

Lipid class and alkane distribution in settling particles of the upper Laurentian Great Lakes*

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Abstract—Sediment traps were deployed at up to 6 depths at seven stations in Lakes Superior, Michigan, and Huron for 2 months during the summer of 1984. Total organic carbon, total lipid, lipid classes, and alkanes were measured in the collected material to gain information on the composition, sources, and fate of particulate organic matter in the Great Lakes. Total aliphatic hydrocarbon was a large component of all samples, accounting for more than 15% of the extractable lipids. Particles collected at 10-m depth in Lake Huron had especially high relative contributions (more than 65% of total lipids) of total aliphatic hydrocarbons at the three stations examined. The high proportion of aliphatic hydrocarbon appears not to have originated from customary pollution sources. The alkane distribution was strongly dominated by even-numbered carbon chains of unknown origin. Algae are a possible source for the unsaturated hydrocarbons that were present at relatively elevated levels in settling particles. *Botryococcus braunii*, sampled from Lake Michigan had as much as 80% of its lipids in the form of hydrocarbons. Wax and sterol esters constituted less than 10% of the lipids in trap material except in samples from mid-depths in Lake Huron where high levels of these compounds may have resulted from elevated amounts of calanoid copepod debris or swimmers entering the traps.

Key words—Great Lakes, sediment traps, lipid classes, lipids, hydrocarbons, alkanes, particles

INTRODUCTION

The lipid composition of particulate matter in aquatic environments can provide information on the nature and origin of the particles as well as on their role in food web dynamics and contaminant transfer. As metabolic fuels that are directly or indirectly transferred across trophic levels, some types of lipids, especially those containing fatty acids (e.g. triglycerides and wax esters), are important components in energy transfer from phytoplankton to invertebrates and fish, whereas others (e.g. some hydrocarbons and lipid breakdown products) are more refractory and can serve as biogeochemical indicators of diagenetic processes in the water column and sediments. Because of their hydrophobic nature, lipids in particles may also modulate pollution dynamics.

Examination of lipid composition of particles in the Great Lakes has been used as a tool to determine their probable origin. For example, measurements of alkanes, fatty acids, and free aliphatic and alicyclic alcohols in sediment trap material in southeastern Lake Michigan (Meyers *et al.*, 1980, 1984) indicated that settling particles were predominantly of aquatic origin. However, there was also a terrigenous com-

ponent, especially in near-surface and near-bottom settling matter. Vertical profiles of lipids can also provide information on the location and sources of these high-energy reduced organic compounds. For example, in marine environments, lipid concentrations were elevated near density discontinuities (Parrish *et al.*, 1988b).

Despite the usefulness of lipids as indicators of biogeochemical processes, little information is available on particulate lipid composition in the Great Lakes except for a few studies in southeastern Lake Michigan (Meyers *et al.*, 1980, 1984; Gardner *et al.*, 1989). We compare here the composition of different lipid classes in settling particles collected during summer stratification at different depths in the 3 upper Laurentian Great Lakes. The data provide new insights into biogenic production and transport of hydrophobic compounds in the Great Lakes.

METHODS

Arrays of sediment traps were deployed at seven stations in Lakes Superior, Michigan, and Huron for 2 months between 8 July and 17 September 1984 (Fig. 1). Traps were placed at up to 6 depths at each station (Fig. 2). The shallowest traps were deployed at 10 m in the surface mixed layer, the next traps were at 35 m, in the vicinity of the thermocline, and the deepest ones were placed about 5 m above bottom. The sediment trap design and sample-handling procedures are described by Eadie *et al.* (1984). The

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cylindrical traps had an i.d. of 10 cm and an aspect ratio of 5:1. A powder funnel at the bottom of the cylinder emptied directly into a 500 ml polyethylene bottle. Prior to deployment, the sample bottles were filled with 25 ml of CHCl_3 and distilled water. The bottles were continuously saturated with the poison; a pool of CHCl_3 remained in the bottles upon retrieval. Chloroform inhibits bacterial activity in sediment traps by more than 99% when present at concentrations of at least half-saturation (Lee *et al.*, 1989), but it is not an effective poison when it is present at low concentrations (e.g. 1 ml per 3927 ml; Gundersen and Wassman, 1990).

