Evaluation of Organic Geochemical Proxies in Sediments as Recorders of the History of Biogeochemical Dynamics in Lake Erie over the Last Century

by

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A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
(Oceanography: Marine Geology and Geochemistry)
in The University of Michigan
2008

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To My Parents

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Abstract

Against a background of a well documented and reconstructed paleoenvironmental history of Lake Erie over the last century, the reliability and accuracy of commonly used organic geochemical proxies from sediments in paleoenvironment reconstructions were evaluated.

Carbon cycling in Lake Erie is reflected by stable carbon isotopes of total organic carbon and calcium carbonate ($\delta^{13}C_{org}$ and $\delta^{13}C_{caco3}$), total organic carbon concentrations (TOC) and calcium carbonate concentrations ($CaCO_3$). $\delta^{13}C_{org}$ and TOC both record changes in lacustrine productivity and nutrient loadings reliably and directly. $CaCO_3$ contents are primarily controlled by decomposition of TOC in the hypolimnion and sediments, reflecting the carbon cycling between the epilimnion and hypoliminion/sediment. The carbon cycling process indicated by $\delta^{13}C_{caco3}$ variations is complicated and appears to relate to primary productivity, temperature variations, phosphorus distributions and/or the recycling of ^{12}C in the epilimnion.

Although stable nitrogen isotopes ($\delta^{15}N$) reflect nitrogen cycling, they also record multiple biogeochemical processes, including anthropogenic inputs, denitrification, primary productivity and establishment of invasive species at different stages of lacustrine history, rendering the interpretations of $\delta^{15}N$ as paleoenvironmental proxies difficult.

The concentrations of biomarker molecules, including hydrocarbons (HCs), fatty acids (FAs) and fatty alcohols (OLs), reliably record changes of lacustrine productivity while their molecular distributions reflect various aspects of paleoenvironmental conditions. The degree of post-burial diagenesis is closed linked with the abundance of branched and unsaturated FAs. When used together, carbon-chain lengths of FAs and OLs may reliably reflect the relative importance between terrigenous and aquatic sources for organic matter. Speculatively, uncommon HC distributions originate from microorganisms inhibiting an oil-contaminated environment.

The effects of spatial and temporal variability of sediment cores on paleoenvironmental reconstructions are investigated by comparing four cores sampled at a common location but in different years, i.e., 1982, 1988, 1991 and 2003. The approximately consistent temporal trends of organic geochemical proxies in these four cores suggest both spatial and temporal variability are not significant enough in biasing long-term paleoenvironmental interpretations. Nevertheless, the differences among the cores in year-to-year proxy variations and proxy values, which are mainly accounted by spatial variability of sediment cores, indicate that high-resolution (i.e. annual) paleoenvironmental interpretations may not be reliable.

Chapter I
Introduction

Organic geochemical proxies, referring to some resistant biomarker molecules and their stable isotopic compositions, are especially informative as "geochemical fossils" or "geochemical fingerprints" in marine and lacustrine sediments because of their wide applications in tracing the biogeochemical processes and providing information about original producers in past ecosystem. The successful application of organic geochemical proxies in paleoenvironment reconstructions depends on two assumptions. The first assumption, which has been widely tested in numerous studies, is that these proxies record information about specific producers or/and biogeochemical processes. For example, alkanes with long carbon chains ($\geq C_{27}$) are generally attributed to terrestrial higher plants while short chain analogues ($\leq C_{21}$) are usually associated with bacterial and algae sources (e.g. Meyers, 1997). As another, stable carbon isotopic compositions of organic carbon ($\delta^{13}C_{org}$) in lacustrine sediments with a predominance of aquatic sources often record the preferential utilization of ^{12}C during the carbon uptake by phytoplankton (e.g. Meyers, 1997). The second assumption is that these proxies are relatively resistant to diagenetic alterations after organic matter is buried in sediment, and hence they preserve information about the original depositional sources and their environments. This assumption is also widely supported by many studies that show negligible alterations of these proxies after they are buried in sediment. For instance, $\delta^{13}C_{org}$ compositions are very similar in two sediment cores sampled six years apart in the Lake Ontario (Hodell and Schelske, 1998), and the atomic ratio between carbon and nitrogen (C/N_{at}), a well established proxy indicating sedimentary sources, was observed to be stabilized by the sediment burial (Ertel and Hedges, 1985; Talbot and Johannessen, 1992).

Despite numbers of successful examples in utilizing organic geochemical proxies in paleoenvironmental reconstructions, concerns regarding the reliability of these two assumptions on which the accuracy of these proxies rely have been raised recently. The first assumption, the exclusivity of some widely used proxies to specific depositional sources or biogeochemical processes, was questioned as the result of advances in technology allowing studies to be performed under diverse environmental settings and in various organisms. As an example, stable carbon isotope compositions of calcium carbonate ($\delta^{13}C_{caco3}$) in lacustrine sediments have been widely used as a proxy indicting the amounts of primary productivity until the recent discovery showing that they may be significantly altered by the chemoautotrophic and methanotrophic microbes living in the oxic-anoxic interface in eutrophic lakes (Hollander and Smith, 2001). For another example, the compounds with short carbon chains ($\leq C_{20}$), which were originally associated with the aquatic sources, have been discovered in various organisms including algae, higher plants, bacteria and fungi (e.g. Carmack et al., 1976; Ueki and Suto, 1979; Rieley et al., 1991; Meyers et al., 1997). The question of "which biogeochemical process or primary source mainly determines the changes of organic geochemical proxies" has more potential answers from recent discoveries, resulting in more challenging paleoenvironmental interpretations of proxies.

The debates on the first assumption, while raising some concerns in paleoenvironmental interpretations, have been minor compared to the concerns arising from the doubts about the second assumption that diagenesis has negligible alterations on organic geochemical proxies. Numerous field and laboratory studies have shown that diagenetic processes have the potential to generate significantly biased environmental records by altering values of organic geochemical proxies through pathways including but not limited to several following ones: (1) selective preservation of resistant organic matter and preferential loss of reactive fractions (e.g. Tu et al, 2004); (2) replacement of biomarkers produced by primary sources with those related to microbial utilization and resynthesis in the sediment (e.g. Meyers and Ishiwatari, 1993); (3) chemical transformations(e.g. Cranwell et al., 1987). These various diagenetic pathways may have different effects on the original organic matter compositions, and even the same diagenetic process may affect organic matter differently under different circumstances,

making it difficult to identify the diagenetic process that is responsible for a certain change in the values of organic proxies. Therefore, more debates arise when it comes to the effects on the organic geochemical proxies related to post-burial diagenesis. Potential effect of diagenesis are illustrated by stable carbon and nitrogen isotope compositions ($\delta^{13}C$ and $\delta\ ^{15}N$), which may become more enriched or depleted as the result of isotopic fractionations of microbial metabolisms, depending on the oxygen concentrations of the surrounding environment (Lehmann et al., 2002). Meanwhile, other biogeochemical processes, such as the selective loss of isotopically enriched or depleted components, hydrolysis, etc., may further complicate the diagenetic signals by shifting $\delta^{13}C$ and $\delta\ ^{15}N$ in uncertain directions (Macko et al., 1987; Bada et al, 1989).

The concerns about the reliabilities of organic geochemical proxies in paleoenvironmental reconstructions have recently been raised much more often than ever as reconstructing high-resolution paleoenvironmental records becomes one of the most important goals in paleoenvironmental studies. This challenge is not surprising given that any offset of these assumptions that may be erased sufficiently not to affect the patterns of environmental records in thousands or millions of years, may be preserved in centennial, annual, seasonal, or even monthly records that have not achieved diagenetic equilibrium. These concerns are the motivation of this study, with a main goal to evaluate the reliability of some widely used organic geochemical proxies in reconstructing high-resolution environmental records in relatively young sediment records.

To do so, it is important to have a reference against which the accuracy and reliability of organic geochemical proxies can be assessed. Lake Erie is an ideal site because changes in its ecosystem over the last century have been so rapid and dramatic that they have attracted scientific attention, which has documented and reconstructed a comprehensive record of the lacustrine ecosystem over the last century, including lacustrine productivity, biological communities, allochthonous inputs from human activities and natural sources, and dissolved oxygen concentrations in the hypolimnion, etc. (e.g. Hartman, 1973; Munawar et al., 1999). By comparing these well-established environmental records with the reconstructed environmental record from the organic matter preserved in Lake Erie sediment in this study, not only the reliability of the

organic geochemical proxies are evaluated, but also the diagenetic alterations of some proxies are identified without the confusion often encountered in paleoenvironmental studies that arises from distinguishing the proxy changes related with environmental changes and those due to diagenetic alterations.

Even better, the dramatic changes of ecosystem in Lake Erie over the course of last century due to anthropogenic perturbations provide various environmental settings under which the behaviors and the reliability of organic proxies can be evaluated. The most distinct change is its primary productivity, which has increased slowly since the early 1800s, mostly due to increased nutrient loadings from European settlement, until early ~1950s, when the primary productivity rose dramatically, fueled by significant increases in phosphorus (P) inputs to Lake Erie as the result of rapid urbanization and industrialization. Fortunately, this increase reached an end point in the early to mid-1970s as the result of the common efforts of the U.S. and Canada governments in reducing P overloads, and the primary productivity has been decreasing steadily thereafter (Munawar et al., 1999). The frequent changes of lacustrine productivity in Lake Erie allow us to study the behaviors of the organic geochemical proxies under different trophic status and at their transitional stages. Many other environmental factors further add to the variability of the ecosystem of Lake Erie, such as the wide establishment of invasive species over the entire basin (e.g., *Dreissena polymorpha*, commonly known as the zebra mussel and *D. bugensis*, commonly known as the quagga mussel), significant water level fluctuations, and anthropogenic trace compound contaminations. (Munawar and Munawar, 1999; Dusini, 2005). Thus, many fast-changing environmental factors in Lake Erie allow evaluations of organic geochemical proxies under different environmental scenarios, which provide references to future studies done under a wide range of lacustrine settings.

With a thorough understanding of various changes in Lake Erie ecosystem as an interpretive background, the reliability of a set of most commonly used proxies in paleoenvironmental reconstructions were evaluated in this study. Chapter II focuses on several classical organic geochemical proxies that reflect the carbon cycle in the lacustrine ecosystems, which include total organic carbon contents (TOC), calcium carbonate contents ($CaCO_3$), $\delta^{13}C_{org}$ and $\delta^{13}C_{caco3}$. Chapter III deals with variations of

the $\delta^{15}N$ record, which has always been a complicated proxy involving many biogeochemical processes that may potentially affect nitrogen cycles and hence has created complications in paleoenvironmental interpretations. This study identified the main biogeochemical processes in determining $\delta^{15}N$ records in the sediment of Lake Erie at different stages of lacustrine ecosystem. Chapter IV concentrates on a set of biomarker molecules including hydrocarbons, fatty acids and fatty alcohols. These three groups of molecules have different sources and reactivities, allowing assessment of their reliabilities in recording different aspects of environmental changes.

While Chapter II to IV focuses on evaluation of organic geochemical proxies using the knowledge of environmental changes in Lake Erie as the reference, Chapter V takes this evaluation to a new level by comparing proxies in multiple sediment cores sampled at approximately the same location but at different years (i.e.1982, 1988, 1991, and 2003). Compared to Chapter II ~ IV, the methodology used in Chapter V puts more emphasis on testing the second assumption behind the proxy applications, that post-burial diagenesis generally is not strong enough to bias paleoenvironmental interpretations. Previous field and laboratory studies aiming to test this assumption both have had limitations in their methods. Field studies assumes that either any changes in proxies with the burial depth are from post-burial diagenesis, which is only valid if original depositional sources and environment did not change (e.g. Matsuda and Koyama, 1977; Haddad et al., 1992), or they assume that depth-related changes in the sediment record reflect environmental changes (e.g. Zhou et al., 2005). Laboratory studies, on one hand, are incomparable to natural environments, where complex biogeochemical processes are constantly interacting with each other, and on the other hand, often restrict the simulations in days or months at most, while natural diagenesis may occur in years or even decades (e.g. Macko et al., 1994). This study compared the proxies in sediment cores sampled at several times over 21 years to overcome these limitations. Additionally, it was discovered the sediment cores were sampled at close but not exactly the same locations, providing an opportunity to examine if the spatial variability of sediments affects the reliabilities of organic geochemical proxies in reflecting environmental changes.

Finally, the major findings of this study are summarized and thoughts on future research directions are given in Chapter VI.

References

Bada, J. L., M. J. Schoeninger, and A. Schimmelmann. 1989. Isotopic fractionation during peptide-bond hydrolysis. Geochimica Et Cosmochimica Acta **53:** 3337-3341.

Carmack, C. L., J. D. Weete, and W. D. Kelley. 1976. Hydrocarbons, fatty-acids and sterols of cronartium-fusiforme aeciospores. Physiological Plant Pathology **8:** 43-49.

Cranwell, P. A., G. Eglinton, and N. Robinson. 1987. Lipids of aquatic organisms as potential contributors to lacustrine sediments .2. Organic Geochemistry **11:** 513-527.

Dusini, D. S. 2005. The effect of Lake Erie water level variations on sediment resuspension. M.S. thesis, Ohio State University.

Ertel, J. R., and J. I. Hedges. 1985. Sources Of Sedimentary Humic Substances - Vascular Plant Debris. Geochimica Et Cosmochimica Acta **49:** 2097-2107.

Haddad, R. I., C. S. Martens, and J. W. Farrington. 1992. Quantifying early diagenesis of fatty-acids in a rapidly accumulating coastal marine sediment. Organic Geochemistry **19:** 205-216.

Hartman, W. L. 1973. Effects of exploitation, environmental changes, and new species on the fish habitats and resources of Lake Erie. Technique report no. 22, Great Lakes Fishery Commission, U. S. Bureau of Sport Fisheries and Wildlife, Biological Station, Sandusky, Ohio.

Hodell, D. A., and C. L. Schelske. 1998. Production, sedimentation, and isotopic composition of organic matter in Lake Ontario. Limnology and Oceanography **43:** 200-214.

Lehmann, M. F., S. M. Bernasconi, A. Barbieri, and J. A. Mckenzie. 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. Geochimica Et Cosmochimica Acta **66:** 3573-3584.

Macko, S. A., M. H. Engel, and Y. R. Qian. 1994. Early diagenesis and organic-matter preservation - a molecular stable carbon-isotope perspective. Chemical Geology **114:** 365-379.

Macko, S. A., M. L. Fogel, P. E. Hare, and T. C. Hoering. 1987. Isotopic fractionation of nitrogen and carbon in the synthesis of amino-acids by microorganisms. Chemical Geology **65:** 79-92.

Matsuda, H., and T. Koyama. 1977. Early diagenesis of fatty-acids in lacustrine sediment .1. identification and distribution of fatty-acids in recent sediment from a freshwater lake. Geochimica Et Cosmochimica Acta **41:** 777-783.

Meyers, P. A. 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Organic Geochemistry **27:** 213-250.

Meyers, P. A., and R. Ishiwatari. 1993. Lacustrine organic geochemistry - an overview of indicators of organic-matter sources and diagenesis in lake-sediments. Organic Geochemistry **20:** 867-900.

Munawar, M., T. Edsail, and I.F. Munawar I F (eds), 1999. State of Lake Ere: past, present and future. Backhuys Publishers. Leiden, The Netherlands.

Rieley, G., R. J. Collier, D. M. Jones, and G. Eglinton. 1991. The biogeochemistry of Ellesmere Lake,UK .1. source correlation of leaf wax inputs to the sedimentary lipid record. Organic Geochemistry **17:** 901-912.

Talbot, M. R., and T. Johannessen. 1992. A high-resolution paleoclimatic record for the last 27,500 years in tropical west Africa from the carbon and nitrogen isotopic composition of lacustrine organic-matter. Earth and Planetary Science Letters **110:** 23-37.

Tu, T. T. N., S. Derenne, C. Largeau, G. Bardoux, and A. Mariotti. 2004. Diagenesis effects on specific carbon isotope composition of plant n-alkanes. Organic Geochemistry **35:** 317-329.

Ueki, A., and T. Suto. 1979. Cellular fatty-acid composition of sulfate-reducing bacteria. Journal of General and Applied Microbiology **25:** 185-196.

Zhou, W., S. Xie, P. A. Meyers, and Y. Zheng. 2005 Reconstruction of late glacial and Holocene climate evolution in southern China from geolipids and pollen in the Dingnan peat sequence. Organic Geochemistry **36**: 1272-1284.

