Chapter 9

Biogeochemical Marker Profiles in Cores of Dated Sediments from Large North American Lakes

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Hydrocarbon and fatty acid components of sediments from two large remote lakes in northern Canada, Lake Athabasca and Great Slave Lake, are compared with those from two large lakes in the heavily populated Great Lakes Basin, Lakes Ontario and Erie. Studies concentrated on modern sediments dating back 70-150 years, the period during which anthropogenic effects due to development would be expected for these basins. Normal alkane and fatty acid biogeochemical markers are useful for tracking the impacts of land-use changes to the sediments of these lakes. Carbon preference indices indicate the predominance of natural sources, and point to events and trends related to petroleum contamination in all four lakes, especially the Great Lakes. Normal alkane and fatty acid biogeochemical markers yielded different assessments of the relative amounts of aquatic sources of organic matter, suggesting that diagenetic processes alter the aquatic fatty acid profiles and affects their reliability as source indicators. The ratio of unsaturated to saturated n-C_{16} acids appears to be diagnostic of depositional conditions that affect early diagenesis of fatty acids. Application of the biogeochemical marker approach to these lakes highlighted the differences in the degree of development in their watersheds.

The extractable lipid fraction of lake sediments contains hydrocarbon and fatty acid components that are a combination of biologically synthesized lipids and diagenetically modified materials. Anthropogenically derived materials, primarily hydrocarbons, which result from petroleum transport and use, also contribute to the lipids extracted from modern

sediments *(1, 2)*. Changes in the downcore distribution patterns of *n*-alkanes can be used to indicate historical changes in a lake's watershed due to anthropogenic impacts and/or natural causes *(1-4)*. Normal fatty acid distributions have likewise been used to indicate impacts of land use and climate changes on lakes *(5, 6)*.

This paper compares recent investigations of the depositional history of two large lakes in a remote area of northern Canada, Lake Athabasca and Great Slave Lake, with those from two large lakes in the heavily populated Great Lakes Basin, Lakes Ontario and Erie. Our studies have concentrated on modern sediments dating back 70-150 years, the period during which anthropogenic effects due to development would be expected for these basins. Previous work has been reported on these Great Lakes cores for a variety of natural and anthropogenic components. The purpose of this paper is to compare source and diagenetic impacts on the hydrocarbon and fatty acid distribution in the sediments of the northern lakes with the Great Lakes. This is done using biogeochemical markers derived by examining *n*-alkane and fatty acid concentrations from the northern lakes sediments and re-examining these same parameters by means we have not used previously for the Great Lakes cores.

Total organic carbon (TOC) profiles of sediment cores give an overall view of the changes that occur in a lake's watershed over time, representing both anthropogenic and natural perturbations to the mix of organic components entering the lake. The biogeochemical markers used in this paper are derived from the distributions of *n*-alkanes and *n*-fatty acids. Carbon Preference Indices (CPI), which are derived from *n*-alkane distributions *(7, 8)*, can be used to indicate the degree of contamination from petroleum and its products. Terrestrial and aquatic plant contributions to lake sediments can be determined from both *n*-alkane and fatty acid distributions. These indirectly measure processes that can influence the input of terrestrially derived organic matter (*e.g.* deforestation) and those that influence primary productivity (*e.g.* nutrient inputs). The ratio of two commonly occurring fatty acids, *n*-hexadecenoic acid (n-$C_{16:1}$) and *n*-hexadecanoic acid (n-$C_{16:0}$) can be used to indicate the degree to which diagenic processes (*e.g.* microbial degradation) affect organic matter after deposition *(2, 3, 9-10)*.

Sampling and Methodology

Coring. Sediments were collected from Lake Athabasca (1992) and Great Slave Lake (1994) using a 10 cm i.d. gravity corer through the ice in late winter. Sediments from Lake Ontario (1981) and Lake Erie (1982) were collected as 6.5 cm i.d. subcores from box cores taken aboard the *CSS Limnos* during summer. Locations of the four lakes are shown in Figure 1 and site information for each are given in Table I. In all cases several replicate cores were collected. Cores were kept cold (4±2 ° C) until extrusion could be done. Sectioning was done, within a few hours of collection, with cores aligned vertically using an hydraulically controlled extruder. Sections of sediment from 0.5 - 2 cm thick were placed into pre-cleaned glass jars, and the sediment samples were frozen immediately. Section thicknesses were selected according to the expected sedimentation rate for each site and generally were thinner on the top of the core and thicker further down.

