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Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes

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Abstract

The organic matter content of lake sediments contains information that helps to reconstruct past environmental conditions, evaluate histories of climate change, and assess impacts of humans on local ecosystems. The elemental, isotopic, and molecular compositions of organic matter buried in sediment provide evidence of the biota that have lived in a lake and its catchment area, and they serve as proxies of organic matter delivery and accumulation. Sedimentary records from the North American Great Lakes provide examples of applications of organic geochemistry to paleolimnological reconstructions. The records of these lakes date from retreat of the Laurentide ice sheet around 12 ka, include the mid-Holocene Hypsithermal, and show consequences of recent human changes. Low C_{org}/N_{total} ratios indicate that most of the sediment organic matter in the Great Lakes is from algal production, yet changes in biomarker molecule compositions also show that varying amounts of land-plant organic matter have been delivered to the lakes. Elevated algal productivity that accompanies nutrient enrichments of lake waters is recorded as excursions to less negative $\delta^{13}C$ values in the organic matter of sediments that were deposited in the 1960s and 1970s. Increased organic carbon mass accumulation rates mirror the isotopic excursions in most parts of the Great Lakes. Accumulations of petroleum residues and pyrogenic polycyclic aromatic hydrocarbons in sediments identify fluvial and eolian delivery of organic matter components to different parts of the Great Lakes. Emerging applications of multiple and novel organic geochemical proxies to paleolimnological reconstructions are promising, yet some potentially important measurements remain underutilized.

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1. Introduction

Subaqueous sediments hold information from which histories of past climates and former environmental conditions can be reconstructed. Marine sediments contain unparalleled chronicles of global changes that have unfolded over millions of years, yet lake sediments provide valuable and often unique paleoenvironmental and paleoecological records. Lakes generally have higher sedimentation rates and greater rates of primary production than the oceans, so short-term processes that affect organic matter delivery and burial are amplified in

their sediment records. In addition, lake sediments contain evidence of paleoclimatic and paleoenvironmental changes on continents that record local and regional responses to the global histories provided by deep-sea sediments.

The organic matter content of lake sediments can be small or large, but its paleolimnological importance is always great. Its composition includes a variety of elemental, isotopic, and molecular indicators, or proxies, that can be used to reconstruct paleoenvironments of lakes and their surrounding land areas. The organic matter originates from the complex mixture of lipids, carbohydrates, proteins, and other biochemical components produced by the various organisms that have lived in and around the lake. As an accumulation of “geochemical fossils”, the organic matter components in lake sediments provide information that can be used to

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reconstruct natural and human-induced changes in local and regional environmental systems.

Examples of paleoenvironmental reconstructions that are based on the organic matter compositions of sediment records from lakes in different parts of the world are summarized by Meyers and Ishiwatari (1993ab), Meyers (1997), Dean (1999), Meyers and Lallier-Verges (1999) and Meyers and Teranes (2001). This overview will first describe the principles behind common organic geochemical parameters employed in paleolimnological reconstructions, then illustrate some of their applications in the Laurentian Great Lakes of North America, which is a large freshwater system that integrates a variety of regional environments and encompasses a range of sedimentary settings, and finally discuss emerging trends and some of the future perspectives of organic geochemical applications to paleolimnology.

2. Paleolimnological proxies

Paleolimnological proxies provide information from which paleoenvironmental changes can be inferred. Many such proxies are contained in the amount and composition of organic matter in lacustrine sediments. Organic matter in most sediments is a mixture of components from many sources and with variable degrees of preservation. During sinking and incorporation into bottom sediments, over 90% of the initial material initially contributed from the source organisms is typically remineralized (Eadie et al., 1984). Some organic matter components are more susceptible to remineralization than others, and some components undergo partial alteration. The consequence is that the composition of sedimented organic matter is modified from its starting composition shortly after its formation. Once in the lake bottom, remineralization and alterations continue, but generally at slower rates. Despite these very early diagenetic changes, sedimentary organic matter retains important paleoenvironmental information about its origins and about how it was delivered and deposited. Common organic geochemical proxies used in paleolimnological reconstructions and the kinds of information that they provide are listed in Table 1.

The two most important types of proxy information provided by sedimentary organic matter are the origin of the organic matter and the abundance of the various biota that produced it. The dominant source of organic matter to lake sediments is the various plants that have lived in and near the lake. Plants can be divided into two geochemically significant groups on the basis of their bulk biochemical compositions: (1) non-vascular plants that contain little or no cellulose and lignin and that have relatively large proportions of nitrogen-rich proteinaceous material, such as phytoplankton, and (2) vascular plants that contain large proportions of woody

tissues and that can be relatively rich in waxy hydrocarbons, such as grasses, shrubs, and trees on land and emergent macrophytes in lakes. The CHNO elemental compositions of the organic matter derived from these two broad groupings of plants retain these general source distinctions.

Microbes in the water and sediment of lakes and the soil of the lake watershed are the principal agents of remineralization. They rework and degrade aquatic and land-derived organic matter and diminish their amounts. While doing this, they create new forms of organic matter and thereby add to the mixture of different organic matter components in sediments. In general, components from aquatic sources are more susceptible to microbial reworking than are materials from land plants. Organic matter in lacustrine sediments consequently often includes a large and relatively durable fraction of land-derived organic residues.

Lake systems are diverse, and the sources and alterations of organic matter are geographically and temporally variable. Nonetheless, useful generalizations can be made about the different kinds of elemental, isotopic, and molecular organic geochemical proxies that provide evidence of the origins and depositional histories of sedimentary organic matter and hence paleoenvironmental conditions.

2.1. Concentration of total organic carbon

The concentration of total organic carbon (TOC) is a fundamental proxy for describing the abundance of organic matter in sediments. Typical organic matter contains approximately 50% carbon, so the concentration of organic matter in sediment is equivalent to about twice the TOC value. TOC concentration is a bulk value that represents the fraction of organic matter that escaped remineralization during sedimentation. TOC concentrations are influenced by both initial production of biomass and subsequent degree of degradation, so they integrate the different origins of organic matter, delivery routes, depositional processes, and amount of preservation. It is common for sediment TOC concentrations to vary substantially from place to place within a lake (Table 2) because these multiple factors interact in sometimes complicated ways. However, it is also often possible to separate the effects of these factors. For example, Tenzer et al. (1997) were able to distinguish between in-lake and land sources of organic matter and to describe the impacts of hydraulic sorting on the organic matter contents of surficial sediment during sediment focusing in Pyramid Lake, Nevada. Contributions of land-derived material to sediment organic matter become minor beyond a few hundred meters from shore in this large, mesotrophic lake.

TOC concentrations are expressed in weight/weight ratios and are therefore influenced by other sediment

Table 1

Some of the organic geochemical proxies that have been used in paleolimnological reconstructions and representative examples of studies that illustrate their applications

Measured property	Proxy information	Example
Organic carbon concentration	Amount of organic matter	Generic
Organic carbon mass accumulation rate	Organic matter delivery rate	Hodell and Schelske (1998), Jellison et al. (1996)
C _{organic} /N _{total} ratio	Identification of proportions of algal and land-plant organic matter	Meyers (1994), Kaushal and Binford (1999)
δ ¹³ C _{organic}	Proportions of C ₃ and C ₄ plants, enhanced algal productivity	Talbot and Johannessen (1992), Hodell and Schelske (1998)
δ ¹⁵ N _{total}	Identification of proportions of algal and land-plant organic matter, evidence of nitrogen fixation, enhanced algal productivity	Peterson and Howarth (1987), Hodell and Schelske (1998), Brenner et al. (1999), Teranes and Bernasconi (2000)
<i>n</i> -Alkane composition	Contributions from algae, aquatic macrophytes, and land plants	Bourbonniere and Meyers (1996b), Ficken et al. (2000)
<i>n</i> -Akanoic acid composition	Contributions of land-plant waxes	Rieley et al. (1991)
Branched and unsaturated fatty acid composition	Microbial and algal contributions, extent of microbial reworking	Cranwell (1976), Goossens et al. (1989)
<i>n</i> -Alkanol composition	Contributions from algae, aquatic macrophytes, and land plants	Rieley et al. (1991), Ficken et al. (1998a)
Sterol composition	Proportions of algae and land-plants	Volkman (1986)
Polycyclic aromatic hydrocarbon components	Delivery routes of organic matter	Wakeham et al. (1980a, b), Eadie (1984)
Pigment composition	Algal paleoassemblages	Zullig (1981); Swain (1985)
Compound-specific δ ¹³ C	Origins of individual biomarkers	Rieley et al. (1991), Brincat et al. (2000), Huang et al. (2001)
Lignin derivatives	Amount of land-plant organic matter, former land-plant assemblages	Hedges and Mann (1979), Leopold et al. (1982)
Rock-Eval hydrogen and oxygen indices	Identification of proportions of algal and land-plant organic matter	Talbot and Livingstone (1989), Ariztegui et al. (2000)

components. TOC can be both diluted by addition of clastic sediment particles and concentrated by dissolution of carbonate minerals in sediment (e.g., Dean, 1999). TOC concentrations commonly increase as sediment grain size decreases (e.g., Thompson and Eglinton, 1978). A consequence is that concentrations can become larger in deeper parts of lake basins where fine-grained sediments slowly settle than in shallower parts where coarser sediments rapidly accumulate (Table 2). For these reasons, mass accumulation rates (MARs) of

organic carbon are more useful measures of delivery and preservation of organic matter than TOC percentages. MARs are expressed as mass of TOC per unit of lake bottom area per unit of time, typically mg cm⁻² y⁻¹. Reliable sediment dating is obviously important to calculating meaningful MAR values.

Organic carbon MARs are especially useful to paleolimnology for identification of changes in delivery rates of organic matter to lake sediments (cf., Meyers and Lallier-Vergés, 1999). Often the proportions of lake-

Table 2

Surface-sediment organic carbon concentrations, atomic $C_{\text{org}}/N_{\text{total}}$ ratios, and $\delta^{13}C_{\text{org}}$ values (PDB) that reflect differences in delivery of organic matter with increasing distance from shore in Lake Victoria, East Africa (Talbot and Laerdal, 2000), and with greater water depth in Pyramid Lake, Nevada (summarized from Tenzer et al., 1997)

Sample location	TOC (%)	C/N (atomic)	$\delta^{13}C_{\text{org}}$ (‰)
<i>Lake Victoria</i>			
Swampy margin	35.9	16.4	−20.6
100 m offshore	38.6	17.5	−20.5
200 m offshore	31.2	12.3	−20.5
300 m offshore	27.6	16.1	−20.6
400 m offshore	12.1	11.6	−19.6
<i>Pyramid Lake</i>			
20 m depth	0.6	6.7	−24.9
30 m depth	0.9	9.4	−24.9
40 m depth	1.3	7.4	−24.5
50 m depth	1.6	10.8	−26.4
60 m depth	2.2	9.8	−26.1
70 m depth	2.9	9.3	−27.9
90 m depth	3.5	9.1	−27.5
100 m depth	3.6	8.7	−27.8

derived and land-derived organic matter can be estimated by determinations described later in this overview, allowing calculation of separate MARs for the TOC from these two origins (e.g., Sifeddine et al., 1996). Increases and decreases in primary productivity that result from paleoenvironmental changes can also be inferred from organic carbon MAR records. However, post-burial degradation of organic matter can diminish the apparent accumulation rates of TOC in lake bottoms. In sediments with oxic pore-waters, post-burial diagenesis will continue to decrease the mass of TOC until burial below the oxic–anoxic interface. For example, Hodell and Schelske (1998) compared the concentration of organic carbon in two sediment cores that were collected 6 years apart from the same location in Lake Ontario. They concluded that microbial processing created a 20% decrease in the mass of organic matter that had remained buried in the lake bottom for the 6 years.

2.2. Organic matter C/N ratios

Fresh organic matter from lake algae, which are protein-rich and cellulose-poor, has molar C/N values that are commonly between 4 and 10, whereas vascular land plants, which are protein-poor and cellulose-rich, create organic matter that usually has C/N ratios of 20 and greater (Meyers, 1994). These fundamental differences in organic matter composition generally survive sinking and sedimentation. The proportions of sedimentary organic matter that originate from these two general

sources can consequently be distinguished by their characteristic C/N ratios.

Elevated $C_{\text{org}}/N_{\text{total}}$ values identify large proportions of land-plant organic matter in lake sediments, such as evident in nearshore areas of Lake Victoria (Table 2). Similarly, Kaushal and Binford (1999) document an increase in sediment $C_{\text{org}}/N_{\text{total}}$ ratios from 16 to 25 that corresponds with deforestation around 1780 of the watershed of Lake Pleasant, Massachusetts. This environmental change apparently enhanced delivery of both land-plant organic matter and land-derived sediment to the lake, inasmuch as sedimentation rates increased sufficiently to dilute TOC concentrations.

Sedimentary C/N ratios sometimes give misleading indications of bulk organic matter origin. The most common problem happens because most analysts measure the carbon and nitrogen contents that remain in sediment samples after removal of carbonate carbon and thereby obtain a residual nitrogen value that combines both organic nitrogen and inorganic nitrogen. In most sediments, inorganic nitrogen concentrations are small compared to those of organic nitrogen, and this analytical approach yields GIN ratios that faithfully represent organic matter origins. In sediments having low organic matter concentrations (TOC <0.3%), however, the proportion of inorganic nitrogen can sometimes be a large fraction of the residual nitrogen, and C/N ratios based on residual nitrogen could be artificially depressed. Because most lake sediments contain 1% or more TOC, $C_{\text{org}}/N_{\text{total}}$ values are normally reliable indicators of organic matter sources in paleolimnologic reconstructions.

2.3. Carbon stable isotopic composition

The carbon isotopic composition of organic matter in lake sediments is important to assessing organic matter sources, for reconstructing past productivity rates, and for identifying changes in the availability of nutrients in surface waters. Increases in the accumulation rates of organic matter and its $^{13}C/^{12}C$ ratio have been widely used as an indicator of enhanced aquatic productivity in lakes (e.g., Hollander and McKenzie, 1991; Hollander et al., 1992; Hodell and Schelske, 1998; Brenner et al., 1999). Phytoplankton (C_3 algae) preferentially utilize ^{12}C to produce organic matter that averages 20‰ lighter than the $^{13}C/^{12}C$ ratio of their dissolved inorganic carbon (DIC) source (cf., O'Leary, 1988; Wolfe et al., 2001). Sedimentation of algal organic matter consequently removes ^{12}C from surface-water DIC reservoirs. As availability of DIC becomes depleted, the $^{13}C/^{12}C$ ratio of the remaining inorganic carbon increases and produces a subsequent increase in the $\delta^{13}C$ values of newly produced organic matter. Increased productivity therefore yields an increase in the $\delta^{13}C$ of organic matter that is produced in the lake and becomes buried in its sediment.