Chapter II
Processes Affecting Carbon Cycling in Lake Erie During Cultural Eutrophication Over the Last Century as Indicated by Stable Isotope Compositions of Sedimentary Organic and Inorganic Carbon

Abstract

A ~106cm sediment core from Eastern Lake Erie Basin was examined to investigate the biogeochemical processes in this large lake during its cultural eutrophication over the last century. We measured stable carbon isotopes of total organic carbon and calcium carbonate ($\delta^{13}C_{TOC}$ and $\delta^{13}C_{caco3}$) as well as the total organic carbon concentrations (TOC) and calcium carbonate concentrations ($CaCO_3$). $\delta^{13}C_{TOC}$ and TOC, showing a strong positive correlation throughout the core, both recorded the changes in lacustrine productivity and nutrient loadings reliably and directly. $CaCO_3$ contents had a negative correlation with TOC through the whole core, suggesting $CaCO_3$ concentrations were primarily controlled by the decomposition of TOC in the hypolimnion and the sediments. We observed a decoupling between the temporal patterns of $\delta^{13}C_{TOC}$ and $\delta^{13}C_{caco3}$. While both $\delta^{13}C_{TOC}$ and $\delta^{13}C_{caco3}$ showed similar responses to the most severe eutrophication, the temporal trends of $\delta^{13}C_{caco3}$ diverged from those of $\delta^{13}C_{TOC}$ before and after this period, suggesting these two proxies independently traced carbon cycling in the lake. The cause for the divergence is not exactly known, but perhaps it is associated with temperature variations, phosphorus distributions in the water column or the recycling of ^{12}C in the epilimnion. This study provided important insights into the processes affecting carbon cycling in Lake Erie during the progress of cultural eutrophication and the recovery of the lake ecosystem after eutrophication.

1. Introduction

No other lake as large as Lake Erie has experienced as many significant changes in its ecosystem over the last century (Hartman 1973). Lake Erie went through an ecological decline from ~1800 to ~1972, a recovery and rehabilitation from ~1972 to present, and a succession of invasions of nonindigenous species starting as early as 1882

(Leach 1999; MacIsaac 1999). Human impacts included the cultural eutrophication of Lake Erie prior to the early 70s, which resulted from significant increases in nutrient loadings and let to deterioration of dissolved oxygen, rapid changes in the types and abundances of phytoplankton, zooplankton and benthic organisms, and the collapse of commercial fisheries (e.g. Hartman 1973; Wright and Tidd 1933; Carr and Hiltunen 1965; Davis 1964; Leach 1999). Fortunately, the rapid eutrophication moderated in the early to mid 70s because of the wide public alert to the degraded state of the lake and the consequent efforts to improve the lake ecosystem and to reverse the human impacts (Leach 1999). The Great Lakes Water Quality Agreements of 1972 and 1978 were established by the governments of the United States and Canada to restrict the overload of phosphorus. Subsequently, decreases in eutrophic species, recovery of fisheries, and improvements in water quality were seen (Makarewicz 1993; Hatch et al. 1987; Leach 1999). Introduction of large numbers of invasive species, which had significant impacts on food chain compositions, trophic structures and contamination dynamics, has been recognized to be another significant perturbation of the Lake Erie ecosystem over the last century (MacIsaac 1999). For example, zebra mussels were introduced into Lake Erie in the late 1980s. These became the focus of research projects because they played a significant role in lake recovery processes by reducing turbidity, altering nitrogen and phosphorus dynamics, and affecting aquatic communities and sedimentary environments (Nicholls and Hopkins 1993; Nicholls et al. 1999; Howell et al. 1996).

An understanding of the biogeochemical processes active during cultural eutrophication is important for formulating effective regulations to help recovery of the lacustrine ecosystem and to prevent further eutrophication. Environmental data from direct measurements in the lower Great Lakes, however, are only available for the last 20-30 years (Schelske and Hodell 1995). Consequently, sediment-record reconstructions of paleoproductivity and carbon cycling processes before and during cultural eutrophication in Lake Erie and Lake Ontario have been used (Schelske and Hodell 1995; Bourbonniere and Meyers, 1996; Hodell et al. 1998; Hodell and Schelske 1998). Stable carbon isotope values of total organic matter ($\delta^{13}C_{TOC}$) have proved to be reliable indictors of paleoproductivity even though the amounts of organic matter in the

sediment records may be diminished by post-depositional diagenesis (Schelske and Hodell 1995). Stable carbon isotope values of calcium carbonate ($\delta^{13}C_{caco3}$) have been observed to diverge from$\delta^{13}C_{toc}$ during the eutrophication recovery process (i.e. after 1970s) in the Lake Ontario (Schelske and Hodell 1991; Hodell et al. 1998). Although the divergence has been attributed to seasonal carbon cycles (Schelske and Hodell 1991), a robust explanation for this divergence remains to be found. The primary factors in controlling the concentrations of calcium carbonate in the sediments of Lake Ontario were attributed to either summer temperature variations (Hodell et al., 1998) or primary productivity (Schelske and Hodell 1991), while the major factors in controlling sedimentary calcium carbonate concentrations in Lake Erie are still enigmatic (Schelske and Hodell 1995).

Here, we presented a high-resolution (1cm/year) TOC, $CaCO_3$, $\delta^{13}C_{TOC}$ and $\delta^{13}C_{caco3}$ paleoproductivity record from sediments collected at the Eastern Basin Reference Site in Lake Erie (Fig.2-1). Our aim is to characterize the carbon cycles and the sedimentary environmental changes in Lake Erie as the lake has experienced eutrophication, rehabilitation and species invasions. Compared to the study by Schelske and Hodell (1995), we provide a sedimentary record that is one decade more recent, which is particularly valuable in assessing the effects of eutrophication recovery measures and their impacts on the sedimentary environment. More specifically, we further examined the relations between $\delta^{13}C_{TOC}$ and $\delta^{13}C_{caco3}$ variations, which have shown decoupling in Lake Ontario during eutrophication recovery processes (Schelske and Hodell 1991) and have attracted research interests in other lacustrine settings (Hollander and Smith 2001; Teranes and Bernasconi 2005; Myrbo and Shapley 2006). The hypothesis that $\delta^{13}C_{TOC}$ is a reliable indictor of paleoproductivity while TOC concentration is not owing to early diagenesis (i.e. oxidation) was further tested. Moreover, by comparing the documented environmental changes and the sedimentary record, our study provided important insights into how the sediments were imprinted by the significant changes in the water column during cultural eutrophication over the last century. Hence, this study also provided important references to assess the assumptions of paleolimnologists who used sedimentary records to reconstruct prehistoric paleoenvironmental changes.

2. Sampling Site

Lake Erie (Fig.2-1) is centered at latitude 42º15'N and longitude 81º15' W. It is 388 km long, 92 km wide and has a surface area of about 25,690 km^2 and a volume of 484 km^3. The lake receives the outflow of Lake Superior, Huron and Michigan and covers a total drainage area about 418,679 km^2. In the Lake Erie region, summers are short, hot and humid, and winters are cold with some snow. The maximum surface temperature in midlake averages ~ 24º and usually occurs in early August. Lake Erie water is bicarbonate rich and has a pH averaging 8.3.

Lake Erie is bathymetrically divided into three basins. The shallow western basin, containing 5% of the lake's total volume, is close to large urban areas and rivers that bring pollutants to the lakes. It is therefore the most vulnerable to anthropogenic impacts of the three basins. The central basin constitutes 63% of the total lake's volume. The deep eastern basin has the maximum depth (64m) among the three basins and makes up 32% of total lake volume. The eastern basin is more resistant to human impacts and environment changes compared to the other two basins because it is farther away from river inputs and it is deeper than the other two basins.

Our sampling site is located at the center of the eastern basin. A Benthos gravity corer was used to collect a sediment core of about 106 cm at 42º31.0'N and 79º53.6'W in 2003 (Fig.2-1). The water depth at this site is about 60 m. The core was cut into 1cm intervals and packed into separate bags in the field. The bags were stored in a freezer after transport to the NOAA Great Lakes Environmental Research Laboratory in Ann Arbor, MI.

3. Methods

Age control for the core was based on the identification of a bomb spike in ^{137}Cs profile data (A.D. 1963). The ages were counted using a mean sedimentation rate of 1cm/year in the core. The sediment core represented the depositional record from 1909 to 2003.

Samples were freeze dried and ground to a fine powder. Calcium carbonate concentrations of each sample were measured by the carbonate bomb technique, which yielded a carbonate-free residue suitable for organic carbon analysis. Elemental compositions (C, %) and stable isotope analysis ($\delta^{13}C$, ‰) were measured with the elemental analysis- isotope ratio mass spectrometry (EA-IRMS) flow through system at

the Laboratory of Isotope Geochemistry at the University of Arizona. Total organic carbon concentrations (TOC, wt%) were expressed on a whole-sediment basis after adjusting for the measured percentage of calcium carbonate. $\delta^{13}C_{TOC}$ values were reported in standard per mil (‰) delta notation relative to the Peedee Belemnite. Suess corrections were applied to the $\delta^{13}C_{TOC}$ and $\delta^{13}C_{caco3}$ to remove the isotopic shifts caused by fossil fuel combustion as recommended by Schelske and Hodell (1995). The Suess correction factor was calculated by subtracting the measured $\delta^{13}C$ values of atmospheric CO_2 at each year from the average $\delta^{13}C$ value of pre-industrial atmospheric CO_2 (i.e. –6.49‰). Annual $\delta^{13}C$ values of atmospheric CO_2 were obtained from Francey et al.' (1999) measurements of $\delta^{13}C$ ratios in air extracted from Antarctic ice core and firn samples. The correction factor, which was linearly interpolated to correlate to the age of the sediments if necessary, was added to the measured $\delta^{13}C$ values of organic carbon and $CaCO_3$ in this study. The isotopic fractionation between $\delta^{13}C$ values of TOC and $CaCO_3$, ϵ_{TOC},, was calculated after Teranes and Bernasconi (2005) as :

$$\epsilon_{TOC} = 1000\ (((\delta^{13}Ccaco3 + 1000)/(\ \delta^{13}Corg + 1000))-1) \quad (1)$$

The Pearson test (two-tailed) was conducted using SPSS 14.0 to examine bivariate correlations among different paleoenvironment proxies.

4. Results

The stratigraphic trends of $\delta^{13}C_{org}$ and TOC contents, which are strongly positive correlated ($r=0.847$, $P<0.0001$, $n=105$), both show a rapid increase from 1950 to 1972, followed by an overall decreasing trend after 1972 (Fig.2-2). $\delta^{13}C_{caco3}$ variations do not parallel the trends of $\delta^{13}C_{TOC}$. $\delta^{13}C_{caco3}$ values show a rapid increase as a response to the rapid eutrophication from 1969 to 1974, but they do not show corresponding increases to the rapid eutrophication from 1950-1969 nor a corresponding decrease to the eutrophication recovery process after 1972 (Fig.2-2). $CaCO_3$ concentrations inversely correlate with TOC concentrations throughout the core (Fig.2-2). In fact, the Peterson correlation r is –0.627 ($p<0.0001$, $n=105$), verifying a significant negative correlation between $CaCO_3$ and TOC contents.

5. Discussion

5.1. The positive relation between TOC and $\delta^{13}C_{org}$: reliable proxies for primary productivity

$\delta^{13}C_{TOC}$ values have been demonstrated to closely approximate the historical trends of primary productivity, P loadings and the changes of lake trophic status in the lower Great Lakes (Schelske and Hodell 1991, 1995; Hodell and Schelske 1998). Phytoplankton primary productivity in the epilimnion is often considered to be the most significant biogeochemical influence on the carbon isotopic composition of lacustrine sedimentary carbon (e.g. Schelske et al. 1988; Hollander and McKenzie 1991). Increased uptake of dissolved CO_2 in the epilimnion during periods of high productivity selectively diminishes the availability of ^{12}C and hence causes a shift to larger $\delta^{13}C$ values. Additionally, enhanced bicarbonate utilization can occur when elevated phytoplankton uptake lowers the availability of dissolved CO_2, which also leads to organic matter with higher $\delta^{13}C$ values (e.g. Hollander and Smith 2001). The TOC concentration in sediments has also been found to be an excellent proxy for past primary productivity, although it varies with many other environmental factors including precipitation, temperature, oxic conditions, etc. (Meyers and Ishiwatari 1993; Meyers 2003; Zhou et al. 2004, 2005; Robinson et al. 2000). More organic matter is transported out of the epilimnion and deposited in the sediments during enhanced primary productivity (Schelske and Hodell 1995; Hodell and Schelske 1998). Specific to our study, Schelske and Hodell (1995) attributed the observed divergence between organic carbon accumulations at the surface sediment and the documented productivity variations in Lake Erie to post-burial diagenesis in sediments overlain by oxic waters.

The stratigraphic trends of $\delta^{13}C_{TOC}$ and TOC in our core, paralleling each other, reflect the changes of nutrient loadings and primary productivity directly (Fig.2-2). Both proxies show rapid increases between ~1950-~1972, recording the rapid increases in aquatic primary productivity within this time period. After 1972, both proxies begin to decrease, responding to the relaxation of nutrient stress as the result of establishment of P-abatement agreements. Our observations agree with and Schelske and Hodell's (1995) study on the sediment cores from Lake Erie, which also showed the rapid increases in TOC and $\delta^{13}C_{TOC}$ between 1950s-1970s and the gradual decreases after the early 1970s. However, the increases in $\delta^{13}C_{TOC}$ in 1990 from the sediment of Ontario observed by Hodell and Schelske (1998), which were speculated to be associated with the establishment of invasive of zebra mussels in the lower Great Lakes, are not observed in

this study, suggesting that the mussel invasions may not be the factor causing this increase in $\delta^{13}C_{TOC}$ in Ontario. To further prove the reliability of these proxies in reflecting nutrient loadings in the lake, we compare $\delta^{13}C_{TOC}$ and the documented TP contents in the Eastern basin of Lake Erie. TP contents between 1983-2003 were the calculated average values from measurements during April at various depths (0~50m) by EPA survey (personal communication with Kenneth W. Klewin and David C. Rockwelland, Environmental Protection Agency, USA) and those between 1970-1979 were estimated from Makarewicz and Bertram (1991). Both TP and $\delta^{13}C_{TOC}$ show an overall decreasing trend from 1970-2003 (Fig.2-3a), further supporting that $\delta^{13}C_{TOC}$ is a direct and reliable proxy for productivity changes related to changes in nutrient loadings. Our conclusion is consistent with the previous studies in the lower Great Lakes (Schelske and Hodell 1991, 1995; Hodell and Schelske 1998), again showing that the $\delta^{13}C_{TOC}$ in lake sediments is a reliable proxy for lacustrine primary productivity and nutrient loadings. TOC concentrations in the sediments of Lake Erie, which are positively correlated with $\delta^{13}C_{TOC}$ values, also reliably trace the variations in primary productivity and trophic status of the lake.

5.2 The inverse relation between TOC and $CaCO_3$: carbon cycle in the water column and the sediments

As discussed earlier, the TOC concentration in sediments is primarily controlled by primary aquatic productivity. The authigenic precipitation of $CaCO_3$ in the Great Lakes, commonly referred to as whiting events, is most intense during late summer and early fall when high water temperature has reduced the solubility of $CaCO_3$ and the biological primary productivity has removed the epilimnetic CO_2, increased the pH of waters, and consequently promoted the precipitation of $CaCO_3$ (Strong and Eadie 1978; Hodell et al. 1998). Hence, a high $CaCO_3$ concentration in sediments generally corresponds to enhanced productivity and/or high epilimnion temperature (Hodell et al. 1998). However, $CaCO_3$ concentrations are also sensitive to $CaCO_3$ dissolution occurring in the hypolimnion and in bottom sediments, where temperature and pH values determine the extent of dissolution of $CaCO_3$. (Dean 2002).

$CaCO_3$ and TOC concentrations show a strong inverse relation through the whole core ($r=-0.627$, $P<0.0001$, $n=105$). The concentration decreases in TOC of several

tenths of a percent were accompanied by a several percent increase in $CaCO_3$ (Fig.2-2), indicating dilution of one component by another is not the primary reason for this inverse correlation. Dean (1999, 2002) also observed an inverse relation between $CaCO_3$ and TOC concentrations in sediments from Minnesota lakes. He argued that the CO_2 produced by decomposition of TOC in the hypolimnion and in the sediments lowers the pH values of water and expedites the dissolution of $CaCO_3$ produced in the epilimnion. This situation often occurs at sediments containing high amounts of TOC (12% suggested in Dean (1999)'s study) or in the lakes with seasonally anoxic hypolimnion (Dean 1999). Although our core contains low TOC contents (0.7-1.6%), the anoxic conditions in the lake bottom caused by the cultural eutrophication in Lake Erie (Hartman 1973) produces conditions conducive to this process. Hence, although more $CaCO_3$ precipitates at enhanced epilimnetic productivity, the greater decomposition of TOC in the hypolimnion and the sediments produces more organic acids, causing greater dissolution of $CaCO_3$, and lowering the amounts of $CaCO_3$ in the Lake Erie sediments. Hence, $CaCO_3$ dissolution seems to be the primary control of $CaCO_3$ contents in the sediments of Lake Erie.

