

Biogeochemistry of organic matter in the Laurentian Trough, II. Bulk composition of the sediments and relative reactivity of major components during early diagenesis

J.C. Colombo ^{a,*}, N. Silverberg ^b, J.N. Gearing ^c

^a *Département d'Océanographie, Université du Québec à Rimouski, 310 Allé des Ursulines, Rimouski, Québec G5L 3A1, Canada*

^b *Fisheries and Oceans, Maurice Lamontagne Institute, 850 Route de la Mer, P.O. Box 1000, Mont-Joli, Québec G5H 3Z4, Canada*

^c *Department of Chemistry, University of Massachusetts at Dartmouth, North Dartmouth, MA 02747, USA*

Received 7 June 1994; accepted 23 June 1995

Abstract

The organic carbon of 280–320 m deep Laurentian Trough sediments at landward and seaward sites (13–24 mg C/g) consisted of carbohydrates (15–22%), hydrolysable amino acids (7–13%), lipids (1–5%), labile proteins (0.3–1%) and a non-characterized fraction (62–74%). Amino acids, proteins and uncharacterized compounds accounted for 21–43, 0.9–4 and 51–78%, respectively, of total nitrogen (1.2–2.2 mgN/g). A clear reactivity trend (pheopigments \gg lipids $>$ proteins $>$ amino acids \approx nitrogen $>$ carbon $>$ carbohydrates) was deduced from the concentration decreases between settling particles and surficial sediments. This was confirmed by one-year inventories in the top cm, burial rates at 35 cm depth, and one-*G* model calculations. Lipids were a dominant substrate near the sediment–water interface whereas carbohydrates and amino acids constituted the principal energy sources deeper in the sediment. In the porewaters, DOC levels were low (2–6 mg/l) in the top 4 cm, indicating rapid removal (i.e. consumption, irrigation, diffusion), and increased with depth (8–12 mg/l), reflecting the buildup of refractory products. There were also clear compositional changes of DOC with depth. Geographical differences in water column fluxes were recorded in the sediments. The organic contents and C/N ratios were higher at the landward site due to higher rates of sedimentation, bioturbation and terrestrial and total organic inputs. At the seaward station, the lower rates of these processes and stronger marine influence resulted in lower C/N ratios and a more complete decay of organic matter within the top 35 cm sediments.

1. Introduction

Even in deep environments, the benthic community and the chemical composition of sediments are influenced by processes occurring far above in the

sunlit surface layers of the ocean. The production of large, rapidly sinking particles permits the downward transport of labile organic matter (OM) to the sea floor (Graf, 1989). This process is relevant to the question of the fate of anthropogenic CO₂ since it permits the transference of carbon from surface layers into deep ocean waters and sediments. During this passage the biochemical patterns entering from the euphotic zone are edited by the action of different organisms which consume, metabolically alter

* Corresponding author's present address: Environmental Chemistry Chair, Facultad Cs. Naturales y Museo, Universidad Nacional de La Plata, Paseo del Bosque s/n, La Plata, 1900, Argentina.

and ultimately degrade the OM. This results in a preferential loss of the more labile compounds and the incorporation of organism-specific signatures (Downs and Lorenzen, 1985; Neal et al., 1986; Wakeham and Lee, 1989).

After deposition, the transformation of OM continues through selective degradation, mixing and continued sedimentation of other material. Thus, factors such as primary productivity, water depth, sedimentation rate, benthic production, bioturbation and oxygen concentration are responsible for the amount, vertical distribution and chemical makeup of organic matter preserved in the sediments (Hargrave, 1975; Müller and Suess, 1979; Berner, 1980; Aller and Mackin, 1984; Emerson et al., 1985; Jorgensen et al., 1990; Cowie and Hedges, 1991). In order to understand the relative importance of these processes, it is necessary not only to characterize and quantify the organic matter but also to identify its major sources. Two types of analyses have principally been used to attack this problem: elemental analysis and individual biomarker compounds. The former approach uses carbon and nitrogen (and occasionally other elements) to quantify the behavior of organic matter; it can also provide some limited indication of the sources. The examination of individual biomarker compounds has been mainly confined to the more long-lived lipid groups such as hydrocarbons, sterols, and fatty acids. These compounds can be very specific as regards sources. However, they often are not affected by the same processes, or with rates analogous to those which control the fate of the total organic matter. A complement to these two strategies is the measurement of the principal biochemical components of OM - proteins, carbohydrates, and lipids. These major classes can help determine both sources and the parameters controlling the diagenetic fate of OM. Through the years, several authors have noted the need for such information, particularly for data on a wider range of chemical classes in contrasting depositional environments (Degens, 1965; Dumas and Saliot, 1977; Hamilton and Hedges, 1988), but few published studies have met this need (Gough and Mantoura, 1990). The urgent need for a better understanding of the sources, fluxes, reactivity and early diagenesis of OM on a global biogeochemical scale has been recently emphasized (Farrington, 1992).

In our study of the organic geochemistry of the Laurentian Trough, we examined the composition and the early diagenesis of OM, using all three tactics - elemental analysis, bulk molecular composition and individual biomarker compounds. Results from the first two are given here for sediments, following up a similar treatment of the settling particles in the previous paper. Our objective was to examine the response of underlying sediments to the events occurring at the surface in two contrasting sites along the terrestrial-marine gradient in the Estuary, sampled during spring and mid-summer. Particular aims were: (1) to describe the bulk organic composition of these sediments, (2) to study the distribution, relative reactivity and early diagenesis of different OM fractions, and (3) to determine if the geographical trends observed in the OM input from the water column were reflected in underlying sediments.

2. Materials and methods

2.1. Field sampling

The study area and the sampling strategy were described in the preceding paper on settling particles (Colombo et al., 1995a). Undisturbed bottom sediments were recovered during each period of sediment trap deployment, from 280 m (*S*) and 320 m depth (*L*), using a 0.1 m² box corer. The cores were subsampled immediately upon recovery in a glove box under a forced flow of nitrogen gas using a stainless steel spatula (5 successive scrapings in the top cm, then 1 cm thick slices every 1 cm down to 5 cm depth and at 5 cm intervals down to 35 cm depth). Porewater from each subsample was immediately extracted using a Reeburgh-style squeezer (Reeburgh, 1967) fitted with precombusted Whatman glass fiber filters (1.2 and then 0.7 μ m). Filtered porewater samples were collected in acid-washed precombusted amber bottles. All samples were stored at -20 or -40°C until analysis.

2.2. Chemical analysis

Porewater dissolved organic carbon (DOC) was measured using a dry combustion method (Gordon

and Sutcliffe, 1973; Krom and Sholkovitz, 1977). Aliquots of 5–10 ml porewater were acidified with 85% orthophosphoric acid and then evaporated at 45°C under strictly controlled, non-contaminating conditions. Approximately 40–80 mg of the resulting salts were combusted at 720°C in a Perkin Elmer Model 240 elemental analyser and quantified using acetanilide as standard. The precision of the measurements was $14.9 \pm 11.9\%$ ($n = 13$).

Sediment total organic carbon (TOC), total nitrogen (TN), carbohydrates (CH_2O), proteins (PROT), lipids (LIP), and pheopigments (PHEO) were measured using the methods described in the preceding paper (Colombo et al., 1995a). For TOC and TN, 30–50 mg of oven-dried sediments (141–184 h at 60°C) were introduced into the elemental analyzer. For the other analyses, wet sediment subsamples were taken after a thorough homogenization (10–15 mg for CH_2O ; ~ 300 mg for PROT; and 20–30 g for lipids). The results are expressed on a dry-weight basis. Dissolved carbohydrates (DCH_2O) were measured in 1 ml aliquots of porewaters with the same phenol-sulfuric acid method used for solid phase CH_2O (Colombo et al., 1995a). The precision of the analyses averaged $5.1 \pm 4.6\%$ ($n = 13$). Total hydrolyzable (THAA), dissolved free (DFAA) and combined amino acids (DCAA), were measured by reverse-phase high performance liquid chromatography using o-phthalaldehyde derivatization and fluorescence detection. A more comprehensive discussion of amino acid methods and data is published elsewhere (Colombo et al., 1995b).

3. Results and discussion

3.1. Bulk organic composition

Table 1 presents the composition of sediments collected at both stations and sampling periods in the Laurentian Trough. The carbon and nitrogen contents (13–24 mg/g TOC and 1.2–2.2 mg/g TN) are similar to those previously reported for Lower St. Lawrence Estuary muds (Bouchard, 1983; Silverberg et al., 1987; Gearing and Pocklington, 1990). The bulk composition of organic matter in these sediments has not been previously measured. Results are presented in Fig. 1 as a percentage of total organic

carbon. Carbohydrates are the most abundant characterized component of TOC (15–22%), followed by THAA (7–13%), lipids (1.3–5.5%) and proteins (0.3–1%). The non-characterized (NONCH) fraction (62–74% TOC) probably contains recalcitrant humic-type geopolymers, which usually account for a major fraction of TOC in sediments (10–70%; Mayer, 1985). THAA-N represent a high proportion of TN (21–43%), whereas labile proteins account for only 0.9–4% TN.

The bulk molecular composition of Laurentian Trough surficial (0–3 cm) sediments is compared with that reported for other marine environments in Table 2. Because these parameters have not been frequently measured in marine sediments, Table 2 is spotty, with relatively more information on special environments (e.g. highly productive Peru and Namibian shelf regions; Mangrove Lake, a coastal pond with reducing sapropels). The concentrations of TOC and TN in the St. Lawrence fall in the lower range of the reported values along with other oxic, nearshore environments such as Buzzards Bay, Dabob Bay, and the continental margin off New England.

Carbohydrates, which include polyhydroxylated compounds ranging in size from 5–6 carbon sugars to large biopolymers (i.e. starches, cellulose), have been measured with a robust technique which extracts most combined carbohydrates (Mopper, 1977). St. Lawrence sediments contain relatively high proportions of CH_2O compared with the New England shelf, San Diego Trough and Dabob Bay (Table 2). The absolute concentrations in the top 0–3 cm are also high (6–12 mg/g) compared with other oxic sediments, 0.5–3 mg/g off California (Degens, 1965, 1967) and 3.3 mg/g in Dabob Bay (Cowie and Hedges, 1984), but are lower than those reported for anoxic areas, 10 mg/g in Saanich Inlet (Hamilton and Hedges, 1988), and ≈ 40 mg/g for the Black Sea (Mopper, 1977). CH_2O are much higher in vascular plants than in algae (Cowie and Hedges, 1984); terrestrial soils average 10–50 mg/g (Degens, 1967). The abundance of CH_2O in both sediments and settling particles from the St. Lawrence may thus reflect the contribution of OM from terrestrial sources.