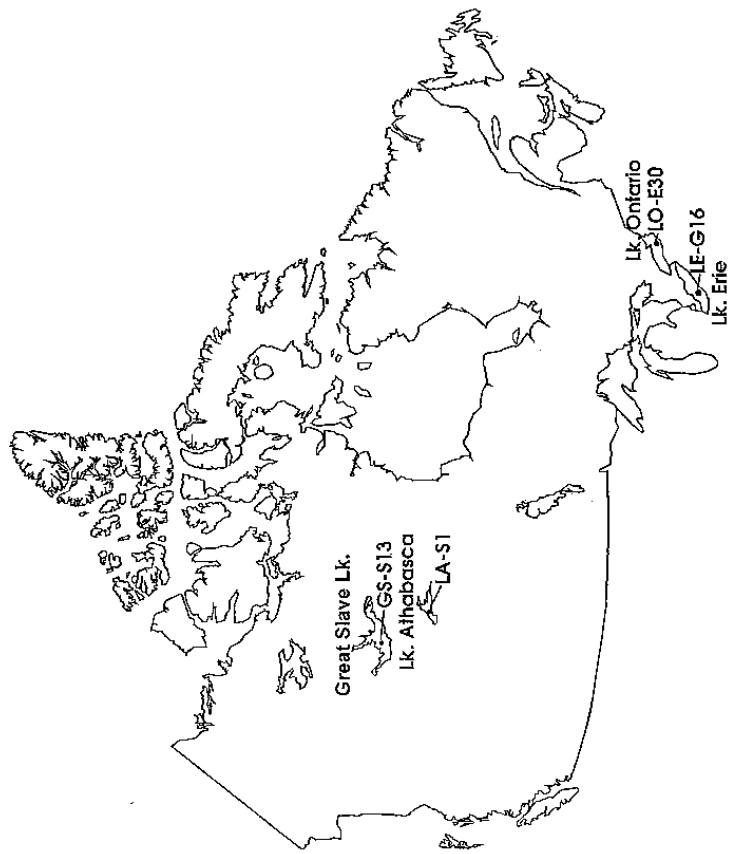

Figure 1. Map of Canada showing study lakes and coring locations.

Cores from each lake were evaluated for overall quality according to slice by slice descriptions recorded during extrusion. Two cores were selected from the replicates collected at each lake for use in this study. One was used for geochronology and bulk physical and chemical determinations; the other was used for organic geochemical analyses. Information used for core selection and the depth of the upper oxidized interval at each coring location are included in Table I.

Geochronology. One of the cores selected from each site was freeze-dried, dated using the ^{210}Pb method *(11-13)* and confirmed by the ^{137}Cs method *(11, 12, 14)*. The average modern mass sedimentation rate determined from the ^{210}Pb profile was applied to the downcore cumulative dry weight distribution, assigning deposition dates to the midpoints of the intervals sampled. All data presented here are plotted according to these ^{210}Pb deposition dates to allow easier comparisons among the cores. Geochronological parameters are listed for each site in Table I.

Total organic carbon. TOC was determined by dry catalytic oxidation of carbonate-free sediment (de-calcified using sulfurous acid) at 950-1000°C on aliquots of the same cores used for dating. Quantitation was done using NDIR detection on either Leco IR12 or Perkin-Elmer instruments. Precision of replicates was within 3% of the mean at the 20 mg/g level.

Extractable lipids. Hydrocarbons, fatty acids and other lipids were isolated from sediments by 2 x 24 h Soxhlet extraction with azeotropic toluene/methanol. The combined Soxhlet extracts constitute the "unbound" or extractable lipid fraction of the organic matter in the sediments. These are concentrated, saponified to break esters, methylated with BF_3/methanol and fractionated to isolate several lipid classes on alumina/silica gel columns *(11,15)*. The first eluent from the columns, hexane/toluene (85:15), contains hydrocarbons and the second eluent, toluene (100%), contains fatty acid methyl esters. Other classes were not considered for this work. After concentration both fractions were analyzed by capillary gas chromatography with flame ionization detection (FID). Samples were injected, on-column, using 30 m x 0.32 mm i.d. fused silica columns (SE30, DB1 or DB5 -- 0.25 µm film thickness). The gas chromatographs used were either a Carlo Erba 4160 or Hewlett Packard 5890.

Quantitation was accomplished by adding internal standards to the sediment samples before the extraction procedure. For *n*-alkanes the internal standard was either *n*-hexatriacontane (*n*-C_{36}) or *n*-octatriacontane (*n*-C_{38}), both of which were shown to occur below detection limits or in negligible quantities during preliminary tests of a few sediment samples. For fatty acids, either *n*-heptadecanoic acid (*n*-$C_{17:0}$) or *n*-nonadecanoic acid (*n*-$C_{19:0}$) was used as the internal standard after testing for negligible occurrence. Inclusion of the internal standards at the beginning of the procedure by injecting them onto the sediment assures that any losses resulting from subsequent operations are accounted in the final results. Quantitation of the integrated gas chromatographic results for all of the *n*-alkanes and fatty acids determined were done by applying FID response factors relative to the internal standards used. These response factors were calculated from daily runs of mixtures of authentic standards covering the range of analytes determined in each class. For the few

analytes not represented in the mixtures, the response factors were estimated by averaging the factors determined for the adjacent homologs.

Table I. Location, Identification and Geochronological Parameters from the Four Coring Sites

Lake and Date (Site ID)	Latitude N	Longitude W	Water Depth (m)
L. Athabasca, 1992, (LA-S1)	59° 02.7'	110° 13.4'	12
Great Slave L., 1994, (GS-S13)	61° 24.2'	114° 59.8'	61
L. Ontario, 1981, (LO-E30)	46° 32.2'	76° 54.1'	233
L. Erie, 1982, (LE-G16)	42° 00.0'	81° 36.1'	24

Site ID	[1]GCH Core	[1]BGM Core	[2]Oxid. Layer cm	Mass Sed. Rate g/cm^2/yr	[3]Date at ^{137}Cs Maximum	Geochronology Reference
LA-S1	1C	1D	5-6	0.072	1957	*11*
GS-S13	13C	13E	4-5	0.043	1966	*13, 14*
LO-E30	RNC	LIP	3-4	0.044	1960	*12*
LE-G16	SC5	SC8	7-8	1.360	1963	[4]JAR

