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Biogeochemistry of organic matter in the Laurentian Trough, I. Composition and vertical fluxes of rapidly settling particles

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Abstract

Settling particles from duplicate free-drifting sediment traps were collected at 150 m depth in May and July at a landward and a seaward site in the 350 m deep Laurentian Trough. The total organic carbon (TOC) fluxes were high (95–454 mg/m^2/d), comparable to those reported for Dabob Bay (a similar moderately productive deep coastal environment) and for the highly productive Peru upwelling region. The TOC (26–67 mg C/g) consisted of lipids (17–37%), carbohydrates (7.9–16%), hydrolysable amino acids (8.4–16%), labile proteins (0.3–2.6%), and a non-characterized fraction (40–64%). Amino acids, proteins and uncharacterized compounds accounted for 24–42, 1–10 and 58–76%, respectively, of total nitrogen (2.3–7.7 mg N/g). The pigment fraction was largely dominated by pheopigments (0.06–1.15 mg/g vs 0.004–0.15 mg/g for chlorophyll *a*). C/N and C/pigment ratios indicated that on average, about half of the carbon flux was of terrigenous origin. Marine sources included a dominant zooplanktonic contribution, indicated by the abundance of fecal pellets, lipids and pheopigments, and a smaller contribution from fresh algae. Cluster and correlation analyses confirmed the decoupling of pigment and TOC fluxes and the strong zooplanktonic influence of the trap material. Despite large day-to-day and inter-trap variability, clear differences were observed in the fluxes, TOC content and composition at both sampling sites and months. Such trends are attributed to the relative contribution from terrestrial and marine sources and seasonal patterns of primary production.

1. Introduction

The settling of organic matter (OM) in the oceans, chiefly in the form of large, rapidly sinking aggregates, controls the site of nutrient regeneration, links the pelagic and benthic food webs (Billet et al., 1983; Graf, 1989), and affects the transport of biogenic and anthropogenic compounds to the sediments (Honjo, 1980; Fowler and Knauer, 1986). The vertical transport of OM is also of immediate concern to the question of global warming due to strong post-industrial increases in greenhouse gases, notably CO_2. The transport of organic-rich particles below the surface layer of the oceans effectively sequesters carbon in deep ocean waters and sediments (Sarmiento and Sundquist, 1992). Although upward fluxes, particularly in the form of lipids, have also been recognized (Grimalt et al., 1990), modelling of

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the transport of carbon has concentrated on the downward flux, including terms for new and regenerated primary production and depth-dependent consumption (Eppley and Peterson, 1979; Suess, 1980; Platt and Harrison, 1985; Pace et al., 1987).

Coastal and continental margin areas are of particular concern since they are commonly regions of high CO_2 fixation through primary production, high sedimentation rates and intense OM burial (Holser et al., 1988). Furthermore, very active regeneration and early diagenetic mineralization occur at depths shallow enough to permit a more efficient return of metabolic products to the surface layer of the coastal ocean. Our understanding of coastal areas is still restricted by the small number of published studies on organic chemistry. Few of these studies even present information on the bulk composition of total organic matter.

1.1. Setting and previous work

The Laurentian Trough, a U-shaped, glacially overdeepened valley, extends 1200 km from the Atlantic continental slope, across the entire Gulf of St. Lawrence and Lower St. Lawrence Estuary to its head near the mouth of the Saguenay Fjord (Fig. 1). With depths greater than 300 m and width up to 50 km, it dominates the 30–40 m deep narrow shelf-like platforms on the flanks of the Estuary. The absence of a sill and the broadly estuarine circulation induce the intrusion of a 200 m thick bottom layer of virtually unmodified North Atlantic water throughout the Trough. This gives the Lower St. Lawrence, or Maritime Estuary, a unique character: an upper continental margin environment with a strong terrigenous influence (see El-Sabh and Silverberg, 1990, for comprehensive review articles). These characteristics make the Lower St. Lawrence Estuary a convenient laboratory to study "oceanic" processes in a coastal area.

Much has been learned about trace-metal biogeochemistry and early diagenetic processes (see review by Silverberg and Sundby, 1990), but little is yet known about the chemistry of OM in the Lower St. Lawrence Estuary (Gearing and Pocklington, 1990). There are some studies concerning the bulk carbon,

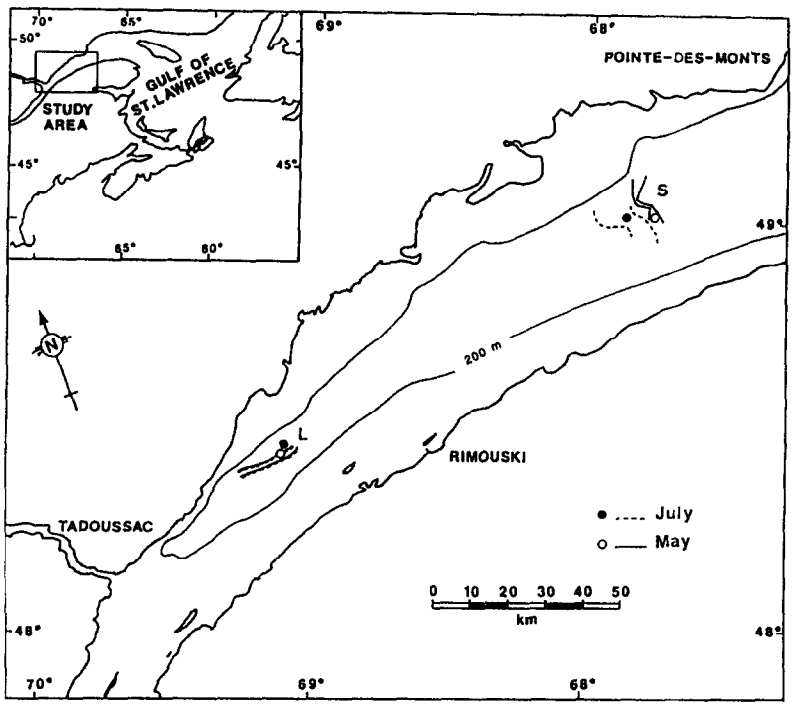

Fig. 1. Landward (L) and seaward (S) coring sites and trajectories followed by the traps during the May and July sampling periods in the Lower St. Lawrence Estuary.

nitrogen and isotopic composition of suspended material and sediments (Pocklington and Leonard, 1979; Strain and Tan, 1979; Bouchard, 1983; Sundby et al., 1983; Tan and Strain, 1983; Pocklington and Tan, 1987), and a few dealing with individual organic compounds such as phenols, ketones, fatty acids and hydrocarbons (Rodier and Khalil, 1982; Gagné and Brindle, 1985; Nichols and Johns, 1986; Gearing and Pocklington, 1990; Pelletier et al., 1991). Significant geographic and seasonal, as well as small-scale, variations in the sedimentation rate and the flux and quality of OM have been noted during several years of sediment trap deployments in the Estuary (Bouchard, 1983; Silverberg et al., 1985, 1986, 1987, 1991). However, the detailed organic composition of settling particles and sediments is still largely unknown.

This and the following paper (Colombo et al., 1995a) are the first of a study designed to provide basic information on the organic composition of settling particles and bottom sediments of the deep Lower Estuary. In conjunction with the examination of a series of more specific biomarkers, they will allow the interpretation of the sources and variation of the OM flux and the early diagenesis in the underlying sediments. This first paper outlines the bulk composition and fluxes of OM in the Estuary. In order to provide broader understanding of the organic chemistry, two sites, separated by 120 km along the land–sea gradient within the Lower Estuary, have been sampled during contrasting seasons: spring (high runoff) and mid-summer (high marine production).

2. Materials and methods

2.1. Field sampling

Sampling was carried out in May and July 1988 aboard the research vessels *L.M. Lauzier* and *Petrel V*, at a landward (48°26′N, 69°07′W; station *L*) and a seaward site (49°01′N, 67°49′W; station *S*) in the Lower St. Lawrence Estuary (Fig. 1). Rapidly sinking particles were intercepted at 150 m depth, with duplicate, unpoisoned, free-drifting sediment traps modelled after the design of Staresinic (Staresinic et al., 1978), each with four cylinders and a total collecting surface of ~ 0.5 m^2. Operating within the suspended particulate matter minimum, the traps avoided sampling the euphotic zone and the material resuspended from the bottom (Silverberg et al., 1985).