Lipids, defined as compounds soluble in organic solvents and only slightly soluble in water, include

Table 1
Organic composition of sediments collected at a landward and seaward stations in the Lower St. Lawrence Estuary

Depth (cm)	TOC (mg/g)		TN (mg/g)		CH ₂ O (mg/g)		PROT (mg/g)		THAA (mg/g)		LIPIDS (mg/g)		PHEO (μg/g)		DOC (mg/l)		DCH ₂ O (mg/l)	
	May	July	May	July	May	July	May	July	May	July	May	July	May	July	May	July	May	July
Landward																		
0.0–0.2	21.4	23.0	1.90	1.98	10.7	10.3	0.40	0.36			1.47	1.36	13.9	15.7	2.90	4.03	1.66	2.60
0.2–0.4	21.4	22.7	1.90	2.02	8.60	11.2	0.20	0.57	5.98	6.12	1.44	1.23	19.1	19.9	3.73	4.14	1.66	2.03
0.4–0.6	21.2	23.8	1.86	2.07	7.46	10.4	0.30	0.45			1.44	1.23	19.1	19.9	3.13	3.95	1.51	1.86
0.6–0.8	20.9	23.2	1.85	2.07	7.18	10.7	0.44	0.32	5.40	6.00	1.19	1.16	14.7	13.4	2.45	3.69	1.35	2.74
0.8–1	21.5	23.9	1.89	2.15	8.45	11.6	0.26	0.28							3.31	5.18	1.62	2.51
1–2	20.3	23.3	1.79	2.11	10.3	9.79	0.33	0.20	5.52	5.69	1.43	1.73	16.9	18.9	2.95	5.71	1.27	3.18
2–3	20.0	22.8	1.83	1.92	11.7	11.5	0.63	0.33	6.52	5.79	1.46	1.42	14.2		2.44	4.55	1.43	3.98
3–4	19.4	20.4	1.74	1.76	8.52	9.47	0.31	0.30	4.66	4.75	0.95	1.47	8.98	14.0	2.92	5.26	4.52	4.68
4–5	18.9	19.0	1.60	1.67	8.64	9.02	0.23	0.22	4.73	4.27	1.15	1.23	8.71	11.5	6.76	6.06	3.13	6.81
9–10	19.0	18.0	1.59	1.44	7.78	7.53	0.28	0.19	4.64	3.92	1.33	1.23	8.23	11.8	9.28	7.95	6.90	7.87
14–15	17.9	17.1	1.45	1.39	6.29	7.17	0.27	0.11	3.60	3.05	1.13	1.00	6.71	7.79	9.43	7.36	7.14	8.04
19–20	16.4	16.3	1.37	1.27	6.10	6.54	0.24	0.14	3.63	2.87	1.12	0.98	6.36	3.33	11.6	7.95	4.92	6.98
24–25	16.7	16.6	1.46	1.33	6.18	6.55	0.19	0.21	2.67	2.81	1.32	1.14	4.46	4.40	8.33	9.35	4.76	6.72
29–30	16.2	15.4	1.36	1.26	5.68	6.39	0.19	0.16	2.99	3.18	1.36	0.95	5.82	4.47	9.75	9.02	6.27	7.16
34–35	14.6	14.9	1.26	1.17	5.70	6.22	0.18	0.06	2.70	2.33	1.09	0.70	2.71	4.45	12.0	10.8	7.30	7.07
0–3 cm																		
Average	21.0	23.3	1.86	2.05	9.21	10.8	0.37	0.36	5.86	5.90	1.40	1.37	15.8	17.0	2.99	4.46	1.50	2.70
SD	0.6	0.5	0.04	0.09	1.87	0.73	0.15	0.13	0.59	0.21	0.13	0.30	2.46	3.45	0.50	0.79	0.17	0.77
Seaward																		
0.0–0.2	17.7	17.8	1.77	1.99	7.58	9.52	0.11	0.20			0.92	0.82	16.1	9.79	3.76	2.95	1.39	2.47
0.2–0.4	17.9	19.0	1.89	1.94	8.54	9.18	0.25	0.23	5.17	4.26	0.92	0.82	16.1	9.79	10.1	3.63	2.03	2.03
0.4–0.6	17.7	18.1	1.79	1.85	6.33	9.63	0.29	0.23			1.02	1.04	13.6	12.3	4.88	3.14	4.43	2.30
0.6–0.8	18.6	22.1	1.82	2.14	8.99	9.40	0.26	0.24	4.64	5.03	0.86	0.89	14.5	9.91	4.54	3.05	1.56	2.03
0.8–1	18.4	21.6	1.85	2.25	8.12	12.1	0.51	0.19							3.99	3.56	1.64	2.87
1–2	20.6	20.9	1.88	2.10	8.70	11.0	0.40	0.42	4.65	4.87	0.79	1.01	13.8	9.47	4.14	3.20	2.25	2.47
2–3	18.2	18.6	1.83	1.94	6.05	9.59	0.19	0.29	4.95	5.48	0.81	0.86	9.55	8.18	3.42	3.54	2.21	3.00
3–4	17.5	19.1	1.73	1.98	7.86	9.62	0.37	0.24	4.92	5.19	0.77	0.72	8.52	7.17	6.05	6.84	2.70	3.54
4–5	15.3	16.6	1.50	1.68	6.32	8.78	0.22	0.30	3.06	3.93	0.82	0.74	7.06	3.08	6.88	6.44	3.28	5.21
9–10	15.3	14.3	1.49	1.46	7.70	6.39	0.16	0.07	2.78	3.08	0.72	0.72	5.68	5.28	9.05	8.55	8.07	7.25
14–15	15.5	13.6	1.55	1.30	6.24	6.38	0.13	0.06	2.53	3.42	0.60	0.31	5.87	3.62	9.75	10.5	9.34	9.64
19–20	13.7	13.8	1.46	1.52	5.97	6.49	0.12	0.18	2.00	2.51	0.47	0.37	5.21	3.69	8.08	7.57	6.56	7.69
24–25	13.1	13.5	1.39	1.45	6.07	5.41	0.15	0.11	3.30	2.58	0.37	0.37	4.54	3.89	7.80	9.67	6.80	9.59
29–30	13.6	14.4	1.43	1.56	5.69	6.52	0.26	0.12	2.66	2.52	0.33	0.42	4.51	4.16	6.79	8.48	6.47	8.84
34–35	13.4	14.0	1.40	1.54	5.60	6.02	0.15	0.02	2.07	2.46	0.31	0.27	3.85	3.31	8.32	9.64	6.92	8.66
0–3 cm																		
Average	18.5	19.7	1.83	2.03	7.76	10.1	0.29	0.26	4.85	4.92	0.88	0.93	13.5	9.93	4.98	3.30	2.25	2.45
SD	1.1	1.9	0.05	0.15	1.26	1.16	0.14	0.08	0.30	0.59	0.10	0.11	2.71	1.66	2.50	0.30	1.23	0.41

many well-studied groups of chemicals including hydrocarbons, sterols, fatty acids and fatty alcohols. Absolute concentrations in St. Lawrence surficial sediments (0.8–1.5 mg/g) are similar to those reported for the Hudson Canyon off New York (0.1–1.4 mg/g; Farrington and Tripp, 1977). In terms of relative composition (Table 2), St. Lawrence sediments are in the range of other oxic marine sediments.

Proteins, the third of the major biochemical classes in organisms, are low in the Trough sediments. The method used gives the quantity of proteins “available” or subject to enzymatic attack, so that comparison with other areas is difficult. Using the same methodology, Mayer et al. (1988) reported values of 0.05–0.4 mg/g for Gulf of Maine sediments, which is similar to our results (0.1–0.6 mg/g; Table 1).

THAA include the amino acids contained in proteins but also those liberated from other geopolymers. THAA concentrations in St. Lawrence surficial sediments (4.3–6.5 mg/g) are comparable to those reported for oxic sediments off California (2–4 mg/g; Degens, 1965) and Dabob Bay (4.8–7.6 mg/g; Cowie and Hedges, 1992). Degens (1967) reported a value of 5 mg/g as an average for marine argillaceous muds. The relative contribution of THAA to TOC in the St. Lawrence is at the low end of the range for oxic sediments (Table 2).

The concentration of dissolved OM (DOM) in the sediment porewaters of the Laurentian Trough is also comparable to that reported for oxic marine sediments. The levels of DOC throughout the sediment cores range from 2.4 to 12 mg/l (Table 1), within the range of values reported for oxic near-shore and oceanic sediments, 0.7–15 mg/l (Krom and Westrich, 1980). Higher DOC concentrations (~3–50 mg/l) have been measured in organic-rich sediments from Chesapeake Bay and Cape Lookout Bay (Burdige and Homstead, 1994; Alperin et al., 1994). Dissolved CH₂O levels (1.3–9.6 mg/l) are similar to those reported for deep oxidized sediments from the Pacific (2.2–6.9 mg/l) whereas in reducing environments the concentrations are usually higher

(12–64 mg/l; Romankevich, 1984). The bulk composition of porewater DOC is presented in Fig. 2. Dissolved CH₂O (DCH₂O) forms a high proportion of characterized DOC (12–45%); dissolved free (DFAA) and combined amino acids (DCAA) together account for about 2.8–26% DOC. The non-characterized fraction represents 40–75%.

3.2. Comparison with sediment-trap material

Settling particles intercepted at 150 m depth contained in general much higher concentrations of all bulk parameters than did the underlying sediments (Fig. 3). Only the traps collected during conditions of strong terrestrial influence (*L May*) showed concentrations more comparable to those in the sediment (TOC, 29; TN, 2.6; CH₂O, 7.2; THAA, 6.8; PROT, 0.9; LIP, 11; PHEO, 0.07 mg/g; Colombo et al., 1995a). The average loss of TOC from settling particles to 0–3 cm sediments is 53% with a range between 38 and 98% for the other organic components. The different reactivity of the components resulted in a change of the TOC composition. A rapid loss of lipids and proteins and a relative enrichment in the CH₂O and non-characterized “humic” fractions was observed in the sediments relative to settling particles (Fig. 1). This relative persistence of CH₂O probably reflects the contribution of resistant terrestrial (cellulose) or marine plant structural polysaccharides. The relative preservation of CH₂O during diagenesis has previously been attributed to the presence of structural water-insoluble heteropolysaccharides complexed to the mineral matrix (Romankevich, 1984).

