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Joel Clemence Henry

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Nathaniel Ostrom
Major professor

Peggy Ostrom

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ELEMENTAL, MOLECULAR, AND CARBON ISOTOPIC EVIDENCE OF REDUCED ALGAL PRODUCTIVITY AND EARLY DIAGENESIS IN LAKE ERIE, 1968-1982

By

Joel Clemence Henry

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ABSTRACT

ELEMENTAL, MOLECULAR, AND CARBON ISOTOPIC EVIDENCE OF REDUCED ALGAL PRODUCTIVITY AND EARLY DIAGENESIS IN LAKE ERIE, 1968-1982

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The $\delta^{13}C$ composition of lacustrine organic sediments typically reflects the $\delta^{13}C$ content of the primary sources of organic matter, but may be diagenetically altered. The $\delta^{13}C$ content of organic sediments from Lake Erie decreases from -24.9‰ to -25.9‰ between 1968 and 1982 (^{210}Pb dating), coincident with reduced historical phosphorous loadings to the lake. Organic sediments deposited in the eastern basin of Lake Erie are derived primarily from autochthonous sources, as indicated by low organic C/N, and the persistance of low molecular weight (C_{14}-C_{20}) n-alkanes. The absence of correlations between elemental, isotopic, and molecular abundances, and the apparent absence of change in the relative contributions from algal and terrestrial sources, suggests that the shift in $\delta^{13}C$ is related to neither a change in source or diagenetic alteration, but to changes in $[CO_2]_{aq}$ as a function of the algal productivity and trophic state of Lake Erie.

This thesis is dedicated in memory of my father,
Clemence James Henry
1922 - 1991

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Introduction

1.1 Purpose of Study

The trophic status of Lake Erie has been a major environmental concern during the latter half of this century. Excessive anthropogenic loading of phosphorus has resulted in enhanced algal productivity and the deterioration of water quality in the lake (Mortimer, 1987), a process known as eutrophication. The eutrophication of Lake Erie received national attention during the 1960's when large mats of algae washed up on beaches to rot, fouling the shoreline of the lake (Burns, 1985). Less spectacular, but more damaging to the lake, was the decomposition of the detrital remains of the surplus algal biomass on the bottom of the lake. Increased sediment oxygen demand led to widespread anoxia in the hypolimnion of the central basin during the annual period of summer stratification (Burns, 1985). Low oxygen concentrations eliminated species of fish and insects, precipitating the "death" of the world's largest freshwater fishery (Burns, 1985).

Remedial measures undertaken since the 1970's have successfully reduced the phosphorus load to Lake Erie at the cost of large public expenditures (Mortimer, 1987; Fraser, 1987; Rosa, 1987). In response to environmental regulations, the Lake Erie fishery has since recovered, and the phytoplankton biomass has been significantly reduced (Makarewicz and Bertram, 1991), yet questions remain regarding the extent of bottom-water anoxia (Boyce et al., 1987). Numerical models have been developed to describe the relationships between nutrient concentrations, productivity, and anoxia, but the associated mechanisms are not yet fully understood (Lam and Schertzer, 1987). Definitive evidence of the beneficial effects of phosphorus reduction needs to be demonstrated if the high cost of remediation imposed by legislation such as the Clean Water Act is to be justified.

Organic geochemical studies of the sediments of eutrophic lakes have previously been used to characterize changes in trophic status (reviewed and summarized by Meyers and Ishiwatari, 1993a). The carbon isotopic composition[1] of organic sediments may provide an indication of trophic state, owing to an inverse relationship between the concentration of aqueous CO_2 and the $\delta^{13}C$ composition of the organic constituents of phytoplankton (Degens et al., 1968; Deuser et al., 1968; Stuvier, 1975; Arthur et al., 1985; McCabe, 1985; Dean et al., 1986; O'Leary, 1988; Freeman and Hayes, 1992; Rau et al., 1992). The detrital remains of phytoplankton comprise only a small fraction of organic sediments, yet may preserve a time-integrated geochemical record of the concentration of aqueous CO_2 in surface waters (Jasper and Hayes, 1990; Rau et al., 1991, 1992; Meyers and Horie, 1993). Fluctuations in the concentration of aqueous CO_2 could in turn serve as a proxy by which changes in algal productivity may be inferred (Schelske and Hodell, 1991; Rau et al., 1992; Shemesh et al., 1993).

Recent evidence suggests that the $\delta^{13}C$ composition of the bulk organic

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[1] The stable isotopic composition of carbon, denoted $\delta^{13}C$, describes the ratio of $^{13}C/^{12}C$ in a sample relative to a given standard. Isotopic compositions of samples are reported relative to a standard, in per mil notation, in which $R = {}^{13}C/{}^{12}C$, and

$$\delta^{13}C\ (‰) = [(R_{sample}/R_{standard}) - 1] \times 1000$$

Carbon isotopic compositions in this study are reported relative to PDB, a Cretaceous belemnite from the Peedee formation of South Carolina.

sedimentary fraction may also reflect the trophic status of lakes (Schelske and Hodell, 1991). Sediment cores recovered from Lake Erie and Lake Ontario exhibit maximum $\delta^{13}C$ values in organic material deposited during the early 1970's (Schelske and Hodell, 1991; Meyers, unpublish. data). This peak is coincident with the period of maximum historical phosphorus loading to the lakes, suggesting that changes in trophic status are responsible for the observed isotopic shift.

In addition to the availability of aqueous CO_2, the $\delta^{13}C$ of organic sediments may be affected by diagenetic alteration, and allochthonous sources of organic matter. Extensive microbial reprocessing of organic compounds leads to the formation of secondary and tertiary organic products, with the potential alteration of $\delta^{13}C$ values (Spiker and Hatcher, 1984; Hayes, 1993; Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993a). Allochthonous material derived from terrestrial sources tends to be isotopically lighter than phytoplankton, such that any change in the magnitude of the relative contributions from aquatic or terrestrial sources would likely affect the $\delta^{13}C$ of the organic sediments (Stuvier, 1975; Jasper and Gagosian, 1989).

The intent of this study is: 1) to present evidence indicating that the recent change in the $\delta^{13}C$ of the sedimentary organic matter of Lake Erie may be attributed to changes in algal productivity, rather than a change in source or degree of diagenetic activity, and 2) to use the relative abundance of individual hydrocarbons to develop an understanding of the trophic state of Lake Erie. Hydrocarbon distributions and organic C/N are used to characterize the sources of organic matter contributing to the lake sediments, and to assess the effects of early diagenesis on lake sediments. Variations in the isotopic composition of organic sediments are interpreted in the context of inferred sources, diagenetic trends, and the known trophic history of Lake Erie.

1.2 Lake Erie

Lake Erie is the fourth largest of the Laurentian Great Lakes by area, with a surface area of 25,300 km^2 (Figures 1, 2). The lake averages 70 km in width, and extends 390 km on a southwest to northeast axis along the border of the United States and Canada. Due to its relatively shallow depth, Lake Erie is the smallest of the Great Lakes in volume (470 km^3). Despite its location as the southernmost of the Great Lakes, most of the lake surface freezes in winter. From fall until spring, the water column is well-mixed from top to bottom. The lake rapidly stratifies in the spring, and the epilimnion warms rapidly to approximately 23°C (Sly, 1976; Burns, 1985).

The lake is typically divided into the western, central, and eastern basins, each of which exhibit unique physical and limnological characteristics. The Detroit River flows into the western basin, providing the bulk of the hydrologic input to the lake. Together with the Maumee River at Toledo, these rivers deliver a large load of suspended material to the lake. The high nutrient content of riverine inputs has resulted in the western basin being the most eutrophic of the three. The central basin, which extends from Pelee Island in the west to Pennsylvania Ridge in the east, is noted for the development of bottom-water anoxia during summer stratification (Burns and Ross, 1972; Burns et al., 1976; Rosa and Burns, 1987). The eastern basin, the deepest of the three, is shielded from the bottom-water anoxia of the central basin by the Pennsylvania Ridge, an underwater sill at a depth of about 15 m. The deepest portion of the eastern basin, at a maximum depth of 60 m, acts as a natural sediment trap where rapid sedimentation has been observed (Mortimer, 1987). Sediments deposited here preserve an integrated biogeochemical record of inputs and processes which affect the entire lake (Mortimer, 1987).

Lake Erie and its watershed have undergone dramatic change during the past 150 years. The clearance of land for farming and timber greatly increased the degree of soil erosion. The discovery of coal and iron in the Great Lakes basin, coupled with the industrial revolution, made the Great Lakes a suitable location for industry (Burns, 1985). The cities of Detroit, Cleveland, Toledo, and Erie thrived on the commerce and transportation that the Great Lakes provided. The watershed of Lake Erie is presently home to approximately 13 million people. Detailed synopses of the geology, climate, and anthropogenic changes in the Lake Erie basin are available in the literature (e.g. Sly, 1976; Burns, 1985).

Anthropogenic enrichment of phosphate and nitrate prior to 1970 led to the eutrophication of Lake Erie. Eutrophication began with the clearing of forests in the early 1800's, which increased the amount of terrestrial runoff into the lake (Burns, 1985). Nutrient loadings increased steadily with population growth until 1945, when the increase became exponential owing to the replacement of soap by phosphate detergents, and the widespread use of nitrogen and phosphate fertilizers (Burns, 1985).

Geochemical and biological changes in Lake Erie associated with eutrophication have been the subject of extensive investigations, the results of which are summarized in numerous reviews (Beeton, 1969; Kemp et al., 1972; Burns and Ross, 1972; Dobson et al., 1974; Kemp et al., 1976; Mortimer, 1987; El-Shaarawi, 1987). Productivity of phytoplankton increased dramatically as a result of eutrophication, and the species composition of the lake shifted to include several nuisance and eutrophic species of phytoplankton (Auer and Canale, 1982; Burns, 1985; Makarewicz, 1987). The populations of fish and other fauna decreased dramatically, due to the increased sediment oxygen demand associated with the degradation of the excess algal biomass (Makarewicz and Bertram, 1991). Depletion of oxygen from the bottom waters of the central basin during summer stratification imposed anoxic conditions throughout the hypolimnion (Burns and Ross, 1972).

Anthropogenic loading of soluble, reactive forms of phosphorus has been identified as the primary cause of the eutrophication of Lake Erie (Burns et al., 1976). The Great Lakes Water Quality Agreement (1972) between the United States and Canada set target levels for the reduction of tributary phosphorus loadings, with the primary goal being the reduction of bottom water anoxia within the central basin (Boyce et al., 1987). This resulted in significant declines in phosphorus loadings to Lake Erie through tertiary treatment of effluent phosphorus, construction of new sewage treatment facilities, and limitations on detergent phosphorus (Boyce et al., 1987; Rosa, 1987; Fraser, 1987; Makarewicz and Bertram, 1991). The effectiveness of these abatement programs is demonstrated by an 80% decrease in phosphorus delivered to the lake by the Detroit River (Fraser, 1987). Improvements in the Lake Erie fishery, and reduction of total chlorophyll concentrations, indicate a positive response to phosphorus abatement (Makarewicz, 1987; Makarewicz and Bertram, 1991). Extensive modelling has been performed to describe the ecology of Lake Erie, linking the nutrient supply, the dynamics of water mass mixing, sediment/water exchange processes, and consumers such as zebra mussels with the effects of eutrophication (Burns et al., 1976; DiToro, et al., 1987; Lam et al., 1987; Lam and Schertzer, 1987; Wu and Culver, 1991; Nicholls and Hopkins, 1993).

1.3 Carbon isotopes

Carbon has two stable isotopes, consisting of approximately 98.9% ^{12}C, and 1.1% ^{13}C. Kinetic and equilibrium isotope effects produce variations in the distribution of carbon isotopes among reservoirs of organic and inorganic materials. The distribution of carbon isotopes in atmospheric CO_2, photosynthetic production, and organic and inorganic sediments has been useful for providing insight into the flux and cycling of carbon between these reservoirs (McKenzie, 1986; Ostrom, 1989; Hayes, 1993).

Variation in the relative abundance of ^{13}C to ^{12}C is a consequence of isotopic discrimination, or fractionation. The slight difference in the mass of the isotopes results in different vibrational frequencies (equilibrium effects) or reaction rates (kinetic effects) for isotopically distinct molecules of the same compound (McKenzie, 1986). A given molecule containing ^{13}C has a lower vibrational frequency and lower zero-point energy than the same molecule containing ^{12}C. Bonds formed by the heavier isotope are therefore stronger and less reactive. At a given kinetic energy, isotopically heavier molecules such as $^{13}CO_2$ will tend to diffuse more slowly than $^{12}CO_2$, and tend to be slightly less available for reaction (Faure, 1986).

Isotopic fractionation may occur during diffusion, dissolution, phase change, and a variety of other kinetic and equilibrium reactions (Freeman and Hayes, 1992; Hayes, 1993). Fractionation factors, abbreviated as α, may be calculated for equilibrium reactions as $\alpha = R_a/R_b$, or $\alpha = K^{12}C/K^{13}C$ for kinetic reactions, where $R = {}^{13}C/{}^{12}C$, a is the initial state or substrate, b is the final state or product, and K is the rate of reaction. Fractionation is may be expressed in ‰ notation as the difference between the isotopic composition of the substrate and the product molecules in a given reaction, where $\Delta = \delta^{13}C_s - \delta^{13}C_p$, or occasionally as $\epsilon = (\alpha - 1) * 1000$, where $\epsilon \approx \Delta$.

Isotopic compositions of samples are determined through the use of stable isotope ratio mass spectrometers, which determine the relative abundance of isotopes to six decimal places (atom percent). The linkage of an isotope ratio mass spectrometer with a gas chromatograph (GC-irMS) permits the isotopic analysis of individual organic compounds (Matthews and Hayes, 1978; Hayes et al., 1990; Ricci et al., 1994; Bakel et al., 1994).

1.3.1 Photosynthetic fractionation of organic carbon

Kinetic and equilibrium isotopic fractionations account for the depletion of ^{13}C in photosynthetically produced organic matter relative to PDB (O'Leary, 1988). Atmospheric CO_2 has a $\delta^{13}C$ value of approximately -8‰, due to the equilibrium fractionation associated with the dissolution and hydration of CO_2 in water (Fogel, 1993). The isotopic composition of atmospheric CO_2 is becoming increasingly lighter due to the combustion of isotopically light (approximately -30‰) fossil fuels

(O'Leary, 1988; Keeling et al., 1989). Diffusion of CO_2 through air or water, transport of CO_2 through cell membranes, and carboxylation of various enzymes all demonstrate significant kinetic isotope effects, resulting in discrimination against the heavier isotope.

In complex biochemical processes such as photosynthesis, the overall degree of isotopic fractionation is not the sum of the fractionations associated with individual steps, but rather is primarily a function of the fractionation associated with the rate-limiting step (O'Leary, 1988). This principle is illustrated by a comparison of the isotopic fractionation and carbon isotopic composition of C_3 and C_4 plants. These two plant types differ in the sequence of carboxylation steps leading to the assimilation of CO_2. Plants using the C_3 (Calvin-Benson) mechanism produce compounds depleted in ^{13}C by -24 to -34‰ relative to PDB, whereas plants using the C_4 (Hatch-Slack) mechanism produce compounds depleted by only -10 to -20‰ (O'Leary, 1988). The C_3 uptake mechanism concludes with the carboxylation of ribulose bisphosphate (RuBP), which fractionates carbon by up to -29‰ (Roeske and O'Leary, 1984). The C_4 mechanism similarly utilizes RuBP for the final step in its carboxylation sequence, but a previous step involves the carboxylation of phosphoenolpyruvate (PEP). The carboxylation of PEP, which fractionates carbon by approximately -8 to -12‰, is the rate-limiting step of the carboxylation sequence for C_4 plants (O'Leary, 1988; Meyers and Ishiwatari, 1993a). Nearly all inorganic carbon, regardless of isotopic mass, will be incorporated into organic matter once it passes this threshold step. The isotopic fractionation of C_4 plants is generally less than that of C_3 plants because the smaller kinetic fractionation of PEP is expressed rather than that of RuBP.

The isotopic composition of primary productivity is determined not only by the isotopic fractionation associated with carboxylation of enzymes, but also may be affected by the $\delta^{13}C$ of the inorganic carbon assimilated, and the isotopic fractionation associated with the diffusion of CO_2 through the cell membrane. The diffusion of CO_2 through the cell membrane becomes the rate-limiting step to production if the rate of enzymatic carboxylation exceeds the net rate of transport of CO_2 into the cell, depleting the internal supply of CO_2. Again, the expressed isotopic fractionation primarily reflects the fractionation associated with the rate-limiting step, but in cases where two reactions in a series may be rate-limiting, the expressed fractionation describes the extent to which the reactions jointly share the rate-limiting role. Isotopic fractionation associated with diffusion is much smaller than that of either enzymatic carboxylation, such that an increase in the $\delta^{13}C$ of photosynthetic production may be interpreted as the increased importance of diffusion as the rate-limiting step (O'Leary, 1988).

The concentration of dissolved CO_2 within a cell is a function of the rate of diffusion of CO_2 into the cell, the rate of leakage of CO_2 out of the cell, and the rate of assimilation of CO_2 into the biomass (Fogel and Cifuentes, 1993; Hayes, 1993). Low levels of CO_2 external to the cell result in a reduced rate of diffusion of dissolved CO_2 into the cell, which limits the rate at which CO_2 is assimilated and reduces the degree of isotopic discrimination. The degree to which the availability of CO_2 is rate limiting in plants has been mathematically modelled by Farquhar et al., (1982), and Hayes (1993) as

$$\delta^{13}C_{algae} = \delta^{13}C_{atm} + a + (b - a)(C_i/C_e) \qquad \text{(eq. 1)}$$

where *b* is the fractionation attributed to carboxylation of the enzyme, and *a* is the small fractionation (-4.4‰) associated with the transport of CO_2 across the cell membrane. The term C_i/C_e, where C_i and C_e are the respective internal and external concentrations of CO_2, describes the flux of CO_2 into and out of the cell, and incorporates both the availability and the rate of diffusion of CO_2. If CO_2 is abundant, $C_e = C_i$, and the carboxylation fractionation (*b*) is fully expressed. If CO_2 becomes depleted, the rate of carboxylation may exceed the rate of diffusion, such that any internal CO_2 is utilized regardless of isotopic mass. As C_i/C_e approaches zero, photosynthetic fractionation approaches the fractionation associated with diffusion (Fogel and Cifuentes, 1993).

1.3.2. Isotopic fractionation in phytoplankton

The depletion of CO_2 becomes particularly pronounced in aquatic systems, in which the concentration of aqueous CO_2, and subsequently the $\delta^{13}C$ of phytoplankton, fluctuates based on biological demand and solubility of CO_2 (Stuvier, 1975; Fontugne and Duplessy, 1978; Rau et al., 1989; Hollander and McKenzie, 1991; Ho and Meyers, 1994). In aquatic production, full enzymatic fractionation becomes partially reduced by the degree to which the availability of CO_2 limits the rate of reaction. During periods of high productivity, aqueous CO_2 may become depleted, resulting in increased, or less negative $\delta^{13}C$ values. Enhanced CO_2 demand in eutrophic lakes might, therefore, be recorded in the phytoplankton community of the lake, and their sedimentary molecular remains. The degree of photosynthetic fractionation and its relation to aqueous CO_2 has been useful in the reconstruction of paleo-pCO_2 levels

(Jasper and Hayes, 1990; Rau et al., 1991; Freeman and Hayes, 1992). The expectation that changes in trophic status may be preserved in the isotopic composition of organic sediments may be inferred from the results of such studies.

Recent evidence suggests that growth rates of phytoplankton may provide an improved predictor of algal $\delta^{13}C$ values (Fry and Wainwright, 1991; Laws, 1995). The $\delta^{13}C$ of phytoplankton has also been related to the species composition of the phytoplankton biomass, climate, the active transport and assimilation of dissolved CO_2 and HCO_3^-, and other factors (Stuvier, 1975; Gearing et al., 1984; Descolas-Gros and Fontugne, 1990; Takahashi et al., 1990; Falkowski, 1991; Fogel and Cifuentes, 1993; Goericke et al., 1994). Future research may further establish relationships between these parameters and the availability of aqueous CO_2, or describe and discriminate between the causes of isotopic fractionation in phytoplankton.

1.3.3 Photosynthetic fractionation of inorganic carbon in lakes

Preferential assimilation of ^{12}C into the organic constituents of phytoplankton increasingly enriches the remaining pool of aqueous CO_2 in the heavier isotope. The $\delta^{13}C$ of photosynthetically produced organic matter will therefore increase not only because of reduced photosynthetic fractionation, but also because of the reduced availability of the lighter isotope (Deuser, 1970; McKenzie, 1986; Shemesh et al., 1993). The isotopic composition of the inorganic pool is reflected in the isotopic composition of carbonate precipitates. Changes in the $\delta^{13}C$ of carbonate precipitates have previously been used to provide an indication of productivity in lacustrine environments (Schelske and Hodell, 1991; Hollander and McKenzie, 1991).