[1]GCH - Geochronology Core ID, BGM - Biogeochemical Marker Core ID from field notes
[2]Thickness of brown oxidized layer at top of each core overlying grey sediment
[3]Date from ^{210}Pb method at which the 1963 ^{137}Cs maximum occurs
[4]Robbins, J. A., NOAA / GLERL, Ann Arbor, MI, unpublished data

Quality Assurance. Standard laboratory practices include the determination of total procedural blank for 1 extraction in 12, and running 1 of several laboratory reference standards in every 12 extractions. This latter practice served to test the robustness of the procedures by showing that only small variations occurred even though several analysts carried out the laboratory work. As well, results from replicate extractions of the laboratory standards provide an estimate of the reproducibility of the procedures. Typical results for reproducibility of fatty acid determinations are illustrated by data from 6 determinations of a Lake Ontario laboratory reference standard analyzed by 3 technicians over a 2 year period. The precision for total fatty acids (from total FID area), *n*-$C_{16:0}$, and *n*-tetracosanoic acid (*n*-$C_{24:0}$) were 11%, 9% and 7% respectively, expressed as relative standard error.

Data reported are corrected, when necessary, for small amounts of cross contamination occasionally found in total procedural blanks. Rarely were individual *n*-alkane or fatty acid components identified in the blank runs in significant quantities. Most often no correction was needed at all. The practical detection limit based on 5 g sample

size was 10 ng/g for individual *n*-alkanes and 5 ng/g for individual fatty acids based on analysis of the signal-to-noise ratio from several representative chromatograms.

Tests conducted during method development showed that 95% of the extractable lipids were isolated during the first 24 hours of Soxhlet extraction, but a second 24 hour extraction was always done to allow for sample-to-sample variations. The ratio of "unbound" fatty acids (extractable as defined here) to "bound" fatty acids (extractable by saponification after "unbound" was removed) from a Lake Ontario surficial sediment was 33:1. This was not tested for other sediments.

The Great Lakes sediments used for this study were freeze-dried before extraction with the chamber temperature maintained at 20° C. Interest in more volatile components of sediments for related work prompted the adoption of wet extraction techniques for the northern lakes sediments and involved only minor modifications to the procedures *(11)*. Volatility tests in our laboratory showed no effect of prolonged evaporation for *n*-alkanes greater than *n*-C_{14}, so a significant effect of freeze-drying is unlikely for the compounds used here as biogeochemical markers.

Total Organic Carbon

Concentrations of TOC increase in the upper parts (post 1940) of cores taken from each of the lake basins (Figure 2). The most recent increase is much less for the northern lakes, but can be considered higher than background for all lakes. In addition, one of the Great Lakes cores (LO-E30) shows evidence for a prior increase in TOC beginning about 1860 (Figure 2). The earlier increase has been attributed to deforestation coincident with settlement in the lower Great Lakes basin *(3, 16-19)*. The later increase in TOC for all cores coincides with increases in development and industrial activity, and is especially evident in the Great Lakes cores. TOC concentrations in the contemporary sediments from the northern lakes are the same (10-15 mg/g) as the pre-settlement levels in the lower Great Lakes. The cores from Lake Athabasca and Lake Erie exhibit several excursions in the TOC profiles (Figure 2). The coring sites for these two lakes were shallower than the other two sites (Table I) and may have been influenced by wave action during storms.

n-Alkane Source Indicators

Natural biological precursors of sedimentary organic matter generally contain a wide range of *n*-alkanes. These components typically exhibit a strong predominance of odd carbon numbered homologs over those of even chain length (*2*). Thermogenic (petroleum generation) processes that act on sedimentary organic matter after deep burial modify the *n*-alkane distribution so that no carbon number predominance remains *(20)*. This lack of odd over even predominance can be used in environmental geochemistry to assist in identifying sediments contaminated with petroleum or its by-products.

Two principal sources dominate natural inputs of hydrocarbons to modern lake sediments; photosynthetic algae from aquatic sources, and vascular land plants. The former are represented by *n*-alkane distributions dominated by C_{17} *(2, 11, 21)* while the latter contain large proportions of C_{27}, C_{29}, and C_{31} *n*-alkanes that originate in epicuticular wax coatings *(2, 5, 22-25)*. In modern sediments, *n*-alkanes from natural sources are usually augmented by those from contamination sources.

Carbon Preference Indices for *n*-Alkanes. The CPI, as originally proposed by Bray and Evans *(7)* and Cooper and Bray *(26)*, has been used widely in petroleum geochemistry as a maturity indicator. Using a mathematical expression that reduces the ratio of odd carbon to even carbon chain length *n*-alkanes to a single value, oil-containing mature sediments tend to show no predominance and yield a CPI value of unity. Immature sediments contain largely unmodified *n*-alkanes and show higher odd predominance (CPI >1). In a recent paper *(8)*, a mathematical shortcoming of the original Bray and Evans expression was described, and an improved expression was proposed. We have adopted the newer expression for use in this paper.