In contrast, temperature variations have been postulated as the most important control on sedimentary $CaCO_3$ contents in the downstream Lake Ontario (Hodell et al. 1998). Without a direct measurement of water temperature of Lake Erie, it is hard to assess the influence of temperature on its sedimentary $CaCO_3$ concentrations. Interestingly, we observed that the annual surface temperature variations of Erie, Pennsylvania (local climatological data publications from National Climatic Data Center, www7. ncdc. Noaa.gov/IPS/LCDPubs) have a negative relation on TOC contents through the core while also showing a positive relation with CaCO3 concentrations in some limited depositional periods (i.e.~1914-~1923 and ~1940-~1978, Fig.2-3 b,c). Our observation suggests that primary productivity was higher at lower temperatures and vice versa. Even though it has been established that P loadings are the main factor determining the variations in primary productivity during the cultural eutrophication of Lake Erie (Hartman 1973; Schelske and Hodell 1995; Leach 1999; the previous discussion of this paper), the low temperature could enhance P availability by shortening the summer stratified period (Findlay et al. 2001; Johnson et al. 2003). At lower

temperatures, the lake more likely experiences a shorter stratified period, has more time to recycle nutrients between the epilimnion and hypolimnion, and hence has a higher primary productivity. The temperature variations, therefore, likely act together with P loadings in determining the primary productivity in Lake Erie. The dramatic increases in TOC deposition starting in the early 1950s were mainly caused by the increased human P loadings but may have also been boosted by the recorded decreases of temperature starting then. Similarly, the increases in the temperature of the late 1970s may also have contributed to the decreasing trend in TOC contents after the early 1970s. The several years' difference between the occurrence of decreases in TOC contents and the increases of the temperatures, however, either reflects the difference between water temperature of Lake Erie and air temperature of Erie, PA or suggests that nutrient loadings are the primary factor initiating the changes in the TOC concentrations. The impacts of temperature variations on $CaCO_3$ concentrations are less consistent in our core compared to those on TOC contents. Generally, more $CaCO_3$ will be precipitated at high temperatures because of the decreased solubility of $CaCO_3$ and high pH values in the epilimnion due to the more intense removal of CO_2 as the result of a longer stratification period (Hodell et al. 1998). The positive correlation between $CaCO_3$ contents and the temperature variations appear only at some depositional periods (Fig.2-3c), perhaps suggesting that temperatures have some influence on $CaCO_3$ contents in the sediments within some periods. The lack of the consistency of this positive correlation through the core, however, indicates that the $CaCO_3$ contents in the sediments are primarily controlled by the dissolution of $CaCO_3$ in the hypolimnion and in the sediments due to the decomposition of organic matter.

5.3 The decoupling of $\delta^{13}C_{TOC}$ and $\delta^{13}C_{caco3}$: independent proxies tracking carbon cycles in the Lake Erie

Different models have been developed based on different lake basins describing how $\delta^{13}C$ values of TOC and $CaCO_3$ record the response of lacustrine carbon cycle to seasonal and long-term changes in primary productivity in the lakes (McKenzie 1985; Hollander 1989; Hollander and Smith 2001; Teranes and Bernasconi 2005). Many studies found that the $\delta^{13}C$ values of sedimentary TOC and $CaCO_3$ often parallel each other (McKenzie 1985; Hollander and Smith 2001; Lojen et al. 1997). In the earlier models,

phytoplankton primary productivity in the epilimnion was considered as the most significant biogeochemical influence on the carbon isotope of lacustrine sedimentary carbon (e.g. McKenzie 1985; Hollander and McKenzie 1991). $\delta^{13}C$ values of both TOC and $CaCO_3$ are high as a consequence of enhanced phytoplankton productivity because of the progressively enriched ^{13}C carbon sources in the epilimnion and the decreased carbon isotopic fractionation during carbon uptake by phytoplankton (e.g. McKenzie 1985; Hollander and McKenzie 1991). Interpretation of sedimentary $\delta^{13}C$ records in terms of changes of trophic status became more complicated when more recent work brought forward the importance of microorganisms on the variations of carbon isotopes of sedimentary carbon, especially in lakes with seasonal water column anoxia (Hollander and Smith 2001; Lehmann et al. 2004). During periods of enhanced eutrophication, when the oxic-anoxic interface is close to the surface, biomass created by chemoautotrophic and methanotrophic microbes is generally more depleted in ^{13}C than algal biomass by -15 to -40‰ (Kelly et al. 1998, Summons et al. 1994) and can contribute significant quantities of ^{13}C depleted CO_2 to the epilimnion carbon reservoir. The recent lake eutrophication model developed from two highly productive lakes, Lake Mendota (Wisconsin) and Lake Greifen (Switzerland), that both incorporated contributions of microbial biomass, showed that the excursions of $\delta^{13}C$ values of sedimentary carbon were controlled by the relative importance of algae and microorganisms during the progress of cultural eutrophication (Hollander and Smith 2001). When the lake is at relatively moderate level of eutrophication, $\delta^{13}C$ values of TOC and $CaCO_3$ in the sediments both display negative excursions because of (1) the additions of ^{13}C depleted carbon from chemoautotrophic and methanotrophic organisms living in the hypolimnion and the sediments and/or (2) the phytoautotrophic assimilation of ^{13}C depleted CO_2 produced by oxidation of biological methane. At more severe eutrophication, ^{13}C-enriched carbon produced from algae is able to overwhelm the ^{13}C-depleted biomass and cause an increase in the $\delta^{13}C$ of sedimentary TOC and $CaCO_3$ (Hollander and Smith 2001).

The decoupling of the temporal patterns of $\delta^{13}C$ values between TOC and $CaCO_3$, however, has been observed in many other studies (Hodell et al. 1998; Schelske and Hodell 1991; Teranes and Bernasconi 2005). Various mechanisms have been proposed

to explain the decoupling, most of which were related with the different seasonal carbon cycles when the TOC and the $CaCO_3$ are produced (Hodell et al. 1998; Schelske and Hodell 1991; Teranes and Bernasconi 2005). Schelske and Hodell (1991) found a discrepancy of $\delta^{13}C$ values between TOC and $CaCO_3$ in the sediments of Lake Ontario in responding to lake recovery from eutrophication as P loading decreased. They attributed this discrepancy to the seasonal cycle of carbon in the lake and suggested that $\delta^{13}C_{TOC}$ was determined by springtime primary productivity whereas $\delta^{13}C_{caco3}$ mostly reflected late summer productivity. The decoupling of $\delta^{13}C$ values of TOC and $CaCO_3$ was also observed during the eutrophication of Lake Baldeggersee, Switzerland (Teranes and Bernasconi 2005). During the hypertrophic period in Baldeggersee, $\delta^{13}C_{caco3}$ values became larger, whereas $\delta^{13}C_{TOC}$ became smaller. Teranes and Bernasconi (2005) argued that the $\delta^{13}C_{caco3}$ trend mainly reflected surface-water primary productivity because $CaCO_3$ precipitation was mainly confined to the epilimnion due to light limitations of the photoautotrophic producers. However, $\delta^{13}C_{TOC}$ responded to the combined effects from both primary productivity and microbial biomass, the latter of which was mostly produced at the anoxic-oxic interface or the anoxic part of the water column and added ^{13}C depleted carbon to the sedimentary organic matter because of the shallowing of anoxic-oxic interface at severe eutrophication. They also suggested that ϵ_{TOC}, the isotopic difference between the TOC and $CaCO_3$, was a more effective indicator of lake trophic status than either $\delta^{13}C_{TOC}$ or $\delta^{13}C_{caco3}$ alone. Overall, it is hard to generalize the behavior of $\delta^{13}C$ values of sedimentary TOC and $CaCO_3$ in response to transitions of the eutrophic status of the lakes, which differ depending on the biological communities, biogeochemical processes and many specific environmental conditions of the individual lake.

Although a positive correlation exists between the variations of $\delta^{13}C_{caco3}$ and $\delta^{13}C_{TOC}$ in our sediment core ($r=0.446$, $P<0.0001$), $\delta^{13}C_{caco3}$ trends do not closely parallel those of $\delta^{13}C_{TOC}$ (Fig.2-2), suggesting that changes in primary productivity with the transitions of eutrophic status are not the only important control on $\delta^{13}C_{caco3}$ values. In contrast to $\delta^{13}C_{TOC}$, whose stratigraphic trends closely approximate the changes in primary productivity and nutrient loadings, $\delta^{13}C_{caco3}$ shows a dramatic increase only in responding to the most rapid eutrophication increase between 1969-1974. The lack of

response in $\delta^{13}C_{caco3}$ to eutrophication before 1969, as well as to the lake recovery after 1974, however, suggests other factors also influence the variations of $\delta^{13}C_{caco3}$ values.

The isotopic difference between organic matter and $CaCO_3$ - ϵ_{TOC} - has been employed as an effective proxy to identify the contributions of microbial biomass. ϵ_{TOC} values greater than 32‰ were identified as a indictor for the bacterial inputs in both marine and lacustrine sediments (Hayes 1993; Teranes and Bernasconi 2005). The ϵ_{TOC} values (25-27.2‰) in our study are relatively small, suggesting no significant contributions of microbial inputs to the sedimentary carbon. The temporal variations of the ϵ_{TOC} values closely follow those of $\delta^{13}C_{TOC}$, reflecting the variations of primary productivity and nutrient loadings.

$\delta^{13}C_{caco3}$ continuously increases after 1974 while $\delta^{13}C_{TOC}$ decreases due to the decreases in primary productivity as the lake remediation program proceeded. As mentioned earlier, a similar discrepancy between $\delta^{13}C$ values of TOC and $CaCO_3$ was observed in the sediments of downstream Lake Ontario that were attributed to the differences in primary productivity at different seasons (Schelske and Hodell 1991). The observation that the summer TP concentrations in the water column of Lake Ontario have not showed proportionate decreases compared to the annual TP concentrations during the processes of recovery from eutrophication led the authors to believe that summer productivity did not decrease as significantly as annual productivity. Hence, $\delta^{13}C_{caco3,}$ which mainly reflected the productivity during late summer in Lake Ontario, did not decrease even after the lake remediation program had effectively decreased the $\delta^{13}C_{TOC}$ values (Schelske and Hodell 1991). In Lake Erie, this explanation may also partially account for the discrepancy observed in our study, inasmuch as the decreases of August TP concentrations from 1982-2003 in the Eastern Lake Erie Basin were ~ 40% less than those in April, when TP concentrations at various depths are mostly equal because of lake overturn and hence represent well the annual whole water column conditions (personal communication with Kenneth W. Klewin and David C. Rockwelland, Environmental Protection Agency, USA). However, the increases of $\delta^{13}C_{caco3}$ are still puzzling as TP concentrations during August showed an overall decreasing trend from 1982 to 2003. Furthermore, in a subsequent study of sediments from Lake Ontario, $\delta^{13}C_{caco3}$ values were observed to decrease after the 1980s (Hodell et al. 1998). The

six years lag in decreases of $\delta^{13}C_{caco3}$ in Lake Ontario were explained either by the lagged response to P abatement in the late 70s or by the response to the establishment of zebra mussels in the late 1980s, which have dramatically lowered phytoplankton standing crop, zooplankton biomass, and TP concentrations in upstream Lake Erie (Hodell et al. 1998). Our study suggests that zebra mussel establishment may not be responsible for this lagged response of $\delta^{13}C_{caco3}$ as no correspondent decrease occurs in $\delta^{13}C_{caco3}$ in the sediments of Lake Erie. Another important factor that may affect $\delta^{13}C_{caco3}$ values is temperature. Greater $\delta^{13}C_{caco3}$ values are produced in years with early thermal stratification and a warmer summer, because longer thermal stratification causes more photosynthetic removal of ^{12}C from the epilimnion and produces a more ^{13}C enriched pool in the epilimnion (Hodell et al. 1998). Hence, the continuously increasing $\delta^{13}C_{caco3}$ values after 1970s may be accounted for by the increases in temperature during late 1970s (Fig.2-3d). Overall, the reason for the absent or lagged response of $\delta^{13}C_{caco3}$ to the lake recovery from eutrophication observed in Lake Erie and Lake Ontario is not adequately understood and warrants more studies of $CaCO_3$ precipitation in Great Lakes to elucidate its mechanism.

Similarly, $\delta^{13}C_{caco3}$ does not show correspondent increases to the increase in primary productivity before 1969. $\delta^{13}C_{caco3}$ decreases from 1950-1956, when the rapid eutrophication occurred as reflected by the dramatic increases in both TOC concentrations and $\delta^{13}C_{TOC}$ within this period. This decrease of $\delta^{13}C_{caco3}$ may also be attributed to the decreases of temperature from 1950-1972, which resulted in a shorter thermally stratified period, less removal of epilimnetic ^{12}C, and lower $\delta^{13}C_{caco3}$ values. The seasonal variations of TP concentrations in Lake Erie may also play a role in this lack of the response of $\delta^{13}C_{caco3}$ to the increased productivity. Direct measurements of TP contents in Lake Erie between 1982-2003 from Environmental Protection Agency (Personal communications) show that the TP contents in the epilimnion are lower than those in the hypolimnion during August, which can be accounted by the lack of the P resuspension from the sediments in August (You et al 2007). We suggest, therefore, that the relatively low TP concentrations in the epilimnion in August may not be enough to cause the apparent responses in $\delta^{13}C_{caco3}$. Another possible explanation may lie in the compensatory effects from epilimnetic organic matter recycling because of the

well-developed thermocline during late summer. The recycling of carbon sources in the epilimnion, which diminishes the effects of ^{13}C enrichment due to the increases in primary productivity by returning ^{12}C depleted carbon sources for the phytoplankton, should be more intense when $CaCO_3$ is largely precipitated because of a well-developed thermocline. Hence, the $\delta^{13}C_{caco3}$ incorporates the ^{13}C-depleted carbon and does not show positive excursions in response to the gradual increasing primary productivity. In contrast, TOC is mostly deposited during the spring lake overturn period, and hence, $\delta^{13}C_{TOC}$ is less affected by the recycled carbon and shows increasing trends owing to the increases in the annual primary productivity.

Our study suggests that $\delta^{13}C_{caco3}$ and $\delta^{13}C_{TOC}$ values record the carbon cycles in the lakes independently, which agrees with the studies on Lake Ontario (Schelske and Hodell 1991) and Lake Baldeggersee (Teranes and Bernasconi 2005). However, the behavior of $\delta^{13}C$ values of sedimentary carbon among Lakes Erie (this study), Ontario (Schelske and Hodell 1991) and Baldeggersee (Teranes and Bernasconi 2005) are different and, consequently, the mechanism for the decoupling between $\delta^{13}C_{caco3}$ and $\delta^{13}C_{org}$ must be different in these three lakes. In Baldeggersee, $\delta^{13}C_{caco3}$ appears to respond mainly to surface-water productivity whereas $\delta^{13}C_{org}$ reflects the incorporation of microbial biomass (Teranes and Bernasconi 2005). In our study, there is no evidence showing significant microbial inputs. $\delta^{13}C_{caco3}$ values in Lake Ontario show a lagged response to the P abatement program while those in Lake Erie do not show any response. In Erie, $\delta^{13}C_{TOC}$ is a reliable indicator of surface water primary productivity, while $\delta^{13}C_{caco3}$ only responds to the dramatic increases in productivity when eutrophication is the most intense. The relatively gradual changes in primary productivity before and after the most severe eutrophication period are not reflected in $\delta^{13}C_{caco3}$. The reason for the lack of the response in $\delta^{13}C_{caco3}$ to productivity variations is not exactly known. It may be related to temperature variations, uneven P distributions in the water column, and carbon recycling in the epilimnion. Improved understanding of the mechanism of $\delta^{13}C_{caco3}$ variations observed in both Lake Erie (this study) and Lake Ontario (Schelske and Hodell 1991) requires additional studies of $CaCO_3$ in the Great Lakes. Overall, the sedimentary carbon isotope record observed in this study is not completely consistent with previous models describing carbon isotope excursions during eutrophication processes (e.g.

McKenzie 1985; Hollander 1991; Hollander and Smith 2001). Our study suggests the eutrophication model differs between different lake basins and hence local settings need to be well known before interpreting the stable carbon isotope records are attempted.

