques are described in detail elsewhere (Burdige and Gardner, 1998; Burdige and Zheng, 1998).

All collected pore waters were filtered through 0.45 μm Gelman Nylon Acrodisc filters without exposure to ambient air, and aliquots divided into different storage vessels for later analysis. Samples for DCHO and total DOC analyses were filtered into separate 8 ml cleaned glass vials sealed with Teflon-lined silicone septa, acidified to pH 2 with 6 N HCl, and then quick frozen and stored frozen until analysis. All glass and plasticware used in this study were cleaned as described in Burdige and Homstead (1994).

2.3. Dissolved and Solid Phase Analyses

Dissolved organic carbon was determined by high temperature catalytic oxidation using a Shimadzu TOC-5000 total carbon analyzer (Burdige and Homstead, 1994; Burdige and Gardner, 1998). Solid phase POC and PCHOs were determined on frozen sediment samples collected during previous studies at these sites (Burdige and Homstead, 1994; Burdige and Gardner, 1998). Frozen samples were thawed, dried and ground in a mortar and pestle, fumed with concentrated HCl to remove carbonates, and finally redried and reground before being analyzed for POC using a Carlo Erba NCS elemental analyzer (Verardo et al., 1990).

2.4. Carbohydrate Analyses

Bulk carbohydrate concentrations in sediments and in pore waters were determined using the MBTH procedure of Johnson et al. (1981) as modified by Pakulski and Benner (1992). In this technique, polysaccharides (or other monomeric sugars contained in polymeric natural substances) are first hydrolyzed to individual monosaccharides (aldoses) and then oxidized to alditols. The terminal alditol glycol groups are next oxidized to formaldehyde, which was finally quantified spectrophotometrically after reaction with MBTH (3–methyly–2–benzothiazolinone hydrazone hydrochloride).

In the analytical procedures we used here we also chose not to preconcentrate pore water samples before analysis (Pakulski and Benner, 1992), given the high concentrations of DCHOs in pore waters as compared to the water column. Thus in the initial step of the analysis of pore water DCHOs, concentrated sulfuric acid was simply added to pore water samples to make them 1.2 M in H_2SO_4, followed by hydrolysis at 100°C for 3 h. This modification also eliminates the 2 h

Table 2. Recoveries of standard monomeric sugars and polysaccharides.

Compound	Recovery (%)*	PB recovery (%)**		Recovery ratio***
Monomeric sugars[a]				
Xylose	61 ± 6	87		0.7
Glucosamine	104 ± 4	74		1.4
Glucuronic acid	74 ± 5	75		1.0
Polysaccharides[b]				
Raffinose	85 ± 7	95		0.9
Stachyose	81 ± 9	89		0.9
			Mean	0.96

* Based on total carbohydrate determinations using the MBTH method.

** Recoveries reported by Pakulski and Benner (1992) for 10 μM standard solutions.

*** The ratio of our recovery to that reported by Pakulski and Benner (1992).

[a] Based on triplicate analyses of 5 μM and 40 μM standard solutions.

[b] Based on triplicate analyses of 3, 5 and 10–30 μM standard solutions.

room temperature pretreatment of freeze-dried samples in 12 M H_2SO_4 prior to their subsequent 10-fold dilution and high temperature hydrolysis. Although this concentrated sulfuric acid pretreatment has been reported to yield slightly higher carbohydrate recoveries (Pakulski and Benner, 1992; Skoog and Benner, 1998), our recoveries of standard carbohydrates (Table 2) were similar to those reported by Pakulski and Benner (1992). Replicate analyses of sediment samples yielded results that agreed to within ±12% (n = 17 individual samples run in duplicate or triplicate).

All carbohydrate concentrations reported here were based on standard curves constructed from glucose standards hydrolyzed and analyzed along with samples, yielding total carbohydrate concentrations that are "glucose equivalent" concentrations. Glucose equivalent concentrations were multiplied by 6 to express concentrations on a per-mole-carbon-basis, since each glucose molecule contains 6 carbon atoms (see Pakulski and Benner, 1992, for additional details).

A selected number of pore water samples were analyzed for some dissolved aldoses by sulfuric acid hydrolysis and high performance anion exchange chromatography with pulsed ampometric detection (HPAEC-PAD; Skoog and Benner, 1998). This procedure separates and quantifies seven individual aldoses (fucose, rhamnose, arabinose, galactose, glucose, mannose and xylose).

3. RESULTS

3.1. Particulate Carbohydrates

Concentrations of sediment PCHOs ranged from ~0.3 to 4 mg C/gdw (see Fig. 1 and a complete tabulation of this data in the Appendix). At all sites PCHO concentrations generally followed POC concentrations and PCHOs were ~5–9% of the sediment POC (Table 1). Relative PCHO concentrations were slightly higher in the estuarine Chesapeake Bay sediments (~6–9%; average value for all sites = 7.8 ± 2.0%) than they were in the mid-Atlantic shelf/slope break sediments (average value = 5.1 ± 0.7%). These two averages are statistically different (two sample t-test, $p < 0.001$). The absolute and relative concentrations of PCHOs observed here are similar to values reported in other coastal marine and continental margin sediments (Cowie and Hedges, 1984; Steinberg et al., 1987; Hamilton and Hedges, 1988; Cowie et al., 1992; Martens et al., 1992).

At all sites except sta. N3 in the northern Chesapeake Bay relative PCHO concentrations were essentially constant with depth. At this site there was an apparent increase with depth in the relative concentration of PCHOs, although this trend was likely related to an increase with depth in absolute PCHO concentrations. The causes of this are not well understood. They may be related to the occurrence of non-steady state diagenetic processes in these sta. N3 sediments that result from, e.g., recent temporal changes in sediment organic matter deposition. Unfortunately, we are unable to further examine such possibilities with our existing data.

3.2. Dissolved Carbohydrates

Concentrations of DCHOs in these sediment pore waters ranged from ~30 to 400 μM, and generally increased with depth in a manner similar to total DOC (Figs. 2 and 3). Dissolved carbohydrates represented between 5 and 30% of the total DOC in sediment pore waters, although one core from sta. AI on the shelf/slope break had much higher relative DCHO concentrations (~50–60%) than all of the other shelf/slope break cores. Relative DCHO concentrations were also generally lower (~5–15%) in the Chesapeake Bay sediments than they were in the shelf/slope break sediments (~20–30%). In all offshore shelf/slope break sediments, relative DCHO concentrations were essentially constant with depth, while in the Chesapeake Bay sediments (particularly sta. M3), relative DCHO concentrations decreased with depth (Figs. 2 and 4).

Concentrations of individual aldoses in selected pore water samples are reported in Table 3. In these samples ~30 to 50% of the total DCHOs could be identified as individual aldoses (Table 4). Dissolved glucose was the predominant aldose (28%), with the following order of abundance for the remaining aldoses: xylose (16%); fucose, rhamnose and galactose (each average value between 12 and 14%); mannose (10%); arabinose (7%). Total aldose yields (total individual aldose concentrations as a % of DOC) were higher in the shelf/slope break pore waters (>9%) than they were in the estuarine Chesapeake Bay pore waters (less than ~5% in all estuarine samples and less than 3% in all but one of these samples).