In practice CPIs should be referenced to the same range of *n*-alkanes to compare values among samples. Our analytical procedures allowed reliable quantitation of *n*-alkanes from C_{15} through C_{35} in all samples from the lake sediments studied. Within this wide range of *n*-alkanes are included all of the aquatic, terrestrial and petroleum alkanes described above which commonly are found in the lipid extracts of modern sediments *(2, 20)*. We define here three CPIs using the formulas in equation 1. The overall CPI (equation 1a) incorporates all natural *n*-alkanes contributed by aquatic algae and vascular land plants as well as contaminants from transport and use of petroleum and its products in the watershed.

$$CPI = \left(\sum \text{Odds } C_A \ldots C_B + \sum \text{Odds } C_C \ldots C_D \right) / 2 \left(\sum \text{Evens } C_E \ldots C_F \right) \quad (1)$$

Overall $CPI_{15\text{-}35}$ (CPI):	A=15, B=33, C=17, D=35, E=16, F=34	(a)
Low $CPI_{15\text{-}25}$ (LCPI):	A=15, B=23, C=17, D=25, E=16, F=24	(b)
High $CPI_{25\text{-}35}$ (HCPI):	A=25, B=33, C=27, D=35, E=26, F=34	(c)

If CPI is calculated for only the lower half of the range determined (equation 1b), the resulting low carbon preference index (LCPI) is more influenced by algal and bacterial sourced biogenic *n*-alkanes and lighter petroleum products such as fuel oils *(20)*. CPI calculated from only the higher end of the *n*-alkane distribution (HCPI, equation 1c) should be influenced by inputs from natural higher land plant sources as well as heavier petroleum products such as crude and lubricating oils *(20)* and possibly combustion products. Examples of end-member values from the literature and this work are given in Table II .

High Carbon Preference Index. The CPI value of around 2 is characteristic of the organic matter deposited over the past 100-150 years at three of the four locations studied. Only the LO-E30 core showed consistently lower values, centering around a CPI of 1.4. The downcore patterns of HCPI at all four sites (Figure 3) parallel closely the downcore CPI patterns except that values are shifted higher about 1 unit. For this reason only the former will be discussed.

The fact that HCPI values >1.5 are common at all sites suggests a mixed natural and contaminant source of alkanes to all four lakes. For all lakes, HCPI values >3 occur only episodically, which implies that natural higher plant sources of alkanes, though always a major contributor to these sediments, are sometimes deposited in greater proportions. A possible explanation for such episodic increases in HCPI is a greater contribution from topsoil containing degraded leaf litter eroded from the watershed, caused by forest clearance, urbanization or periods of unusual rainfall. This is a plausible explanation for the increasing trend shown for LO-E30 between 1940-1960. The urban population of Canada nearly doubled from 8 to 14 million between 1941 and 1961 *(27)*, much of this growth

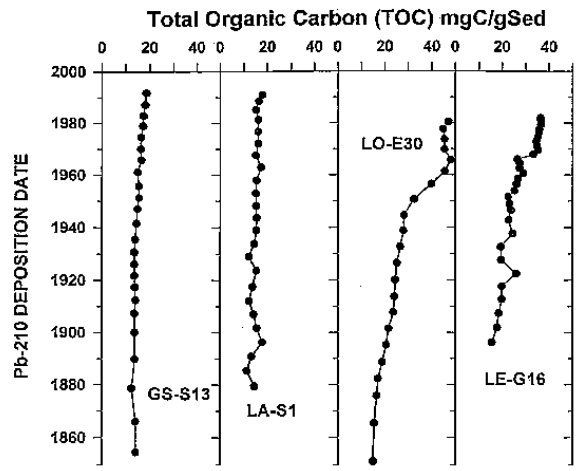

Figure 2. Downcore concentrations of TOC in the four dated cores of sediments from large North American lakes identified in Figure 1 and Table I.

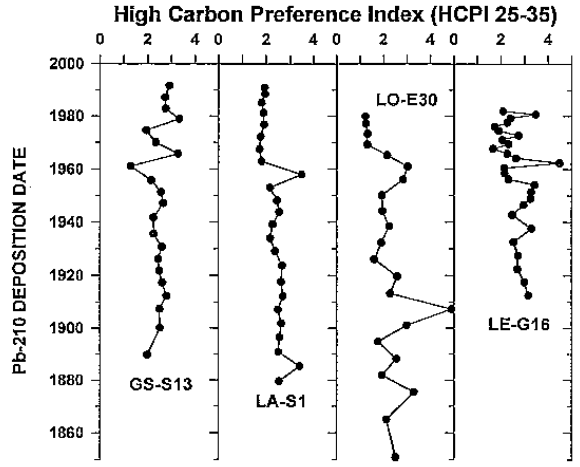

Figure 3. Downcore distributions of High Carbon Preference Index (HCPI) for the n-alkane range: C25 - C35, from sediments of four large North American lakes identified in Figure 1 and Table I.

occurred in southern Ontario. Likewise, the increase between 1940 and 1950 in the LE-G16 core could reflect similar urbanization in the Lake Erie watershed (Figure 3).

The overall HCPI trend for GS-S13 over the past 100 years is a slightly increasing one except for some lower and higher excursions between 1960 and 1980 (Figure 3). The suggestion from this pattern is that higher land plant hydrocarbons have been gradually increasing in relative proportion, but that occasional periods of lower input of these *n*-alkanes or incidents of contamination by heavier petroleum products influenced the HCPI distribution.

