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Lipid biogeochemistry in the Laurentian Trough: I—fatty acids, sterols and aliphatic hydrocarbons in rapidly settling particles

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Abstract—Sinking particles intercepted at 150 m depth in May and July at landward (L) and seaward (S) sites in the Laurentian Trough contained 540–2910 $\mu g\ g^{-1}$ of fatty acids (FA), 54–990 $\mu g\ g^{-1}$ of sterols and 101–184 $\mu g\ g^{-1}$ of aliphatic hydrocarbons. The vertical fluxes averaged 7.2, 3.1 and 0.8 $mg\ m^{-2}\ d^{-1}$, respectively. FA fluxes (greater at site L) and concentrations (higher at S and during July) reflected the terrestrial–marine gradient and the seasonal patterns of primary production in the estuary. Unresolved anthropogenic hydrocarbons (UCM) displayed an opposite trend. The sources and behaviour of individual lipid biomarkers were evaluated by multivariate techniques. FA 16:0 and 16:1, heneicosahexaene and 24-methylcholest-5-en-3β-ol were the most consistent tracers of an early diatom bloom sampled at the seaward site. FA 14:0 and 15:0, squalene and 24-methylcholesta-5,22E-dien-3β-ol also traced this event but were less specific. The summer increase of primary production was reflected by cholestanol, 24-methylenecholesterol, 24-norcholesta-5,22E-dien-3β-ol, 24-ethylcholesta-5,22E-dien-3β-ol and dinosterol. Zooplanktonic pristane, unsaturated FA, cholesterol and cholesta-5,22E-dien-3β-ol, were abundant in all the traps. At the landward site, cholesterol and cholesta-5,22E-dien-3β-ol covaried with dinosterol, suggesting a dinoflagellate contribution as well. These samples were very heterogeneous and showed variable inputs from higher plants (stigmastanol, FA 24:0, 26:0, long-chain *n*-alkanes), petrogenic hydrocarbons (*n*-alkanes, UCM) and plankton (unsaturated FA, cholesterol), reflecting the combined contribution from the Upper St. Lawrence Estuary, Saguenay Fjord and a periodic upwelling.

Key words—settling particles, lipid sources and fluxes, fatty acids, sterols, aliphatic hydrocarbons, Laurentian Trough

INTRODUCTION

In 1988, we began a project to study the composition, fluxes and early diagenesis of organic matter (OM) in the Laurentian Trough, a 300–350 m deep depositional channel which allows entry of North Atlantic waters far into the heart of the continent and drainage of the Great Lakes and the St. Lawrence Basin (Fig. 1). The questions addressed were: (1) what is the chemical composition of the rapidly settling organic material which constitutes the main source of energy to the sediments, and (2) to what extent does this chemistry reflect source material and/or its alteration by water column and sedimentary processes. The study of several bulk organic parameters, as well as the amino acid composition in settling particles and underlying sediments from two contrasting sites, revealed that the vertical flux of OM in the Lower St. Lawrence Estuary contains a strong terrigenous component, and that zooplanktonic influences dominated over those of fresh phytoplankton (Colombo *et al.*, 1996a,b; Colombo *et al.*, submitted). A distinct land–sea gradient is apparent in terms of sedimentation rates and relative marine contribution. The characterized portion of total organic carbon (TOC) consisted of lipids (17–37 %), carbohydrates (7.9–16 %), hydrolyzable amino acids (8.4–16 %), and labile proteins (0.3–2.6 %). However, little information was obtained from these data on particular sources of OM, i.e. different algae, zooplankton, vascular plants, anthropogenic material and bacteria. Lipids were examined in more detail to fill this gap.

Although lipids usually represent a small fraction of TOC, their diversity and specificity makes them useful compounds to study sources and follow the transformation of OM. This has led to the development and use of the "biomarker approach" (e.g. Brassell and Eglinton, 1983; Johns, 1986; Saliot *et al.*, 1991). Fatty acids are among the most abundant biomarkers, but they are considered to be relatively nonspecific source indicators. On the other hand, they are one of the few indicators of bacterial contributions and may also distinguish marine from terrigenous and algal from zooplanktonic inputs (Gillan and Johns, 1986; Wakeham and Lee, 1989). Aliphatic hydrocarbons are more specific, with com-

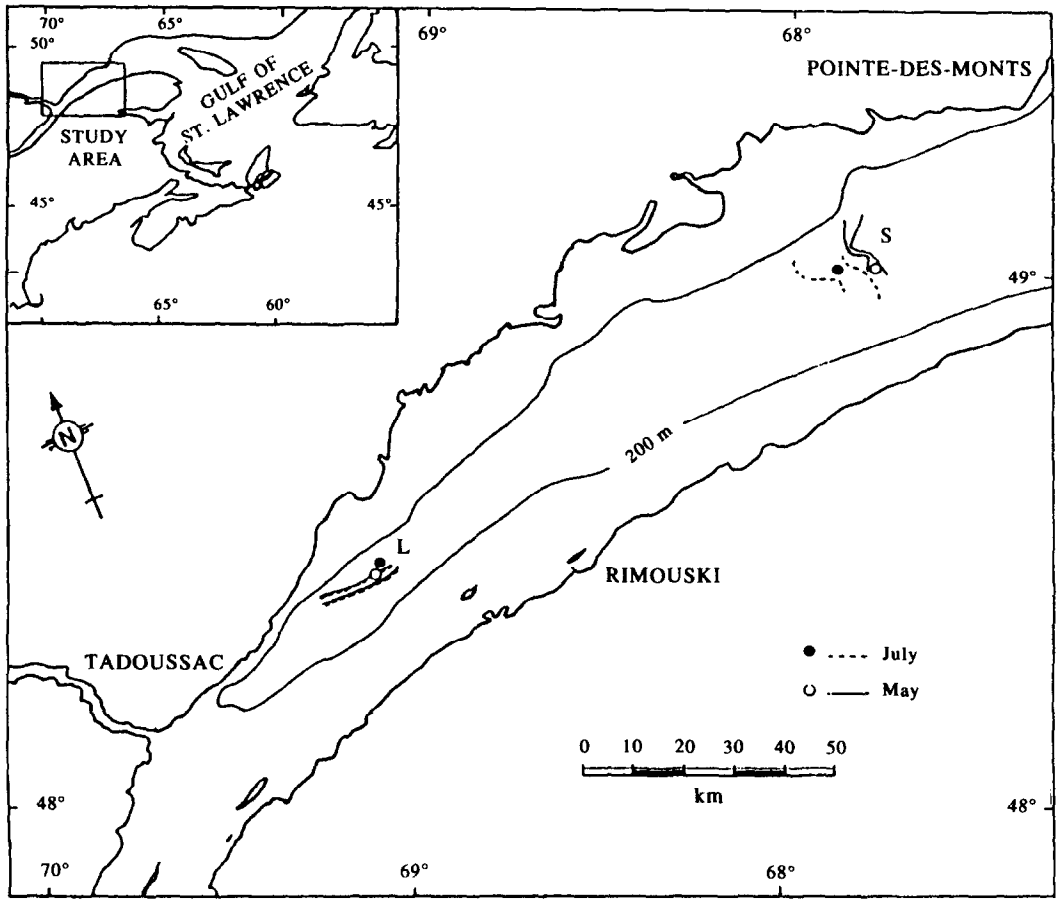

Fig. 1. Trajectories followed by the free-drifting sediment traps and coring sites at both stations (L: landward, S: seaward) and sampling periods in the Laurentian Trough.

pounds characteristic of algae, zooplankton, vascular plants and anthropogenic contamination (e.g. Blumer *et al.*, 1971; Volkman and Maxwell, 1986; Colombo *et al.*, 1989). Sterols are among the most specific and diverse lipid biomarkers and can trace the contribution from different algae, higher animals, vascular plants, and sewage contamination (e.g. Hatcher and McGillivary, 1979; Huang and Meinschein, 1979; Volkman, 1986).

The principal limitations of the "biomarker approach" are related to the wide distribution of some compounds, the different reactivity of the components, and the multiplicity of processes (biological, chemical, physical and geochemical) which transform the original source signals. Approaches taken to minimize these problems include using relative and absolute concentrations instead of presence/absence, and the quantification of several biomarkers from different lipid classes.

In this paper we report the results for more than 60 compounds from three lipid classes which were analyzed to characterize the sources of OM and evaluate their sensitivity. The subsequent decay of these lipids in detailed profiles of underlying sediments is presented in a following paper.

MATERIALS AND METHODS

Sampling

A detailed description of the study area and sampling methods is presented in previous papers (Colombo *et al.*, 1996a,b). Briefly, settling particles were intercepted with two unpoisoned, free-drifting sediment traps suspended at 150 m depth at a landward site (L; 48° 26'N and 69° 07'W) and a seaward site (S; 49° 01'N and 67° 49'W) in the Laurentian Trough (Fig. 1). After 8–30 h deployment, the traps were recovered and the samples collected in 2 l glass jars. The water was decanted, the few swimmers were eliminated and the material was then split for weighing, chemical analysis, and microscopic examination. The samples were stored at −20 or −40 °C until analysis.