Strong differences in the concentration and composition of OM between settling particles and sediments were noted previously, both in coastal (Furlong and Carpenter, 1988; Hedges et al., 1988; Cowie and Hedges, 1991) and deep marine environments (Emerson et al., 1985; Wakeham and Lee, 1989; Wakeham, 1990). In the deep sea, much of the loss of OM occurs during relatively long residence times in the water column and near the sediment–water

Notes to Table 1:

TOC = total organic carbon; TN = total nitrogen; CH₂O = carbohydrates; PROT = proteins; THAA = total hydrolyzable amino acids; PHEO = pheopigments; DOC = dissolved organic carbon; DCH₂O = dissolved carbohydrates; SD = standard deviation.

interface. In contrast, settling times in the Laurentian Trough are only about one day (Colombo et al., 1995a), while bioturbational mixing is 2–3 orders of

magnitude greater than deep-sea rates (Sundby and Silverberg, 1985; Silverberg et al., 1986). While some portion of the arriving organic matter is de-

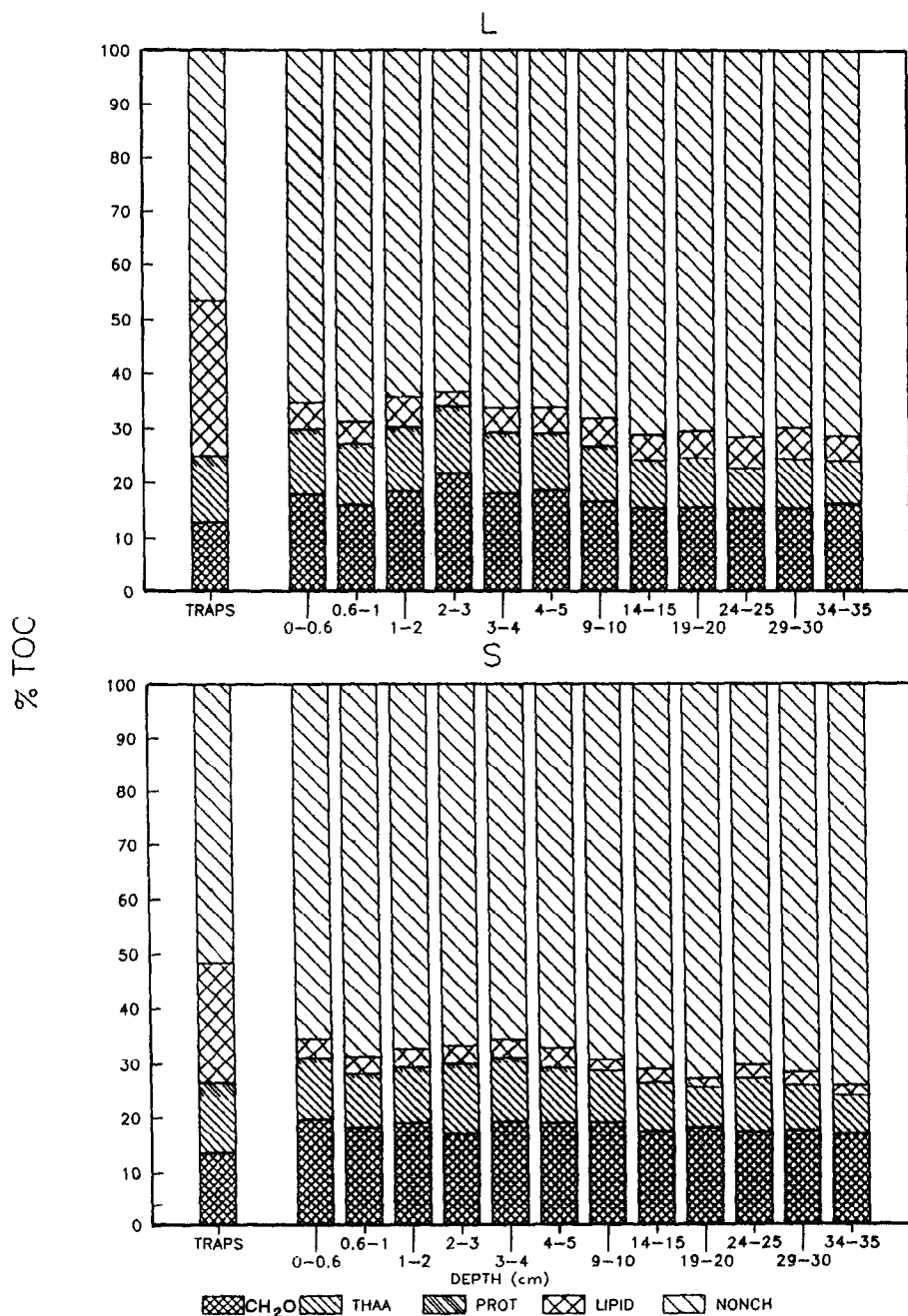


Fig. 1. Proportion of TOC represented by carbohydrates (CH₂O; conversion factor, 0.4), total hydrolyzable amino acids (THAA; cf. 0.44), proteins (PROT; cf. 0.44), lipids (LIP; cf. 0.75), and uncharacterized compounds (NONCH) in settling particles and underlying sediments at both stations. Average results from May and July samplings are shown. PROT is included in the THAA contribution.

Table 2
Organic composition of surficial (0–3 cm) sediments collected in the Lower St. Lawrence Estuary compared to that reported for other marine sediments

Region	Depth (m)	TOC (mg/g)	TN (mg/g)	as % of TOC					References
				LIPID-C	CH ₂ O-C	PROT-C	THAA-C	NONCH-C	
St. Lawrence									
L	320	22	1.9	4.2	18	0.7	12	65	this study
S	280	19	1.9	3.4	18	0.6	11	66	this study
Mangrove Lake marine sapropel	2	390	36	20	37	5.5	—	20 *	Hatcher et al. (1982, 1983)
Buzzards Bay Massachusetts	17	19–20	2–3	—	—	—	16–23	—	Henrichs and Farrington (1987)
Continental shelf Gulf of Mexico	30–60	5.8–36	—	3.4–5.4	—	—	—	—	Gearing et al. (1976)
Continental margin New England	80	16	—	—	4#(5#)	—	10	—	Steinberg et al. (1987)
Dabob Bay Puget Sound	110	22–36	2–3	—	7#	—	—	—	Prahl et al. (1980); Cowie and Hedges (1984)
Saanich Inlet British Columbia	210	47	5	—	11#	—	—	—	Hamilton and Hedges (1988)
Namibian Shelf Equatorial Atlantic	106	46	—	4	22	—	11	50 **	Klok et al. (1984)
San Diego Trough	—	10	—	10	5	—	15	70	Degens, 1967
Peru Upwelling Equatorial Pacific	92–506	32–75	4–9	—	—	—	25–38	—	Henrichs and Farrington (1984); Henrichs et al. (1984)
Hudson Canyon	140–1000	7–32	—	1–2.3	—	—	—	—	Farrington and Tripp (1977)

^a Hummin, ^b residual, chiefly aliphatic and organo-sulfur compounds and kerogens.

= Sum of individual sugars.

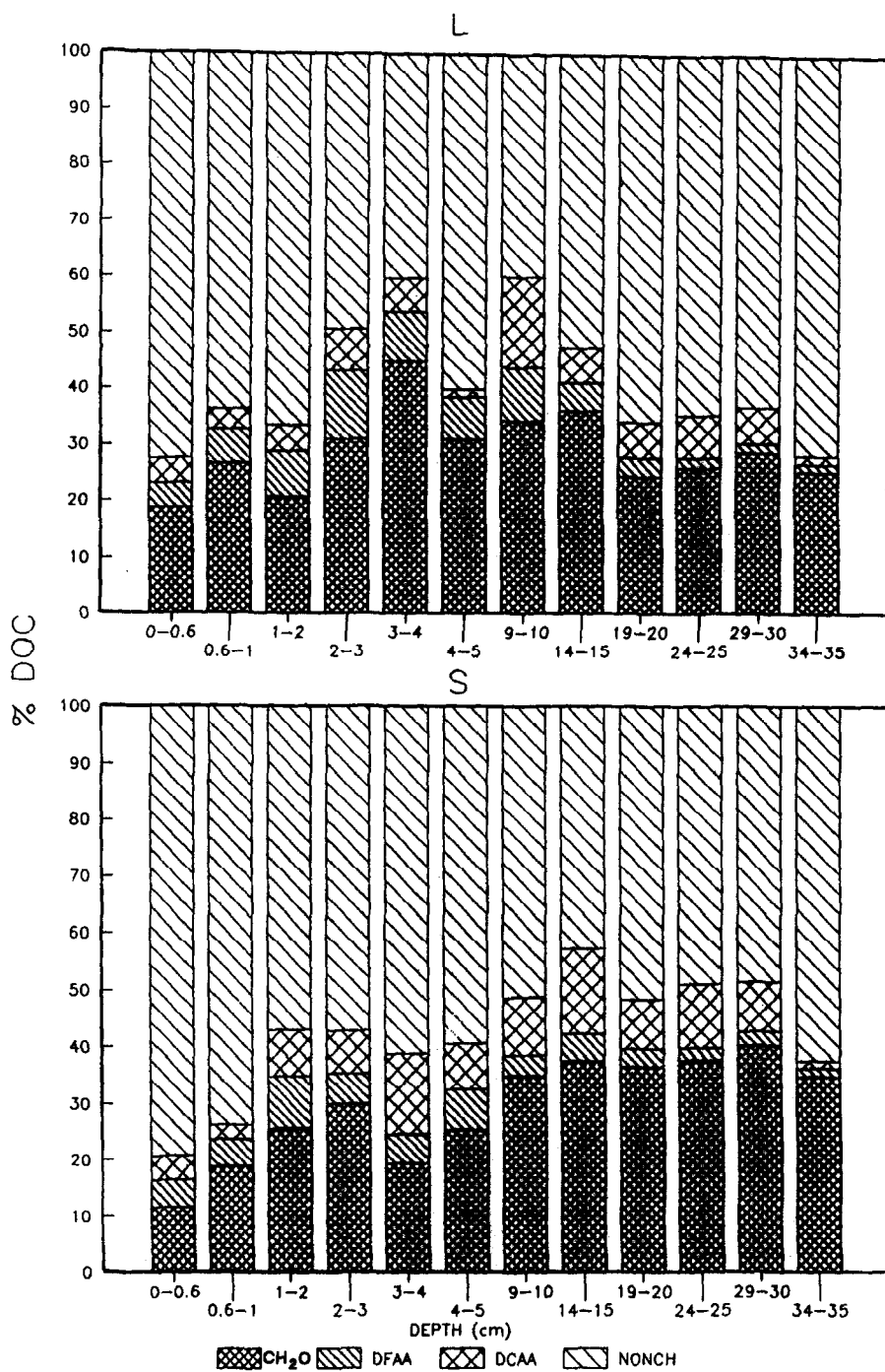


Fig. 2. Proportion of DOC represented by dissolved free (DFAA) and combined amino acids (DCAA) and dissolved carbohydrates (DCH₂O) in porewaters (average results from May and July).

graded at the interface itself (and thus would not influence diagenetic changes within the sediment and its porewaters), Silverberg et al. (1985) estimated

that, at a site intermediate to *L* and *S*, a significant percentage of the daily influx was mixed and degraded below the interface.