Before deployment, each of the cylinders were filled with submicron-filtered surface water (10 m) pumped with a submersible stainless steel Grundfos pump equiped with a teflon-lined hose. To obtain a denser medium and restrict the exchanges with surrounding waters, a solution containing ~ 2.25 kg of NaCl was added to each cylinder (salinity increase of ~ 15). The trajectories followed by the traps were tracked by radar. After a collection period of 8–30 h (Table 1) the traps were recovered. Once on deck, the few remaining suspended or disturbed particles were allowed to settle in the terminal tubes of the cylinders (~ 1 h). The samples were then collected into 2 l glass jars. After sedimentation of the material, the surplus water was decanted. Many living and dead swimmers (mostly copepods) were eliminated during the decantation step. The remainder were carefully eliminated with glass pipets. A small aliquot of material from one cylinder was retained for a rapid on-board microscopic examination. The material from the four cylinders was then combined and made up to a 500 ml suspension. While stirring, three 10 ml subsamples were removed for mass flux determination, CHN analysis and preservation. The bulk sample was then allowed to resettle and most of the remaining water was siphoned off. The particulate material for organic chemistry determinations was stored at -20 or -40°C until analysis.

2.2. Chemical analysis

Total organic carbon (TOC) and total nitrogen (TN) were determined on samples that had been oven-dried at 55°C and finely powdered with a mortar and pestle. Approximately 20–50 mg were combusted at 800°C in a Perkin-Elmer Model 240 elemental analyser. No attempt was made to correct for the inorganic carbon content because other studies in the area (Bouchard, 1983; Sundby et al., 1983) indicated that inorganic carbon formed only a very small fraction ($< 2\%$) of total carbon in sediment samples. Daily blanks and acetanilide standards were run during the CHN determinations. The average reproducibility of the measurements was $1.2 \pm 1.1\%$ ($n = 12$) for TOC and $2.5 \pm 2.4\%$ ($n = 12$) for TN.

Table 1
Total particle flux and organic composition of settling particles collected in May and July at a landward (*L*) and seaward (*S*) stations in the Lower St. Lawrence Estuary

Station	Date	Hr	Total particle flux	Concentration mg/g d.w.										
			(g/m2/d)	TOC	TN	CH_2O	THAA	PROT	LIPID	CHLa	PHEO	C/N	fCHLa	fPHEO
L	May 12	25	10.5	25.7	2.31	6.00	5.60	0.59	12.8	0.004	0.06	11.1	0.48	3.68
L	May 12	22	11.5	34.2	3.13	10.2	8.05	2.04	8.20	0.006	0.08	10.9	0.55	3.55
L	May 13	8	5.41	27.4	2.51	5.40	6.74	0.16	13.0	0.004	0.07	10.9	0.44	3.78
Mean		18	9.14	29.1	2.65	7.20	6.80	0.93	11.3	0.004	0.07	11.0	0.49	3.67
SD		9	3.27	4.50	0.43	2.62	1.23	0.99	2.72	0.001	0.01	0.12	0.06	0.11
L	July 15	28	11.3	40.3	4.50							8.96		
						15.4	12.0	2.00	14.0	0.155	1.00		13.7	39.0
L	July 15	26	11.3	36.7	4.10							8.95		
Mean		27	11.3	38.5	4.30	15.4	12.0	2.00	14.0	0.155	1.00	8.95	13.7	39.0
SD		1	0.00	2.55	0.28							0.00		
L Mean		23	10.2	33.8	3.48	11.3	9.42	1.47	12.7	0.080	0.54	9.98	7.10	21.3
Sd		9	1.53	6.65	1.17	5.80	3.71	0.76	1.89	0.107	0.66	1.45	9.34	25.0
S	May 9	23	6.85	44.9	5.10							8.80		
						14.8	13.0	2.35	16.0	0.136	1.07		10.7	37.2
S	May 9	21	6.91	41.4	4.80							8.63		
S	May 10	20	2.73	47.6	5.77	17.8	17.2	2.25	18.6	0.142	1.15	8.25	10.2	36.2
S	May 10	19	3.74	48.2	5.39	10.0	9.19	1.23	12.2	0.138	0.98	8.94	9.73	30.5
Mean		21	5.06	45.5	5.27	14.2	13.1	1.94	15.6	0.139	1.07	8.66	10.2	34.6
SD		2	2.15	3.10	0.41	3.94	4.03	0.62	3.22	0.003	0.09	0.30	0.49	3.62
S	July 17	19	2.24	66.2	7.70							8.60		
						23.7	20.2	3.44	16.9	0.067	0.55		3.49	12.7
S	July 17	19	1.55	64.0	7.60							8.42		
S	July 18	19	1.86	63.7	7.00							9.10		
						24.1	19.1	3.74	15.1	0.047	0.52		2.45	11.9
S	July 18	18	1.49	66.9	7.30							9.16		
Mean		19	1.79	65.2	7.40	23.9	19.6	3.59	16.0	0.057	0.54	8.82	2.97	12.3
SD		1	0.34	1.59	0.32	0.28	0.78	0.21	1.27	0.014	0.02	0.37	0.74	0.57
S Mean		20	3.42	55.4	6.33	19.0	16.4	2.77	15.8	0.098	0.80	8.74	6.59	23.5
SD		1	2.31	13.9	1.51	6.86	4.59	1.16	0.28	0.058	0.38	0.12	5.12	15.8
Grand mean		21	6.82	44.6	4.90	15.2	12.9	2.12	14.2	0.089	0.67	9.36	6.84	22.4
SD		4	4.24	15.3	1.98	6.85	5.28	1.10	2.12	0.071	0.46	1.10	6.16	17.1

Hr = hours deployment; TOC = total organic carbon; TN = total nitrogen; CH_2O = carbohydrates; THAA = total hydrolyzable amino acids; PROT = proteins; CHLa = chlorophyll *a*; PHEO = pheopigments; fCHLa = TOC/CHLa ratio in phytoplankton (34, Downs and Lorenzen, 1985) divided by the measured TOC/CHLa ratio; fPHEO = TOC/PHEO in herbivore fecal pellets (15, Downs and Lorenzen, 1985) divided by the measured TOC/PHEO ratio; SD = standard deviation.

Undried material was used for all the other organic analyses (in some cases the material from duplicate traps had to be pooled). Carbohydrate (CH_2O) measurements were carried out using the phenol-sulphuric acid method (Liu et al., 1973). Approximately 55 mg of wet material was reacted with 10% phenol solution and concentrated sulphuric acid. The absorbance was read in a Perkin-Elmer Lambda 3B UV/VIS spectrophotometer at 485 nm against a reagent blank with a sediment/sulphuric acid interaction correction. A starch solution was used as a standard. The average reproducibility of the determinations was $5.3 \pm 5.1\%$ ($n = 37$).

Proteins (PROT) were measured using a modified Coomassie blue dye binding method, which includes an enzymatic digestion to overcome the interference with humic substances (Mayer et al., 1986). Approximately 350 mg wet sediment was extracted with 0.1 *N* NaOH at 60°C for 2 h, then centrifuged and the supernatant neutralized with HCl. An aliquot was incubated with a protease solution at 70°C for 2 h. The dye was added to both the protease hydrolysed and unreacted extracts and the absorbance was read at 595 nm. The difference between both readings represented the protein available for enzymatic attack. A solution of bovine serum gamma globulin was used for calibration. The average reproducibility of the analysis was $11.4 \pm 7\%$ ($n = 13$).

Total lipids (LIP) were measured gravimetrically. About 2–4 g wet material were centrifuged and then extracted with 4 ml of an acetone–petroleum ether mixture (1:1). The samples were shaken, sonicated for 15 min and centrifuged. The organic phase was collected and dried over pre-extracted Na_2SO_4. The lower aqueous phase was extracted with petroleum ether. This extraction scheme was repeated 3 times. The organic phases were combined, dried and concentrated to 1 ml by rotoevaporation and under a N_2 stream. A 100 μl aliquot of this extract was dried at 50°C in preweighed micro-vials. Lipid contents were obtained by reweighing the vials in a Mettler Model M3 electrobalance and correcting for a procedural blank. The same lipid extract was purified and fractionated by column chromatography for the analysis of hydrocarbons by capillary gas chromatography (Colombo et al., 1989) and other compounds. Only selected results are included here.