Chemical analysis

Approximately 2–4 g wet weight of the trap material was extracted with a 1:1 acetone–petroleum ether mixture and sonication (3 × 15 min). The combined organic phases were dried, concentrated and stored under nitrogen at −20 °C. Fatty acids were converted to methyl esters (FAMES) by acid-cata-

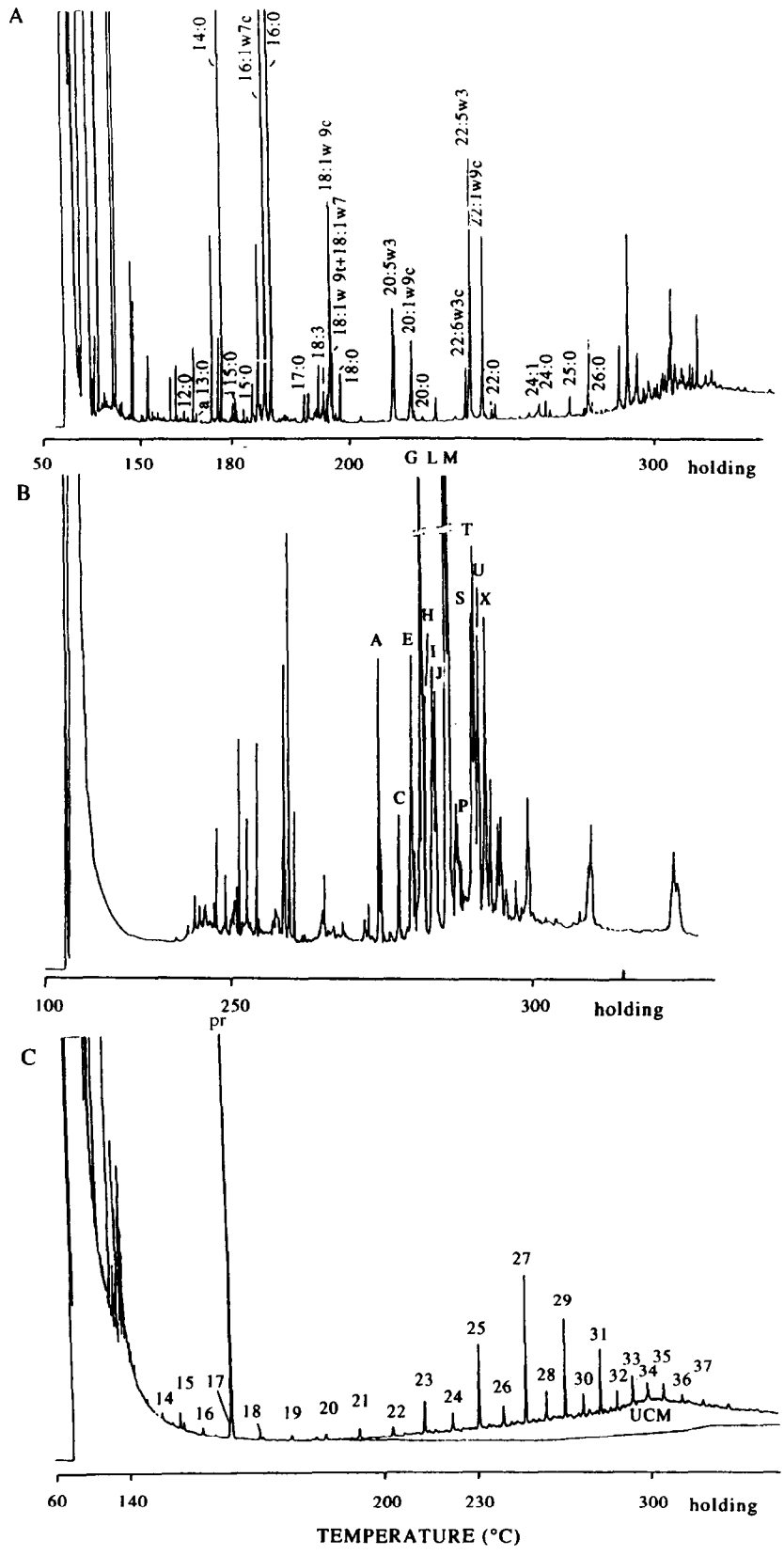

Fig. 2. Representative gas chromatograms of fatty acid methyl esters (A), sterols (B) and aliphatic hydrocarbons (C) in rapidly settling particles. Peaks numbered 14 to 37 in the chromatogram of hydrocarbons are *n*-alkanes with that chain length and pr indicates pristane. Sterol identification is as in Table 2.

lyzed transesterification reacting 50 μl of lipids in toluene with 1 % sulphuric acid in methanol at 50 °C overnight. The esters were extracted with hexane, dried, concentrated to 200 μL and analyzed using a Varian 600 gas chromatograph equipped with an on-column injector programmed from 50 to 300 °C at 20 °C min^{-1}, a 0.25 mm × 30 m J & W DB5 capillary column, and a flame ionization detector (FID) operating at 320 °C. The oven temperature was programmed from 50 °C (2 min hold) to 150 °C at 16 °C min^{-1}, then to 180 °C (2 min) at 4 °C min^{-1} and to 200 °C (1 min) at 2 °C min^{-1} with a final ramp of 4 °C min^{-1} to 300 °C (6 min hold). Fatty acid (FA) assignments were done by comparison of retention times with authentic standards (Polyscience Corp., Alltech, Supelco) which included *n*-C_{11}–C_{30}, 16:1(*n*-7), 18:1(*n*-9), 18:1(*n*-7), 20:1, 22:1, 24:1, 18:2(*n*-6), 18:3, 20:2, 20:3, 20:4, 22:5, 22:6, branched-chain C_{13}–C_{16} FA and 22 C_{11}–C_{20} saturated, monoenoic, hydroxy and branched bacterial FA. The response factor of the standards was used for quantification. Results were corrected for the recovery yield tested with FA 11:0, 17:0 and 25:0 (74 ± 2.3 %).

Hydrocarbons and sterols were fractionated in 30 × 1 cm glass columns packed with 7 g of activated silica gel, 5 g of deactivated aluminium oxide, 2 cm of activated copper and 3 cm of Na_2SO_4. The columns were eluted with 17 ml hexane (F1: aliphatic hydrocarbons); 21 ml hexane–methylene chloride 1:1 (F2: aromatic + chlorinated hydrocarbons); and 25 ml of methanol (F3: sterols). Heneicosahexaene ($C_{21:6}$) and squalene ($C_{30:6}$) eluted in F2 which was analyzed using the same GC conditions as F1.

The aliphatic fractions were concentrated to 100–200 μl under a N_2 flow and analyzed in the Varian 600 GC with the on-column injector programmed from 60 to 300 °C at 40 °C min^{-1} and the same column and FID used for FAMES. The oven temperature was programmed from 60 °C (1 min hold) to 140 °C (1 min) at 16 °C min^{-1}, then to 200 °C at 3 °C min^{-1} and to a final plateau at 300 °C (12 min hold) at 4.5 °C min^{-1}. Structural assignments were carried out by comparison of retention times with authentic standards (Alltech, Thetakit) which included *n*-C_{15}–C_{26}, *n*-C_{28}, *n*-C_{30}, *n*-C_{32}, *n*-C_{34}, *n*-C_{36}, *n*-C_{38}, *n*-C_{40} alkanes, pristane and phytane. The average response factor of the standards was used for quantification. The unresolved complex mixture (UCM) was measured by planimetry and quantified using the *n*-alkane response factor. The recovery yield averaged 93 ± 13 % (n = 39).

The sterol fractions (F3) were evaporated to dryness under a N_2 flow at 40 °C and subsequently derivatized to produce trimethylsilylethers (100 μl BSTFA:TMCS 10:1 v/v, 2 h at 40 °C). The extracts were evaporated with N_2, redissolved in 150 μl of toluene and analyzed in the Varian 600 GC with the on-column injector programmed from 100 to 300 °C at 40 °C min^{-1}, the same column and the FID operating at 325 °C. The oven temperature was programmed from 100°C (1 min hold) to 250 °C (1 min hold) at 15 °C min^{-1} and then to 300 °C (12 min hold) at 3 °C min^{-1}. Compound identification was done by comparison of retention times with six standards (lanosterol, sitosterol, stigmasterol, campesterol, cholestanol and cholesterol) and by comparison with published chromatograms (Lee *et al.*, 1979; Smith *et al.*, 1982; Volkman, 1986; Volkman *et al.*, 1987). The average response factor of the available standards was used for quantification. The results were corrected for the recovery yield of the procedure (71 ± 13 %).

Figure 2 shows representative chromatograms of fatty acids, aliphatic hydrocarbons and sterols in settling particles. Sterols G–H, I–J, L–M and S–T were incompletely separated. L–M and S–T were the most critical pairs and in some samples (site L May 12, site L May 13, site S May 10; Table 2) they could not be discriminated, thus peaks L and T include the contribution of M and S respectively. The identity assignments of major peaks were confirmed by GC–MS analysis of selected samples performed with a Hewlett Packard 5890A GC operated with the same column and conditions described for FAMES and sterols, and interfaced to a VG TS250 run in the EI mode (70 eV) with a 0.9 d^{-1} scan time over a 50–650 m range (resolution: 700 daltons). The GC–MS analysis of the sterol fraction revealed that in the traps (but not in the sediments) peak U contained isofucosterol (m/z 386 and M^+ = 484) coeluting with stigmastanol (m/z 383, 398 and M^+ = 488). Thus the prevailing vascular plant biomarker U, contains some algal contribution of isofucosterol (Volkman, 1986).

RESULTS AND DISCUSSION

Geographic and temporal trends of lipid classes

Tables 1–3 give the relative composition, total concentrations and fluxes of the lipid classes examined in each trap as well as their average by station and sampling period. Figure 3 shows the average concentrations and fluxes (±1 SD). Fatty acids were the most abundant lipids (1430 ± 800 μg g^{-1}) followed by sterols (580 ± 380 μg g^{-1}), unresolved hydrocarbons (UCM, 104 ± 22 μg g^{-1}), and resolved aliphatic hydrocarbons (RESHC, 26 ± 7.1 μg g^{-1}). The fluxes averaged 7.2 ± 4.4, 3.1 ± 3.5, 0.7 ± 0.5 and 0.15 ± 0.07 mg m^{-2} d^{-1}, respectively. The concentrations and fluxes of lipids measured in the St. Lawrence are similar to those reported for other deep nearshore areas such as Dabob Bay and the Peru upwelling (Prahl *et al.*, 1980; Wakeham *et al.*, 1984) which are also comparable in terms of the total carbon flux (Colombo *et al.*, 1996a).