4. DISCUSSION

4.1. The Role of PCHO Remineralization in Sediment POC Remineralization

The near-constant relative PCHO concentrations in these sediments suggest that there is no significant selective preservation or utilization of carbohydrates as compared to total sediment POC during the early diagenesis of these Chesapeake Bay and shelf/slope break sediments. As a result, these relative concentrations (~5–10%; see Table 1) also correspond approximately to the fraction of sediment POC remineralization (or C_{ox}) accounted for by PCHO remineralization. In Figure 5 our results are compared with similar results from other coastal sediments. In the bioturbated sediments of Dabob Bay (Cowie and Hedges, 1992) PCHO remineralization accounts for a percentage of C_{OX} that is similar to that seen in these other nearshore sediments. This percentage is slightly higher (~15%)

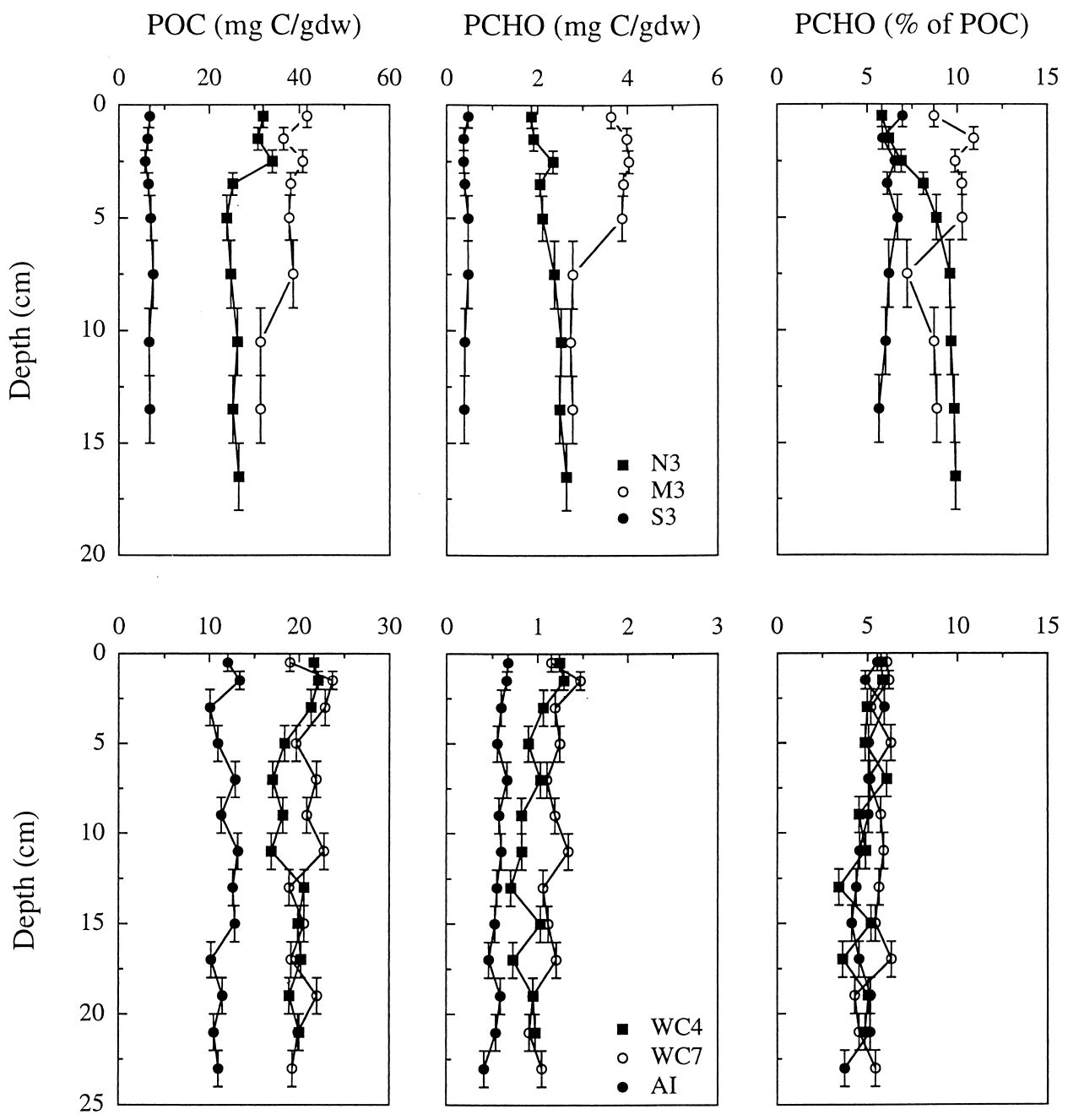

Fig. 1. Depth profiles of solid phase particulate organic carbon (POC), particulate carbohydrates (PCHOs), and relative PCHO concentrations (PCHO as a % of POC), in the sediments at: [upper panels] sta. S3 in southern Chesapeake Bay (●), sta. M3 in the mid-Chesapeake Bay (○) and sta. N3 in the northern Chesapeake Bay (■); [lower panels] mid-Atlantic shelf/slope break stations WC4 (■), WC7 (○) and AI (●). For the Chesapeake Bay profiles, the values shown here are averages based on cores collected at these stations on three different sampling dates (see the Appendix for sample dates and the complete data sets). These POC data are from Burdige and Homstead (1994) and Burdige et al. (1995). For the shelf/slope break profiles, all cores were collected in 7/94 (cruise CH X). These data are also tabulated in the Appendix.

in the anoxic sediments of Cape Lookout Bight (Martens et al., 1992) and Saanich Inlet (Hamilton and Hedges, 1988). However, given the uncertainties in all of these rate estimates, these results suggest that carbohydrate remineralization is a near-constant fraction of total carbon remineralization in all of these coastal and margin sediments (also see the best-fit line through this data in Fig. 5).

For further comparison, these results can be compared with those obtained in studies of the post-depositional, oxic remineralization (or "burn-down") of organic matter in a pelagic