Freeze-dried samples were stored in the dark at -20°C until analysis within 6 months. Subsamples of this material were extracted for lipid analysis by microtechniques (Gardner *et al.*, 1985) or combusted in a CHN analyzer to determine organic carbon and nitrogen. One portion of each extract was used to determine total lipids gravimetrically; a second portion was stored (for <2 months) at 4°C under nitrogen for lipid class or alkane analysis.

Lipid extracts were applied to Chromarods (silica-coated quartz rods) for separation and class analysis by thin-layer chromatography (TLC) with flame ionization detection (FID) in an Iatroscan (Parrish 1987a; Parrish *et al.*, 1988a). Two to four subsamples were obtained from material collected at 10 m in Lakes Superior, Michigan, and Huron, as well as at deeper depths at the two southern Lake Huron stations. Each extract was applied to one or more Chromarods so that 2–10 Iatroscan determinations were made for each trap. Typical TLC/FID chromatograms from sediment trap extracts are shown and discussed in Parrish (1987a). Total procedural blanks for TLC/FID analyses were obtained on each day that samples were extracted. A maximum of 5 lipid classes was detected in these blanks; the level of any class in the blank was normally <15% of that observed in a sample. The total analytical precision for extracts of the same material was better than $\pm 20\%$ coefficient of variation. For 26 of the extracts, the entire sample allocated for lipid-class determination was spotted on Chromarods and the results



Fig. 1. Sediment trap station locations in the three upper Laurentian Great Lakes.

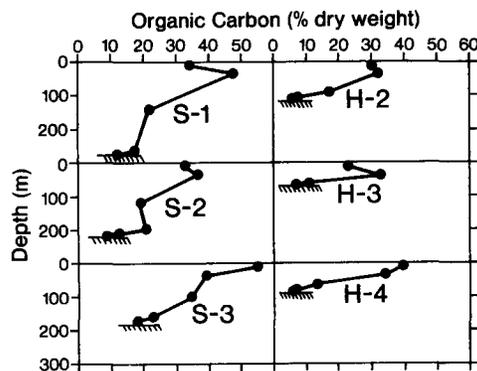


Fig. 2. Vertical profiles of organic carbon content (% dry weight) of settling particles collected from Lakes Superior and Huron. See Fig. 1 for station locations.

were summed to allow a direct comparison between gravimetric and TLC/FID results. After blank corrections, the sum of the Iatroscan-measured lipid classes was on average $74 \pm 9\%$ of the gravimetric value.

For alkane analysis, the chloroform extract was applied to an activated silica gel column (0.6×10 mm). The alkanes were eluted with 12 ml of pentane, evaporated to 1 ml under nitrogen, and analyzed on a gas chromatograph (HP 5890) equipped with a 25 m BP-1 capillary column (Supelco) and a flame ionization detector. An external standard with equal concentrations of $n\text{-C}_{16}$ – $n\text{-C}_{36}$ was used to establish retention times. Sample peaks were confirmed by analyzing portions of sample extracts spiked with standards.

Botryococcus braunii was collected on 21 September 1989, from Lake Michigan at a 100-m deep station offshore from Grand Haven, Michigan. A $64 \mu\text{m}$ mesh net, 0.5 m in dia, was trolled at the water surface to collect floating *B. braunii*. Concentrated *B. braunii* were dried at 55°C under nitrogen and analyzed for lipids as described for trap materials.

RESULTS

The greatest mass flux at both 10 and 35 m occurred at the Lake Michigan station (Table 1). The amount of organic carbon, its flux, and its ratio to nitrogen were generally higher in particles from the 35-m traps than in those from the 10-m traps at a given station (Table 1, Fig. 2).