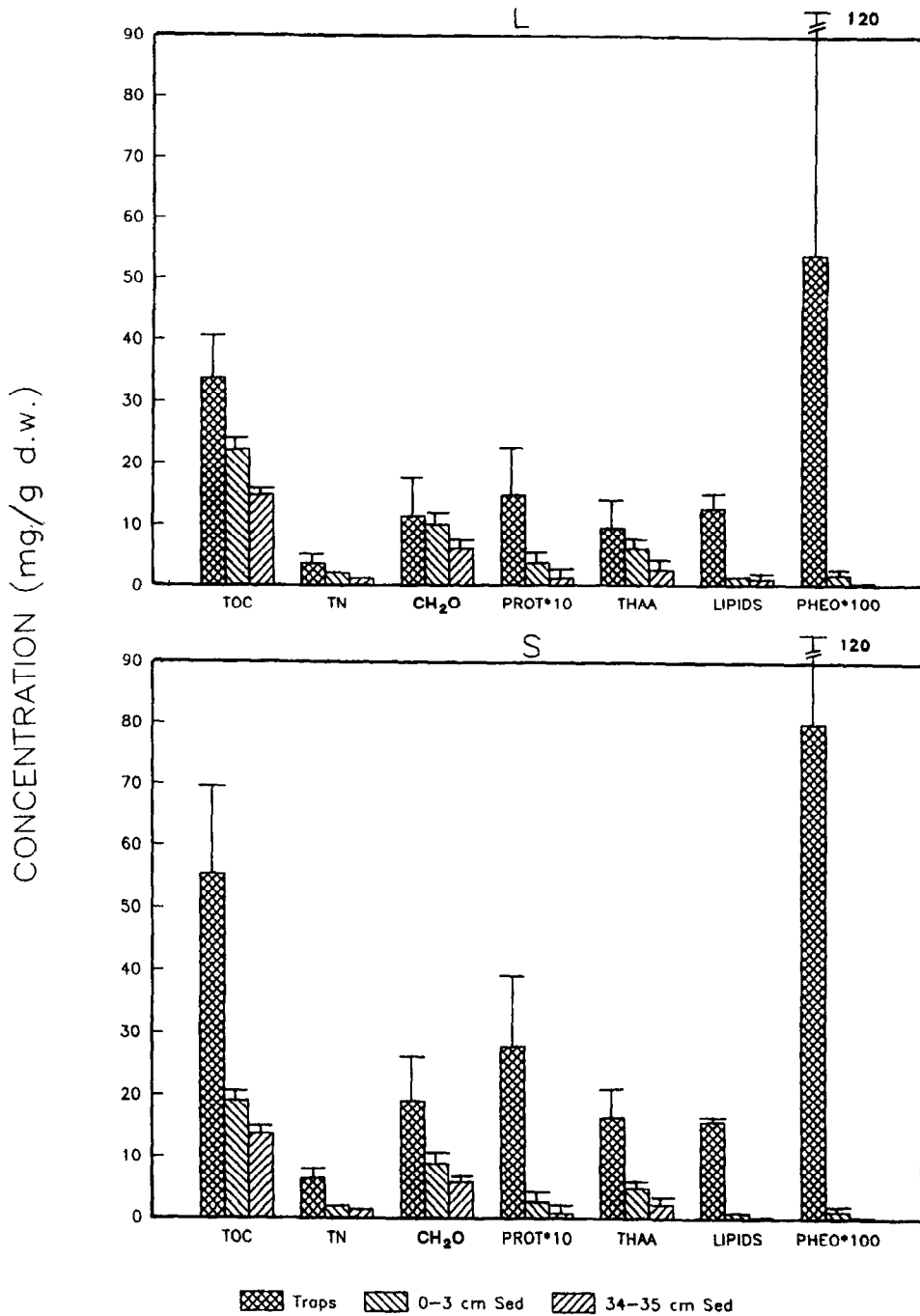


Fig. 3. Average of May and July concentrations of measured parameters in sediment traps, surficial sediments (0–3 cm), and bottom sediments (34–35 cm).

Better defined sedimentation rates, near-surface carbon gradients and bioturbation coefficients are required to evaluate the situation at the present sites, but both the greater influx and mixing rates at *L* suggest a high proportion of diagenetic mineralization of OM, rather than loss to the water column (cf. with sediment accumulation efficiencies in relative reactivity section). Lateral input of already-degraded sedimentary OM, perhaps of concern at *L*, could also contribute to the differences between the traps and surficial sediments. An additional factor might be the loss of organic-rich flocculent material at the sediment–water interface during boxcore sampling.

3.3. Distribution of solid phase OM with depth in the sediment

The loss of OM with depth in the sediment is much less dramatic than that between the traps and surficial sediments (the loss of TOC between 0–3 and 35 cm deep sediments is ~31% vs. 50% between settling particles and 0–3 cm sediments). The depth–concentration profiles (Figs. 4–6) show that most of the solid phase degradation occurs within the top 5 cm. The patterns are not smooth in this zone of intense bioturbation (90% of the macrofauna are found in the top 5 cm; Ouellet, 1982). More regular decreases in concentration with depth are apparent for some components (e.g. lipids and pheopigments) indicating that their greater reactivities are able to sustain steep gradients in spite of biological mixing (see section on relative reactivity below). The percentages of the whole-core decrease of TOC and TN lost in the first 5 cm are 42–43% at *L* and 58–74% at *S*, respectively. Below 5 cm, the concentrations of the different components continue to decline slowly at *L* and are nearly constant at *S*. This difference in the mineralization rate of OM at the two stations is related to the sedimentation rates: 0.6–1.6 cm/yr at *L* and ~0.2 cm/yr at *S* (see section on geographical trends below).

The proportion of carbon contributed by each of the different characterized components also decreases with depth in the cores (Fig. 1). The decrease

is stronger for proteins and THAA and only slight for CH₂O. The contribution of PROT, THAA, LIP and CH₂O decrease from approximately 0.7 to 0.3, 11 to 7.3, 3.8 to 3.1, and 18 to 16% TOC, respectively. A similar decrease is observed for the nitrogen fraction, with THAA-N going from 39 to 25 and Prot-N from 2.6 to 1.3% TN. Conversely, the non-characterized fraction of TOC increases with depth in the cores from 66 to 73% TOC. These changes reflect the preferential degradation of most of the components studied and the relative increase of the uncharacterized fraction, possibly enriched in more refractory “humic” type material, during the decay of OM.

3.4. Distribution of porewater OM with depth in the sediment

The concentration of dissolved organics also changed with depth, showing patterns opposite to those of the solid phase components (i.e. low surface values and subsequent increases with depth, Fig. 4). The surface zone of most intense OM mineralization in the solid phase (0–5 cm), where production of dissolved compounds would be expected to be highest, in fact coincides with minimal porewater DOM levels. Removal processes, i.e. diffusion, irrigation and consumption, must be very intense.

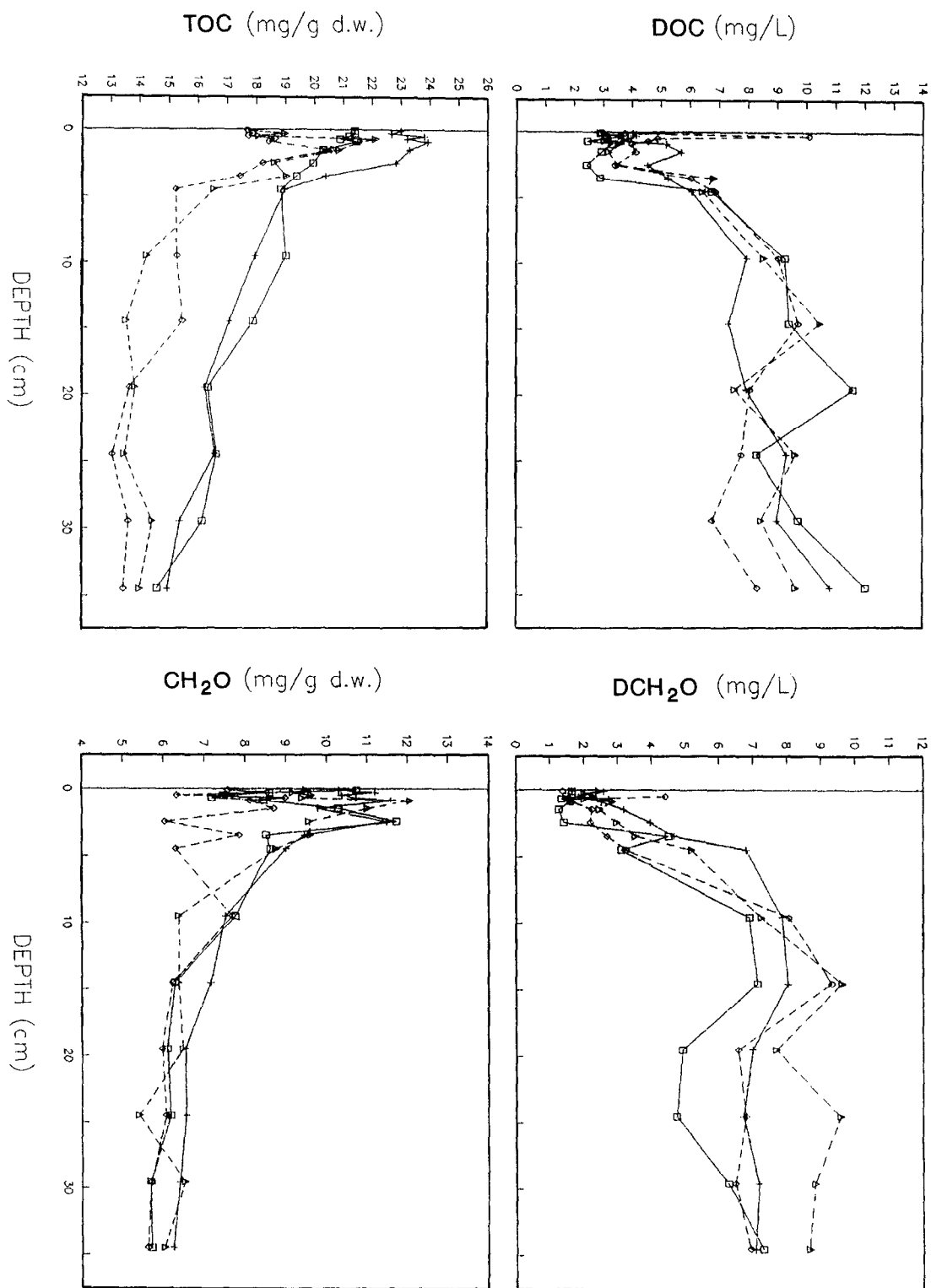
The concentration difference of DOC between the water column average (1.4 mg/l; Gearing and Pocklington, 1990) and the top 0.1–0.3 cm sediments (2.9–10 mg/l) can be used to estimate the diffusive flux (*J*) out of the sediment according to:

$$J = D_s \frac{d[\text{DOC}]}{dz}$$

(Berner, 1980) using 1×10^{-6} cm²/s as the effective molecular diffusion coefficient (*D_s*). These calculations provided a mean *J_{DOC}* of 20 mg C/m²/d. This value is equivalent to only 13% of the average carbon loss (input fluxes – burial rates) or 22% of carbon burial in these sediments (see section on reactivities below).