Lake-derived organic matter that is produced by phytoplankton using dissolved CO_2 in isotopic equilibrium with the atmosphere is usually isotopically indistinguishable from organic matter produced by C_3 plants in the surrounding watershed. The lack of difference between $\delta^{13}\text{C}$ values of algal and land-plant organic matter is notably different from the distinctive difference between the isotopic compositions of marine algae and continental organic matter (e.g., Meyers, 1994). Algal organic matter in lakes nonetheless usually has a distinctly different carbon isotopic composition than material produced by C_4 plants growing either on land or the lake bottom. However, when the availability of dissolved atmospheric CO_2 ($\delta^{13}\text{C} = -7\text{‰}$) is limited and lake algae begin to use dissolved HCO_3^- ($\delta^{13}\text{C} = 1\text{‰}$) as their source of carbon, their isotopic compositions become heavier than those of land plants. Situations where HCO_3^- becomes important include periods of high productivity during which the availability of dissolved CO_2 becomes diminished (Keeley and Sandquist, 1992; Hollander and McKenzie, 1991; Bernasconi et al., 1997) and in waters where the ratio of HCO_3^- to CO_2 is kept elevated by an alkaline pH (e.g., Hassan et al., 1997). In such cases, $\delta^{13}\text{C}$ values of algal organic matter can increase to reach as high as -9‰ , which is in the range of C_4 plants. In other cases, delivery of large amounts of isotopically light soil DIC ($\delta^{13}\text{C} \cong -12\text{‰}$) to a lake can

lead to in-lake production of isotopically light algal organic matter ($\delta^{13}\text{C} \cong -32\text{‰}$). The possibility of these different excursions in isotopic source signatures is a potent reminder that multiple proxies should be employed in paleolimnologic studies.

The distinctive $\delta^{13}\text{C}$ values of C_3 and C_4 plants can be used together with the characteristic C/N values of algal and land-plant tissues to help identify the major sources of organic matter in lake sediments (e.g., Fig. 1). However, these values are general guidelines and should be thoughtfully evaluated when being applied. Deviations from the generalized $\delta^{13}\text{C}$ and C/N values sometimes occur, and they can represent natural variations in biochemical compositions, diagenetic modifications of initial compositions, or valuable evidence of paleoenvironmental changes.

2.4. Nitrogen stable isotopic composition

Although not as widely used as a paleolimnologic proxy as $\delta^{13}\text{C}$ values, nitrogen isotopic compositions can similarly help to identify sources of organic matter to lakes and to reconstruct past productivity rates (e.g., Herczeg et al., 2001; Talbot, 2002). Application of $\delta^{15}\text{N}$ values to identify organic matter sources is founded on the difference between the $^{15}\text{N}/^{14}\text{N}$ ratios of the inorganic nitrogen reservoirs available to plants in water

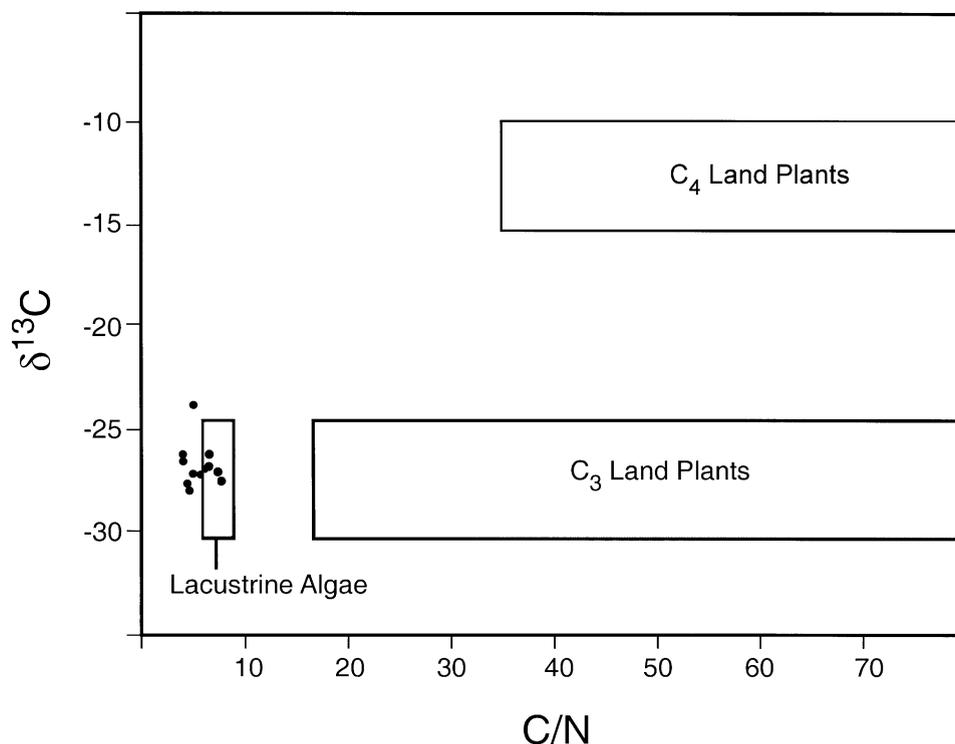


Fig. 1. Generalized $\delta^{13}\text{C}$ and C/N values of major sources of plant organic matter to lake sediments (Meyers, 1994). Data from Core 81-E30 (Silliman et al., 1996) demonstrate the dominance of algal organic matter in the sediments of Lake Ontario.

and those on land. The $\delta^{15}\text{N}$ value of dissolved NO_3^- , which is the most common form of dissolved inorganic nitrogen (DIN) used by algae, is typically 7–10‰ greater than that of the atmosphere-derived N_2 that is made available to land plants by nitrogen fixers in soil (cf., Peters et al., 1978). The isotopic difference between these two sources of nitrogen is roughly preserved in the $\delta^{15}\text{N}$ values of organic matter from algae (+8.5‰) and from C_3 land plants (+0.5‰) (e.g., Peterson and Howarth, 1987).

However, additional factors complicate interpretations of the nitrogen isotopic composition of organic matter in lake sediments. An increase in $\delta^{15}\text{N}$ values might record deliveries of isotopically heavy nitrate ($\delta^{15}\text{N}=10\text{--}25\text{‰}$) from farm runoff and human sewage (Teranes and Bernasconi, 2000), or it might indicate denitrification of DIN in anoxic bottom water. Shifts in phytoplankton or heterotroph assemblages will influence the $\delta^{15}\text{N}$ of sedimented organic matter (Peterson and Fry, 1987). A 6‰ difference in $\delta^{15}\text{N}$ values that exists between organic matter settling in Lake Ontario in the summer and in the winter has been attributed to the dominance of isotopically light phytoplankton detritus during the summer and isotopically heavy organic matter from heterotrophic sources during the winter (Hodell and Schelske, 1998). An abundance of nitrogen-fixing cyanobacteria, which directly fix atmospheric N_2 , leads to lower $\delta^{15}\text{N}$ values in sedimented organic matter (Fogel and Cifuentes, 1993). Shifts to low (–1 to 3‰) $\delta^{15}\text{N}$ values in sediments deposited in Florida lakes since the early 1900s record increases in the contributions of nitrogen-fixing cyanobacteria to organic matter production as eutrophication of these lakes increased (Brenner et al., 1999). Low $\delta^{15}\text{N}$ values ($\sim 3\text{‰}$) in Lake Victoria sediments suggest that nitrogen fixation has been an important process in this lake throughout the Holocene (Talbot and Laerdal, 2000). Although these factors complicate interpretations of $\delta^{15}\text{N}$ values, they should be viewed as opportunities to refine and improve paleolimnologic reconstructions.

2.5. Biomarker molecule proxies

Biological marker (biomarker) molecules are compounds that characterize certain biotic sources and that retain their source information after burial in sediments, even after some alteration. Biomarkers in geologically old sediments and rocks are usually stabilized derivatives of their precursor compounds.

Some of the stabilizing changes include saturation of double bonds, substitution of hydrogen for hydroxyl and carboxylic acid groups, and aromatization of rings. Carbon skeletons generally retain their source-distinctive structures. Most lake sediments are not more than Holocene in age, and some of the biomarker compounds that they contain are little-altered from their

initial forms. However, some lakes, especially those in tectonically active settings, have accumulated sediments for million-year time periods, and organic matter alterations can be advanced in these settings. A number of reviews provide details about the biomarker contents of lake sediments (e.g., Cranwell, 1982; Johns, 1986; Müller, 1987; Sanger, 1988; Meyers and Ishiwatari, 1993a,b). Summaries of applications of selected biomarkers are given here.

2.5.1. Aliphatic hydrocarbon compositions

Because of their low susceptibility to microbial degradation relative to other types of organic matter, aliphatic hydrocarbons are generally robust recorders of the origins of organic matter in lake sediments. The two principal sources of biotic hydrocarbons to lake sediments are: (1) algae, bacteria, and vascular plants that live within a lake and (2) vascular plants that live around it. Because these sources produce distinctively different suites of hydrocarbons, their characteristic molecules serve as proxies for delivery of organic matter. The hydrocarbon compositions of many aquatic algae and photosynthetic bacteria are dominated by the C_{17} *n*-alkane (e.g., Blumer et al., 1971; Giger et al., 1980; Cranwell et al., 1987), and the abundances of this and related compounds reflect lacustrine paleoproductivity rates. Organic matter production in some lakes is dominated by submerged and floating macrophytes, rather than algae, and the *n*-alkane distributions of these non-emergent vascular plants commonly maximize at C_{21} , C_{23} , or C_{25} (Cranwell, 1984; Ficken et al., 2000).

Vascular plants on land or along the edges of lakes contain large proportions of C_{27} , C_{29} , and C_{31} *n*-alkanes in their epicuticular waxy coatings (e.g., Eglinton and Hamilton, 1963, 1967; Cranwell, 1973; Cranwell et al., 1987; Rieley et al., 1991). Abundances of these waxy hydrocarbons reflect the amount of organic matter transported to lakes from the surrounding land. Furthermore, *n*-alkane distributions in sediments provide an approximate record of the kinds of plants that have populated the watershed. In watersheds where grasses dominate, C_{31} is the major sediment *n*-alkane, whereas C_{27} and C_{29} are more abundant in lake sediments where trees dominate (Cranwell, 1973). Emergent macrophytes have *n*-alkane distributions dominated by the long-chain components typical of most land plants (Ficken et al., 2000). Ternary plots of the relative proportions of the C_{27} , C_{29} , and C_{31} *n*-alkanes in sediments can be used to reconstruct past abundances of grasses, shrubs, coniferous trees, and deciduous trees in the vicinity of a lake (e.g., Schwark et al., 2002).

Branched alkanes are also common in lacustrine sedimentary records. The origins of many of these compounds have not yet been identified, but they are known for some. The isoprenoid hydrocarbons, pristane and phytane, are usually found in young lake sediments.

Pristane has two principal sources: (1) digestive tract preprocessing of phytol sidechain of chlorophyll *a* by planktonic herbivores (Blumer et al., 1963) and (2) erosion of sedimentary rocks that contain pristane reated during later diagenesis. Pristane is occasionally not found in the sediments of a lake (e.g., Ho and Meyers, 1994), which indicates that the types of animals that produce this hydrocarbon are absent from the food chain of the lake and that the watershed has not contributed ancient hydrocarbons to the sediments. Methanogenic bacteria, which exist beneath the zone of bioturbation of most lake sediments, are an important source of phytane (Risatti et al., 1984). Phytane therefore records methanogenesis in the lake bottom. Cyanobacteria contribute 7- and 8-methyl heptadecane to lake sediments (Fillee et al., 2001), which indicates organic matter production under low-oxygen conditions in the photic zone.

However, it is important to remember that hydrocarbons normally constitute a very small fraction of the total organic matter in both biota and in sediments. In addition, diagenetic losses of the non-hydrocarbon components of the total organic matter may exaggerate the importance of various sources implied by absolute amounts of biomarker hydrocarbons. This exaggeration is particularly true for land-plants, which tend to produce proportionally more *n*-alkanes than algae. Because of the likelihood that the importance of hydrocarbon proxies might be amplified in lake sediment records, their information needs to be interpreted cautiously.

Despite this caveat, relative amounts of hydrocarbon biomarkers present in sediments have proved to be very useful in reconstructing paleoenvironmental histories of lake systems. As one example, Silliman and Schelske (2003) document a dramatic drop in the ratio of long-chain ($C_{27} + C_{29} + C_{31}$) to short-chain ($C_{15} + C_{19} + C_{23}$) *n*-alkanes that corresponds to a shift from macrophyte to algal dominance of organic matter production in Lake Apopka, Florida. This trophic shift followed agricultural development of the watershed in the mid-1940s and consequent increased nutrient delivery to the lake.

Hydrocarbons from petroleum contamination have augmented biotic hydrocarbons since the late 1800s in sediments of lakes near urban areas (Wakeham, 1977a,b; Meyers, 1987; Bourbonniere and Meyers, 1996a). Petroleum hydrocarbons can be distinguished from biological hydrocarbons by two distinctive characteristics: (1) absence of the characteristic odd-carbon chain-length dominance of biological hydrocarbons, and (2) presence of a vastly greater diversity of molecular structures than found in biological hydrocarbon mixtures (e.g., Meyers and Takeuchi, 1981). This latter characteristic results in a complex mixture of hydrocarbons in sediment extracts that cannot be separated by high resolution capillary gas chromatography, giving rise to the term “unresolved complex mixture” or UCM.

2.5.2. Carboxylic acid compositions

Carboxylic acids in lake sediments typically originate from multiple sources. The *n*-C₁₆ and *n*-C₁₈ alkanolic and alkenolic acids are ubiquitous components of biota, whereas the even-chain C₂₄–C₃₀ *n*-alkanoic acids originate principally from the waxy coatings of land plants. The long-chain *n*-acid components of organic matter in lake sediments therefore represent transport of land-derived debris to the lake bottom. Unsaturated *n*-C₁₆ and *n*-C₁₈ acids are major constituents of the lipids of freshwater algae, yet they are rapidly degraded by microbes during and after sedimentation (Cranwell, 1976). The microbes contribute their own distinctive biomarker acids to the sediments. For example, *normal* and *anteiso* C₁₅ alkanolic acids have been used as indicators of microbial biomass in lake sediments (Cranwell et al., 1987; Goossens et al., 1989), and they represent in situ production of secondary lipids at the expense of primary organic matter.