Vertical profiles of the total lipid content of sediment-trap material (Fig. 3) were similar for most stations; the amount of lipid, expressed as a proportion of dry weight, usually peaked in the 35-m trap with steep declines below 35 m at all stations. The 35-m peak was generally small or absent in the Lake Superior materials, probably because seasonal thermal stratification was not well-developed in this lake. The mixed layer temperature was 4°C in Lake Superior during deployment (8 July), as compared to mixed-layer deployment temperatures of $15\text{--}20^\circ\text{C}$ in

Table 1. Mass fluxes and atomic ratios of settling particles at 10 and 35 m

	Sediment trap stations						
	Superior			Michigan 18	Huron		
	1	2	3		2	3	4
<i>10-m Traps</i>							
Mass flux ($\text{g m}^{-2} \text{d}^{-1}$)	0.16	0.27	0.14	0.57	0.25	0.35	0.13
C/N atomic ratio of particles	—	—	—	11.5	10.6	11.5	10.7
Organic carbon flux ($\text{mg m}^{-2} \text{d}^{-1}$)	55	88	77	20	72	78	51
<i>35-m Traps</i>							
Mass flux ($\text{g m}^{-2} \text{d}^{-1}$)	0.19	0.16	0.11	0.43	0.27	0.39	0.29
C/N atomic ratio of particles	—	—	—	15.7	13.5	13.3	13.1
Organic carbon flux ($\text{mg m}^{-2} \text{d}^{-1}$)	91	59	43	24	82	113	91

the other two lakes. The pattern in the ratios of total lipid to total organic carbon (Fig. 4) resembled that for the ratios of total lipid to dry weight. Both ratios often peaked at 35 m and then declined with depth. Lipid to carbon ratios ranged from 0.1 for particles from the 63-m trap at Sta. 3 in Lake Huron to 0.9 in the 35-m trap at Sta. 3 in Lake Superior. The average ratio of lipid to organic carbon was 1:2.

Lipid class analysis of particles from 10-m sediment traps in the 3 upper Great Lakes indicated that the aliphatic hydrocarbons (HC), ranged from 15% in Lake Michigan to more than 65% of the total lipids at all stations in Lake Huron (Fig. 5). The mean contribution of the major neutral acyl lipids, including the wax and sterol esters (WE), the triglycerides (TG), and the free fatty acids (FFA), ranged from 0.8% for WE at Sta. 4 in Lake Huron to 29% for TG at Sta. 1 in Lake Superior. The remaining neutral lipids in the sediment trap samples were acyclic and cyclic alcohols. Acyclic alcohols accounted for <3% of the Iatroscan-measured total lipid mass and were not detected in some samples. The mean contribution of the cyclic alcohols, the sterols (ST), ranged from 1.1% at Sta. 2 in Lake Huron to 4.4% in Lake Michigan. The mean contribution of polar lipids, i.e. "the acetone-mobile polar lipids" (AMPL) and the phospholipids (PL), ranged from 2.2% for PL at Sta. 3 in Lake Superior to 40% for AMPL in Lake Michigan. Chlorophyll, or its breakdown products, likely contributed to the AMPL peak, as most extracts had a green tinge.

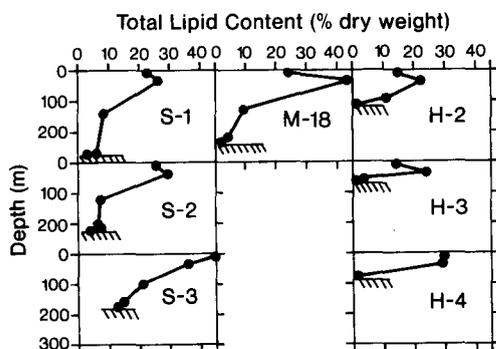


Fig. 3. Vertical profiles of lipid content (% dry weight) of settling particles in Lakes Superior, Michigan, and Huron. See Fig. 1 for station locations.

The relative proportions of lipid classes in particles from 3 depths at the 2 southern Lake Huron stations are shown in Fig. 6(a). Note, on deployment the 10-m traps were at the base of the surface mixed layer and above a large transparency minimum, while the 35-m traps were at the base of the thermocline and immediately below the transparency minimum. At the time of recovery, the 35-m traps were still at the base of the thermocline, but the mixed layer had deepened and the discrete transparency minimum had disappeared. The lipid class flux patterns at these two stations [Fig. 6(b)] suggest that particulate HC were transported through the water column. In contrast, wax esters and phospholipids were produced at depths between the 10 and 35 m traps, as was AMPL at Sta. 3. However, unlike HC, high fluxes of these lipid classes were not generally observed in the deep traps. Aliphatic hydrocarbons constituted a major proportion of the organic carbon at 10 m, whereas wax and sterol esters were the major lipid components of the organic carbon pool at 35 m (Fig. 7). The relative concentration of hydrocarbon decreased approx. 10-fold from the 10 m trap to the 83 m (5 m above bottom) trap at Lake Huron Sta. 4 (Fig. 7). The relative composition of the *n*-alkanes also changed with depth (Fig. 8).