Calcium carbonate is formed in the epilimnion of lakes as microbial tests of microorganisms, and as a biogenically induced precipitate. As CO_2 is depleted from the epilimnion through uptake by photosynthesizers, disequilibrium occurs in the bicarbonate-carbonate buffer system. As pH rises, $CaCO_3$ is precipitated, often nucleating on algae (Stabel, 1986). Carbonate sediments are basically in isotopic equilibrium with the inorganic carbon from which they are formed (McKenzie, 1986), but a -8‰ fractionation accompanies the equilibrium between CO_2 and HCO_3^-. The exact magnitude of fractionation is dependent upon temperature, and whether calcite or aragonite is precipitated (Hayes, 1993). The isotopic composition of the inorganic carbon source nonetheless may be approximated from the $\delta^{13}C$ of the carbonate sediments (Jasper and Hayes, 1990; Shemesh et al., 1993), therefore changes in the $\delta^{13}C$ of the carbonate sediments reflect the $\delta^{13}C$ of the dissolved CO_2 utilized by phytoplankton.

Calcium carbonate tends to precipitate in temperate lakes in summer, rather than during the spring bloom when the bulk of the algal matter is precipitated (Lean et al., 1987; Schelske and Hodell, 1991). In such cases, the springtime $\delta^{13}C$ of the dissolved CO_2 carbon source might not necessarily be reflected in summer carbonate precipitates, and the exact magnitude of photosynthetic fractionation may not be accurately calculated.

1.4 Sedimentary Organic Matter

Sedimentary organic matter consists of a complex mixture of lipids, carbohydrates, proteins, and other biochemicals which represent the detritus of biota formerly living in the lake and its watershed (Leenheer et al., 1984; Ho and Meyers, 1993; Meyers and Ishiwatari, 1993b). The type and amount of sedimentary organic compounds is a function of the sources of organic matter in the lacustrine environment, and the diagenetic processes affecting its fate. Organic matter deposited in sedimentary layers forms a geological record of these sources and processes. Variations in the distribution of compounds contained in these sediments may be interpreted as changes in the community structure of the lacustrine environment (Cranwell, 1973; Meyers and Ishiwatari, 1993a).

Terrestrial higher plants and autochthonous phytoplankton comprise the primary sources of organic matter to lakes (Meyers and Ishiwatari, 1993a). The relative proportion of these sources at a given location varies with respect to lake morphology, watershed topography, and the relative abundance of terrestrial and aquatic plants (Meyers and Ishiwatari, 1993a). Secondary sources of organic matter include the microbial biomass, and airborne particles such as pollen (Meyers and Ishiwatari, 1993a). Recent sediments are frequently characterized by petroleum-related compounds, such that anthropogenic sources constitute a small but important source of organic matter (Wakeham and Carpenter, 1976; Giger et al., 1980).

Only a fraction of the organic matter deposited or produced in lakes survives diagenetic alteration to become preserved in the sediments (Eadie et al., 1984). Water-soluble components of primary producers are easily remineralized by bacteria in the epilimnion, greatly reducing the total amount of organic material present (Vallentyne, 1962; Eadie et al., 1984; Meyers and Ishiwatari, 1993b). Hydrophobic compounds tend to remain or become associated with sinking particles, where they are subject to further alteration en route to the sediment-water interface (Parrish et al., 1992; Meyers and Eadie, 1993; Wakeham and Lee, 1993). Once deposited, physical processes such as bioturbation and resuspension continually reexpose the organic matter to microbial reworking (Leenheer et al., 1984). Below the oxic/anoxic boundary, anaerobic bacteria continue the decomposition process (Meyers and Ishiwatari, 1993a).

The collection of processes affecting the fate of organic compounds during deposition, burial, and low temperature sedimentation is known as diagenesis. The degree of diagenetic alteration in a lacustrine environment is a function of the oxicity of the sediment, the degree of bioturbation, the microbial community, and the rate of deposition of sinking particles (Leenheer et al., 1984). The rate of diagenetic alteration of organic matter is compound-specific, as easily oxidizable substituent groups are preferentially degraded. As a result, less reactive compounds become dominant in sediments, and more reactive compounds are preferentially reutilized and remineralized (Meyers and Ishiwatari, 1993a; deLeeuw and Largeau, 1993). Relative to compounds from aquatic sources, terrestrially-derived compounds are generally more resistant to diagenetic alteration, and subsequently the ratio of terrestrial to aquatic compounds increases with depth in sediments (Cranwell, 1984; Meyers and Ishiwatari, 1993a).

Molecules which resist alteration, and are derived from known biological origins, are referred to as biological markers, or more commonly, biomarkers (Peters and Moldowan, 1993). These compounds assist in the identification of source organisms, the reconstruction of paleoenvironmental conditions, and the subsequent diagenetic and thermal history of sediments (Summons, 1993). Lipids as a group tend to be more resistant to alteration relative to carbohydrates and proteins, and thus have found particular utility in paleolimnological studies (Kemp and Johnston, 1979).

1.4.1 Bulk organic indicators of source and diagenesis

Elemental abundances have been widely used as indicators of source and diagenesis. The relative contributions of terrestrial and aquatic sources of sedimentary organic matter may be discerned using the ratio of organic carbon to organic nitrogen. Phytoplankton are high in nitrogen rich proteins, while lacking cellulose. Consequently the organic C/N of phytoplankton typically ranges between about 4 and 10 (Muller, 1977; Ostrom, 1989; Meyers and Ishiwatari, 1993a). Terrestrial plants have a higher cellulose and lower protein content, and therefore C/N ranges between 14 and 30, to as high as 100 (Godell, 1972; Ostrom, 1989; Meyers and Ishiwatari, 1993b). Fluctuations in C/N may be indicative of changes in the relative contributions from these sources (Ho and Meyers, 1994). An increase in the C/N with depth is generally indicative of preferential diagenetic loss of aquatic, nitrogen rich compounds (Muller, 1977; Macko et al., 1993)

The isotopic composition of organic carbon may also be used to provide information regarding the various sources of organic matter. Terrestrially-derived organic matter tends to be isotopically lighter than aquatic production, although the range of values for these two reservoirs varies widely (Meyers and Benson, 1988; O'Leary, 1988). Consequently, variation in the $\delta^{13}C$ of sedimentary organic matter may indicate a change in the relative contributions from terrestrial and aquatic sources, or a change in the $\delta^{13}C$ of the terrestrial or aquatic organic material. An increase in the $\delta^{13}C$ of terrestrial compounds may be related to an increase of C_4 relative to C_3 vegetation in the watershed (Sackett et al., 1986; Bourbonniere et al., 1991).

In some sedimentary environments, diagenetic alteration affects the $\delta^{13}C$ of organic matter. The $\delta^{13}C$ of the organic sediments may become increasingly heavier during reprocessing, as isotopically light CO_2 and CH_4 is preferentially respired by microorganisms (Hayes, 1993). Preferential preservation of less reactive compound classes could also affect $\delta^{13}C$ values, as the $\delta^{13}C$ of compounds which comprise sedimentary organic matter varies widely (Spiker and Hatcher, 1984). In lacustrine sedimentary environments with low organic carbon content, however, the $\delta^{13}C$ of organic sediments does not seem to be significantly affected by diagenesis, as most of the alteration occurs during deposition (Rea et al., 1980; Meyers and Eadie, 1993; Meyers and Horie, 1993).

1.4.2. Geolipid indicators of source

Geolipids are operationally defined as the fraction of organic sediments which may be isolated by extraction from sediments using an organic solvent (Meyers and Ishiwatari, 1993a). The low susceptibility of lipids to diagenetic alteration has led to their utilization in a wide range of geochemical studies (Leenheer et al., 1984; Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993a). The lipid fraction in sediments is comprised of a mixture of hydrocarbons including alkanes, alkenes, aromatics, alcohols, steroids, esters, aldehydes, ketones, fatty acids, and carotenoids

(Cranwell, 1982). These compound classes may be partitioned using one of several methodologies outlined in the literature (e.g. Cranwell, 1978; Leenheer et al., 1984). Chromatographic separation of these compound classes, and quantification of individual members of homologous series, has led to the development of several quantitative indexes that may be used to describe the relative magnitude of terrestrial and aquatic sources. Carbon-chain length distribution patterns and odd-even ratios of n-alkanes, n-alcohols, and n-alkanoic acids assist in the assessment of terrestrial, aquatic, microbial, and petroleum sources (Cranwell, 1982; Colombo et al., 1989).

The n-alkane homologous series has found particular utility in sediment studies due to its persistance, abundance, and ubiquity. Distributions of n-alkanes have been reported in marine (Kvenvolden et al., 1987; Sandstrom, 1988), lacustrine (Brooks et al., 1976; Ishiwatari et al., 1980; Meyers et al., 1984; Albaiges et al., 1984), polluted (Wakeham and Carpenter, 1976; Ishiwatari et al., 1994), and pristine (Ho and Meyers, 1994) sediments. Distributions of n-alkanes in the biota and sediments of eutrophic lakes have also been reported (Reed, 1977; Giger et al., 1980). Decay rates of n-alkanes during sedimentation have been investigated, describing patterns of early diagenetic activity (Parrish et al., 1992; Meyers and Eadie, 1993). Sedimentary n-alkanes have also been a common subject of compound-specific isotopic analysis (Kennicutt and Brooks, 1990; Bakel et al., 1994; Collister et al., 1994; Ishiwatari et al., 1994; Lichtfouse et al., 1994; Spooner et al. 1994).

Several n-alkane indexes have been employed to quantitatively describe sources of organic matter, and to assess diagenetic alteration (Columbo et al., 1989). The short/long index (eq. 2) describes the relative contributions from terrestrial and aquatic sources, and the preferential preservation of terrestrially-derived organic matter (Ho and Meyers, 1994). In general, short-chain n-alkanes, primarily n-C_{14}

$$\text{Short/long index} = \frac{nC_{27} + nC_{29} + nC_{31}}{nC_{15} + nC_{17} + nC_{19}} \qquad \text{(eq. 2)}$$

through n-C_{20}, are considered to be derived primarily from aquatic production (Clark and Blumer, 1967; Han and Calvin, 1969; Gelpi et al., 1970). Long-chain n-alkanes (C_{25}-C_{35}) are produced as terrestrial plant waxes (Eglinton and Hamilton, 1967; Cranwell, 1973). Compound-specific isotopic analysis has recently called some of these generalizations into question, however (Collister et al., 1994a; Lichtfouse et al., 1994; Spooner et al., 1994).

The presence of petroleum contamination in sediments, and patterns of diagenetic alteration, may be described by the odd-even preference (Eq. 3; Ho and Meyers, 1994). A predominance of odd-carbon number chains is indicative of naturally produced compounds (Kvenvolden et al., 1987), whereas low or no predominance indicates increasing petroleum contamination, or diagenetic alteration (Colombo et al., 1989; Ho and Meyers, 1994). The dominance of even-numbered n-alkanes has been observed in a few sediments, and is thought to indicate microbial activity (Nishimura and Baker, 1986; Grimalt and Albaiges, 1987; Kennicutt and Brooks, 1990).

$$OEP_i = \frac{C_{i-2} + 6C_i + C_{i+2}}{4C_{i-1} + 4\,C_{i+1}} \qquad \text{(eq. 3)}$$

Compound-specific stable isotopic analysis of n-alkanes has proved useful in sediment studies by providing further information regarding the mechanisms by which organic compounds are formed. The isotopic composition of terrestrial n-alkanes are significantly different from that of n-alkanes produced by phytoplankton, based on the limited supply of CO_2 in aquatic environments (Freeman et al., 1994). Studies have combined lipid distributions and isotopic analysis to describe terrestrial (Reiley et al., 1991; Spooner et al., 1994; Collister et al., 1994a), aquatic (Bakel et al., 1994; Freeman et al., 1994), microbial (Hayes et al., 1990; Collister et al., 1994b), and petroleum (Ishiwatari et al., 1994) origins of sedimentary organic matter.

1.5 Synopsis

The cultural eutrophication and subsequent remediation of Lake Erie offers an opportunity to gain a better insight into the interpretation of sedimentary records. A fraction of the organic compounds produced in Lake Erie and its watershed are deposited and preserved in its sediments. These organic sediments exhibit maximum $\delta^{13}C$ values coincident with the maximum loading of phosphorus to Lake Erie, suggesting that phytoplankton are the primary source of organic matter in the lake, and that the $\delta^{13}C$ of these phytoplankton is related to changes in productivity.

The $\delta^{13}C$ of the organic sediments may also be attributed to changes in the sources of organic matter contributing to the lacustrine environment. Sources of organic matter are assessed using the ratio of organic carbon to organic nitrogen, geolipid abundances, and various n-alkane distribution indexes. Source changes are distinguished from diagenetic alterations through the careful interpretation of geochemical data. Compound-specific isotopic analysis may be used to provide further evidence linking the $\delta^{13}C$ of the sediments with productivity-induced changes in the $\delta^{13}C$ of phytoplankton. Using elemental abundances, compound-class fractions, and n-alkane distributions, variations in the $\delta^{13}C$ of the organic sediments may be assessed with regard to recent changes in the trophic history of Lake Erie.

Methods

2.1. Sample collection and preparation

A box core with a depth of 40 cm was collected from the Eastern basin of Lake Erie in 1982, and sectioned at 1 cm intervals for the top 20 cm, and at 5 cm intervals for the lower 20 cm for this study. Sediment samples were stored wet, but frozen, in glass containers for 12 years prior to analysis. In preparation for analysis, wet sediment samples were freeze-dried for 48 hrs in the original glass containers. Each sample contained approximately 10 g dry sediment. Samples were ground to a uniform grain size using a metal spatula. Dried sediments were stored in a freezer to discourage the readsorption of water and to retard microbial activity.

Sediments were made available for this study courtesy of Dr. Brian Eadie, NOAA Ann Arbor. Approximate ages were calculated using ^{210}Pb dating techniques by John Robbins of the Great Lakes Environmental Research Lab.

2.2 C/N composition and bulk $\delta^{13}C$ analysis

In preparation for elemental and isotopic analysis, inorganic carbon was removed by acidification. Approximately 500 mg of freeze-dried sediment was acidified using 2N HCl to remove carbonate, dried at 45°C, and ground into a fine powder using a metal spatula. Approximately 15 mg of each acidified sample was weighed into an 8 x 5 mm aluminum cup (Microanalysis). Organic carbon and organic nitrogen percent compositions were determined by combustion within a Carlo Erba 1500 elemental analyzer, where the gas abundance was quantified using a calibrated standard. The $\delta^{13}C$ composition of the bulk sediment samples was determined using a Prism stable isotope mass spectrometer (VG Isotech) interfaced with the Carlo Erba elemental analyzer, following the method of Wong et al. (1992).

2.3 <u>Solvent extraction of organic compounds</u>

Unbound hydrocarbons were removed from the sediment matrix by solvent extraction methods. Soxhlet and sonication extraction procedures were compared in this study to assess the efficiency of extraction of organic matter from the sediment matrix. Quartz distilled dichloromethane (Sigma, HPLC grade) was used for the extraction of non-polar and polar compounds in both methodologies.

Sonication utilizes high-energy ultra-sonic waves to break up the sediment matrix and expose particles to the extracting solvent. A Vibracell (Sonics and Materials, Inc.) equipped with a microtip was used for this extraction. Approximately 3 g of sediment and 20 mL of dichloromethane (DCM) were placed in a 100 mL round-bottom flask. The sample was sonicated in a pulsed mode for 5 minutes (P. Meyers, pers. commumnication). After sonication, the entire contents of the flask was transferred to a centrifuge tube and spun for 12 minutes to separate the solvent from the sediment. An IEC Clinical Centrifuge, with a maximum speed of 4450 rpm when equipped with a fixed angle rotor, was used for centrifugation. The solvent and organic extract was pipetted off the top into a 50 mL round bottom flask. Rotoevaporation was used to reduce the volume of solvent to approximately 2 mL. The concentrated solvent was transferred to a small vial and dried under a stream of filtered air.

Soxhlet extraction combines evaporation and condensation in a semi-enclosed system to continuously rinse powdered sediments in clean, hot solvent. A volatile solvent is heated in a round-bottom solvent flask at the base of the apparatus. Solvent vapors are directed through a sidearm, bypassing the extraction vessel in which the sediment sample is contained. The hot vapors are condensed above the extraction vessel, and dripped onto the sediment. The sediment sample is held in a porous cellulose extraction thimble (25 x 80 mm) through which solvent may flow but sediment particles are retained. When the level of solvent in the extraction vessel reaches the level of a sidearm siphon, the solvent and extracted organic matter are drained to the solvent flask. Organic extracts become concentrated in the solvent flask while the solvent continues through repeated cycles of evaporation and condensation.

Extraction thimbles were precleaned with DCM in the extraction apparatus for 4 hours. In the comparison study of soxhlet and sonication extraction procedures, approximately 4 g of Lake Huron sediment was placed in the thimble (8 g of each sample was used for the extraction of the Lake Erie sediments). A total volume of approximately 80 mL of DCM was used in the extraction. The thimble and sediment were moistened with DCM to reduce splashing of the sediment out of the thimble and into the solvent flask. The remaining DCM was placed in the solvent flask. Clean glass beads (Soxhlet extracted for 4 hrs in DCM) were added to the solvent flask to reduce bumping. Sediments were extracted for 7 hours. Following extraction, DCM was removed by rotovaporation until a residual volume of about 2 mL was obtained. The residual 2 mL of solvent and organic extract was dried under a stream of filtered air.

Significantly higher extraction efficiency, combined with minimal sample handling, led to the selection of soxhlet extraction as the chosen method (see Section 3.1 for a comparison of the results).

2.4 Column Chromatography

Separation of organic compound classes was performed by silica gel/alumina column chromatography using a methodology similar to that of Bakel et al. (1994). This method does not result in isotopic fractionation of n-alkanes during separation (Bakel et al., 1994). Hydrocarbons were adsorbed onto silica gel (J.T. Baker, 60-200 mesh) while polar compounds were retained by alumina (Alltech, 60-200 mesh). Three compound classes were isolated from each of 11 samples through the elution with solvents of increasing polarity. Aliphatic compounds, including straight chain, branched, and cyclic alkanes and alkenes, were eluted with 15 mL n-hexane, and aromatic compounds were eluted with 15 mL of a 2:1 hexane/DCM solution. A column wash of 15 mL of methanol eluted the remaining polar compounds. The flow rate for all solvents was 0.5 mL per minute. Acidic compounds such as carboxylic acids were irreversibly retained on the column.

2.4.1 Preparation of silica gel and alumina

During initial tests of the extraction methodology for polar compounds, it was discovered that columns which were not loaded with the extracted organic material (blanks) often eluted a greater abundance of polar material than columns which had been loaded with the organic extract. The origin of this polar material is presumably due to the colloidal suspension of polar silica and alumina particles into the methanol. Filtration of silica gel suspended in methanol revealed that particles smaller than 0.45 μm became suspended in methanol and could be easily transferred to the weighing vial and included in the quantification of the polar fraction. Consequently both the silica gel and alumina were thoroughly cleaned with a methanol (Omnisolve, J. T. Baker) slurry in an attempt to remove fine grained particles. Methanol containing the dissolved particles was decanted and recycled, and replaced with clean methanol. This procedure was repeated 15 times for each resin.

After the silica gel and alumina were dried, the resins were placed into clean scintillation vials, plugged with ashed glass wool, and set in an aluminum foil covered beaker inside the GC oven. Silica gel and alumina were deactivated during the methanol rinse, and had to be reactivated at high temperature to restore its ability to separate molecules on the basis of polarity. Silica gel and alumina used for the separation of Lake Erie sediments were reactivated at 305°C in a GC oven. To minimize the readsorption of water, neither the silica gel nor alumina were removed from the GC oven until the columns were ready to be filled.

2.4.2 Efficiency of compound class separation as a function of activation temperature

Silica gel and alumina resins were activated at 100°C, and at 305°C, to determine the effects of activation temperature on chromatographic separation of compound classes. Two chromatographic columns were constructed, from resins activated at 100°C, and from resins activated at 305°C. A standard solution of three alkanes and one aromatic compound was separated on these columns. The standard solution contained between 5 to 10 μmol each of C_{17}, C_{18}, pristane, and phenanthrene. Phenanthrene is a non-polar tricyclic aromatic compound which closely approximates the weight and retention time of the alkanes used in this experiment. Alkanes were eluted from the columns using n-hexane. At 5 mL intervals, 1 μL of n-hexane eluent was sampled and injected into a GC/MS to test for the presence of phenanthrene in the eluent. The simultaneous elution of phenanthrene and alkanes from the column activated at 100°C indicates that the activation of silica gel and alumina at 305°C provided more efficient separation between aliphatic and aromatic compounds than resins activated at 100°C (see Section 3.2 of results).

2.4.3 Activation of Cu powder

A thin layer of activated purified Cu powder (Fisher) on the silica gel/alumina column was required for the removal of elemental sulfur. Within a few hours of use, approximately 4 g of Cu powder was activated by rinsing with 3N HCl for a few minutes. Excess HCl was decanted, and the Cu was rinsed three times with 20 mL Omnisolve methanol. Excess methanol was decanted, and the Cu dried by warming the beaker in water, and continually stirring the Cu paste until dry. Careful attention was necessary to avoid oxidation of the Cu powder as a consequence of drying the Cu too slowly. If the Cu is oxidized, it cannot be reactivated by the same method.