Carboxylic acids are more sensitive to degradation and modification than most types of lipid biomarkers. Meyers and Eadie (1993) calculate that the remineralization rate of total *n*-alkanoic acids is four times that of bulk organic matter and ten times that of *n*-alkanes in particles sinking in Lake Michigan. Degradation of carboxylic acids continues after their incorporation into lake bottoms; some acids are more susceptible to diagenesis than others. For example, ratios of C_{16:1}, C_{18:1}, C_{18:2}, and C_{18:3} to their corresponding alkanolic acids decrease by a factor of 10 in the upper 8 cm of sediment in Lake Haruna, Japan (Kawamura et al., 1980). The virtual absence of unsaturated acids below this depth, which corresponds to only 120 y of burial history, illustrates the sensitivity of these originally abundant components to microbial reworking. Because of their susceptibility to degradation, carboxylic acids are often more useful as indicators of the amount of organic matter recycling in lake sediments than as recorders of the original sources of organic matter. As such, the acids serve an important function in paleoenvironmental reconstructions by providing a relative measure of the reliability of source information from other biomarker compounds.

2.5.3. Alkanol compositions

Alkanol distributions in sediments have not been nearly as widely applied in paleolimnological reconstructions as either aliphatic hydrocarbons or carboxylic acids, yet they contain equally useful information about organic matter sources and preservation in sedimentary records. Epicuticular waxes of land plants contain *n*-alkanols that have an even number of carbon atoms from C₂₂ to C₃₀ (Eglinton and Hamilton, 1967; Rieley et al., 1991). In contrast, aquatic algae and bacteria generally have *n*-alkanol distributions dominated by C₁₆ to C₂₂ components (Robinson et al., 1984; Volkman et al.,

1999). Moreover, individual species of plants often have distinctive chain-length patterns within these generalized distributions (e.g., Ficken et al., 1998a). The common mono-unsaturated isoprenoid alkenol, phytol, is derived from chlorophyll and can be diagenetically reduced to dihydrophytol over time. Either molecule consequently is a general biomarker for organic matter produced by photoautotrophy, but each can represent a different history of delivery to sediments (Schultz and Quinn, 1974).

Some studies have employed *n*-alkanols as parts of the suites of *n*-alkyl lipids that were used to reconstruct lacustrine sedimentary records. Filley et al. (2001) document changes in the relative proportions of C₂₂ to C₃₀ *n*-alkanols at a major lithologic transition at ~3 ka in sediments of Mud Lake, Florida. A dominance of the *n*-C₂₄ alkanol is interpreted to record emergence of cyanobacteria as major producers of the organic matter in the younger part of this sediment record, which accumulated under essentially modern climatic conditions that became established subsequent to drier conditions in the early Holocene. Ficken et al. (1998b) identify changes in the proportions of algal, land-plant, and aquatic macrophyte inputs of organic matter delivered to sediments of Lake Nkunga in East Africa over the past 40 ky. Distributions of *n*-alkanols are usually dominated by the C₂₆, C₂₈, and C₃₀ biomarkers for land-plants, but some sediment horizons contain large proportions of the C₂₄ component, which may indicate enhanced importance of submerged macrophytes or cyanobacteria at the times corresponding to these horizons. Lake Nkunga has gradually become shallower over time as it has filled with sediment. In addition, local climate was drier during the last glacial period. These factors have impacted delivery of organic matter to the lake sediments.

2.5.4. Sterol compositions

Sterols and their derivatives are important paleoenvironmental biomarker compounds. The presence or absence of double bonds and methyl groups at various positions on the carbon framework, the length of the branched sidechain at the C₁₇ position, and the stereochemistry of the substituent bonds create a variety of compounds (e.g., Volkman, 1986). The structural diversity of sterols and the stanols and steranes derived from them provides information about the origins and diagenetic alterations of organic matter in lake sediments.

The relative amounts of C₂₇ and C₂₉ sterols help to identify the contributions of algal and land-plant organic matter in marine sediments (Huang and Meinschein, 1976, 1979), and this source distinction applies equally to lakes. Cholesterol is the dominant sterol in algae from Lake Suwa (Japan), whereas 24-ethylcholesterol (β -sitosterol) is the major sterol in vascular plants in and around this lake (Nishimura and Koyama, 1977;

Nishimura, 1977). Similarly, Rieley et al. (1991) report that tree-leaf waxes contain C₂₈ and C₂₉ sterols but lack C₂₇ sterols. However, the distinction between algal and higher plant sterol compositions is not perfect. For example, Matsumoto et al. (1982) have reported 24-ethylcholesterol to be the dominant sterol in epibenthic blue-green algae from saline lakes in Antarctica. Absence of land vegetation rules out contributions of organic matter from living vascular plants to these lakes, yet high ratios of C₂₉/C₂₇ sterols in their sediments resemble those of temperate-zone lakes that receive terrigenous organic matter.

Changes in sterol compositions with depth in lake sediments can indicate paleolimnological changes. Sediments throughout a 6-m core from Motte Lake, France, contain gorgostanol, believed to be derived from microbial reduction of gorgosterol (22,23-methylene-23,24-dimethyl-cholest-5-en-3 β -ol), which is probably produced by the dinoflagellate phytoplankton abundant in this lake (Wünsche et al., 1987). The deepest core sections contain aplystanol [24,26-dimethyl-5 α (H)-cholestan-3 β -ol]. Both of the sterol precursors of the saturated stanols are found in marine algae; freshwater algae evidently also synthesize the precursors. The absence of aplystanol in the upper parts of the core suggests a change in algal populations has occurred in Motte Lake. The sources of total organic matter to the sediment presumably also changed, although not necessarily exactly in the same proportions as the sterol sources.

2.5.5. Polycyclic aromatic hydrocarbon compositions

Polycyclic aromatic hydrocarbons (PAHs) do not occur naturally in organisms, yet they are ubiquitous components of lacustrine sediments (e.g., Laflamme and Hites, 1978; Hites et al., 1980). They are the products of organic matter alteration and are created by: (1) microbial modification of biogenic precursors shortly after burial in sediment, (2) low-temperature diagenesis over long periods of geological time, or (3) high-temperature rearrangements of organic matter combustion products into polynuclear aromatic molecules. Nearly all PAH molecules originate principally from one of these three processes, making the compositions of these compounds useful as tracers of organic matter transport and indicators of geochemical transformation processes in lake sediments (e.g., Eadie, 1984).

PAHs derived by alteration of biogenic precursors can reflect the kinds of plants living near a lake and thereby serve as paleoecological proxies. For example, sediments of Lake Washington, near Seattle, contain large concentrations of retene, whereas those of Greifensee, Switzerland, contain negligible amounts (Wakeham et al., 1980a). The postulated precursor of retene is abietic acid, a component of pine resin (Simoneit, 1977; Wakeham et al., 1980a). Similarly, pimanthrene, for which resin-derived pimaric acid is the probable precursor, and a

wide range of triterpenoid hydrocarbons derived from amyrin precursors are abundant in the sediments of Lake Washington but not in those of Greifensee. These differences reflect the fact that conifers are abundant around Lake Washington, but they are not so common around Greifensee. Once created, most PAHs are considered to be relatively robust molecules that can preserve source information in sediments.

2.5.6. Pigment compositions

Higher plants, algae, and microbes synthesize a variety of pigmented organic compounds for use in photosynthesis. Chlorophyll *a* is the most common, but aquatic plants have evolved carotenoid compounds that enable photosynthesis in the absence of the red wavelengths absorbed by chlorophyll *a* (cf. Swain, 1985; Sanger, 1988). All pigment biomarkers contain multiple double bonds, which are molecular features that increase their susceptibility to postdepositional alterations. Consequently, these biomarkers need to be interpreted cautiously, yet they can yield unparalleled information for paleolimnological reconstructions.

Changes in aquatic primary producers can be inferred from the types of carotenoid pigments that are present in sediments. In one example, progressive eutrophication of Esthwaite Water in the English Lake District is recorded by increases in the concentrations of the carotenoids indicative of cyanophytes (Griffiths, 1978). Diminished concentrations of these biomarkers in the uppermost, most eutrophic sediments suggest replacement of cyanophytes by other algae. Similarly, a century-long history of the eutrophication of Zürichsee, Switzerland, is recorded in the pigment contents of its sediments (Züllig, 1981). Algal assemblages changed as nutrient fluxes increased, and the sediment pigments track the algal succession. Finally, Schouten et al. (2001) conclude from changes in carotenoid compositions in sediments of Ace Lake, Antarctica, that green-colored and brown-colored strains of green sulfur bacteria have exchanged dominance at different times in the past, which is evidence of climate-driven changes in the depth of the chemocline in this meromictic lake.

2.5.7. Lignin derivatives

Lignins are phenolic polymers synthesized by higher plants to construct parts of their vascular and structural systems. Nearly all vascular plants grow on land; some exist as emergent vegetation in lakes. The lignin fraction of sediment organic matter therefore largely records the contribution and preservation of land-plant materials. Lignin-containing plant debris is delivered to lakes principally by rivers and streams, although some lakes receive important amounts from shoreline flora. In addition, pollen, which can be carried to lakes by winds, contains lignin (e.g., Hu et al., 1999). Gymnosperms and angiosperms synthesize distinctive types of lignin com-

ponents (Hedges and Mann, 1979). As a consequence, past changes in watershed vegetation can be inferred from the kinds of lignin found in sediment records. Moreover, lignin is relatively resistant to diagenesis, making its sedimentary record longer-lived than many other forms of organic matter.

Molecular analysis of lignin derivatives follows an aggressive oxidation that breaks down the biopolymer into phenolic monomers (Hedges and Parker, 1976; Hedges and Mann, 1979). A measure of the relative contributions of non-woody land-plant tissues is given by a high C/V (cinnamyl/vanillyl) ratio, which is the sum of *p*-coumaric acid plus ferulic acid concentrations divided by the sum of the three vanillyl phenols. However, Hu et al. (1999) demonstrate that lignin from spruce pollen yields much higher C/V ratios than conifer needles and can bias source assignments in sediment rich in conifer pollen. Gymnosperm sources of land-plant residues have historically been distinguished from angiosperm sources by a low S/V (syringyl/vanillyl) ratio, which is the sum of the amounts of the three syringyl phenols divided by the sum of the vanillyl phenols.

In their classic reconstruction of the Holocene history of Lake Washington from lignin contents of sediments, Hedges et al. (1982) identify four stages in the post-glacial succession of watershed plants around this lake. At the base of the 11-m sediment core, low S/V and C/V ratios indicate an approximately equal mixture of plant tissues from woody (conifers) and nonwoody (ferns) gymnosperms. Between 10 m and 8 m in the core, high S/V and C/V ratios suggest a predominance of non-woody angiosperms (grasses), although pollen data suggest that pines dominated the watershed during this interval (Leopold et al., 1982). Pine pollen is exceptionally small and easily carried by wind, so its abundance probably reflects eolian transport from outside the watershed. High S/V and low C/V ratios from 7 to 4 m suggest large contributions of angiosperm wood, a conclusion that is consistent with the abundance of alder pollen. A decrease in the S/V ratio and a constant C/V ratio between 4 m to the core top indicates a gradual replacement of deciduous trees by conifers, which is also consistent with the pollen record (Hedges et al., 1982; Leopold et al., 1982).

2.5.8. Compound-specific carbon isotope ratios

The isotopic compositions of individual compounds isolated from the mix of molecules that constitute sediment organic matter are useful to paleolimnological studies. In particular, carbon isotope analyses of individual biomarker compounds provide a powerful source of paleoenvironmental information that complements the $\delta^{13}\text{C}$ values of bulk organic matter. Compound-specific carbon-isotope GC-IRMS has become the method of choice to determine the origin of a given organic compound, to explore the effects of diagenesis,

and to reconstruct paleodepositional settings in ways that neither bulk organic matter characterizations nor traditional biomarker analyses can individually provide.

Compound-specific carbon isotope analyses have proven particularly useful to identifying origins of organic matter components in cases where several sources are possible. Rieley et al. (1991) compared the $\delta^{13}\text{C}$ values of individual C_{25} to C_{29} *n*-alkanes extracted from sediments of Ellesmere, England, to those from the leaves of different species of trees overhanging the lake. Their analyses reveal that willow leaves appear to be the major source of the sedimentary *n*-alkanes. Brincat et al. (2000) similarly employed $\delta^{13}\text{C}$ values of waxy *n*-alkanes to test the hypothesis that the C_3 plants that have dominated the post-glacial flora around Lake Baikal, Siberia, succeeded a flora dominated by C_4 tundra plants during the last glacial period (Qiu et al., 1993). This paleoenvironmental interpretation is based on a 3‰ shift to more negative TOC $\delta^{13}\text{C}$ values that occurs in sediments of this lake at the end of the glacial period. In contrast to the bulk carbon values, the leaf-wax $\delta^{13}\text{C}$ values remain between -31.0 and -31.5% throughout the entire sediment record, which indicates that C_3 plants have remained the dominant vegetation around Lake Baikal since 20 ka. The explanation for the $\delta^{13}\text{C}$ shift is instead more likely to be from increased delivery of isotopically light soil-derived DIC to the photic zone of the lake as local climate became wetter. Algal uptake of this carbon produced isotopically light organic matter.

Changes in the delivery of land-plant and aquatic organic matter to the sediments of Sacred Lake, Mt. Kenya, from 40 ka to the present have been identified using lipid biomarker $\delta^{13}\text{C}$ values (Huang et al., 1999). Plant-wax $\delta^{13}\text{C}$ values reveal a succession from late-glacial vegetation dominated by C_4 grasses and sedges (values of -20 to -18%) to post-glacial vegetation dominated by C_3 plants (values of -34 to -27%). Unsaturated hydrocarbon biomarkers that are specific to algae undergo a dramatic excursion from values of -5.1% at the glacial maximum to values of -30.3% in the early Holocene. The isotopic shift reveals that the low $p\text{CO}_2$ of the last glacial maximum simultaneously favored C_4 grasses in the lake catchment and restricted isotopic discrimination by algae in the lake waters.