Lower values of HCPI, approaching that of unity, occur occasionally in the data from GS-S13 and LE-G16, and over the last decade for LO-E30. Such low HCPI values suggest sporadic incidents of petroleum contamination for the former two lakes and a very recent increase in the supply of petroleum related contaminants to Lake Ontario sediments. A three-fold increase between 1940 and 1970 in the content of hydrocarbons constituting an unresolved complex mixture (UCM) in the LO-E30 sediments was reported previously *(4)*. The LA-S1 core (Figure 3) shows a distinct shift to consistently lower (<2) HCPI from a prior near constant value of >2. This pattern suggests influence from oil sands surface mining and upgrading activities in the region which experienced major development beginning in the 1960s *(30)*, see also Table II.

Low Carbon Preference Index. In Figure 4 the LCPI data from the northern lakes show very consistent values over the past 100 years. LCPI values for the LA-S1 core are a nearly unchanging 1.5 except for a brief excursion to 1.9 in the 1940s. Likewise the GS-S13 core yielded values from 1.3-1.5 for all sections except for a period when the LCPI of the sedimentary organic matter doubled in the 1920s suggesting a shift to increased autochthonous biogenic sources of *n*-alkanes (Table II). The Great Lakes cores exhibit more variable and generally lower values of LCPI. The LO-E30 core shows all values <1.5 over the past 150 years trending downward to unity since the 1920s with the exception of an excursion to even preference (<1) in the 1940s and one to higher odd preference in the early 1960s (Figure 4). The LE-G16 core shows a LCPI trend opposite to the LO-E30 core, increasing more sharply from a value of about 1 in 1940 to 1.8 in 1980, suggesting increasing autochthonous biogenic sources.

Terrestrial and Aquatic Indicators. Terrestrial plants and aquatic algae have very different *n*-alkane distributions, longer chain ($>C_{20}$) alkanes being more typical of the leaf waxes of land plants and short chain *n*-alkanes are more common in aquatic algae *(21-23, 25)*. The sum of *n*-alkane concentrations: ($C_{27} + C_{29} + C_{31}$) can be used as a measure of the inputs of *n*-alkanes from terrestrial plants, and the sum: ($C_{15} + C_{17} + C_{19}$) indicates *n*-alkanes from aquatic sources. Previous work *(3)* used the "terrestrial/aquatic ratio" for hydrocarbons (TAR_{HC}), a simple ratio of these two sums (Table II), as a measure of the relative amounts that these sources contribute to sediments. The advantage of using a ratio is that large episodic changes in total organic contribution to sediments are normalized and data from several cores can often be plotted on the same scale. Trends in TAR_{HC} can be used to indicate changes in source to the sediments, but they work better when the trends are mostly due to changes in terrestrial sources. When aquatic sources predominate, the TAR_{HC} decreases to values of <1 (Table II) and changes are less evident. Other shortcomings of ratios are that opposing trends are masked and small absolute trends are dampened. For this work we use the simple sums as biogeochemical markers.

Table II. Examples of End-Member Values for *n*-Alkane Biogeochemical Marker Ratios

	[1]CPI	[1]LCPI	[1]HCPI	[1]TAR_{HC}	Reference
L. Ontario Phytoplankton	8.9	10	1.5	0.02	This work
Algal Ooze	5.2	-	-	-	*28*
[2]White Spruce Needles	1.8	1.2	2.2	10	*29*
[3]Spruce Needles	1.5	1.4	1.5	29	This work
Continental Plants	4 - 7	-	-	-	*20*
[4]Oil Sands Mine Drainage	1.3	1.5	1.2	2.8	This work
[5]Oil Sands Refinery Effluent	1.2	1.3	1.1	0.65	This work
Oil Shales	1.1	-	-	-	*20*

[1]See text for definitions.
[2]*Picea glauca* from Matthei Botanical Gardens, Ann Arbor, MI.
[3]*Picea* sp. from Burlington, ON, near heavy industrial area.
[4]Suspended particulates in strip mine drainage, Ft. McMurray, AB.
[5]Suspended particulates from process water discharge, Ft. McMurray, AB.

The profiles of terrestrial and aquatic indicators for Lake Ontario (Figure 5) show that this lake previously experienced lesser inputs of both land based and algal *n*-alkanes. In the early part of the 20th century some small episodic increases occurred in both aquatic and terrestrial *n*-alkanes. Around 1940 the inputs of both types of *n*-alkanes began to increase and by 1960 the increased inputs became significant. More recently, inputs of *n*-alkanes from vascular plant sources have exceeded by 2-3 times the input of aquatic *n*-alkanes (Figure 5). These trends follow the growth in urban population in the Great Lakes basin as mentioned previously *(19)*. Increases in biogenic silica and total phosphorus have been shown to occur at about the same time in another of the replicate cores from this Lake Ontario site *(18)* and decrease of total phosphorus loadings to the lake in the 1970s *(31)* could explain the leveling off that is evident in the aquatic *n*-alkane profile (Figure 5). The longer chain *n*-alkanes likely originate from multiple sources related to anthropogenic activities, such as soil erosion, sewage inputs, and petroleum inputs from urban runoff, industrial emissions, shipping, etc. The suggestion of petroleum inputs are consistent with recent UCM increases in this core *(4)* and HCPI data (Figure 3), and points to a limitation in the use of these longer chain *n*-alkanes as terrestrial markers without also obtaining evidence of petroleum influence.