6. Conclusion

Our study employs a sediment core from Lake Erie to reconstruct paleoproductivity and carbon cycling over the last century, when the lake ecosystem was subjected to a series of anthropogenic impacts. We have reached several major conclusions:

1. Our study confirms the hypothesis of Schelske and Hodell (1995) that sedimentary $\delta^{13}C_{TOC}$ is a reliable indicator for paleoproductivity in Lake Erie when corrected for the Suess Effect. Sedimentary TOC concentrations also record changes in primary productivity faithfully in lakes with uniform sedimentation rates.
2. The inverse correlation between $CaCO_3$ and TOC concentrations in the sediments provides information about the carbon cycling processes between the epilimnion and hypolimnion/sediments. Sedimentary $CaCO_3$ contents in Lake Erie are primarily controlled by the decomposition of TOC, which produces organic acid, lowers pH values and causes the dissolution of $CaCO_3$ in the hypolimnion and the sediments. Neither paleoproductivity or the temperature variations play the major role in determining the $CaCO_3$ concentrations in the sediments of Lake Erie.
3. We observed a decoupling of $\delta^{13}C_{caco3}$ and $\delta^{13}C_{TOC}$ in Lake Erie, which is also found in the downstream Lake Ontario (Schelske and Hodell 1991). The decoupling of $\delta^{13}C_{TOC}$ and $\delta^{13}C_{caco3}$ suggests that these two proxies track relatively independent parts of the carbon cycle in Lake Erie. The mechanism for why $\delta^{13}C_{caco3}$ is not a direct proxy for the paleoproductivity is not clear. However, it may be associated with temperature variations, P distributions in the epilimnion and hypolimnion at different seasons, and recycling of carbon in the epilimnion during thermally stratified periods.

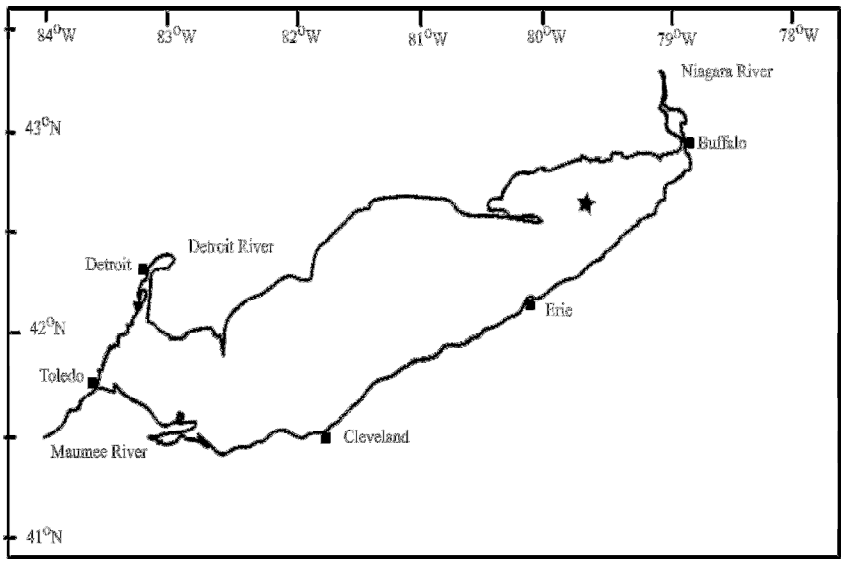

Fig. 2-1 Map of the Lake Erie study area. The star locates the Eastern Basin (EB) Reference Site where the sediment core was obtained in 2003 from a water depth of 60m.

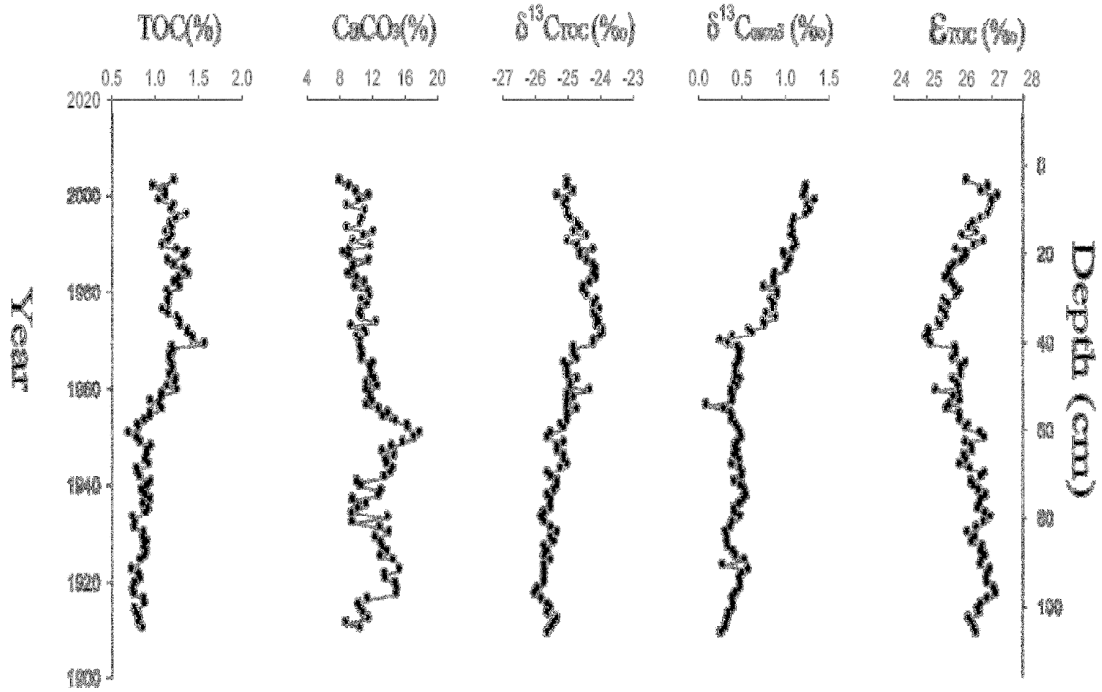

Fig. 2-2 Paleoenvironmental proxies (TOC concentrations, $CaCO_3$ concentrations, $\delta^{13}C_{TOC}$, $\delta^{13}C_{caco3,}$ and ϵ_{TOC} values) of the sediment core from the Eastern Lake Erie Basin Reference Site.

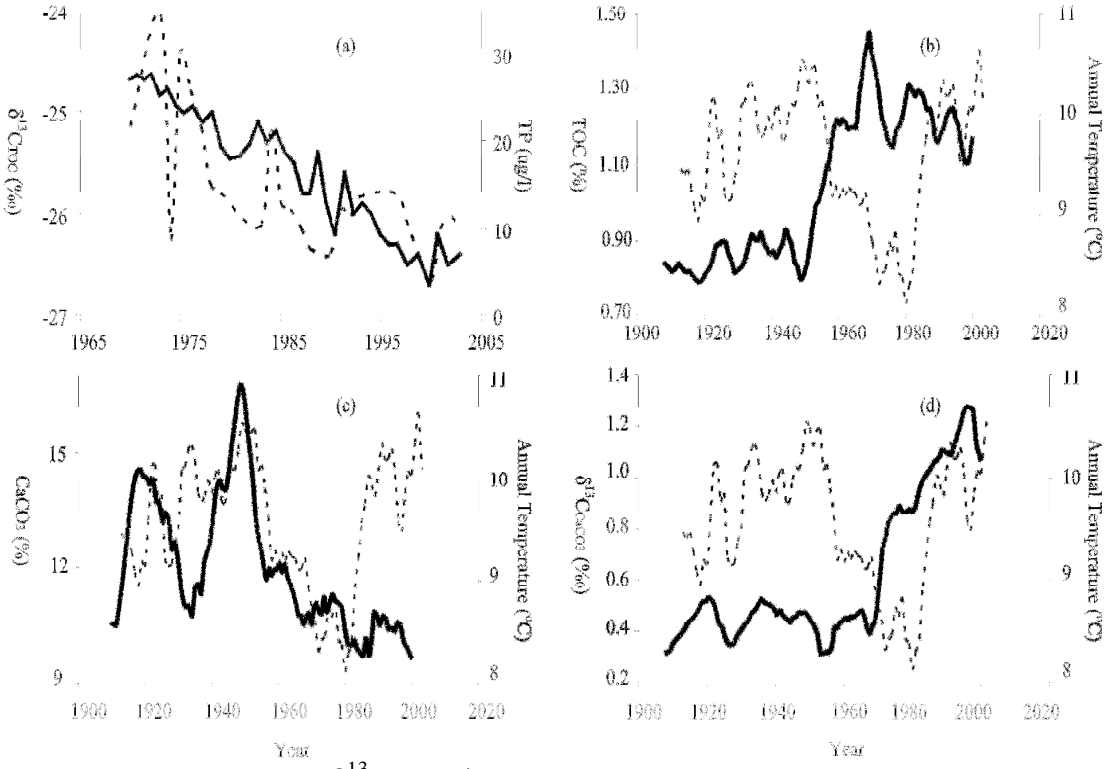

Fig. 2-3 (a) Variations of $\delta^{13}C_{TOC}$ (‰) of the sediment core (solid line) and total phosphorus (TP) contents (dashed line) in the Lake Erie from 1970 to 2003. TP contents were summarized from Makarewicz and Bertram (1991) and the data from Environmental Protection Agency; (b) Variations of 5-point moving average of TOC (wt %) (solid line) in the sediment core and 5-point moving average of annual temperatures of Erie, PA (dashed line) between 1909 to 2003; (c) Variations of 5-point moving average of $CaCO_3$ (wt%) in the sediment core (solid line) and 5-point moving average of annual temperature of Erie, PA (dashed line) between 1909 to 2003; (d) Variations of 5-point moving average of $^{13}C_{caco3}$ (‰) in the sediment core solid line) and 5-point moving average of annual temperature of Erie, PA (dashed line) between 1909 to 2003; Annual temperature variations at Erie, PA were summarized from local climatological data publications from National Climatic Data Center, www7. ncdc. Noaa.gov/IPS/LCDPubs

References

Bourbonniere, R. A., and P. A. Meyers. 1996. Sedimentary geolipid records of historical changes in the watersheds and productivities of Lakes Ontario and Erie. Limnology and Oceanography **41:** 352-359.

Carr, J. F., and J.K. Hiltunen. 1965. Changes in the bottom fauna of western Lake Erie from 1930 to 1961. Limnology and Oceanography **10**: 551-569.

Davis C C. 1964. Evidence for the eutrophication of Lake Erie from phytoplankton records. Limnology and Oceanography **3**: 275-283.

Davis, C. C. 1969. Seasonal distribution, constitution, and abundance of zooplankton in Lake Erie. Journal of fishery research bulle. Journal of the Fisheries Research Board of Canada **26**: 2459-2476.

Dean, W. 1999. The carbon cycle and biogeochemical dynamics in lake sediments. Joural of Paleolimnology **21**: 375-393.

Dean, W. 2002. A 1500-year record of climatic and environmental changes in Elk Lake, Clearwater County, Minnesota II: geochemistry, mineralogy, and stable isotopes. J Paleolimnol **27**: 301-319.

Findlay, D. L., S. E. M. Kasina, M. P. Stainton, K. Beaty and M. Lyng. 2001. Climatic influences on algal populations of boreal forest lakes in the Experimental Lakes Area. Limnology and Oceanography **46**: 1784-1793.

Francey, R. J., C. E. Allison, D. M. Etheridge, C. M. Trudinger, I. G. Enting, M. Leuenberger, R. L. Langenfelds, E. Michel and L. P. Steele. 1999. A 1000-year high precision record of $\delta^{13}C$ in atmospheric CO_2. Tellus **51B**: 170-193.

Hartman, W. L. 1973. Effects of exploitation, environmental changes, and new species on the fish habitats and resources of Lake Erie. Technique report no. **22**, Great Lakes Fishery Commission.

Hatch, R. W., S. J. Nepszy, K. M. Muth, and C. T. Baker. 1987. Dynamics of the recovery of the western Lake Erie walleye (*Stizostedion viterum vitreum*) stock. Canadian Journal of Fisheries and Aquatic Sciences **44** (Suppl 2): 15-22.

Hayes, J. M. 1993. Factors controlling ^{13}C contents of sedimentary organic compounds: Principles and evidence. Marine Geology **113**: 111-125.

Hayes, J. M., H. Strauss, and A. J. Kaufman. 1999. The abundance of 13C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800Ma. Chemical Geology **161**: 103-125.

Hodell, D. A., and C. L. Schelske. 1998. Production, sedimentation and isotopic composition of organic matter in Lake Ontario. Limnology and Oceanography **43**: 200-214.

Hodell, D. A., C. L. Schelske, G. L. Fahnenstiel, and L. L. Robbins. 1998. Biologically induced calcite and its isotopic composition in Lake Ontario. Limnology and Oceanography **43**: 187-199.

Hollander, D. J., and J. A. McKenzie. 1991. CO_2 control on carbon isotope fractionation during aqueous photosynthesis: A paleo-CO_2 barometer. Geology **19**: 929-932.

Hollander, D. J., and M. A. Smith. 2001. Microbially mediated carbon cycling as a control on the $\delta^{13}C$ of sedimentary carbon in eutrophic Lake Mendota (USA): New models for interpreting isotopic excursions in the sedimentary record. Geochimica Et Cosmochimica Acta **65**: 4321-4337.

Howell, E. T., C. H. Marvin, R. W. Bilyea, P. B. Kauss and K. Somers. 1996. Changes in environmental conditions during *Dreissena* colonization of a monitoring station in eastern Lake Erie. Journal of Great Lakes Research **22**: 744-756.

Johnson, L., G. Kling, J. Magnuson, and B. Shuter. 2003. Changes in lake productivity and eutrophication. Confronting climate change in the Great Lakes Region Technical Appendix http://www.ucsusa.org/greatlakes/

Kelley, C. A., R. B.Coffin, and L. A. Cifuentes. 1998. Stable isotope evidence for alternative bacterial carbon sources in the Gulf of Mexico. Limnology Oceanography **43**: 1962-1969.

Leach, J. H. 1999. Lake Erie: passages revisited. In: Munawar M, Edsail T, Munawar I F (eds) State of Lake Ere: past, present and future. Backhuys Publishers. Leiden, The Netherlands, pp 5-22.

Lehmann, M. F., S. M.Bernasconi, J. A. McKenzie, A. Barbieri, M. Simona, M. Veronesi. 2004. Seasonal variation of the $\delta^{13}C$ and $\delta^{15}N$ of particulate and dissolved carbon and nitrogen in Lake Lugano: Constraints on biogeochemical cycling in a eutrophic lake. Limnology and Oceanography **49**: 415-429.

MacIsaac, H. J. 1999. Biological invasions in Lake Erie: past, present and future. In: Munawar M, Edsail T, Munawar I F (eds), State of Lake Ere: past, present and future. Backhuys Publishers. Leiden, The Netherlands, pp 305-322.

Makarewicz, J. C. 1993. Phytoplankton biomass species composition in Lake Erie, 1970

to 1987. Journal of Great Lakes Research **19**: 258-274.

Makarewicz, J. C., and P. Bertram. 1991. Evidence for the restoration of the Lake Erie ecosystem. Bioscience **41**: 216-223.

McKenzie, J. A. 1985. Carbon isotopes and productivity in the lacustrine and marine environment. In: Stumm W (Ed), Chemical processes in lakes. Wiley, New York, pp 99-117.

Meyers, P. A. 2003. Application of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. Organic Geochemistry **34**: 261-289.

Meyers, P. A., and R. Ishiwatari. 1993. Lacustrine organic geochemistry: an overview of indicators of organic matter sources and diagenesis in lake sediments. Organic Geochemistry **20**: 867-900.

Myrbo, A., and M. D. Shapley. 2006 Seasonal water-column dynamics of dissolved inorganic carbon stable isotopic compositions ($\delta^{13}C_{DIC}$) in small hardwater lakes in Minnesota and Montana. Geochimica Et Cosmochimica Acta **70**: 2699-2714.

Nicholls, K. H., and G. J. Hopkins. 1993. Recent changes in Lake Erie (North Shore) phytoplankton: cumulative impacts of Phosphorus loading reductions and the zebra mussel introduction. Journal of Great Lakes Research 19: 637-647.

Nicholls, K. H., Standke, S. J., and G. J. Hopkins. 1999. Effects of dreissenid mussels on nitrogen and phosphorus in north shore waters of Lake Erie. In: Munawar M, Edsail T, Munawar I F (eds) State of Lake Ere: past, present and future. Backhuys Publishers. Leiden, The Netherlands, pp 5-22.