2.4.4 Chromatographic techniques

Columns consisted of 25 mL glass burets fitted with teflon stopcocks. Ashed glass wool was used to plug the bottom of the buret. The buret was filled with n-pentane (HPLC grade, Sigma). Approximately 1.5 g (4 mL) of silica gel was placed in the buret and allowed to settle for a few minutes. The silica gel was covered with approximately 1.8 g (2 mL) of alumina. A thin layer (0.2 mL) of acid-washed powdered Cu metal (Fisher) was placed on top of the column for the removal of elemental sulfur. Columns remained in pentane overnight to allow additional packing, and to reduce the likelihood of channel development.

Just prior to the introduction of the sample, the packed column was rinsed using the overlying 25 mL of n-pentane. Twelve hours prior to chromatographic separation, the organic extract of the sediment sample was diluted to 2.0 mL with n-hexane. After the extract was loaded onto the column, sample vials were rinsed 3 times with 1 mL of n-hexane (HPLC grade, Sigma) and this material was also introduced to the column. Flow rates were set at approximately 0.5 mL/min. Collection of the eluent began immediately. An additional 10 mL of n-hexane were added to the column to elute the aliphatic fraction with a total of 15 mL n-hexane. Aromatics were eluted from the column by elution with 15 mL of 2:1 hexane/DCM, and the polar compounds were removed with 15 mL of Omnisolve methanol. After collection, solvent was removed from the individual fractions by rotoevaporation to a volume of 2 mL. Concentrated extracts were quantitatively transferred to preweighed, ashed glass vials, and dried under a stream of filtered air.

2.5 Gas Chromatography / Mass Spectroscopy

The abundance and identity of major components of the aliphatic fraction were determined by gas chromatography - mass spectrometry (GC/MS), using an HP 5890 Series II gas chromatograph, fitted with a DB-5 (32 μm i.d. x 25 m) column, and interfaced with an HP 5971 mass spectrometer. Helium was used as the carrier gas and kept at a constant head pressure of 13 Pa. Injector, detector, and transfer line temperatures were all set at 305°C. The GC oven temperature was set at 100°C for 5 minutes, increased at a rate of 5°C per minute to a maximum of 305°C, and held at 305°C for 10 minutes. The mass spectrometer operated in electron impact mode. An initial mass scan of the sedimentary aliphatic fraction from M/Z 30 to 500 provided an identification of each n-alkane based on the presence of the molecular ion. Subsequent analyses for quantification of the concentration of n-alkanes were performed using a mass scan from M/Z 30 to 200. Branched and cyclic alkanes and alkenes were tentatively identified through comparison with literature spectra (Giger et al., 1980; Kvenvolden et al., 1987; Schoell et al., 1994).

2.6 Quantification of unresolved complex mixture and alkanes

Samples of extracted aliphatic compounds were diluted with 250 μL of n-hexane spiked with 0.05 nmol/μL phenanthrene. Injections of 1 μL were made into the column. Phenanthrene was used as an internal standard, such that the concentration of sample peaks was quantified relative to the phenanthrene peak.

The mixture of compounds that did not produce individual peaks but contributed to a rise in baseline during GC/MS analysis is referred to as the unresolved complex mixture, or UCM. The absolute concentration of UCM was not calculated due to differences in the response of MS detector for phenanthrene, and the variety of molecules comprising the UCM. The relative abundance of UCM was calculated, however, by establishing the area under the baseline relative to the peak area of the phenanthrene internal standard in each sample, and then by comparing the ratio of UCM:phenanthrene in each sample, relative to the sample with the largest ratio. The area under the baseline was limited to between 10 minutes and 50 minutes. The area under the baseline, and the peak area of phenanthrene was approximated by enlarging the chromatograms to a standard scale and display size, and cutting out and weighing the paper beneath the curves.

A series of standards, each containing 0.05 nmol/μL phenanthrene, was used for the purpose of quantification of n-alkanes in the sedimentary extract. Four standards of known concentrations were used to calculate a linear regression to which known concentrations of various n-alkane standards could be compared. Each standard contained eight even-numbered n-alkanes (C_{18}, C_{20}, C_{22}, C_{24}, C_{26}, C_{30}, C_{34}, C_{36}). Regression equations were developed that describe the relationship between n-alkane concentration, in terms of the ratio of n-alkane peak area to phenanthrene peak area. The results of these regressions are summarized in Appendix B1. Regression equations vary in slope because the response of the MS detector varies according to the chain length of the n-alkanes. For n-alkanes present in sediment samples, but not available as standards, the regression equation of the most similar n-alkane was used for quantification (Appendix B2).

The results of the regression equations needed to be corrected to account for incomplete recovery of individual n-alkanes during silica gel/alumina column chromatography. The percent recovery of n-alkanes was quantified using a 0.4 nmol/μL n-alkane standard. A 0.5 mL aliquot of the 0.4 nmol/μL standard was pipetted onto each of two columns, prepared with silica gel and alumina as previously described. The compounds were eluted, concentrated, dried, redissolved, and injected into the GC/MS as previously described. Integrated GC/MS peaks were quantified using calculated regression lines. The percent recovery of the individual n-alkane standards are summarized in Section 3.3. The corrected concentration of individual sedimentary n-alkanes was calculated by adding the amount of n-alkanes injected onto the column, to the amount of n-alkanes lost on the silica gel/alumina column.

Results of Method Development

3.1 <u>Sonication vs. soxhlet extraction</u>

The efficiency of sonication and soxhlet extraction techniques were compared previous to the solvent extraction of organic matter from the Lake Erie sediment samples. Triplicate analysis of a Lake Huron surficial sediment demonstrated that soxhlet extraction consistently extracted a greater mass of total organic matter, and aliphatic hydrocarbons than did sonication (Table 1). An average of 1.51 $\pm$ 0.10 mg of organic material was extracted per gram of dry Lake Huron surficial sediment by soxhlet extraction, but only 0.92 ± 0.05 mg/g of dry sediment was extracted by sonication. Similarly, 0.35 ± 0.06 mg of aliphatic compounds per gram of dry sediment were extracted by soxhlet extraction, but only 0.28 ± 0.01 mg/g of dry sediment were extracted by sonication. Previous studies have also favored soxhlet extraction over sonication (Weaver, 1988; Brillis and Marsden, 1990).

3.2 Activation of silica gel and alumina

Based on the separation of n-C_{17}, n-C_{18}, pristane, and phenanthrene, the activation of silica gel and alumina at 305°C led to better separation of aromatic from aliphatic hydrocarbons than activation at 100°C (Table 2). The alkanes n-C_{17}, n-C_{18}, and pristane were present, and phenanthrene was absent, in both the 0 - 5 ml and the 5 - 10 mL eluent fractions of columns activated at both 100°C and 305°C. Small alkane peaks persisted in the 10 - 15 mL eluent fraction collected from the column using silica gel and alumina activated at 100°C, but no alkanes were eluted from the column constructed from silica gel and alumina activated at 305°C. A trace molecular ion peak at $M^+ = 178$ indicated the presence of phenanthrene in the eluent fraction from both columns. In the 15 - 20 mL eluent fraction of the column activated at 100°C, a pronounced molecular ion of phenanthrene was present, and alkane peaks persisted. The 15 - 20 mL eluent fraction from the column activated at 305°C contained a minimal phenanthrene molecular ion, and no trace of the alkanes.

3.3 Sample Recovery

The percent recovery of n-alkane standards from the silica gel/alumina column varies with chain length (Table 3). The shortest n-alkane standard, C_{18}, exhibits the lowest percent recovery at 75%, whereas long-chain n-alkanes (C_{34}, C_{36}) are nearly quantitative in their recovery. The loss of low molecular weight n-alkanes is attributed in part to higher vapor pressures of these compounds relative to high molecular weight n-alkanes, which result in their preferential vaporization during concentration of the sample. In addition, low molecular weight n-alkanes may be retained on the silica gel/alumina column. The absence of n-alkanes in the eluent beyond 15 mL (see Section 3.2) suggests that if short-chain n-alkanes are retained on the column, they are irreversibly bound, and that no memory effect is present during column chromatography.

Experimental Results

Sedimentary organic matter recovered from Lake Erie was characterized by: 1) the elemental and isotopic composition of the bulk organic fraction, 2) the concentration of total hydrocarbons extracted from the sediment, and the abundance of aliphatic, aromatic, and polar compound classes contained therein, and 3) the distribution and concentration of n-alkanes, isoprenoid alkanes, and unresolved compounds within the aliphatic fraction. Sediment samples from various depths were used to determine the primary sources of organic matter contributing to the lacustrine environment, and to evaluate early diagenetic activity within the sediments. Source and diagenetic information was used to provide a basis for attributing changes in the $\delta^{13}C$ content of the sediments.

4.1 Sedimentation rate and mixed depth

The age-depth relationship of the core was calculated using ^{210}Pb dating techniques (Robbins and Edgington, 1975; Eisenreich et al., 1989). The bottom of the core was calculated to have been deposited in 1968, fourteen years prior to collection of the core (Figure 3, Table 4). The mixed depth was calculated to have been 10.5 cm, equivalent to a cumulative weight of 2.84 g/cm^2. The mass sedimentation rate was determined to have been 0.88 g/cm^2/yr, much higher than previously reported estimates from the eastern basin (Mortimer, 1987; Robbins et al., 1989).

Maximum values of ^{210}Pb activity in the sediment core occured at depths between 6 and 11 cm. In the absence of sediment mixing, the highest ^{210}Pb activity occurs at the sediment-water interface, and decreases with depth. The pattern of ^{210}Pb activity is suggestive of selective feeding patterns by benthic animals such as oligochaete worms (Matisoff and Robbins, 1987). Oligochaete worms are common in the upper 15 cm of Lake Erie sediments, and are a likely organism responsible for the observed sediment mixing (McCall and Fisher, 1979; Fisher et al., 1980; McCall and Tevesz, 1982; Robbins et al., 1989).

4.2 Removal of elemental sulfur

Elemental sulfur was removed as CuS from the aliphatic fraction of sedimentary organic compounds to avoid co-elution with n-alkane peaks during GC/MS separation. Sulfur was present in samples taken from 11 cm and below, but removed as CuS, as evidenced by a black coating of CuS on the activated Cu powder. The presence of elemental sulfur approximates the depth of the oxic/anoxic boundary. The co-occurence of the bottom of the mixed layer with the presence of sulfur suggests that sediments in the mixed layer remain oxic due to bioturbation.

4.3 Elemental Abundance

Carbon and nitrogen elemental abundances of the organic sedimentary fraction are reported as percent organic carbon and percent organic nitrogen relative to total sedimentary material, and as C/N (Figures 4, 5, 6). The range in percent organic carbon is small (2.04% to 2.47%), with an average of 2.26 ± 0.11%. The depth profile for percent organic carbon is characterized by a series of maxima and minima, with maxima occuring approximately every four samples. Percent nitrogen ranges between 0.241% and 0.311%, with an average of 0.274 ± 0.016%. The depth profile of percent organic nitrogen is also characterized by a similar series of maxima and minima. Comparison of the trends in percent organic carbon and percent organic nitrogen shows that maxima and minima co-occur in most instances. The ratio of organic carbon to organic nitrogen averages 9.60 ± 0.38. The organic C/N profile is not characterized by series of maxima and minima.

Procedural reproducibility for elemental analysis was established through the triplicate analysis of a Lake Superior surficial sediment sample (Table 5). The precision was determined to be ± 0.06 and ± 0.02 for percent organic carbon and nitrogen, respectively. Error associated with the measurement of percent organic carbon and nitrogen is propagated in the calculation of C/N. The propagated error[2] associated with C/N is calculated as ± 0.58.

Net depletion of organic matter in older sediments relative to surficial sediments is an indicator of microbial remineralization of organic carbon and nitrogen. There appears to be no trend in percent organic carbon as proceeding from the bottom to the top of the core. Values of percent organic nitrogen increase slightly from the bottom to the top of the core. Differences in both percent organic carbon and percent organic nitrogen between maxima and subsequent minima are the most striking feature of the data. The significance of these differences was considered using procedural reproducibility. If a criteria of 2σ was established to statistically discriminate between two points, several of the differences between maxima and subsequent minima in percent organic carbon and nitrogen are significant. The largest difference in percent organic carbon between a minimum and the next subsequent maximum is 0.30%, five times greater than the precision. The largest difference in percent organic nitrogen between a minimum and the following maximum is 0.054%, exceeding the precision by a factor of three.

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[2]Propagated error for a quotient is calculated by adding in quadrature the fractional uncertainties associated with two independent measurements,

$$\delta q/q = [(\delta c/c)^2 + (\delta n/n)^2]^{1/2} \qquad \text{(Taylor, 1982)}$$

in which δx is the uncertainty associated with the measured value x.

4.4 Carbon isotopic composition of the bulk organic sedimentary fraction

The $\delta^{13}C$ composition of sedimentary organic matter extracted from Lake Erie generally exhibits a trend of ^{12}C enrichment through the 1970's (Figure 7). The maximum $\delta^{13}C$ value of -24.9‰ was recorded in sediments deposited in 1970, two years following the maximum phosphorus loading to Lake Erie (Fraser, 1987; Rosa, 1987), and again in 1977. The minimum $\delta^{13}C$ value of -25.9‰ is recorded in sediments deposited in 1981.

The $\delta^{13}C$ depth profile is characterized by a series of maxima and minima at intervals of 3 - 4 cm. These variations do not co-occur with the maxima and minima exhibited by percent organic carbon and nitrogen. The criteria of 2σ was again used to consider statistical significance of variability in the data. Procedural reproducibility was established as 0.2‰ through $\delta^{13}C$ analysis of Lake Superior surficial sediment (Table 8). The largest difference in $\delta^{13}C$ values between maxima and subsequent minima (0.7‰) exceed the procedural reproducibility by more than 3σ, indicating that variations in the $\delta^{13}C$ content of the sediments may be significant.

4.5 Total extractable hydrocarbons

The amount of organic material extracted from Lake Erie sediments samples varied within a small range (1.14 $\pm$ 0.09 mg/g dry sediment) between 1978 and the top of the core (Figure 8). Sediments deposited during 1976-1977 contained as high as 2.07 mg/g dry sediment, nearly twice the amount extracted from the most recent sediments. Procedural reproducibility was established by triplicate analysis of a Lake Huron surficial sediment, which yielded an average of 1.15 $\pm$ 0.07 mg/g dry sediment (Table 6).

4.6 Geolipid compound classes

Chromatographic separation of the organic extract yielded three fractions containing aliphatic, aromatic, and polar compounds (Figures 9a, b, c). All three organic fractions exhibited a loss of mass in the upper five centimeters of the core that was likely due to early diagenetic degradation. The aliphatic fractions contained an average of 0.29 $\pm$ 0.07 mg/g dry sediment, the aromatic fractions an average of 0.15 $\pm$ 0.03 mg/g dry sediment, and the polar fractions an average of 0.41 $\pm$ 0.07 mg/g dry sediment.

4.7 Unresolved complex mixture

The size of the UCM provides an indication of the abundance of branched and cyclic aliphatic compounds present in the sediments (Giger et al., 1980). The concentration of these unresolved compounds is greatest at the bottom of the core, a consequence of the diagenetic alteration of primary molecules to branched and cyclic compounds. Maxima in the concentration of the unresolved compounds occur during 1970 and 1979 (Figure 10).

4.8 Normal and branched alkane abundances

Eighteen n-alkanes (C_{14}-C_{31}) and two branched alkanes (pristane and phytane) were separated, identified, and quantified using GC/MS. Absolute abundances are reported in μg/g of sediment. Normalized abundances are reported relative to the n-alkane of highest concentration. Hydrocarbon indexes quantify the relative distribution of short to long n-alkanes, and odd to even n-alkane chain lengths.

The absolute and normalized distributions of n-alkanes may be described as bimodal distributions, which are generally characteristic of sediments with mixed terrestrial and algal sources of organic matter (Giger et al., 1980; Ho and Meyers, 1993). In terms of absolute abundance, heptadecane (C_{17}) is the most abundant n-alkane in the distribution, followed by C_{29} or C_{31} as the secondary mode (Figures 11a-d). Normalized abundances of n-alkanes generally exhibit the same pattern as absolute abundances (Figures 12a-d). In general, the absolute abundance of short-chain n-alkanes (C_{14} - C_{20}) tends to increase from the bottom to the top of the sediment core, but the abundance of mid (C_{21}-C_{24}) and long- (C_{25}-C_{31}) chain n-alkanes tends to remain constant.

Hydrocarbon indexes quantitatively describe changes in the distribution of n-alkanes that occur with depth in the sediment core. The odd-even preference (eq. 2, Figure 13), is a ratio of odd to even chain length n-alkanes, calculated as a running average over a range of five consecutive hydrocarbons (Ho and Meyers, 1994). The odd-even preference (OEP) approaches unity as n-alkanes are increasingly altered through diagenetic activity, or as petroleum becomes an increasingly large fraction of sedimentary organic matter. Values of >1.0 are generally indicative of primary production, either algal or terrestrial (Ho and Meyes, 1994). Values of < 1.0 have been associated with bacterial assemblages in marine sediments (Kennicutt and Brooks, 1990). The OEP ranges from a maximum of 10.57 for a distribution centered around C_{29}, to a minimum of 1.17 for a distribution centered around C_{20}. The highest OEP values are centered around C_{17} and C_{29}, the dominant n-alkanes for the algal and terrestrial portions of the distributions.

The ratio of short to long chain lengths compares the absolute abundance of three algal n-alkanes (C_{15}, C_{17}, C_{19}) to three terrestrial n-alkanes (C_{27}, C_{29}, C_{31}), providing an approximate ratio of algal to terrestrial sources of organic matter (Figure 14). A short/long index of < 1.0 indicates a predominance of terrestrial n-alkanes, whereas a ratio of > 1.0 indicates primarily algal compounds. The ratio increases abruptly over time from an average of 0.92 ± 0.11 for the seven samples at 11 cm and below, to an average of 1.48 ± 0.15 for the four samples at 10 cm and above. The increase of algal n-alkanes relative to terrestrial n-alkanes indicates either a sudden change in the sources of organic matter, or a difference in the nature of diagenetic processes operating above and below the mixed depth. The abundance of pristane tends to increase over time, from a minimum of 0.36 μg/g of dry sediment at the bottom of the core, to a maximum of 2.19 μg/g at the top. The concentration of phytane remains relatively constant over time, averaging 0.26 ± 0.09 μg/g of dry sediment (Figures 15a, b).

Discussion

The previously observed temporal relationship between historical phosphorus loadings and the $\delta^{13}C$ content of bulk organic sediments suggests that a record of trophic status is preserved in the $\delta^{13}C$ content of lake sediments (Schelske and Hodell, 1991). Changes in $\delta^{13}C$, however, may be attributed to changes in source, as well as diagenetic alterations of organic matter deposited in the lake. The objective of this discussion is to describe the sources of organic matter contributing to the depositional environment, and to document evidence of early diagenetic alteration of the organic sediments. Elemental, isotopic, and molecular data indicate that source changes and diagenesis play a limited role in altering the $\delta^{13}C$ content of organic sediments deposited between 1968 and 1982.

5.1 Sedimentation rate and mixed depth

The high sedimentation rate at this site in the eastern basin of Lake Erie permits excellent resolution in the upper 20 cm of the core, such that as many as four 1-cm samples are associated with one year of sediment deposition. The mixed depth of the core, at approximately 10.5 cm, was slightly greater than the average depth of bioturbation in the Great Lakes (Robbins and Edgington, 1975). The detection of elemental sulfur in sediments below the mixed depth suggests that sulfate-reducing bacteria were active below 10 cm.

Series of maxima and minima in the percent organic carbon, percent organic nitrogen, and the organic $\delta^{13}C$ content indicate that the sediment core is not homogenized by sediment mixing processes. Rather, it is likely that benthic feeders such as oligochaete worms mix sediment in such a manner that features within the sedimentary record are preserved. Tubificid oligochaetes selectively feed on organic rich sediments, consuming bacteria associated with organic particles (Brinkhurst and Austin, 1979; Robbins et al., 1989). Sediments are ingested by oligochaetes at depth, and excreted at the sediment-water interface. Selective feeding on organic material will tend to concentrate organic compounds in the form of fecal pellets at the sediment surface (Matisoff and Robbins, 1987). The rate of advection of buried sediments to the sediment-water interface is exceeded, however, by the sedimentation rate in the eastern basin of Lake Erie (McCall and Fisher, 1979). The high sedimentation rate, combined with selective feeding patterns, is most likely responsible for the high resolution present in this sediment core.

5.2 Elemental Abundances

The organic carbon and nitrogen content of sediments provides an information regarding the sources of organic matter, and the degree of diagenetic alteration of the organic sediments. Diagenetic activity, such as the microbial remineralization of organic matter, tends to reduce the amount of organic carbon and nitrogen preserved in sediments. Rates of diagenetic alteration, however, are compound-specific, as labile compounds such as carbohydrates are preferentially degraded (Meyers and Ishiwatari, 1993a). Despite the diagenetic alteration of the organic contents of sediments, the ratio of organic carbon to organic nitrogen has often provided a good indicaton of the sources of organic matter contributing to lacustrine environments.