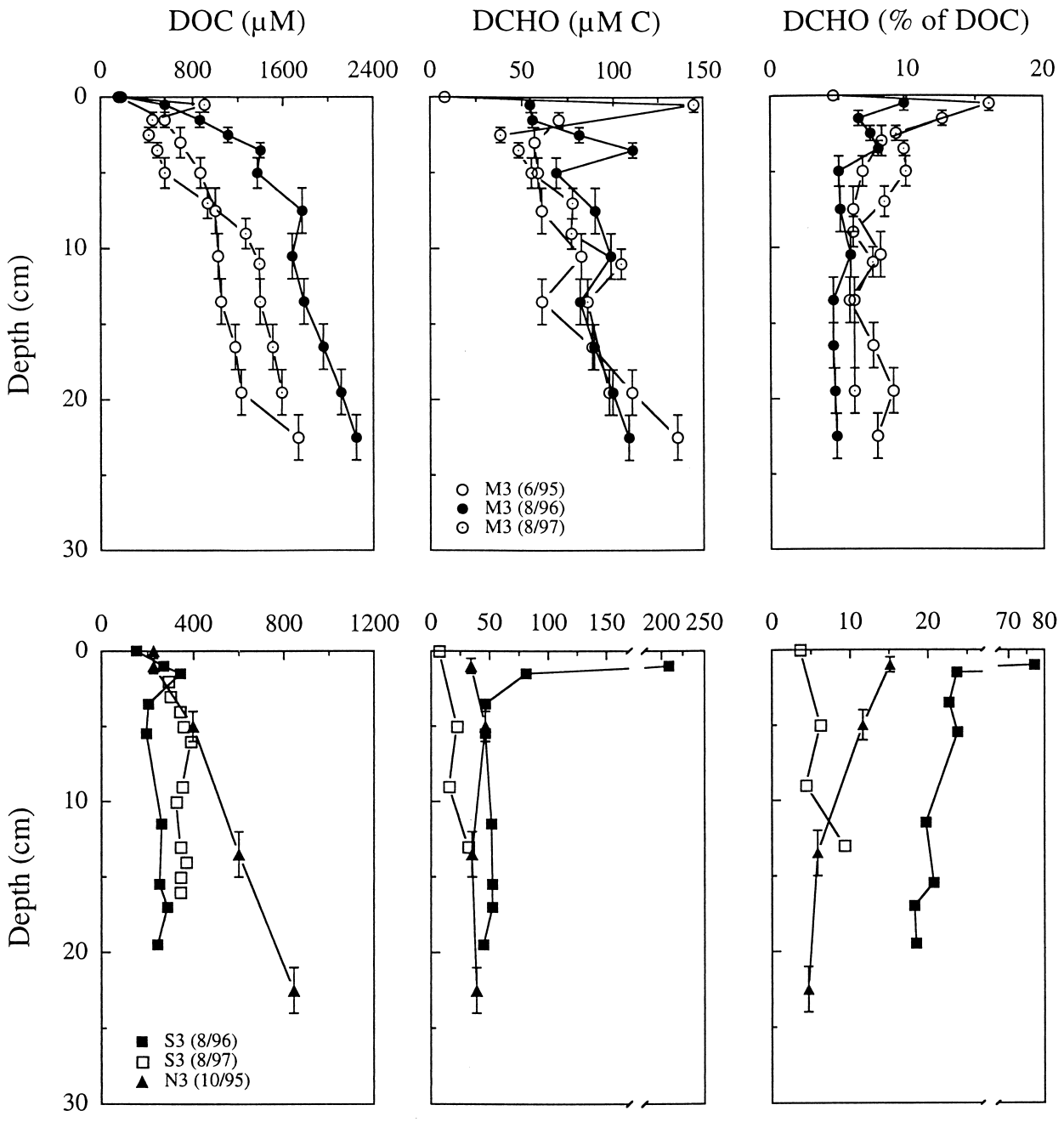

Fig. 2. Pore water depth profiles of DOC, dissolved carbohydrates (DCHO), and relative DCHO concentrations (DCHO as a % of DOC) in Chesapeake Bay sediments. Upper panels: cores collected at sta. M3 in 7/95 (CH XIV; ○), 8/96 (CH XVII; ●) and 8/97 (CH XIX; ⊙). Lower panels: cores collected at sta. N3 in 10/95 (CH XV; ▲), and sta. S3 in 8/96 (CH XVII; ■) and 8/97 (CH XIX; □).

turbidite on the Madeira Abyssal Plain (the MAP-f turbidite, deposited in a water depth of 5,400 m; Cowie et al., 1995). Here carbohydrate remineralization also accounted for a percentage of POC remineralization (5–6%) that is similar to that observed in coastal and continental margin sediments. However, a rough estimate of the carbon oxidation rate in this turbidite when it was diagenetically active (ca. 140 kyr BP) suggests that it was 10–100 times smaller than the lowest C_{ox} value in Fig. 5 (also see Wilson et al., 1985, for similar carbon oxidation rates calculated with a pore water diffusion-reaction model for other nearby turbidite systems currently undergoing active, oxic burn-down diagenesis).

Other workers have also noted the lack of selective carbohydrates remineralization in several of these same coastal sediments (Sannich Inlet and Dabob Bay; Cowie and Hedges, 1984; Hamilton and Hedges, 1988; Cowie et al., 1992). At the

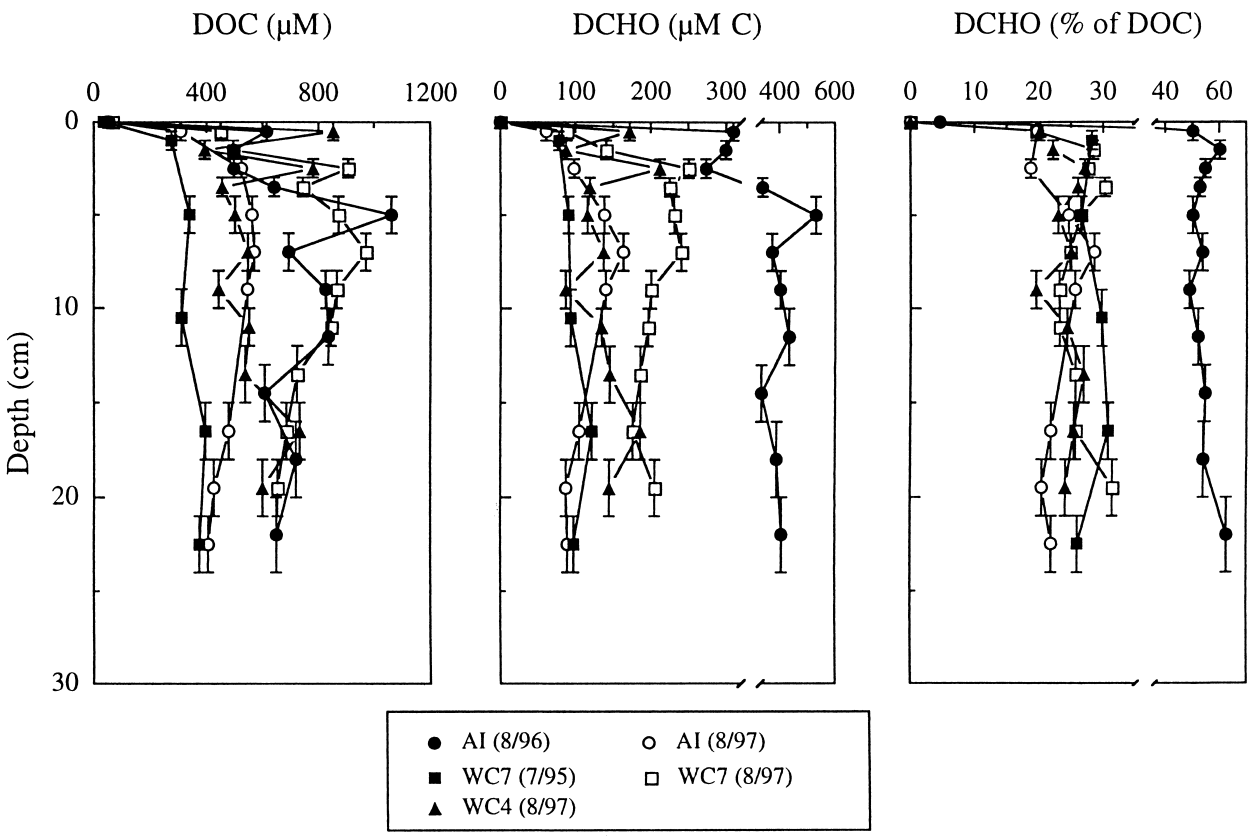

Fig. 3. Pore water depth profiles of DOC, dissolved carbohydrates (DCHO), and relative DCHO concentrations (DCHO as a % of DOC) in the shelf/slope break sediments. Cores were collected in 7/95 (CH XIV; sta. WC7 = ■), 8/96 (CH XVII; sta. AI = ●) and 8/97 (CH XIX; sta. WC4 = ▲, WC7 = □ and AI = ○).

same time though, the continual diagenesis of organic matter also fractionates this material by preferentially consuming more reactive components over those that are more refractory. Therefore as organic matter is diagenetically altered, its bulk reactivity decreases (Middelburg, 1989; Burdige, 1991) and its chemical composition changes (Lee and Wakeham, 1988; Cowie and Hedges, 1994). However, the discussion above suggests that when PCHO remineralization is now examined over a 3–4 order of magnitude range in C_{ox} values, we see that the highly-altered organic matter undergoing remineralization in the MAP f-turbidite has a carbohydrate content similar to (within a factor of ~2–3) the less diagenetically altered and more modern organic matter that is remineralized in coastal and continental margin sediments.

The causes of this observation are not well understood. A possible explanation may stem from the fact that as sediment carbon oxidation rates decrease from Cape Lookout Bight sediments to the MAP f-turbidite, the mode of sediment remineralization changes from being almost exclusively anoxic (sulfate reducing and methanogenic) to being almost completely oxic. During these later stages of diagenesis, some reactive organic matter in sediments may be protected from degradation by either a coating or matrix that can only be decomposed using the O_2 molecule (Cowie et al., 1995; Hedges and Kiel, 1995), or by being tightly bound to mineral surfaces inside of small mesopores on these surfaces (Mayer, 1994a; Mayer, 1994b; Hedges and Kiel, 1995). In this latter case this may occur if the microbial exo-enzymes required to initially degrade this material under anoxic (and perhaps sub-oxic) conditions are too large to enter the mesopores. In contrast, under aerobic conditions degradation of this organic matter may be possible due to the production of activated oxygen species such as the superoxide ion, H_2O_2 or the hydroxyl radical, all of which will be small enough to enter mesopores on sediment surfaces and initiate the remineralization process (Hedges and Kiel, 1995).