Robinson, S G, J. T. S. Sahota, and F. Oldfield. 2000. Early diagenesis in North Atlantic abyssal plain sediments characterized by rock-magnetic and geochemical indices. Marine Geology **163**: 77-107.

Schelske, C. L., and D.A. Hodell. 1991. Recent changes in productivity and climate of Lake Ontario detected by isotopic analysis of sediments. Limnology and Oceanography **36**: 961-975.

Schelske, C. L., and D. A. Hodell. 1995. Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. Limnology and Oceanography **40**: 918-929.

Schelske, C. L., J. A. Robbins, W. S. Gardner, D. J. Conley, and R. A. Bourbonniere. 1988. Sediment record of biogeochemical responses to anthropogenic perturbations of nutrient cycles in Lake Ontario. Canadian Journal of Fisheries and Aquatic Sciences **45**: 1291-1303.

Strong, A. E., and B. J. Eadie. 1978. Satellite observations of calcium carbonate precipitations in Great Lakes. Limnology and Oceanography **23**: 877-887.

Summons, R E, L. L. Jahnke and Z. Roksandic. 1994. Carbon isotopic fractionation in lipids from methanotrophic bacteria: Relevance for interpretation of the geochemical record of biomarkers. Geochimica Et Cosmochimica Acta **58**: 2853-2863.

Teranes, J. L., and S. M. Bernasconi. 2005. Factors controlling $\delta^{13}C$ values of sedimentary carbon in hypertrophic Baldeggersee, Switzerland, and implications for interpreting isotope excursions in lake sedimentary records. Limnology and Oceanography **50**: 914-922.

Wright, S., and W. M. Tidd. 1933. Summary of limnological investigations in western Lake Erie in 1929 and 1930. Transactions of the American Fishery Societies **63**: 271-285.

Zhou, W., X. Yu, A. J. Jull, G. Burr, J. Xiao, X. Lu, and F. Xian. 2004. High-resolution evidence from southern China of an early Holocene optimum and a mid-Holocene dry event during the past 18,000 years. Quaternary Research **62**: 39-48.

Zhou, W., S. Xie, P. A. Meyers, and Y. Zheng. 2005 Reconstruction of late glacial and Holocene climate evolution in southern China from geolipids and pollen in the Dingnan peat sequence. Organic Geochemistry **36**: 1272-1284.

You, B., J. Zhong, C. Fan, T. Wang, L. Zhang, and S. Ding. 2007. Effects of hydrodynamics processes on phosphorus fluxes from sediment in large, shallow Taihu Lake. Journal of Environmental Sciences **19**: 1055-1060.

Chapter III

δ ^{15}N Values in Lake Erie Sediments: Indicators of Nitrogen Biogeochemical Dynamics During Lake Eutrophication

Abstract

Changes in organic carbon and nitrogen concentrations and stable isotope compositions in a century-long sediment core from the Eastern Basin (EB) of Lake Erie defined five stages in the history of the eutrophication of this lake that included its onset, peak, and amelioration. Pronounced variations in stable nitrogen isotope (δ^{15}N) values reflected significant perturbations in N dynamics within the lake during the onset of accelerated eutrophication in the 1950s. δ^{15}N values increased from the bottom to the top of the sediment core, indicating that the denitrification that accompanied the development of anoxic bottom waters of the Central Basin (CB) modified the nitrogen cycle in Lake Erie as cultural eutrophication proceeded. The δ^{15}N values reached a maximum that reflected the productivity peak in 1968-1970 or/and strong dissolved oxygen (DO) depletion in the hypoliminion of the CB. δ^{15}N values remained high for a decade after lake productivity began to drop after nutrient deliveries decreased. A subsequent progressive decrease in δ^{15}N values after 1991 was most likely related to the establishment and growth of large populations of filter-feeding zebra mussels in the lake, which furthered the decreases in primary productivity. δ^{15}N record in the sediments from the Lake Erie EB largely reflected the variations of primary productivity as well as the denitrification process in the lake basin, which was closely related with the DO depletion in the hypoliminion of the CB during summer stratification, combined with the resuspension and eastward transport of CB sediments into the EB and beyond. External human N inputs, however, can introduce significant alterations of the δ^{15}N record and overprint the isotopic signals within the lake basin.

1. Introduction

The Lake Erie ecosystem has experienced a series of significant changes over the last century (Hartman 1973). The lake went through an ecological decline from ~1850 to ~1972, a recovery and rehabilitation from ~1972 to present, and a succession of invasions of nonindigenous species starting as early as 1882 (Leach 1999; MacIsaac 1999). The cultural eutrophication of Lake Erie, largely due to the increased human phosphorus (P) inputs to the lake, began in the mid-1900s and caused many significant changes in the aquatic ecosystem including increases in aquatic productivity, deterioration of DO concentrations, and changes in biological community compositions (Hartman, 1973). Fortunately, cultural eutrophication reached an end in the mid-1970s because of the limits imposed on P loadings to the lake. Rehabilitation of the ecosystem, including improvement of water quality, decreases in phytoplankton productivity, and recovery of fisheries, have been observed in Lake Erie since the 1970s (Leach 1999). Besides cultural eutrophication, the invasion of nonindigenous species is another factor causing significant changes in the ecosystem of Lake Erie over the last century. In particular, two non-native species of mussel, *Dreissena polymorpha* (commonly known as the zebra mussel) and *D. bugensis* (commonly known as the quagga mussel) proliferated within Lake Erie beginning in the late 1980s and attracted many scientific concerns because of their significant effects on the native biota and the entire lacustrine ecosystem (Upsdell, 2005).

The stable isotope compositions of organic matter in lacustrine sediments are important recorders of past environments because they provide evidence about the biological sources and past depositional environments of the organic matter (Meyers and Ishiwatari 1993). Stable carbon isotope values of organic matter ($\delta^{13}C_{org}$) in the sediment records from Lake Erie have been shown to be reliable and direct proxies of changes in aquatic productivity during this lake's cultural eutrophication over the last century (Schelske and Hodell 1995). $\delta^{15}N$ compositions of lacustrine sediments have not been as widely used in paleoenvironmental reconstructions because the multiple processes involved in N biogeochemical cycles complicate interpretations of the $\delta^{15}N$ records (Bernasconi et al. 1997). For example, different temporal patterns of $\delta^{15}N$ records were observed in the sediments from Florida lakes as the trophic status of the lakes changed. $\delta^{15}N$ values decreased in Lakes Clear Hollingsworth and Parker with

increasing nutrient enrichment, but they did not show a consistent trend in Lake Griffin as it also became more enriched in nutrients (Brenner et al. 1999). When relying on $\delta^{15}N$ in the sediments to reconstruct changes in the past N dynamics, the critical point is to clarify the most significant biogeochemical processes that control the $\delta^{15}N$ records in the sediments.

This study presents the first complete high resolution $\delta^{15}N$ record (1.1cm/year) for the last century of sediment accumulation in the EB of Lake Erie. The well-documented/reconstructed eutrophication history of Lake Erie provides an ideal background to evaluate the use of $\delta^{15}N$ values in sediment records to reconstruct past changes in nitrogen biogeochemical dynamics. Moreover, we present several classic paleoenvironmental proxies including total organic carbon (TOC), $\delta^{13}C_{org}$, and atomic carbon and nitrogen ratios ($C:N_{at}$) for a better understanding of the local sedimentary environmental conditions in the EB. With a good knowledge of the changes in biogeochemical processes that potentially affect the $\delta^{15}N$ values, the primary goal of this study is to identify the most significant process recorded in the $\delta^{15}N$ values in the sediments of EB.

Moreover, the rapid and significant changes in the Lake Erie ecosystem over the last century allow evaluation of the sedimentary $\delta^{15}N$ values as a record of past changes in N cycling under different scenarios. This large-lake setting provides a special opportunity to examine the response of $\delta^{15}N$ records in sediments to variations in trophic status, anthropogenic inputs, and the establishment of invasive species. Hence, the second goal of this study is to examine the behaviors of the sedimentary $\delta^{15}N$ records when the lacustrine environmental settings were subjected to rapid and dramatic shifts.

Overall, our study provides important insights into the major biogeochemical processes affecting sedimentary $\delta^{15}N$ records when a lacustrine ecosystem experiences rapid changes, which presents an important basis for assessing how $\delta^{15}N$ compositions reflected past changes in N dynamics during different environmental settings of this or any lake.

2. Sampling Site

Lake Erie (Fig.3-1) was formed as the result of melting of Laurentide glaciers about 12 kyrs ago (Upsdell 2005). It is 388 km long and 92 km wide, and it has a surface area of about 25,690 km^2 and a volume of 484 km^3 (Hartman 1973). The lake receives the outflow from upstream lakes Superior, Huron and Michigan through the Detroit River and consequently has a total drainage area of about 418,679 km^2 (Hartman 1973; Makarewicz and Bertram 1991). It drains into Lake Ontario through the Niagara River (Makarewicz and Bertram 1991). In the Lake Erie region, summers are short, hot and humid while winters are cold with some snow. The average maximum surface temperature in midlake can reach ~ 24º and usually occurs in early August (Hartman 1973). Lake Erie water is bicarbonate rich and has an average pH of 8.3 (Hartman 1973).

Lake Erie is bathymetrically divided into three basins by subaqueous moraines (Upsdell, 2005). The shallow western basin (WB) averages 8m in depth and contains 5% of the lake's total volume. The CB constitutes 63% of the total lake's volume and has a maximum depth of 25 meters (Hartman 1973). The deep EB has the maximum depth of 64m of the three basins and makes up 32% of total lake volume (Hartman 1973). The CB and EB thermally stratify during summer while the shallow WB does not (Hartman 1973).

The status of lake eutrophication is classified in terms of either the amount of biological productivity or the extent of DO depletion in the hypoliminion or sometimes both. The three basins of Lake Erie were affected by cultural eutrophication between ~1945 to ~1972 in different ways. The WB is close to large urban areas and rivers that bring pollutants to the lakes (Hartman 1973) and therefore, it had the highest P concentrations, experienced the highest biological productivity of the three basins and was considered as a eutrophic basin. The shallowness of the WB prevented the occurrence of DO depletion in its bottom (Berner and Berner, 1996). Although surface water productivity of the CB was considered only mesotrophic, DO depletion in the hypoliminion of the central basin during summer stratification justifies its classification as eutrophic (Berner and Berner, 1996). Being farther away from river inputs and deeper than the other two basins, the EB is more tolerant of human effects and environment changes compared to the other two basins The EB was considered as mesotrophic in the matter of both surface productivity and DO depletion (Berner and Berner, 1996).

Our sampling site is located at the center of the eastern basin (see Fig.3-1). A Benthos gravity corer was used to collect a 106 cm sediment core at 42º31.0'N and 79º53.6'W in September 2003 (Fig. 3-1). The water depth at this site was about 60 m. The core was cut into 1cm intervals and packed into separate bags in the field that were stored in a freezer after transport to the NOAA GLEREL in Ann Arbor, MI.

3. Methods

Age determination for the core was based on the identification of the 1963 bomb spike in the ^{137}Cs profile data (Fig. 3-2). ^{137}Cs was measured on a carefully calibrated gamma counting system with a counting error of less than 3%. The ages of the 1-cm core sections were established using a mean sedimentation rate of 1.1 cm/year in the core. The 106 cm sediment core represented the depositional record from 1909 to 2003.

Samples were freeze dried and ground to a fine powder. Calcium carbonate concentrations of each sample were measured by the carbonate bomb technique, which yielded a carbonate-free residue suitable for organic carbon analysis. Analysis of TOC (%), total nitrogen (TN, %), $\delta^{13}C_{org}$ and $\delta^{15}N$ was done using the elemental analysis-isotope ratio mass spectrometry (EA-IRMS) flow through system of the Laboratory of Isotope Geochemistry at the University of Arizona. $\delta^{13}C_{org}$ and $\delta^{15}N$ values were reported in standard per mille (‰) delta notation relative to the Peedee Belemnite and atmospheric N_2, respectively. Suess Effect corrections were applied to the $\delta^{13}C_{org}$ to compensate for the atmospheric carbon isotopic shifts caused by fossil fuel combustion as recommended by Schelske and Hodell (1995). The Suess Effect correction factor was calculated by subtracting the measured $\delta^{13}C$ values of atmospheric CO_2 at each year from the average $\delta^{13}C$ value of pre-industrial atmospheric CO_2 (i.e. –6.49‰). Annual $\delta^{13}C$ values of atmospheric CO_2 were obtained from the measurements of $\delta^{13}C$ ratios in air extracted from Antarctic ice core and firn samples (Francey et al. 1999). TOC concentrations were adjusted to a whole-sediment basis from the measured $CaCO_3$ concentrations. $C:N_{at}$ ratios were calculated based on the measured carbonate-free TOC and TN and their atomic weights.

4. Results

The variations of TOC, $\delta^{13}C_{org}$, $\delta^{15}N$, and $C:N_{at}$ ratios with depth in the sediments were shown in Fig.3-3. We divided the eutrophication history of Lake Erie into five

stages according to the variations of the geochemical proxies through the core (see Fig.3-3). TOC and $\delta^{13}C_{org}$ values, showing similar temporal trends throughout the core, were used to reflect the productivity history of Lake Erie, which corresponded to the eutrophication history reconstructed by Schelske and Hodell (1995) and the documented nutrient loadings and productivity changes (Hartman, 1973; Makarewicz and Bartram 1991). The $C:N_{at}$ ratio was used as a proxy to assess changes in the primary source of organic matter in the sediments. Phytoplankton, zooplankton, bacteria and benthic plants have low $C:N_{at}$ values (4-10), whereas terrestrial vascular plants generally have $C:N_{at}$ values of 20 and greater (Meyers and Ishiwatari 1993). $C:N_{at}$ values, ranging from 7.3 to 8.9, indicated aquatic organisms as the primary sources while the variations of $C:N_{at}$ reflected the changes in the relative importance of different sedimentary sources. The variations of $\delta^{15}N$ values, used to reconstruct N biogeochemical dynamics, will be detailed in the discussion section.

Stage I: pre-eutrophication from 1909 ~ 1950:

This stage was characterized by fairly invariant values of all proxies. Both $\delta^{13}C_{org}$ and TOC were relatively constant, suggesting minor changes in the primary productivity during this period. This observation was consistent with previous reports showing that the Lake Erie EB was not significantly affected by eutrophication before the 1950s (Hartman 1973) because it is farther away from the pollution sources (Detroit, Raisin and Maumee Rivers) relative to the other two basins. The moderate variations of $\delta^{15}N$ values at this period suggested moderate changes in N dynamics within the lake at this stage.

Stage II: the beginning of rapid eutrophication from ~1950 to ~1966:

Cultural eutrophication began to show effects on the Eastern Basin in the early 1950s. Primary productivity increased rapidly at this stage, as suggested by the rapid increases in both $\delta^{13}C_{org}$ and TOC values. $\delta^{15}N$ showed significant variations, suggesting that dramatic changes in N dynamics were occurring rapidly at this period. $C:N_{at}$ values show a decreasing trend, indicating some major changes were occurring in the sedimentary sources at this period.

Stage III: eutrophication maximum from ~1966 to ~1970:

Eutrophication continued to increase during this period. $\delta^{13}C_{org}$ and TOC showed their most pronounced increases during this short period, suggesting dramatic increases in

primary productivity. Both $\delta^{13}C_{org}$ and TOC reached their maxima, indicating that the lake reached its most eutrophic status. Both $\delta^{15}N$ values and $C:N_{at}$ showed gradually increasing trends within this period, suggesting the occurrence of the modifications of N cycling and organic matter sources at this stage.

Stage IV: recovery from eutrophication from ~ 1970 to ~1990.

The lake began to show signs of recovery and rehabilitation from eutrophication due to the mandated efforts to limit P inputs. $\delta^{13}C_{org}$ and TOC values both decreased, indicating decreases in lacustrine productivity due to the decreased anthropogenic P inputs. $\delta^{15}N$ values were relatively constant, suggesting the response of N cycling to the eutrophication recovery was relatively resistant or slower compared to C cycles. $C:N_{at}$ values also showed minor variations, perhaps indicating that there were no major changes in sedimentary sources at this period.

Stage V: expansion of the zebra mussel population after 1990:

The biogeochemical effects of the rapidly expanding presence of the zebra mussels in Lake Erie that had first been reported in 1988 begin to be seen in the sediment record. Both TOC and $\delta^{13}C_{org}$ values continued to show a general decreasing trend, likely as a response to the continuously decreasing biological productivity as the lake proceeded to recover from eutrophication. A consistently decreasing trend in $\delta^{15}N$ values after 1990 indicated a persistent change in N cycling in the lake.