Table 1. Relative composition, total concentrations and fluxes, of fatty acids measured at 150 m depth at a landward and a seaward station in the Lower St. Lawrence Estuary

	% Total									Means						
Station	Landward				Seaward					Landward			Seaward			
Month	May	May	May	July	May	May	May	July	July	May	SD	July	May	SD	July	SD
Day	12	12	13	15	9	10	10	17	18							
Fatty Ac.																
12:0	—	0.3	—	—	0.2	0.2	—	0.1	0.5	0.1	0.2	—	0.2	0.1	0.3	0.3
a13:0	—	0.2	—	—	—	0.1	—	0.1	0.2	0.1	0.1	—	—	0.1	0.1	0.1
14:0	5.4	6.8	5.5	9.7	11.5	12.2	11.0	9.8	9.5	5.9	0.8	9.7	11.5	0.7	9.7	0.2
i15:0	0.8	0.6	0.3	0.4	0.3	0.3	—	0.4	0.4	0.6	0.2	0.4	0.2	0.2	0.4	0.0
a15:0	0.6	0.6	0.4	0.3	0.3	0.3	—	0.3	0.3	0.5	0.1	0.3	0.2	0.2	0.3	0.0
15:0	0.5	0.6	0.6	0.6	1.2	1.2	1.4	0.7	0.6	0.6	0.1	0.6	1.2	0.1	0.6	0.1
i16:0	—	—	—	0.3	0.3	0.3	—	0.4	0.3	—	—	—	0.2	0.2	0.3	0.0
16:1	10.1	14.0	12.3	16.3	22.0	24.0	20.0	16.0	17.0	12.1	1.8	16.3	22.0	2.0	16.1	0.8
16:0	13.3	12.4	15.1	20.5	34.2	41.3	50.0	25.0	20.0	14.0	1.4	20.5	42.0	7.9	22.1	3.6
18:2	0.6	—	1.0	1.1	0.4	—	—	1.0	1.2	0.5	0.5	1.1	0.1	0.2	1.1	0.1
18:1(*n*-7)	1.5	2.5	1.8	2.8	2.3	2.3	2.8	3.9	2.4	1.9	0.5	2.8	2.5	0.3	3.2	1.1
18:1(*n*-9)	8.9	11.0	11.0	12.3	5.1	4.5	5.4	13.0	9.8	10.1	1.1	12.3	5.0	0.4	11.3	2.2
18:0	3.1	2.6	3.7	1.9	2.7	2.8	3.6	2.6	1.9	3.1	0.6	1.9	3.0	0.5	2.2	0.5
20:5	9.5	7.1	5.9	6.9	3.8	2.7	2.2	3.5	4.0	7.5	1.8	6.9	2.9	0.8	3.7	0.4
20:1	10.0	10.2	7.9	6.6	4.2	1.6	—	3.7	4.9	9.4	1.3	6.6	1.9	2.1	4.3	0.8
20:0	1.2	0.5	0.6	0.2	0.2	—	—	0.2	0.2	0.8	0.4	0.3	0.1	0.1	0.2	0.0
22:6	0.7	0.7	0.9	1.5	0.5	0.5	—	1.9	2.0	0.7	0.1	1.5	0.3	0.3	2.0	0.1
22:5	17.1	14.0	14.3	8.5	3.8	2.2	—	8.9	13.0	15.1	1.8	8.5	2.0	1.9	11.0	2.9
22:1	11.1	9.7	9.6	5.5	4.7	1.1	0.9	4.9	7.0	10.1	0.8	5.5	2.3	2.1	6.0	1.5
22:0	1.1	1.8	1.8	0.7	0.7	0.7	0.9	0.5	0.4	1.6	0.4	0.7	0.8	0.1	0.4	0.1
24:1	1.7	1.1	2.0	0.9	0.3	—	—	0.7	0.6	1.6	0.5	1.0	0.1	0.2	0.6	0.1
24:0	1.8	2.5	2.7	1.4	0.9	0.9	1.1	0.8	0.7	2.3	0.5	1.4	1.0	0.1	0.7	0.1
26:0	1.1	1.4	2.7	0.9	0.5	0.5	1.0	0.7	0.5	1.7	0.9	0.9	0.7	0.3	0.6	0.2
Tot. Conc. ($\mu g\ gdw^{-1}$)	540	1110	660	1300	1530	1760	740	2350	2910	770	300	1300	1340	530	2630	400
Tot. Flux ($mg\ m^{-2}\ d^{-1}$)	5.7	13.0	3.6	15.0	10.5	4.8	2.8	4.4	4.9	7.3	4.8	15.0	6.0	4.0	4.7	0.4

—: Below detection limits.
SD: standard deviation.

Previous studies of the bulk organic composition of the settling particles revealed consistent geographical and temporal trends related to the position of the stations along the land–sea gradient and the seasonal cycle of primary production. The fluxes were greater at station L, the concentrations of OM were higher at the site S, and increased in July at both stations (Colombo *et al.*, 1996a). Terrestrial inputs (highest in the spring runoff) are attenuated with time and distance from the river while marine *in situ* production, which produce particles enriched in OM, predominates at station S and during the summer.

In general, excluding the UCM, lipids followed the trends of bulk parameters (average fluxes 1.3–1.7 times higher at site L, concentrations 1.4–2.4 times higher at S with a 0–775 % increase in July), but showed high variability (Fig. 3). This is probably related to the greater sensitivity of the biomarkers to the contribution of specific OM sources. Fatty acids, which accounted for 2.4 % TOC in our traps, similar to proteins, better reflected the changes of bulk organic components and displayed similar seasonal changes. In contrast, RESHC levels were higher at station S (ranges overlapping with site L in May), but showed no seasonal trend, while sterols presented a marked July increase at site L and high, constant values at station S, similar to the behaviour of pigments (Colombo *et al.*, 1996a).

A different trend is observed for the UCM, the unresolved hump below the *n*-alkanes taken as indicative of petrogenic pollution, although recycled, multiple-source material could also contribute (Colombo *et al.*, 1989). The pattern appears to be opposite to that of bulk organic components or fatty acids (concentrations usually higher at site L and during May), but due to the variability, the differences are not significant (Fig. 3). The UCM/RESHC ratios reflect more clearly the decrease of petrogenic inputs with distance from the river and during July (5.8 ± 1 to 4.4 at station L and 3.6 ± 0.9 to 2.8 ± 0.2 at site S, from May to July; Table 3).

Geographic and temporal trends of individual compounds

To characterize specific sources of OM, we examined the relative distribution of individual biomarkers, interpreting the information in the context of the consistent geographic and temporal trends observed for bulk organic components. These earlier data indicated that on average, about half of the carbon flux was of terrigenous origin, with higher values during the spring runoff at site L (70 %). Among marine sources, the zooplanktonic contri-

Table 2. Relative composition, total concentrations and fluxes of sterols measured at 150 m depth at a landward and a seaward station in the Lower St. Lawrence Estuary

		% Total									Means						
	Station	Landward				Seaward					Landward			Seaward			
	Month	May	May	May	July	May	May	May	July	July	May	SD	July	May	SD	July	SD
	Day	12	12	13	15	9	10	10	17	18							
Sterol																	
A		3.8	3.0	2.6	3.7	5.6	5.0	5.7	6.8	6.5	3.1	0.6	3.7	5.4	0.4	6.6	0.2
C		3.3	2.0	1.4	2.1	4.5	6.1	3.7	4.6	5.1	2.2	0.9	2.1	4.8	1.2	4.9	0.3
E		6.0	13.7	2.6	5.0	3.2	2.7	3.4	4.7	4.5	7.4	5.7	5.0	3.1	0.3	4.6	0.2
G		20.2	36.3	11.1	25.0	12.4	13.2	12.3	13.2	13.3	23.0	13.0	25.0	13.0	0.5	13.2	0.0
H		3.2	—	1.2	3.1	1.1	1.3	1.0	2.2	2.4	1.5	1.6	3.1	1.1	0.1	2.3	0.2
I		8.5	—	7.9	6.1	11.5	10.2	10.2	7.4	7.5	5.5	4.7	6.1	10.6	0.7	7.4	0.0
J		2.8	14.3	5.0	3.7	6.5	6.3	3.9	5.4	6.3	7.3	6.1	3.7	5.6	1.4	5.8	0.6
L		13.5	3.9	21.0	17.4	12.0	18.0	8.5	17.1	18.0	13.0	8.5	17.4	13.0	4.8	17.4	0.5
M		4.3	—	-	11.1	18.0	13.4	24.5	6.4	6.6	1.4	2.5	11.1	19.0	5.6	6.5	0.2
P		1.1	—	1.6	1.3	2.6	3.4	4.1	4.1	5.5	0.9	0.8	1.3	3.4	0.8	4.8	1.0
S		8.2	—	12.1	4.4	1.1	—	—	0.9	2.1	6.8	6.2	4.4	0.4	0.6	1.5	0.8
T		18.4	15.0	15.0	7.0	14.2	13.0	15.4	17.2	14.0	16.1	2.1	7.0	14.2	1.2	15.4	2.5
U		3.4	5.0	19.0	4.8	2.7	2.5	2.6	3.0	3.1	9.1	8.5	4.8	2.6	0.1	3.1	0.0
X		3.6	7.4	—	4.0	5.0	5.2	4.6	6.3	5.9	3.7	3.7	4.0	4.9	0.3	6.1	0.3
Tot. Conc. ($\mu g\ gdw^{-1}$)		140	54	140	980	990	860	520	840	670	112	50	980	790	240	760	120
Tot. Flux ($mg\ m^{-2}\ d^{-1}$)		1.5	0.6	0.8	11.0	6.8	2.4	1.9	1.6	1.1	1.0	0.5	11.0	3.7	2.7	1.4	0.3

—: Below detection limits.
SD: standard deviation.
A = 24-norcholesta-5,22E-dien-3β-ol.
C = 5β-cholestan-3β-ol(coprostanol).
E = cholesta-5,22E-dien-3β-ol.
G = cholest-5-en-3β-ol (cholesterol).
H = 5α-cholestan-3β-ol (cholestanol).
I = 24-methylcholesta-5,22E-dien-3β-ol (24α crino-diatomsterol;24β brassicasterol).
J = 24-methyl-5α-cholest-22E-en-3β-ol.
L = 24-methylcholesta-5,24(28)-dien-3β-ol (24-methylenecholesterol).
M = 24-methyl-5α-cholest-24(28)-en-3β-ol + 24-methylcholest-5-en-3β-ol (24αcampesterol;24β 22-dihydrobrassicasterol).
P = 23,24-dimethyl-5α-cholest-22E-en-3β-ol + 24-ethylcholesta-5,22E-dien-3β-ol (24α stigmasterol; 24β poriferasterol).
S = 23,24-dimethylcholest-5-en-3β-ol.
T = 23,24-dimethyl-5α-cholestan-3β-ol + 24-ethylcholest-5-en-3β-ol (24α sitosterol; 24β clionasterol) + 24-ethylcholesta-5,24(28)E-dien-3β-ol (fucosterol).
U = 24-ethyl-5α-cholestan-3β-ol (stigmastanol) + 24-ethyl-5α-cholest-24(28)E-en-3β-ol + 24-ethylcholesta-5,24(28)Z-dien-3β-ol (isofucosterol).
Z = 4α,23,24-trimethyl-5α-cholest-22-en-3β-ol (dinosterol).

bution predominated over that of algae, but an unexpectedly important phytoplankton bloom, evidenced by the abundance of pigments and chain forming diatoms, was sampled at the seaward station in May (Colombo *et al.*, 1996a).