Elemental abundances of 2.26 $\pm$ 0.11%, and 0.274 $\pm$ 0.016% (Figures 4, 5) for organic carbon and nitrogen, respectively, are relatively high compared with marine sediments, low for lacustrine sediments, but typical for large, deep lakes such as the Laurentian Great Lakes (Meyers and Horie, 1993). The low organic content of Lake Erie is consistent with earlier studies of Lake Michigan, in which the abundance of autochthonous and allochthonous organic matter is significantly reduced, to varying degrees, during deposition (Meyers and Eadie, 1993). The absence of significant change in percent carbon, and the simultaneous increase in the nitrogen content between the oldest and youngest sedimentary layers, suggests that labile, nitrogen-rich compounds are more susceptible to alteration relative to carbon-rich compounds. In general, aquatic compounds tend to be more labile, with lower carbon contents, than terrestrial compounds (Meyers and Ishiwatari, 1993a). The preferential loss of labile components typically leads to depositional records biased in favor of terrestrial organic matter (Cranwell, 1984; Canuel and Martens, 1993).

The series of maxima and minima in percent organic carbon and nitrogen appear significant, as differences between maxima and subsequent minima exceed the precision associated with elemental analysis. The origin of the variation could be related to changes in rates of primary productivity, deposition, degradation of organic matter, or variation in inorganic inputs (Canuel and Martens, 1993). The vertical flux of hydrophobic organic matter in the Great Lakes is related to the types and amounts of sedimenting particles. Seasonal variability determines the types and amounts of the particles, derived primarily from shoreline erosion, biotic production, and resuspension (Baker and Eisenreich, 1989). Wide variations in percent organic carbon and percent organic nitrogen may, therefore, represent seasonal and time-integrated changes in the nature of sedimenting particles.

The organic C/N content of sediments is used to provide an indication of terrestrial and aquatic productivity (Meyers and Ishiwatari, 1993a). The organic C/N of Lake Erie sediments averages 9.62 ± 0.38, suggesting that the sediments are dominated by autochthonously-produced organic matter (Figure 6). A mass balance approach may be used to approximate the relative magnitude of aquatic and terrestrial contributions to organic sediments. For a conservative estimate of algal contributions to Lake Erie, average C/N for phytoplankton and land plants are assumed to be 6 and 20, respectively (Meyers and Ishiwatari, 1993a). Using these estimates, it is calculated that phytoplankton contribute approximately 74% of the organic matter to the sediments. Based on these calculations, algae may be inferred to be the primary source of organic matter in Lake Erie, and terrestrial plants are inferred to constitute a secondary source of organic material.

The slight apparent decrease in C/N values between the bottom and the top of the core does not appear to be significant, given that the variation is less than 2σ. The absence of significant variation in C/N between the top and the bottom of the sediment core indicates that there is no evidence for a change in the relative proportion of terrestrial and algal sources of organic matter between 1968 and 1982.

5.3 Carbon isotopic composition of bulk organic sediments

The $\delta^{13}C$ content of the organic sediments of Lake Erie exhibits a trend of increasing enrichment of ^{12}C toward the present (Figure 7). The trend in ^{12}C enrichment is consistent with the findings of previous Great Lakes studies (Schelske and Hodell, 1991; Bourbonniere et al., 1991). The isotopically heaviest organic carbon is present in sediments deposited in 1970, two years following the maximum loading of anthropogenic phosphorus to Lake Erie (Fraser, 1987). Between 1970 and 1982, organic matter deposited on the bottom of the lake has become isotopically lighter, coincident with previous records of phosphorous reductions (Fraser, 1987;

Rosa, 1987).

Sediment $\delta^{13}C$ values between -25.9‰ and -24.9‰ are consistent with a mixture of aquatic and terrestrial sources of organic matter, although the relative contributions of terrestrial and aquatic sources cannot be quantified. Freshwater algae generally have $\delta^{13}C$ values of -25 to -28‰, within the range of $\delta^{13}C$ values associated with land plants of approximately -25 to -30‰ (O'Leary, 1988; Meyers and Ishiwatari, 1993a; Fogel and Cifuentes, 1993). Isotope ratios consequently cannot be used to quantify the relative contributions of organic matter from aquatic and terrestrial sources in Lake Erie.

Possible explanations for the enrichment of ^{12}C in Lake Erie sediments deposited during the early 1980's include a change in the relative size of algal and terrestrial contributions of organic matter, and the preferential remineralization of isotopically light carbon compounds. If the $\delta^{13}C$ content of the bulk organic sediments is primarily a function of the sources of organic matter, then variations in $\delta^{13}C$ values should correspond to a changes in C/N. If $\delta^{13}C$ values are affected by diagenetic alteration, evidence of diagenetic activity, such as trends in percent organic carbon and nitrogen proceeding from the bottom to the top of the core, should be apparent. Downcore decreases in percent organic carbon and nitrogen were not observed, and therefore suggest that early diagenesis was not a dominant factor controlling the elemental or isotopic content of the sediments.

When considered together, elemental and isotopic evidence suggests that the change in the $\delta^{13}C$ content of bulk organic sediments is not associated with a change in source. If the shift in $\delta^{13}C$ values were related to a source change, a correlation should exist between $\delta^{13}C$ and C/N (Meyers and Benson, 1988). Organic C/N and $\delta^{13}C$ values show no such correlation ($r^2 = 0.04$). The absence of change in C/N between the bottom and the top of the core suggests that the relative contributions of autochthonous and allochthonous material has remained constant.

The possibility remains that the $\delta^{13}C$ shift may be related to recent changes in the proportion of C_3 vs. C_4 plants in the watershed of Lake Erie. Terrestrial C_3 plants are isotopically lighter than C_4 grasses (O'Leary, 1988). An increase in the contribution from C_3 plants relative to C_4 vegetation could therefore lead to the progressive depletion of ^{13}C in sediments (Sackett et al., 1986). Compound-specific isotopic analysis of long-chain, terrestrial n-alkanes could be used to relate possible changes in the $\delta^{13}C$ content of organic sediments to changes in watershed vegetation patterns (Collister et al., 1994a; Spooner et al., 1994).

The absence of correlation ($r^2 = 0.14$) between percent organic carbon and $\delta^{13}C$ values supports the interpretation that the shift in $\delta^{13}C$ composition is not related to diagenetic activity. The trend of ^{12}C enrichment between 1970 and 1982 could be explained in terms of the preferential remineralization of isotopically light carbon, such that surficial sediments undergo the least alteration, retaining more ^{12}C and giving the appearance of ^{12}C enrichment. No evidence of ^{12}C remineralization, however, is provided by the percent organic carbon profile, as the oldest sediments do not differ significantly from the youngest in percent organic carbon content.

Previous studies have also indicated that diagenesis does not significantly alter the $\delta^{13}C$ of organic sediments containing typically low (< 2-3%) concentrations of organic carbon (Jasper and Hayes, 1990; Fontugne and Calvert, 1992; Meyers and

Horie, 1993). Based on this generalization, the low carbon content of the Lake Erie sediments (2.26 ± 0.06) suggests that diagenesis has little effect on the $\delta^{13}C$ content of the sediments.

The absence of a change in source, and the lack of evidence concerning the remineralization of isotopically light carbon, supports the theory that the $\delta^{13}C$ content of the bulk organic sediments reflects the $\delta^{13}C$ composition of the predominant source of organic matter, namely algae. The overall shift in $\delta^{13}C$ values suggests that the $\delta^{13}C$ content of autochthonous production has changed between 1970 and 1982. Significant variations in the $\delta^{13}C$ content of the core may be related to seasonal or interannual changes in the source, type, and amount of sedimenting particles, which affects the nature of the organic matter delivered to the sediments (Baker and Eisenreich, 1989). Maximum values in the $\delta^{13}C$ content of the sediments may also reflect periodic influx of organic matter from the central basin of the lake, which is more eutrophic than the eastern basin (Burns, 1985).

5.4 Total extractable hydrocarbons

The concentration of total extractable hydrocarbons in the sediments of Lake Erie remained constant throughout the upper 16 cm of the sediment, averaging 1.14 ± 0.09 mg/g dry sediment (Figure 8). Below 16 cm, in sediments deposited during 1976-1977, higher concentrations of organic matter were extracted, reaching a maximum of 2.07 mg/g dry sediment. The significant peak in total extractable hydrocarbons did not coincide with an increase in aliphatic, aromatic, or polar compounds. The increase in organic matter could represent an increase in terrestrial erosion into the lake, as erosion of shoreline bluffs could have delivered a large amount of highly refractory terrestrial organic material to the lake.

5.5 Abundance of aliphatic, aromatic, and polar compounds

The concentration of aliphatic, aromatic, and polar compounds in the sediments remains nearly constant throughout the core, with the exception of the top 5 cm of sediment (Figures 9a, b, c). Within the top 5 cm, the concentration of each of these compound classes increases toward the surface, and indicates the diagenetic loss of labile, predominantly aquatic compounds in surficial sediments.

5.6 Relative concentration of unresolved complex mixture

The relative concentration of the UCM indicates that diagenesis has altered the distribution of compounds within the aliphatic fraction (Figure 10), even if there is no apparent decrease in the absolute concentration of aliphatic compounds (Figure 9a). The relative magnitude of the UCM decreases between the bottom and the top of the core, consistent with the limited diagenetic alteration of the surficial sediments. Deeper sediments tend to be characterized by larger concentrations of branched and cyclic hydrocarbon compounds, as diagenetic alteration of organic matter decreases the ratios of O/C and H/C with time (Peters and Moldowan, 1993).

5.7 Distribution of n-alkanes

The distribution of n-alkanes in the sediments of Lake Erie is a bimodal distribution, with modes at C_{17}, and at C_{29} or C_{31}. Bimodal distributions of n-alkanes are characteristic of sedimentary environments having multiple sources of organic matter (Giger et al, 1980; Ho and Meyers, 1993). Heptadecane (C_{17}) is the most abundant n-alkane in phytoplankton (Gelpi, 1970; Giger et al., 1980) and its dominance throughout the core is a good indication that algae comprise the primary source of organic matter in Lake Erie (Figures 11a-d). The second most abundant n-alkane is either C_{29} or C_{31}, indicating that a large terrestrial component is also present. The dual terrestrial and algal sources are in agreement with conclusions drawn from organic C/N.

The odd-even preference (OEP) similarly indicates that multiple sources of n-alkanes contribute to Lake Erie sediments. High OEP values are indicative of natural sources of organic matter, whereas values of 1.0 indicate extensive diagenetic alteration, or petroleum contamination. The highest odd predominances occur at C_{17} and C_{31}, indicating algal and terrestrial origins of n-alkanes. High OEP values also occur around C_{24}, suggesting the presence of a possible third natural source of n-alkanes not observed in the abundance distributions (Figure 13).

Although C_{17} remains the dominant n-alkane throughout the sediment core, the relative proportion of algal to terrestrial n-alkanes changes with depth. The increase of 0.5 in the short/long n-alkane index for sediments at 10 cm and above, relative to 11 cm and below, suggests that algal organic matter may be preferentially consumed by oligochaete worms, bacteria, and other organisms in the mixed layer of the sediments (Figure 14). The absence of change in organic C/N between 10 and 11 cm indicates that the variation in the short to long index is not related to a change in the relative contributions of organic matter from aquatic and terrestrial sources. The preferential loss of labile compounds often leads to depositional records biased in favor of terrestrial sources (Canuel and Martens, 1993; Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993; Bakel et al., 1994). The loss of short-chain n-alkanes relative to long-chain n-alkanes is consistent with the conclusions that distinct algal and terrestrial sources of n-alkanes contribute to Lake Erie sediments, and that rates of diagenetic alteration vary considerably between different organic fractions, compound classes, and molecules.

The presence of pristane and phytane in sediments has previously been utilized as indicators of oxic/anoxic deposition (Didyk, 1978). One of the primary biosynthetic pathways of these molecules is through the oxic or anoxic decomposition of phytol, the alcohol side-chain of chlorophyll *a*, during later diagenesis (Peters and Moldowan, 1993; Ho and Meyers, 1993). In recent sediments, however, the presence of pristane reflects the decomposition of chlorophyll *a* in the digestive tract of copepods (Blumer et al., 1963; Ho and Meyers, 1994). Large fluctuations in pristane concentration throughout the sediment core indicate the annual variability of zooplankton grazing communities (Figure 15a). The concentration of phytane remains relatively constant with depth, indicating a different formative process, which has varied little during the 14 years of sediment deposition (Figure 15b).

Conclusions

The isotopic composition of the sediments of Lake Erie exhibits a significant decrease in ^{13}C content between 1968 and 1982. Elemental and isotopic data suggest that the decrease in ^{13}C is not related to a change in diagenetic activity, nor to a change in the relative distribution of terrestrial and aquatic sources of organic matter. Therefore, it is likely that the isotopic shift is due to a decrease in the algal productivity, a response related to diminished phosphorus loadings to Lake Erie.

The primary source of organic matter contributing to the Lake Erie sedimentary environment is algae, as indicated by organic C/N and n-alkane distributions. The distributions of n-alkanes suggests that terrestrial sources of organic matter contribute a secondary, but significant fraction of organic matter. Organic C/N indicates that the relative proportion of source inputs has changed little between 1968 and 1982. The relative magnitude of contributions from each source is difficult to assess, due to the preferential diagenetic alteration of aquatic, short-chain n-alkanes, and the lack of definitive C/N endmembers for autochthonous and allochthonous production in the Lake Erie watershed.

Series of maxima and minima in percent organic carbon, percent organic nitrogen, and organic $\delta^{13}C$ content are evident in the sediment record. In addition, variations in ^{210}Pb activity indicate that sediments were not completely homogenized, despite a mixed depth of 10.5 cm, and reflect selective feeding patterns by benthic organisms. Selective feeding and high rates of sedimentation are most likely responsible for the high degree of resolution present in this sediment core.

The diagenetic alteration of organic matter affects individual molecules, compound classes, and the bulk organic fraction to different degrees. Early diagenetic alteration of the organic sediments is apparent in variations of the concentrations of n-alkanes, compound classes, and chromatographically unresolved compounds. The absence of significant change in the percent organic carbon content of the sediments suggests, however, that diagenetic alteration alone is insufficient to affect the $\delta^{13}C$ of the bulk organic fraction.

Future studies may utilize the distribution and isotopic composition of additional organic fractions, such as n-alkanols and n-alkanoic acids to further distinguish between the various sources of organic matter. Isotopic analysis may also be useful for determining the significance and origins of the maxima and minima observed in percent organic carbon, percent organic nitrogen, and the $\delta^{13}C$ content of bulk organic matter.

APPENDICES

APPENDIX A: TABLES AND FIGURES

Table 1: Comparison of the efficiencies of sonication and soxhlet extraction methods.

Extraction Technique	mg extracted organics per g of dry sediment	mg extracted aliphatics per g of dry sediment
Sonication	0.92 +/- 0.05	0.28 +/- 0.01
Soxhlet	1.51 +/- 0.10	0.35 +/- 0.06

Table 2: Comparison of alkane and aromatic separation based on the activation temperature of silica gel and alumina.

Eluent fraction (mL)	100°C	305°C
0 - 5	alkanes - trace phenanthrene - none	alkanes - trace phenanthrene - none
5 - 10	alkanes - large peaks phenanthrene - none	alkanes - large peaks phenanthrene - none
10 - 15	alkanes - small peaks phenanthrene - trace	alkanes - none phenanthrene - trace
15 - 20	alkanes - small peaks phenanthrene - larger trace	alkanes - none phenanthrene - trace

Table 3: Percent recovery of n-alkane standards from silica gel/alumina column chromatography.

n-alkane	Percent Recovery
C_{18}	74.8
C_{20}	81.8
C_{22}	84.2
C_{24}	87.5
C_{26}	90.6
C_{30}	95.4
C_{34}	98.6
C_{36}	102.1

Table 4: Age-depth relationship of Lake Erie sediment core as determined by ^{210}Pb dating methods.

Sediment Depth (cm)	Approximate year
1	1982.75
2	1982.50
3	1982.25
4	1982.00
5	1981.67
6	1981.33
7	1981.00
8	1980.67
9	1980.33
10	1980.00
11	1979.67
12	1979.33
13	1979.00
14	1978.67
15	1978.33
16	1978.00
18	1977.00
20	1976.50
22	1976.00
24	1975.00
26	1974.00
28	1973.50
30	1973.00
32	1972.00
34	1971.00
36	1970.00
38	1969.00
40	1968.00

Table 5: Calculation of the precision of percent organic carbon, percent organic nitrogen, and $\delta^{13}C$ of bulk organic sediments using Lake Superior surficial sediment.

Sample	% organic C	% organic N	$\delta^{13}C$ (‰)
LS 1383	3.440	0.399	-26.80
LS 1383	3.436	0.376	-26.47
LS 1383	3.338	0.371	-26.75
Average	3.404	0.382	-26.67
St. Dev.	0.058	0.015	0.18

Table 6: Calculation of the precision of geolipid extraction by Soxhlet extraction methods using Lake Huron surficial sediments.

Sample	organic extract (mg/g dry sediment)
LH Oct1	1.10
LH Oct2	1.12
LH Oct3	1.23
Average	1.15
St. Dev.	0.07

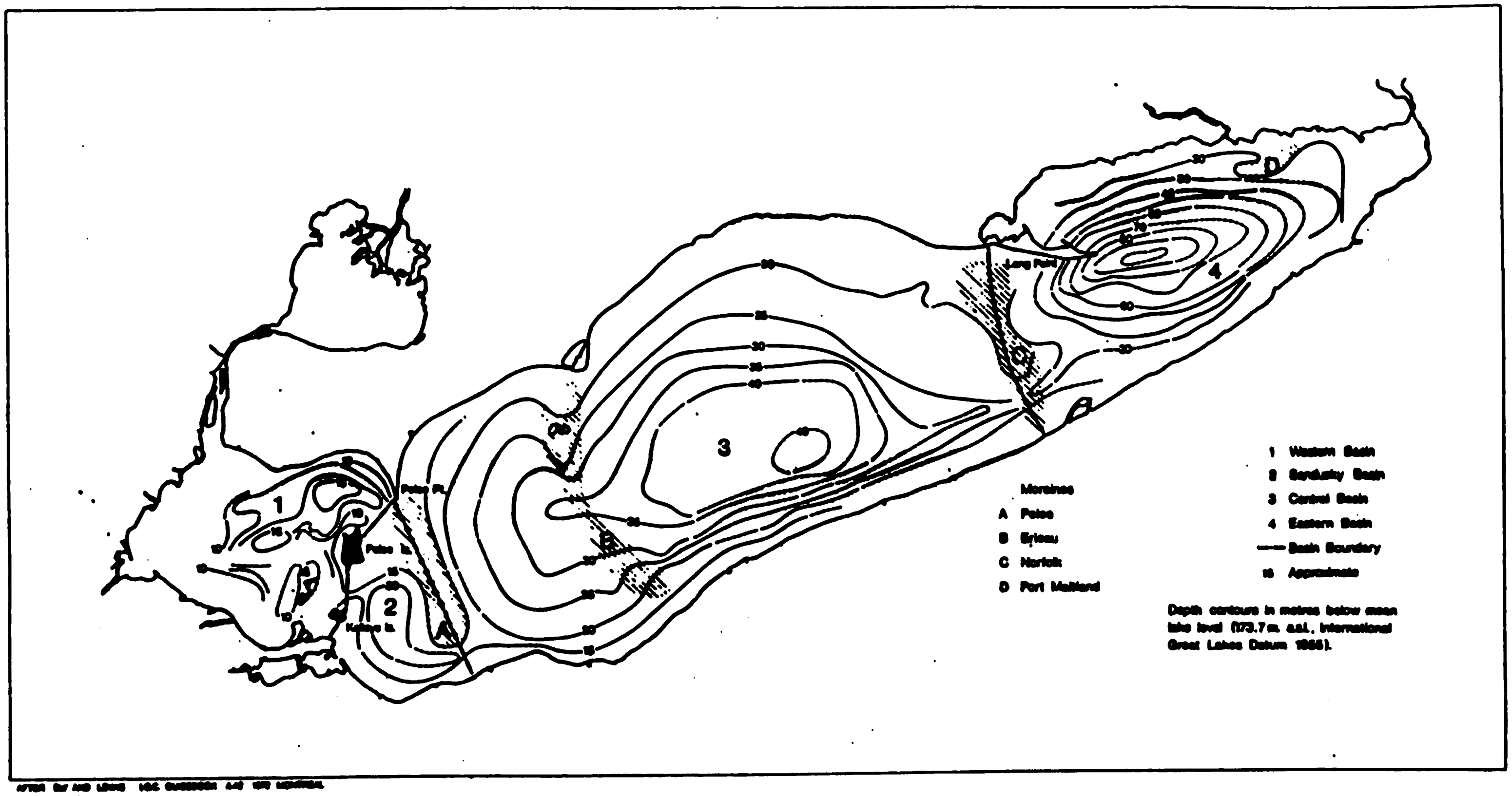

Figure 1: Inferred bathymetry of Lake Erie (after Sly and Lewis, 1972; Burns, 1985)

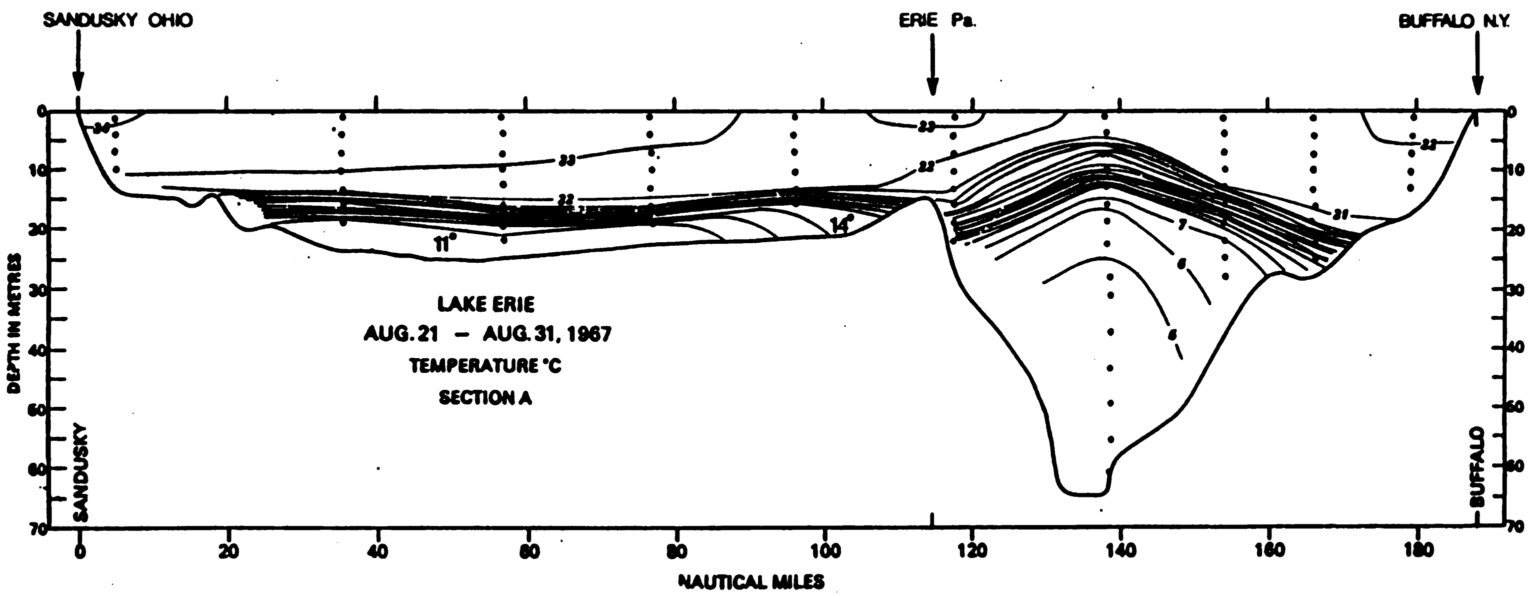

Figure 2: Cross-section of the central and eastern basins of Lake Erie showing mid-summer thermal stratification (Burns, 1985).