Overall, the proxies in the sediment core reconstructed a complete history of eutrophication development in the Eastern Basin of Lake Erie over the last century, including pre-development, development, deterioration, and rehabilitation, which showed a good correspondence with the documented eutrophication history.

5. Discussion

5.1. $\delta^{15}N$ interpretive background

Interpretation of $\delta^{15}N$ records in sediments is more complicated than for $\delta^{13}C_{org}$ because $\delta^{15}N$ compositions are affected by many factors, including degree of nitrate utilization associated with primary productivity (e.g. Altabet and Francois, 1994), different nitrogen sources (e.g. Hodell and Schelske 1998), denitrification and diagenesis (e.g. Altabet et al. 1995) and the biological N cycles in food webs (e.g. Gu et al. 1996).

Primary productivity is most commonly considered in evaluating the variations of $\delta^{15}N$ records in sediments. Enhanced aquatic primary productivity draws down dissolved nitrate, which decreases isotopic discrimination in favor of ^{14}N during N uptake by phytoplankton owing to N limitation and consequently yields larger $\delta^{15}N$ values (Altabet and Francois 1994).

Allochthonous N inputs alter the $\delta^{15}N$ values of organic matter in lake sediments by affecting the mix of $\delta^{15}N$ values of dissolved nitrogen sources in the lake (Ostrom et al. 1998; Lehmann et al. 2004a). The $\delta^{15}N$ values of external N sources fall in a wide range. Generally, $\delta^{15}N$ values of atmospheric depositions are relatively low and range between -10 and 0‰ (Hodell and Schelske 1998). Higher plants surrounding the lakes could have lower $\delta^{15}N$ values than algae living within the lake because they assimilate atmospheric N_2 made available to them by nitrogen-fixing soil microbes (Brenner et al. 1999). Agriculture runoff contains a range of $\delta^{15}N$ values (organic N in soil, 0~ +9‰, fertilizer with NO_3^-, -5~+7‰, fertilizer with NH_4^+, -6 to +5‰: Heaton 1986; Faure and Mensing 2005) while domestic sewage is generally enriched in ^{15}N ($\delta^{15}N$ of 3 ~ 12‰, Hodell and Schelske 1998). The high variability of $\delta^{15}N$ values of external N sources, consequently, may cause positive or negative excursions of $\delta^{15}N$ values in the lake sediment record. For example, Ostrom et al. (1998) suggested that the low $\delta^{15}N$ value in nitrate in Lake Superior was derived from atmospheric deposition. Lehmann et al. (2004a) associated a marked positive shift in the $\delta^{15}N$ of sedimenting particulate organic matter in Lake Lugano in 1994/1995 with the introduction of a denitrification stage in wastewater treatment.

Diagenesis also has great potential to alter the $\delta^{15}N$ values. Although some studies showed negligible alterations in $\delta^{15}N$ contents of sedimentary particles resulting from diagenesis (e.g. Meyers and Eadie 1993), other studies reported N isotopic shifts with different magnitudes and directions. The variations of nitrogen isotope ratios of organic matter during diagenesis were primarily attributed to two possible causes: (1) preferential loss of ^{14}N and (2) bacterial secondary N. The preferential loss of ^{14}N was mostly observed in the denitrification process, where ^{14}N is preferentially removed when NO_3^- is partially converted into N_2, and consequently, the residual NO_3^- is ^{15}N-enriched. This process was well established by the several studies that showed an increase of

nitrogen isotope ratios of organic matter with depth of the sediments (e.g. Altabet and Francois 1994). Bacterial secondary N affects the δ^{15}N values of primary N in different directions. Bacteria may produce more enriched δ^{15}N protein (Macko et al. 1987, Bada et al, 1989) or ^{15}N-depleted nitrogen (Macko and Estep, 1984), depending on the biosynthetic pathways. The N-isotope shifts caused by bacteria fractionation have been suggested as potential indicators of oxygen depletion at the water-sediment interface because aerobic and anaerobic bacteria generate the N-isotope shifts in contrasting directions (Sachs and Repeta 1999).

Biological community compositions have also been reported to be important in determining δ^{15}N values by affecting the nitrogen pools used by primary producers, the frequency with which nitrogen cycles through the food web, and different metabolic pathways (Upsdell 2005). For example, N_2- fixing cyanobacteria display little fractionation and generate δ^{15}N values similar to atmospheric N_2 (Gu et al. 1996). By contrast, non-N_2 fixers, which generally utilize ammonium or nitrate, can have considerable isotopic variations and result in organic matter with various δ^{15}N values. As an example, primary producers assimilating ammonium are more enriched in ^{15}N than those utilizing nitrate (Upsdell 2005). Further, the apparent N-isotope enrichment varies with different phylogenetic groups even with the same nitrogen pool. For example, diatoms show relatively small N-isotope fractionation (ε=-1.0‰±0.9) and green algae have larger fractionation (ε=-3.4‰±0.4) during nitrate assimilation (Lehmann et al. 2004b). Moreover, δ^{15}N values increase by 3-4‰ with each trophic transfer due to metabolic pathways that preferentially eliminate the lighter isotope (Hodell and Schelske 1998; Upsdell 2005).

Keeping in mind all the potential processes affecting the temporal trends in δ^{15}N, we will discuss the variations of δ^{15}N in reflecting past changes in N cycles at the different stages of cultural eutrophication in the Lake Erie record to distinguish the most important factors controlling δ^{15}N variations.

5.2. Denitrification: The overall positive shift of δ^{15}N values from Stage I to Stage III

After the significant fluctuations in δ^{15}N values during Stage II, δ^{15}N values showed an overall increase. The average of δ^{15}N values in from Stage III to V was about 0.7‰ more positive than those at Stage I (Fig. 3-3). We believed this overall increase in

$\delta^{15}N$ values was most likely related with the increased denitrification before and after the rapid cultural eutrophication of the lake. Previous studies have shown the significance of the effects of denitrification on $\delta^{15}N$ values in the sediments of Lake Erie. Hodell and Schelske (1998) suggested this denitrification signal in Lake Erie was transported downstream as far as Lake Ontario and contributed at least partially to the increase of $\delta^{15}N$ values in sediment cores from Lake Ontario.

The increase in $\delta^{15}N$ values in our core also can be attributed to the intensification of anoxia in the CB. Summer stratification anoxia was widely observed in the hypoliminion since ~1930s in the CB of the Lake Erie and has not shown long term decreases even after the decreases of P loadings after 1970 (Hodell and Schelske 1998; Schloesser et al. 2005), while the anoxia or hypoxia was rarely observed even at the most eutrophic status in the EB. There is a strong west to east flow within the lake. The outflows of Lakes Superior, Michigan, and Huron enter Erie via the Detroit River ($5465 m^3$/sec, Hartman, 1973) and exit the lake via the Niagara River. Moreover, the hydraulic residence time of the lake is less than two years. The shallow WB and CB are subject to frequent and persistent sediment resuspension during spring and fall, resulting in the eastward transport of those materials into the EB and beyond. Hence, sediments carrying the denitrification signal of the CB were redeposited in the EB and contributed to the positive $\delta^{15}N$ signals in the EB. The overall positive shift of $\delta^{15}N$ values from the bottom to the surface of the core is the result of the seasonal anoxia in the CB.

$\delta^{15}N$ values were more positive after Stage II, suggesting that this stage was a critical period for the intensification of the DO depletion in CB. Given that Stage II was the stage of development of rapid eutrophication in the Lake Erie, our study again proves that the rapid increases in primary productivity were the fundamental cause for the development of anoxic conditions in the Lake Erie.

5.3. Moderate variations in N dynamics in Stage I: gradual eutrophication (1909-1950)

The $\delta^{15}N$ values during Stage I displayed frequent variations without an apparent trend, which may suggest the moderate variations in N dynamics during the progress of slow eutrophication. According to the documented history and the variations of TOC and $\delta^{13}C_{org.}$, the lake went through relatively moderate changes in ecosystem within Stage I compared to Stage III-V. However, the $\delta^{15}N$ values showed greater variations in Stage I

than those in Stage III to V. This contradiction was most likely due to the lack of the treatment of wastewater, which did not begin until ~1970 in Lake Erie, at Stage I. In other words, the anthropogenic inputs added much more noise to $\delta^{15}N$ in Stage I than those at Stage III, IV and V. Thus, the frequent variations of $\delta^{15}N$ in Stage I reflected the changes of N dynamics due to the anthropogenic inputs, however, the lack of the consistent trend in $\delta^{15}N$ suggest these changes are relative compared to those during Stage III to V.

5.4. Initiation of changes in N dynamics at Stage II: the beginning of rapid eutrophication(1950-1966)

The frequent and dramatic fluctuations in $\delta^{15}N$ record during Stage II (Fig.3-3), when the EB began to show strong effects from eutrophication, suggested that rapid increases in cultural eutrophication caused significant instability in N dynamics within the lake basin. The rapid increase in productivity during this stage was not directly seen in $\delta^{15}N$ records. The cause for these significant fluctuations is not known but is most likely related to the increases in anthropogenic N inputs, which are the only factors that can be imagined to cause such a significant change in $\delta^{15}N$ values within such a short period. Further, the changes in $C:N_{at}$ values provided collateral evidence for the changes in anthropogenic N inputs. We noticed that the beginning of the strong variability of the $\delta^{15}N$ values (~1950) was accompanied by the decreases of $C:N_{at}$ values while the end of the variability (~1962) was accompanied by the increases of $C:N_{at}$ values. Thus, we believed the strong variability of $\delta^{15}N$ values was caused by the changes of the sedimentary sources. The decreased $C:N_{at}$ values most likely reflected higher inputs of nitrogen from agricultural fertilizer and animal wastes; similarly lowered values were also observed in the tributaries of Lake Erie (Upsdell 2005). Agricultural fertilizers have $\delta^{15}N$ compositions similar to atmospheric N_2, but their isotopic compositions can become enriched or depleted after being applied to the soil and exhibit a wide range of $\delta^{15}N$ values (-5 to +7‰) (Hodell and Schelske 1998). Moreover, sewage inputs, most of which were untreated before ~1970, were likely to have increased at this period with the increase of urban and suburban populations and would have added further variations in the $\delta^{15}N$ signals within the lake. Hence, increased anthropogenic N inputs were most likely the major reason for the significant variations of $\delta^{15}N$ values at this period. The

beginning of the rapid increases in TOC and $\delta^{13}C_{org}$ values further support our interpretation of significant increases in human inputs at this time.

Although N inputs may be the most important cause for the significant variations of $\delta^{15}N$ records at this period, we cannot completely exclude other potential factors causing the shifts of the $\delta^{15}N$ values. First, DO depletion in the hypoliminion of the CB was observed to significantly increase during this period (Hartman, 1973; Berner and Berner, 1996), which would have transported more positive $\delta^{15}N$ signals to the EB due to denitrification. Second, phytoplankton communities and the foodchain structure within Lake Erie were subjected to significant changes due to the rapid increases in cultural eutrophication at this period (i.e. ~1950 to ~1970) (e.g. Davis 1969; Hartman 1973), which may have added more variations to the $\delta^{15}N$ values. However, these factors were masked by the significant variability of the allochthonous inputs.

Overall, the strong variability of $\delta^{15}N$ values in the sediments was evidence of significant changes of the N cycling dynamics when the lake was undergoing rapid cultural eutrophication. Given the rapid changes in $\delta^{15}N$ values over short intervals and the accompanying $C:N_{at}$ changes, we believed that the human N inputs were the major cause for the abnormal $\delta^{15}N$ values at this period.

5.5. Nitrate utilization and denitrification at Stage III: the maximum of eutrophication (1966 to 1970)

Eutrophication reached its peak in Stage III and resulted in the maximum level of lacustrine productivity of the last century. Surprisingly, the $\delta^{15}N$ records did not show fluctuations as significant as those at Stage II even though anthropogenic inputs were expected to be maximum at this stage. Given the accompanying increases in $C:N_{at}$ values, this lack of the variability in $\delta^{15}N$ perhaps reflected the decreases in anthropogenic N inputs for unknown reasons, and hence, the signals from anthropogenic inputs were likely to be superseded by those from the biogeochemical N cycles within the lake basin. The gradual increases in $\delta^{15}N$ values at this period were most likely caused by two major changes in N dynamics within the lake. First, primary productivity reached such a high point that it was able to overcome all other sources and dominated the $\delta^{15}N$ variability during this period although various biogeochemical processes affecting $\delta^{15}N$ signals were occurring. The abundant primary productivity led to limited nitrate supplies, resulting in

decreased N isotope fractionation during nitrate assimilation and elevated $\delta^{15}N$ values. Again, the increases of $C:N_{at}$ values, suggesting that external N input from fertilizers and animal manure became less significant than those at Stage II, provided further evidence that organic matter from phytoplankton became more dominant at this stage. Second, the rapid eutrophication intensified DO depletion in the bottom of the CB, further promoting denitrification and subsequently transporting a more positive signal to the EB. Supporting evidence exists in the observation that anoxia of the CB of Lake Erie increased significantly from the 1930s to the 1970s (Hodell and Schelske 1998). Hence, the gradual increase in $\delta^{15}N$ values from ~1966 to ~1970 reflected the rapid increases in phytoplankton productivity during cultural eutrophication and/or the growth of annual DO depletion in the hypoliminion of the central basin.

5.6. Denitrification at Stage IV: recovery and rehabilitation

As concluded above, larger $\delta^{15}N$ values appeared to be good indictors of the rapid increases in primary productivity in Lake Erie during Stage III. However, $\delta^{15}N$ values did not decrease as the immediate responses to the gradual decreases in primary productivity beginning in the early 70s. This lack of response may be related to two factors: First, the wastewater treatment involving denitrificaion began at ~1970 and added more positive $\delta^{15}N$ signals. The relatively constant pattern in $\delta^{15}N$ values between 1970 to1991 may be the result of the counteracting effects of the positive shifts from anthropogenic inputs and the negative shifts caused by the decreases in primary productivity. Second, as discussed earlier, the DO depletion in the CB has not shown any long term decrease after all of the P reduction efforts (Schloesser et al. 2005). This lack of the response to the decreases in primary productivity may suggest that the increases in the $\delta^{15}N$ values in the Stage III were mainly caused by the DO depletions in the CB, which has not changed, instead of the rapid increases in primary productivity.

5.7. Changes in N dynamics at Stage V: invasion of zebra mussels

Instead, $\delta^{15}N$ values began to show a delayed decrease at ~1991. The decreases of the $\delta^{15}N$ values corresponded with the time when the invasive zebra mussels proliferated and spread to the central and eastern basins of Lake Erie (Upsdell 2005), suggesting that changes in N dynamics were likely caused by this invasive species. It is interesting to note that Hodell and Schelske (1998) have speculatively related the

increases in $\delta^{13}C_{org}$ in sediments deposited after 1990 in the sediments from Lake Ontario to the establishment of zebra mussels in the entire lake basin of Lake Erie. In this study, similar changes in $\delta^{13}C_{org}$ were not seen while the decreases of $\delta^{15}N$ values after 1991 may be attributed to the invasions of zebra mussels. While previous studies have shown that zebra mussels have posed important changes in N biogeochemical dynamics in the lake ecosystem (e.g. Nicholls and Hopkins 1993; Upsdell 2005), the direction of the $\delta^{15}N$ shifts in the sediments were uncertain as zebra mussels can change N cycles in various ways. First, they can alter $\delta^{15}N$ values by affecting the primary productivity in the lake. These filter feeders have been observed to dramatically decrease phytoplankton standing crops in nearshore areas (Schelske and Hodell 1995), which would have further relieved the N limitation in the lake during eutrophication recovery and contributed to the decreases in the $\delta^{15}N$ values. Second, zebra mussels have been observed to stimulate the growth of cyanobacteria in Lake Erie. However, cyanobacteria in the lake have not been observed to fix N_2 directly. Thus, they generated $\delta^{15}N$ values in the range of other phytoplankton and were unlikely the cause for the negative shifts in the $\delta^{15}N$ values of the sediments. Third, zebra mussels have been observed to increase the denitrification rate of the sediment (Bruesewitz et al., 2006), which will add to the positive shifts in the $\delta^{15}N$ signals, and hence, is not the major cause for the negative $\delta^{15}N$ shifts in the sediments. Four, zebra mussels also significantly increased excretion of ammonium (Gardner et al., 1995; Lavrentyev et al., 2000), which generally has more positive $\delta^{15}N$ values than nitrate (Upsdell, 2005). Actually, increases in $\delta^{15}N$ values of suspended particulate organic matter in nearshore sites of Lake Erie have been associated with the ammonium excreted by the mussels, which can be an alternative of nitrate as the nitrogen pool for primary production (Upsdell 2005). This change also cannot be the primary cause for the observed negative shifts in $\delta^{15}N$ values in the sediments as it would have led to the shifts in the direction opposite to our observation.