Fatty acids

The most abundant FA in settling particles are 16:0 (12–50 % total), 16:1 (10–24 %), 18:1(*n*-9c) (4.5–13 %), 14:0 (5.4–12 %), 22:5 (0–17 %) and 22:1, 20:1 and 20:5 (1–11 % each; Table 1; Fig. 4). This dominance of C_{14}–C_{22} FA is typical of plankton and has been reported for settling particles in other freshwater and marine environments (Tanoue and Handa, 1980; Saliot *et al.*, 1982; Meyers *et al.*, 1984; Kawamura *et al.*, 1987; Wakeham and Lee, 1989; Reemtsma *et al.*, 1990; Reemtsma and Ittekkot, 1992). Fatty acids 14:0, 16:0, 16:1(*n*-7), 20:5, 22:5 and 22:6 are abundant in phytoplankton, while 16:0, 18:1(*n*-9), 18:0, 20:5 and 22:6, often predominate in zooplankton. Diatoms are rich in 14:0, 16:0 and 16:1 FA and low in C_{18} homologues. In contrast, 18:1, 18:2, 18:3 and 18:4 predominate in flagellates and freshwater algae while 18:5 and 22:6 are abundant in dinoflagellates (Kattner *et al.*, 1983; Mayzaud *et al.*, 1989; Wakeham and Lee, 1989; Ahlgren *et al.*, 1990; Hama, 1991). However, higher plants also contain C_{16}–C_{18} fatty acids together with their more specific saturated C_{22}–C_{32} series (Matsuda and Koyama, 1977).

The relative distribution of the three principal fatty acids in diatoms (14:0, 16:0 and 16:1) shows a clear pattern with a maximum at site S in May (Fig. 4), consistent with the existence of an early phytoplankton bloom. The lower percentages observed in July when the contribution of 18:1(*n*-9), 22:5 and 22:6 increase, suggest a stronger relative input from zooplankton and also dinoflagellates, as suggested by the increase of dinosterol (see sterols). However, as mentioned previously, C_{14}–C_{16} FA are not exclusive to diatoms and they are also found in higher plants, green algae or bacteria (Matsuda and Koyama, 1977; Kayama *et al.*, 1989). These are potential sources in the station L May traps, whose terrestrial nature was reflected by the abundance of

Table 3. Relative composition, total concentrations and fluxes of aliphatic hydrocarbons measured at 150 m depth at a landward and a seaward station in the Lower St. Lawrence Estuary

	% Total									Means						
Station	Landward				Seaward					Landward			Seaward			
Month	May	May	May	July	May	May	May	July	July	May	SD	July	May	SD	July	SD
Day	12	12	13	15	9	10	10	17	18							
Hydroc.																
n-C14	—	0.6	—	—	—	—	—	0.3	—	0.2	0.4	—	—	0.0	0.2	0.2
n-C15	0.1	0.6	—	0.4	—	0.3	—	0.8	0.8	0.2	0.3	0.4	0.1	0.2	0.8	0.0
n-C16	0.3	0.6	—	—	—	—	—	0.4	0.5	0.3	0.3	—	—	0.0	0.4	0.1
n-C17	0.7	1.5	—	—	0.9	—	—	—	—	0.7	0.7	—	0.3	0.5	—	0.0
PRIS	22.0	34.0	35.0	27.2	36.1	39.3	33.3	47.2	53.0	30.1	7.2	27.2	36.2	3.0	50.0	3.9
n-C18	—	0.9	—	0.5	0.5	0.3	0.7	0.3	0.3	0.3	0.5	0.5	0.5	0.2	0.3	0.0
PHYT	—	0.7	—	0.2	0.2	0.2	0.5	0.1	0.1	0.2	0.4	0.2	0.3	0.2	0.1	0.0
n-C19	0.6	1.1	—	0.6	0.5	0.5	—	0.5	0.3	0.5	0.5	0.6	0.4	0.3	0.4	0.1
FICHT	0.6	0.9	—	0.6	—	0.3	—	—	—	0.5	0.5	0.6	0.1	0.2	—	0.0
n-C20	0.4	1.0	—	0.6	—	0.6	0.5	0.5	0.3	0.5	0.5	0.6	0.4	0.3	0.4	0.1
HEH	0.7	0.8	—	4.2	16.1	12.0	6.1	2.5	3.2	0.5	0.4	4.2	11.3	5.0	2.8	0.5
n-C21	2.3	1.9	2.5	1.2	0.9	1.1	1.1	0.9	0.8	2.2	0.3	1.2	1.1	0.1	0.9	0.1
n-C22	3.6	1.7	2.2	1.2	0.7	1.4	1.1	0.8	0.8	2.5	1.0	1.2	1.1	0.4	0.8	0.1
n-C23	6.0	4.2	4.8	3.1	2.0	2.9	4.4	2.5	2.2	5.0	0.9	3.1	3.1	1.2	2.4	0.2
n-C24	5.3	2.4	2.2	1.5	1.3	2.1	3.5	1.1	1.1	3.3	1.7	1.5	2.3	1.1	1.1	0.0
n-C25	8.1	5.5	7.3	6.5	2.5	4.0	7.1	6.5	5.3	7.0	1.3	6.5	4.5	2.3	5.9	0.8
n-C26	5.7	2.8	3.0	2.2	1.9	2.6	5.4	1.4	1.4	3.8	1.6	2.2	3.3	1.9	1.4	0.0
n-C27	8.5	7.8	8.8	9.9	4.5	4.4	7.4	9.8	8.2	8.4	0.5	9.9	5.4	1.7	9.0	1.1
n-C28	5.7	2.6	3.1	3.3	2.4	2.4	3.4	1.7	1.5	3.8	1.7	3.3	2.7	0.6	1.6	0.1
SQUAL	3.1	5.3	5.4	5.9	9.9	8.8	7.3	3.7	1.8	4.6	1.3	5.9	8.7	1.3	2.8	1.4
n-C29	6.8	7.5	8.1	8.2	4.1	4.3	5.3	6.8	6.2	7.5	0.7	8.2	4.5	0.7	6.5	0.4
n-C30	4.2	2.3	2.7	3.0	2.3	2.1	2.5	1.3	1.4	3.0	1.0	3.0	2.3	0.2	1.4	0.1
n-C31	5.1	5.6	6.1	6.6	3.1	3.4	3.7	4.6	4.4	5.6	0.5	6.6	3.4	0.3	4.5	0.1
n-C32	2.5	1.9	1.4	2.5	1.9	1.6	1.7	1.2	1.3	1.9	0.6	2.5	1.7	0.2	1.3	0.1
n-C33	3.4	2.0	2.7	3.1	2.1	1.6	1.8	1.5	1.8	2.7	0.7	3.1	1.8	0.2	1.6	0.2
n-C34	1.7	1.3	2.2	2.5	1.4	1.7	1.8	1.6	1.0	1.8	0.5	2.5	1.7	0.2	1.3	0.4
n-C35	1.3	0.9	2.4	2.2	1.3	1.0	1.5	1.2	1.6	1.5	0.8	2.2	1.2	0.3	1.4	0.3
n-C36	0.3	0.4	—	1.2	1.0	0.7	—	0.6	0.8	0.2	0.2	1.2	0.6	0.5	0.7	0.1
n-C37	0.1	0.3	—	0.8	0.8	0.6	—	—	—	0.1	0.1	0.8	0.5	0.4	-	0.0
CPI	1.4	3.0	2.8	3.1	1.9	1.8	1.7	5.5	4.9	2.4	0.8	3.1	1.8	0.1	5.2	0.5
Tot. Conc. ($\mu g\ gdw^{-1}$)																
RESHC	29.0	17.0	16.2	21.0	26.0	37.4	24.2	28.4	34.1	21.0	7.1	21.0	29.1	7.3	31.3	4.0
UCM	155.0	118.4	85.0	91.4	94.0	102.4	109.4	86.0	93.0	119.4	35.0	91.4	102.0	7.9	89.4	4.7
UCM/ RESHC	5.3	7.0	5.2	4.4	3.6	2.7	4.5	3.0	2.7	5.9	1.0.	4.4	3.6	0.9	2.9	0.2
Fluxes ($mg\ m^{-2}\ d^{-1}$)																
RESHC	0.3	0.2	0.1	0.2	0.2	0.1	0.1	0.1	0.1	0.2	0.1	0.2	0.1	0.0	0.1	0.0
UCM	1.6	1.4	0.5	1.0	0.6	0.3	0.4	0.2	0.2	1.1	0.6	1.0	0.4	0.2	0.2	0.0

—: Below detection limits.
SD: standard deviation.
PRIS: Pristane.
PHYT: Phytane.
FICHT: Fichtelite.
HEH: Heneicosa-3,6,9,12,15,18-hexaene.
SQUAL: Squalene; CPI: 2(n-C27 + n-C29)/n-C26 + (2n-C28) + n-C30.
RESHC: Resolved hydrocarbons.
UCM: Unresolved complex mixture.

sand grains and a C/N ratio of 11 (Colombo *et al.*, 1996a).

The abundance of unsaturated fatty acids in our samples (31–70 % of total FAMES), which are known to be more susceptible to degradation than the saturated homologues, reflect the relative freshness of the material collected in the traps. All the major unsaturated acids, 18:1(*n*-9), 20:5, 20:1, 22:5 and 22:1, follow a broadly similar pattern: high proportions at site L, particularly in May, and increasing values in July at station S (Fig. 4). This pattern is more difficult to interpret than the clear-cut trend of diatom FAMES. This is possibly related to the mixed origin of unsaturated FAMES: green algae, flagellates, dinoflagellates, diatoms and zooplankton could contribute to these acids (Ahlgren *et al.*, 1990; Reemtsma *et al.*, 1990; Reemtsma and Ittekkot, 1992).