Lake Erie has experienced increased anthropogenic phosphorus loadings throughout the 20th century, but especially since the 1940s *(32-33)* and greater aquatic plant contributions to the sedimentary *n*-alkanes is evidenced by the decreasing trend of TAR_{HC} after 1970 *(3)*. Profiles of the terrestrial and aquatic *n*-alkane markers are very complex with considerable cyclic variability evident for both sources throughout the 20th century (Figure 5). Note that the cycles for both sources are in phase, suggesting that overall

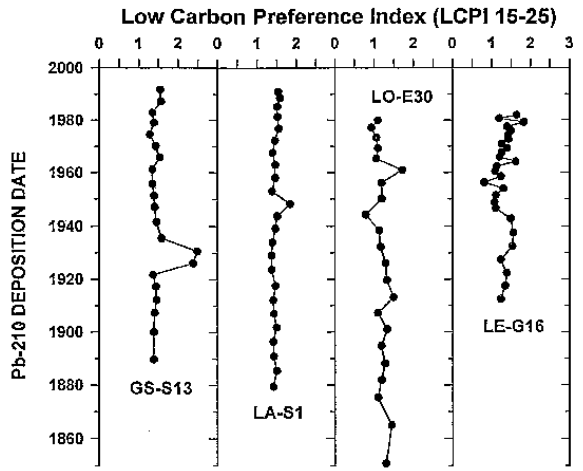

Figure 4. Downcore distributions of Low Carbon Preference Index (LCPI) for the n-alkane range: C15 - C25, from sediments of four large North American lakes identified in Figure 1 and Table I.

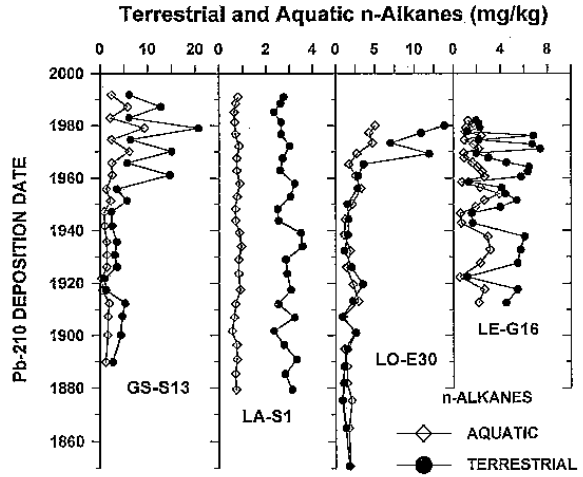

Figure 5. Downcore distributions of n-alkane terrestrial and aquatic biogeochemical markers from sediments of four large North American lakes identified in Figure 1 and Table I. Aquatic = ($C_{15} + C_{17} + C_{19}$), Terrestrial = ($C_{27} + C_{29} + C_{31}$).

watershed effects may be largely responsible for these fluctuations. A comparison of the *n*-alkane data with historical lake level data *(33)* reveals that the periods of high *n*-alkane inputs from either source are associated somewhat with periods of higher water levels. This suggests that erosion of bluffs *(34)* and agricultural land can provide inputs of terrestrial *n*-alkanes and nutrients which can increase phytoplankton productivity. Although cultural loadings of phosphorus to Lake Erie have increased dramatically since the 1940s *(33)* the aquatic *n*-alkane signal is equally high at times before 1940 as it is after that date (Figure 5).

Great Slave Lake shows in-phase cyclic inputs of *n*-alkanes from both terrestrial and aquatic sources since the 1960s. The fluctuating behavior began earlier (1950) for the terrestrial *n*-alkanes (Figure 5). A few of the values for the GS-S13 core are the highest values for both aquatic and terrestrial *n*-alkanes of all the cores. This lake receives input from the Peace River system which flows through major forested regions of British Columbia and Alberta which have seen recent growth in forest products industries. These may be the sources of the terrestrial *n*-alkanes in the sediment. In contrast to the GS-S13, core the LA-S1 core shows the lowest and least variable contents of both terrestrial and aquatic n-alkanes of all the four cores (Figure 5). Lake Athabasca sediments have received a constant input of aquatic *n*-alkanes for the last 100 years and a nearly constant input of terrestrial *n*-alkanes, with some cyclic behavior over the same period. The Athabasca river drains forestry, agricultural and oil producing regions of Alberta, but most of its flow exits into the Peace River system after entering only the far southwestern part of Lake Athabasca *(35)*.

Fatty Acid Source and Diagenesis Indicators

Downcore profiles for certain normal fatty acids can also be used to infer changes in source input to lake sediments. Fatty acids are about ten times more degradable than hydrocarbons *(36-37)* and much more abundant in these sediments *(3, 11)*. Thus, there is a greater potential for fatty acid profiles to be modified by post-depositional processes such as microbial reworking *(38-39)*. This property can be used to advantage in assessing the extent of microbial reworking, but also indicates that caution must be used when ascribing source changes on the basis of labile biogeochemical markers *(29)*.

Terrestrial and Aquatic Indicators. Like the *n*-alkanes, long chain fatty acids are dominant components of the waxy coatings of leaves, flowers and pollen originating from land plants *(25)*, and shorter chain acids are produced by all plants but are the dominant lipid components of algae *(40)*. Aquatic source normal fatty acids can be represented by the sum: ($C_{12:0} + C_{14:0} + C_{16:0}$), and terrestrial sources by the sum of three longer chain acids: ($C_{24:0} + C_{26:0} + C_{28:0}$). A fatty acid ratio (TAR_{FA}) was defined and used in a similar way to the TAR_{HC} ratio *(3)*. Higher values of TAR_{FA} may indicate increased input of terrigenous sources of lipid matter to the sediments, but they may also indicate preferential degradation of shorter chain fatty acids relative to longer ones *(29, 36, 41-43)*.