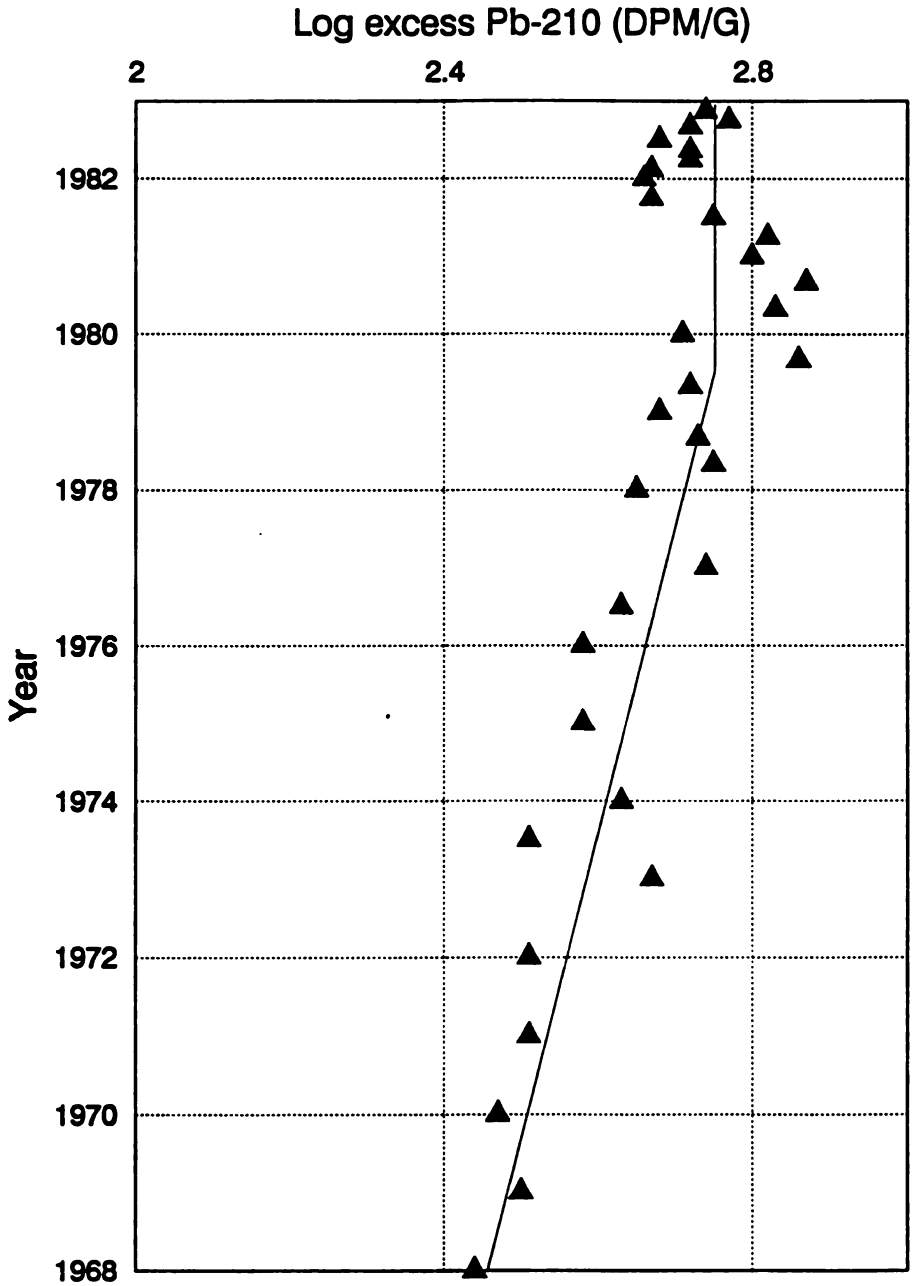

Figure 3: Mixed depth and sediment dating inferred from excess ^{210}Pb activity.

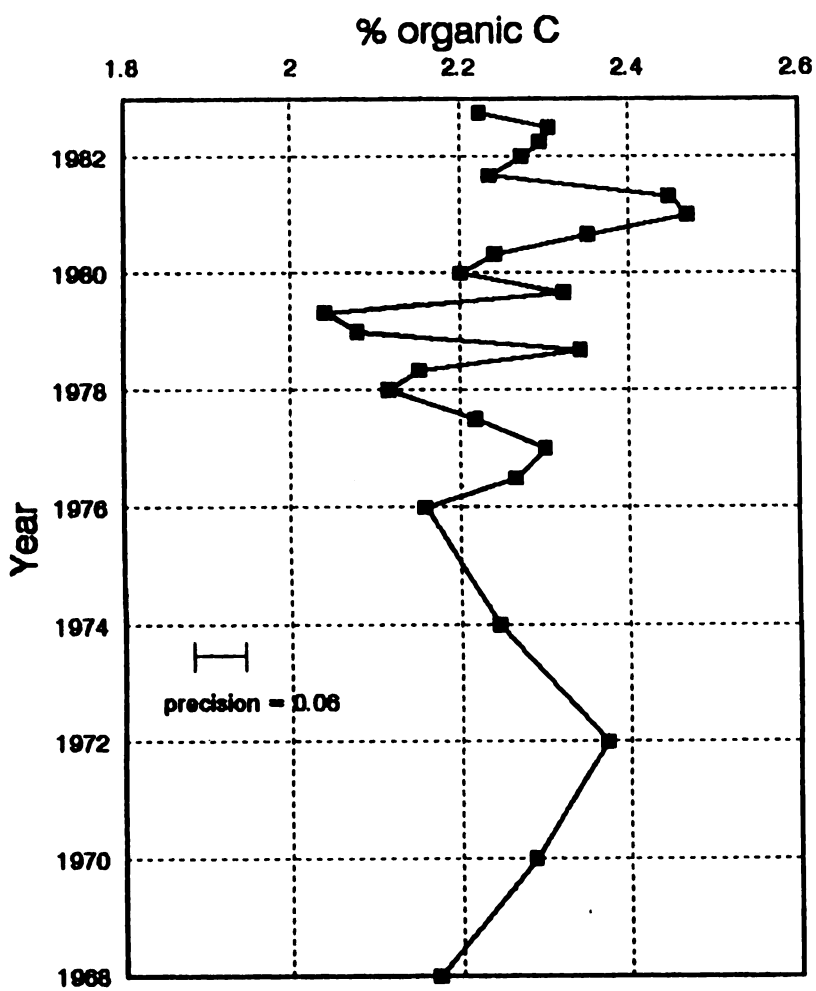

Figure 4: Percent organic carbon in sediments from the eastern basin of Lake Erie.

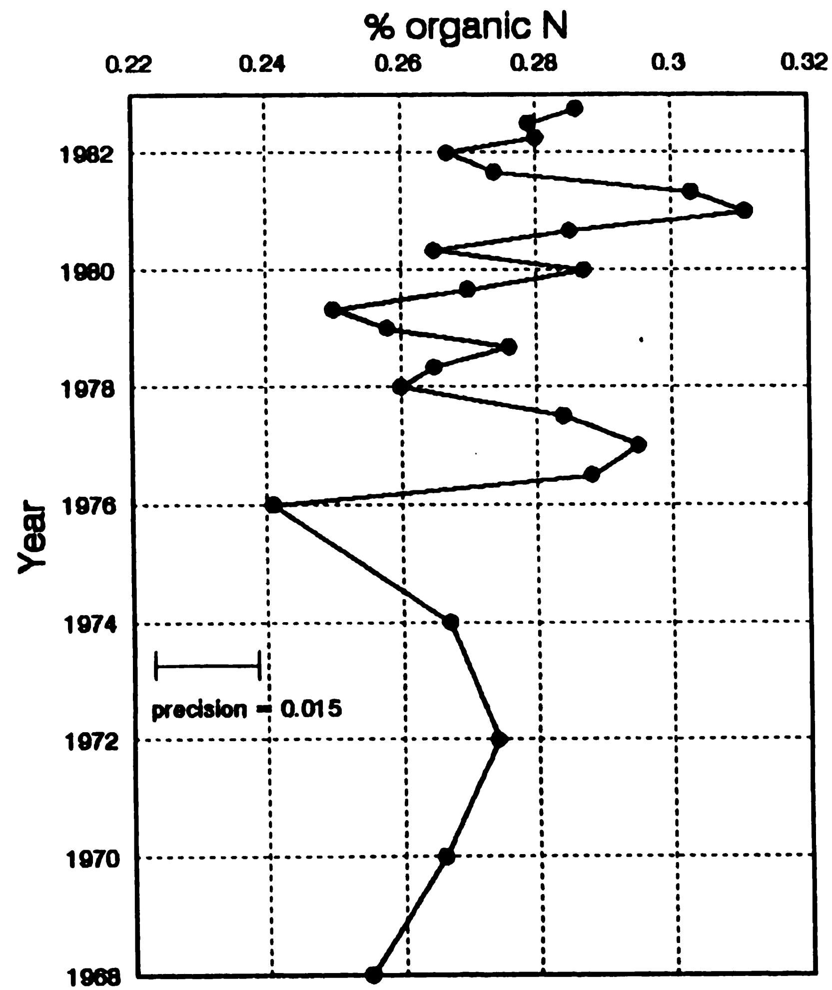

Figure 5: Percent organic nitrogen in sediments from the eastern basin of Lake Erie.

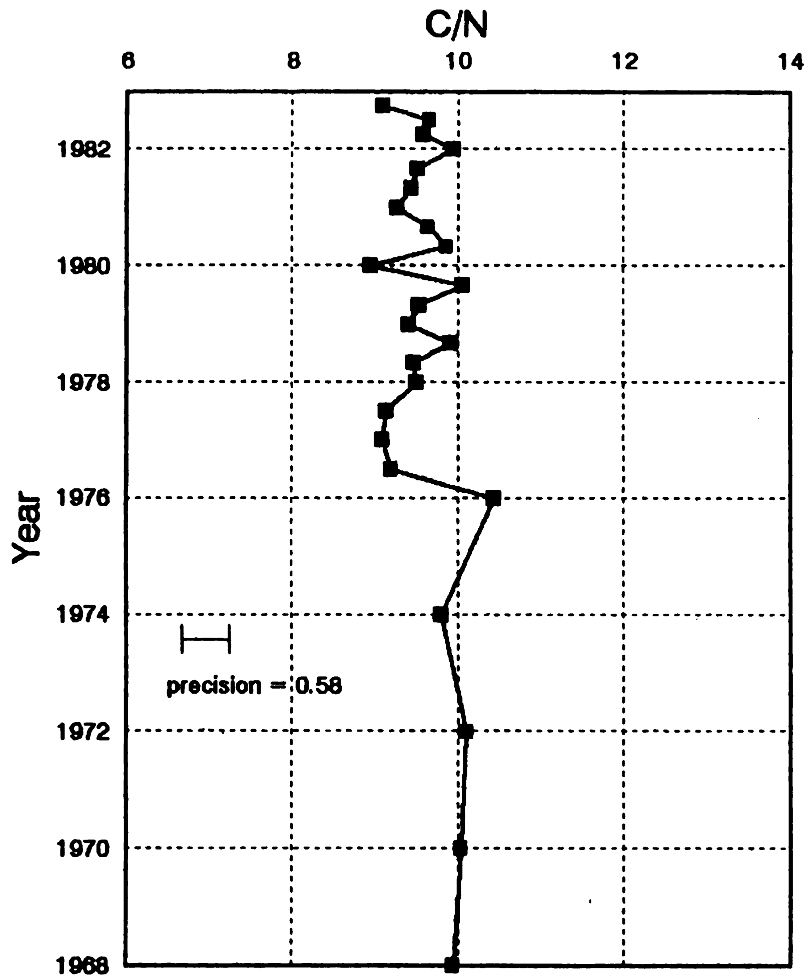

Figure 6: Organic C/N of Lake Erie sediments.

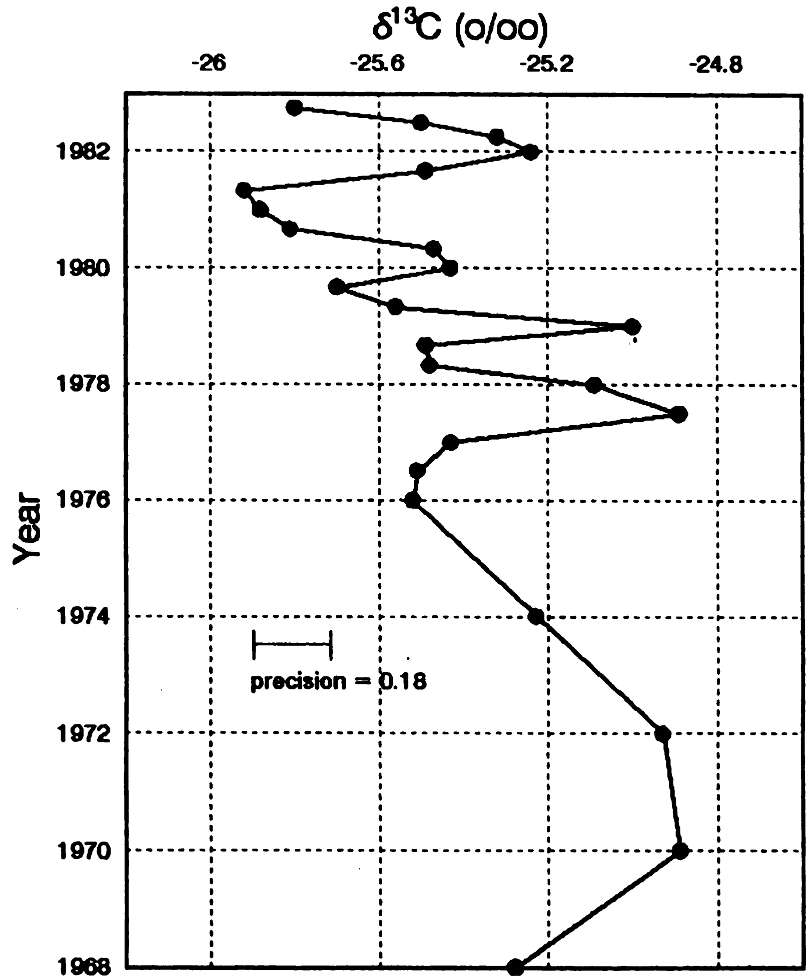

Figure 7: Carbon isotopic composition of Lake Erie organic sediments.

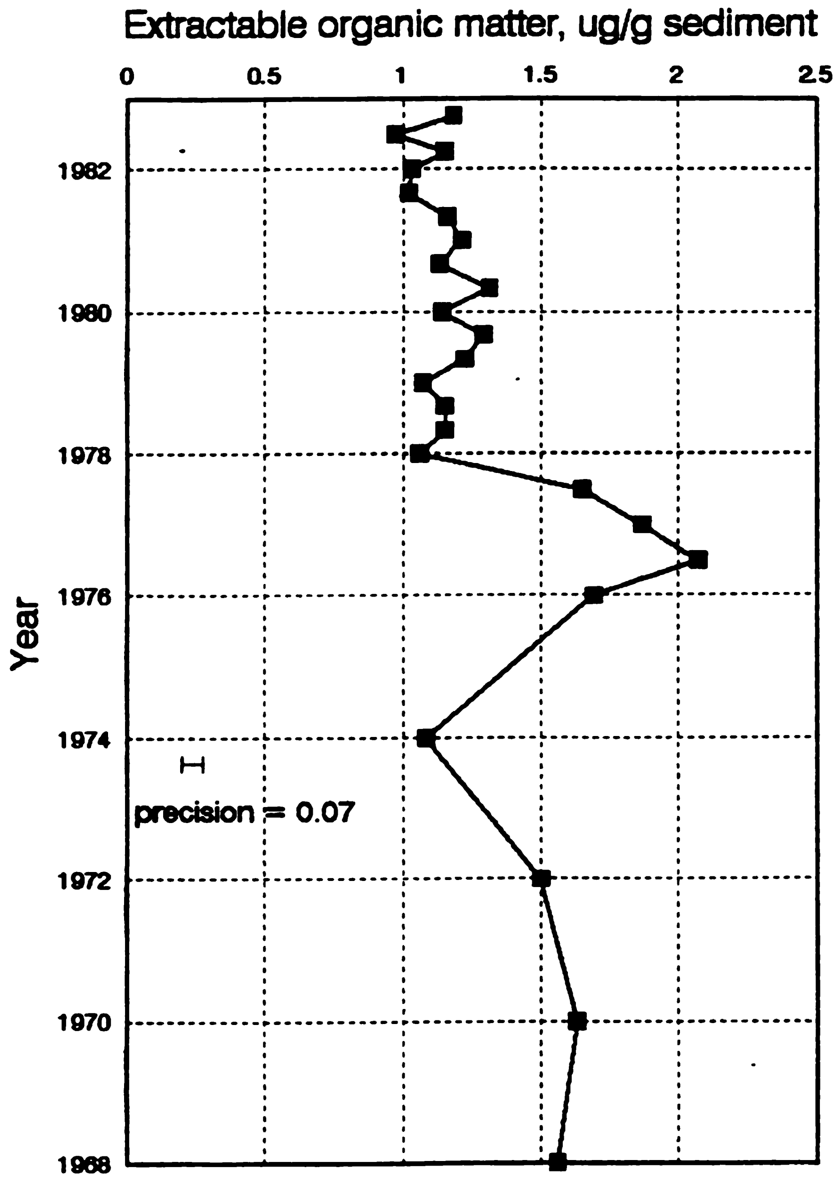

Figure 8: Concentration of organic material obtained from Lake Erie sediment core by Soxhlet extraction using dichloromethane.

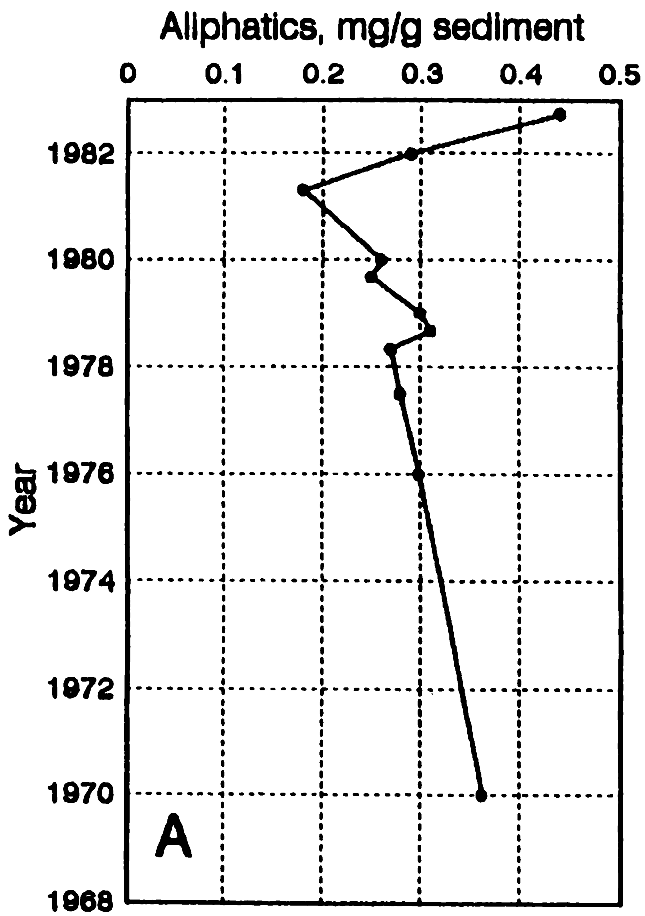

Figure 9a: Concentration of aliphatic material extracted from Lake Erie sediments.