The *n*-alkane distribution at all depths in Lake Huron (Fig. 8) and at 10 m in the different lakes (Fig. 9) was unusual because it was dominated by

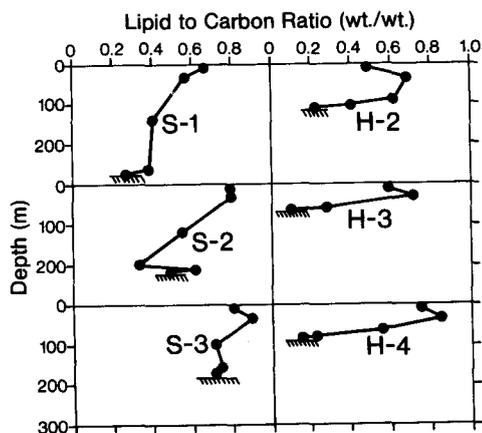


Fig. 4. Vertical profiles of the mass ratio of lipid to carbon in settling particles in Lakes Superior and Huron. See Fig. 1 for station locations.

even numbered carbon chains. The major alkane in all traps was $n\text{-C}_{20}$ except for the Lake Michigan trap, where $n\text{-C}_{18}$ dominated. Iatroscan-measured total aliphatic hydrocarbons and GC-measured total alkanes were quantitatively compared in extracts of the 10 m trap material from Sta. 4 in Lake Huron. Gas chromatographically measured alkanes accounted for only 8% of the aliphatic hydrocarbons, suggesting that the majority of the aliphatic hydrocarbons were not simple alkanes.

Botryococcus braunii collected from Lake Michigan contained $39 \pm 3\%$ ($n = 5$) lipids relative to dry weight. Hydrocarbons accounted for more than 80% of the Iatroscan-measured lipids in *B. braunii* (data not shown). We did not investigate the nature of most of these hydrocarbons, but gas chromatographic analysis of the lipid extracts indicated that n -alkanes constituted $<0.02\%$ of the hydrocarbons in this organism. Even numbered alkanes were not predominant among the detected alkanes.

DISCUSSION

The particle mass flux at the Lake Michigan station (Table 1) was similar to that reported for 35 m by Meyers *et al.* (1980) during the summer in southern Lake Michigan. The mass fluxes at the stations in the other 2 Great Lakes were lower than those in Lake Michigan. The total organic carbon content of particles in the 10 and 35-m sediment traps in the 3 upper

Great Lakes (Fig. 2) were similar but generally higher than values previously reported for similar depths in southeastern Lake Michigan (Meyers *et al.*, 1980, 1984). The C/N ratios of those particles (Table 1) were quite high for fresh aquatic organic matter (cf. Meyers *et al.*, 1984; Wakeham *et al.*, 1984) and suggest the presence of nitrogen-poor organic matter such as carbohydrates, lignin, and lipids. Such classes predominate in reworked aquatic particles depleted of labile nitrogen-containing compounds, in particles of terrigenous origin, and in organisms, or detrital particles, rich in lipids.