Terrestrial fatty acid inputs to the GS-S13 and LA-S1sites have been constant at the same 10 mg/kg level for 80 and 100 years respectively (Figure 6). As well, the LO-E30 core shows constant input of these fatty acids from 1850 through 1930, with only a slight increase for the next two decades. Likewise The LE-G16 core received constant input of terrestrial fatty acids from 1910-1960. The Great Lakes cores contain from 3-10 times as much terrestrial fatty acids as the northern lakes. Both the LO-E30 and LE-G16 cores

exhibit significant increases in terrestrial sourced fatty acids beginning in 1950 and 1960 respectively (Figure 6). The most recent trends for the terrestrial fatty acids for both of these Great Lakes are significant decreases, leaving behind a subsurface maxima. As terrestrial fatty acids are less susceptible to degradation *(29, 36, 41-43)*, we can treat the profiles as indicating source changes with more certainty. If we do so, these profiles fit very well with the history of urbanization in these watersheds as described previously.

The lower portions of all cores are characterized by low levels of aquatic fatty acids, the lowest levels in each core (Figure 6). The GS-S13, LO-E30 and LE-G16 cores all show increases in aquatic fatty acid content beginning at 1950, and the LA-S1 core begins to increase at 1930. The aquatic fatty acid content of all cores increases progressively towards the present with the highest value near the surface that is 3-10 times the background value for a given core. The aquatic fatty acid profiles for LO-E30 and LE-G16 could be explained by cultural inputs of nutrients *(31,33)*, but no such mechanism is known for the increases shown for GS-S13 and LA-S1 (Figure 6). Based on phytoplankton biomass Munawar and Munawar *(44)* classified Lake Erie as eutrophic in the early 1970s. Certainly such conditions would imply a greater concentration of aquatic fatty acids in the surface sediments, as is seen in the LE-G16 core. By that measure, the concentrations of aquatic fatty acids in the surficial sediments of the other three lakes correctly suggest that they are all oligotrophic.

Another view of the aquatic fatty acid profiles is that they are influenced by diagenetic processes such as microbial degradation during settling and after deposition. The shape of the profiles from GS-S13, LA-S1 and LE-G16 are all similar and is consistent with decreases over time of an initial high input of aquatic fatty acids. As well the rate of decrease is higher in the upper few cm for each core, the oxidized zone (Table I), where aerobic microbial activity is normally vigorous. The aquatic fatty acid profile of the LO-E30 core appears to result from even more vigorous degradation. This is consistent with the relatively low surface value resulting from selective microbial degradation during the long transport to this site which is by far the deepest of all (Table I), a process which has been measured in sediment trap studies in the Great Lakes *(37)*.

Indicators of Post-Depositional Alteration. Although all fatty acids are susceptible to microbial degradation *(36, 43)*, unsaturated fatty acids are especially labile and are preferentially removed during early diagenesis in lake sediments *(38)*. We have used changes in the ratio of $n\text{-}C_{16:1}$ to $n\text{-}C_{16:0}$ (US16) as an indicator of the intensity of diagenetic activity. Under conditions that favor microbial degradation (*e.g.* low sedimentation rate, oxidized surface sediments, higher temperatures, longer water column residence time) lower values for US16 would be expected. Conversely, high sedimentation rate would tend to preserve organic matter by quick burial so that it remains in the oxidized zone for less time. Lower temperatures tend to limit microbial activity and a shallow water column exposes sinking particles to oxic microbial action for shorter periods. These latter conditions serve to preserve the ratio closer to the original, sometimes higher, US16 value of the depositing organic matter.

Comparisons of US16 values on cores from different depositional environments must be made cautiously since multiple depositional factors are concerned as mentioned above, and source changes and duration of settling time are also important variables. We are not certain what the original US16 ratio is for any of the lakes studied, but a laboratory culture of *Asterionella formosa*, a common freshwater diatom, yielded a value of 3.8 for

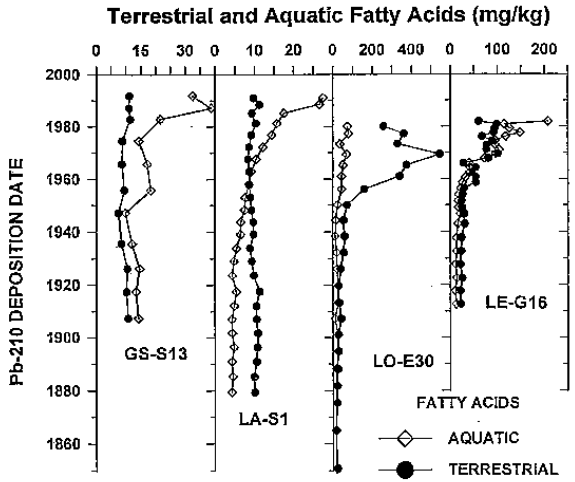

Figure 6. Downcore distributions of fatty acid terrestrial and aquatic biogeochemical markers from sediments of four large North American lakes identified in Figure 1 and Table I. Aquatic = ($C_{12:0} + C_{14:0} + C_{16:0}$), Terrestrial = ($C_{24:0} + C_{26:0} + C_{28:0}$).