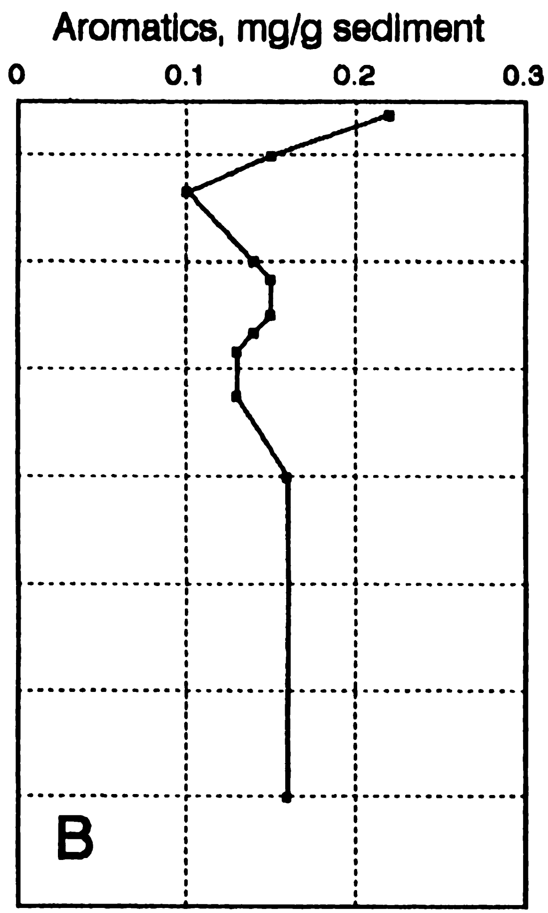

Figure 9b: Concentration of aromatic material extracted from Lake Erie sediments.

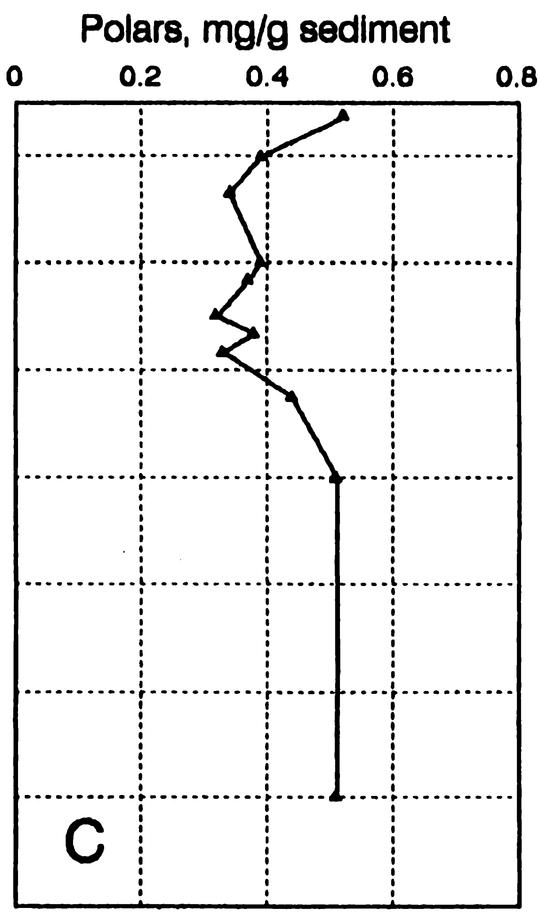

Figure 9c: Concentration of polar material extracted from Lake Erie sediments.

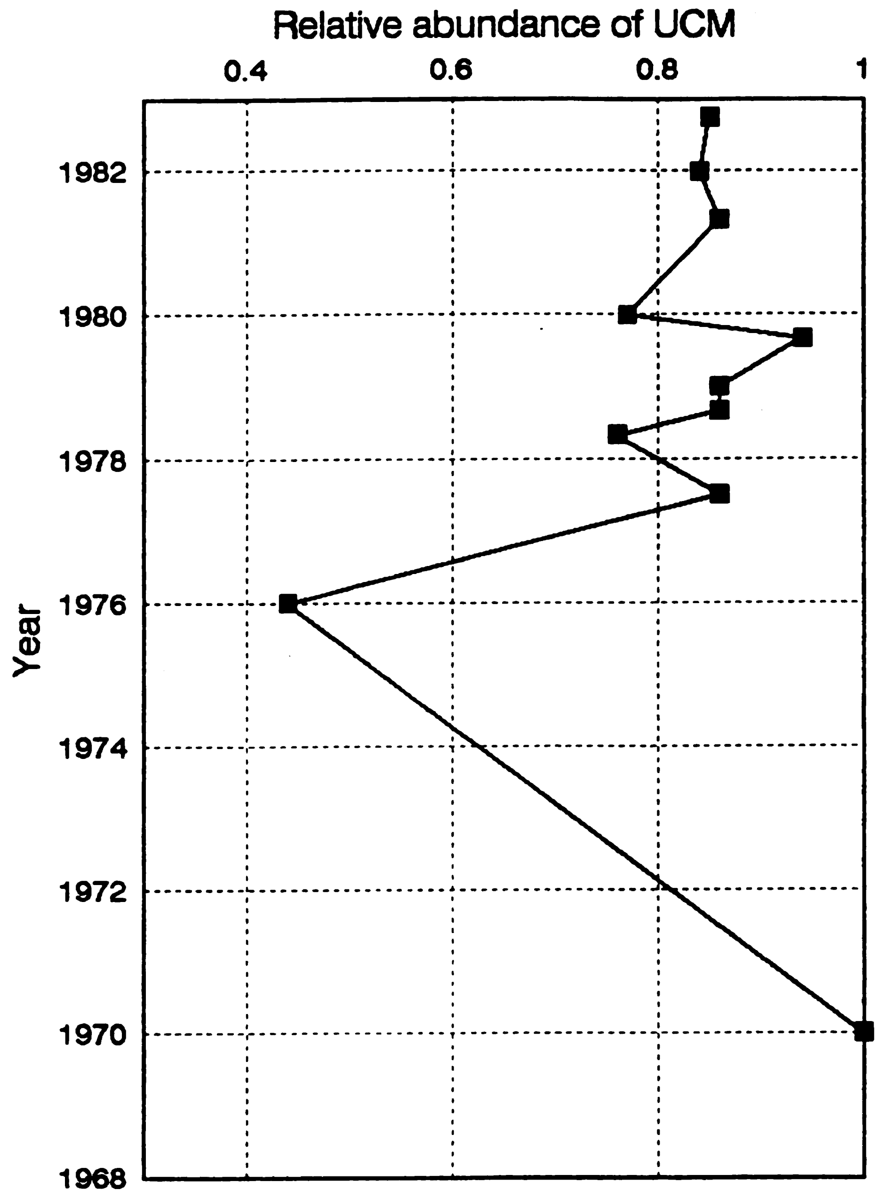

Figure 10: Relative abundance of unresolved complex mixture in Lake Erie sediments.

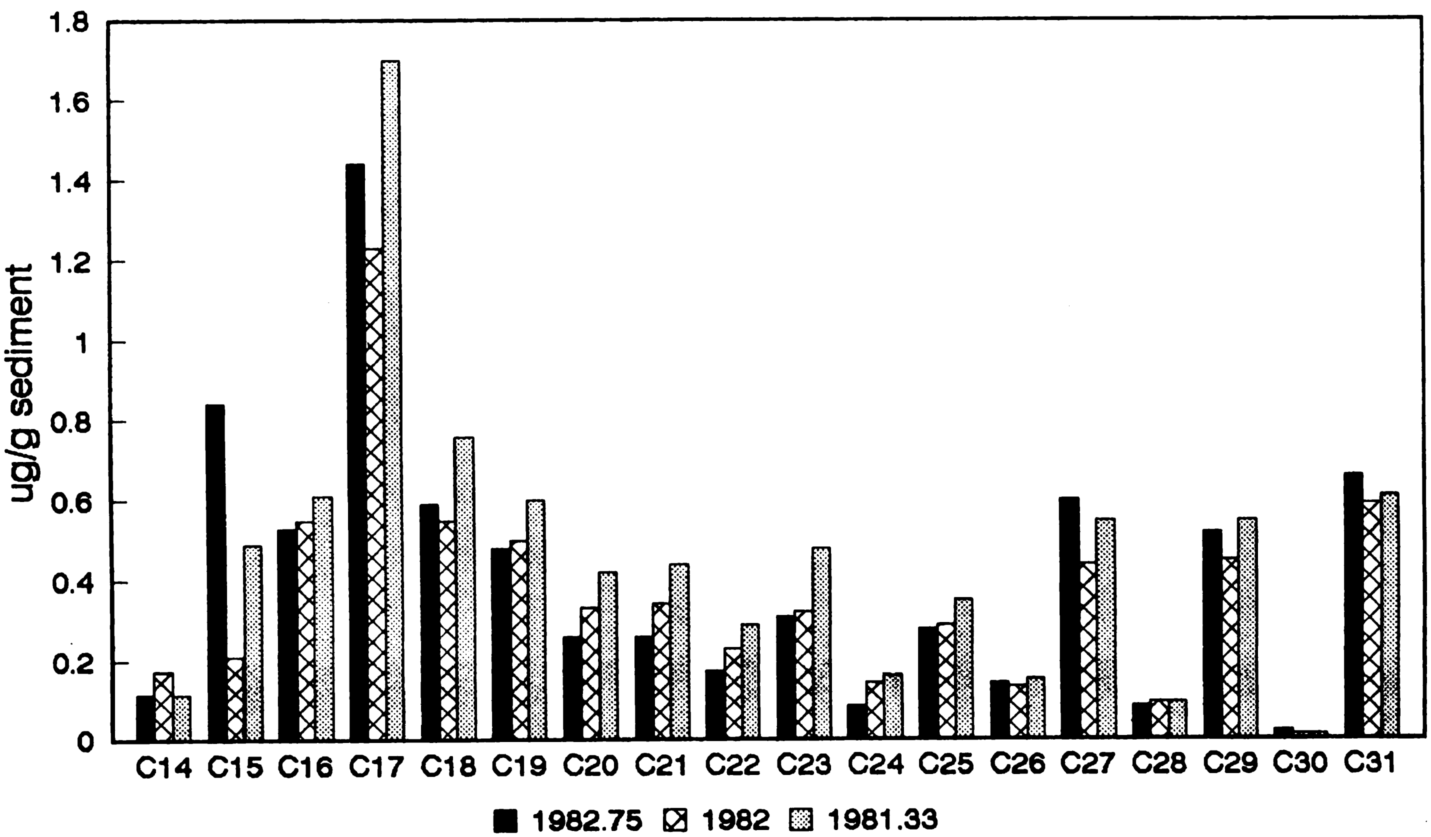

Figure 11a: **Absolute abundance of n-alkanes extracted from Lake Erie sediments, 1981 - 1982.**

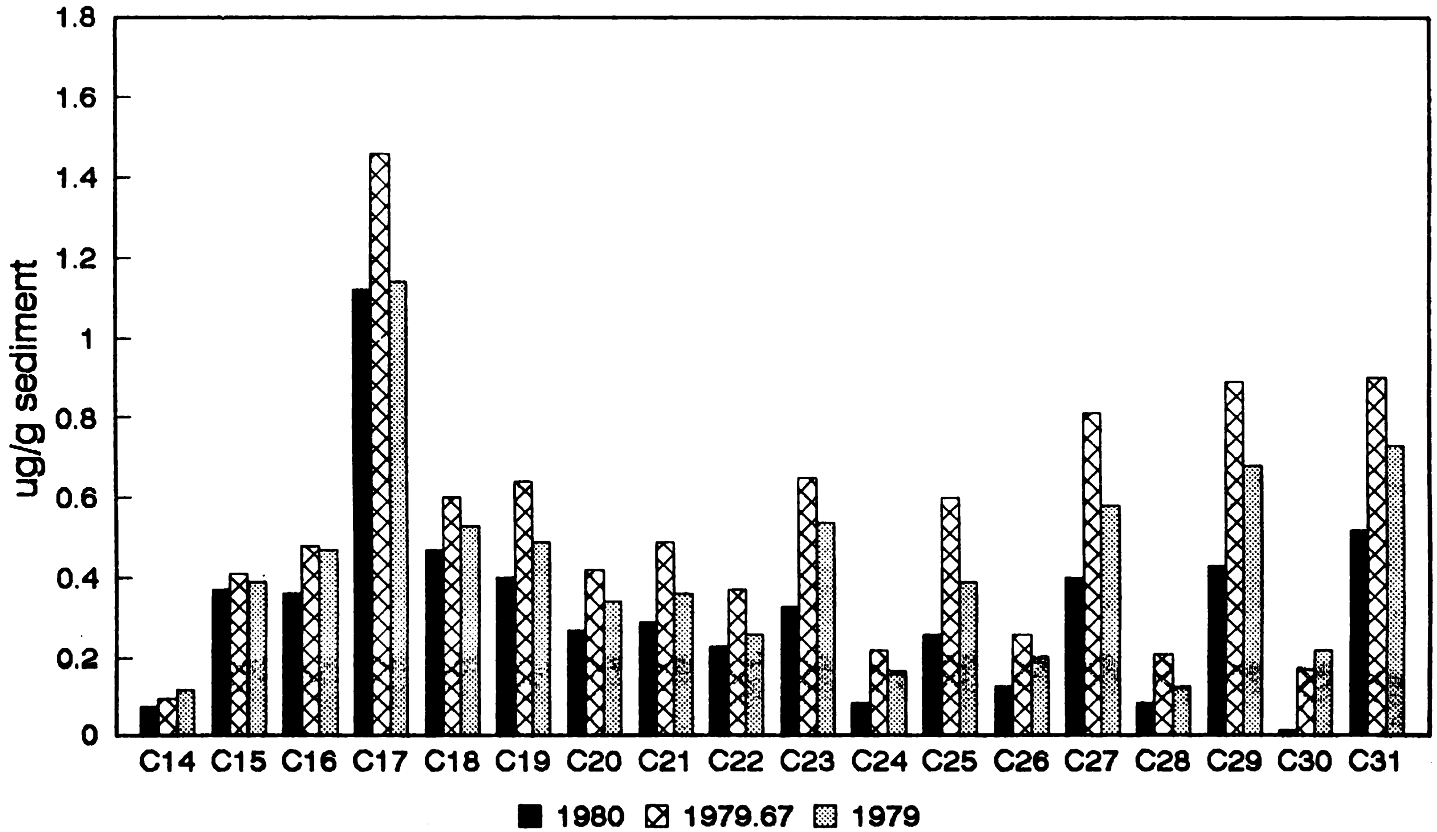

Figure 11b: **Absolute abundance of n-alkanes extracted from Lake Erie sediments, 1979 - 1980.**

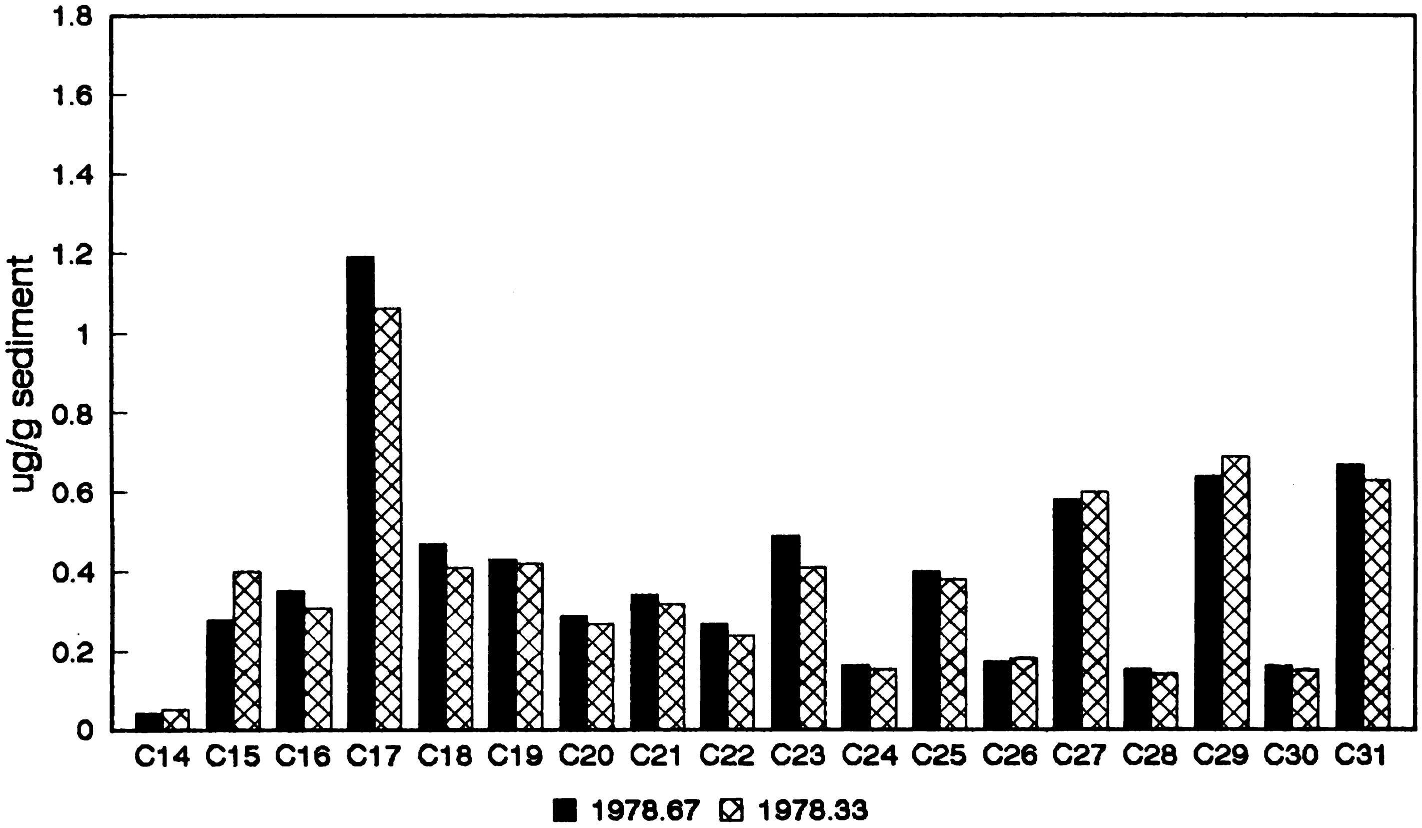

Figure 11c: **Absolute abundance of n-alkanes extracted from Lake Erie sediments, 1978.**

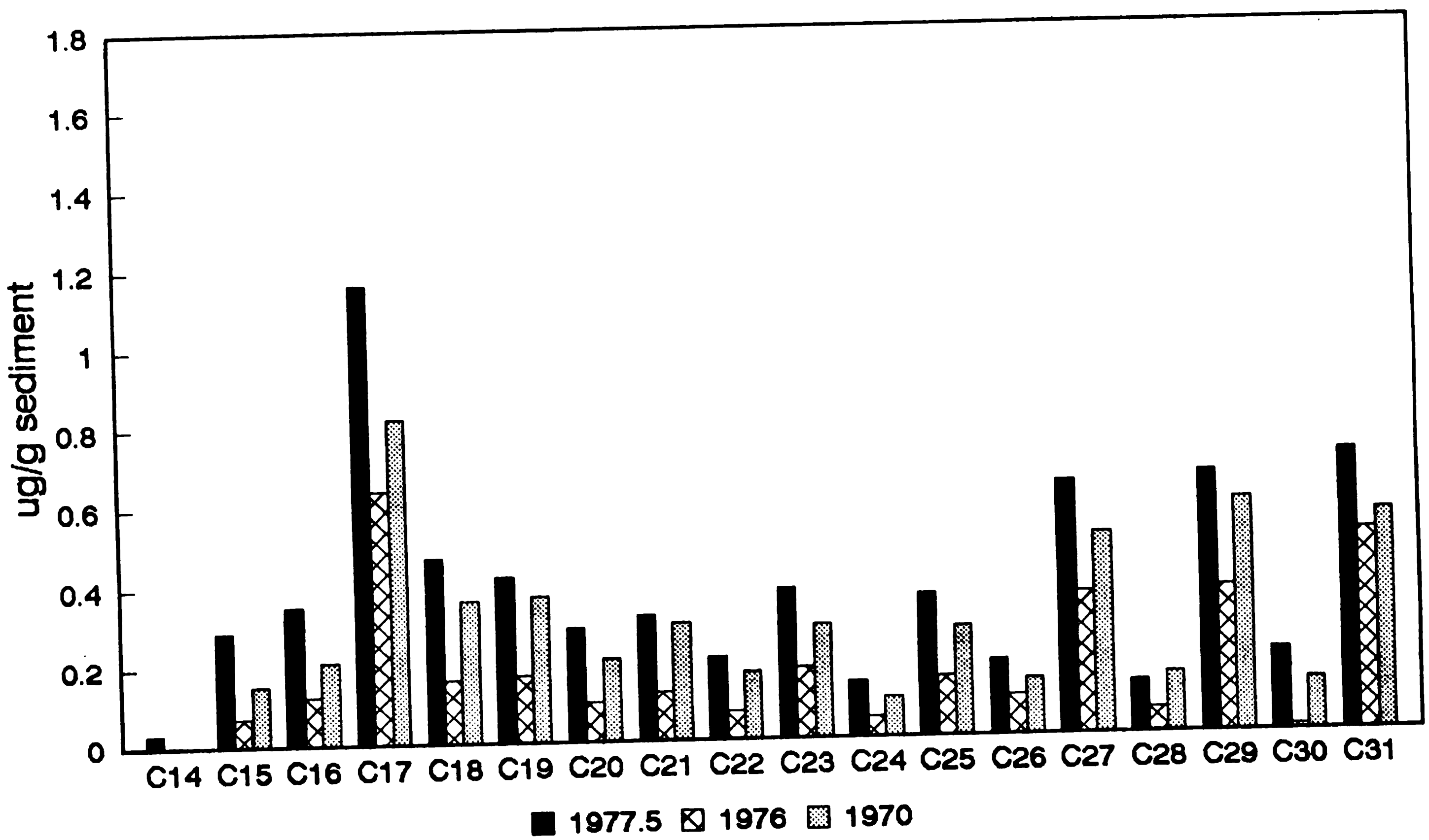

Figure 11d: Absolute abundance of n-alkanes extracted from Lake Erie sediments, 1970 - 1977.