A small contribution of bacterial lipids is evidenced in the fatty acid composition of settling particles. Bacterial FA such as branched-chain i15:0 and a15:0 and cis-vaccenic acid, 18:1(*n*-7) (Johns *et al.*, 1977; Perry *et al.*, 1979; Gillan *et al.*, 1983), account for only 2.5–4.6 % of total FAMES in our trap material. The proportion of branched-chain a15:0 and i15:0 is highest at the landward site

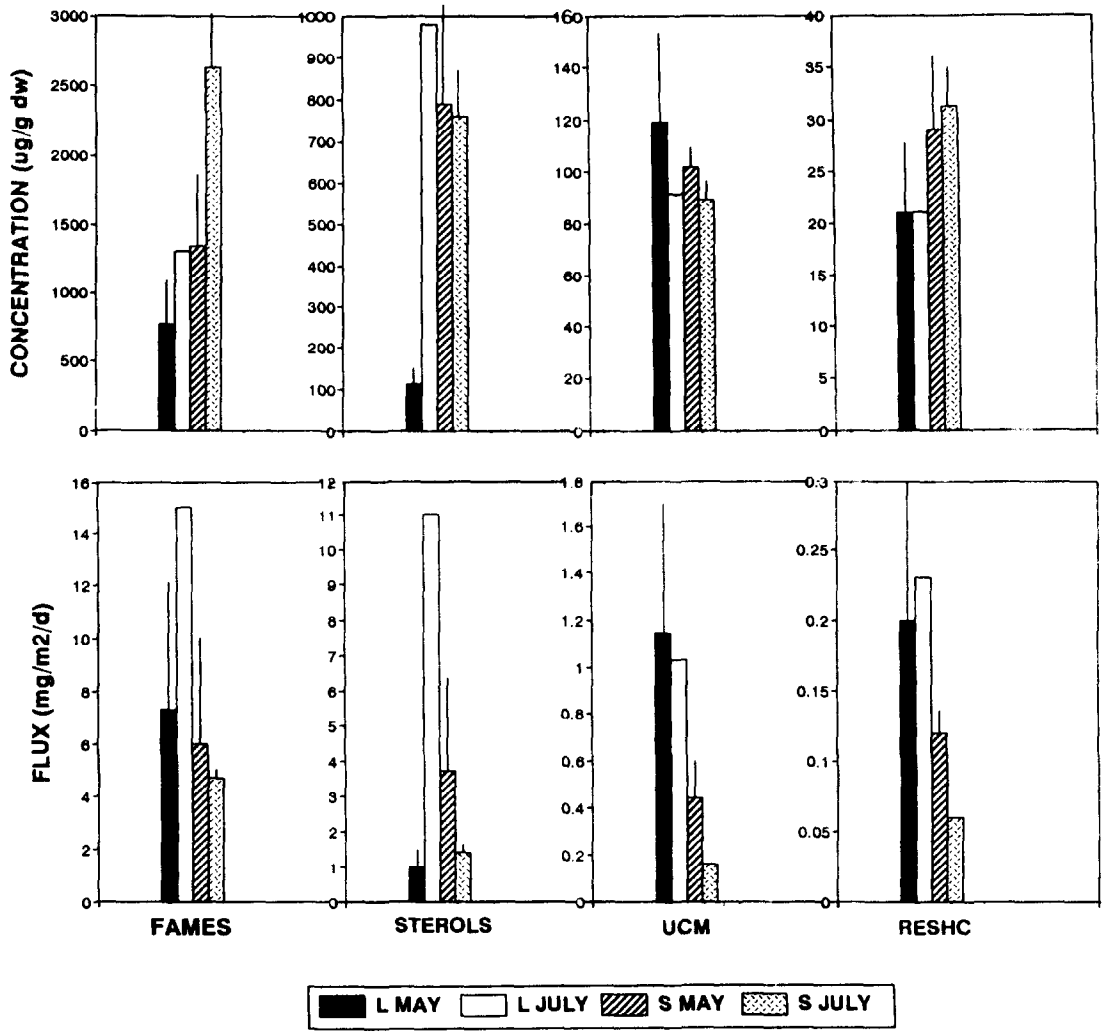

Fig. 3. Average concentrations and fluxes of total fatty acid methyl esters (FAMES), sterols, unresolved hydrocarbons (UCM) and resolved aliphatic hydrocarbons (RESHC) measured in May and July at landward (L) and seaward (S) sites in the Laurentian Trough.

during the spring runoff (Table 1) which may reflect the contribution from the Upper Estuary where bacterial abundances are an order of magnitude higher (Painchaud *et al.*, 1987). The distribution of 18:1(*n*-7) shows a different trend (higher values at station S and during July) possibly reflecting the influence of planktonic sources (Reemtsma *et al.*, 1990).

The contribution of terrestrial FA in settling particles is small ($C_{22} + C_{24} + C_{26}$ = 1.6–7.2 % total FAMES) compared to that of planktonic FA, and to previous C/N results which indicated a terrestrial contribution of 40–70 % TOC (Colombo *et al.*, 1996a). This disproportionately strong marine signature possibly results from the higher abundance of fatty acids in lipid-rich planktonic organisms relative to terrestrial OM, which due to recycling and degradation is normally enriched in refractory components such as lignin and cellulose. In spite of this apparent skewness, the proportions of marine and terrestrial FAMES effectively reflect the position of the stations along the land–sea gradient and the seasonal variation of the signals. The proportion of terrigenous 22:0, 24:0 and 26:0 FA is higher at site L and decreases in the summer (L–S, 5.6–2.5 to 3–1.7) while that of marine FA 14:0, 16:1 and 16:0 is higher at station S (75–48 %) and increases in July at L (32 to 46 %). The marine:terrestrial 16:0/24:0 ratios, clearly reflect this trend: high values at site S, particularly during the spring diatom bloom (42–31), and a strong shift from terrestrial to more marine conditions in July at L (6.1–14).

In summary, fatty acids reflected the contribution from diatoms (14:0, 16:1, 16:0), vascular land plants (22:0, 24:0, 26:0) and bacteria (i15:0, a15:0 and partially 18:1(*n*-71)). The abundant unsaturated FA are attributed to mixed planktonic sources.

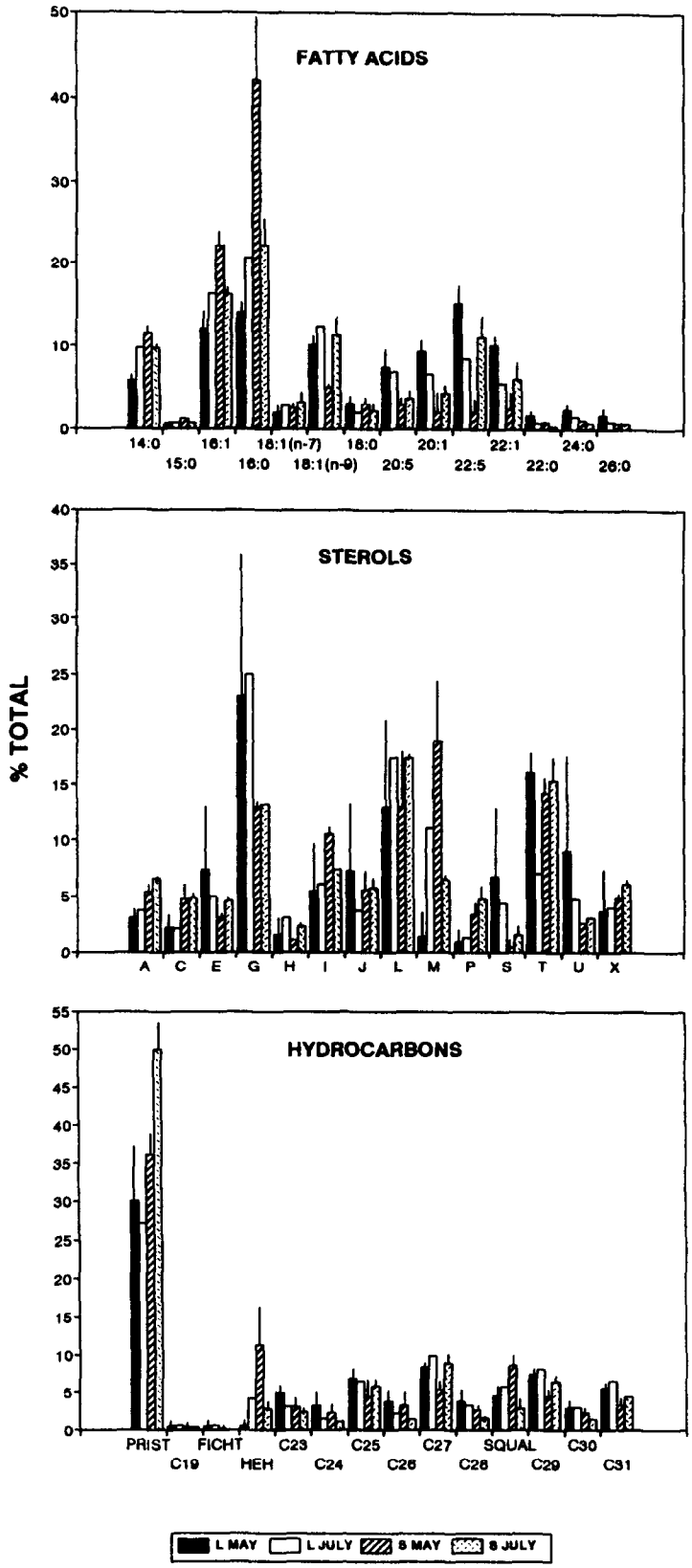

Fig. 4. Relative composition of fatty acids, sterols and hydrocarbons for the four samplings.

Sterols

The sterol composition of settling particles (Table 2; Fig. 4) was dominated by cholesterol (G; 11–36 % total sterols), 24-methylenecholesterol (L; 3.9–21 %), campesterol (M; 0–24 %), sitosterol (T; 7–18 %), 24-methyl-5α-cholest-22E-en-3β-ol (J; 2.8–14 %) and brassicasterol–diatomsterol (C_{24} R/S epimers are not distinguished; I, 0–11 %).

The phytoplanktonic pattern observed for pigments and fatty acids 14:0, 16:0, 16:1 is also followed by campesterol (M) and brassicasterol–diatomsterol (I). Campesterol, which has been found in some dinoflagellates and diatoms (Volkman, 1986), seem to be more specific because it shows a clear-cut trend (L–S, 1.4–19 to 11–6.5 % from May to July), very similar to that of HEH ($C_{21:6}$) an hydrocarbon abundant during periods of active diatom growth (see next section). The pattern of sterol I is less marked (maxima at site S in May but high at L) suggesting the presence of other non-diatom sources. This compound has been found in several algal groups, and is a major sterol in diatoms and coccolithophores (Volkman *et al.*, 1981; Smith *et al.*, 1982; de Leeuw *et al.*, 1983; Gagosian *et al.*, 1983a). The most common diatoms in the St. Lawrence are from the genera *Chaetoceros* and *Thalassiosira* (Levasseur and Therriault, 1987) which contain abundant campesterol (36–38 %) and lower amounts of I (12 %) whereas in *Phaeodactylum, Navicula, Nitzchia* and *Cyclotella* sp., diatomsterol largely predominates (91–100 %; Volkman, 1986). Brassicasterol (24R/βI) is also present in some higher plants (Volkman, 1986), which may explain the relatively high values at the landward station (Fig. 4).

Three other sterols, while not showing as clear a pattern of diatom maxima in May at site S as campesterol and diatomsterol, are associated in the literature with algae. 24-Norcholesta-5,22E-dien-3β-ol (A; 2.6–6.8 % in our samples), has been ascribed to diatoms by Smith *et al.* (1982). 24-Methylenecholesterol (L) and stigmasterol (P; 0–5.5 % in our traps) are also common in Prymnesiophycean algae, diatoms and dinoflagellates (Huang and Meinschein, 1979; Volkman, 1986). The proportion of A and P in our traps is higher at site S and increases in July (Fig. 4). Sterol L also increases in July, but the variability is high, particularly at the landward site in May, suggesting the presence of other sources. A higher relative abundance of algal sterols in July is consistent with a summer increase of primary production, provided that the species causing the spring bloom at site S contained little of these three compounds, e.g. *Chaetoceros* sp. has 38 % M, 12 % I, 2 % L and no P whereas *Thalassiosira pseudonana* contains 36 % M and no I, L or P (Volkman, 1986).