Low surface porewater DOM concentrations have

Fig. 4. Depth concentration profiles of organic carbon and carbohydrates in the solid phase and dissolved in porewaters (both stations and sampling periods). □ = *L* May, + = *L* July; ◇ = *S* May; △ = *S* July.



been reported by Krom and Westrich (1980) and by Chin and Gschwend (1991) who suggested that they could result from the mineralization of DOM by microbes and from diffusion and bioirrigation into overlying waters. Benthic DOC fluxes have been recognized as a potentially important pathway in the oceanic carbon cycle (comparable to the riverine DOC and POC inputs and to the remineralization and burial of carbon in the sediments; see Burdige and Homstead, 1994, and references therein). The latter authors reported that molecular diffusion appeared to control benthic fluxes in Chesapeake Bay, even at a heavily bioturbated site where DOC fluxes were unexpectedly low. The stimulation of DOC consumption by macrofauna or bacteria due to enhanced oxygen transport through bioirrigation was proposed as a possible explanation of this apparent contradiction.

The ventilation and irrigation of burrows in Laurentian Trough sediments can contribute to the loss of subsurface DOM to the overlying waters and to the stimulation of microbial activity through enhanced transport of oxidants and oxidation end products (Rhoads, 1974; Aller, 1982; Sundby et al., 1983; Aller and Aller, 1986). The tendency, best seen in the May cores, for DOC and DCH_2O to develop a minimum at 2–3 cm down in the cores (Fig. 4), suggests an intense consumption of DOM, possibly enhanced by irrigation. The gradual shift of the chemical composition of DOC with sediment depth indicates that consumption is likely a relevant factor determining the fate of DOM in these sediments.

As far as we know, this is the first time that dissolved free and combined amino acids and dissolved carbohydrates have been measured simultaneously in sediment porewaters. The relative contribution of these components to DOC shows marked changes with sediment depth. The contribution of DFAA is more important in the top 5–10 cm, where they represent 3.6–12% DOC; below this depth DCAA are relatively more abundant (6.5–15 vs. 1.7–4.9% DOC for DFAA). The two fractions represent only about 1.4% DOC each in the bottom of the cores. In contrast, the contribution of DCH_2O in-

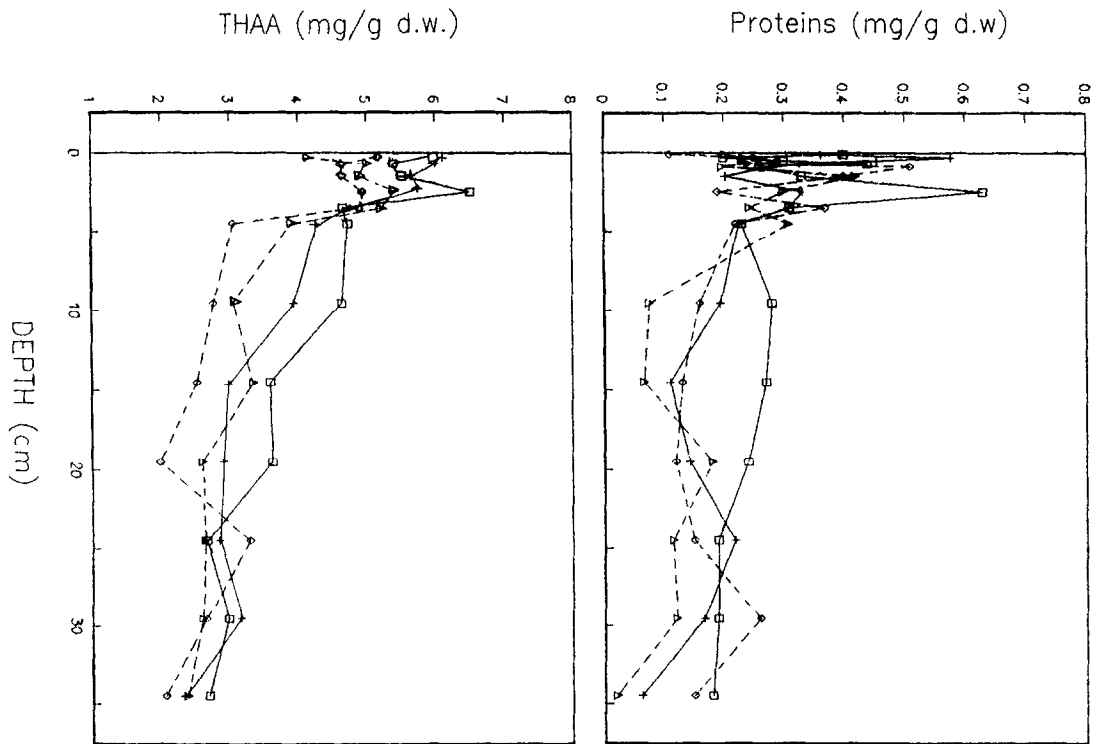
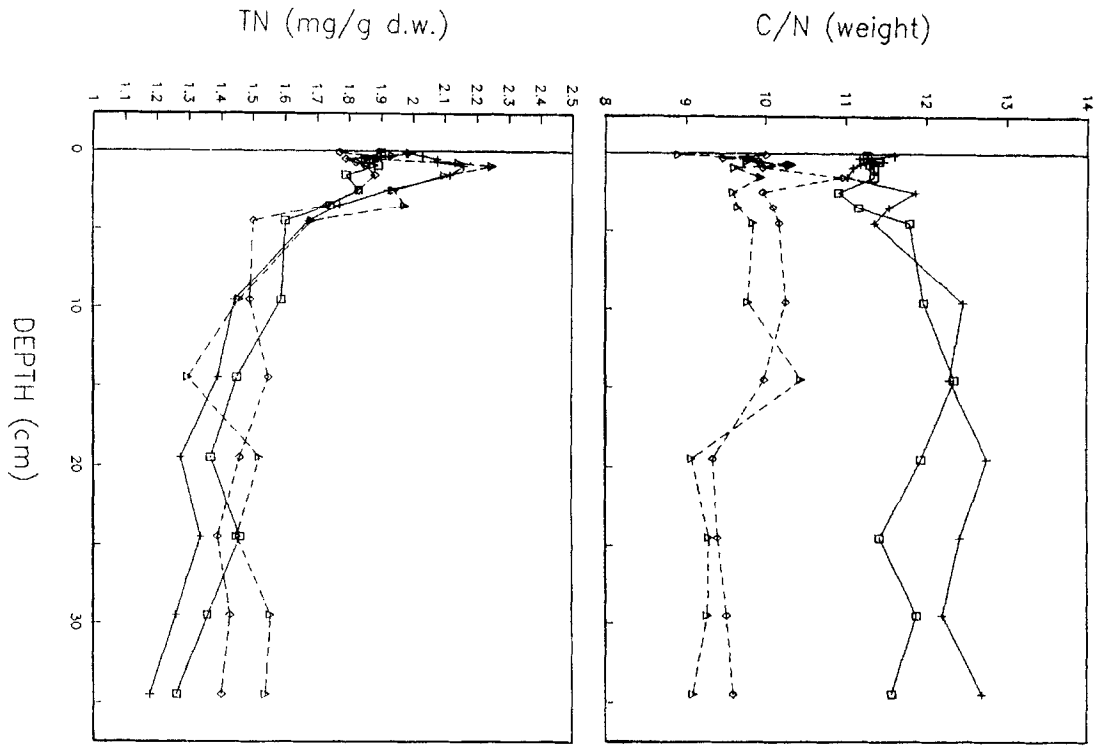
creases with sediment depth (from 11–19 to 25–40% DOC; Fig. 2). This pattern is consistent with a progressive consumption of DOM from more labile (DFAA) to more recalcitrant (DCH_2O) components with sediment depth. Geopolymerization (e.g. Maillard condensation of amino acids and CH_2O) or adsorption may be also important factors determining the amount and composition of DOC. The high proportion of uncharacterized DOC at the top of the cores indicates the presence of some other labile components which would be rapidly consumed. Volatile fatty acids may be included in this fraction as they are important intermediaries in the degradation of OM, present high turnover rates and make up a substantial fraction of porewater DOC (Sansone and Martens, 1982; Barcelona, 1984; Sansone, 1986).

3.5. Relative reactivity of OM components during early diagenesis

The reaction rates of the organic components were examined using different approaches - comparison of concentrations in the traps and in surface sediments; comparison of inventory remaining in the top 0–3 cm; input vs. burial rates; and one-*G* model calculations - all of which yield similar results in terms of relative rapidity of mineralization: PHEO > LIP > PROT > TN ≈ THAA > TOC > CH_2O . An important corollary of this is that lipids are important substrates near the sediment–water interface whereas CH_2O and THAA would constitute the principal energy sources in deeper sediment layers.

In the first instance, the mean sediment trap concentrations of the different components were compared with those in 0–3 cm surficial sediments. Overall, the parameters showing the least change were carbohydrates, TOC, TN, and THAA, whereas proteins and especially lipids and pheopigments were the most reactive. The magnitude of this difference (expressed as the percentage of the original trap concentrations) gives a first indication of the relative reactivity of the components: CH_2O (38%) < TOC (54%) < THAA (58%) ≤ TN (60%) < PROT (85%) < LIP (92%) < PHEO (98%). Some of the variabil-

Fig. 5. Solid phase profiles of total nitrogen, C/N ratios, total hydrolyzable amino acids, and proteins. □ = L May; + = L July; ◇ = S May; △ = S July.



ity correlated with geographic differences, with more apparent loss occurring at *S* (77% vs. 55% at *L*). The extent of sedimentary degradation and the relative reactivity of the components indicated by these results are comparable to those reported for Dabob Bay where 30–40% syringyl phenols, 60% TOC, 70% TN, 65–75% of neutral sugars, 90% of plankton lipids and 99% of pigments were degraded near the sediment–water interface (Hedges et al., 1988).