4.2. Dissolved Carbohydrates—Comparisons with Other Studies

In the water column, DCHO concentrations are generally less than ~30 μM (e.g., Pakulski and Benner, 1994) and are much lower than those observed here in sediment pore waters (Figs. 2 and 3). In both cases DCHOs represent ~20–30% of the DOC, although the range in relative DCHO concentrations in pore waters is larger than that observed in the water column (particularly when our results are compared with other pore water DCHO studies; see the discussion below for further details).

In contrast to sediment carbohydrate studies, there is little

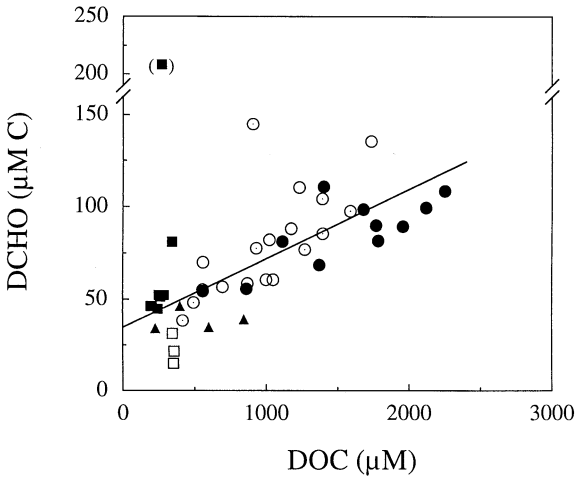

Fig. 4. Absolute concentrations of dissolved carbohydrates (DCHO) versus DOC in Chesapeake Bay sediment pore waters. Also shown is the best-fit straight line through the data (slope = 3.7 ± 0.5%; r = 0.75, $p < 0.001$). Symbols: ○ = sta. M3 (7/95); ● = sta. M3 (8/96); ⊙ = sta. M3 (8/97); ■ = sta. S3 (8/96); □ = st. S3 (8/97); ▲ = sta. N3 (10/95). As discussed in Burdige and Gardner (1998), concentration-concentration plots such as this one should be linear and pass through the origin if DCHOs are a constant fraction of total DOC. Since the best-fit y-intercept here is significantly different than zero (35 ± 6 μM), this implies that relative DCHO concentrations (which are the slopes of lines between the origin and a particular data point or a point on the best-fit line) decrease with increasing total DOC. Since DOC concentrations increase with depth in these sediments (Fig. 2), this then predicts that relative DCHO concentrations decrease with depth in Chesapeake Bay sediments (particularly at sta. M3), consistent with these depth plots.

past work on DCHOs in sediment pore waters that can be used for comparative purposes. Lyons et al. (1979) observed DCHO concentrations in Bermuda carbonate sediments ranging from ~10–400 μM C, values that are comparable to those observed here. In these Bermuda sediments DCHOs generally represent ~10–20% of the DOC. However in some cores values as high as 50% were observed (particularly near the sediment-water interface) and in these sediments relative DCHO concentrations decreased with depth over the upper ~60 cm of the sediments. In the organic-rich, anoxic sediments of Cape Lookout Bight NC, Arnosti and Holmer (1999) observed DCHO concentrations of ~300 μM C near the sediment surface, which increased with depth to ~1200 μM C at 6–8 cm and then decreased slightly with depth to 16 cm (the maximum depth of

Table 4. Individual aldose concentrations compared to total DOC concentrations in selected pore water samples.

Station	Depth (cm)	Total aldoses (TA; μM)	DOC (μM)	TA/DCHO (%)*	TA/DOC (TAY; %)**
M3	1.5	4.11	450.6	54[a]	5.2
M3	16.5	6.18	1509.1	36[b]	2.4
S3	3.0	0.99	298.4	29[c]	1.9
S3	15.0	1.52	342.6	39[c]	2.6
WC7	1.5	6.58	400.1	42[d]	9.5
WC7	11.0	8.96	567.3	40[d]	9.1

All samples were collected in 8/97 on cruise CH XIX.

* Total DCHO concentrations were not determined in these samples due to sample volume limitations. They were therefore estimated with the reported DOC concentrations and relative DCHO concentrations (the DCHO/DOC ratio) shown in Figs. 2 and 3 (see notes a–d below). Here, and in the total aldose yield calculations, aldose concentrations were converted from μM individual aldoses to μM aldose carbon by multiplying these concentrations by 5.75 (assuming, based on the aldose mole percentages listed in Table 3, that the average aldose in these pore water samples had 5.75 carbon atoms).

** Also referred to as total aldose yield (TAY).

[a] Based on a relative DCHO concentration of 9.6% for samples from depths of 2.5–5 cm in this core (see Fig. 2).

[b] Based on a relative DCHO concentration of 6.6% for samples from depths of 11–20 cm in this core (see Fig. 2).

[c] Based on a whole core average relative DCHO concentration of 6.6% (see Fig. 2).

[d] Based on a whole core average relative DCHO concentration of 22.6% (see Fig. 3).

Table 3. Aldose concentrations in selected pore water samples.*

Station	Depth (cm)	Total aldoses (μM)	Fuc (%)	Rha (%)	Ara (%)	Gal (%)	Glu (%)	Man (%)	Xyl (%)
M3	1.5	4.11	14	16	8	14	23	8	17
M3	16.5	6.18	11	15	14	15	21	8	15
S3	3.0	0.99	13	12	4	12	35	8	16
S3	15.0	1.52	10	11	4	11	39	10	15
WC7	1.5	6.58	12	11	6	14	28	10	19
WC7	11.0	8.96	13	13	6	16	22	14	15
Average (all pore water samples)			12	13	7	14	28	10	16
Water column**			8	6	7	11	37	13	11
T-test results***			0.07	0.01	0.64	0.38	0.09	0.02	0.00

* All pore water samples were collected in 8/97 on cruise CH XIX. Total aldose concentrations are μM, while individual aldoses are mole percentages of the total aldose pool. Abbreviations: Fuc = fucose; Rha = rhamnose; Ara = arabinose; Gal = galactose; Glu = glucose; Man = mannose; Xyl = xylose.

** Averages calculated from aldose concentrations in 9 samples (water depths 2–4,000 m) collected at two sites in the equatorial Pacific (data from Skoog and Benner, 1998).

*** These t-test results give the probability that these pore water and water column samples come from populations with the same means. T-tests were done on complete data sets.

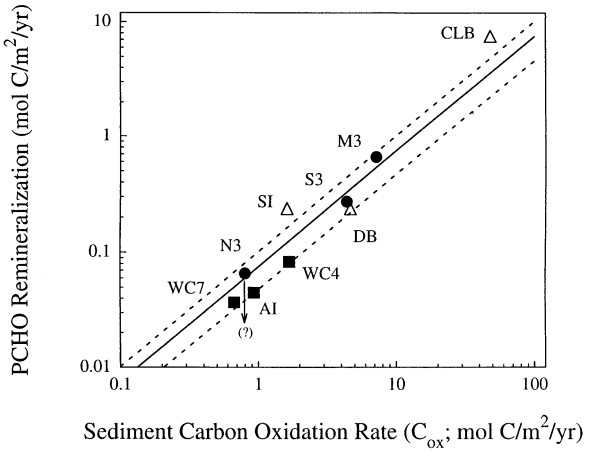

Fig. 5. Carbohydrate remineralization rates versus sediment carbon oxidation rates (C_{ox}) in Chesapeake Bay (●), shelf/slope break (▲) and other coastal (△) sediments. The arrow on the sta. N3 point indicates that if there is selective preservation of carbohydrates in these sediments (see section 3.1) then this value is an upper limit of the carbohydrate remineralization rate. The solid line in this figure is the best-fit of this data to the equation PCHO remin. = b · C_{ox} with a best-fit b value of 7.5 ± 1.3% (the dashed lines represent lines for ±2 standard deviations of this b value). Values of C_{ox} for the Chesapeake Bay and shelf/slope break sediments were taken from Table 1, while carbohydrate remineralization rates were calculated as described in the text using data in this table. Values for the other coastal sites were taken from the literature (CLB = Cape Lookout Bight: Martens et al., 1992; DB = Dabob Bay: Cowie and Hedges, 1984 and Cowie and Hedges, 1992; SI = Sannich Inlet: Hamilton and Hedges, 1988, and Cowie et al., 1992).

the core they examined). Near the sediment surface DCHOs accounted for ~80% of the total DOC, although this value decreased to 40% with depth. Similar trends were seen in our Chesapeake Bay cores, particularly at sta. M3 (see Figs. 2 and 4). However, the magnitude of depth changes in relative DCHO concentrations observed at sta. M3 (from ~10–15% near the sediment surface to ~5–7% below 10 cm) was much smaller than that observed in the Cape Lookout Bight or Bermuda sediments.