Overall, it seemed that the negative shifts observed in the sediments were mainly associated with the decreases in primary productivity, which have been further stimulated by the invasion of zebra mussels. Although zebra mussels can potentially cause changes in the $\delta^{15}N$ values of organic matter in various ways, the decreases in the N isotopic fractionation during N uptake seemed to be the most significant process in Lake Erie

since the sediments record is a result of the integration of many processes occurring in the whole water column, in which the most important process generally stands out.

5.8. What did the $\delta^{15}N$ values preserve in the sediment record?

The $\delta^{15}N$ values in the 100-yr sedimentary record indicated various changes in N dynamics in Lake Erie as its cultural eutrophication proceeded. We summarized the most likely biogeochemical processes affecting $\delta^{15}N$ variations at different stages: (1) the variations in $\delta^{15}N$ values before 1950 suggested that minor changes due to anthropogenic inputs were occurring in N dynamics within the lake when it was experiencing gradual cultural eutrophication. (2) During the rapid increase in eutrophication between 1950 - 1966, $\delta^{15}N$ values fluctuated dramatically, indicating significant instability in N dynamics that was most likely associated with the increases of anthropogenic N inputs. (3) The apparent increases in $\delta^{15}N$ values between 1968-1970 were reflectors of enhanced primary productivity when the P-driven eutrophication reached its maximum or/and the annual DO depletion in the hypolimnion of the CB peaked. (4) After 1991, the gradual decreases in $\delta^{15}N$ may be the result of the establishment of zebra mussels, which further reduced the amounts of lacustrine productivity. 5) The overall positive shift of $\delta^{15}N$ values after 1966 relative to those before 1950 indicated greater denitrification because of the development of anoxic lake-bottom waters in the CB during eutrophication.

The overview of our data shows that three important processes were preserved in the $\delta^{15}N$ records: denitrification, primary productivity and anthropogenic inputs. These three processes may add or cancel each other or one of them may dominate the $\delta^{15}N$ signals, depending on different environmental settings. Our study showed that, even in the same lake, $\delta^{15}N$ variations in the sediments recorded different aspects of the N dynamics as the lacustrine ecosystem changed. In paleolimnological studies, $\delta^{15}N$ record in the lacustrine sediments have more complex behaviors than $\delta^{13}C$ and should not be oversimplified as an indictor of any single biogeochemical process without a background knowledge of the lake history or/and supporting evidence from other environmental proxies.

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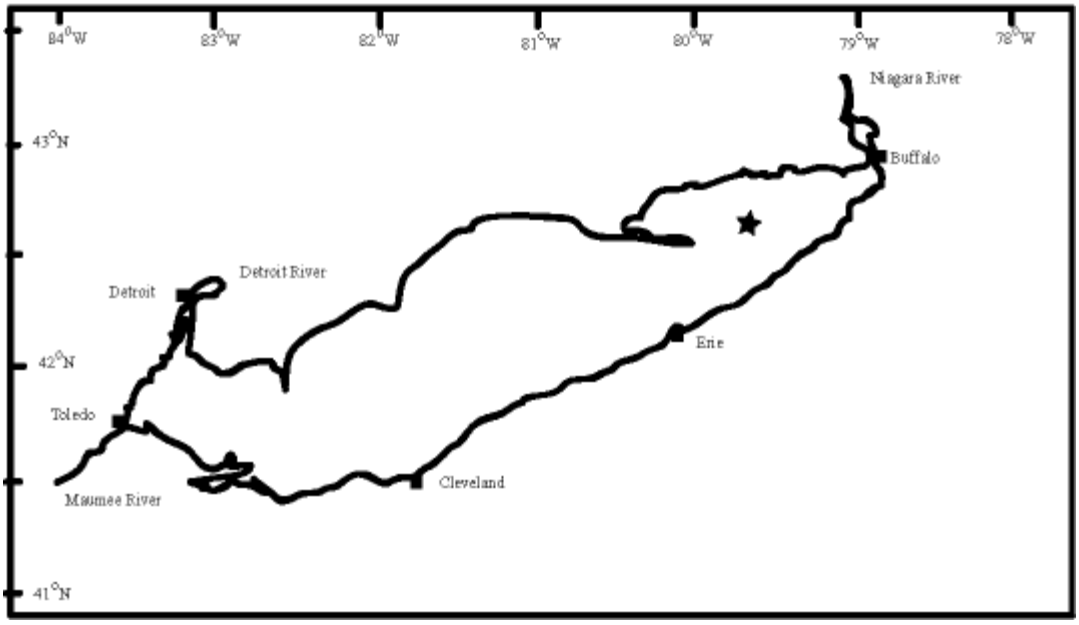

Fig. 3-1 Map of the Lake Erie study area. The star locates the Eastern Basin (EB) Reference Site where the sediment core was obtained in 2003 from a water depth of 60m.

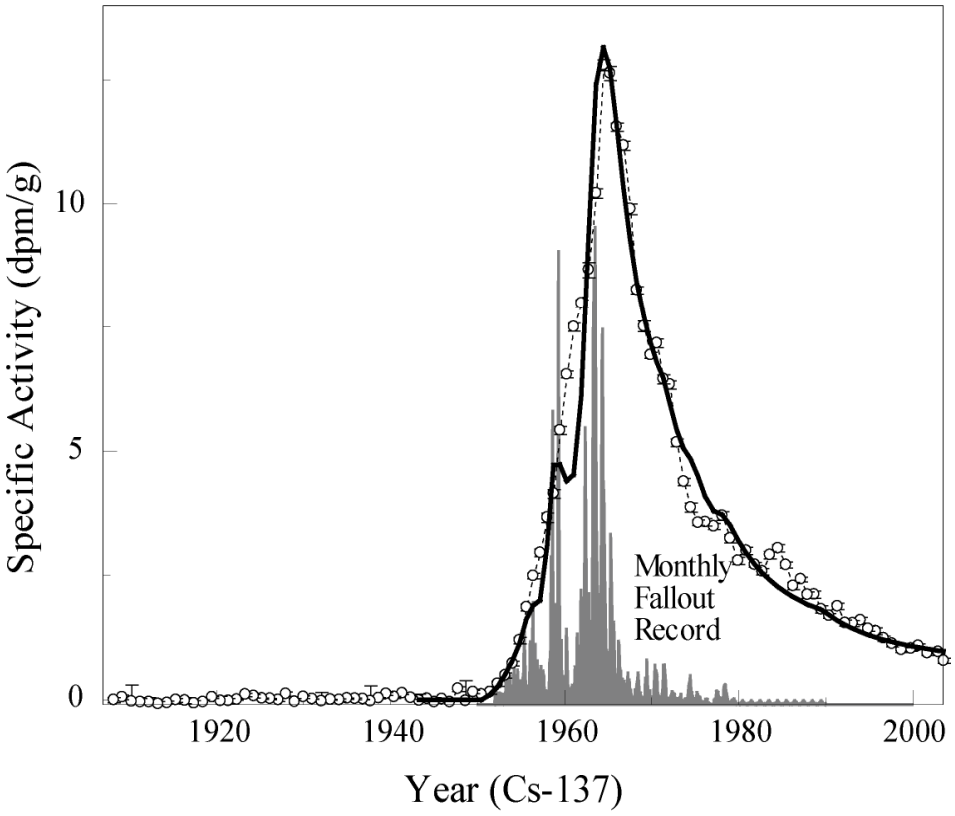

Fig. 3-2 The Cs-137 profile. The open circles are the measured specific activity of ^{137}Cs in the sediment; the gray bar indicated the monthly fallout record of the Great Lakes regions (Robbins1985) and the solid line represents the results from STA Model simulations (System Time Average Model, Robbins et al. 2000).

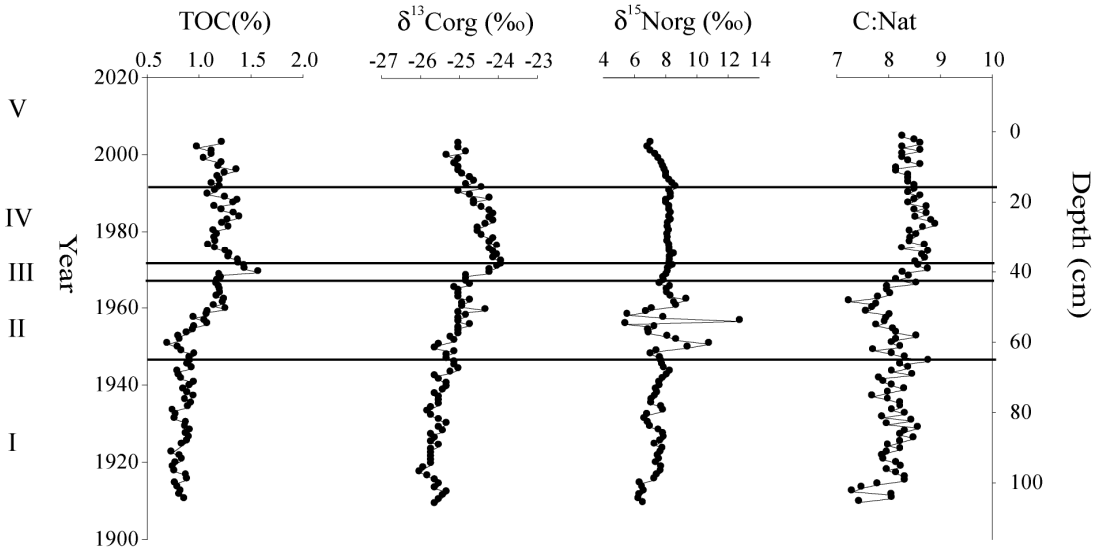

Fig. 3-3 Paleoenvironmental proxies (TOC concentrations, $\delta^{13}C_{org}$, $\delta^{15}N$ and $C:N_{at}$) of the sediment core from the Eastern Lake Erie Basin Reference Site. I to V represents five stages of eutrophication history which are divided according to the variations of these paleoenvironment proxies.

References

Altabet, M. A., and R. Francois. 1994. Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization. Global Biogeochemcial Cycles **8**: 103-116.

Altabet, M. A., R. Francois, D. W. Murray and W. L. Prell. 1995. Climate-related variations in denitrification in the Arabian Sea from sediment N^{15}/N^{14} ratios. Nature **373**: 506-509.

Bada, J. L., M. J. Schoeninger, and A. Schimmelmann. 1989. Isotopic fractionation during peptide-bond hydrolysis. Geochimica Et Cosmochimca Acta **53**: 3337-3341.

Bernasconi, S. M., A. Barbieri, and M. Simona. 1997. Carbon and nitrogen isotope variations in sedimenting organic matter in Lake Lugano. Limnology and Oceanography **42**: 1755-1765.

Berner, E. K., and R. A. Berner. 1996. Global environment: water, air, and geochemical cycles, Prentice-Hall Inc.

Brenner, M., T. J. Whitmore, J. H. Curtis, D.A. Hodell, and C. L. Schelske. 1999. Stable isotope (δC^{13} and δN^{15}) signatures of sedimented organic matter as indicators of historic lake trophic state. Journal of Paleolimnology **22**: 205-221.

Bruesewitz, D. A., J. L. Tank, M. J. Bernot, W. B.Richardson, and E. A. Strauss. 2006. Seasonal effects of the zebra mussel (*Dreissena polymorpha*) on sediment denitrification rates in Pool 8 of the Upper Mississippi River. Canadian Journal of Fisheries and Aquatic Sciences **63**:957-969.

Davis, C. C. 1969. Seasonal distribution, constitution, and abundance of zooplankton in Lake Erie. Journal of the Fisheries Research Board of Canada. **26**: 2459-2476.

Faure, G., and T. M. Mensing. 2005. Isotopes principles and applications. 3rd ed. John Wiley & Sons, Inc.

Francey, R. J., C. E. Allison, D. M. Etheridge, C. M. Trudinger, I. G. Enting, M. Leuenberger, R. L. Langenfelds, E. Michel, and L. P. Steele. 1999. A 1000-year high precision record of $\delta^{13}C$ in atmospheric CO_2. Tellus **51B**: 170-193.

Gardner, W.S., J. F. Cavaletto, T. H. Johengen, J. R. Johnson, R. T. Heath, and J. B. Cotner. 1995. Effects of the zebra mussel, *Dreissena polymorpha*, on community

nitrogen dynamics in Saginaw Bay, Lake Huron. Journal of Great Lakes Research **21**:529-544.

Gu, B. H., C. L. Schelske, and M. Brenner. 1996. Relationship between sediment and plankton isotope ratios (δ^{13}C and δ^{15}N) and primary productivity in Florida lakes. Canadian Journal of Fisheries and Aquatic Sciences **53**: 875-883. Hartman, W. L. 1973. Effects of exploitation, environmental changes, and new species on the fish habitats and resources of Lake Erie. Technique report no. 22, Great Lakes Fishery Commission, U. S. Bureau of Sport Fisheries and Wildlife, Biological Station, Sandusky, Ohio.

Heaton, T. H. E. 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere - a review. Chemical Geology **59**: 87-102.

Hodell, D. A., and C. L. Schelske. 1998. Production, sedimentation and isotopic composition of organic matter in Lake Ontario. Limnology and Oceanography **43**: 200-214.

Lavrentyev, P. J., W. S. Gardner, and L. Y. Yang. 2000. Effects of the zebra mussel on nitrogen dynamics and the microbial community at the sediment-water interface. Aquatic Microbial Ecology **21**: 187-194.

Leach, J H. 1999. Lake Erie: passages revisited, p. 5-22. *In* M. Munawar, T. Edsail and I. F. Munawar [eds.], State of Lake Erie: past, present and future. Backhuys Publishers.

Lehmann, M. F., S. M. Bernasconi, A. Barbieri, M. Simona, and J. A. McKenzie. 2004a. Interannual variation of the isotopic composition of sedimenting organic carbon and nitrogen in Lake Lugano: A long-term sediment trap study. Limnology and Oceanography **49**: 839-849.

Lehmann, M. F., S. M. Bernasconi, J. A. McKenzie, A. Barbieri, M. Simona, and M. Veronesi. 2004b. Seasonal variation of the δ^{13}C and δ^{15}N of particulate and dissolved carbon and nitrogen in Lake Lugano: Constraints on biogeochemical cycling in a eutrophic lake. Limnology and Oceanography **49**: 415-429.

MacIsaac, H. J. 1999. Biological invasions in Lake Erie: past, present and future, p. 305-322. In M. Munawar, T. Edsail, and I. F. Munawar [eds.], State of Lake Ere: past, present and future. Backhuys Publishers. Leiden, the Netherlands.

Macko, S. A., and M. L. Estep. 1984. Microbial alteration of stable nitrogen and carbon isotopic compositions of organic matter. Organic Geochemistry **6**: 787-790.

Macko S. A., M. L. Fogel, P. E. Hare, and T. C. Hoering. 1987. Isotopic fractionation of nitrogen and carbon in the synthesis of amino acids by microorganisms. Chemical Geology **65**: 79-92.

Makarewicz, J. C. 1993. Phytoplankton biomass species composition in Lake Erie, 1970 to 1987. Journal of Great Lakes Research **19**: 258-274.

Makarewicz, J. C., and P. Bertram. 1991. Evidence for the restoration of the Lake Erie ecosystem-water quality, oxygen levels, and pelagic function appear to be improving. Bioscience **41**: 216-223.

Meyers, P. A., and B. J. Eadie. 1993. Sources, degradation and recycling of organic matter associated with sinking particles in Lake Michigan. Organic Geochemistry **20**: 47-56.

Meyers, P. A., and R. Ishiwatari. 1993. Lacustrine organic geochemistry: an overview of indicators of organic matter sources and diagenesis in lake sediments. Organic Geochemistry **20**: 867-900.

Nicholls, K. H., and G. J. Hopkins. 1993. Recent changes in Lake Erie (North Shore) phytoplankton: cumulative impacts of phosphorus loading reductions and the zebra mussel introduction. Journal of Great Lakes Research **19**: 637-647.

Ostrom, N. E., D. T. Long, E. M. Bell, and T. Beals. 1998. The origin and cycling of particulate and sedimentary organic matter and nitrate in Lake Superior. Chemical Geology **152**: 13-28.

Robbins, J. A. 1985. Great Lakes regional source functions. NOAA Tech. Memo ERL-GLERL-**56**: p. 22

Robbins, J. A., C. Holmes, R. Halley, M. Bothner, E. Shinn, J. Graney, G. Keeler, M. tenBrink, K. A. Orlandini, and D. Rudnick. 2000. Time-averaged fluxes of lead and fallout radionuclides to sediments in Florida Bay. J. Geophysical Research-Oceans **105**: 28805-28821.