Within the sediments, there remains considerable divergence in the loss rates. Between the top 0–3 cm and the bottom of the cores, TOC and TN decrease by 31% (18–24 to 13–15 and 1.8–2.2 to 1.2–1.5 mg/g, respectively; Figs. 4 and 5). CH₂O levels drop more, ≈ 38% (6–12 to 5.6–6.2 mg/g, Fig. 4) while THAA experience an even stronger decay, ≈ 56% (4.3–6.5 to 2.1–2.7 mg/g, Fig. 5). The concentrations of lipids (0.8–1.5 to 0.3–1.1 mg/g, Fig. 6) and proteins (0.1–0.6 to 0.02–0.18 mg/g, Fig. 5) are more irregular, but show overall losses of 48 and 68%, respectively. The PHEO fraction

(chiefly pheophorbide a with 11–27% pheophytins) shows the most rapid attenuation, losing 74% with depth (8.2–20 to 2.7–4.4 μg/g, Fig. 6).

The second approach assumes that the trap measurements are representative of both the average composition and the average annual fluxes to the sediment surface. The inventories of the organic components and mineral fraction were calculated for the top 3 cm. These values for each organic component were then normalized to represent one year's average accumulation according to the following equation:

one year inventory

$$= \frac{0-3 \text{ cm inventory}}{\text{annual mineral flux}} \times \frac{\text{annual mineral flux}}{0-3 \text{ cm mineral inventory}}$$

The one-year inventory for each compound was then divided by the annual influx to estimate the accumulation efficiencies. The results, presented in

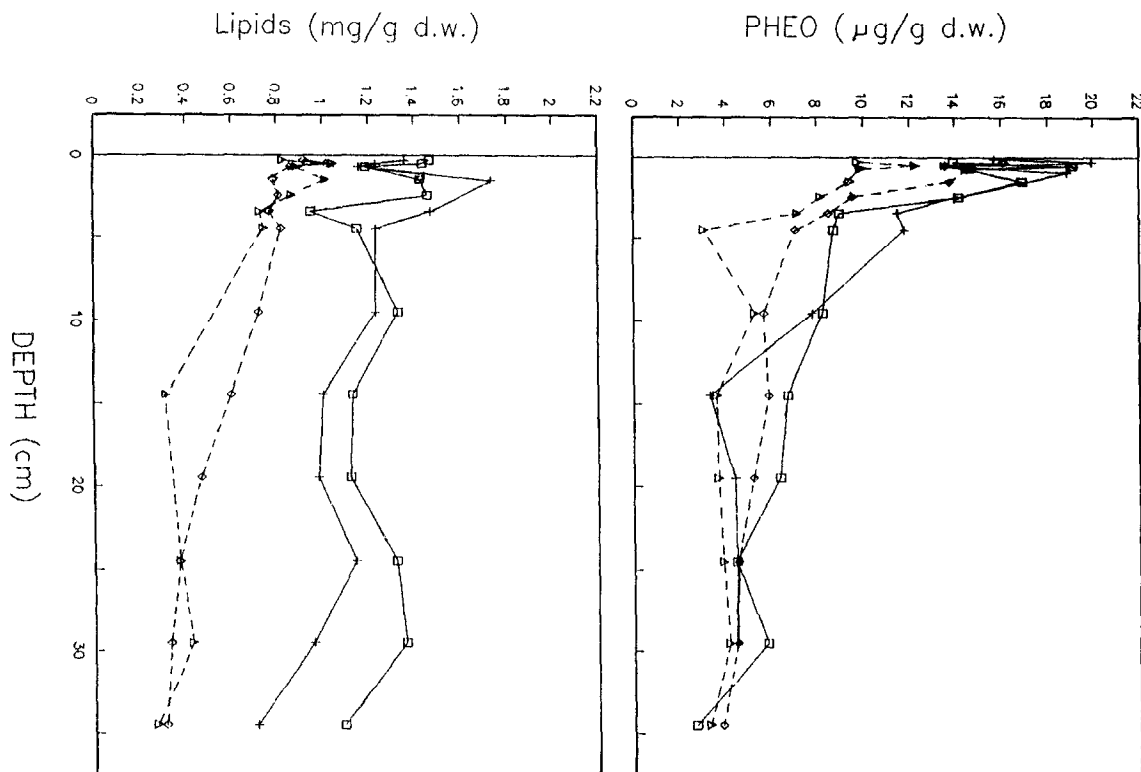


Fig. 6. Solid phase profiles of total lipids and pheopigments. □ = *L* May; + = *L* July; ◇ = *S* May; △ = *S* July.

Table 3, indicate that a grand mean of $67 \pm 27\%$ of the water column organic fluxes ($56 \pm 32\%$ at *L* and $79 \pm 16\%$ at *S*) is degraded near the sediment–water interface. As in the previous calculations, carbohydrates are clearly the most persistent fraction; TOC, TN and THAA are accumulated with similar efficiencies (30–60%) and PROT, LIP and PHEO show the lowest values. Lipid decay accounts for a major fraction of TOC loss (30–68%), followed by THAA (13–14%) and CH_2O (3–12%).

The third approach examines the loss rates over the entire depth of the cores. The rates of input at the surface were compared with burial rates calculated using the stable, low residual concentrations at 35 cm depth, multiplied by the bulk sedimentation rate (ω), and corrected for porosity. At station *L*, these results may overestimate the actual burial rates because some profiles continue a slow decrease at depth (Figs. 4 and 5). For the calculations, the trap-derived ω -values were used (0.6–0.2 cm/yr,

L–*S*). ^{210}Pb data yield comparable values at *S* (0.23 cm/yr) but much higher results at *L* (1–1.6 cm/yr; Silverberg et al., 1986; Smith, pers. commun., 1991; C. Gobeil and M. Lebeuf, pers. commun., 1992). This discrepancy may be due to a lack of trap samples during high sedimentation events and/or to the modification of apparent ^{210}Pb activity gradients by deep bioturbation (Silverberg et al., 1986). Thus, the burial rates at *L* are considered as provisional estimates. The complex pattern of seasonal sedimentation, the possibility of strong horizontal gradients and perhaps of lateral inputs are still not well understood at this site.

The burial rates ranged over four orders of magnitude, from 0.0005 mg/cm²/yr for PHEO to 6 mg/cm²/yr for TOC and are consistently higher at *L*, reflecting the higher sedimentation rates. The burial rates of TOC (1.9–6 mg/cm²/yr; *S*–*L*), are in the range of values predicted by the models which relate burial rates and sedimentation rates; about

Table 3

One-year inventories of the different components in the top 0–3 cm sediments and burial rates at 35 cm depth compared with the average water column fluxes

Component	Station	Inventory (mg/cm ² /yr)	Burial rate (mg/cm ² /yr)	Trap fluxes (mg/cm ² /yr)	Inventory efficiency (% trap flux)	Burial efficiency (% trap flux)
Mineral ^a	<i>L</i>	350	402	350	100	115
	<i>S</i>	112	134	112	100	120
CH	<i>L</i>	3.83	2.46	4.21	91.0	58.4
	<i>S</i>	1.02	0.80	2.37	43.0	33.8
TOC	<i>L</i>	7.97	6.10	12.6	63.2	48.5
	<i>S</i>	2.24	1.89	6.88	32.6	27.5
TN	<i>L</i>	0.70	0.50	1.30	53.8	38.5
	<i>S</i>	0.22	0.20	0.79	27.8	25.7
THAA	<i>L</i>	2.15	1.04	3.50	61.4	29.7
	<i>S</i>	0.57	0.31	2.03	28.1	15.1
PROT	<i>L</i>	0.13	0.05	0.55	23.6	9.09
	<i>S</i>	0.03	0.01	0.34	10.3	3.53
LIPIDS	<i>L</i>	0.53	0.37	4.73	11.2	7.82
	<i>S</i>	0.10	0.04	1.96	5.10	2.04
PHEO	<i>L</i>	0.0057	0.0015	0.20	2.85	0.75
	<i>S</i>	0.0013	0.0005	0.10	1.30	0.49

Inventories and burial rates are the average of both cores taken at each station.

Inventory: $C \times p(1 - \phi)$, where C is concentration, p is sediment density (2.65 g/cm³), and ϕ is porosity.

Burial rate: $\omega \times C \times p(1 - \phi)$, where ω is sedimentation rate (0.6 cm/yr at *L*, 0.2 cm/y at *S*).

^a Residual fraction after the subtraction of organic matter (TOC \times 1.8).

1–10 mg C/cm²/yr for sedimentation rates of 0.1–1 cm/yr (Henrichs and Reeburgh, 1987; Ingall and Cappellen, 1990). The burial efficiencies at 35 cm depth ranged from 0.5% for PHEO to 58% for CH₂O and were 1.5–3.8 times higher at *L* (Table 3). The values obtained for TOC (27–48%), TN (26–38%) and THAA (15–30%) are very similar to those reported for Dabob Bay and Saanich Inlet (35–36, 28–30 and 15–20%, respectively; Cowie and Hedges, 1991). The percentages of the trap flux which disappear between the surface inventory and 35 cm depth are: 0.8–2.1% for PHEO < 3.1–3.4% for LIP < 2–15% for TN ~ 5–15% for TOC ~ 6.8–14% for PROT < 9–33% for CH₂O ~ 13–32% for THAA (S–L). The higher losses of THAA and CH₂O (26–31 and 26–29% of TOC loss, respectively), shows that they are the most important substrates in the subsurface sediment. The order of disappearance (lipids at the surface and CH₂O and THAA in the subsurface) is likely related to the energy yields when consumed by benthic organisms or bacteria, 19.3 kcal/g for lipids vs. 4.1–5.4 kcal/g for CH₂O and proteins (Martin et al., 1981).