As is the case for total DOC, DCHO pore water concentration gradients near the sediment-water interface predict the occurrence of a benthic flux of DCHOs from the sediments to the overlying waters (e.g., see Burdige et al., 1999, and references therein). This DCHO benthic flux has the potential to play an important role in pelagic (bottom water) carbon cycling, depending in part on the biogeochemical reactivity of pore water dissolved carbohydrates in the water column (see discussions in Skoog and Benner, 1998 for further details).

4.2.1. Controls on DCHO concentrations with depth

In several of these sediments (i.e., the estuarine Chesapeake Bay sediments, Cape Lookout Bight sediments, and some Bermuda sediments) relative DCHO concentrations decrease with depth. In contrast, DCHOs appeared to be a relatively constant fraction of the pore water DOC in the shelf/slope break sediments. The factors controlling pore water DOC concentrations (in general) and DCHO concentrations (in particular) at depth are not well understood (see discussions in Burdige and Gardner, 1998). However, an understanding of these controls will be important in further elucidating the role of pore water DOC in sediment carbon preservation (Nissenbaum et al., 1971; Tissot and Welte, 1978; Krom and Westrich, 1981; Hedges, 1988; Mayer, 1994a; Mayer, 1994b; Hedges and Kiel, 1995; Alperin et al., 1999; Burdige et al., 1999). In particular, the occurrence of recognizable dissolved carbohydrates at depth in pore waters may play some role in controlling particulate carbohydrate preservation in sediments, although this depends on the "mechanism(s)" of sediment carbon/carbohydrate preservation, and the forms of these DCHOs in pore waters (e.g., free monomeric aldoses, dissolved polysaccharides, sugars associated with and/or incorporated into "humic" substances). More detailed studies of the processes affecting DOC and DCHO cycling in sediments, and the chemical makeup of pore water DOC will be needed to further examine these possibilities.

4.2.2. Dissolved aldoses

In these pore waters individual aldoses represented ~30–50% of the DCHOs (Table 4). Total aldose concentrations were correlated with DCHO concentrations ($r = 0.98$, $p < 0.05$; plot not shown here), indicating that aldoses are a constant fraction of the pore water DCHOs in these sediments. In the water column, recognizable aldoses represent a similar (~40–50%; Borch and Kirchman, 1997) to significantly lower (~7–20%; Skoog and Benner, 1998) percentage of the MBTH-determined dissolved carbohydrate pool. In addition, the chemical composition of the aldose fraction in pore waters is different from that in the water column, since there is a significant ($p < 0.1$) difference between pore waters and the water column in relative concentrations of 5 out of 7 aldoses (Table 3). These observations suggest that pore water dissolved carbohydrates are different than those in the water column in terms of their composition and presumably structure. Such differences may be related to several factors, including: the importance of non-aldose carbohydrates such as sugar alcohols or amino sugars in these different environments; the sources of carbohydrates to the different environments (e.g., marine vs. terrestrial organic matter); structural changes to individual aldoses incorporated into refractory DOC molecules that may allow them to still be recognized by the MBTH procedure but not by the HPAEC-PAD technique; differences in the mechanisms of carbohydrate remineralization (presumably oxic in the water column vs. predominantly sub-oxic and anoxic in these sediments). More detailed studies of carbohydrate cycling in these different environments will be needed to further examine these suggestions.

4.3. DCHO Concentrations in Estuarine vs. Continental Margin Sediments

In examining the controls on DCHO concentrations in these sediments, we will use the recently proposed pore water DOC size/reactivity (PWSR) model (Burdige and Gardner, 1998). In this model it is assumed that the overall remineralization of sediment POC to inorganic nutrients occurs by the production and consumption of DOC intermediates of increasingly smaller molecular weights. At the same time, the model also assumes

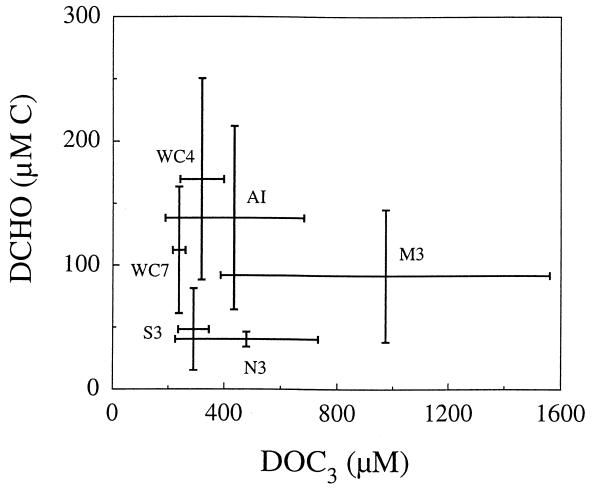

Fig. 6. Pore water dissolved carbohydrate concentrations (DCHO) versus concentration of pore water DOC with a molecular weight less than 3 kDa (DOC_3; data from Burdige and Gardner, 1998). Since the two sets of measurements are not necessarily based on the analysis of both quantities on the same pore water samples, we have chosen here to simply use station averages and ranges.

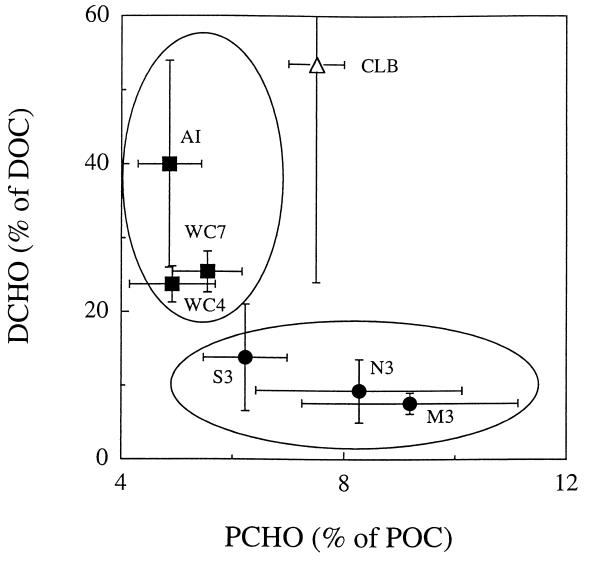

Fig. 7. Average relative concentrations of dissolved carbohydrates (DCHO) versus particulate carbohydrates (PCHO) in Chesapeake Bay (●) and shelf/slope break (■) sediments. Results taken from Table 1 and Figs. 3 and 4. The Cape Lookout Bight (CLB) value is based on data in Arnosti and Holmer (1999) and Martens et al. (1992).

that during POC remineralization there is some small net production of relatively low molecular weight DOC (referred to here as polymeric low molecular weight DOC, or pLMW-DOC). This pLMW-DOC is proposed to be much less reactive than other high (and low) molecular weight DOC intermediates of sediment POC remineralization, and therefore represents the majority of the pore water DOC accumulating with depth in marine sediments.