For the determination of chlorophyll *a* (CHLa) and pheopigments (PHEO), 1 μl of the total lipid extract was diluted with acetone and subjected to the standard fluorometric method (Strickland and Parsons, 1972). The average yield of the entire procedure, tested by the addition of a standard solution of chlorophyll *a* to a sediment sample, was $73 \pm 9\%$ ($n = 3$). The average reproducibility of the measurements was $\pm 8.3\%$ ($n = 3$). To obtain more information on the individual pigment composition and to confirm the fluorometric data, three samples were subjected to HPLC pigment analysis (Mantoura and Llewellyn, 1983). The results indicated that the fluorometric method overestimated pheopigment values by an average of 13%. The concentrations were recalculated using correction factors based on the HPLC data.

Total hydrolyzable amino acids (THAA) were measured by pre-column o-phthaldialdehyde derivatization and reverse-phase HPLC separation of the components, followed by fluorescence detection (Lindroth and Mopper, 1979; Dawson and Liebezeit, 1983). A more comprehensive discussion of amino acid methods and data is published elsewhere (Colombo et al., 1995b).

3. Results and discussion

3.1. General nature of trap material

The manner of collection of the particles makes it difficult to know their original character in the water column (Alldredge and Silver, 1988). The funnelling of particles into a common, narrow collector can create artificial aggregation of already "sticky" marine snow. The subsequent agitation during sample recovery and treatment undoubtedly breaks up the loose aggregates into smaller ones. Large particles sinking through the water column have been observed in the Laurentian Trough both during submersible dives (Syvitski et al., 1983) and with floc cameras (Heffler et al., 1991). These include many sand-sized particles, several mm long string aggregates, cm-sized globular aggregates (e.g. *Oikopleura* houses) and even meter-long ropes of mucus, sometimes festooned with clumps and strings.

During the 1 h resettling period before removing our samples from the traps, it was common to ob-

serve 2–5 mm semi-spherical aggregates settling through the transparent terminal tubes of the cylinders. At *S*, we clocked their descent at 1–3 s/cm, or an average of over than 400 m/day. Although this may possibly represent an overestimation of the "in-situ" sinking rates due to an artificial aggregation in the traps, it suggests a very rapid transit of the particles through the water column (< 1 day).

The fresh subsamples of our trap material were examined immediately on board using a dissecting scope. Portions of the preserved subsamples were later examined in the laboratory with a high-power microscope (Fig. 2). Much of the material still consisted of broken up marine snow ("fluffy" aggregates) and a variety of fecal pellets. Tests of centric diatoms (*Coscinodiscus* sp.) were common in the samples. Other particles included: sand grains, most evident at *L* in May; diatom chains, particularly evident at *S* in May; and parts of other organisms (e.g. copepods, tintinnids, dinoflagellates). All these components were often agglutinated in amorphous aggregates (marine snow).

The fecal pellets collected were often elongated with pinched or broken ends and many were about 300–700 μm long ("stick" pellets). Other shapes included oval, spheric, and larger broken pellets. The pellets typically had a dark brown colour and a compact appearance. Many presented partially or totally degraded peritrophic membranes. Within broken pellets, fine particulate matter (clay minerals) and occasional diatom fragments could be observed. The pellets were not identified according to species. However, the appearance and sizes of many of the observed pellets suggested that they were produced by copepods (Corner et al., 1986). Copepods represent 79–90% of the total zooplankton in the estuary, with *Calanus finmarchicus* and *C. hyperboreus* as the dominant species (Runge and Simard, 1990). Larger pellets may have belonged to other animals such as euphausiids. Large dense patches of the euphausiids *Thysanoessa raschi* and *Meganyctiphanes norvegica* have been observed at 75 and 150 m depth, respectively, along the northern edge of the Laurentian Trough (Simard et al., 1986). The presence of these copepod and euphausiid species during our trap deployments was confirmed by vertical tows (150–0 m) made with a 333 μm mesh plankton net. Aggregates produced by other non-crustacean organisms, i.e. ctenophores, appendicularians and fish, whose distributions are poorly documented in the Estuary, may also be components of our samples.

3.2. Variability

Table 1 presents the total mass flux and the organic composition of the settling particles for each of the trap deployments. The data show considerable scatter. High variability between cylinders of the same trap and between simultaneous traps has been shown to be a common characteristic at an intensively sampled site between stations *L* and *S*. Temporal trends were best discerned when data from multiple traps were averaged (Silverberg, 1991).

The variability observed in the data includes the analytical error, the differences between same-day and successive-day traps, and changes between sampling periods and stations. Considering the precision of the analyses (TOC, ± 1.2; TN, $\pm 2.5\%$), the contribution of the analytical error to the total variability in TOC and TN is relatively small. The data base is very small for definitive statistical analysis; however, in order to evaluate the validity of between-station and between-month differences, analysis of variance (ANOVA) and non-parametric Mann-Whitney tests were performed.

For the ANOVA, the largest data set available was used (total mass flux, TOC and TN). A logarithmic transformation of the data was applied to minimize the effect of the inhomogeneous variance detected for the total flux in May (Bartlett's test). One-way ANOVA results indicated that the day to day variability was of the same order of magnitude as the inter-trap variation. Only in two cases was it possible to distinguish ($p < 0.06$) between successive sampling days (total flux in May and TN in July at *S*; between-day variability, 92 and 88%, respectively). This high inter-trap variance suggests a high degree of patchiness in the downward flux of material. A nested ANOVA design carried out with the data from *S* indicated that this small-scale variability accounted for a small fraction of the total variance (inter-trap, 1.9–6.5; between-day, 3.2–23%) when compared to the between-month differences (71–95%). A similar evaluation was not feasible for *L* due to the scarcity of data.

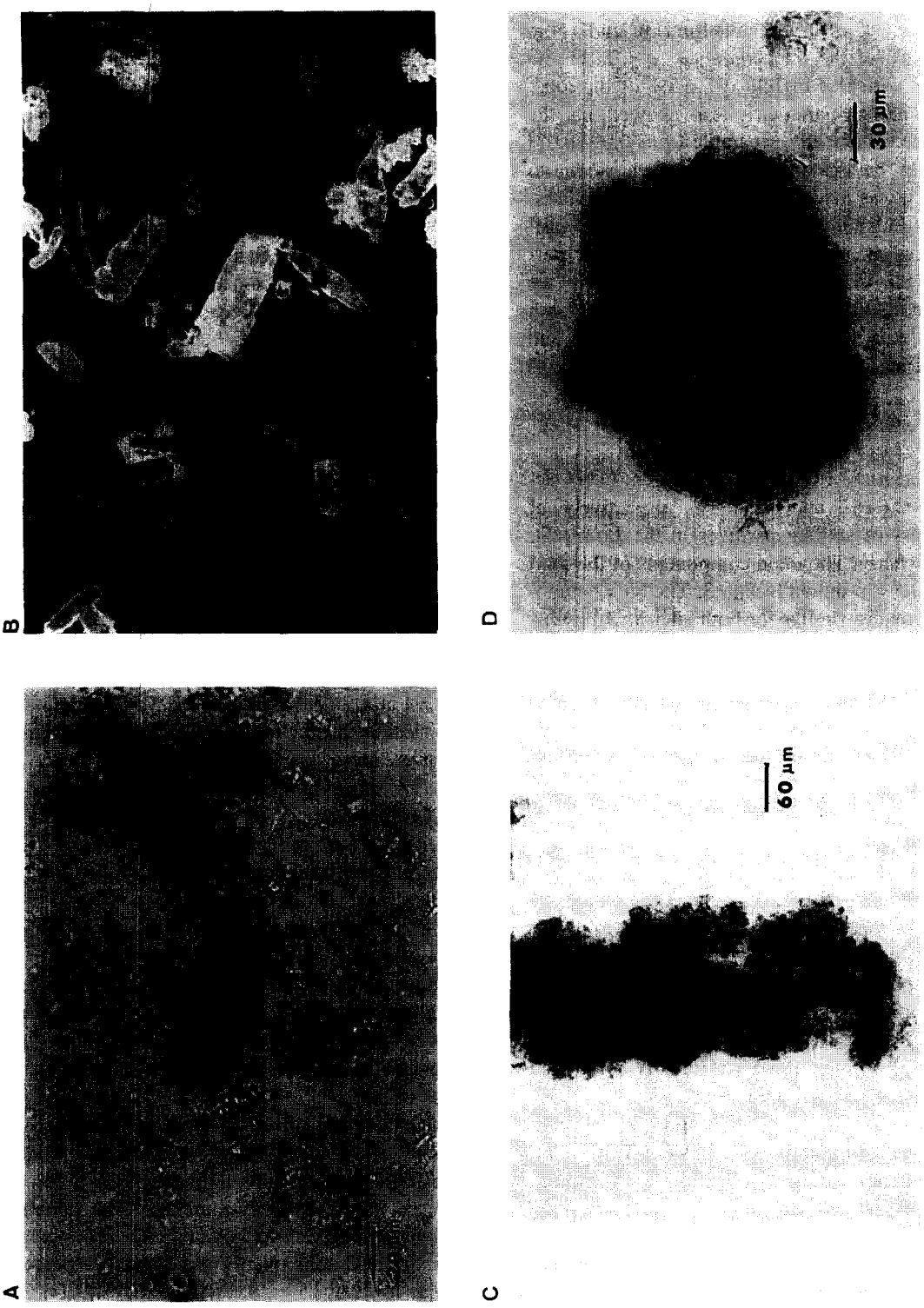

Fig. 2. Photomicrographs of selected sediment trap samples. (A) Sample with abundant mineral grains collected at *L* in May. (B) Material collected at *S* in May. (C,D) Diatom aggregates collected at *S* in May.