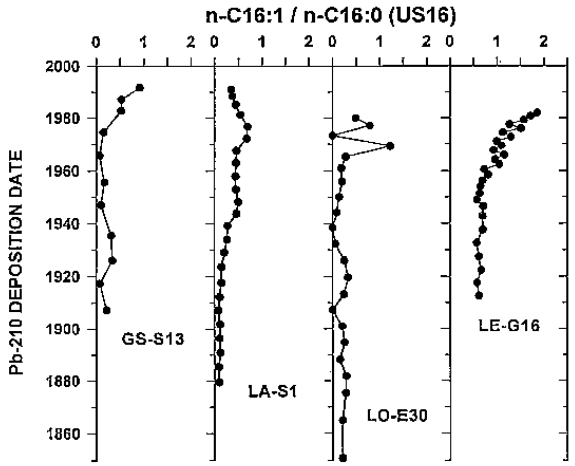

Figure 7. Downcore distributions of fatty acid Unsaturated / Saturated Ratio ($n\text{-}C_{16:1} / n\text{-}C_{16:0}$), from sediments of four large North American lakes identified in Figure 1 and Table I.

US16 *(45)*. Thus, the high value found for the LE-G16 core (Figure 7) and the gradual nature of the downcore decline in US16 suggests that microbial degradation of deposited fatty acids is inhibited at this site. This could be caused by the high sedimentation rate (Table I) and periodic occurrence of summertime hypolimnetic anoxia *(32)*. The high ratio could also indicate, in this case, a high algal input in line with results discussed above (Figure 6).

Like the LE-G16 core, the GS-S13 core shows a gradual downcore decrease in US16 value. The sedimentation rate is not as high at GS-S13, and hypolimnetic anoxia should not occur at this site. At the depth of this site the year-round temperature is 4° C *(46)*. Such conditions could aid in preservation of fatty acids and slow down degradation rates and could conceivably result in a profile similar to that from LE-G16. The Lake Athabasca coring site is the shallowest of the four sites studied (Table I) and its summer bottom water temperature can reach 9° C *(35)*. The US16 profile (Figure 7) shows evidence of a gradual stepwise decrease at depths which correspond to 1980 and sooner. The most recent values show an increasing trend with depth, which suggests that source changes may have obscured diagenetic effects

The US16 profile for the LO-E30 core is unique (Figure 7). Excluding a few sections near the top of the core, the LO-E30 core shows mostly low US16 values that are among the lowest found. Part of the explanation for this may be that much of the early diagenesis of the lower molecular weight fatty acids occurs during settling of the sediments as they make their way to this deep site.

Conclusions

TOC concentration profiles from the northern lakes record only very small increases in organic matter delivery over the past 100 years in contrast to those from the Great Lakes which show progressively greater delivery of organic matter to the sediments in response to anthropogenic perturbations in the watershed.

The overall CPI indicates natural sources of hydrocarbons predominate in all lakes, but incidents of petroleum contamination may be recorded by the HCPI profiles of the Lake Erie and Great Slave Lake cores. The Lake Athabasca core, and to an even greater extent the Lake Ontario core, show evidence for modern trends in HCPI that suggest persistent contamination by petroleum or its products. Focusing the CPI on lower molecular weight *n*-alkanes (LCPI) shows that the northern lakes are largely unchanged in the past 70-100 years with respect to *n*-alkane sources. Lake Ontario results indicate a slow progression to unity indicating increasing contamination by light petroleum products and the Lake Erie results show that natural sources of *n*-alkanes have increased progressively since the 1940s.

Normal alkane biogeochemical markers show consistent dominance of higher plant sources over the past 100 years for both Lake Athabasca and Great Slave Lake and over the past 70 years for the Lake Erie core. For the Lake Ontario core the predominance of terrestrially sourced *n*-alkanes occurs only over the past 25 years. The Lake Erie and Great Slave Lake cores show cyclic changes in both aquatic and terrestrial *n*-alkanes. Only the Lake Ontario core shows clear modern increases in aquatic sources for *n*-alkanes.

Fatty acid biogeochemical markers show no changes in the amount of terrestrial fatty acids input into Great Slave Lake or Lake Athabasca over the past 100 years. Both Lake Ontario and Lake Erie show modern increases in terrestrial fatty acid inputs and constant values before 1950. The sediment concentrations of fatty acids from aquatic

sources appear to be influenced by diagenetic processes, before and after deposition, to varying degrees, for all four lakes. Post-depositional alteration profoundly affects the concentrations of these fatty acids so that they are not reliable as source indicators. The ratio of unsaturated to saturated n-C_{16} acids (US16) appears to be diagnostic of depositional conditions that affect early diagenesis of fatty acids. Such conditions as sedimentation rate, temperature, and settling time appear to explain the downcore patterns of US16 for all four lakes.

Evidence from all of these biogeochemical markers suggests that the northern lakes have not had substantial impact from anthropogenic hydrocarbon sources, nor has the trophic status of these lakes been impacted by human activities. The Great Lakes cores show evidence of petroleum contamination, increases in terrestrial sourced components and increases in organic matter from aquatic sources since the mid 20th century as a result of human activities in the lower Great Lakes basin.

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