Filley et al. (2001) utilize the $\delta^{13}\text{C}$ values of a suite of biomarker compounds to reconstruct changes in delivery of organic matter to the sediments of Mud Lake, Florida, over the past five millennia as climate became wetter and the local water table rose. They conclude from their compound-specific isotope analyses that biomarkers indicative of vascular plants (lignin monomers, C_{29} and C_{31} *n*-alkanes, C_{26} *n*-alkanol), cyanobacteria (7- and 8-methyheptadecanes), and phytoplankton (C_{17} *n*-alkane) are robust representatives of organic matter sources. Moreover, the biomarker $\delta^{13}\text{C}$ values refine the history of paleolimnological changes that the $\delta^{13}\text{C}$ and

$\text{C}_{\text{org}}/\text{N}_{\text{total}}$ values of bulk sediment organic matter only roughly record.

2.6. Rock-Eval hydrogen index

The majority of organic matter in sediments consists of macromolecules that cannot be characterized by usual chemical analyses. Pyrolysis uses heat to break the large molecules into smaller molecules that can then be chemically identified. One type of pyrolysis that has been shown to be of real value to paleolimnology is Rock-Eval pyrolysis, which was initially developed to evaluate the hydrocarbon potential of petroleum source rocks (Espitalié et al., 1985; Peters, 1986). This procedure approximates elemental analysis of the organic matter in sediment. A Rock-Eval parameter that has proved particularly useful to paleolimnological studies is the Hydrogen Index (HI), which represents the amount of hydrocarbons generated from the total organic matter and is expressed in $\text{mg HC g}^{-1} \text{C}_{\text{org}}$. HI values are surrogates for the elemental H/C ratios of organic matter (Espitalié et al., 1985).

TOC concentrations and HI values often vary through lacustrine sedimentary sequences and indicate changes in organic deposition under different paleoenvironmental and paleoecological conditions (e.g., Talbot and Livingstone, 1989; Hollander et al., 1992; Ariztegui et al., 1996; Wilkes et al., 1999; Talbot and Laerdal, 2000). A correspondence between elevated TOC and HI values is often found in some sediment intervals and implies periods of greater algal paleoproductivity. Of particular interest to paleolimnological studies, variations in the HI values of sedimentary organic matter appear to reflect changes in algal communities. Ariztegui et al. (2001) note a correspondence between elevated HI values and periods during the history of Lago di Albano, Italy, that were dominated by cyanobacteria production. In contrast, sediments having lower HI values were deposited during times when diatom production was dominant.

3. The Great Lakes and Holocene environmental changes

Lakes Superior, Huron, Michigan, Saint Clair, Erie, and Ontario comprise the Laurentian Great Lakes (Fig. 2). Their collective volume ($24,620 \text{ km}^3$) exceeds that of Lake Baikal ($23,000 \text{ km}^3$)—the world's single largest lake—and represents over 20% of the fresh water on the planet. The total surface area of the lake system is impressively large ($245,240 \text{ km}^2$), yet the land areas that drain into the lakes are only two or three times those of their surface areas (Table 3). As a consequence, many parts of the lakes are not directly influenced by land runoff, and sediments in these areas provide histories of



Fig. 2. The Laurentian Great Lakes of North America, their drainage basins, and important study sites discussed in this overview. Overall flow of water is from Lake Superior and Lake Michigan through Lakes Huron, Erie, and Ontario and to the North Atlantic Ocean via the St. Lawrence River.

Table 3
Physical and hydraulic features of the Laurentian Great Lakes

	Surface area (km ²)	Drainage basin (km ²)	Mean depth (m)	Greatest depth (m)	Residence time (y)
Lake Superior	82,100	127,700	147	405	185
Lake Huron	59,600	134,000	59	229	30
Lake Michigan	57,800	118,000	85	281	70
Lake St. Clair	1080	^a	4	6	<1
Lake Erie	25,700	78,000	19	64	2.7
Lake Ontario	18,960	64,030	86	244	8

^a Included in Lake Erie drainage basin.

predominantly lacustrine processes. Except in Erie and Saint Clair, water depths of 100 m to more than 200 m are common. The minor water turbulence at these depths and the absence of large bottom-dwelling animals combine to minimize sediment disturbance in the lake floors. However, annual turnover keeps the lake waters well-oxygenated and bottom sediments are therefore bioturbated. Age resolutions in sediment cores are ~2 years in high-deposition areas such as the Eastern Basin of Lake Erie and some nearshore locations and less than

a decade in most parts of the Great Lakes (Robbins and Edgington, 1975).

Sedimentary records in the Great Lakes date from retreat of the Laurentide ice sheet from the lake basins about 12,000 years ago (Larson and Schaetzl, 2001). Although continuous at most locations, records are sometimes punctuated by hiatuses that reflect slumping, underwater erosion, and changes in lake level resulting from postglacial isostatic rebound and downcutting of drainage channels (cf. Rea et al., 1980, 1981; Larson and

Schaetzl, 2001). Lake levels became stabilized at essentially modern depths about 4000 years ago, yet the differences between volumes of the individual lakes create a range of hydraulic residence times (Table 3). Sediment cores from sites located fairly close to each other often contain very different spans of paleolimnologic history and therefore allow interesting comparisons of their organic geochemical contents.

Following retreat of the glaciers, land ecosystems in the Great Lakes region began a progression from tundra to boreal forests to mixed temperate forests dominated by deciduous trees in the south and coniferous ones in the north. After the first permanent European colonies were established around 1700, the pace of environmental change increased, and it especially accelerated after completion of the Erie Canal in 1825. Forests were clear-cut and replaced by farmland, towns and cities grew, heavy industry became established, and some parts of the lakes evolved from being oligotrophic to becoming eutrophic as nutrient loadings increased. Evidence of many of these changes is recorded in the amount and composition of the organic matter in lake sediments that were deposited at the various stages of the paleoenvironmental history of the region.

4. Organic geochemical evidence of postglacial environmental changes in the Great Lakes region

The range of sedimentation rates that exist in the Great Lakes can provide interesting and sometimes unique opportunities to compare how delivery of organic matter has changed over their postglacial history. Both expanded and condensed sediment records can be obtained. Moreover, sediment cores can be collected that contain very different periods of the Great Lakes depositional record but monitor essentially the same location.

4.1. Comparison of early postglacial and recent organic matter contributions to Lake Huron

Comparison of sediment cores from two closely spaced locations in southern Lake Huron show dramatically different histories of organic matter accumulation in early postglacial and recent times. Core 75-58 consists of a 1–2 cm veneer of modern sediment on top of glaciolacustrine clay deposited ~12 ka, whereas Core 75-12, which is less than 7 km away, contains a ²¹⁰Pb-dated continuous accumulation of the most recent 400 y of sediment (Meyers et al., 1980). Glaciolacustrine clay is common to glaciated regions like the Great Lakes. It consists of rock flour and other fine-grained sediment components that settled from meltwater in periglacial lakes as glaciers receded.

In general, fine-sized sediments contain higher concentrations of organic carbon and biomarker compounds than coarser sediments (cf. Thompson and Eglinton, 1978; Meyers and Takeuchi, 1979; Tenzer et al., 1997). However, the fine-grained glaciolacustrine clays of Core 75-58 have lower concentrations of organic carbon, fatty acids, and hydrocarbons than the silty clays of Core 75-12 (Meyers et al., 1980). TOC concentrations average only 1% in Core 75-58 but are between 2.5 and 3.3% in Core 75-12 (Fig. 3). Because glacial meltwaters deliver large amounts of rock flour to periglacial lakes, the turbidity of lake water and sediment accumulation rates are increased. Shallow light penetration probably limited algal production of organic matter to a thin photic zone, and the organic matter delivered to lake sediments was probably diluted by the high accumulation rates of the glaciolacustrine clays. Also, pollen assemblages indicate that tundra-type grasses and shrubs dominated postglacial vegetation in the catchment (Jacobson et al., 1987). Delivery of land-derived organic matter to Lake Huron was therefore probably minor.

Comparison of the *n*-alkane compositions of the two sediment records confirms that the glaciolacustrine clays contain less land-derived lipid material than modern sediments. Meyers et al. (1980) employed the ratio of the C₂₉ to C₁₇ *n*-alkanes as a proxy for land-derived versus algal contributions of hydrocarbons. This ratio remains around 1–2 throughout Core 75-58, whereas it fluctuates between 2 and 12 in Core 75-12 except for a short-lived excursion to 25 at the 8-cm depth horizon (Fig. 3). The higher values of this ratio indicate delivery of greater proportions of land-plant debris to recent sediments of Lake Huron than immediately after retreat of the Laurentide Glacier.

4.2. Impacts of Holocene climate change on organic matter deliveries to Lake Ontario

Postglacial North American climate has varied substantially (Jacobson et al., 1987; Kutzbach, 1987; Webb et al., 1987), and evidence of the variations exists in sediments of the Great Lakes region. A brief interlude of post-Younger-Dryas cold climate (the Preboreal Oscillation, 9.6 ¹⁴C ka) is preserved as variations in CaCO₃ concentrations in sediments of Seneca Lake (Anderson et al., 1997), which drains into Lake Ontario (Fig. 2). The mid-Holocene Hypsithermal (~9–5 ¹⁴C ka) is recorded as a period of warm and dry climate in much of the American Midwest (Krishnamurthy et al., 1995; Dean et al., 1996; Hassan et al., 1997) but as a time of warm and wet climate in the eastern Great Lakes area (Dwyer et al., 1996; Silliman et al., 1996).

A particularly useful proxy for the prehistoric paleotemperature history in the Great Lakes region is the concentration of calcite in sediments laid down at different

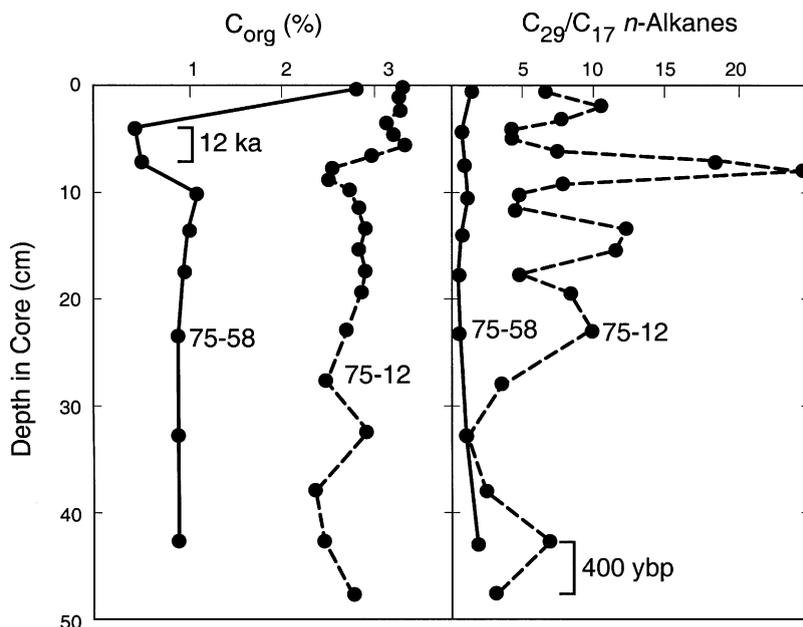


Fig. 3. Comparison of concentrations of organic carbon and ratios of land-plant and algal *n*-alkanes in southern Lake Huron sediments from Core 75-12 (water depth 91 m), which records the most recent 400 years, and Core 75-58 (water depth 73 m), in which a sandy layer containing 0.4% TOC separates a veneer of modern sediment from periglacial sediment. From Meyers et al. (1980).

times. Because the bedrocks and soils of the region are rich in limestone, the waters of the lakes are “hard”—they are near saturation with respect to calcium carbonate. Precipitation of CaCO_3 is easily induced by both warming of surface waters and removal of dissolved CO_2 from lake waters by algae. In the modern lakes, for example, episodes of calcite precipitation (“whitings”) are common during summer stratification. Moreover, sediment cores from different parts of the Great Lakes region show systematic elevations in CaCO_3 concentrations that record times of warmer climate. Concentrations are highest deposited during the Holocene Hypsithermal in sediments of Lake Ontario (Silliman et al., 1996), Seneca Lake (Anderson et al., 1997), and Cayuga Lake (Mullins, 1998). This pattern has been interpreted to be a result of warmer summers, which produced earlier seasonal stratification and lengthened the time available for algal removal of $\text{CO}_2(\text{aq})$ from the surface waters (Mullins, 1998).

Silliman et al. (1996) employed elevated CaCO_3 concentrations to identify the Holocene Hypsithermal in the postglacial record of organic matter delivery to eastern Lake Ontario that they spliced together with a 1.5-m gravity core and a 12-m piston core from Station E30 in the Rochester Basin in 1981. Piston cores often fail to capture the softer, upper part of sediment columns; about 110 cm was lost at this location. Absolute age dating of this long sediment record was challenging. The upper part of the record was dated using excess ^{210}Pb (Bourbonniere and Meyers, 1996b), but radiocarbon

ages of bulk organic matter isolated from the sediments were unreasonably old because of relatively large proportions of geologically old detrital material. However, radiocarbon dating of the ostracods present in some sediment horizons provided ages that agree with the elevated concentrations of CaCO_3 (Fig. 4). In addition, Silliman et al. (1996) noted that mean sediment grain-size is simultaneously elevated with calcite concentrations, which indicates that climate in the Lake Ontario area was wetter as well as warmer during the Hypsithermal.

Several stages in the evolution of the postglacial Lake Ontario environment are evident in the sediment record (Fig. 4). Low concentrations of CaCO_3 and TOC in the basal 2 m of the core correspond to glaciolacustrine clay. Low C/N values indicate that algal production was essentially the sole source of organic matter to Lake Ontario for the first several thousand years of its postglacial history. TOC concentrations remain below 1% until the beginning of the Hypsithermal about 9 ka. If TOC concentrations are taken as a proxy for algal productivity, then productivity gradually grew from initially low levels until the recent past, when it greatly increased. Silliman et al. (1996) measured the bulk carbon isotopic composition of a small number of sediment samples from the piston core; the $\delta^{13}\text{C}$ values vary narrowly between -25.5 and -28.0 ‰, which is characteristic of both lacustrine algae and C_3 land plants. A plot of these $\delta^{13}\text{C}$ values against the $\text{C}_{\text{org}}/\text{N}_{\text{total}}$ ratios of the same samples implies that the organic matter is predominantly algal in origin (Fig. 1).