In Figure 6, it can be seen that DCHO concentrations in these sediment pore waters are essentially independent of concentrations of pore water DOC in the <3 kDa size fraction (DOC_3; data from Burdige and Gardner, 1998). This implies that the accumulation of DCHOs in sediment pore waters is independent of, and not directly related to, the production of DOC_3. Since the biogeochemical properties of the DOC_3 pool appear to be controlled by pLMW-DOC (see Burdige and Gardner, 1998, for further details), this suggests that DCHOs may be preferentially found in the high molecular weight (HMW) pore water DOC pool. Dissolved carbohydrates therefore likely represent some of the initial HMW intermediates produced and consumed during sediment POC remineralization. We note that Arnosti and Holmer (1999) reached similar conclusions about the role of DCHOs in sediment POC remineralization based on pore water DCHO concentrations and potential polysaccharide hydrolysis rate measurements in Cape Lookout Bight sediments. We also note that the high molecular weight fraction (>1 kDa) of DOC in marine surface waters is preferentially enriched in carbohydrates (Benner et al., 1992), consistent with our suggestion.

Using pore water molecular weight data from the same estuarine and continental margin sediments studied here, Burdige and Gardner (1998) proposed that remineralization processes in continental margin sediments are more controlled by the oxidative or hydrolytic processes that produce and consume the initial HMW-DOC intermediates of POC remineralization. In these sediments the remineralization processes affecting HMW-DOC cycling apparently provide more of an initial "upstream" bottleneck in the overall POC remineralization process, allowing HMW-DOC to accumulate to a greater extent in continental margin sediment pore waters. In contrast, in estuarine sediments the later fermentative or perhaps terminal respiratory processes appear to exert a greater overall control on carbon remineralization (also see Arnosti et al., 1994). The fact that relative DCHO concentrations are higher in these shelf/slope break sediments than they are in the estuarine Chesapeake Bay sediments (section 3.2 and Figs. 2 and 3) is consistent with this suggestion, if pore water DCHOs are indeed preferentially found in the HMW-DOC pool (as discussed above). Furthermore, the total aldose yields in Table 4 provide additional evidence in support of differing controls on carbon remineralization in these sediments, since water column studies have shown that TAYs generally decrease as organic matter is diagenetically altered (Hedges et al., 1994; Skoog and Benner, 1998). Therefore, shelf/slope break sediment pore waters would be expected to contain a higher percentage of "reactive" DOC intermediates than that found in the estuarine Chesapeake Bay sediments, as is seen in this table.

4.4. Uncoupling of PCHO and DCHO Concentrations

A comparison of the dissolved and particulate carbohydrate data from these sediments illustrates an interesting trend (Fig. 7). Whereas PCHOs (as a % of POC) vary by only a factor of ~2 (from 5–10%), DCHOs (as a % of DOC) vary over a much wider range (from ~10% to up to 60%). Furthermore, the Chesapeake Bay and shelf/slope break data appear to cluster in two distinct regions.

The slightly lower relative PCHO concentrations in these mid-Atlantic shelf/slope break sediments versus the estuarine

Chesapeake Bay sediments (also see Table 1) could be indicative of either a slightly higher contribution of marine (vs. terrestrial) organic matter to these offshore sediments (Cowie and Hedges, 1984), or a greater amount of pre-depositional diagenesis of the organic matter in these sediments (Hedges et al., 1994). Unfortunately, we are unable to differentiate between these two possibilities with our existing data (see similar discussions in Cowie and Hedges, 1984).

Regardless of the causes of these differences in PCHO concentrations, the results in Figure 7 clearly demonstrate that DCHO concentrations are not simply positively related to the amount of PCHO in the sediments (or the amount of carbohydrate being remineralized). Arnosti and Holmer (1999) have noted a similar "uncoupling" of dissolved and particulate carbohydrate concentrations in Cape Lookout Bight sediments, although their results do not appear to follow the general trends seen in our data set. If we assume that DCHOs are produced from PCHOs during sediment remineralization processes, then it seems likely that differences in these remineralization processes in estuarine vs. shelf/slope break sediments may explain the observations in Figure 7. In fact, the differing controls on carbon remineralization in these sediments discussed in section 4.3 do appear to explain the observed differences in relative DCHO concentrations in these sediments. As such, these differing controls then also plays a major role in explaining the uncoupling of DCHO and PCHO concentrations in these sediments.

5. SUMMARY AND CONCLUSIONS

1. Particulate carbohydrates represented ~5–9% of the POC in estuarine (Chesapeake Bay) and mid-Atlantic shelf/slope break (continental margin) sediments. Relative carbohydrate concentrations were slightly higher in the Chesapeake Bay sediments (~6–9%) than they were in the shelf/slope break sediments (~5%). This may be due to either a slightly higher contribution of marine organic matter to these offshore sediments, or to a greater amount of pre-depositional diagenesis of this material.
2. There was no selective preservation of carbohydrates in these sediments, and PCHO remineralization was also ~5–9% of sediment POC oxidation (or C_{ox}). When compared with results from other coastal sediments and a pelagic turbidite, PCHO remineralization (as a percentage of C_{ox}) did not vary by more than a factor of ~2–3 over a 3–4 order of magnitude range in C_{ox} values. The causes of this are not well understood, but may be related to specific effects associated with the remineralization of highly altered organic matter mixtures under aerobic conditions.
3. Dissolved carbohydrates (DCHOs) in sediment pore waters ranged from ~30 to 400 μM, increased with depth in a manner similar to total DOC, and represented ~10 to 55% of the pore water DOC. In estuarine sediments this percentage decreased with sediment depth, while in continental margin sediments it was constant with depth (upper ~30 cm). The occurrence of recognizable DCHOs at depth in pore waters may play some role in controlling PCHO preservation in sediments. However, this depends on the mechanisms of sediment carbon/carbohydrate preservation, and the forms of DCHOs in pore waters.
4. Of the DCHOs in these pore waters ~30 to 50% could be identified as individual aldoses (monomeric neutral sugars), and total aldose yields were higher in the continental margin sediment pore waters (>9%) than they were in the estuarine sediment pore waters (<5%). When compared with water column data, these observations suggest that there are differences in pore water versus water column DCHOs in terms of their composition and presumably structure.
5. All of these observations suggested that pore water DCHO concentrations are primarily controlled by sediment remineralization processes. Pore water DCHOs may be preferentially found in the HMW-DOC pool, likely occurring as some of the initial HMW intermediates produced and consumed during sediment POC remineralization. These results also support past suggestions about the differing controls on carbon remineralization processes in continental margin versus estuarine sediments. Finally, these observations suggest that there is an uncoupling between PCHO and DCHO concentrations in sediments, which further indicates the importance of sediment remineralization processes in controlling pore water DCHO concentrations.

Acknowledgments—We would like to thank the captain and crew of the R/V Cape Henlopen for their assistance in sample collection, and two anonymous reviewers for their comments on an earlier version of this manuscript. This work was supported by a grant from the US National Science Foundation to D.J.B. (OCE-930212). Partial ship time support was also provided by a grant from the Office of Naval Research (Marine Environmental Quality and Harbor Processes Programs). A.S. would like to thank the Swedish National Science Foundation (NFR) for their support while she was a post-doctoral researcher at University of Washington, and would also like to thank John Hedges for graciously receiving her in his lab at U.W.

REFERENCES

Alperin M. J., Martens C. S., Albert D. B., Suayah I. B., Benninger L. K., Blair N. E., and Jahnke R. A. (1999) Benthic fluxes and porewater concentration profiles of dissolved organic carbon in sediments from the North Carolina continental slope. *Geochim. Cosmochim. Acta* **63,** 427–448.

Arnosti C. and Holmer M. (1999) Carbohydrate dynamics and contributions to the carbon budget of an organic-rich coastal sediments. *Geochim. Cosmochim. Acta* **63,** 353–403.

Arnosti C., Repeta D. J., and Blough N. V. (1994) Bacterial degradation of polysaccharides in anoxic marine sediments. *Geochim. Cosmochim. Acta* **58,** 2639–2652.

Benner R., Pakulski J. D., McCarthy M., Hedges J., and Hatcher P. G. (1992) Bulk chemical characteristics of dissolved organic matter in the ocean. *Science* **255,** 1561–1564.