For the between-station differences, the one-way ANOVA showed significant results for TOC and TN in May (86–92% of the total variance, $p < 0.01$) and for all three variables in July (97–98% of the total, $p < 0.01$). The non-parametric tests showed that the stations were statistically separable ($p = 0.09$–0.01) for the eight parameters analyzed, even when no consideration was made for seasonality. These statistical results indicate that although small-scale variability is present, it represents a relatively low percentage of the total variance. For this reason, we chose to use the mean values for each site and month (Table 1) to best interpret the geographical and temporal trends.

3.3. Bulk organic composition

Organic carbon (TOC) and nitrogen (TN) accounted for 2.6–6.7 and 0.2–0.8%, respectively, of the total mass of settling particles in the Lower St. Lawrence Estuary. The main components of the total organic matter are shown in Fig. 3. The bulk composition was broadly similar for both sites and months. In terms of their contribution to characterizable TOC, lipids were the most abundant components (17–37%), followed by CH_2O (7.9–16%), THAA (8.4–16%) and proteins (0.3–2.6%). For TN, THAA and proteins accounted for 24–42 and 1–10%, respectively. Protein-N represented 2.7–29% of THAA-N, indicating that the major part of THAA was not in the form of labile proteins.

The remaining fraction of the organic matter (40–64% TOC and 58–76% TN) has not been characterized. Much of this was probably refractory in nature and a significant proportion possibly consisted of humic compounds. Information about humics is mainly confined to bottom sediments. In estuaries they account for 10–70% of sedimentary TOC (Mayer, 1985). Lignin, another refractory compound usually found in coastal areas, makes up 0.5–3.3% of sediment trap TOC in Dabob Bay, Washington (Hedges et al., 1988) and about 3.8% of TOC in St. Lawrence Estuary sediments (Gearing and Pocklington, 1990).

Few analyses of sediment trap material reported in the literature include more than a small proportion of the total organic matter. Table 2 compares the bulk composition of Laurentian Trough OM with that of other marine environments. The concentrations of TOC in St. Lawrence material fall in the lower range of reported values. However, for similar depths, they are comparable to those of other non-open ocean sites. The bulk composition seems to be rather characteristic: it shows a high contribution of lipids and CH_2O, and relatively low protein and THAA percentages. It appears to most resemble the very fresh, organic-rich macroaggregates collected in surface waters from Santa Barbara Channel, but is much lower in nitrogenous compounds. This may be related to the contribution of low-protein terrestrial matter and/or the partial degradation of the trap material. The high lipid content suggests an important zooplanktonic influence (see section on sources below).

3.4. Geographical and temporal patterns

Clear differences in OM concentrations for both sites and months are evident in Fig. 4. The concentration of OM is higher at the seaward site and increases at both stations during July. PHEO is the sole parameter which shows a different trend, suggesting unexpectedly important phytoplankton production at L in July and S in May. C/N ratios were significantly higher at L in May (11) and remained at lower, more constant values (8.7–9) in the other three samplings (Table 1).

These differences in the concentration and composition of OM reflect the position of the stations relative to the terrigenous–marine gradient along the estuary. The terrestrial signal, high mineral content and C/N ratio (i.e. vascular plant debris, lignin), is most strongly seen at L, particularly during the spring runoff (May). Marine production is relatively more important at S, even in May. This is reflected in a 22–88% higher content of all organic components at S as compared to L (Fig. 4) and in the C/N ratios (Table 1).

The temporal difference is explained by the stronger contribution of marine production relative to terrestrial inputs in July. This produces a 30–115% increase in the organic content of the particles at both sites from May to July (Fig. 4). The increase of the individual components expressed as a percentage of May levels is ($S - L$): PROT (85–115%) > CH_2O (68–113%) > THAA (49–78%) > TN((40–62%) ≥

TOC (43–32%) > lipids (2.6–24%). The higher percentage increase generally observed at *L* indicates a more drastic shift from terrestrial to marine sources at this landward site. The stronger seasonal change of PROT, CH_2O, and THAA suggests a greater dependence on marine productivity for these fractions. The other parameters are more conservative, perhaps reflecting the presence of humic substances. The proportion of TOC and TN contributed by the individual components also generally increases in July, when there is a stronger contribution of marine biogenic matter (Fig. 3).

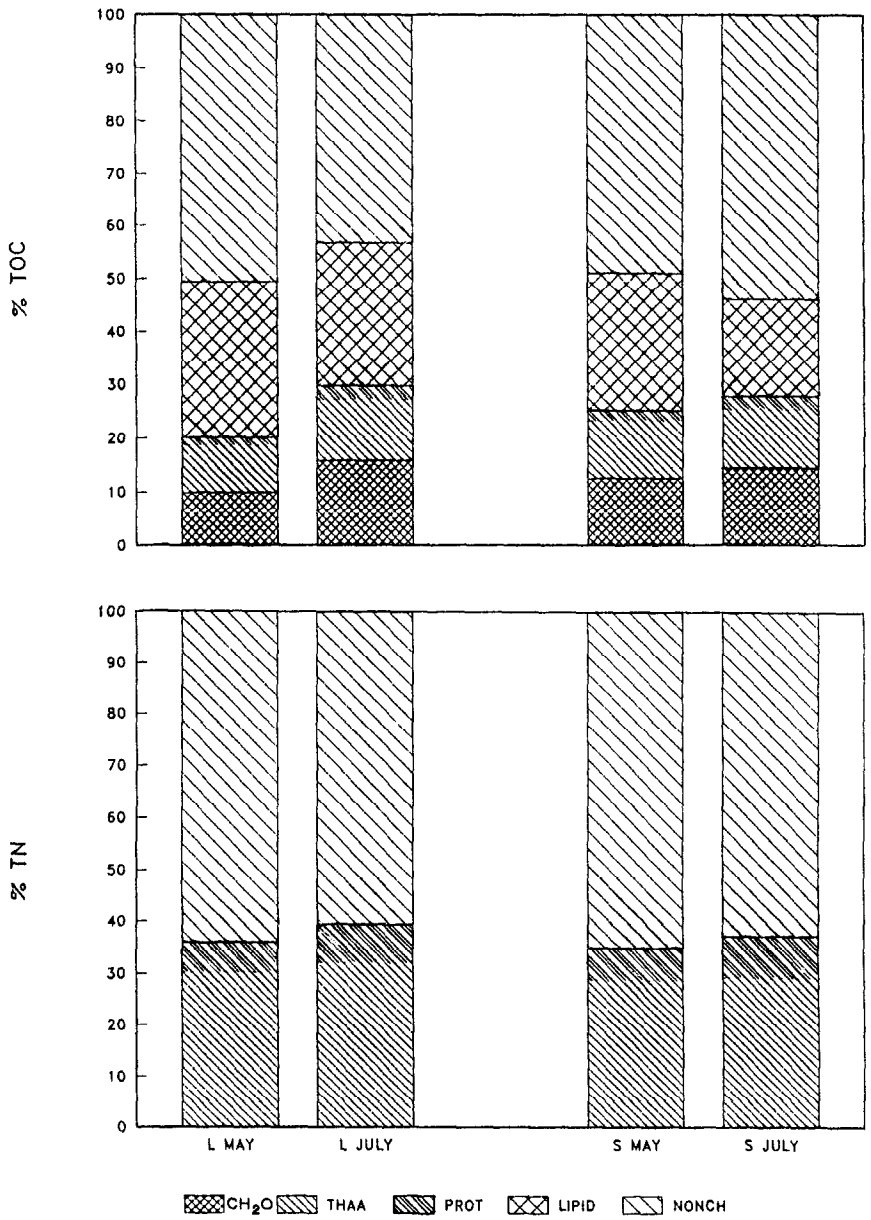

Fig. 3. Proportion of total organic carbon and nitrogen represented by the different components. Abbreviations are defined in the text. The carbon conversion factors used are: 0.75 for LIP, 0.4 for CH_2O, 0.44 for THAA and PROT. For nitrogen, 0.14 was used for THAA and 0.16 for PROT. PROT is included in the THAA contribution.