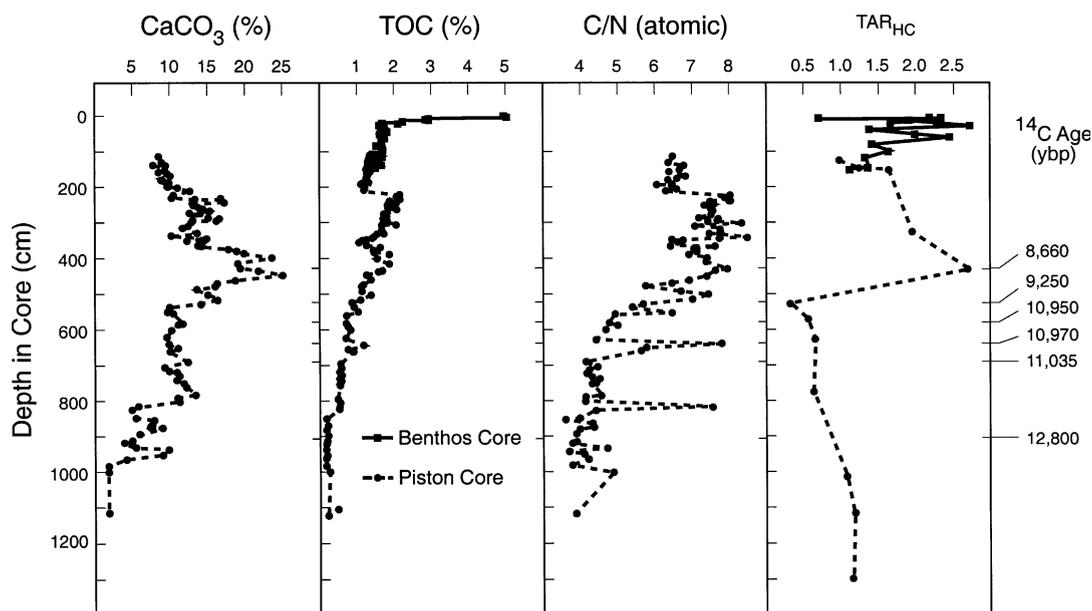


Fig. 4. Concentrations of calcium carbonate and organic carbon, $C_{\text{org}}/N_{\text{total}}$ atomic ratios, and n -alkane terrigenous/aquatic ratios (TAR) in sediments of Gore 81-E30 (water depth 233 m) from the Rochester Basin of Lake Ontario. Data from Silliman et al. (1996).

Some increase in delivery of land-derived organic matter to Lake Ontario appears to have accompanied the wetter climate of the Hypsithermal. The C/N values peak ~ 8 at the same time that CaCO_3 concentrations reach their highest levels (Fig. 4). Part of this increase in C/N values probably reflects greater wash-in of land-plant organic matter, although algal production remained dominant. TOC concentrations also increased during this paleoenvironmental stage, which supports the possibility of greater delivery of land-derived organic matter.

Silliman et al. (1996) applied several ratios of terrigenous/aquatic biomarkers as proxies to infer Holocene changes in delivery of land-plant waxes to Lake Ontario. Their terrigenous/aquatic ratio of hydrocarbons (HC) is defined as:

$$\text{Terrigenous/Aquatic Ratio (TAR}_{\text{HC}}) = \frac{(C_{27} + C_{29} + C_{31})}{(C_{15} + C_{17} + C_{19})}$$

The principle for this proxy is that C_{27} , C_{29} , and C_{31} n -alkanes are characteristic of land plant waxes, whereas C_{15} , C_{17} , and C_{19} n -alkanes represent algal input (Eglinton and Hamilton, 1963; Cranwell et al., 1987). TAR_{HC} values are low until the onset of the Hypsithermal, when they increase significantly (Fig. 4). This change probably records both more wash-in of land-derived materials, as evident also in the increase in sediment grain-size, and the establishment of well-developed forests to provide the land-plant debris that was transported into the lake. The ratio drops at the end of the Hypsithermal and then rises in younger sediments as European settlement of the Great Lake region disturbed catchment areas.

5. Organic geochemical evidence of human environmental changes in the Great Lakes region

Human activities began to have a noticeable impact on delivery of organic matter to the Great Lakes starting in the early 19th century in Lake Ontario and spreading westward (Schelske et al., 1983). Forests were clear-cut to open land for agriculture as European settlement expanded into the region. Expansion of cities in the second half of the century created a demand for lumber, which was met by harvesting of remaining forests. The last virgin forests—in northern Michigan, northern Wisconsin, and southwest Ontario—were cut down in the early 20th century. The change from forests to farm fields destabilized soils and produced a burst in delivery of land-plant litter and soil-derived nutrients to the lakes. Subsequent to this first, major environmental change, growth of industrial centers, which started in the early 20th century and exploded in mid-century, created an increasingly greater flow of poorly treated, nutrient-rich wastewater into the Great Lakes.

5.1. Changes in origins of organic matter delivered to lake sediments

Several lines of organic geochemical evidence show changes in the amounts and types of organic matter delivered to the Great Lakes as a result of the human environmental impacts. An increase in TOC concentrations between 10 and 6 cm in Core 75-12 from the southeastern part of Lake Huron coincides

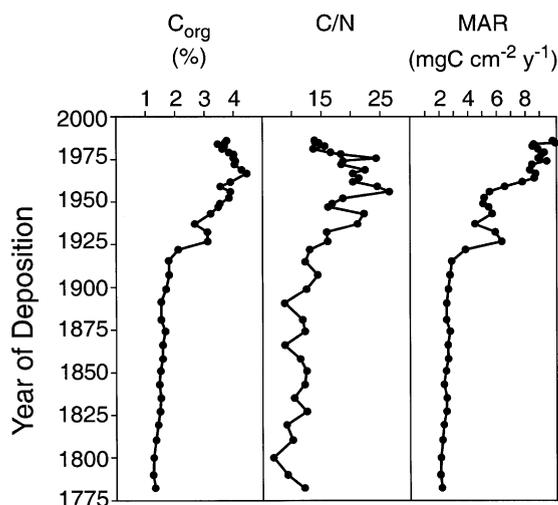


Fig. 5. Concentrations and mass accumulation rates of organic carbon and C_{org}/N_{total} atomic ratios in sediment from Lake George (water depth 13 m) on the Michigan–Ontario border (Fig. 2). Changes in these parameters reflect increased delivery of land-plant organic matter and increased algal productivity since 1925. Data from Tenzer et al. (1999).

with a peak in C_{29}/C_{17} *n*-alkane ratios (Fig. 3). This sediment horizon corresponds to ~ 1900 , the time that agricultural land-clearing peaked nearby in the Province of Ontario. The simultaneous increase in TOC concentrations and in the proportion of land-plant/algal hydrocarbons indicates that runoff of soil nutrients increased algal productivity at the same time that delivery of land-plant waxes was temporarily magnified as litter from deforestation washed into this part of Lake Huron. Unlike the C_{29}/C_{17} ratio, TOC concentrations remain enhanced, which shows that increased nutrient delivery from agricultural runoff continued to enhance algal productivity from 1900 through 1975 when this sediment core was collected (Meyers et al., 1980).

Small lakes are often more sensitive to environmental impacts than lakes as large as Lake Huron. The sediments of Lake George, which is situated in the St. Marys River that flows from Lake Superior into Lake Huron (Fig. 2), record both local changes in the immediate watershed and a succession of changes associated with growth of industries upstream in the twin cities of Sault Ste. Marie, Ontario, and Sault Ste. Marie, Michigan.

TOC concentrations in a sediment core collected from Lake George in 1986 change with depth and record changes in organic matter delivery and preservation (Fig. 5). C/N ratios are elevated above values of 20 in sediments deposited between 1975 and 1937, which roughly corresponds to the interval in which organic carbon concentrations also are elevated. Typical Great Lakes phytoplankton have a C/N ratio of 7, whereas

leaves and needles from trees representative of the Lake George watershed have C/N ratios between 17 and 42 (Tenzer et al., 1999). These sediments evidently include large proportions of land-plant-derived material in their organic matter contents. In older sediments, C/N ratios fluctuate between values of 5 and 15 and indicate smaller and variable proportions of land-derived organic matter. The major source of organic matter in these older sediments is probably principally from algae. Based on the C/N ratio profile, contributions of land-plant-derived organic matter did not increase coincident with the beginning of lumbering in the 1870s, but they became important with the growth of municipalities and consequent land-use changes that accompanied industrial development along the St. Marys River after 1900.

Organic carbon mass accumulation rates (C_{org} MARs) are better measures of changes in organic matter accumulation in sediments than TOC concentrations because they compensate for changes in bulk sedimentation rates and for sediment compaction. The C_{org} MARs are 8–10 $mgC\ cm^{-2}\ y^{-1}$ in sediments deposited from 1986 to 1964, decrease to less than 3 $mgC\ cm^{-2}\ y^{-1}$ at the 1900 horizon, and are below 2.5 $mgC\ cm^{-2}\ y^{-1}$ in sediments deposited prior to 1850 (Fig. 5). The C_{org} MAR values of the pre-1900 sediments are similar to those of other moderately productive lakes, and the post-1964 values are markedly higher than most modern lakes (Meyers and Lallier-Vergès, 1998a). Environmental changes during the twentieth century have clearly enhanced burial of organic matter in the sediments of Lake George.

Because hydrocarbons degrade about one-fourth as fast as total organic matter during sedimentation (Meyers and Eadie, 1993), changes in their compositions can be used as relative indicators of changes in organic matter origins. Bourbonniere and Meyers (1996b) report that hydrocarbon concentrations at two locations in Lake Ontario fluctuate in sediments deposited since ~ 1910 but are fairly constant in older sediments. In contrast, TOC concentrations smoothly increase starting around 1900. The difference probably indicates a change in hydrocarbon content of the organic material supplied at different times to the sediments. Greater TAR_{HC} ratios correspond to higher hydrocarbon concentrations, which suggests that intervals of larger inputs of plant-wax components delivered from watershed regions started early in the 20th century.

5.2. Changes in rates of algal production of organic matter

Conversion of formerly forested areas to farm fields increased erosion of soil, release of soil nutrients, and production of algal organic matter in the Great Lakes starting in the early 19th century (Schelske et al., 1983). The increase in primary productivity was gradual until

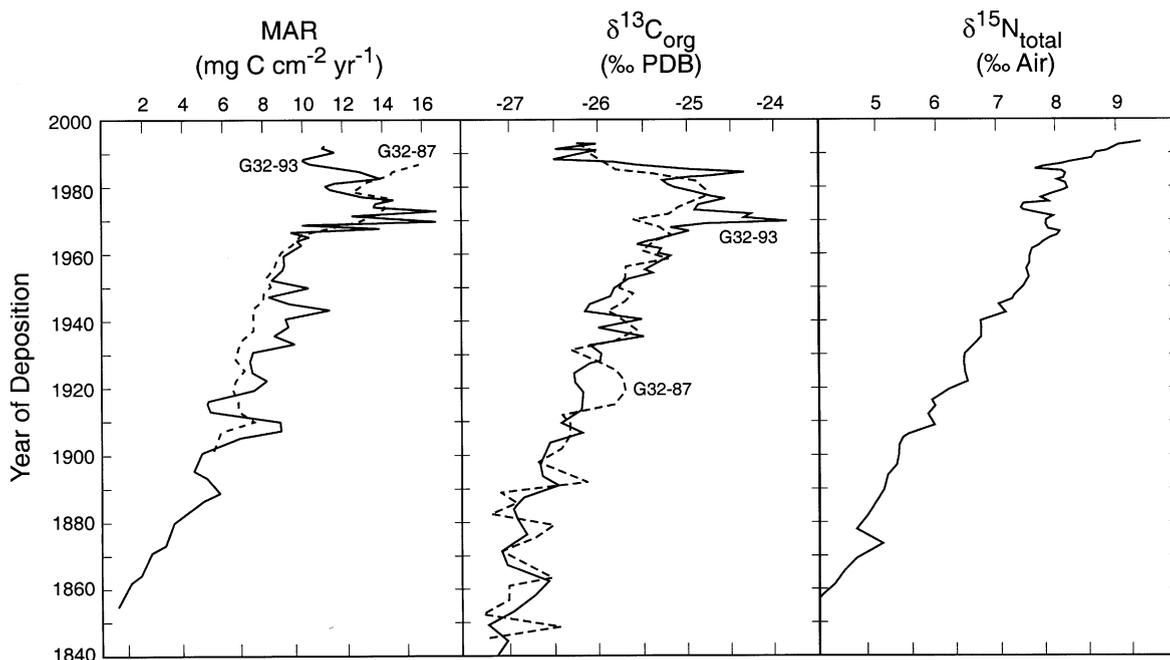


Fig. 6. Comparison of mass accumulation rates of organic carbon and $\delta^{13}\text{C}$ values in sediment cores collected in 1987 and 1993 and $\delta^{15}\text{N}$ values in the 1993 core from Site G32 (water depth 158 m) in the Rochester Basin of Lake Ontario. The three parameters track changes in algal productivity in this lake. Despite the in situ loss of 20% of the sediment organic carbon during the 6-year difference between collection of Core G32-93 and Core G32-87, $\delta^{13}\text{C}$ values are unaffected. Data from Hodell and Schelske (1998).

1950, when accelerated population growth magnified nutrient delivery to the lakes and greatly bolstered algal production of organic matter. As an example, organic carbon concentrations in the sediments of Lake Ontario tripled over their pre-agricultural levels by 1975, and most of this increased occurred after 1950 (Bourbonniere and Meyers, 1996b).

A widespread indicator of enhanced delivery of nutrients to the Great Lakes has been an excursion to larger $\delta^{13}\text{C}$ values of organic matter in sediments as increased algal removal of ^{12}C left the remaining dissolved inorganic carbon isotopically heavier (e.g., Schelske and Hodell 1991, 1995; Hodell and Schelske, 1998; Ostrom et al., 1998; Silliman et al., 2001). The $\delta^{13}\text{C}$ record of sediments deposited over the past century in Lake Ontario illustrates the effects of enhanced algal productivity (Fig. 6). Algal growth began to be stimulated in this lake by watershed deforestation, which occurred between 1820 and 1850 (Schelske et al., 1983) and resulted in increased delivery of soil-derived phosphorus to the lake. Schelske et al. (1988) note that organic carbon concentrations in Lake Ontario cores follow the increases in phytoplankton abundance expected from the phosphorus enrichments. Organic carbon mass accumulation rates increase gradually in response to the higher productivity until about 1975, when they start to drop (Fig. 6). The $\delta^{13}\text{C}$ values of buried organic carbon reflect the productivity increase

by becoming over 2‰ less negative, maximizing at -24.5% in sediments deposited in 1975–1980 (Fig. 6). The subsequent shift to more negative values in more recent sediments mirrors a mandated decrease in dissolved phosphate delivery to the Great Lakes. These changes in organic carbon mass accumulation rates and carbon isotope values are evidence that improved wastewater treatment can successfully reverse eutrophication.