The highest concentrations of organic carbon (Fig. 2) and lipids (Fig. 3) occurred in particles collected at 10 and 35 m. Below 35 m, the organic carbon content and the ratio of lipid to carbon generally both decreased with depth (Fig. 4). This result may reflect a greater lability of lipid compounds over some other components of the organic carbon pool (Gardner *et al.*, 1989). The peaks in lipids at 35 m could be directly or indirectly associated with a deep chlorophyll layer caused by *in situ* phytoplankton growth and phytoplankton sedimentation (Fahnenstiel and Scavia, 1987a,b). The magnitudes of the lipid content and the C/N ratios indicate preferential loss of proteinaceous material either by further sinking or breakdown and/or preferential lipid synthesis within or above the thermocline. The average density difference between the two layers may have impeded further sinking of more buoyant lipid-containing material; pycnoclines in the marine

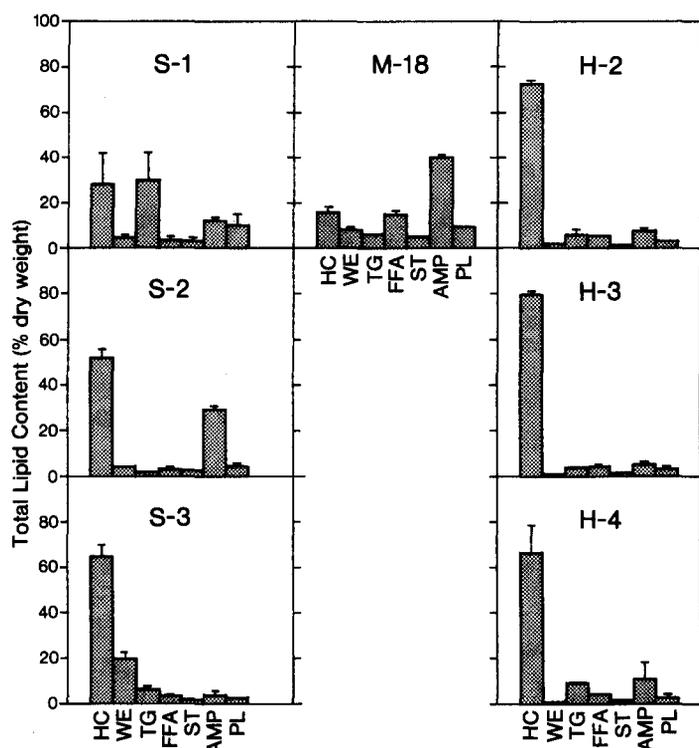


Fig. 5. Iatroscan-measured lipid class composition (%) in 10-m sediment traps collected from Lakes Superior, Michigan, and Huron. Error bars extend 1 standard deviation from the mean.

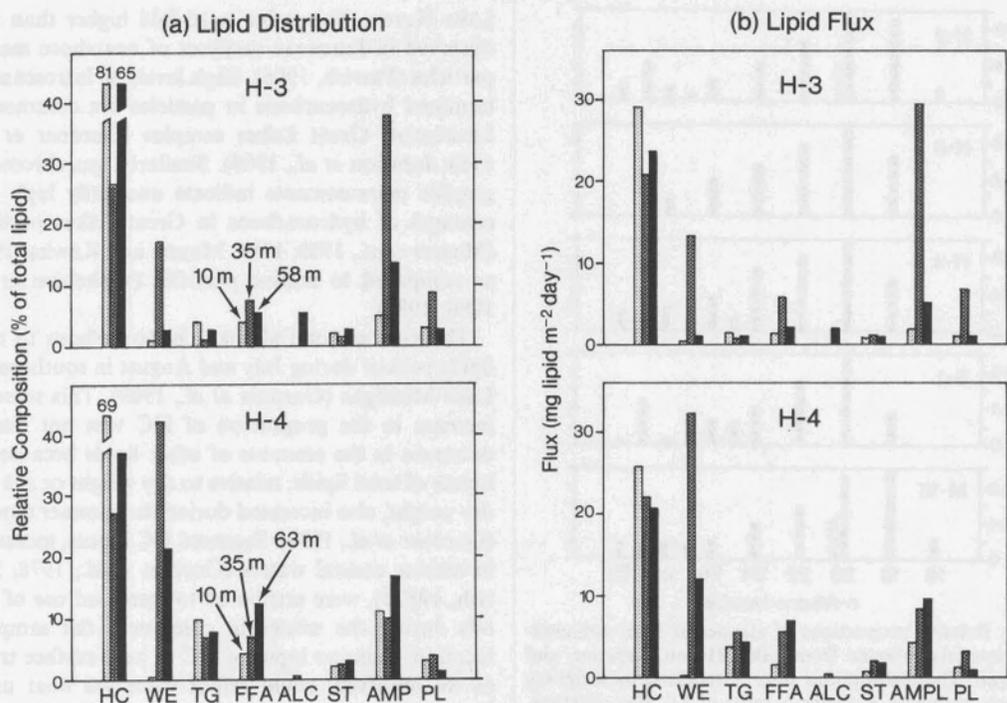


Fig. 6. Percent lipid class composition (a) and lipid flux (b) of sediment-trap materials collected from three depths at two sites in southern Lake Huron.