Borch N. H. and Kirchman D. L. (1997) Concentrations and composition of dissolved combined neutral sugars (polysaccharides) in seawater determined by HPLC-PAD. *Mar. Chem.* **57,** 85–95.

Boschker H. T. S., Bertilsson, S. A., Dekkers E. M. J., and Cappenberg T. E. (1995) An inhibitor-based method to measure initial decomposition of naturally occurring polysaccharides in sediments. *Appl. Environ. Microbiol.* **61,** 2186–2192.

Burdige D. J. (1991) The kinetics of organic matter mineralization in anoxic marine sediments. *J. Mar. Res.* **49,** 727–761.

Burdige D. J. and Gardner K. G. (1998) Molecular weight distribution of dissolved organic carbon in marine sediment pore waters. *Mar. Chem.* **62,** 45–64.

Burdige D. J. and Homstead J. (1994) Fluxes of dissolved organic carbon from Chesapeake Bay sediments. *Geochim. Cosmochim. Acta* **58,** 3407–3424.

Burdige D. J., Huang C. M., Krishna N., and Scully Jr. F. E. (1995) Aliphatic amines in Chesapeake Bay sediments. *Mar. Chem.* **51,** 45–54.

Burdige D. J. and Zheng S. (1998) The biogeochemical cycling of dissolved organic nitrogen in estuarine sediments. *Limnol. Oceanogr.* **43,** 1796–1813.

Burdige D. J., Berelson W. M., Coale K. H., McManus J., and Johnson K. S. (1999) Fluxes of dissolved organic carbon from California continental margin sediments. *Geochim. Cosmochim. Acta* **63,** 1507–1515.

Cowan J. L. W. and Boynton W. R. (1996) Sediment-water oxygen and nutrient exchanges across the longitudinal axis of Chesapeake Bay: seasonal patterns, controlling factors and ecological significance. *Estuaries* **19,** 562–580.

Cowie G. L. and Hedges J. I. (1984) Carbohydrate sources in a coastal marine environment. *Geochim. Cosmochim. Acta* **48,** 2075–2087.

Cowie G. L. and Hedges J. I. (1992) The role of anoxia in organic matter preservation in coastal sediments: relative stabilities of the major biochemicals under oxic and anoxic depositional conditions. *Org. Geochem.* **19,** 229–234.

Cowie G. L. and Hedges J. I. (1994) Biochemical indicators of diagenetic alteration in natural organic matter mixtures. *Nature* **369,** 304–307.

Cowie G. L., Hedges J. I., and Calvert S. E. (1992) Sources and reactivity of amino acids, neutral sugars, and lignin in an intermittently anoxic marine environment. *Geochim. Cosmochim. Acta* **56,** 1963–1978.

Cowie G. L., Hedges J. I., Prahl F. G., and deLange G. J. (1995) Elemental and biochemical changes across an oxidation front in a relict turbidite: An oxygen effect. *Geochim. Cosmochim. Acta* **59,** 33–46.

Ferdelman T. A. (1994) Oceanographic and geochemical controls on sulfur diagenesis in coastal sediments. Ph.D., Univ. of Delaware.

Hamilton S. E. and Hedges J. I. (1988) The comparative geochemistries of lignins and carbohydrates in an anoxic fjord. *Geochim. Cosmochim. Acta* **52,** 129–142.

Hedges J. I. (1988) Polymerization of humic substances in natural environments. In *Humic substances and their role in the environment* (eds. F. C. Frimmel and R. C. Christman), pp. 45–58. J. Wiley & Sons.

Hedges J. I., Cowie G. L., Richey J. E., Quay P. D., Benner R., Strom M., and Forsberg B. R. (1994) Origins and processing of organic matter in the Amazon River as indicated by carbohydrates and amino acids. *Limnol. Oceanogr.* **39,** 743–761.

Hedges J. I. and Kiel R. G. (1995) Sedimentary organic matter preservation: An assessment and speculative synthesis. *Mar. Chem.* **49,** 81–115.

Henrichs S. M. (1992) Early diagenesis of organic matter in marine sediments: Progress and perplexity. *Mar. Chem.* **39,** 119–149.

Hernes P. J., Hedges J. I., Peterson M. L., Wakeham S. G., and Lee C. (1996) Neutral carbohydrate geochemistry of particulate material in the central equatorial Pacific. *Deep-Sea Res.* **43,** 1181–1204.

Jahnke R. A. (1988) A simple, reliable, and inexpensive pore water sampler. *Limnol. Oceanogr.* **33,** 483–487.

Johnson K. M., Burney C. M., and Sieburth J. M. (1981) Doubling of production and precision of the MBTH spectrophotometric assay for dissolved carbohydrates in seawater. *Mar. Chem.* **10,** 467–473.

Kemp W. M., Sampou P., Mayer M., Henricksen K., and Boyton W. R. (1990) Ammonium recycling versus denitrification in Chesapeake Bay sediments. *Limnol. Oceanogr.* **35,** 1545–1563.

Krom M. D. and Westrich J. T. (1981) Dissolved organic matter in the pore waters of recent marine sediments; a review. In *Biogéochemie de la matière organique à l'interface eau-sédiment marin*, pp. 103–111. Colloques Internationaux du C.N.R.S.

Lee C. and Wakeham S. G. (1988) Organic matter in seawater: Biogeochemical processes. In *Chemical Oceanography* (ed. J. P. Riley and R. Chester); Vol. 9, pp. 1–51. Academic Press.

Lyons W. B., Gaudette H. E., and Hewitt A. D. (1979) Dissolved organic matter in pore waters of carbonate sediments from Bermuda. *Geochim. Cosmochim. Acta* **43,** 433–437.

Martens C. S., Haddad R. I., and Chanton J. P. (1992) Organic matter accumulation, remineralization and burial in an anoxic marine sediment. In *Productivity, accumulation, and preservation of organic matter in recent and ancient sediments* (eds. J. K. Whelan and J. W. Farrington); pp. 82–98. Columbia Univ. Press.

Martin W. R. and McCorkle D. C. (1993) Dissolved organic carbon concentrations in marine pore waters determined by high-temperature oxidation. *Limnol. Oceanogr.* **38,** 1464–1479.

Marvin-DiPasquale M. C. and Capone D. G. (1998) Benthic sulfate reduction along the Chesapeake Bay central channel. I. Spatial trends and controls. *Mar. Ecol. Prog. Ser.* **168,** 213–228.

Mayer L. M. (1994a) Relationships between mineral surfaces and organic carbon concentrations in soils and sediments. *Chem. Geol.* **114,** 347–363.

Mayer L. M. (1994b) Surface area control of organic carbon accumulation in continental margin sediments. *Geochim. Cosmochim. Acta* **58,** 1271–1284.

McCarthy M., Hedges J., and Benner R. (1996) Major biochemical composition of dissolved high molecular weight organic matter in seawater. *Mar. Chem.* **55,** 281–297.

Middelburg J. J. (1989) A simple rate model for organic matter decomposition in marine sediments. *Geochim. Cosmochim. Acta* **53,** 1577–1581.

Mopper K., Dawson R., Liebiezeit G., and Ittekot V. (1980) The monosaccharide spectra of natural waters. *Mar. Chem.* **10,** 55–66.

Nissenbaum A., Baedecker M. J., and Kaplan I. R. (1971) Studies on dissolved organic matter from interstitial waters of a reducing marine fjord. In *Advances in Organic Geochemistry* (eds. H. R. von Gaerter and H. Wehner), pp. 427–440. Pergamon Press.

Pakulski J. D. and Benner R. (1992) An improved method for the hydrolysis and MBTH analysis of dissolved and particulate carbohydrates in seawater. *Mar. Chem.* **40,** 143–160.

Pakulski J. D. and Benner R. (1994) Abundance and distribution of carbohydrates in the ocean. *Limnol. Oceanogr.* **39,** 930–940.