Another algal sterol which does not follow the pattern of M and I, is dinosterol (X, 0–7.4 % in our samples). This compound is considered a reliable biomarker for dinoflagellates (de Leeuw *et al.*, 1983; Volkman, 1986). However, some diatoms such as *Navicula* sp. also contain small amounts of dinosterol (2.6–3.6 %; Volkman *et al.*, 1993). In the St. Lawrence, the most common dinoflagellates are *Dinophysis acuminata* and, particularly, *Protogonyaulax tamarensis*, which can be the dominant phytoplankton species during late summer (Cembella *et al.*, 1988). The distribution of sterol X in our samples suggests a greater contribution of dinoflagellates at station S during the summer but shows high, variable values at site L in May (Fig. 4). At this site, dinosterol is correlated with cholesterol ($r = 0.99$) and sterol E ($r = 0.93$), also abundant in some dinoflagellates (Volkman, 1986), suggesting that these organisms could contribute to the maxima of E and G observed at site L (Fig. 4; see below).

The abundance of cholesterol (G; 11–36 % in our samples) and also of cholesta-5,22E-dien-3β-ol (E; 2.6–14 %), is a common feature of sinking particles collected in marine environments and is considered to reflect the input of zooplankton carcasses, molts and feces (Gagosian *et al.*, 1983b; Wakeham, 1987). The abundance of these two sterols as well as that of copepod fecal pellets, lipids, pristane and pheopigments in our traps (Colombo *et al.*, 1996a) all indicate the importance of zooplankton inputs. However, the almost opposite trends of cholesterol and pristane, another zooplankton tracer (see next section), suggests the existence of independent sources for each compound.

Cholesterol is rather unspecific and is present in a wide range of organisms: from phytoplankton to fish or mammals (Morris and Culkin, 1977). Among algae, cholesterol is abundant in dinoflagellates (26–100 % total sterols), some Haptophycea (small flagellates) and to a lesser degree in diatoms, which also contain sterol E (Volkman *et al.*, 1981; Volkman, 1986). The covariation of dinosterol with cholesterol and sterol E at site L, suggests that dinoflagellates are an important additional source of both sterols. The differential excretion of cholesterol and pristane by copepods could also contribute to the decoupling of these compounds. In contrast to pristane, cholesterol is excreted in significant amounts (up to 4 ng per pellet; Volkman, 1986) possibly due to excess conversion and to the release of gut epithelial tissue (Harvey *et al.*, 1987). Thus, copepod fecal pellets are a source of cholesterol, but not of pristane.

The stanol 5α-cholestan-3β-ol (H), is also usually assigned to plankton (Nishimura and Koyama, 1977). The pattern of H in our samples (L–S, 1.5–1.1 to 3.1–2.3 %, from May to July) is similar to that of 24-methylenecholesterol, supposedly algal (Fig. 4). This saturated sterol together with its 5β epimer (coprostanol), is also produced by reduction

of cholesterol. Coprostanol is produced by intestinal microflora of higher animals, and has been used as a sewage tracer (Hatcher and McGillivary, 1979). This compound makes up 1.4–6.1 % of total sterols in our samples, and its higher contribution at the seaward site suggests the prevalence of a marine source. Algal sources of coprostanol have been proposed to explain its covariation with phytosterols, HEH and phytol in particles from Bedford Basin (Pocklington *et al.*, 1987). In Antarctic sediments, coprostanol has been attributed to marine mammal feces (Venkatesan *et al.*, 1986).

The contribution of terrestrial sterols is evidenced by stigmastanol (U) and 24-ethylcholesterol (T). Sterol U is a well characterized vascular plant marker (Nishimura, 1977), and shows a clear terrestrial pattern (highest at site L in May, and low at the seaward site; Fig. 4). Surprisingly, 23,24-dimethylcholest-5-en-3β-ol (S), displays a similar pattern. However, as has been observed for other sterols, the variability is high at station L in May, suggesting the contribution from multiple sources, e.g. dinoflagellate and higher plants as suggested by the negative correlation of U and S with dinosterol ($r = -0.79$, -0.97). 24-Ethylcholesterol (T) is a less specific terrestrial tracer and has been found in diatoms, prymnesiophyceae, chlorophyceae, and cyanobacteria (Volkman, 1986). It has been attributed to algae in sediments from the Peru upwelling region (Smith *et al.*, 1983) and to a mixed algal–terrestrial source in suspended particles of the Chang Jiang Estuary and adjacent East China Sea (Sicre *et al.*, 1994). The pattern of sterol T in our traps, high during terrestrial (site L, May) and marine conditions (site S, Fig. 4), indicates that both vascular plants and algae are equally important sources of 24-ethylcholesterol in the St. Lawrence.

In summary, the sterol composition of settling particles denotes the contribution from phytoplankton (A, P, L), including diatoms (M, I) and dinoflagellates (X), zooplankton (G, E, also partially contributed by dinoflagellates) and vascular plants (U and T, partially contributed by algae).

Hydrocarbons

All the samples analyzed showed a strong predominance of the C_{19} acyclic isoprenoid pristane, which accounted for 22–53 % of total resolved aliphatic hydrocarbons. The next most abundant components were the highly unsaturated n-$C_{21:6}$ hydrocarbon heneicosa-3,6,9,12,15,18-hexaene (HEH; 0–16 %), the C_{30} acyclic isoprenoid, squalene (1.8–9.9 %) and C_{25}, C_{27}, C_{29}, and C_{31} n-alkanes (2.5–9.9 % each; Table 3; Fig. 4).

The major phytoplanktonic hydrocarbon detected in the traps is HEH. This compound is the most abundant hydrocarbon in diatoms, dinoflagellates and other algae groups (Blumer *et al.*, 1971; Nichols *et al.*, 1988; Nevenzel, 1989). High concentrations of HEH have been associated with times of rapid cell division such as the spring bloom in the Kiel Bight dominated by diatoms from the genera *Detonula, Chaetoceros* and *Skeletonema* (Osterroht *et al.*, 1983). The relative abundance of HEH in our samples reflects the phytoplanktonic pattern already noted for pigments even more clearly than fatty acids or sterols (Fig. 4): highest during the spring diatom bloom at site S (11 vs. 2.8 % in July), and a marked increase in July at site L (from 0.5 to 4.2 %). This pattern supports the interpretation of HEH as a reliable indicator of periods of active diatom growth. Other hydrocarbons usually found in algae, i.e. n-C_{15}, n-C_{17} (Blumer *et al.*, 1971), are poorly represented in our traps (0.1–1.5 %; Table 3) probably reflecting the dominance of diatoms containing chiefly HEH.

Squalene, which is an intermediate in the biosynthesis of cholesterol, follows a broadly similar trend to HEH (Fig. 4) suggesting a common origin, i.e. diatoms. However, the pattern is less marked, similar to that of sterol I (maxima at site S in May but high at L), indicating other sources. Squalene has been found in a variety of organisms: in diatom cultures (Volkman *et al.*, 1983), in some Antarctic sea-ice diatom communities (26 % total RESHC; Nichols *et al.*, 1988), in green algae (4–25 % total RESHC with no HEH; Nevenzel, 1989), in salp fecal pellets (high in squalene and HEH; Matsueda *et al.*, 1986), and in some fish and their feces (high in squalene and dietary pristane; Prahl *et al.*, 1985).

Pristane is a well known biomarker of zooplankton, particularly of calanoid copepods, which produce it from phytol in chlorophyll-a from their diet (Volkman and Maxwell, 1986). It is the major hydrocarbon in the dominant species in the St. Lawrence (*Calanus finmarchicus* and *C. hyperboreus*), constituting 0.5–1 % of total dry weight (Nevenzel, 1989). As a consequence of food web transfer, pristane is also abundant in some jellyfish, echinoderms, molluscs and planktophagous fish (Nevenzel, 1989).

The interpretation of pristane in sediment traps is difficult because, due to its high content in copepods, the collection of a few swimmers could introduce a significant bias (two 150 μg copepods with a 0.7 % pristane content could increase our values by 10–40 %). However, it was rare to see many swimmers in our unpoisoned, short-term traps and the few which were present have been carefully eliminated. In addition, pristane shows no correlation ($r = -0.40$) with cholesterol, also abundant in copepod carcasses, but it display a significant relationship with carbon ($r = 0.86$), which would not be affected by a few swimmers, revealing a real, unbiased zooplanktonic influence to the vertical flux of matter (Colombo *et al.*, 1996a).

Pristane averaged 36 % of total RESHC in our traps. Its relative distribution shows low values at

station L during both samplings (mean = 27–29 %) and higher values at site S, particularly in July (36–50 %). As copepods seem to limit the release of important amounts of pristane in their feces, the most likely source of this compound are their carcasses and fecal material from higher level consumers (Prahl *et al.*, 1985).

The other major group of resolved hydrocarbons present in St. Lawrence settling matter are *n*-C_{21} to C_{33} *n*-alkanes with odd carbon predominance. The conventional interpretation of this series is that it is derived from terrestrial vascular plants. Our data indicate that in addition to vascular plants, other sources could contribute to such *n*-alkanes. Although the relative contribution of these compounds is higher at the landward site (56 ± 8.2 % vs. 38 ± 7.3 % at site S), some of the components most prominent in vascular plants (*n*-C_{27}, C_{29}, C_{31}) show higher values in July at both stations (Fig. 4). This distribution contrasts with that of other land plant biomarkers (FA 24:0 and 26:0, stigmastanol), suggesting the presence of some unknown autochthonous contribution. Based on the marked predominance of C_{27}, C_{29} and C_{31}, *n*-alkadienes in the algae *Boctrycoccus braunii*, Lichtfouse *et al.* (1994) warned that long chain odd *n*-alkanes in sediment and water could arise from reduction of algal alkenes. The different distribution patterns of odd and even *n*-alkanes (Fig. 4) suggest independent sources for both series (see below).

Another independent terrestrial tracer present in our samples is the C_{19} diterpenoid hydrocarbon, fichtelite (Barrick and Hedges, 1981). Although the concentrations are very low, its distribution pattern reflects a terrestrial origin: it is detected in three samples from the landward site, two in May and one in July, but only in one trap at site S in May (Table 3).