A final approach involves fitting depth–concentration curves derived from diagenetic models to the vertical profiles. The high variability observed in the bioturbated top few cm of the cores makes it very difficult to determine a realistic surficial concentration and apply a model to the observed distributions. The best exceptions to this situation are the profiles of TOC, TN, THAA and PHEO at *L*. For these profiles, a classic one-*G* model (Berner, 1980; Rice and Rhoads, 1989) was tried to obtain an estimate of the decay constants:

$$G_z = G_u + (G_s - G_u)e^{-\lambda z} \quad (1)$$

where G_z is the concentration of OM at a specified depth z , G_u is the concentration of unreactive OM, i.e. that of the bottom of the core, $G_s - G_u$ is the concentration of reactive OM, with G_s as the concentration in the top 0–3 cm, and λ is the attenuation factor:

$$\lambda = \frac{\omega}{2D_b} - \sqrt{\left(\frac{\omega}{2D_b}\right)^2 + \frac{k}{D_b}} \quad (2)$$

where D_b is the biological mixing coefficient (11.7 cm²/yr for *L*; Sundby and Silverberg, 1985; Silver-

berg et al., 1986), ω is the sedimentation rate (assumed to be 0.6 cm/yr at *L*), and k is the apparent first-order decay constant of the species in question. The values of G_u and G_s were obtained from the profiles. The model was applied to the data assuming constant D_b , ω and k , by a non-linear regression procedure which obtains least-squares estimates of the unknown parameter (λ). The model results are shown in Fig. 7.

The high R^2 -values of the regressions (0.83–0.95; Fig. 7), indicate a good agreement between the data and the model. The reactivities deduced from the first-order decay constants (k) calculated from Eq. 2, are more homogeneous than those obtained from inventory and burial rate calculations but suggest a similar general trend: 0.07–0.16 yr⁻¹ for TOC, 0.10–0.16 yr⁻¹ for TN, 0.11–0.14 yr⁻¹ for THAA and 0.14–0.16 yr⁻¹ for PHED (average residence times of 10.4, 8.0, 7.8 and 6.4 yr, respectively).

To summarize, compatible trends in reactivity were noted when comparing the organic matter composition data from several viewpoints, with four measured parameters (TOC, TN, CH₂O and THAA) being significantly less reactive than the other three (proteins, lipids and pheopigments). Although all seven parameters decreased during the progressive decay of organic matter from sinking particles to deeper sediments, there was a rapid loss of proteins, lipids and pheopigments near the sediment–water interface, whereas CH₂O and THAA accounted for a major fraction of TOC loss in deeper sediment layers.

3.6. Geographical differences

In the preceding paper (Colombo et al., 1995a) we showed that there was considerable difference in the composition and flux of OM in settling particles between the landward and seaward stations. Although both sites displayed high overall OM fluxes, and broadly similar bulk composition, including a significant terrigenous contribution, at site *L* the organic component concentrations were lower, the terrigenous fraction was higher, and the much higher bulk sedimentation rates insured a higher vertical flux of all organic components. The results from the underlying sediments reflect these differences in the input of OM from the water column.

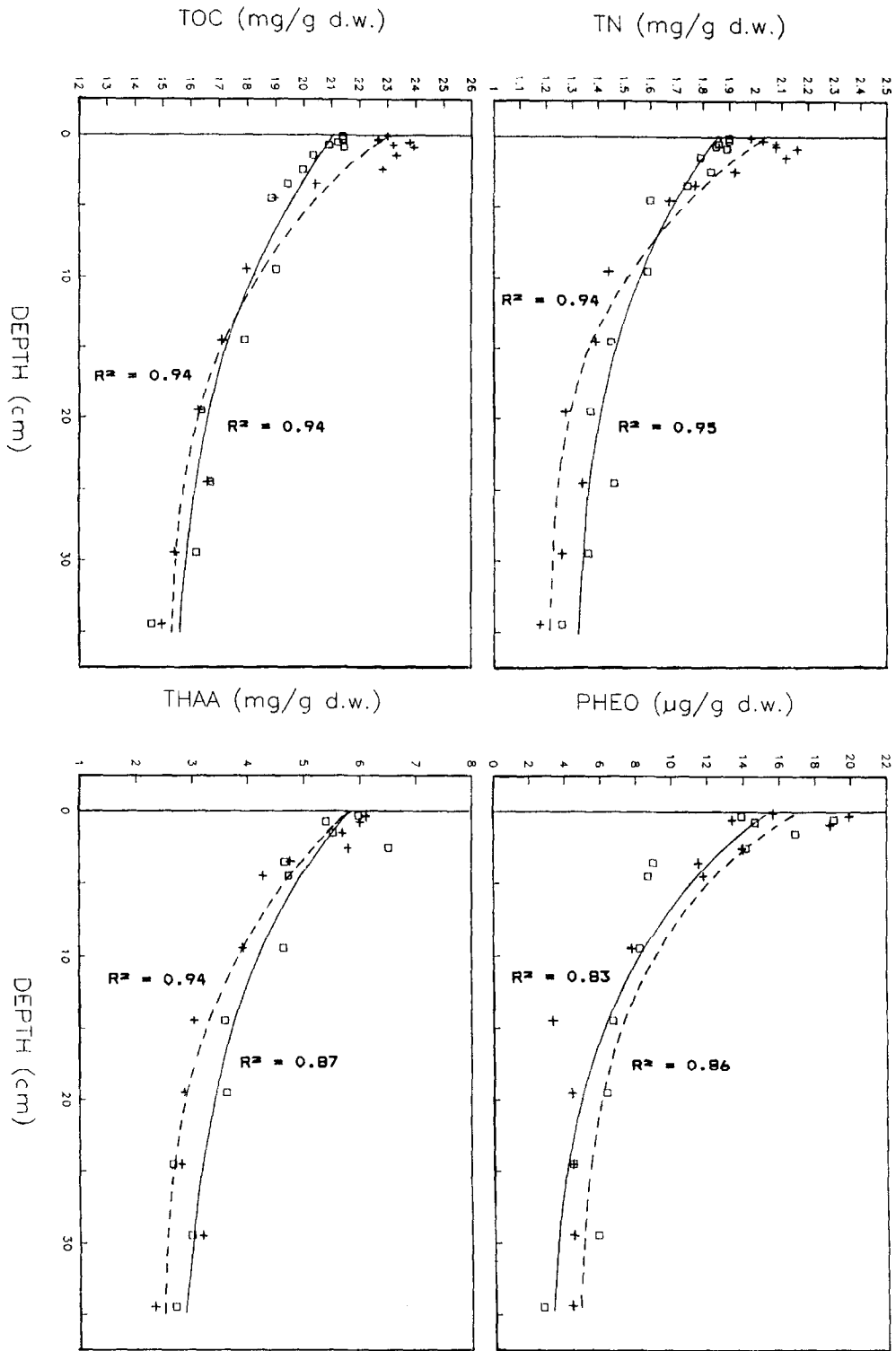


Fig. 7. One-G models fitted to the most regular profiles. \square = L May; + = L July.

Sediments from the landward station have higher C/N ratios throughout the cores (11.6 ± 0.5 vs. 9.8 ± 0.4 at *S*; Fig. 5), and excepting TN, they show higher concentrations of the OM constituents (Figs. 4–6). However, due to the intra-station variability, only the differences in TOC (16%), THAA (20%) and lipid levels (53%) are significant. The differences diminish with depth (8% for TOC, 11% for THAA and 0% for PHEO at 35 cm) as the OM becomes more and more degraded. Using C/N = 13 and C/N = 6 for the terrestrial and marine end members, respectively (Colombo et al., 1995a), the difference in C/N ratios indicates that the terrestrial fraction amounts to ~80% at *L* and 50% at *S*.

The shape of OM profiles also reflects the geographical trend (Figs. 4–6). The slopes of the regressions of the different components and sediment depth in the 5–35 cm section are consistently higher at *L* (2–4 times), reflecting a continuous OM decay with depth. This is also reflected in the slopes of the linear regression between C/N ratios and sediment depth (Fig. 5): at *S* the slopes are negative (-0.016 , -0.020 ; $r = -0.44$, -0.56) whereas at *L* they show more significant positive values (0.016 – 0.043 ; $r = 0.49$ – 0.82). These differences are statistically significant (covariance analysis, $p = 0.05$), for the cores obtained in July, suggesting a continued OM decay with a preferential nitrogen loss at *L*. The depth distribution of the products of OM decay in porewaters also supports this interpretation. The profiles of phosphates, silicates and alkalinity show a marked increase downwards in the cores at *L* while at *S* they are more constant (Bouchard, 1983). The same trend is suggested in DOC profiles (Fig. 4), possibly reflecting the continuous release of OM oxidation products at *L*.

The geographical trends observed in the concentration and depth distribution of OM in these sediments reflect the different ecological conditions determined by the sedimentation rates and OM fluxes at the two sites. The greater sedimentation rates and OM fluxes at *L* combine with the higher rates of bioturbation and the presence of deep-burrowing organisms (Ouellet, 1982) to insure a deeper incorporation of OM in the sediments which results in higher inventories and burial efficiencies. OM is simply not buried as quickly at the seaward site and, even though concentrations in settling particles are higher,

they are also more marine in character, i.e. more readily degradable, so the higher concentrations in the influx are not preserved in the sediments. Thus, although the greatest losses in organic compounds occur in the top few centimetres at both sites, there is very little easily degradable material left below 5 cm depth at *S*, while continued degradation is possible at depth at station *L*.