environment had similar maxima in lipid levels (Parrish *et al.*, 1988b).

Wax and sterol esters accounted for a higher proportion of organic carbon in Lake Huron particles (Figs 5, 6 and 7) than they did in near-shore marine particulate material (Parrish, 1986), especially in the vicinity of the thermocline. Wax esters in sub-thermocline trap material (Figs 6 and 7) likely originated from living zooplankton ("swimmers": cf. Lee *et al.*, 1989; Gunderson and Wassman, 1990) or zooplankton debris. Wax esters are common in deep-water marine zooplankton, especially in situations where short periods of food abundance follow long periods of food deprivation (Sargent *et al.*, 1977), and have also recently been shown to be major lipid components of the Great Lakes hypolimnetic

copepods *Limnocalanus macrurus* and *Scenecella calanoides* (Cavaletto *et al.*, 1989). The zooplankton may assimilate high energy compounds present in the thermocline and accumulate fatty acids into wax esters. Again, as in the marine environment (Parrish *et al.*, 1988b), maximum levels of particulate triglycerides and phospholipids appear to be associated with the density discontinuity (Fig. 7). Although previous studies (Meyers *et al.*, 1980, 1984) showed that organic material in mid-water particles is predominantly of aquatic origin, terrestrial material should also still be considered as a possible contributor to the high lipid values observed at the thermocline. Wax esters from terrestrial plants, for example, might be partially responsible for the WE peak observed at 35 m. More analytical work is necessary to confirm the presence of wax esters in Great Lakes sediment trap material and to elucidate their source. Given

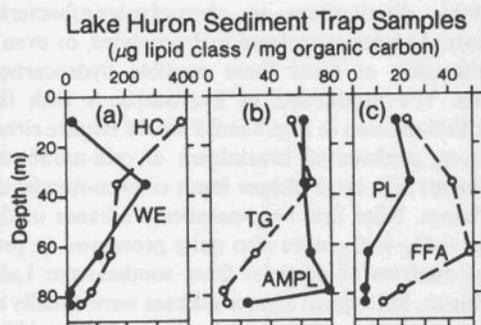


Fig. 7. Vertical profiles of the ratio of lipid classes to organic carbon in sediment-trap samples from Sta. 4 in southern Lake Huron. (a) Aliphatic hydrocarbons and wax and sterol esters. (b) Triglycerides and acetone-mobile polar lipids. (c) Phospholipids and free fatty acids.

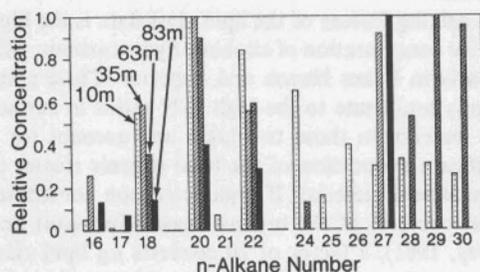


Fig. 8. Relative distribution of *n*-alkanes in sediment-trap materials collected at 4 depths at Sta. 4 in Lake Huron. The distributions were normalized by assigning the most abundant *n*-alkane a value of 1.0.