Some of the lower molecular weight hydrocarbons present in minor amounts (*n*-C_{18}, phytane, *n*-C_{19} and *n*-C_{20}) appear to follow similar terrigenous-source patterns (Table 3), suggesting a petrogenic origin. A petrogenic signal seems to be present as well in the suite of high molecular weight *n*-alkanes. Their carbon preference indexes ($CPI = 2[C_{27} + C_{29}]/[C_{26} + 2C_{28} + C_{30}]$) are low during May ($2.1 \pm 0.6$), similar to values reported for contaminated sediments (CPI < 2; Colombo *et al.*, 1989). Low CPI values may also result from the contribution of bacteria, fungi or yeast which have been suspected to be the origin of unusual even-carbon dominated *n*-alkane distributions ranging from *n*-C_{16} to *n*-C_{36} (Kennicutt and Brooks, 1990). CPI values registered in July (4.5 ± 1.2) are more characteristic of plant waxes.

In summary, hydrocarbon data indicated the contribution of microalgae, chiefly diatoms (HEH and partially squalene); zooplankton (pristane); vascular land plants (*n*-C_{23} to C_{31}) and petrogenic residues (UCM, long chain *n*-alkanes).

MULTIVARIATE ANALYSIS

The discussion of the sources and behaviour of lipids averaged by station and month revealed the principal trends of the data. However, this approach does not adequately reflect the covariation of the many different lipid and bulk organic parameters nor the association of the traps. To evaluate these aspects, a principal component analysis (PCA) was performed using the most effective lipid biomarkers (high discriminatory capacity in PCA previously run for each lipid class), and selected bulk organic data. Even if the data set is admittedly too small to draw definitive conclusions, this more objective evaluation produces a robust pattern and summarizes the data without losing much information.

The PCA were performed with the standardized relative abundance of seven FA (a15:0, 16:1, 16:0, 22:5, 22:1, 24:0, 26:0); nine sterols (C, E, G, I, M, P, S, U, X); ten hydrocarbons (pristane, fichtelite, HEH, squalene, *n*-alkanes C_{24}, C_{26}, C_{27}, C_{28}, C_{29} and C_{31}) plus the UCM/RESHC ratio; and six bulk organic parameters: carbohydrate carbon (CH-C), total hydrolyzable amino acid carbon (THAA-C), protein carbon (PROT-C), chlorophyll-a/pheopigment (CHLa/PHEO) and C/N ratios (Colombo *et al.*, 1996a), and the relative abundance of serine (SER) which is enriched in diatom cell-walls (Colombo *et al.*, submitted). Figure 5 shows the first two principal components with the variables (rays) and samples (boxes) represented in the same plane to facilitate the interpretation. Closely spaced rays are positively correlated variables and opposed rays are negatively correlated parameters.

The first two principal components account for 65 % of the total variance of the data; 48 % the first (PC1) and 17 % the second (PC2). The variables and observations are separated in two main sectors: marine phytoplanktonic + zooplanktonic biomarkers, most predominant at the seaward site (positive PC1); and terrestrial + pollution + planktonic lipids, which are more abundant at the landward station (negative PC1). Within each sector, a further separation into two sub-groups can be made. In the first, phytoplanktonic and diatom-derived biomarkers, from diatomsterol (I) to stigmasterol (P), were most abundant during the spring bloom at the seaward site (+ve PC1, +ve PC2). These parameters show a good correlation with the independent indicators of phytoplanktonic production SER and CHLa/PHEO ratio (high values indicate fresh diatom material). This further supports the strong diatom signature of S May traps, especially those of day 9 and 10 first trap. The second May 10 trap shows a higher contribution of C_{24}, C_{26}, and C_{28} *n*-alkanes. The second group in

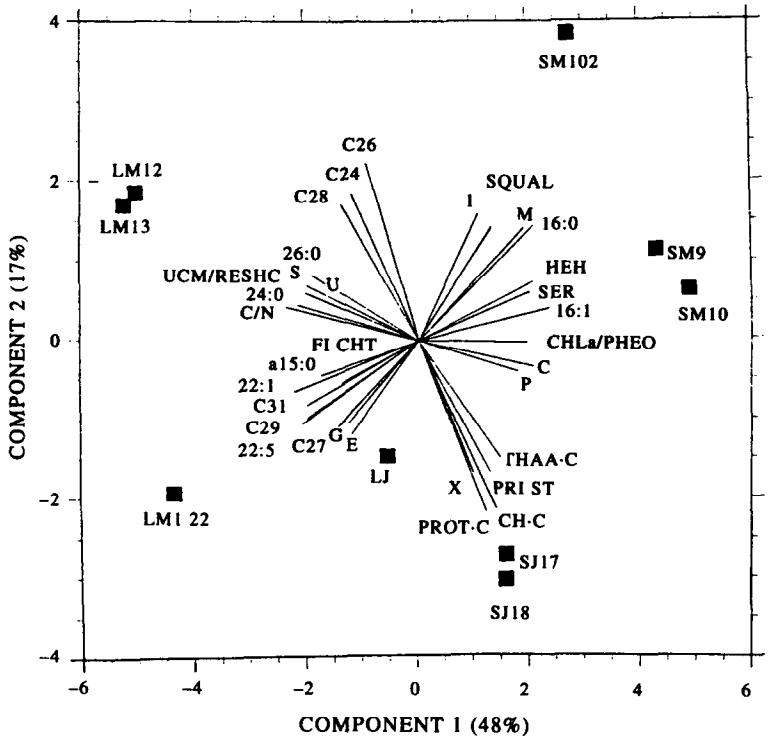

Fig. 5. Principal component analysis performed with 7 fatty acids, 9 sterols, 10 hydrocarbons and 6 bulk organic parameters. The variables are represented by the rays and the traps by the squares. Samples are identified by station (L or S), sampling month (M = May or J = July) and day. The second trap from the same sampling day is identified by a final number 2, i.e. LM122 and SM102.

the "marine" sector includes pristane and dinosterol which predominated at the seaward site in July (+ve PC1, −ve PC2). The higher abundance of the principal biochemicals (amino acids, carbohydrates and proteins) in these traps reflect the importance of the zooplanktonic contributions.

The second "terrestrial" sector is more difficult to interpret due to the overlapping of multiple sources. The more reliable higher plant biomarkers (FA 24:0 and 26:0, sterol U) are correlated with C/N and UCM/RESHC ratios (−ve PC1, +ve PC2) indicating the predominance of terrestrial pollution inputs (Upper St. Lawrence and Saguenay Fjord) in the samples collected at the landward station on May 12, first trap, and 13. The second trap from L May 12 shows a complex lipid signature (−ve PC1, −ve PC2): bacteria (a15:0), zooplankton (cholesterol, cholesta-5,22E-dien-3β-ol, unsaturated FA) and vascular plant related compounds (fichtelite, C_{27}, C_{29}, C_{31} *n*-alkanes). This heterogeneous grouping and the poor correlation of C_{27}, C_{29} and C_{31} *n*-alkanes with other higher plant biomarkers (FA 24:0 and 26:0, sterol U), suggest the contribution of autochthonous sources. The tidally driven upwelling of cold, nutrient-rich waters at the head of the Laurentian Trough induces a strong increase of phytoplanktonic production in the area (Levasseur and Therriault, 1987). Other possible contributors are ctenophores or tunicates whose mucous secretions have been often observed in the Laurentian Trough (Colombo *et al.*, 1996a). The samples collected at site L during July present intermediate terrestrial–marine characteristics.

CONCLUSIONS

The multivariate analysis of lipid biomarkers in rapidly settling particles intercepted at 150 m depth in May and July at two contrasting sites in the Laurentian Trough revealed that a large proportion of the total variance of the data was related to the terrestrial–marine or vascular plant–algae gradient in the estuary. A diatom bloom sampled at the seaward site in May, traced by fatty acids 16:0 and 16:1, heneicosahexaene and campesterol, and the strong zooplanktonic signature (pristane) of the samples collected at this station in July, accounted for a major portion of the total inertia. Additional important factors were the contribution of lipids derived from dinoflagellates (dinosterol, and partially cholesterol and cholesta-5,22E-dien-3β-ol), unidentified plankton (unsaturated fatty acids), higher plants (stigmastanol, long chain odd *n*-alkanes, fatty acids 22:0, 24:0 and 26:0) and pollution (UCM, *n*-alkanes). The grouping of the individual sediment trap samples showed a consistent picture: the most homogeneous clusters were those formed by the traps collected at the seaward site in May (high in

diatom biomarkers) and July (high in zooplankton lipids). The samples collected at the landward site were more heterogeneous and showed variable inputs from vascular plants, pollution and plankton, reflecting the proximity to the Upper St. Lawrence Estuary, Saguenay Fjord, and a periodic upwelling.

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REFERENCES

Ahlgren G., Lundstedt L., Brett M. and Forsberg C. (1990) Lipid composition and food quality of some freshwater phytoplankton for cladoceran zooplankters. *J. Plankton Res.* **12,** 809–818.

Barrick R. C. and Hedges J. I. (1981) Hydrocarbon geochemistry of the Puget Sound region — II. Sedimentary diterpenoid, steroid and triterpenoid hydrocarbons. *Geochim. Cosmochim. Acta.* **45,** 381–392.

Blumer M., Guillard R. R. L. and Chase T. (1971) Hydrocarbons of marine phytoplankton. *Mar. Biol.* **8,** 183–189.

Brassell S. C. and Eglinton G. (1983) The potential of organic geochemical compounds as sedimentary indicators of upwelling. In *Coastal Upwelling its Sediment Record. Part A: Response of the Sedimentary Regime to Present Coastal Upwelling* (Edited by Suess E. and Thiede J.), pp. 545–571. Plenum Press.

Cembella A. D. and Therriault J.-C., Béland P. (1988) Toxicity of cultured isolates and natural populations of *Protogonyaulax tamarensis* from the St Lawrence estuary. *J. Shellfish Res.* **7,** 611–621.

Colombo J. C., Pelletier E., Brochu C., Khalil M. and Catoggio J. (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. (1996a) Biogeochemistry of organic matter in the Laurentian Trough: I — Composition and vertical fluxes of rapidly settling particles. *Mar. Chem.* **51,** 277–293.

Colombo J. C., Silverberg N. and Gearing J. N. (1996b) 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.

Colombo J. C., Silverberg N. and Gearing J. N. (1996c) Amino acid biogeochemistry in the Laurentian Trough: vertical particle flux and early diagenesis. *Geochim. Cosmochim. Acta.* Submitted.

de Leeuw J. W., Rijpstra W. I., Schenck P. A. and Volkman J. K. (1983) Free, esterified and residual bound sterols in Black Sea Unit I sediments. *Geochim. Cosmochim. Acta.* **47,** 455–465.