References

- Aller, R.C., 1982. The effects of macrobenthos on chemical properties of marine sediment and overlying water. In: P.L. McCall and M.J.S. Tevesz (Editors), *Animal Sediment Relations*. Plenum, New York, NY, pp. 53–102.
- Aller, J.Y. and Aller, R.C., 1986. Evidence of localized enhancement of biological activity associated with tube and burrow structures in deep-sea sediments at the HEBBLE site, western North Atlantic. *Deep-Sea Res.*, 33: 755–790.
- Aller, R.C. and Mackin, J.E., 1984. Preservation of reactive organic matter in marine sediments. *Earth Planet. Sci. Lett.*, 70: 260–266.
- Alperin, M.J., Albert, D.B. and Martens, C.S., 1994. Seasonal variations in production and consumption rates of dissolved organic carbon in an organic-rich coastal sediment. *Geochim. Cosmochim. Acta*, 58: 4909–4930.
- Barcelona, M.J., 1984. Dissolved organic carbon and volatile fatty acids in marine sediment pore waters. *Geochim. Cosmochim. Acta*, 44: 1977–1984.
- Berner, R.A., 1980. *Early Diagenesis. A Theoretical Approach*. Princeton Univ. Press, Princeton, NJ.
- Bouchard, G., 1983. Variations des paramètres biogéochimiques dans les sédiments du Chenal Laurentien. Thesis. Univ. Québec, Rimouski, 161 pp.
- Burdige, D.J. and Homstead, J., 1994. Fluxes of dissolved organic carbon from Chesapeake Bay sediments. *Geochim. Cosmochim. Acta*, 58: 3407–3424.
- Chin, Y.-P. and Gschwend, P.M., 1991. The abundance, distribution, and configuration of porewater organic colloids in recent sediments. *Geochim. Cosmochim. Acta*, 55: 1309–1317.
- Colombo, J.C., Silverberg, N. and Gearing, J.N., 1995a. Biogeochemistry of organic matter in the Laurentian Trough, I. Composition and vertical fluxes of rapidly settling particles. *Mar. Chem.*, 51: 277–293, this issue.
- Colombo, J.C., Silverberg, N. and Gearing, J.N., 1995b. Amino acid biogeochemistry in the Laurentian Trough: vertical particle fluxes and early diagenesis. *Geochim. Cosmochim. Acta*, submitted.
- 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., 1991. 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., 1992. Sources and reactivities of amino acids in a coastal marine environment. *Limnol. Oceanogr.*, 37: 703–724.
- Daumas, R.A. and Saliot, A., 1977. The inventory of marine organic chemistry. *Mar. Chem.*, 5: 417–427.
- Degens, E.T., 1965. *Geochemistry of Sediments. A Brief Survey*. Prentice-Hall, Englewood Cliffs, NJ, 342 pp.
- Degens, E.T., 1967. Diagenesis of organic matter. In: G. Larsen and G.V. Chilingar (Editors), *Diagenesis in Sediments*. Elsevier, New York, NY, pp. 343–390.
- Downs, J.N. and Lorenzen, C.J., 1985. Carbon: pheopigment ratios of zooplankton fecal pellets as an index of herbivorous feeding. *Limnol. Oceanogr.*, 30: 1024–1036.
- Emerson, S., Fischer, K., Reimers, C. and Heggie, D., 1985. Organic carbon dynamics and preservation in deep-sea sediments. *Deep-Sea Res.*, 32: 1–21.
- Farrington, J.W., 1992. Marine organic geochemistry: review and challenges for the future. *Mar. Chem.*, 39: 1–4.
- Farrington, J.W. and Tripp, B.W., 1977. Hydrocarbons in western North Atlantic surface sediments. *Geochim. Cosmochim. Acta*, 41: 1627–1641.
- Furlong, E.T. and Carpenter, R., 1988. Pigment preservation and mineralization in oxic coastal marine sediments. *Geochim. Cosmochim. Acta*, 52: 87–99.
- Gearing, J.N. and Pocklington, R., 1990. Organic geochemical studies in the St. Lawrence Estuary. In: M.I. El-Sabh and N. Silverberg (Editors), *Oceanography of a Large-Scale Estuarine System: The St. Lawrence*. Springer, New York, NY, pp. 170–201.
- Gearing P., Gearing, J.N., Lytle, T.F. and Lytle, J.S., 1976. Hydrocarbons in 60 northeast Gulf of Mexico shelf sediments: a preliminary study. *Geochim. Cosmochim. Acta*, 40: 1005–1017.
- Gordon Jr., D.C. and Sutcliffe Jr, W.H., 1973. A new dry combustion method for the simultaneous determination of total organic carbon and nitrogen in seawater. *Mar. Chem.*, 1: 231–244.
- Gough, M.A. and Mantoura, R.F.C., 1990. Advanced analytical methods for the characterization of macromolecular marine organic matter. In E.R. Hilf and W. Tuszynski (Editors), *Mass Spectrometry of Large Non-Volatile Molecules for Marine Organic Chemistry*. World Sci., London, pp. 114–130.
- Graf, G., 1989. Benthic–pelagic coupling in a deep-sea benthic community. *Nature*, 341: 437–439.
- 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.
- Hargrave, B.T., 1975. The importance of total and mixed-layer depth in the supply of organic material to bottom communities. *Symp. Biol. Hung.*, 15: 157–165.
- Hatcher, P.G., Simoneit, B.R.T., Mackenzie, F.T., Neumann, A.C., Thorstenson, D.C. and Gerchakov, S.M., 1982. Organic geochemistry and pore water chemistry of sediments from Mangrove Lake, Bermuda. *Org. Geochem.*, 4: 93–112.
- Hatcher, P.G., Spiker, E.C., Szeverenyi, N.M. and Maciel, G.E., 1983. Selective preservation and origin of petroleum-forming aquatic kerogen. *Nature*, 305: 498–501.
- Hedges, J.I., Clark, W.A. and Cowie, G.L., 1988. Fluxes and reactivities of organic matter in a coastal marine bay. *Limnol. Oceanogr.*, 33: 1137–1152.
- Henrichs, S.M. and Farrington, J.W., 1984. Peru upwelling region sediments near 15°S. 1. Remineralization and accumulation of organic matter. *Limnol. Oceanogr.*, 29: 1–19.
- Henrichs, S.M. and Farrington, J.W., 1987. Early diagenesis of amino acids and organic matter in two coastal marine sediments. *Geochim. Cosmochim. Acta*, 51: 1–15.
- Henrichs, S.M. and Reeburgh, W.S., 1987. Anaerobic mineralization of marine sediment organic matter: rates and the role of anaerobic processes in the oceanic carbon economy. *Geomicrobiol. J.*, 5: 191–237.
- Henrichs, S.M., Farrington, J.W. and Lee, C., 1984. Peru upwelling region sediments near 15°S. 2. Dissolved free and total hydrozable amino acids. *Limnol. Oceanogr.*, 29: 20–34.
- Ingall, E.D. and Van Cappellen, P., 1990. Relation between sedimentation rate and burial of organic phosphorus and organic carbon in marine sediments. *Geochim. Cosmochim. Acta*, 54: 373–386.
- Jorgensen, B.B., Bang, M. and Blackburn, T.H., 1990. Anaerobic mineralization in marine sediments from the Baltic Sea–North Sea transition. *Mar. Ecol. Prog. Ser.*, 59: 39–54.
- Klok, J., Baas, M., Cox, H.C., de Leeuw, J.W., Rijpstra, W.I.C., and Schenck, P.A., 1984. Qualitative and quantitative characterization of the total organic matter in a recent marine sediment (Part II). *Org. Geochem.*, 6: 265–278.
- Krom, M.D. and Sholkovitz, E.R., 1977. Nature and reactions of dissolved organic matter in the interstitial waters of marine sediments. *Geochim. Cosmochim. Acta*, 41: 1565–1573.
- Krom, M.D. and Westrich, J.T., 1980. Dissolved organic matter in the pore waters of recent marine sediments; a review. *Coll. Int. CNRS*, 293: 103–110.
- Martin, D.W., Mayer, P.A. and Rodwell, V.W., 1981. *Harper's Review of Biochemistry*. Lange, Los Altos, CA, 614 pp.
- Mayer, L.M., 1985. Geochemistry of humic substances in estuarine environments. In: G.R. Aiken, D.M. McKnight, R.L. Wershaw and P. Maccarthy (Editors), *Humic Substances in Soil, Sediment, and Water*. Wiley, New York, NY, pp. 211–232.
- Mayer, L.M., Macko, S.A. and Cammen, L., 1988. Provenance, concentration and nature of sedimentary organic nitrogen in the Gulf of Maine. *Mar. Chem.*, 25: 291–304.
- Mopper, K., 1977. Sugars and uronic acids in sediment and water from the Black Sea and North Sea with emphasis on analytical techniques. *Mar. Chem.*, 5: 585–603.
- Müller, D.J. and Suess, E., 1979. Productivity, sedimentation rate, and sedimentary organic matter in the oceans. 1. Organic carbon preservation. *Deep-Sea Res.*, 26: 1347–1362.
- Neal, A.C., Prah, F.G., Eglinton, G., O'Hara, S.C.M. and Corner, E.D.S., 1986. Lipid changes during planktonic feeding sequence involving unicellular algae, *Elminius nauplii* and adult *Calanus*. *J. Mar. Biol. Assoc. UK*, 66: 1–13.
- Ouellet, G., 1982. Etude de l'interaction des animaux benthiques avec les sédiments du Chenal Laurentien. Thesis. Univ. Québec, Rimouski, 188 pp.
- Prah, F.G., Bennett, J.T. and Carpenter, R., 1980. The early

- diagenesis of aliphatic hydrocarbons and organic matter in sedimentary particulates from Dabob Bay, Washington. *Geochim. Cosmochim. Acta*, 44: 1967–1976.
- Reeburgh, W.S., 1967. An improved interstitial water sampler. *Limnol. Oceanogr.*, 12: 163–165.
- Rhoads, D.C., 1974. Organism–sediment relations on the muddy sea floor. *Oceanogr. Mar. Biol. Ann. Rev.*, 12: 263–300.
- Rice, D.L. and Rhoads, D.C., 1989. Early diagenesis of organic matter and the nutritional value of sediment. In: G. Lopez, G. Taghon and J. Levinton (Editors), *Ecology of Marine Deposit Feeders. Lectures and Notes on Coastal and Estuarine Studies*. Springer, New York, NY, pp. 59–97.
- Romankevich, E.A., 1984. *Geochemistry of Organic Matter in the Ocean*. Springer, New York, NY.
- Sansone, F.J., 1986. Depth distribution of short-chain organic acid turnover in Cape Lookout Bight sediments. *Geochim. Cosmochim. Acta*, 50: 99–105.
- Sansone, F.J. and Martens, C.S., 1982. Volatile fatty acid cycling in organic-rich marine environments. *Geochim. Cosmochim. Acta*, 46: 1575–1589.
- Silverberg, N., Edenborn, H.M. and Belzile, N., 1985. Sediment response to seasonal variations in organic matter input. In: A.C. Sigleo and A. Hattori (Editors), *Marine and Estuarine Geochemistry*. Lewis, pp. 69–80.
- Silverberg, N., Nguyen, H.V., Delibrias, G., Koide, M., Sundby, B., Yokoyama, Y. and Chesselet, R., 1986. Radionuclide profiles, sedimentation rates, and bioturbation in modern sediments of the Laurentian Trough, Gulf of St. Lawrence. *Oceanol. Acta*, 9: 285–290.
- Silverberg, N., Bakker, J., Edenborn, H.M. and Sundby, B., 1987. Oxygen profiles and organic carbon fluxes in Laurentian Trough sediments. *Neth. J. Sea Res.*, 21: 95–105.
- 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.
- Sundby, B. and Silverberg, N., 1985. Manganese fluxes in the benthic boundary layer. *Limnol. Oceanogr.*, 30: 372–381.
- Sundby, B., Bouchard, G., Lebel, J. and Silverberg, N., 1983. Rates of organic matter oxidation and carbon transport in early diagenesis of marine sediments. In: *Advances in Organic Geochemistry 1981*. Wiley, New York, NY, pp. 350–354.
- Wakeham, S.G., 1990. Algal and bacterial hydrocarbons in particulate matter and interfacial sediment of the Cariaco Trench. *Geochim. Cosmochim. Acta*, 54: 1325–1336.
- Wakeham, S.G. and Lee, C., 1989. Organic geochemistry of particulate matter in the ocean: The role of particles in oceanic sedimentary cycles. *Org. Geochem.*, 14: 83–96.