Changes in sediment nitrogen isotope compositions of organic matter in Lake Ontario sediments have accompanied the increase in algal productivity of the past century (Fig. 6). Hodell and Schelske (1998) postulate that the increase in organic matter $\delta^{15}\text{N}$ values since the middle of the 19th century indicates increased denitrification in Lake Erie, upstream of Lake Ontario, as a result of progressively longer periods of seasonal bottom-water anoxia as productivity increased. Other possibilities are that the shift could record deliveries of isotopically heavy nitrate ($\delta^{15}\text{N} = 10\text{--}25\%$) from farm runoff and human sewage (e.g., Teranes and Bernasconi, 2000) or changes in the aquatic food-chain of Lake Ontario (e.g., Peterson and Fry, 1987). Because this effect had not reversed as of the time of sampling in 1993 even though organic carbon burial in the lake bottom had decreased to levels comparable to several decades earlier (Fig. 6), increased algal productivity is unlikely to be the cause. This still-unexplained observation is a potent reminder that, in large lakes like

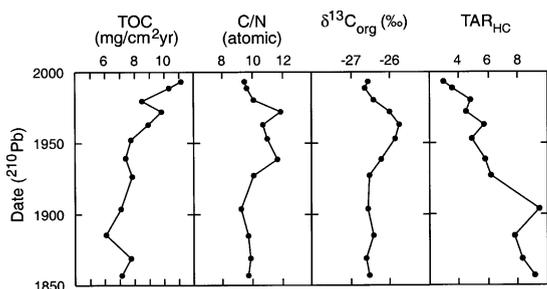


Fig. 7. Mass accumulation rates of total organic carbon (TOC) in sediment from Green Bay core GB32 (water depth 35 m). Organic C/total N and organic carbon $\delta^{13}\text{C}$ values reveal that the type of organic matter that was delivered to Green Bay sediments changed between 1927 and 1980. The progressive decrease in terrigenous/aquatic ratios of *n*-alkanes (sum of C_{27} , C_{29} , C_{31} divided by sum of C_{15} , C_{17} , C_{19}) indicates that the proportion of algal hydrocarbons has increased since the early 20th century. From Silliman et al. (2001).

Ontario, integration of multiple ecological factors in sediment records can make interpretation of a single organic geochemical proxy problematic.

Identification of human impacts on algal organic matter production is generally less complicated in smaller parts of the Great Lakes system where local factors dominate. Silliman et al. (2001) document changes in the amount and type of organic matter delivered to Green Bay, which is the largest bay in Lake Michigan (Fig. 2). The bay has been heavily impacted by agricultural, industrial, and municipal runoff from the surrounding land. Mass accumulation rates of organic carbon increase from $\sim 7\text{--}8\text{ mg/cm}^2/\text{y}$ before 1950 to reach $11\text{ mg/cm}^2/\text{y}$ in sediment deposited in 1994 (Fig. 7). Against this backdrop of relatively smoothly increasing delivery of organic matter, C/N ratios temporarily rise from values of 9–10 to reach 11–12 in sediment deposited between 1940 and 1975. These values indicate that the proportion of land-plant-derived organic matter temporarily increased to $\sim 20\%$ between 1927 and 1980, whereas it was $\sim 10\%$ in pre-1927. At the same time as the excursion in C/N values, organic $\delta^{13}\text{C}$ values increase from a background of -26.6‰ to reach -25.8‰ in sediment deposited ~ 1963 before returning to values around -26.6‰ in shallower sediment (Fig. 7). The isotopic excursion mimics similar patterns found in sediment from Lakes Erie and Ontario (Schelske and Hodell, 1991, 1995; Hodell and Schelske, 1998; Ostrom et al., 1998) that record maxima of cultural eutrophication between 1965 and 1975. The simultaneous excursions in C/N and $\delta^{13}\text{C}$ values suggest that delivery of both land-derived and aquatic organic matter temporarily increased for several decades and has subsequently returned to earlier levels after controls on nutrient delivery were enacted. However, organic carbon MARs do not reflect the decline in delivery

implied by the elemental and isotopic proxies (Fig. 7). One possible explanation is that microbial activity temporarily increased and destroyed evidence of the peak in delivery (Silliman et al., 2001). A more reasonable possibility is that microbial activity has not yet had enough time to diminish the amount of organic matter in the uppermost sediment, in a fashion like that documented by Hodell and Schelske (1998) in Lake Ontario (Fig. 6), to create an MAR profile that resembles those of the two other proxies.

Biomarker compositions indicate that microbial activity modifies the character as well as the amount of organic matter in the sediments of Green Bay. The regular decrease in TAR_{HC} values in younger sediments (Fig. 7) suggests that the relative amount of aquatic organic matter has increased fairly steadily from the mid-1800s to the present. However, this interpretation contradicts the C/N values, which suggest that 80–90% of the organic matter is from algal production. Moreover, the TAR_{HC} profile fails to record the period of elevated algal productivity between 1924 and 1975 that is indicated by organic carbon $\delta^{13}\text{C}$ values. Finally, the TAR_{HC} values in sediments from Green Bay are much higher than in those from Lake Ontario (Bourbonniere and Meyers, 1996b), where algal organic matter is similarly dominant (Silliman et al., 1996). These observations suggest that the TAR_{HC} values over-represent the contributions of land-derived organic matter in the sediments of Green Bay and that the amount of over-representation is greater in deeper sediments. The lower-molecular-weight *n*-alkanes (C_{15} , C_{17} , C_{19}) that typify algae are generally more susceptible to microbial degradation than land-plant *n*-alkanes (e.g., Meyers and Ishiwatari, 1993b). The progressive elevation of TAR_{HC} values in older sediments of Green Bay is probably an artifact of preferential degradation of algal *n*-alkanes (Silliman et al., 2001), and it is therefore strong evidence that fairly deep microbial activity exists in this setting.

A sediment core collected in 1975 from Saginaw Bay of Lake Huron (Fig. 2) records the progressive increase in algal production of organic matter leading up to the 1975–1980 eutrophication peak that is common to the Great Lakes. Concentrations of organic carbon increase abruptly to 2–2.5% at about 1950 in this record (Fig. 8). This time corresponds to the large growth of human population centers in the Great Lakes region that followed World War II. However, TOC concentrations increase more slowly prior to this period, starting approximately with the clearing of land for farming in the Saginaw Bay catchment that followed opening of the Michigan Territory for settlement in 1824. Concentrations of aquatic geolipid biomarkers start to increase in sediments deposited after ~ 1840 (Meyers and Takeuchi, 1981), and relative proportions of land-plant *n*-alkanols, sterols, and *n*-alkanes consequently become smaller (Fig. 8). Part of the increase in the ratios

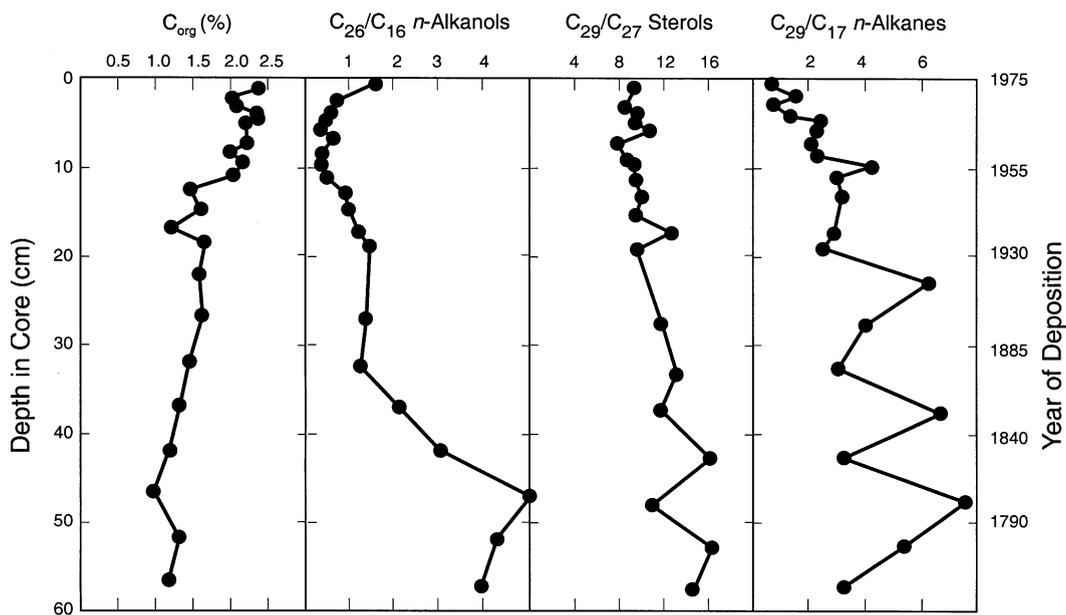


Fig. 8. Concentrations of organic carbon and ratios of land-plant and algal *n*-alkanols, sterols, and *n*-alkanes in sediment from Core 75-30A (water depth 9 m) in Saginaw Bay of Lake Huron (Fig. 2). Progressive eutrophication of the bay is evident in increased organic carbon and decreases in the three biomarker ratios since the advent of agriculture in the mid-1800s. Data from Meyers and Takeuchi (1981).

of C_{26}/C_{16} *n*-alkanols, C_{29}/C_{27} sterols, and C_{29}/C_{17} *n*-alkanes in older sediment may reflect selective diagenetic loss of the algal components, yet the consistent change among these three biomarker ratios indicates instead a progressively larger contribution of algal organic matter towards 1975. In particular, the relative proportions of C_{29} and C_{27} sterols are unlikely to be modified by diagenesis over this relatively short time span (Gaskell and Eglinton, 1976), and so the lowering of the sterol ratio indicates that growth of algal productivity started soon after settlement around Saginaw Bay. In addition, Meyers and Takeuchi (1981) document a progressive increase in the ratio of phytol to dihydrophytol starting early in the 19th century and peaking in 1975 that they interpret to represent greater contributions of algal organic matter over time. Their conclusion is based on the work of Schultz and Quinn (1974), who show that phytol concentrations correlate with chlorophyll and hence with algal biomass in Narragansett Bay, and their determination that dihydrophytol has a constant concentration in Saginaw Bay sediments and evidently is eroded from land.

6. Routes of delivery of fossil fuel hydrocarbons to the Great Lakes

The compositions and the amounts of hydrocarbons in the sediments of the Great Lakes record human-induced environmental changes of the last few centuries.

Two chromatograms of hydrocarbons extracted from sediments of Lake George in the St Marys River (Fig. 2) between Lake Superior and Lake Huron illustrate some of the differences in relative compositions (Fig. 9). The distribution of hydrocarbons in the pre-European settlement sediments (~1782) is dominated by the long-chain *n*-alkanes typical of vascular land-plant waxes. This distribution indicates conditions of moderate to low algal productivity. In marked contrast, the hydrocarbon composition of post-industrialization sediments (1969) is dominated by the UCM that is indicative of petroleum residues, and the contribution of the algal *n*- C_{17} alkane outweighs any of the plant-wax *n*-alkanes. If the contribution of land-plant hydrocarbons is used as a benchmark, then large increases in algal productivity and especially in delivery of fossil fuel residues have added to the “natural” hydrocarbon contents of the sediments. In fact, the change in composition is accompanied by an order of magnitude greater concentration of total extractable hydrocarbons in the 1969 sediment horizon of Lake George (Tenzer et al., 1999), an increase that is mirrored in southern Lake Michigan (Doskey, 2001). A similarly large increase in concentrations of pyrogenic polycyclic aromatic hydrocarbons is found in Great Lakes sediments deposited over the last century (e.g., Eadie, 1984; Helfrich and Armstrong, 1986; Zhang et al., 1993; Simcik et al., 1996).

Anthropogenic delivery of fossil fuel hydrocarbons to recent lake sediments has been documented elsewhere (e.g., Laflamme and Hites, 1978; Hites et al., 1980;

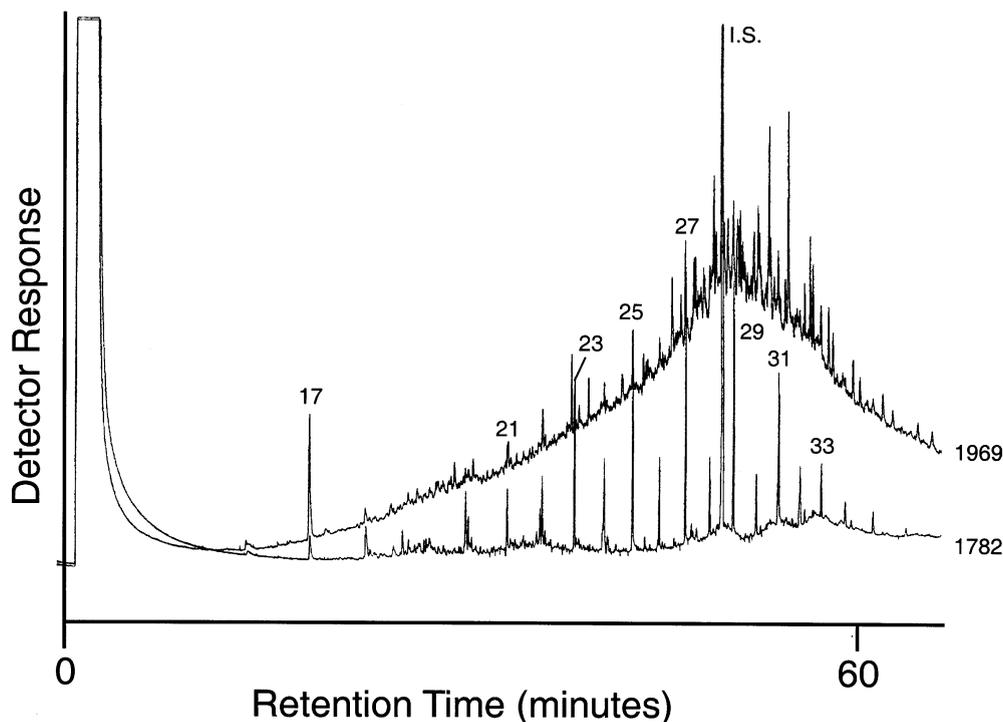


Fig. 9. Comparison of chromatograms of saturated hydrocarbons extracted from two sediment horizons in Lake George on the Michigan–Ontario border (Fig. 2). Numbers identify the peaks corresponding to *n*-alkanes by their carbon atoms; I.S. identifies the internal standard (α -cholestane). The 1969 horizon contains a more complicated composition that includes petroleum residues and a larger algal component than the 1782 horizon, which predates permanent European settlement of this area. The Unresolved Complex Mixture (UCM) diagnostic of petroleum residues is present as the large difference between the detector responses of the 1969 and 1782 traces. From Tenzer et al. (1999).