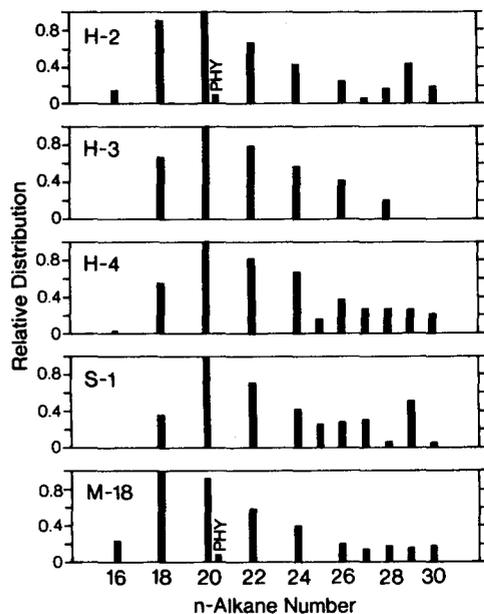


Fig. 9. Relative proportions of alkanes in 10-m sediment-trap materials collected from Lakes Huron, Superior, and Michigan. The distributions were normalized by assigning the most abundant *n*-alkane a value of 1.0. Phy, phytane.

sufficient sediment trap material, the presence of wax esters could be confirmed by magnesium hydroxide thin layer chromatography (Cavaletto *et al.*, 1989), and the relative proportions of wax and sterol esters could be quantified by high temperature glass capillary gas chromatography (Wakeham and Frew, 1982).

Materials collected from below the density discontinuity contained more free fatty acids and acetone-mobile polar lipids than did those collected at 10 or 35 m (Fig. 7). FFA and monoglycerides (a likely contributor to the AMPL peak; Parrish, 1987a) indicate lipid degradation (Parrish, 1988). The proportions of these two classes may have been slightly elevated as a result of sample storage, but the selective increases in the deep water particles indicate *in situ* hydrolysis possibly mediated by zooplankton or bacteria. Plant glycolipids may also have contributed to the AMPL band on Chromarods (Parrish, 1987a), but little is known about their occurrence in aquatic particles.

A striking feature of the lipid class data is the high relative concentration of aliphatic hydrocarbons, particularly in Lakes Huron and Superior. These compounds contribute to the high C/N ratios in surface trap material in those two lakes and account for a significant proportion of the total organic matter in the sediment material. If organic carbon constitutes about one-half of the organic mass (Kennicutt and Jeffrey, 1981), a factor of 20 converts μg lipid class ($\text{mg organic carbon}^{-1}$) (e.g. Fig. 7) to percent by weight. Thus, Iatroscaan-measured total aliphatic hydrocarbons would account for almost 20% of the organic matter in the near-surface trap from Sta. 4 in

Lake Huron. This value is 10-fold higher than that observed in Iatroscaan analyses of nearshore marine particles (Parrish, 1986). High levels of Iatroscaan-determined hydrocarbons in particles are common in Laurentian Great Lakes samples (Gardner *et al.*, 1989; Johnson *et al.*, 1989). Similarly, gas chromatographic measurements indicate unusually high percentages of hydrocarbons in Great Lakes particles (Meyers *et al.*, 1980, 1984; Meyers and Kawka, 1982) as compared to marine particles (Wakeham *et al.*, 1980, 1984).

The ratio of total aliphatic hydrocarbons to total lipids peaked during July and August in southeastern Lake Michigan (Gardner *et al.*, 1989). This seasonal increase in the proportion of HC was not due to decreases in the amounts of other lipids because the inputs of total lipids, relative to dry weight or ash free dry weight, also increased during the summer months (Gardner *et al.*, 1989). Seasonal HC inputs, measured in marine coastal waters (Gordon *et al.*, 1978; Parrish, 1987b), were attributed to increased use of fuel oils during the winter in cities near the sampling location. Summer input of HC to near-surface traps, as we observed, could reflect increased boat usage during summer or alternatively could suggest a significant biogenic contribution.