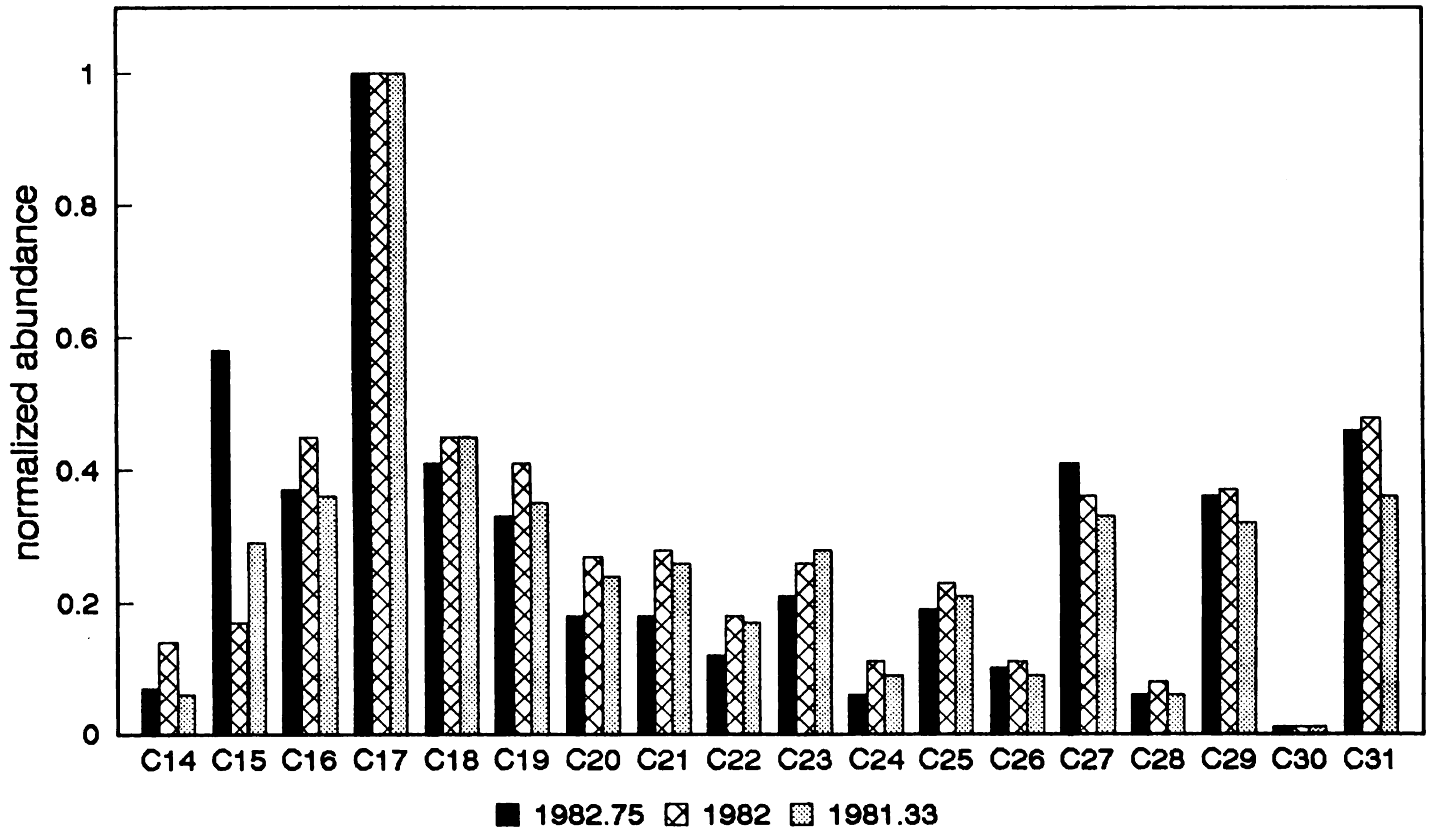

Figure 12a: Normalized abundance of n-alkanes extracted from Lake Erie sediments, 1981 - 1982.

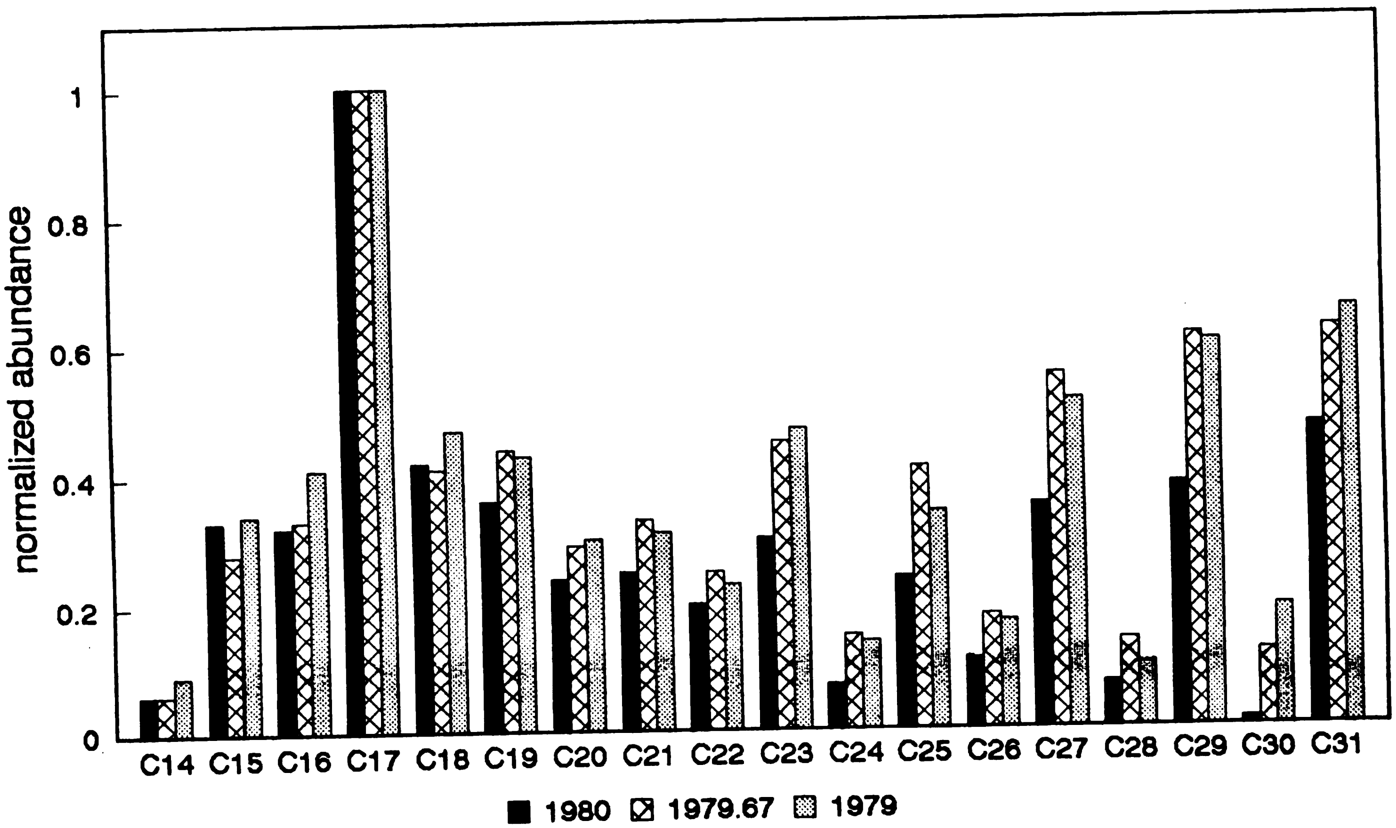

Figure 12b: Normalized abundance of n-alkanes extracted from Lake Erie sediments, 1979 - 1980.

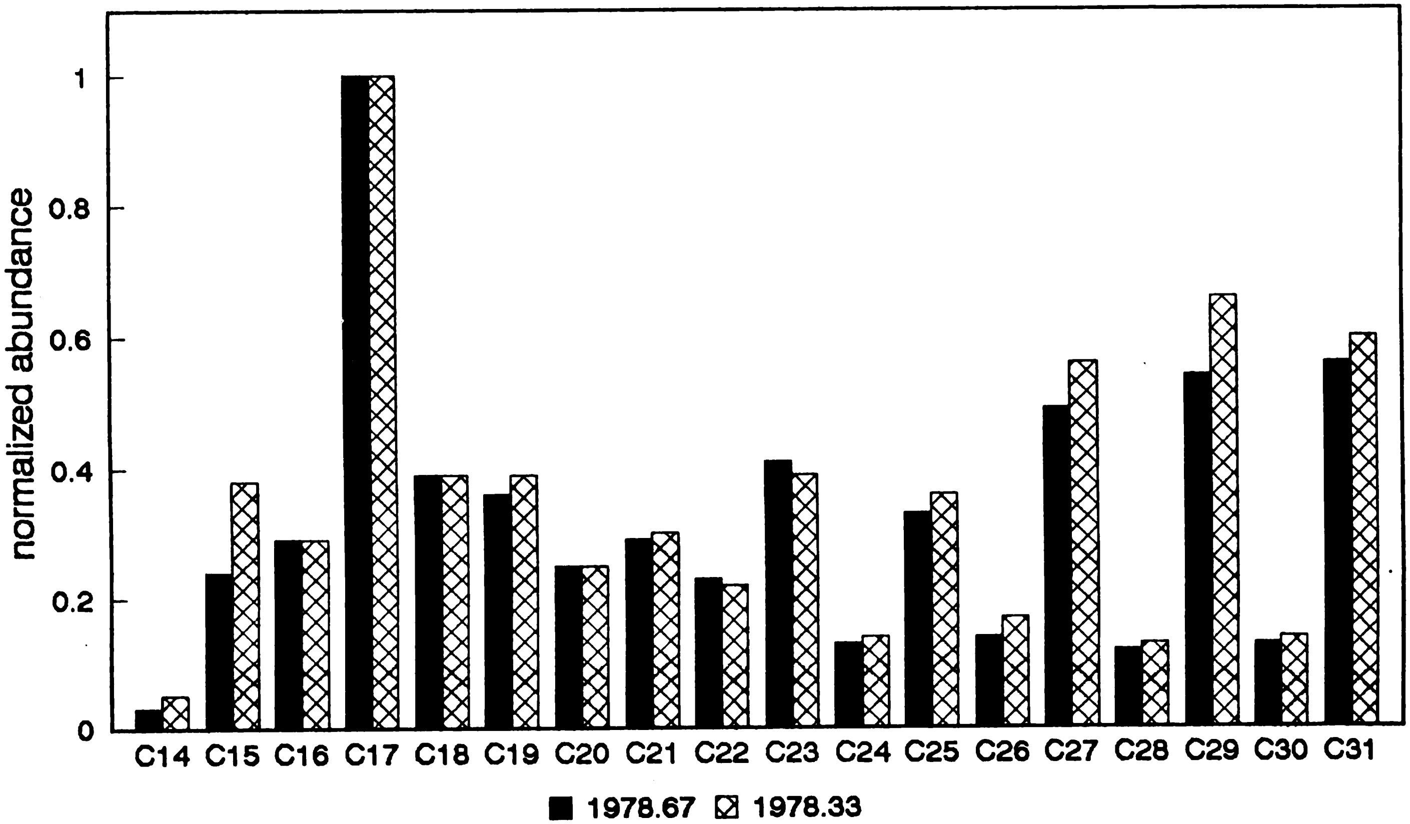

Figure 12c: Normalized abundance of n-alkanes extracted from Lake Erie sediments, 1978.

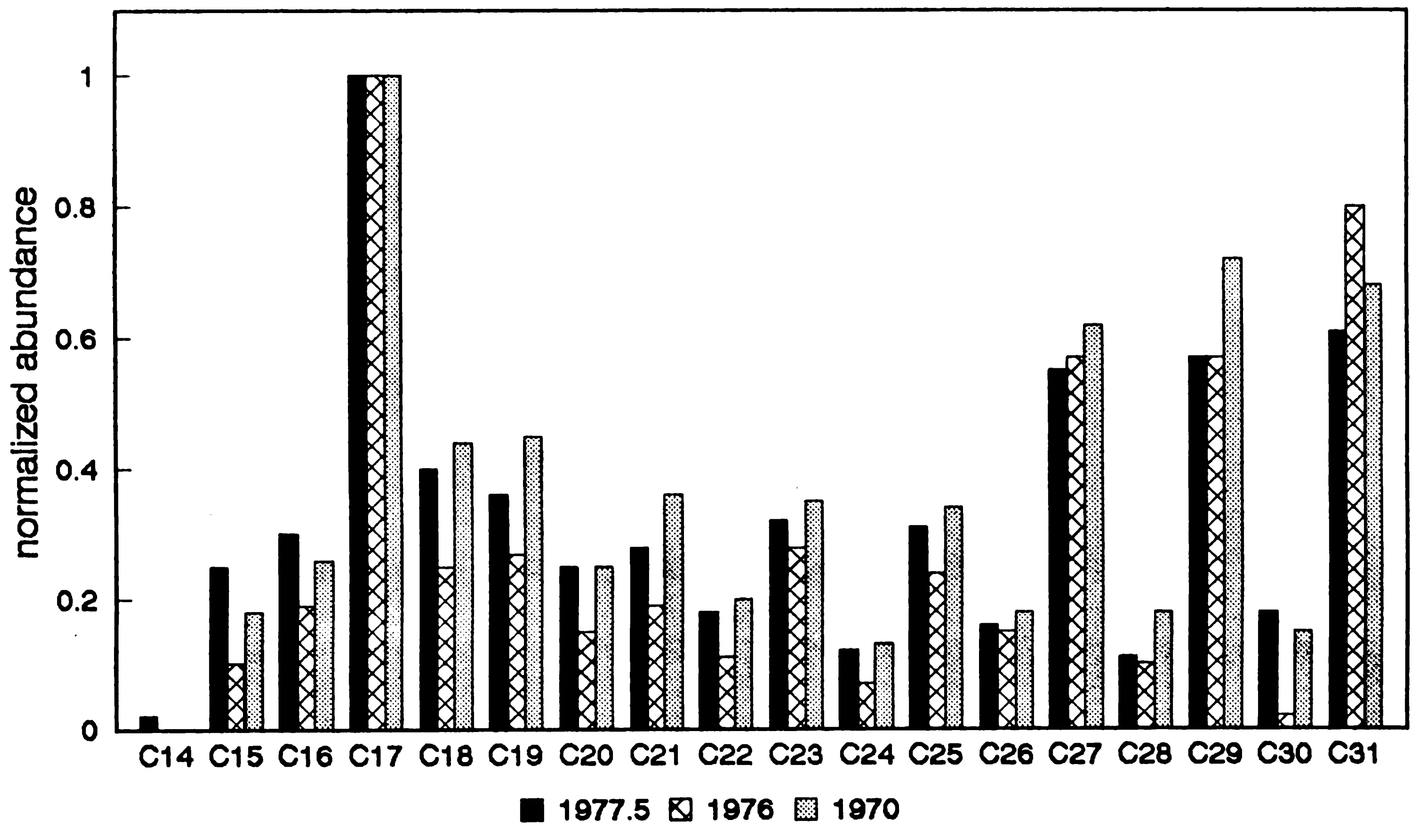

Figure 12d: Normalized abundance of n-alkanes extracted from Lake Erie sediments, 1970 - 1977.

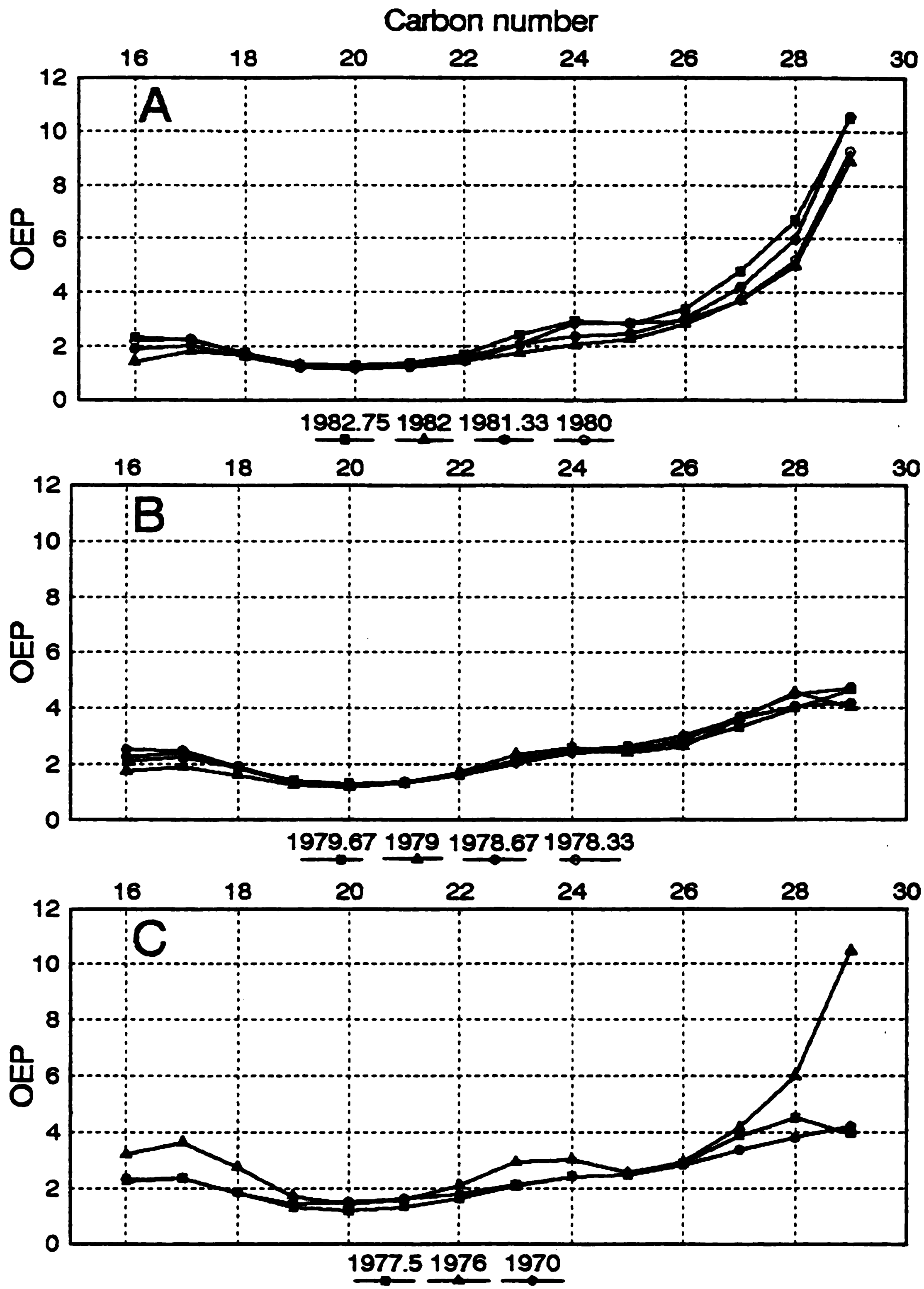

Figure 13: Odd/even preference exhibited by n-alkanes extracted from Lake Erie sediments a) 1980 - 1982; b) 1978 - 1979; c) 1970 - 1977.