Table 2
Organic composition of rapidly settling particles collected in the Lower St. Lawrence Estuary compared to that reported for other marine environments

Region	Depth	TOC	TN	as % of TOC					References
	(m)	(mg/g)	(mg/g)	LIPID-C	CH_2O-C	PROT-C	THAA-C	NONCH-C	
St. Lawrence									
L	150	34	3.5	28	13	1.8	12	47	This study
S	150	55	6.3	22	14	2.2	13	51	This study
Santa Barbara Channel									
Californian Pacific (macroaggregates)	10	135	15.2	24	14	54	–	–	Alldredge (1979)
Dabob Bay									
Puget Sound	60	51	6	–	7	–	–	–	Hedges et al. (1988)
Peru Upwelling									
Equatorial Pacific	50	52 [a]	–	13 [a]	–	–	26 [a]	–	Wakeham et al. (1984b)
Northern North Pacific	100	–	–	–	10	–	–	–	Tanoue and Handa (1987)
VERTEX I	100	233 [a]	–	–	–	–	39	–	Wakeham et al. (1984b)
California Current	250	217 [a]	–	7 [a]	–	–	23–25	–	Lee and Cronin (1984)
PARAFLUX P	378 [a]	318	–	4 [a]	–	–	2 [a]	–	Wakeham et al. (1984b)
Central North Pacific									
Eastern North Pacific	740	230	32	14	–	–	–	–	Matsueda et al. (1986)
PARAFLUX E									
Equatorial North Atlantic	389	100	–	22	–	–	18	–	Lee and Cronin, 1982
Sargasso Sea	3200	45–50	–	–	3–6 [b]	–	8–26	–	Ittekkot et al. (1984)
Breid Bay									
Antarctic	110	–	–	5–14	21–53 [b]	–	15–36	–	Handa et al. (1992)
Bransfield Strait									
Antarctic	323	42	5	–	4 [c]	–	21	–	Liebezeit and von Bodungen (1987)
Drake Passage									
Antarctic	965	28	5	–	9	–	30	–	Wefer et al. (1982)

[a] Calculated from graphs.
[b] Sum of individual sugars.
[c] Monosaccharides.

3.5. Total particle and carbon fluxes

Fig. 5 shows the total mass flux (sedimentation rate) and the TOC and TN fluxes averaged by station and season. The total mass fluxes are consistently much higher at the landward site (9.1–11.3 vs. 5.1–1.8 g/m^2/d at *S*; May–July; Table 1). This agrees with the contrasting sediment accumulation rates calculated for both stations from excess ^{210}Pb data: 16.2 and 2 mm/yr for *L* and *S*, respectively (Silverberg et al., 1986). Including all available sediment trap data (1980–1988), the mass flux averages 13 ± 9.8 g/m^2/d at *L* ($n = 12$) and 3 ± 2.2 g/m^2/d at *S* ($n = 10$). The sediment accumulation rates calculated from these fluxes, 6.4 mm/yr at *L* and 1.5 mm/yr at *S* (density, 2.65 g/cm^3; water content, 50%), are somewhat lower than the results from ^{210}Pb data.

TOC fluxes range from 95 to 454 mg/m^2/d and follow the same trend as the mass fluxes, i.e. higher values at the landward site (averages of 350 ± 120 mg/m^2/d at *L* and 172 ± 78 mg/m^2/d at *S*). The mean TOC fluxes at the two stations agree with the decreasing landward–seaward trend previously observed in the estuary (Bouchard, 1983) and bracket the 5-year average of 32 trap deployments at an intermediate station (198 mg/m^2/d; Silverberg et al., 1986). Including all available sediment trap data, the TOC fluxes vary from 97 to 734 mg/m^2/d at *L* and from 88 to 320 mg/m^2/d at *S*.

These carbon fluxes are high, not only relative to open-sea data, which lie in the range of 3–50 mg/m^2/d at 100–600 m depth (Honjo et al., 1982; Tsunogai and Noriki, 1987); but also considering the data reported for coastal areas: 26–35 mg/m^2/d at 100 m depth in the Santa Monica–San Pedro Basin (Nelson et al., 1987); 12–116 mg/m^2/d at 110 m depth in Breid Bay, Antarctica (Handa et al., 1992); 97–126 mg/m^2/d at 90–200 m depth in the Barents Sea (Wassmann et al., 1994); 72–160 mg/m^2/d at 50–100 m depth in Puget Sound (Baker et al., 1985) and 39–233 mg/m^2/d at 100 m depth during the VERTEX experiment off the California coast (Martin et al., 1987). The TOC fluxes measured in the St. Lawrence are comparable to those reported for Dabob Bay, 21–470 mg/m^2/d at 60 m depth (Downs and Lorenzen, 1985) and 186–386 mg/m^2/d at 30–90 m depth (Hedges et al., 1988) and for the Peru upwelling area, 224–418 mg/m^2/d at 50 m depth (Wakeham et al., 1984a).

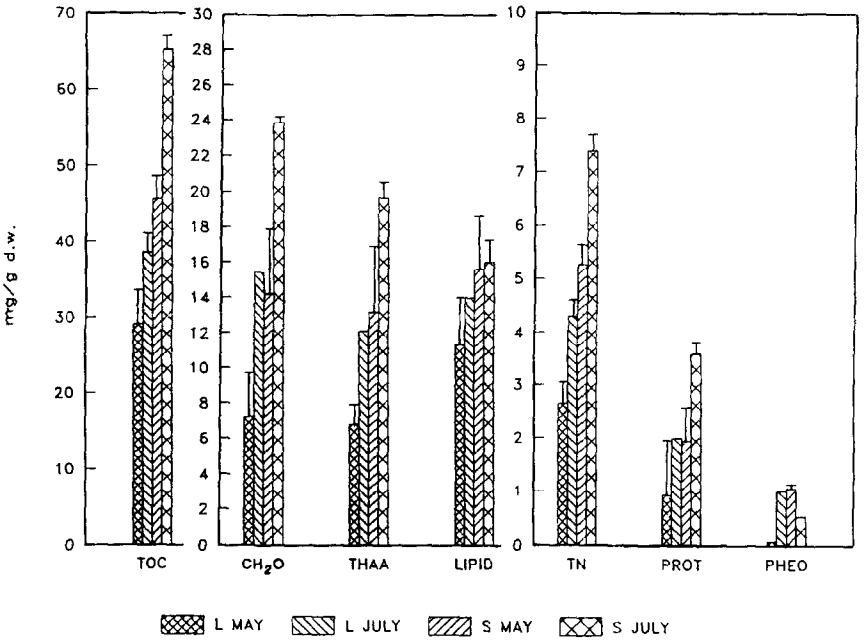

Fig. 4. Geographical and temporal differences in the composition of Laurentian Trough trap material. Note the differences in the vertical scale among the three panels.

Since the organic matter components form a small proportion of the total mass, the variations of their fluxes are controlled by the trends in total mass fluxes. During the May sampling period, the higher OM content of the particles at *S* and the greater total fluxes at *L* (1.8–6.6 times higher) result in similar fluxes of the various OM fractions at both stations, except for PHEO (OM component fluxes = concentration × total particle flux in Table 1). In July, the total particle flux increases at *L* and decreases sharply at *S* resulting in OM fluxes 4–12 times higher at *L* during July.

3.6. Evaluation of the sources of organic matter

The parameters measured can be used to estimate the relative importance of different OM sources, such as terrestrial material and algal and zooplanktonic production. For such determinations, ratios are often more sensitive than absolute concentrations.