To examine these hypotheses, we measured particulate alkanes from 10 m traps in the three lakes and from all depths at Lake Huron Sta. 4 and compared the observed patterns to those expected for hydrocarbons from different sources. The major alkanes in bacteria and phytoplankton are odd-numbered and range from *n*-C₁₅ to *n*-C₂₁, since they are synthesized by decarboxylation of even-numbered fatty acids in the range of C₁₆-C₂₂ (cf. Saliot, 1981; Parrish, 1988). Higher plant hydrocarbons, found in surface waxes in association with wax esters, are also odd numbered and occur in the range of *n*-C₂₅-*n*-C₃₃ (cf. Gurr and James, 1980). On the other hand, petroleum hydrocarbons usually have a broad and fairly uniform *n*-alkane distribution with no preference for odd- or even-numbered carbon chains (cf. Muller, 1987). The alkane distributions in our samples (Figs 8 and 9) differed from these common patterns. They did not resemble distributions in phytoplankton/bacteria, terrestrial plants, petroleum hydrocarbons, or even a combination of these three possible hydrocarbon inputs. The production of hydrocarbons with the distributions seen in Figs 8 and 9 would require either a strong preferential breakdown of odd-numbered *n*-alkanes or a large unique input of even-numbered *n*-alkanes. Note that even-numbered alkanes in the range *n*-C₁₆-*n*-C₂₂ were also quite prominent in previous analyses of particles from southeastern Lake Michigan, but typical algal *n*-alkanes were equally as prominent in these samples (Meyers *et al.*, 1980, 1984; Gardner *et al.*, 1989). In agreement with Meyers *et al.* (1980), the even numbered hydrocarbon, *n*-C₂₀, was the most abundant *n*-alkane in our 10 and 35 m traps, whereas the longer, odd numbered chains, *n*-C₂₇ and

n-C₂₉, were most abundant in the deeper traps. This result may reflect the higher stability of the longer chain, predominantly terrestrially-derived, alkanes as compared to the relatively short alkanes formed by aquatic organisms.

Lake Huron had the highest proportion of aliphatic hydrocarbons among the 10 m trap samples (Fig. 5). The proportions were consistently higher than the maximum of about 50% observed in south-eastern Lake Michigan (Gardner *et al.*, 1989). If most of the hydrocarbons can be related to a single source, then this source is proportionally more prominent in Lake Huron than in the other lakes examined. A common source of hydrocarbons in freshwater lakes is *Botryococcus braunii*. This unicellular alga produces hydrocarbons at levels as high as 80% of its dry mass. The oil it synthesizes consists almost entirely of alkenes with chain lengths from C₁₇ to C₃₄ and with 1–6 double bonds per chain (Wake and Hillen, 1981; Bachofen, 1982). *Botryococcus braunii* is occasionally abundant in the Laurentian Great Lakes (Stoermer, 1978) and has been recorded at levels as high as 26% of the phytoplankton in near-surface waters of southern Lake Huron (Stoermer and Kreis, 1980). The input of hydrocarbons from this (or other functionally similar) species would be disproportionately large relative to its abundance because hydrocarbons usually account for 1% or less of the lipids in aquatic organisms. Our TLC/FID analysis of *B. braunii* from the Great Lakes suggested that this alga could well be the source of the large input of total aliphatic hydrocarbons to the sediment traps, but gas chromatographic examination of the alkanes indicated that it was probably not the direct source of the even-chain normal alkanes in the trap materials.

Although not prominent in *B. braunii*, the even-numbered alkanes could still have a biogenic source. An unusual biosynthetic pathway for hydrocarbons in algae or higher organisms was suggested to account for the predominance of even-numbered hydrocarbons in an Antarctic food chain (Nachman, 1985). The even chain hydrocarbons were thought to have been synthesized from fatty alcohols via dehydration followed by reduction. Also, some bacteria (e.g. Davis, 1968) and fungi (e.g. Jones, 1969) synthesize alkanes with no odd-chain preference or with a slight even-chain predominance. Such organisms may be the source for a strong even-number preference among the alkanes found in a wide variety of sedimentary environments (Grimalt and Albaiges, 1987).

In conclusion, total aliphatic hydrocarbons contribute substantially to the organic carbon and lipid content of settling particles during the summer. These compounds may provide an organic substrate for bacteria, but their role in the trophic transfer of energy to higher organisms may be small because energy from hydrocarbons is not efficiently used or stored by most higher organisms (Muller, 1987). On

the other hand, hydrocarbon laden particles could provide an efficient means of transporting hydrophobic pollutants. Aliphatic hydrocarbons comprise the least polar of the lipid classes so their inclusion in particles would provide a greater degree of hydrophobicity or lipophilicity than would other lipids.

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