Schaffner L. C. (1990) Small-scale organism distributions and patterns of species diversity: Evidence for positive interactions in an estuarine benthic community. *Mar. Ecol. Prog. Ser.* **61,** 107–117.

Sinneghe Damsté J. S., Kok M. D., Köster J., and Schouten S. (1998) Sulfurized carbohydrates: An important sink for organic carbon? *Earth Planet. Sci. Letters* **164,** 7–13.

Skoog A. and Benner R. (1998) Aldoses in various size fractions of marine organic matter: Implications for carbon cycling. *Limnol. Oceanogr.* **42,** 1803–1813.

Skrabal S. A., Donat J. R., and Burdige D. J. (1997) Fluxes of copper-complexing ligands from estuarine sediments. *Limnol. Oceanogr.* **42,** 992–996.

Steinberg S. M., Venkatesan M. I., and Kaplan I. R. (1987) Organic geochemistry of sediments from the continental margin off southern New England, U.S.A.—Part I. Amino acids, carbohydrates and lignin. *Mar. Chem.* **21,** 249–265.

Tissot B. and Welte D. H. (1978) *Petroleum Occurrence and Formation.* Springer-Verlag.

Verardo D. J., Froelich P. N., and McIntyre A. (1990) Determination of organic carbon and nitrogen in marine sediments using a Carlo Erba NA-1500 analyzer. *Deep-Sea Res.* **37,** 157–165.

Whelan J. K. and Emeis K.-C. (1992) Sedimentation and preservation of amino compounds and carbohydrates in marine sediments. In *Productivity, accumulation, and preservation of organic matter in recent and ancient sediments.* (eds. J. K. Whelan and J. W. Farrington); pp. 176–200. Columbia Univ. Press.

Wilson T. R. S., Thomson J., Colley S., Hydes D. J., Higgs N. C., and Sørensen J. (1985) Early organic diagenesis: The significance of progressive subsurface oxidation fronts in pelagic sediments. *Geochim. Cosmochim. Acta* **49,** 811–822.

APPENDIX – Sediment POC and PCHO Concentrations

Depth interval (cm)	POC (mg C/gdw)	PCHO (mg C/gdw)	PCHO (% of POC)
Chesapeake Bay Stations			
station S3, core IIIS12B (10/91)			
0–1	5.90	0.33	5.6%
1–2	5.78	0.33	5.6%
2–3	5.95	0.34	5.8%
3–4	7.28	0.41	5.6%
4–6	7.17	0.46	6.4%
6–9	8.72	0.54	6.2%
9–12	6.47	0.35	5.5%
12–15	7.33	0.40	5.5%
core average			5.8 ± 0.3%
station S3, core IVS23B (3/92)			
0–1	7.46	0.61	8.2%
1–2	7.24	0.46	6.3%
2–3	5.31	0.34	6.3%
3–4	6.30	0.43	6.9%
4–6	7.29	0.57	7.8%
6–9	7.37	0.50	6.7%
9–12	7.11	0.46	6.5%
12–15	6.64	0.38	5.7%
core average			6.8 ± 0.8%
station S3, core VS4C (7/92)			
0–1	6.77	0.46	6.8%
1–2	5.94	0.33	5.5%
2–3	5.82	0.44	7.5%
3–4	5.76	0.34	5.9%
4–6	6.43	0.37	5.7%
6–9	6.38	0.36	5.6%
9–12	6.11	0.37	6.1%
12–15	6.29	0.36	5.8%
core average			6.1 ± 0.7%
station M3, core IIIM18B (10/91)			
0–1	37.70	3.49	9.3%
1–2	31.38	2.34	7.4%
2–3	40.31	3.74	9.3%
3–4	36.20	3.03	8.4%
6–9	32.04	2.52	7.9%
9–12	31.43	2.47	7.9%
12–15	29.35	2.42	8.2%
core average			8.3 ± 0.7%
station M3, core IVM25D (3/92)			
0–1	77.85	18.27	23.5%
1–2	56.11	14.16	25.2%
2–3	44.05	4.71	10.7%
3–4	42.16	5.65	13.4%
4–6	39.26	4.76	12.1%
6–9	45.26	3.56	7.9%
9–12	32.12	3.45	10.7%
12–15	31.50	3.22	10.2%
core average			14.2 ± 6.0%
core average (w/o two surface samples)			10.8 ± 1.7%
station M3, core VM12C (7/92)			
0–1	45.72	3.78	8.3%
1–2	41.57	5.63	13.5%
2–3	37.90	3.64	9.6%
3–4	35.89	3.06	8.5%
4–6	36.10	3.00	8.3%
6–9	38.50	2.26	5.9%
9–12	30.53	2.26	7.4%
12–15	33.16	2.68	8.1%
core average			8.7 ± 2.1%
station N3, core IIIN12C (10/91)			
0–1	40.06	1.98	4.9%
1–2	31.95	2.11	6.6%
2–3	36.85	2.86	7.8%
3–6	26.81	2.71	10.1%
6–9	30.48	3.31	10.9%
9–12	30.20	3.49	11.5%
12–15	28.60	3.43	12.0%
15–18	26.53	2.63	9.9%
core average			9.2 ± 2.4%
station N3, core IVN210B (3/92)			
0–1	25.22	1.69	6.7%
1–2	24.31	1.91	7.8%
2–3	23.85	2.05	8.6%
3–4	21.80	1.91	8.7%
4–6	20.70	1.86	9.0%
6–9	18.59	1.62	8.7%
9–12	21.11	1.81	8.6%
12–15	20.88	1.83	8.8%
core average			8.4 ± 0.7%
station N3, core VN18B (7/92)			
0–1	30.59	1.91	6.2%
1–2	36.06	1.72	4.8%
2–3	41.14	2.12	5.1%
3–4	28.59	2.19	7.6%
4–6	26.98	2.35	8.7%
6–9	25.05	2.17	8.7%
9–12	27.34	2.28	8.3%
12–15	26.13	2.17	8.3%
core average			7.2 ± 1.5%
Mid-Atlantic Shelf/Slope Break Stations			
station WC4, core WC4-1b (7/94)			
0–1	21.62	1.24	5.7%
1–2	22.13	1.29	5.8%
2–4	21.33	1.06	5.0%
4–6	18.36	0.89	4.9%
6–8	17.04	1.03	6.1%
8–10	18.19	0.82	4.5%
10–12	16.89	0.83	4.9%
12–14	20.55	0.70	3.4%
14–16	19.85	1.03	5.2%
16–18	20.24	0.73	3.6%
18–20	18.88	0.95	5.0%
20–22	20.05	0.98	4.9%
core average			4.9 ± 0.8%
station WC7, core WC7-1b (7/94)			
0–1	18.95	1.15	6.1%
1–2	23.70	1.47	6.2%
2–4	22.89	1.19	5.2%
4–6	19.68	1.24	6.3%
6–8	21.93	1.10	5.0%
8–10	20.85	1.19	5.7%
10–12	22.80	1.34	5.9%
12–14	18.88	1.06	5.6%
14–16	20.57	1.12	5.4%
16–18	19.12	1.21	6.3%
18–20	22.02	0.95	4.3%
20–22	19.91	0.91	4.6%
22–24	19.26	1.05	5.4%
core average			5.5 ± 0.6%

(continued)

Depth interval (cm)	POC (mg C/gdw)	PCHO	
		(mg C/gdw)	(% of POC)
station AI, core AI-1b (7/94)			
0–1	12.05	0.67	5.6%
1–2	13.39	0.65	4.9%
2–4	10.08	0.60	5.9%
4–6	10.97	0.56	5.1%
6–8	12.89	0.66	5.1%
8–10	11.34	0.57	5.1%
10–12	13.17	0.60	4.6%
12–14	12.62	0.55	4.4%
14–16	12.85	0.53	4.1%
16–18	10.22	0.46	4.5%
18–20	11.47	0.59	5.2%
20–22	10.51	0.54	5.1%
22–24	11.04	0.41	3.7%
core average			4.9 ± 0.6%