C/N ratios provide an estimate of the proportion of marine and terrestrial carbon, although there are some drawbacks related to their possible variation during OM decay and the choice of the end members (Tan and Strain, 1983; Lancelot and Billen, 1985). A simple mixing model using C/N weight ratios of 6 (Muller, 1977) and 13 (Prahl et al., 1980; Parrish et al., 1992) for the marine and terrigenous and members, respectively, indicated that the terrigenous contribution is very important in the Laurentian Trough. It accounts for ≈ 70% at the landward station in the spring and for ≈ 40% in July. If, instead, a C/N ratio = 15 (highest sediment trap value in the Trough; Silverberg et al., 1985) had been adopted for the terrestrial and member, the terrestrial contribution would still be very significant (30–55%).

The low levels of nitrogenous components (THAA and labile proteins) measured in our trap material result partially from dilution with significant amounts of low-protein terrestrial matter (especially at *L* in May). The preferential consumption of nitrogenous OM in the upper water layers is probably also responsible for the low levels measured in the particles. This is not unexpected since copepods appear to maximize protein ingestion (Penry and Frost, 1991, and references therein).

Pigments, although not very stable, are very sensitive indicators of photosynthetic activity. In our trap samples, the pigment fraction is largely dominated by pheopigments (0.06–1.15 mg/g, ≈ 0.6–7% total

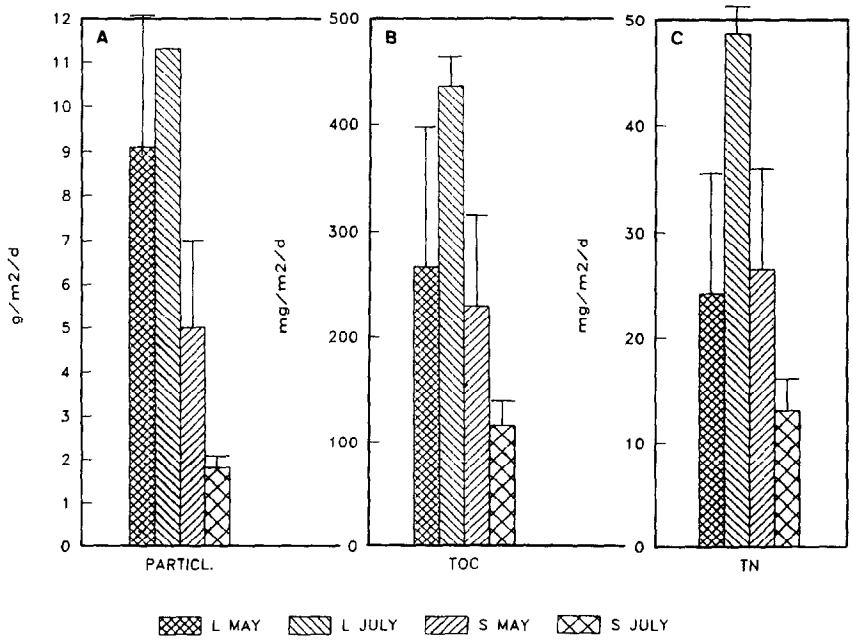

Fig. 5. Total particle (A), carbon (B) and nitrogen (C) fluxes calculated from sediment trap data.

lipids), with very low levels of chlorophyll *a* (0.004–0.15 mg/g, 0.04–1% lipids; Table 1). The HPLC analysis revealed 4 pheopigment peaks: 2 pheophorbides ($\approx$ 87% of total PHEO) and 2 pheophytins ($\approx$ 9%). CHL a (including one allomer) represented 11.3 $\pm$ 4% compared to PHEO. One fucoxanthin and one diadinoxanthin peak were also tentatively identified (S. Roy, pers. commun., 1990). The concentrations of pigments in the trap material show marked temporal changes. At *L*, CHLa and PHEO increase in July, reflecting the tardy spring bloom of the Lower Estuary (Therriault and Levasseur, 1985). At *S*, the pattern is reversed, indicating that we sampled an unexpectedly important phytoplankton bloom in May. This is supported by the microscopic evidence of chain forming diatoms in the traps, abundant phytoplankton in a net tow taken at that time, and low C/N ratios.

According to the literature, the dominance of pheophorbide a is a common feature of trap material and copepod faeces (Nelson et al., 1987; Vernet and Lorenzen, 1987; Roy and Poulet, 1990), while in fresh diatom macroaggregates, pheopigments are much less abundant, 8–28% of total chlorophyll (Alldredge and Gotschalk, 1989). Although dead or senescent algae have now been recognized as potentially important contributors (Head et al., 1994), the degradation of chlorophyll *a* in the guts of herbivorous grazers is considered to be the primary source of pheopigments in the sea. Pheophytin is regarded as an intermediate in this process. Photo-oxidation and coprophagy intensify the degradation of pigments to colourless products not detected by fluorometry. The effect of photodegradation is minimized in rapidly sinking particles which are effective vectors for the transport of pigments to bottom sediments (Welschmeyer and Lorenzen, 1985; Carpenter et al., 1986; Leavitt and Carpenter, 1990).

Downs and Lorenzen (1985) employed C/PHEO ratios to estimate the fraction of carbon derived from recently ingested phytoplankton (fPHEO), in fecal pellets from laboratory-fed copepods and field zooplankton and in trap material from Dabob Bay. Our data base was not specifically generated to apply this model. However, the similarity of the physical environment, and of the TOC and PHEO fluxes (261 and 4.4 vs. 267 and 4.97 mg/m2/d, respectively), as well as the POC/CHLa ratio, $\approx$ 35 during bloom conditions (A. Vézina pers. commun., 1991) vs. a mean of 34 in Dabob Bay, encouraged us to use the Downs and Lorenzen model to obtain some estimate of the importance of herbivory to the vertical TOC flux. We calculated a grand mean of 22 $\pm$ 17% for fPHEO in our samples (Table 1). The averages by station and month reflect the May to July pigment changes: 3.7–39% at *L* and 35–12% at *S*. By performing calculations analogous to fPHEO, we estimated fCHLa, the fraction of TOC directly contributed by algae. fCHLa followed the same trend as fPHEO; a strong increase at *L* (0.5–14%) and a decrease at *S* (10–3%) from May to July.

These calculations with C/pigment ratios indicate that the TOC flux includes an average of 29% algal carbon - 22% recycled and 7% fresh material. This corresponds to an algal carbon flux of 76 mg C/m2/d. The average daily primary production calculated over a 153-day period from May through September, using Therriault and Levasseur's (1985) data, is 745 mg/m^2/d. Our total algal flux alone represents 10% of this value.

The importance of the zooplanktonic influence in the traps, indicated by the abundance of pheopigments, is also suggested by the high lipid content of the particles, since copepods usually contain higher amounts of lipids relative to algae, whereas CH_2O are much more abundant in phytoplankton and higher plants. In samples collected in Nova Scotia, PROT, lipids and CH_2O accounted for 27, 11 and 54% TOC, respectively, in phytoplankton vs. 29, 49 and 1% of TOC in *Calanus finmarchicus* (Mayzaud and Martin, 1975). Head (1992) showed faecal pellets of copepods to be enriched in lipids and proteins compared with their food.

3.7. Statistical grouping of the organic parameters

To examine the covariation of the eight parameters measured in the trap material, a cluster analysis was performed using 1-*r* (Pearson correlation coefficient) as the similarity index (Fig. 6). Data from Colombo et al. (1995c) on two lipid biomarkers indicative of zooplankton (pristane, PRIS) and algae (n-heneicosa-hexaene, HEH) are included in the data set to make the source identifications clearer. Two separate groups are observed, one apparently corresponding to phytoplanktonic carbon (CHLa, PHEO,

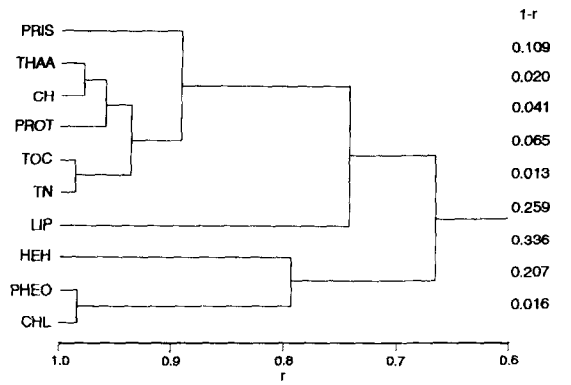

Fig. 6. Dendrogram resulting from single linkage clustering of the eight chemical parameters measured in settling particles plus data from Colombo et al. (1995c) on pristane (PRIS) and heneicosahexaene (HEH). Higher values of the similarity index (1-r, where r is the Pearson correlation coefficient) indicate a weaker correlation.