Wakeham, 1977a,b; Meyers, 1984), so the presence of these components in Great Lakes sediments is not unique. However, a useful feature of the Great Lakes sediment records is that histories of fossil fuel deliveries can be compared in locations that are relatively closely related. Such comparisons allow distinction of local sources from regional sources and enable the fossil fuel residues to be used as proxies for different modes of delivery of organic matter from surrounding land areas.

6.1. Petroleum residues

Petroleum hydrocarbons are commonly delivered to subaqueous sediments in association with suspended particles (Wakeham, 1977a; Nagy et al., 1984; Meyers, 1987), and this mode of delivery appears to be generally true in the Great Lakes. Highest concentrations of petroleum residues in sediments of Lakes St. Clair, Erie, and Ontario are found in areas that are close to major cities and in areas where fine-sized sediment particles can settle (Nagy et al., 1984). Western Lake Erie, which receives the discharge from the heavily industrialized and urbanized Detroit River, has the largest accumulation of petroleum hydrocarbons in this three-lake survey. As

Fig. 9 illustrates, UGMs are dramatic evidence of delivery of petroleum residues to sediments and can therefore be used as a diagnostic indicator of their presence.

UCM profiles in sediment cores reveal differences between local and regional histories of delivery of petroleum residues to the Great Lakes (Fig. 10). UCM concentrations are highest in near-surface sediments of Lake George and decrease irregularly with depth, becoming minor in core intervals deposited prior to *ca* 1900 (Tenzer et al., 1999). This profile records the chronic input of industrial petroleum residues to the St. Marys River system from local sources beginning early in the 20th century. The probable sources, as summarized by Schloesser et al. (1991), are effluents from steel plant rolling mills, paper mill machinery, and chemical plant oil separators. The UCM component of the most recent sediment horizon is lower than in sediments from the 1950s through the 1970s, which is evidence of recent abatement of petroleum hydrocarbon delivery.

Meyers and Takeuchi (1981) report that petroleum residues begin to dominate the hydrocarbons composition of sediments deposited in Saginaw Bay, Lake Huron, starting in the late 19th century (Fig. 10). Furthermore, UCM concentrations diminish with greater

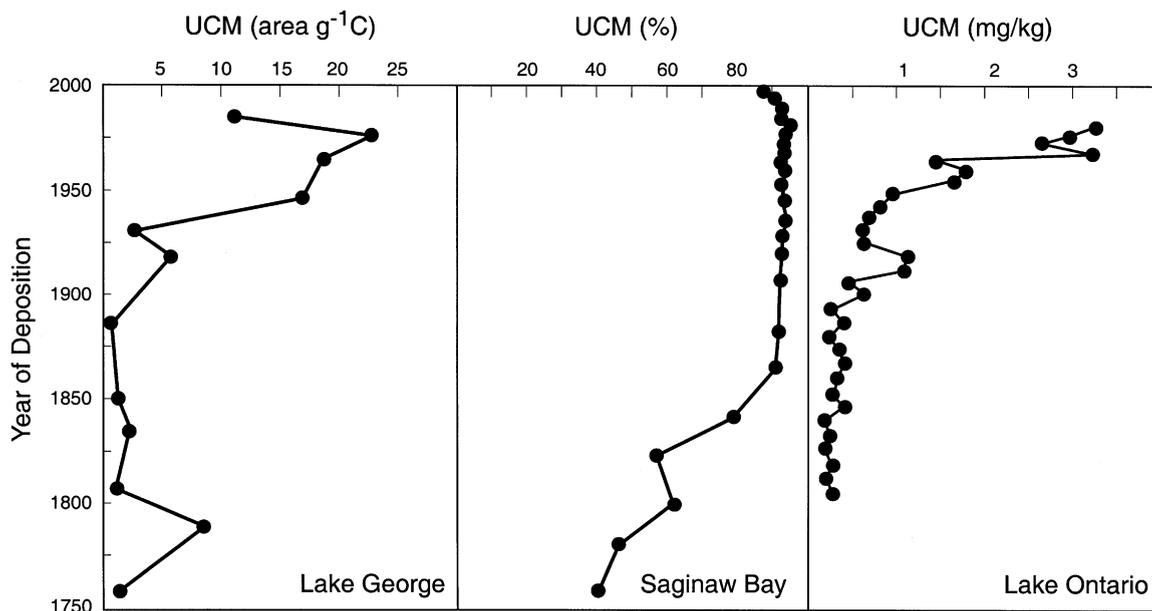


Fig. 10. Comparison of relative contributions of petroleum residues, as evidenced as Unresolved Complex Mixtures (UCM, see Fig. 9) of hydrocarbons, in sediment records from Lake George on the Michigan-Ontario border, Saginaw Bay of Lake Huron, and Core 81-E30 from Lake Ontario. The different histories of UCM accumulation indicate the importance of local sources of river-borne petroleum contamination for the three locations. The three profiles also illustrate different ways to quantify UCM contributions: (1) chromatogram area normalized to organic carbon concentration, (2) percentage of total extractable hydrocarbons, and (3) concentration in dry sediment. Compiled from Tenzer et al. (1999), Meyers and Takeuchi (1981), and Bourbonniere and Meyers (1996a).

distance from the mouth of the Saginaw River (Meyers and Takeuchi, 1979; Meyers, 1984). Because this is the major river entering the bay, local fluvial sources are implicated for the petroleum residues. Effluents from the many heavy industrial complexes within the watershed of the Saginaw River are probably the major source of these contaminants, and their earlier onset than in Lake George sediments agrees with the earlier industrial development of this region. Some fraction of the residues is also likely to have originated from local road runoff (e.g., Wakeham, 1977a,b; Meyers, 1987).

The UCM profile in sediments of Lake Ontario (Bourbonniere and Meyers, 1996a) is similar to the Lake George profile but very different from the Saginaw Bay profile (Fig. 10). The large size of Lake Ontario integrates multiple inputs of organic matter and provides a regional history of deliveries, rather than recording local sources. Consequently, the Lake Ontario profile shows that delivery of petroleum residues remained mostly a local phenomenon until the second half of the 20th century, when it became magnified across the region. The increase corresponds to the widespread growth of suburbs, paved roadways, and motor vehicular traffic starting in the 1960s in the Great Lakes area. Moreover, Bourbonniere and Meyers (1996b) postulate that expansion of paved roadways and of municipal sewage treatment has actually contributed to the magnified delivery of petroleum residues by allowing them to be washed into Lake Ontario in

association with suspended sediment particles rather than remaining sequestered on soil particles on land.

6.2. Pyrogenic polycyclic aromatic hydrocarbons

Several lines of evidence indicate that the major origin of polycyclic aromatic hydrocarbons (PAHs) in Great Lakes sediments appears to be from high-temperature combustion of coal rather than automobile exhaust. First, the molecular distributions of PAHs in sediments from Lake Michigan and Green Bay indicates a high-temperature origin for them (Helfrich and Armstrong, 1986; Zhang et al., 1993). Second, Simcik et al. (1996) note a close similarity between the history of coal use in Illinois and the concentrations of PAHs in sediments of Lake Michigan and therefore conclude that the principal origin of the pyrogenic PAHs is from coke and steel production. Similarly, Karls and Christensen (1998) conclude that coal combustion has been the dominant source of most of the PAHs in Green Bay since the early 1950s.

In addition to their origins, modes of delivery of PAHs and petroleum residues to the Great Lakes differ. Simcik et al. (1996) conclude from similar molecular distributions at 27 different locations in Lake Michigan that airborne transport dominates delivery of PAHs to this lake. However, Smirnov et al. (1998) find that PAH concentrations in Lake Erie are highest near mouths of rivers that drain the important industrial and population

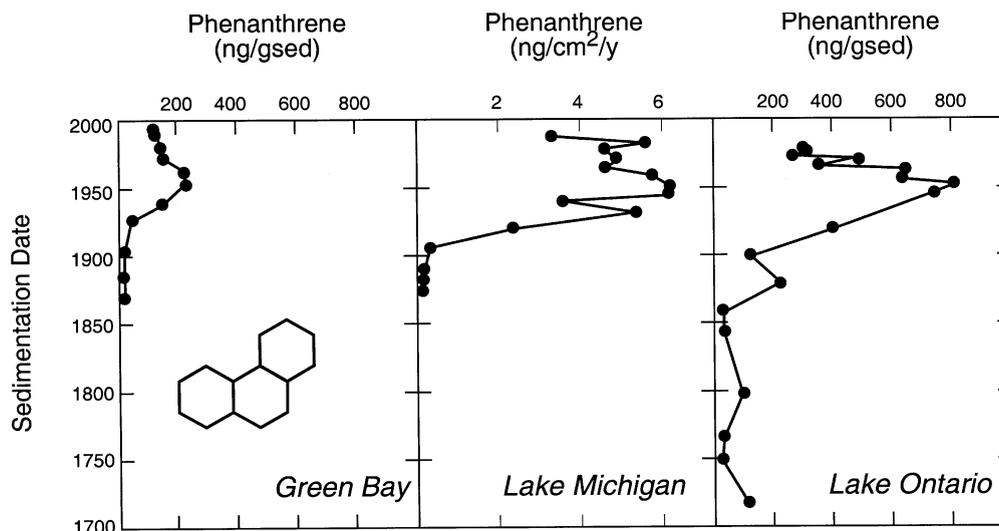


Fig. 11. Comparison of relative contributions of polycyclic aromatic hydrocarbons (PAHs), using phenanthrene as a representative PAH, in sediment records from Green Bay of Lake Michigan, southern Lake Michigan, and Core 81-E30 from Lake Ontario. The similar histories of accumulation at the three separate locations indicate the importance of eolian delivery of PAHs to the entire Great Lakes region. Compiled from Silliman et al. (2001) and Simcik et al. (1996).

centers of Detroit, Cleveland, and Buffalo, which shows that fluvial delivery is at least as important as eolian delivery in some areas of the Great Lakes.

Comparison of the records of accumulation of phenanthrene, a representative pyrogenic PAH, at three locations in the Great Lakes shows that generalizations about delivery routes are sometimes simplistic. The three records—from Green Bay, central Lake Michigan, and the Rochester Basin of Lake Ontario (see Fig. 2)—are similar in having maxima in accumulation in the early 1950s (Fig. 11), which corresponds to the peak in coal combustion in the Great Lakes region (Simcik et al., 1996). The correspondence between the phenanthrene maxima and use of coal suggests that airborne distribution of industrial stack gases and particles has distributed PAHs across the Great Lakes region. Such broadcasting might make PAH deliveries regionally uniform. However, the concentrations of phenanthrene in sediments from Lake Ontario are nearly four times higher than in those from Green Bay, which indicates that local sources of PAHs are important. This contrast is all the more dramatic inasmuch as Green Bay receives the outflow of the Fox River, which has had serious water quality problems. The answer to this puzzle may lie in the fact that Lake Ontario core site E30 is located downwind from Hamilton, Ontario, where a congregation of steel mills, refineries, and other types of heavy industry exists. Stack emissions from these factories have probably contributed a local supply of pyrogenic PAHs that have been carried by winds to Lake Ontario and that have greatly augmented the regional delivery of these anthropogenic materials.

7. Trends and future perspectives in applications of organic geochemistry to paleolimnological reconstructions

The amounts and types of organic matter present in lake sediments provide a history of processes active in the lake water, in the lake catchment, and in the lake bottom. Reconstruction of these processes in former times is the goal of paleolimnology. Organic geochemical measurements have been valuable to many such reconstructions, yet currently evolving advances in approach, analysis, and interpretation promise to refine and enhance future contributions to paleolimnology. Some of these developing trends in applications of organic geochemistry to paleolimnological reconstructions are described below.

7.1. Collection of high-resolution records of organic matter accumulation in sediments

Investigators are increasingly using sedimentary records from lakes to obtain detailed histories of the local paleoenvironment and regional paleoclimate and to identify rapid changes and short-lived events. Sediment accumulation rates in lakes range from as high as several cm per year to a few cm per century. TOC concentrations in lake sediments are commonly 1–10% and often more, and sensitivities of analytical instruments are usually sufficiently high so that the amounts of organic matter components provided by sampling intervals of 1 cm or less in sediment cores is adequate for study. If bioturbation—the mixing of surface sediments by their animal inhabitants—is not extensive,

then sediment layers corresponding to very short periods of paleoenvironmental history can be obtained.

Lakes having varved, or annually laminated, sedimentary records are especially useful to paleolimnology. The laminations result from seasonal climate changes and the existence of oxygen-depleted bottom waters that restrict bioturbation. The presence of varves permits annual age-resolution of paleolimnological records and opens the possibility of collecting thin, non-mixed sediment layers that correspond to different parts of a single year. The combined study of cores of varved sediment and of sediment traps has been used especially effectively in Swiss lakes to identify the impacts of eutrophication on seasonal changes in isotopic compositions of organic matter delivered to bottom sediments (Hollander et al., 1992; Bernasconi et al., 1997; Teranes and Bernasconi, 2000). Studies of this type are important to improving interpretation of organic geochemical parameters in lake sediments.