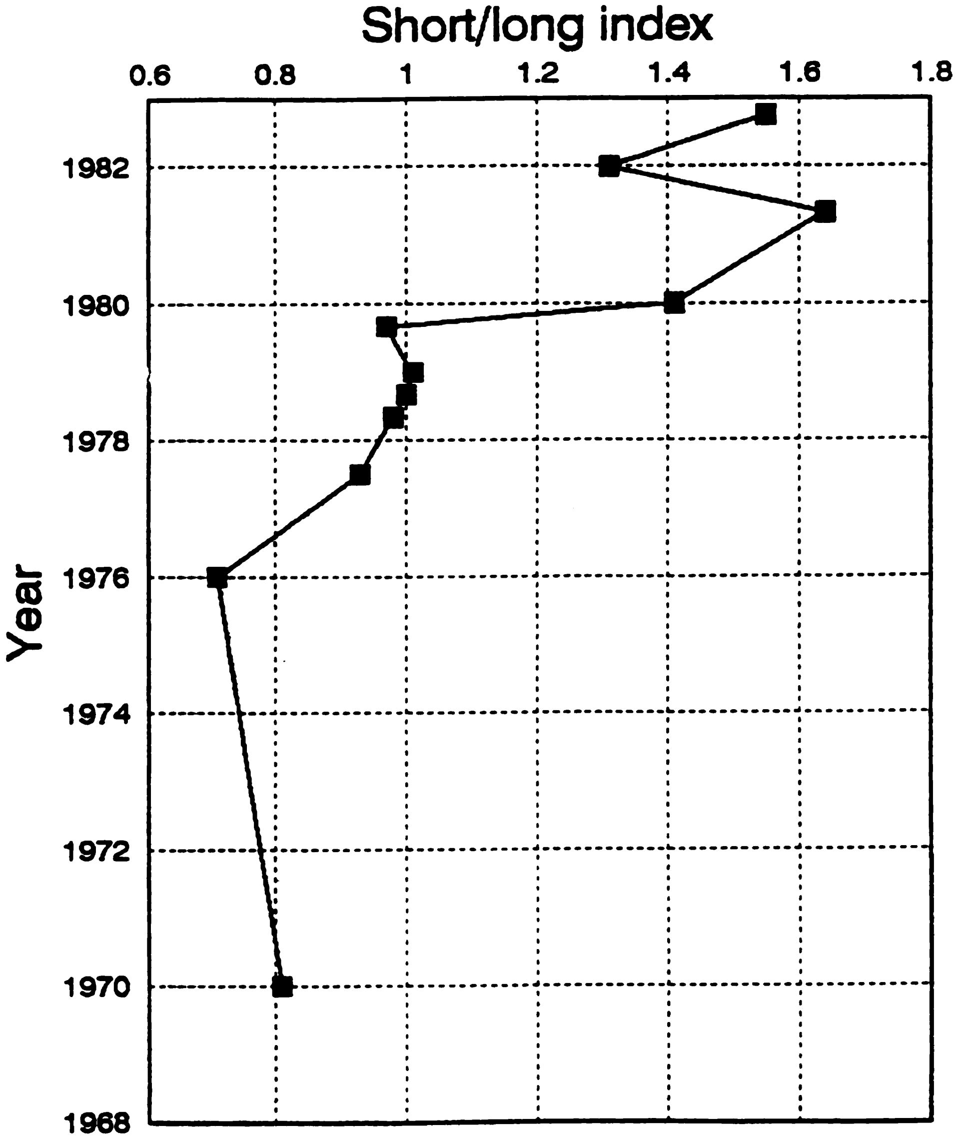

Figure 14: Short/long index of n-alkanes extracted from Lake Erie sediments.

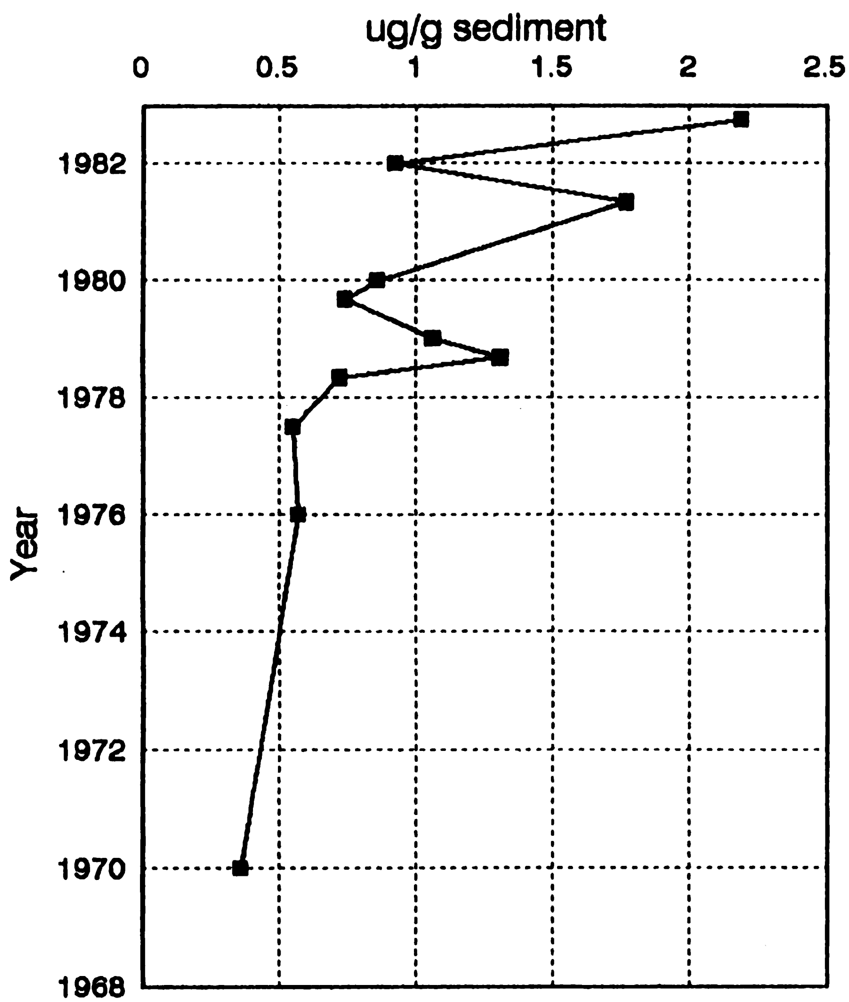

Figure 15a: Absolute abundance of pristane extracted from Lake Erie sediments.

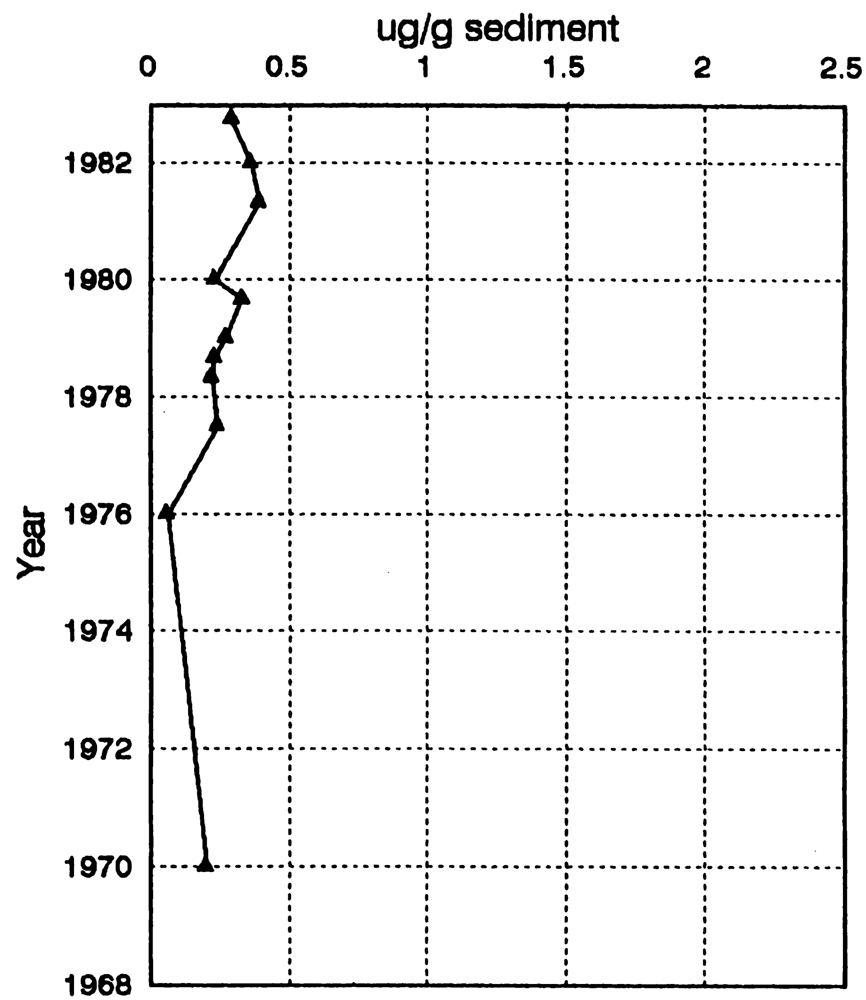

Figure 15b: Absolute abundance of phytane extracted from Lake Erie sediments.

APPENDIX B: ADDITIONAL DATA

Appendix B1: Linear regression of n-alkane standards used in the quantification of sedimentary n-alkanes.

n-Alkane	Slope	Intercept	r^2
C_{18}	30.83	0.335	0.9991
C_{20}	31.78	0.362	0.9992
C_{22}	31.17	0.340	0.9995
C_{24}	28.93	0.309	0.9999
C_{26}	26.61	0.207	0.9999
C_{30}	20.19	-0.017	0.9959
C_{34}	13.46	-0.218	0.9933
C_{36}	10.15	-0.308	0.9835

Appendix B2: Assignments of sedimentary alkanes to linear regressions.

Regression curves (n-alkanes)	Sedimentary alkanes
C_{18}	C_{14}, C_{15}, C_{16}, C_{17}, C_{18}, pristane, phytane
C_{20}	C_{19}, C_{20}
C_{22}	C_{21}, C_{22}
C_{24}	C_{23}, C_{24}
C_{26}	C_{25}, C_{26}, C_{27}
C_{30}	C_{28}, C_{29}, C_{30}, C_{31}

Appendix B3: Percent organic carbon, percent organic nitrogen, and C/N of Lake Erie sedimentary organic matter.

Year	% organic C	% organic N	C/N
1982.75	2.22	0.286	9.09
1982.50	2.31	0.279	9.65
1982.25	2.30	0.28	9.57
1982.00	2.27	0.267	9.95
1981.67	2.24	0.274	9.51
1981.33	2.45	0.303	9.43
1981.00	2.47	0.311	9.26
1980.67	2.35	0.285	9.63
1980.33	2.24	0.265	9.86
1980.00	2.20	0.287	8.94
1979.67	2.32	0.27	10.06
1979.33	2.04	0.25	9.53
1979.00	2.08	0.258	9.41
1978.67	2.34	0.276	9.91
1978.33	2.15	0.265	9.47
1978.00	2.12	0.26	9.49
1977.50	2.22	0.284	9.13
1977.00	2.30	0.295	9.09
1976.50	2.27	0.288	9.19
1976.50	2.16	0.241	10.44
1974.00	2.25	0.267	9.81
1972.00	2.37	0.274	10.10
1970.00	2.29	0.266	10.03
1968.00	2.17	0.255	9.94

Appendix B4: $\delta^{13}C$ values of Lake Erie sedimentary organic matter, in ‰ notation relative to PDB.

Year	$\delta^{13}C$ (‰)
1982.75	-25.80
1982.50	-25.50
1982.25	-25.32
1982.00	-25.24
1981.67	-25.49
1981.33	-25.92
1981.00	-25.88
1980.67	-25.81
1980.33	-25.47
1980.00	-25.43
1979.67	-25.70
1979.33	-25.56
1979.00	-25.00
1978.67	-25.49
1978.33	-25.48
1978.00	-25.09
1977.50	-24.89
1977.00	-25.43
1976.50	-25.51
1976.00	-25.52
1974.00	-25.23
1972.00	-24.93
1970.00	-24.89
1968.00	-25.28

Appendix B5: Concentration of unbound organic matter extracted from Lake Erie sediments, in mg/g dry sediment.

Year	Extractable Organic Matter (mg/g sed)
1982.75	1.18
1982.50	0.97
1982.25	1.15
1982.00	1.03
1981.67	1.02
1981.33	1.16
1981.00	1.21
1980.67	1.13
1980.33	1.31
1980.00	1.14
1979.67	1.29
1979.33	1.22
1979.00	1.07
1978.67	1.15
1978.33	1.15
1978.00	1.06
1977.50	1.65
1977.00	1.87
1976.50	2.07
1976.00	1.69
1974.00	1.08
1972.00	1.50
1970.00	1.63
1968.00	1.56

Appendix B6: Concentration of compound classes in Lake Erie sediment, in mg/g dry sediment.

Year	Aliphatic	Aromatic	Polar
1982.75	0.44	0.22	0.52
1982.00	0.29	0.15	0.39
1981.33	0.18	0.1	0.34
1980.00	0.26	0.14	0.39
1979.67	0.25	0.15	0.37
1979.00	0.3	0.15	0.32
1978.67	0.31	0.14	0.38
1978.33	0.27	0.13	0.33
1977.50	0.28	0.13	0.44
1976.00	0.3	0.16	0.51
1970.00	0.36	0.16	0.51

Appendix B7: Relative abundance of unresolved complex mixture in Lake Erie sediments.

Year	UCM
1982.75	0.85
1982.00	0.84
1981.33	0.86
1980.00	0.77
1979.67	0.94
1979.00	0.86
1978.67	0.86
1978.33	0.76
1977.50	0.86
1976.00	0.44
1970.00	1.00

Appendix B8: Absolute abundances of n-alkanes extracted from Lake Erie sediments, in $\mu g/g$ of dry sediment.

Year	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}
1982.75	0.11	0.84	0.53	1.44	0.59	0.48
1982.00	0.17	0.21	0.55	1.23	0.55	0.50
1981.33	0.11	0.49	0.61	1.70	0.76	0.60
1980.00	0.07	0.37	0.36	1.12	0.47	0.40
1979.67	0.09	0.41	0.48	1.46	0.60	0.64
1979.00	0.11	0.39	0.47	1.14	0.53	0.49
1978.67	0.04	0.28	0.35	1.19	0.47	0.43
1978.33	0.05	0.4	0.31	1.06	0.41	0.42
1977.50	0.03	0.29	0.35	1.16	0.47	0.42
1976.00	0	0.07	0.12	0.64	0.16	0.17
1970.00	0	0.15	0.21	0.82	0.36	0.37

Appendix B8, continued

Year	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}
1982.75	0.26	0.26	0.17	0.31	0.08	0.28
1982.00	0.33	0.34	0.23	0.32	0.14	0.29
1981.33	0.42	0.44	0.29	0.48	0.16	0.35
1980.00	0.27	0.29	0.23	0.33	0.08	0.26
1979.67	0.42	0.49	0.37	0.65	0.22	0.60
1979.00	0.34	0.36	0.26	0.54	0.16	0.39
1978.67	0.29	0.34	0.27	0.49	0.16	0.40
1978.33	0.27	0.32	0.24	0.41	0.15	0.38
1977.50	0.29	0.32	0.21	0.38	0.14	0.36
1976.00	0.10	0.12	0.07	0.18	0.05	0.15
1970.00	0.21	0.30	0.17	0.29	0.10	0.28

Appendix B8, continued

Year	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}
1982.75	0.14	0.60	0.08	0.52	0.02	0.66
1982.00	0.13	0.44	0.09	0.45	0.01	0.59
1981.33	0.15	0.55	0.09	0.55	0.01	0.61
1980.00	0.12	0.40	0.08	0.43	0.01	0.52
1979.67	0.26	0.81	0.21	0.89	0.17	0.90
1979.00	0.20	0.58	0.12	0.68	0.22	0.73
1978.67	0.17	0.58	0.15	0.64	0.16	0.67
1978.33	0.18	0.60	0.14	0.69	0.15	0.63
1977.50	0.19	0.64	0.13	0.66	0.21	0.71
1976.00	0.10	0.36	0.06	0.37	0.01	0.51
1970.00	0.14	0.51	0.15	0.59	0.13	0.56

Appendix B9: Normalized abundances of n-alkanes extracted from Lake Erie sediments.

Year	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}
1982.75	0.07	0.58	0.37	1.00	0.41	0.33
1982.00	0.14	0.17	0.45	1.00	0.45	0.41
1981.33	0.06	0.29	0.36	1.00	0.45	0.35
1980.00	0.06	0.33	0.32	1.00	0.42	0.36
1979.67	0.06	0.28	0.33	1.00	0.41	0.44
1979.00	0.09	0.34	0.41	1.00	0.47	0.43
1978.67	0.03	0.24	0.29	1.00	0.39	0.36
1978.33	0.05	0.38	0.29	1.00	0.39	0.39
1977.50	0.02	0.25	0.30	1.00	0.40	0.36
1976.00	0.00	0.10	0.19	1.00	0.25	0.27
1970.00	0.00	0.18	0.26	1.00	0.44	0.45

Appendix B9, continued

Year	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}
1982.75	0.18	0.18	0.12	0.21	0.06	0.19
1982.00	0.27	0.28	0.18	0.26	0.11	0.23
1981.33	0.24	0.26	0.17	0.28	0.09	0.21
1980.00	0.24	0.25	0.20	0.30	0.07	0.24
1979.67	0.29	0.33	0.25	0.45	0.15	0.41
1979.00	0.30	0.31	0.23	0.47	0.14	0.34
1978.67	0.25	0.29	0.23	0.41	0.13	0.33
1978.33	0.25	0.30	0.22	0.39	0.14	0.36
1977.50	0.25	0.28	0.18	0.32	0.12	0.31
1976.00	0.15	0.19	0.11	0.28	0.07	0.24
1970.00	0.25	0.36	0.20	0.35	0.13	0.34

Appendix B9, continued

Year	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}
1982.75	0.10	0.41	0.06	0.36	0.01	0.46
1982.00	0.11	0.36	0.08	0.37	0.01	0.48
1981.33	0.09	0.33	0.06	0.32	0.01	0.36
1980.00	0.11	0.35	0.07	0.38	0.01	0.47
1979.67	0.18	0.55	0.14	0.61	0.12	0.62
1979.00	0.17	0.51	0.10	0.60	0.19	0.65
1978.67	0.14	0.49	0.12	0.54	0.13	0.56
1978.33	0.17	0.56	0.13	0.66	0.14	0.60
1977.50	0.16	0.55	0.11	0.57	0.18	0.61
1976.00	0.15	0.57	0.10	0.57	0.02	0.80
1970.00	0.18	0.62	0.18	0.72	0.15	0.68

Appendix B10: Odd/even preference of n-alkanes extracted from Lake Erie sediments.

Year	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}
1982.75	2.34	2.22	1.78	1.35	1.29	1.39	1.71
1982.00	1.44	1.85	1.66	1.30	1.23	1.30	1.46
1981.33	1.92	2.05	1.64	1.22	1.17	1.33	1.61
1980.00	2.22	2.27	1.78	1.30	1.19	1.24	1.45
1979.67	2.09	2.26	1.86	1.42	1.30	1.34	1.60
1979.00	1.77	1.92	1.62	1.26	1.19	1.31	1.73
1978.67	2.27	2.41	1.88	1.35	1.23	1.32	1.60
1978.33	2.52	2.48	1.92	1.42	1.30	1.36	1.59
1977.50	2.26	2.36	1.83	1.31	1.21	1.34	1.63
1976.00	3.21	3.64	2.75	1.73	1.42	1.58	2.11
1970.00	2.34	2.35	1.83	1.46	1.50	1.63	1.78

Appendix B10, continued

Year	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}
1982.75	2.42	2.96	2.86	3.40	4.81	6.71	10.50
1982.00	1.76	2.06	2.30	2.84	3.73	5.03	8.90
1981.33	2.06	2.38	2.50	3.06	4.23	6.00	10.57
1980.00	2.08	2.88	2.88	2.97	3.75	5.21	9.28
1979.67	2.13	2.58	2.61	2.78	3.33	4.01	4.67
1979.00	2.35	2.60	2.40	2.65	3.64	4.56	4.03
1978.67	2.13	2.54	2.66	3.02	3.64	4.07	4.19
1978.33	2.05	2.41	2.51	2.89	3.71	4.51	4.75
1977.50	2.10	2.42	2.47	2.89	3.88	4.52	3.96
1976.00	2.93	3.03	2.54	2.94	4.17	6.00	10.49
1970.00	2.12	2.42	2.49	2.82	3.37	3.81	4.21

Appendix B11: Short/long index of n-alkanes extracted from Lake Erie sediments.

Year	Short/Long
1982.75	1.55
1982.00	1.31
1981.33	1.64
1980.00	1.41
1979.67	0.97
1979.00	1.01
1978.67	1.00
1978.33	0.98
1977.50	0.93
1976.00	0.71
1970.00	0.81

Appendix B12: Absolute abundances of pristane and phytane extracted from Lake Erie sediments.

Year	pristane ($\mu g/g$ sediment)	phytane ($\mu g/g$ sediment)
1982.75	2.93	0.39
1982.00	1.23	0.48
1981.33	2.37	0.52
1980.00	1.15	0.31
1979.67	0.99	0.44
1979.00	1.42	0.36
1978.67	1.75	0.31
1978.33	0.96	0.29
1977.50	0.74	0.32
1976.00	0.76	0.08
1970.00	0.48	0.27

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