HEH) and the other including zooplanktonic carbon (LIP, TN, TOC, PROT, CH_2O, THAA, PRIS). There is a poor correlation between the three algal markers and TOC (HEH, $r = 0.25$; CHLa, $r = 0.32$; PHEO, $r = 0.41$). In contrast, the zooplanktonic marker pristane correlates significantly ($n = 9$, $p < 0.05$) with all the bulk parameters (THAA, $r = 0.89$; TOC, $r = 0.86$; TN, $r = 0.85$; CH_2O, $r = 0.85$; PROT, $r = 0.78$; LIP, $r = 0.69$). A partial correlation analysis, which removes the effects due to the covariation with other variables, confirmed the association of pristane with TOC ($r = 0.76$), LIP ($r = 0.55$) and THAA ($r = 0.51$). This suggests that lipids and amino acids are the principal contribution of zooplankton to the vertical flux of carbon. Similar pigment–TOC decouplings and significant pristane–TOC correlations have been interpreted as indicators of important zooplanktonic influence in other coastal environments (Prahl et al., 1980; Baker et al., 1985).

The interpretation of our cluster analysis is complicated by the importance of the terrestrial contribution in the St. Lawrence. The larger group in the cluster, including TOC and TN, contains both compounds high in algal and terrestrial matter (carbohydrates) and compounds higher in zooplankton (lipids and proteins). This cluster may represent both terrestrial and zooplanktonic influences. More certain and detailed interpretation of sources will be provided by the examination of multiple lipid biomarkers (Colombo et al., 1995c).

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References

Alldredge, A.L., 1979. The chemical composition of macroscopic aggregates in two neretic seas. Limnol. Oceanogr., 24: 855–866.

Alldredge, A.L. and Gotschalk, C.C., 1989. Direct observation of the mass flocculation of diatoms blooms: characteristics, settling velocities and formation of diatom aggregates. Deep-Sea Res., 36: 159–171.

Alldredge, A.L. and Silver, M.W., 1988. Characteristics, dynamics and significance of marine snow. Prog. Oceanogr., 20: 41–82.

Baker, E.T., Feely, R.A., Landry, M.R. and Lamb, M., 1985. Temporal variations in the concentration and settling flux of carbon and phytoplankton pigments in a deep fjordlike estuary. Estuarine Coastal Shelf Sci., 21: 859–877.

Billet, D.S.M., Lampitt, R.S., Rice, A.L. and Mantoura, R.F.C., 1983. Seasonal sedimentation of phytoplankton to the deep-sea benthos. Nature, 302: 520–522.

Bouchard, J., 1983. Variations des paramétres biogéochimiques dans les sédiments du Chenal Laurentien. Thesis. Univ. Québec, Rimouski, 161 pp.

Carpenter, S.R., Elser, M.M. and Elser, J.J., 1986. Chlorophyll production, degradation, and sedimentation: implications for paleolimnology. Limnol. Oceanogr., 31: 112–124.

Colombo, J.C., Pelletier, E., Brochu, C., Khalil, M. and Catoggio, J.A., 1989. Determination of hydrocarbon sources using n-alkane and polyaromatic hydrocarbon distribution indexes. Case Study: Rio de La Plata Estuary, Argentina. Environ. Sci. Technol., 23: 888–894.

Colombo, J.C., Silverberg, N. and Gearing, J.N., 1995a. Biogeochemistry of organic matter in the Laurentian Trough, II. Bulk composition of the sediments and relative reactivity of major components during early diagenesis. Mar. Chem., 51: 295–314, 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.

Colombo, J.C., Silverberg, N. and Gearing, J.N., 1995c. Lipid biogeochemistry in the Laurentian Trough, I. Fatty acids, aliphatic hydrocarbons and sterols in rapidly settling particles. In prep.

Corner, E.D.S., O'Hara, S.C.M., Neal, A.C. and Eglinton, G., 1986. Copepod faecal pellets and the vertical flux of biolipids. In E.D.S. Corner and S.C.M. O'Hara (Editors), The Biological Chemistry of Marine Copepods. Clarendon, Oxford.

Dawson, R. and Liebezeit, G., 1983. Determination of amino acids and carbohydrates. In: K. Grasshoff, M. Ehrhardt and K. Kremling (Editors), Methods of Seawater Analysis. Verlag Chemie, Weinheim, 2nd ed., pp. 319–330.

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.

El-Sabh, M.I. and Silverberg, N. (Editors), 1990. Oceanography of a Large-Scale Estuarine System, the St. Lawrence. Springer, New York, NY, Coastal Estuarine Stud., 39, 434 pp.

Eppley, R.W. and Peterson, B.J., 1979. Particulate organic matter flux and planktonic new production in the deep ocean. Nature, 282: 677–680.

Fowler, S.W. and Knauer, G.A., 1986. Role of large particles in the transport of elements and organic compounds through the oceanic water column. Prog. Oceanogr., 16: 147–194.

Gagné, J.-P. and Brindle, J.-R., 1985. Composés phenoliques en milieu cotier: contribution de la région de Baie-Comeau et du Fjord du Saguenay. Nat. Can., 112: 57–64.

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. 170–195.

Graf, G., 1989. Benthic–pelagic coupling in a deep-sea benthic community. Nature, 341: 437–439.

Grimalt, J.O., Simoneit, B.R.T., Gómez-Belinchón, J.I., Fischer, K. and Dymond, J., 1990. Ascending and descending fluxes of lipid compounds in North Atlantic and North Pacific abyssal waters. Nature, 345: 147–150.

Handa, N., Nakatsuka, T., Fukuchi, M., Hattori, H. and Hoshiai, T., 1992. Vertical fluxes and ecological significance of organic materials during the phytoplankton bloom during austral summer in Breid Bay, Antarctica. Mar. Biol., 112: 469–478.

Head, E.J.H., 1992. Comparison of the chemical composition of particulate material and copepod faecal pellets at stations off the coast of Labrador and in the Gulf of St. Lawrence. Mar. Biol., 112: 593–600.

Head, E.J.H., Hargrave, B.T. and Subba Rao, D.V., 1994. Accumulation of a pheophorbide a-like pigment in sediment traps during late stages of a spring bloom: A product of dying algae? Limnol. Oceanogr., 39: 176–181.

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.

Heffler, D., Syvitski, J.P. and Asprey, K.W., 1991. The floc-camera assembly. In: J.P. Syvistski (Editor), Principles, Methods and Application of Particle Size Analysis. Cambridge Univ. Press, New York, NY, pp. 209–221.

Holser, W.T., Schidlowski, M., MacKenzie, F.T. and Maynard, J.B., 1988. Biogeochemical cycles of carbon and sulfur. In: C.B. Gregor, R.M. Garrels, F.T. MacKenzie and J.B. Maynard (Editors), Chemical Cycles in the Evolution of the Earth. Wiley, New York, NY, pp. 105–174.

Honjo, S., 1980. Material fluxes and modes of sedimentation in the mesopelagic and bathypelagic zones. J. Mar. Res., 38: 53–97.

Honjo, S., Manganini, S.J. and Cole, J.J., 1982. Sedimentation of biogenic matter in the deep ocean. Deep-Sea Res., 29: 609–625.

Ittekkot, V., Deuser, W.G. and Degens, E.T., 1984. Seasonality in the fluxes of sugars, amino acids, and amino sugars to the deep ocean: Sargasso Sea. Deep-Sea Res., 31: 1057–1069.

Lancelot, C. and Billen, G., 1985. Carbon–nitrogen relationships in nutrient metabolism of coastal marine ecosystems. Adv. Aquat. Microbiol., 3: 263–321.

Leavitt, P.R. and Carpenter, S.R., 1990. Regulation of pigment sedimentation by photo-oxidation and herbivore grazing. Can. J. Fish. Aquat. Sci., 47: 1166–1176.

Lee, C. and Cronin, C., 1982. The vertical flux of particulate organic nitrogen in the sea: decomposition of amino acids in the Peru upwelling area and the equatorial Atlantic. J. Mar. Res., 40: 227–251.

Lee, C. and Cronin, C., 1984. Particulate amino acids in the sea: effects of primary productivity and biological decomposition. J. Mar. Res., 44: 1075–1097.

Liebezeit, G. and von Bodungen, B., 1987. Biogenic fluxes in the Bransfield Strait: planktonic versus macroalgal sources. Mar. Ecol. Prog. Ser., 36: 23–32.