Although varved lakes exist throughout the world (e.g., Overpeck, 1996), most lake sediments are not varved. Their paleolimnological records nonetheless give good temporal resolutions, sometimes as good as a few years, if sedimentation rates are elevated and sensitive dating methods are used. The time-dependent decay rates of ^{210}Pb (half-life 22 y) for sediment records up to ~150 years old (e.g., Robbins and Edgington, 1975) and ^{14}C (half-life 5730 y) for sediments as old as 40 ky (e.g., Huang et al., 1999) are commonly used. Radiocarbon ages have historically been measured on the bulk organic matter in lake sediments, which often contains some proportion of recycled detrital organic carbon that can make ^{14}C ages 1000–2000 y older than actual sediment ages (e.g., Rea et al., 1980). Sediment ^{14}C ages based on accelerator mass spectrometry (AMS) are becoming routine in paleolimnological reconstructions. AMS ages are not necessarily more accurate than those determined by scintillation counters. However, they can be measured on much smaller amounts of carbon, which permits radiocarbon dating of discrete forms of organic matter such as pollen, leaves, twigs, fish scales, or insect wings found in sediment horizons and thereby minimize the age-biasing from detrital carbon. AMS also allows thinner intervals of sediment sequences to be sampled and radiocarbon dated.

7.2. Expansion of the library of biotic organic matter compositions in lake systems

The generally limited amount of information about the elemental, isotopic, and biomarker compositions of the many kinds of biota that are potential contributors of organic matter to any subaqueous sediments has been a source of frustration to organic geochemists for years. However, a growing number of organic geochemical studies of lake sediments include this important information

from organisms that have been collected from in and around the lake systems under study (e.g., Rieley et al., 1991; Talbot and Johannessen 1992; Ficken et al., 1998a,b, 2000; Tenzer et al., 1999; Herczeg et al., 2001; Sauer et al., 2001; Schwark et al., 2002). Many of these biomarker determinations are useful to studies in other locations.

Expansion of the collection of organic geochemical compositions needs to continue. Quantitative relationships between organic geochemical proxies of lake-derived and land-derived origins of organic matter can probably be defined better as the body of information about the organic matter compositions of source organisms grows. It is also likely that indicator organisms that are characteristic of different types of lacustrine environments can be identified, and their molecular and isotopic compositions can be scanned for new proxies that will refine paleolimnological interpretations based on organic geochemical information.

In addition, the consequences of early diagenesis on the source integrity of organic geochemical proxies needs further assessment. Results of the few existing studies show that a range of susceptibilities to alteration and degradation exists for the variety of organic geochemical proxies available to paleoenvironmental reconstructions. The robustness of proxies needs evaluation so that source identifications based on them are reliable. Lakes provide exceptional settings for studies of early diagenesis in both sediments settling through their water depths and in sediments deposited in their bottoms.

7.3. New applications of compound-specific isotope analyses to paleoenvironmental reconstructions

Use of the $^{15}\text{N}/^{14}\text{N}$, D/H, $^{18}\text{O}/^{16}\text{O}$ and $^{14}\text{C}/^{12}\text{C}$ ratios of selected compounds is less common than of $^{13}\text{C}/^{12}\text{C}$ in paleolimnological studies, yet each ratio conveys special information about the origins of sediment organic matter, cycling of its respective nutrient element, and paleoenvironmental conditions. Demonstrations of the usefulness of compound-specific $\delta^{15}\text{N}$ and $\delta^{14}\text{C}$ values in paleoceanographic reconstructions indicate that these parameters should be very effective in paleolimnologic studies.

Lake systems are far more sensitive to changes in precipitation/evaporation ratios than the oceans because of their much smaller sizes. Therefore, the D/H and $^{18}\text{O}/^{16}\text{O}$ ratios of organic matter created within them, which reflect air mass trajectories and evaporative isotopic distillation, should record their paleohydrologic histories. This expectation is valid. Both the δD and $\delta^{18}\text{O}$ values of lake-derived bulk organic matter have been used to reconstruct Holocene histories of hydrologic change in lake systems (Krishnamurthy et al., 1995; Beuning et al., 1997). A more refined paleoenvironmental

record was obtained by Xie et al. (2000), who employed D/H ratios of the C₂₃ *n*-alkane that is diagnostic of *Sphagnum* in a core from Bolton Fell Moss, Cumbria, England, to explore for effects of climate change on this aquatic environment over the past few centuries. The δD values of the biomarker hydrocarbon increase to -140‰ during two times of warmer climate around 1800 and 1960, and they decrease to -180‰ when climate was cooler around 1870. These fluctuations probably record variations in rates of evaporative distillation of bog waters as air temperatures increased or decreased.

A particularly promising paleolimnological application of compound-specific isotopic analysis is provided by the D/H ratio of aquatic biomarkers. Sauer et al. (2001) have established that the δD of lake water can be reconstructed within 10‰ from the hydrogen isotopic composition of sterols derived specifically from phytoplankton. Use of the aquatic biomarkers eliminates many of the interpretive challenges presented by the multiple sources of bulk sediment organic matter.

7.4. Exploration for molecular paleotemperature proxies

The combination of moisture and temperature defines climate. Organic geochemical proxies that provide information about paleohydrology and paleotemperature are therefore important to paleoclimate reconstructions from lake sediment records. The δD and $\delta^{18}O$ values of lake-derived organic matter discussed in section 7.3 are good proxies for water balances within lakes, and $\delta^{13}C$ values of land-derived organic matter, which identify proportions of C₃ and C₄ plants, serve as proxies for the availability of water on lands around lakes. Several molecular paleotemperature proxies derive from the biochemical requirement for organisms to maintain a constant fluidity of their cell membranes and external coatings (c.f., Brassell, 1993). The basis for these proxies is that the melting points of homologous organic molecules decrease as the number of carbon-carbon double bonds increases.

Aquatic organisms contain saturated and unsaturated fatty acids in their cell membranes, and the proportion of unsaturated acids increases in organisms that inhabit cooler waters. Kawamura and Ishiwatari (1981) applied variations in the ratio of sedimentary *n*-C_{18:2} and *n*-C_{18:0} acids to reconstruct changes in the surface-water paleotemperature of Lake Biwa, Japan. High values of the C_{18:2}/C_{18:0} ratio correspond to periods of cooler climate and presumably cooler surface water in the Holocene history of this lake. However, application of the ratio to older parts of the sedimentary record was prevented by the progressive degradation of the unsaturated acid with greater sediment age. This approach has rarely been applied to paleolimnologic studies since its initiation, yet it may have potential to other Holocene sedimentary sequences.

The alkenone unsaturation index has found wide application in reconstructions of sea-surface paleotemperature histories (c.f., Brassell, 1993). The source of alkenones is coccolithophorids, a group of marine algae, yet alkenones also are found in some lacustrine sediments. Algal assemblages in brackish and salt-water lakes evidently contain relatives to the marine species that produce long-chain unsaturated ketones, and these temperature-sensitive biomarkers have been reported in the sediments of salty lakes (Li et al., 1996; Thiel et al., 1997). Alkenones have also been detected in the sediments of some freshwater lakes. For example, Cranwell (1985) reported the presence of C₃₇–C₃₉ unsaturated methyl and ethyl ketones in the sediments of three English lakes but their absence in those of three others, and Volkman et al. (1988) reported alkenones in the sediments of a freshwater lake in Antarctica. Zink et al. (2001) surveyed 27 lakes in Europe and North America and found alkenones in sediments of 13 of them. The variable occurrence of the ketones in lake sediments suggests that algal populations differed in the lakes, possibly in response to different environmental conditions. The presence of alkenones in some lake settings offers the tantalizing possibility of estimating local paleotemperature histories and thereby improving continental paleoclimate reconstructions. However, Zink et al. (2001) caution that sedimentary records of alkenones are rarely continuous. Furthermore, the specific source of these freshwater ketones remains to be identified before the full paleolimnological potential of these biomarkers can be realized.

A potential land-based paleotemperature proxy independent of the aquatic unsaturation indices exists in the *n*-alkane compositions of epicuticular waxes of land plants. The basis of this proxy is that chain-lengths of *n*-alkanes evidently increase in warm climates and decrease in cool ones as plants attempt to maintain an optimal and constant viscosity of their waxy coatings. Poynter et al. (1989) utilize the Average Chain-Length (ACL) of land-plant wax *n*-alkanes extracted from marine sediments to identify relative changes in temperature on the continents where they postulated the plants grew. The same approach has promise in reconstructing paleotemperature records of lacustrine sedimentary sequences. However, changes in *n*-alkane composition because of climate-caused shifts in plant assemblages can overwhelm the paleotemperature information of ACL values (e.g., Huang et al., 1999) and complicate interpretation of this proxy.

7.5. Use and reconciliation of multiple paleolimnological proxies

Multiple processes are active in lake systems. Hence, multiple proxies should be employed in paleolimnological reconstructions. Pollen, fossils of aquatic biota,

sediment grain-size and mineralogy, organic matter components, and trace metal contents of sediment yield respectively important information. An incomplete and potentially misleading reconstruction can result if only one or two organic geochemical proxies are used. Use of several independent proxies in addition to organic geochemical parameters helps not only to improve interpretations of paleoenvironmental changes in lake systems but also to identify more of the processes that have participated in the changes.

Modern studies increasingly apply multiple proxies to paleoenvironmental and paleoecological reconstructions. A good example is a combined biomarker-pollen reconstruction of the succession of post-glacial to early Holocene vegetation surrounding Lake Steisslingen in southern Germany (Schwark et al., 2002). Pollen of grasses and herbs is accompanied by the dominance of C_{31} *n*-alkane in post-glacial lake sediment. Concordant increases in birch pollen and the C_{27} *n*-alkane indicate replacement of these pioneering plants by birch forests, which were first replaced by pines (*n*- C_{29} and *n*- C_{31} dominance) during the Younger Dryas and then eventually by a mixed oak–elm–beech–hazel forest (*n*- C_{29} dominance) in the early Holocene. Moreover, the combination of pollen and *n*-alkane compositions allows detailed identifications of climate change not evident in sole use of either proxy.

However, applications of multiple proxies sometimes give contradictory indications of past conditions. Such contradictions demand reconciliation, and they represent opportunities to refine and better understand the paleoenvironmental settings that the proxies imply. Comparison of the pollen and lignin proxies of early Holocene land vegetation in the sediments from Lake Washington provides a classic example of contradictory paleoenvironmental evidence. The pollen indicate extensive pine forests in the catchment (Leopold et al., 1982), whereas the lignin compositions indicate grasses (Hedges et al., 1982). The answer to the problem is in how these proxies are delivered to lake sediments—pollen are carried by wind, whereas lignin-bearing plant debris is carried by streams. The pine trees that produced the pollen were not in the Lake Washington catchment, and their pollen do not accurately indicate the local early Holocene paleoconditions. Instead, the pollen record wind trajectories from where the pine forests existed, probably on the Olympic Peninsula 30 km upwind to the west.

Comparison of bulk and biomarker $\delta^{13}C$ values in sediments from Lake Erie provides another illustration of how proxies sometimes fail to be consistent. Bulk organic carbon isotope compositions record the classic excursion to heavier values that accompanies the eutrophication peak of the mid-1970s in the Great Lakes (Schelske and Hodell, 1991). However, the $\delta^{13}C$ values of the C_{17} *n*-alkane biomarker, which is

considered representative of algae (Blumer et al., 1971; Filley et al., 2001), remain steady at -31‰ throughout the bulk carbon isotopic excursion (Ostrom et al., 1998). The isotopic composition of this biomarker, above all others, should reflect eutrophication! Several explanations are possible for this unresolved problem. First, the C_{17} *n*-alkane may not be a valid proxy for algal productivity in this lake system and instead is derived from land plants, which would not be affected by nutrient loading of the lake. Second, algae may synthesize *n*-alkanes by pathways that are not impacted by changes in the dissolved carbon isotopic composition, a possibility that challenges much of our understanding of biosynthetic pathways. Third, algal *n*- C_{17} may be more sensitive to diagenetic degradation than land-derived *n*- C_{17} , a possibility that challenges much of our thinking about diagenesis. Problems such as this example should be considered as challenges that will ultimately improve identification of proxies, interpretation of data, and reconstruction of past paleoenvironments.

7.6. *Lacustrine–marine paleoclimate correlations*

Ocean sediment records provide broad perspectives of changes in climate and of responses to global forcing functions such as orbital insolation cycles. In contrast, lake sediments are the best archives of continental climate histories, and they can yield unique records of how local and regional climates respond to global changes. Furthermore, lake sediment records commonly have the time-resolution to reveal details about climate change that are not available from marine records. Comparisons and combinations of marine and lacustrine records of climate histories can consequently amplify and extend understanding of how climate change has evolved.

Examples of lacustrine–marine paleoclimate correlations demonstrate the effectiveness of combining these different types of paleoclimate records. The climate of Japan is especially sensitive to glacial–interglacial cycles because sea-surface temperatures of the Sea of Japan alternate between being cold during glacial times and warm during interglacial times, which changes the amount of moisture in the airmasses that flow over Japan. The difference in climate regimes affects precipitation, which impacts delivery of soil nutrients to Japanese lakes and hence lake productivities. Meyers and Takemura (1997) employ TOC mass accumulation rates to identify connections between the last five glacial–interglacial cycles and variations in production of aquatic organic matter in Lake Biwa, Japan. Changes in delivery of moisture from the ocean can also affect the types of land vegetation in lake catchments. Huang et al. (2001) use the $\delta^{13}C$ of plant-wax *n*-alkanes in the sediments of two lakes in Central America to identify shifts in C_3 and C_4 plant dominance that record local

precipitation histories over the past 20 ky. Using non-organic proxies, Baker et al. (2001) document from mineralogical changes that wet-dry periods preserved in a 50-ky sediment record of an ephemeral lake on the Bolivian Altiplano correspond to global precessional (20-ky) cycles and millennial-scale Heinrich Events in the North Atlantic. Similarly, Rodbell et al. (1999) employ changes in sediment character in Laguna Palca-cocha, Ecuador, as a proxy for local rainy periods to establish that ENSO events in the nearby Pacific Ocean remained infrequent between 15 and 7 ka before increasing to modern levels about 5000 years ago. Finally, Ariztegui et al. (2000) show that deposition of organic matter increased simultaneously in the Adriatic Sea, the Tyrrhenian Sea, and in two lakes in central Italy during the Holocene Hypsithermal, verifying that the regional change to wetter climate that instigated formation of the S₁ Mediterranean sapropel also impacted climate on land. Although not all of these studies employed organic geochemical analyses as paleoclimate proxies, addition of some of the many proxies provided by organic matter in sediments to the other types of independent proxies will enhance and refine future paleolimnological reconstructions.

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