Gagosian R. B., Nigrelli G. E. and Volkman J. K. (1983a) Vertical transport and transformation of biogenic organic compounds from a sediment trap experiment off the coast of Peru. In *Coastal Upwelling, its Sediment Record. Part A; Responses of the Sedimentary Regime to Present Coastal Upwelling* (Edited by Suess E. and Thiede J.), pp. 241–272. Plenum Press, New York.

Gagosian R. B., Volkman J. K. and Nigrelli G. E. (1983b) The use of sediment traps to determine sterol sources in coastal sediments of Peru. In *Advances in Organic Geochemistry* 1981, (Edited by Bjorøy *et al.*), pp. 369–379 J. Wiley & Sons Ltd.

Gillan F. T. and Johns R. B. (1986) Chemical markers for marine bacteria: fatty acids and pigments. In *Biological Markers in the Sedimentary Record* (Edited by Johns R. B.), pp. 291–309. Elsevier, Amsterdam.

Gillan F. T., Johns R. B., Verheyen T. V., Nichols P. D., Esdaile R. J. and Bavor H. J. (1983) Monounsaturated fatty acids as specific bacterial markers in marine sediments. In *Advances in Organic Geochemistry* 1981 (Edited by Bjorøy *et al.*), pp. 198–206. J. Wiley & Sons Ltd.

Hama T. (1991) Production and turnover rates of fatty acids in marine particulate matter through phytoplankton photosynthesis. *Mar. Chem.* **33,** 213–227.

Harvey H. R., Eglinton G., O'Hara S. C. M. and Corner E. D. S. (1987) Biotransformation and assimilation of dietary lipids by Calanus feeding on a dinoflagellate. *Geochim. Cosmochim. Acta.* **51,** 3031–3040.

Hatcher P. G. and McGillivary P. A. (1979) Sewage contamination in the New York Bight. Coprostanol as an indicator. *Environ. Sci. Technol.* **13,** 1225–1229.

Huang W.-Y. and Meinschein W. G. (1979) Sterols as ecological indicators. *Geochim. Cosmochim. Acta.* **43,** 739–745.

Johns R. B. (1986) *Biological Markers in the Sedimentary Record.* Elsevier, Amsterdam, 364 pp.

Johns R. B., Perry G. J. and Jackson K. S. (1977) Contribution of bacterial lipids to recent marine sediments. *Estuar. Coast. Mar. Sci.* **5,** 521–529.

Kattner G., Gercken G. and Eberlein K. (1983) Development of lipids during a spring plankton bloom in the Northern North Sea. *Mar. Chem.* **14,** 149–162.

Kawamura K., Ishiwatari R. and Ogura K. (1987) Early diagenesis of organic matter in the water column and sediments: microbial degradation and resynthesis of lipids in Lake Haruna. *Org. Geochem.* **4,** 251–264.

Kayama M., Araki S. and Sato S. (1989) Lipids in marine plants. In *Marine Biogenic Lipids, Fats and Oils*, Vol. II, (Edited by Ackman R. G.), pp.3–48. CRC Press Inc, Bbca Raton, Florida.

Kennicutt II M. C. and Brooks J. M. (1990) Unusual normal alkane distributions in offshore New Zealand sediments. *Org. Geochem.* **15,** 193–197.

Lee C., Farrington J. W. and Gagosian R. B. (1979) Sterol geochemistry of sediments from the western North Atlantic Ocean and adjacent coastal areas. *Geochim. Cosmochim. Acta.* **43,** 35–46.

Levasseur M. E. and Therriault J.-C. (1987) Phytoplankton biomass and nutrient dynamics in a tidally influenced upwelling: the role of the NO_3:SiO_4 ratio. *Mar. Ecol. Prog. Ser.* **39,** 87–97.

Lichtfouse E., Derenne S., Mariotti A. and Largeau C. (1994) Possible algal origin of long chain odd *n*-alkanes in immature sediments as revealed by distributions and carbon isotope ratios. *Org. Geochem.* **22,** 1023–1027.

Matsuda H. and Koyama T. (1977) Early diagenesis of fatty acids in lacustrine sediments — II. A statistical approach to changes in fatty acid composition from recent sediments and some source materials. *Geochim. Cosmochim. Acta.* **41,** 1825–1834.

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.

Mayzaud P., Chanut J. P. and Ackman R. G. (1989) Seasonal changes of the biochemical composition of marine particulate matter with special reference to fatty acids and sterols. *Mar. Ecol. Prog. Ser.* **56,** 189–204.

Meyers P. A., Leenheer M. J., Eadie B. J. and Maule S. J. (1984) Organic geochemistry of suspended and settling

particulate matter in Lake Michigan. *Geochim. Cosmochim. Acta.* **48,** 443–452.

Morris R. J. and Culkin F. (1977) Marine lipids: sterols.. *Oceanogr. Mar. Biol. Ann. Rev.* **15,** 73–102.

Nevenzel J. C. (1989) Biogenic hydrocarbons of marine organisms. In *Marine Biogenic Lipids, Fats and Oils*, Vol. 1. (Edited by Ackman R. G.), pp. 3–71. CRC Press, Inc, Boca Raton, Florida.

Nichols P. D., Volkman J. K., Palmisano A. C., Smith G. A. and White D. C. (1988) Occurrence of an isoprenoid C_{25} diunsaturated alkene and high neutral lipid content in Antarctic sea-ice diatom communities. *J. Phycol.* **24,** 90–96.

Nishimura M. (1977) The geochemical significance in early sedimentation of geolipids obtained by saponification of lacustrine sediments. *Geochim. Cosmochim. Acta.* **41,** 1817–1823.

Nishimura M. and Koyama T. (1977) The occurrence of stanols in various living organisms and the behaviour of sterols in contemporary sediments. *Geochim. Cosmochim. Acta.* **41,** 379–385.

Osterroht C., Petrick G. and Wenck A. (1983) Seasonal variation of particulate hydrocarbons in relation to biological parameters. *Mar. Chem.* **14,** 175–194.

Painchaud J., Lefaivre D. and Therriault J.-C. (1987) Box model analysis of bacterial fluxes in the St Lawrence Estuary. *Mar. Ecol. Prog. Ser.* **41,** 241–252.

Perry G. J., Volkman J. K., Johns R. B. and Bavor H. J. Jr. (1979) Fatty acids of bacterial origin in contemporary marine sediments. *Geochim. Cosmochim. Acta.* **43,** 1715–1725.

Pocklington R., Leonard J. D. and Crewe N. F. (1987) Le coprostanol comme indicateur de la contamination fécale dans l'eau de mer et les sédiments marins. *Oceanol. Acta.* **10,** 83–89.

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.

Prahl F. G., Eglinton G., Corner E. D. S. and O'Hara S. C. M. (1985) Faecal lipids released by fish feeding on zooplankton. *J. Mar. Biol. Ass. U.K.* **65,** 547–560.

Reemtsma T., Haake B., Ittekkot V., Nair R. R. and Brockmann U. H. (1990) Downward flux of particulate fatty acids in the Central Arabian Sea. *Mar. Chem.* **29,** 183–202.

Reemtsma T. and Ittekkot V. (1992) Determination of factors controlling the fatty acid composition of settling particles in the water column by principal-component analysis and their quantitative assessment by multiple regression. *Org. Geochem.* **1,** 121–129.

Saliot A., Goutx M., Fevrier A., Tusseau D. and Andrie C. (1982) Organic sedimentation in the water column in the Arabian Sea: relationship between the lipid composition of small and large-size, surface and deep particles. *Mar. Chem.* **11,** 257–278.

Saliot A., Laureillard J., Scribe P. and Sicre M. A. (1991) Evolutionary trends in the lipid biomarker approach for investigating the biogeochemistry of organic matter in the marine environment. *Mar. Chem.* **36,** 233–248.

Sicre M.-A., Tian R. C. and Saliot A. (1994) Distribution of sterols in the suspended particles of the Chang Jiang Estuary and adjacent East China Sea. *Org. Geochem.* **21,** 1–10.

Smith D. J., Eglinton G., Morris R. J. and Poutanen E. L. (1982) Aspects of the steroid geochemistry of a recent diatomaceous sediment from the Namibian Shelf. *Oceanol. Acta.* **5,** 365–378.

Smith D. J., Eglinton G., Morris R. J. and Poutanen E. L. (1983) Aspects of the steroid geochemistry of an interfacial sediment from the Peruvian upwelling. *Oceanol. Acta.* **6,** 211–219.

Tanoue E. and Handa N. (1980) Vertical transport of organic materials in the Northern North Pacific as determined by sediment trap experiments. Part 1. Fatty acid composition. *J. Oceanogr. Soc. Japan.* **36,** 231–245.

Venkatesan M. I., Ruth E. and Kaplan I. R. (1986) Coprostanol in antarctic marine sediments: a biomarker for marine mammals and not human pollution. *Mar. Pollut. Bull.* **17,** 554–557.

Volkman J. K. (1986) A review of sterol markers for marine and terrigenous organic matter. *Org. Geochem.* **9,** 83–99.

Volkman J. K. and Maxwell J. R. (1986) Acyclic isoprenoids as biological markers. In *Biological Markers in the Sedimentary Record, Methods in Geochemistry and Geophysics* (Edited by Johns R. B.), pp. 1-42. Elsevier, Amsterdam.

Volkman J. K., Gillan F. T., Johns R. B. and Eglinton G. (1981) Sources of neutral lipids in a temperate intertidal sediment. *Geochim. Cosmochim. Acta.* **45,** 1817–1828.

Volkman J. K., Farrington J. W., Gagosian R. B. and Wakeham S. G. (1983) Lipid composition of coastal sediments from the Peru Upwelling Region. In *Advances of Organic Geochemistry* 1981 (Edited by Bjorøy *et al.*), pp. 228–240. J. Wiley & Sons Ltd.

Volkman J. K., Farrington J. W. and Gagosian R. B. (1987) Marine and terrigenous lipids in coastal sediments from the Peru upwelling region at 15 °S: sterols and triterpene alcohols. *Geochim. Cosmochim. Acta.* **11,** 463–477.

Volkman J. K., Barrett S. M., Dunstan G. A. and Jeffrey S. W. (1993) Geochemical significance of the occurrence of dinosterol and other 4-methyl sterols in a marine diatom. *Org. Geochem.* **20,** 7–15.

Wakeham S. G. (1987) Steroid geochemistry in the oxygen minimum zone of the eastern tropical North Pacific Ocean. *Geochim. Cosmochim. Acta.* **51,** 3051–3069.

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

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.