Lindroth, P. and Mopper, K., 1979. High performance liquid chromatographic determination of subpicomole amounts of amino acids by precolumn fluorescence derivatization with o-phthaldialdehyde. Anal. Chem., 51: 1667–1674.

Liu, D., Wong, P.T.S. and Dutka, B.J., 1973. Determination of carbohydrate in lake sediment by a modified phenol-sulfuric acid method. Water Res., 7: 741–746.

Mantoura, R.F.C. and Llewellyn, C.A., 1983. The rapid determination of algal chlorophyll and carotenoid pigments and their breakdown products in natural waters by reverse-phase high-performance liquid chromatography. Anal. Chim. Acta, 151: 297–314.

Martin, J.H., Knauer, G.A., Karl, D.M. and Broenkow, W.W., 1987. VERTEX: carbon cycling in the northeast Pacific. Deep-Sea Res., 34: 267–285.

Matsueda, H., Handa, N., Inoue, I. and Takano, H., 1986. Ecological significance of salp fecal pellets collected by sediment traps in the eastern North Pacific. Mar. Biol., 91: 421–431.

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., Schick, L.L. and Betchell, F.W., 1986. Measurement of protein in nearshore marine sediments. Mar. Ecol. Prog. Ser., 30: 159–165.

Mayzaud, P. and Martin, J.-L.M., 1975. Some aspects of the biochemical and mineral composition of marine plankton. J. Exp. Mar. Biol. Ecol., 17: 297–310.

Muller, P.J., 1977. C/N ratios in Pacific deep-sea sediments: effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. Geochim. Cosmochim. Acta, 41: 765–776.

Nelson, J.R., Beers, J.R., Eppley, R.W., Jackson, G.A., McCarthy, J.J. and Soutar, A., 1987. A particle flux study in the Santa Monica–San Pedro Basin off Los Angeles: particle flux, primary production, and transmissometer survey. Cont. Shelf Res., 7: 307–328.

Nichols, P.D. and Johns, R.B., 1986. The lipid chemistry of sediments from the St. Lawrence Estuary. Acyclic unsaturated long chain ketones, diols and ketone alcohols. Org. Geochem., 9: 25–30.

Pace, M.L., Knauer, G.A., Karl, D.M. and Martin, J.H., 1987. Primary production, new production and vertical flux in the eastern Pacific Ocean. Nature, 325: 803–804.

Parrish, C.C., Eadie, B.J., Gardner, W.S. and Cavaletto, J.F., 1992. Lipid class and alkane distribution in settling particles of the upper Laurentian Great Lakes. Org. Geochem., 18: 33–40.

Pelletier, E., Ouellet, S. and Paquet, M., 1991. Long-term chemical and cytochemical assessment of oil contamination in estuarine intertidal sediments. Mar. Pollut. Bull., 22: 273–281.

Penry, D.L. and Frost, B.W., 1991. Chlorophyll a degradation by *Calanus pacificus*: dependence on ingestion rate and digestive acclimatation to food resources. Limnol. Oceanogr., 36: 147–159.

Platt, T. and Harrison, W.G., 1985. Biogenic fluxes of carbon and oxygen in the ocean. Nature, 318: 55–58.

Pocklington, R. and Leonard, J.D., 1979. Terrigenous organic matter in sediments of the St. Lawrence Estuary and the Saguenay Fjord. J. Fish. Res. Board Can., 36: 1250–1255.

Pocklington, R. and Tan, F.C., 1987. Seasonal and annual variations in the organic matter contributed by the St. Lawrence River to the Gulf of St. Lawrence. Geochim. Cosmochim. Acta, 51: 2579–2586.

Prahl, 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.

Rodier, L. and Khalil, M.F., 1982. Fatty acids in recent sediments in the St. Lawrence Estuary. Estuarine Coastal Shelf Sci., 15: 473–483.

Roy, S. and Poulet, S.A., 1990. Laboratory study of the chemical composition of aging copepod fecal material. J. Exp. Mar. Biol. Ecol., 135: 3–18.

Runge, J.A. and Simard, Y., 1990. Zooplankton of the St. Lawrence Estuary: the imprint of physical processes on its composition and distribution. In: M.I. El-Sabh and N. Silverberg (Editors), Oceanography of a Large-Scale Estuarine System, the St. Lawrence. Springer, New York, pp. 296–300.

Sarmiento, J.L. and Sundquist, E.T., 1992. Revised budget for the oceanic uptake of anthropogenic carbon dioxide. Nature, 356: 589–593.

Silverberg, N., 1991. Spatio-temporal variability in the flux of particulate matter in the Laurentian Trough. Annu. Meet. Am. Soc. Limnol. Oceanogr., Halifax, June 10–14.

Silverberg, N. and Sundby, B., 1990. Sediment–water interaction and early diagenesis in the Laurentian Trough. In M.I. El-Sabh and N. Silverberg (Editors), Oceanography of a Large-Scale Estuarine System, the St. Lawrence. Springer, New York, NY.

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.

Silverberg, N., Juniper, K. and Tremblay, G.-H., 1991. Patterns of particle flux and sediment response during the COUPPB project. Annu. Meet. Am. Soc. Limnol. Oceanogr., Halifax.

Simard, Y., de Ladurantaye, R. and Therriault, J.-C., 1986. Aggregation of euphausiids along a coastal shelf in an upwelling environment. Mar. Ecol., 32: 203–215.

Staresinic, N., Rowe, G.T., Shaughnessy, D. and Williams, A.J., 1978. Measurement of the vertical flux of particulate matter with a free-drifting sediment trap. Limnol. Oceanogr., 23: 559–563.

Strain, P.M. and Tan, F.C., 1979. Carbon and oxygen isotope ratios in the Saguenay Fjord and the St. Lawrence Estuary and their implications for paleoenvironmental studies. Estuarine Coastal Mar. Sci., 8: 119–126.

Strickland, J.D.H. and Parsons, T.R., 1972. A Practical Handbook of Seawater Analysis. Fish. Res. Board Can.

Suess, E., 1980. Particulate organic carbon flux in the oceans-surface, productivity and oxygen utilization. Nature, 288: 260–263.

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.

Syvitski, J.P.M., Silverberg, N., Ouellet, G. and Asprey, K.W., 1983. First observations of benthos and seston from a submersible in the Lower St. Lawrence Estuary. Geogr. Phys. Quat., 37: 227–240.

Tan, F.C. and Strain, P.M., 1983. Sources, sinks and distribution of organic carbon in the St. Lawrence Estuary, Canada. Geochim. Cosmochim. Acta, 47: 125–132.

Tanoue, E. and Handa, N., 1987. Monosaccharide composition of

marine particles and sediments from the Bering Sea and northern North Pacific. Oceanol. Acta, 10: 91–99.

Therriault, J.-C. and Levasseur, M., 1985. Control of phytoplankton production in the lower St. Lawrence Estuary: light and freshwater runoff. Nat. Can., 112: 77–96.

Tsunogai, S. and Noriki, S., 1987. Organic matter fluxes and the sites of oxygen consumption in deep water. Deep-Sea Res., 34: 755–767.

Vernet, M. and Lorenzen, C.J., 1987. The relative abundance of pheophorbide a and pheophytin a in temperate marine waters. Limnol. Oceanogr., 32: 352–358.

Wakeham, S.G., Farrington, J.W. and Gagosian, R.B., 1984a. Variability in lipid flux and composition of particulate matter in the Peru upwelling region. Org. Geochem., 6: 203–215.

Wakeham, S.G., Lee, C., Farrington, J.W. and Gagosian, R.B., 1984b. Biogeochemistry of particulate organic matter in the oceans: results from sediment trap experiments. Deep-Sea Res., 31: 509–528.

Wassmann, P., Martinez, R. and Vernet, M., 1994. Respiration and biochemical composition of sedimenting organic matter during summer in the Barents Sea. Cont. Shelf Res., 14: 79–90.

Wefer, G.E., Suess, E., Balzer, W., Liebezeit, G., Muller, P.J., Ungerer, C.A. and Zenk, W., 1982. Fluxes of biogenic components from sediment trap deployment in circumpolar waters of the Drake Passage. Nature, 299: 145–147.

Welschmeyer, N.A. and Lorenzen, C.J., 1985. Chlorophyll budgets: zooplankton grazing and phytoplankton growth in a temperate fjord and the Central Pacific Gyres. Limnol. Oceanogr., 30: 1–21.