Sachs, J. P., and D. J. Repeta. 1999. Oligotrophy and nitrogen fixation during eastern Mediterranean sapropel events. Science **286**: 2485-2488.

Schelske, C. L., and D. A. Hodell. 1995. Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. Limnology and Oceanography **40**: 918-929.

Schloesser, D. W., R. G. Sticker, and T.B. Bridgeman. 2005. Potential oxygen demand of sediments from Lake Erie. Journal of Great Lakes Research **31** (Suppl.2): 272-283.

Upsdell, B. L. 2005. The carbon and nitrogen composition of suspended particulate matter in Lake Erie, selected tributaries, and its outflow. M.S. thesis. Univ. of Waterloo.

Chapter IV
Evaluation of sediment lipid biomarkers as recorders of the history of cultural eutrophication in Lake Erie, 1909-2003

Abstract

Against a background of a well reconstructed and documented paleoenvironmental history, the hydrocarbon (HC), fatty acid(FA) and fatty alcohol (OL) contents of a century-long sediment core from Lake Erie are evaluated on their ability to record the changes in biogeochemical processes accompanying eutrophication. Although the amounts of all three groups of biomarkers are closely linked to changes in primary productivity within the lake, their molecular distributions reflect different aspects of the biogeochemical processes affecting organic matter accumulation. Changes in the relative inputs from terrigenous and aquatic sources are reflected in variations of the molecular distributions of the OLs, whereas the FAs only respond to the dominant aquatic origins. Even-numbered dominance is observed in the n-alkanes with carbon numbers less than C_{22} and the odd-numbered dominance occurs at higher homologues. The even numbered alkenes in a series of C_{16} to C_{22} constitute an important fraction of the HC compositions. The unusual HC distribution is attributed to an uncertain source, most likely from microorganisms living in a close contact with anthropogenic oil contaminants. Post-burial diagenetic alterations of organic matter are especially recorded in the decreases in the unsaturated FAs and branched FAs with depth.

1. Introduction

The lipid biomarker fraction of the organic matter preserved in lake sediment includes the original, biologically synthesized lipid materials within the lake, terrestrial inputs from the watershed, and secondary lipid compounds derived from microbial activities in the water and sediment (Meyers and Ishiwatari, 1993). Biomarkers have been widely used to reconstruct past changes in lacustrine ecosystems because they contain abundant information about the original sedimentary sources and about changes in biogeochemical processes related to aquatic productivity, anthropogenic effects, climatic changes, and post-burial diagenesis. Different groups of biomarkers can provide

different aspects of environmental information in paleoenvironmental reconstructions. Some groups of biomarkers are more resistant to diagenesis and hence are considered more reliable in recording original sedimentary environments, whereas other groups are more sensitive to preservational conditions and can be used as indicators of diagenetic alterations of organic matter (Meyers et al., 1984). For example, HCs are generally considered as the most reliable biomarkers in recording original sedimentary sources whereas FAs are often used to indicate the degree of post-burial diagenesis. Nevertheless, the information recorded by the biomarker molecules may vary under different environmental settings. For instance, the original depositional sources preserved in hydrocarbons may be overprinted by anthropogenic oil contaminants (Pond et al., 2002); the sensitivity of the FAs and OLs in recording post-burial diagenesis may differ because the order of their reactivities vary under different conditions (Muri and Wakeham, 2006). Hence, more studies to examine the behaviors of different biomarker molecules under a known environmental setting will provide important references for paleolimnologists to evaluate the reliability of the biomarkers when reconstructing various prehistorical environmental changes.

The well documented eutrophication history of Lake Erie provides a special opportunity to assess the reliability of different biomarkers in recording the consequences of changes in primary productivity, sedimentary sources, human perturbations and diagenetic alterations during different productivity regimes in a single lake. The eutrophication history includes an ecological decline fueled by excess nutrient delivery from ~1850 to ~1972 and a recovery and rehabilitation from ~1972 to the present (Leach 1999; MacIsaac 1999). The most rapid period of eutrophication began in the ~1950s, during which the lacustrine ecosystem deteriorated so rapidly that it elicited government response in an effort to reduce the phosphorus overload that consequently led to the recovery from eutrophication starting in the mid-1970s. The Lake Erie ecosystem has undergone significant and rapid changes over the last century, including changes in aquatic productivity, alterations of biological communities, and fluctuations in dissolved oxygen concentrations (Hartman, 1973). These changes have attracted research interest in understanding the human effects on the lacustrine ecosystem, and thus they have been reconstructed using organic geochemical proxies (Bourbonniere and Meyers, 1996;

Schelske and Hodell 1995) and their effects documented (Hartman, 1973; Munawar et al., 1991).

Herein, with the well-documented environmental changes in the Lake Erie as an interpretive background, our study evaluates the reliability of three groups of commonly used biomarkers - aliphatic hydrocarbons (HCs), fatty acids (FAs) and fatty alcohols (OLs) - preserved in sediments in recording the composition, origin, and cycling of organic matter as well as related biogeochemical processes when the lacustrine ecosystem experienced rapid changes. Bulk organic paleoenvironmental proxies, including total organic carbon (TOC), stable carbon isotope of organic matter (δ^{13}Corg) and atomic carbon and nitrogen ratios (C/N_{at}) are used to provide background information about the local environmental changes at our sampling site. In particular, we are interested in answering the following questions: (1) Do these three groups of biomarkers react differently to the changes of the lacustrine ecosystem? (2) Which group is more reliable in providing information about the original depositional environment; and which is better in indicating post-depositional diagenetic alterations?

2. Materials and methods

2.1 Sampling Sites

Lake Erie (Fig.4-1) is 388 km long and 92 km wide, with a surface area of about 25,690 km^2 and a volume of 484 km^3 (Hartman 1973). It receives the outflow from upstream Lakes Superior, Huron and Michigan through the Detroit River and drains into Lake Ontario through the Niagara River (Makarewicz and Bertram 1991). Lake Erie water is bicarbonate rich and has an average pH of 8.3 (Hartman 1973).

Lake Erie is bathymetrically divided into three basins by subaqueous moraines (Upsdell, 2005). The Western Basin (WB) has an average depth of 8m and contains 5% of the total lake volume. The WB was most strongly affected by human activities because it is the shallowest and closest to large urban areas and rivers that bring pollutants to the lakes among the three basins (Hartman 1973). During the rapid growth of cultural eutrophication between the 1950s to the 1970s, the WB had the highest biological productivity among the three basins and was considered a eutrophic basin. However, the shallowness of the WB and resulting wave mixing of its bottom waters prevented the occurrence of dissolved oxygen (DO) depletion in its bottom (Berner and

Berner, 1996). The Central Basin (CB) constitutes 63% of the total lake volume, with a maximum depth at 25m (Hartman 1973). Although surface productivity in the CB was not as high as in the WB, it was the only basin that experienced severe DO depletions in its hypolimnion during the period of cultural eutrophication (Berner and Berner, 1996). The Eastern Basin (EB) is the deepest basin, having a maximum depth of 64m, and makes up 32% of the total lake volume (Hartman 1973). The EB is more tolerant of human effects and environmental changes compared to the other two basins and was only considered as mesotrophic even when the cultural eutrophication reached its maximum (Berner and Berner, 1996).

At September, 2003, a 106cm sediment core was collected using a Benthos gravity corer at the center of the EB (42º31.0'N and 79º53.6'W, see Fig.4-1). The water depth at the collecting site was about 60 m when the core was collected. The core was cut into 1cm intervals and packed into separate bags in the field. After they were transported to the Great Lakes Environmental Research Laboratory (Ann, Arbor, MI), they were stored in a freezer before analysis.

2.2 Analyses

Age determination for the core was based on the identification of the 1963 bomb spike in ^{137}Cs profile data, which was measured on a carefully calibrated gamma counting system with a counting error of less than 3%. The ages of the core sections were established using a mean sedimentation rate of 1.1 cm/year in the core. The 106 cm sediment core represents the depositional record from 1909 to 2003 (Lu et al.,submitted).

Sediment samples were freeze dried and ground to a fine powder. Calcium carbonate was dissolved with 3N hydrochloric acid before the analysis of total organic carbon (TOC, %), total nitrogen (TN) and stable carbon isotope (δ^{13}Corg, ‰) with the elemental analysis- isotope ratio mass spectrometry (EA-IRMS) flow through system at the Laboratory of Isotope Geochemistry at the University of Arizona.

Dry samples were extracted with mixture of dichloromethane (DCM) and methanol (V:V=2:1) by sonification for 1 h. A mixture of internal standards containing 4.8 ug 5 α-cholestane (100uL of 1.2mg 5α-cholestane per 25mL DCM), 5.2 ug C_{13} *n*-alkanol (50uL of 2.6mg C_{13} *n*-alkanol per 25mL DCM) and 4.4 ug C_{17} *n*-fatty acid (100uL of 1.1mg C_{17} *n*-fatty acid per 25mL DCM) was added to the extracts. The

extracts were separated by filtration, and the residues were rinsed with dichloromethane. After the extracts were concentrated by rotary evaporation, the solvent was exchanged with hexane. The solvent was blown down to 0.5mL by N_2 before 3mL 6% KOH-methanol (Wt/Wt) was added. The mixture was boiled for 10 minutes to saponify the acidic fractions in the extracts. Neutral fractions were isolated by extraction three times with hexane. Then the acidic fractions were isolated with hexane for three times after acidification to pH<1 with 3N hydrochloric acid. Neutral fractions were silylated with N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) at 60ºC for 30 minutes, and acidic fractions were methylated with 14% BF_3-methanol at 100ºC for 30 minutes before being analyzed by gas chromatography – mass spectrometry (GC-MS; Agilent Technologies 6890N Network GC system- 5973 inert mass selective detector).

Both neutral fractions and fatty acid methyl esters (FAMEs) were analyzed using HP-5MS capillary column with 30m ×0.25 mm i.d. and 0.25μm film thickness. Helium was used as carrier gas at a constant flow rate of 1.5mL/min. The column oven temperature program for neutral fractions was 80-125ºC at 20ºC/min, then to 290ºC at 10ºC/min, then to 300ºC/min at 3ºC/min, and finally to 320ºC/min at 10ºC/min. The temperature program for the FAMEs was 50-160ºC at 20ºC/min, then to then to 290ºC at 10ºC/min, then to 300ºC/min at 3ºC/min, and finally to 320ºC/min at 10ºC/min. Mass spectra were scanned from 50 to 750 amu. Samples were semi-quantified by comparing their peak heights with those of the standards. The concentrations of the biomarkers are presented relative to TOC to compensate for the variations of TOC so that the sediments with more enriched or depleted biomarkers will be identified.

3. Results

3.1. Biomarker abundances

The amounts of HCs, FAs, and OLs (ug/g TOC) overall follow the temporal patterns of the TOC and δ^{13}Corg values, suggesting that the concentrations of these biomarkers in the sediments both faithfully reflect the past changes in the amounts of primary productivity driven by human P inputs (See Fig.4-2). The three stages of eutrophication history including slow eutrophication, rapid eutrophication and recovery are well represented in the changes of the biomarkers. The concentrations of the biomarkers are relatively low and constant before they show a dramatic increase at about

the early to mid-1950s (slow eutrophication stage in Fig.4-2), followed by a relative high concentration from ~late 50s to ~mid 70s (rapid eutrophication stage in Fig.4-2), and then show a decreasing trend afterwards (recovery stage in Fig.4-3). This trend is consistent with the documented and previously reconstructed eutrophication history of Lake Erie, including slow eutrophication before 50s, rapid eutrophication occurring between 50s to mid 70s and the recovery from eutrophication after mid 70s (Hartman, 1973; Munawar et al., 1991; Schelske and Hodell 1995; Lu submitted).

3.2. Unusual patterns of HCs

Generally, the *n*-alkanes produced by natural sources have odd-over-even predominance, which decreases with thermal maturity of the alkanes. The long-chain alkanes ($\geq C_{27}$) generally originate from terrestrial high plants while the short-chains ($\leq C_{21}$) are related to aquatic algae (Meyers, 1997). The HCs in our sediment core show unusual patterns, especially for young geological samples. Fig.4-4 illustrates a typical HC distribution in our sediment samples, which did not significantly change with the depth in the sediments. The *n*-alkanes show even-over-odd predominance in the short-chain molecules ($\leq C_{22}$) and had odd-over-even predominance for long-chain analogues ($>C_{22}$). The odd-numbered short-chain n-alkanes (C_{17} and C_{19}) are present at only trace amounts and were not able to be quantitatively represented in Fig.4-3. In addition to the unusual distributions of even and odd numbered *n*-alkanes, the hydrocarbons also contain a series of alkenes from $C_{16:1}$ to $C_{22:1}$ at high concentrations, which are also uncommon in both the biosphere and geosphere.

3.3. Molecular distributions for FAs and OLs

3. 3.1. Chain length distributions

Generally, long-chain n-FAs and n-OLs (n>20) showing a strong even/odd predominance are believed to be largely derived from waxes of higher plants (Logan and Eglinton, 1994), whereas the source of short chain (n<20) homologues are more difficult to specify because they were widely found in multiple sources including algae, higher plants, bacteria and fungi. (Meyers and Ishiwatari, 1993). However, the short chain compounds in lacustrine sediments are generally related to autochthonous sources (Muri and Wakeham, 2006; Meyers, 2003). Hence, the relative importance of terrigenous and

aquatic sources for sediment lipids can be well reflected by the ratios of long-chain and short-chain biomarkers.

One of the widely used proxies to evaluate the importance between the terrigenous and aquatic sources is derived from the study on Lake Erie by Bourbonniere and Meyers (1996), who eliminated the mid-chain biomarkers (C_{18} to C_{23}) to avoid the effects from aquatic higher plants and defined the terrigenous:aquatic ratio (TAR) of the *n*-fatty acids as

$$TAR= (C_{24}+C_{26}+C_{28})/(C_{12}+C_{14}+C_{16}).$$

Given the similar distributions of FAs and OLs, we applied the same calculation to the *n*-OLs distributions. TAR values for FAs (TAR_{FA}) and OLs (TAR_{FA}) in our sediment core show different temporal patterns. The TAR_{OL} , ranging between 0.43 and 1.53, has relatively high values at the eutrophication recovery stage and lower values when the lake underwent rapid and slow eutrophication. The lowest TAR_{OL} value occurs at the bottom of the sediment core. In contrast, the TAR_{FA} show consistently lower values (all <0.3) than TAR_{OL} and display low variations throughout the core (Fig.4-2).

The biomarker distribution plot (Fig.4-2) displays further differences in carbon number distributions between *n*–Ols and *n*-FAs. The *n*-OLs exhibit bimodal distributions at C_{14} and C_{26} dominating the respective short -chain and long-chain components, with overall decreases of the importance of the long-chain components with depth. The plot of the 21-22cm sediment horizon shows a typical carbon length distribution for the eutrophication recovery period, when both the short- and long-chain components account for important contributions. The distribution at the period of rapid eutrophication, which is demonstrated by the sample at 51-52cm, shows less important contributions from long-chain components relative to the short-chain ones. Long-chain OLs become less significant at the slow eutrophication period, as shown by the 101-102cm distribution. In contrast, the FAs distributions are relatively invariant, with C_{14} and C_{16} dominating the FAs throughout the core (Fig.4-2).

3. 3. 2. Branched biomarkers

Branched (Br) aliphatic FAs and OLs (iso and anteiso-C_{15} and C_{17}) are exclusive to bacterial sources, especially sulfate reducing bacteria (Countway et al., 2007). The production of the branched compounds is derived from the *in situ* bacterial metabolism of

even chain length precursors (Cranwell, 1973; Mudge and Norris, 1997). For example, the *iso*- and *anteiso*-C_{15} compounds are formed by the addition of a methyl group to the straight chain C_{14}. Hence, the variability of the amounts of the branched compounds is an indictor of the extent of bacterial activity, which could reflect the availability of labile organic matter and the environmental conditions affecting the processes of utilization of organic matter by bacteria. Mudge and Norris (1997) have used the ratio between the even-chain-length precursor and the odd-carbon-number methyl derivatives to indicate the degree of bacterial utilization of organic matter.

Iso-and *anteiso*- C_{15} fatty acids are found in our sediment core, and the ratios between br-C_{15} and *n*-C_{14} compounds (br-C_{15}:C_{14}) are plotted with the depth in Fig.4-2. The br-C_{15}:C_{14} for OLs shows smaller values and has relatively invariant trends compared to those for the FAs, which has much higher values in the upper 2.5cm below the sediment surface than in the deeper sediment. During the rapid eutrophication stage, br-C_{15}:C_{14} values for FAs display slight decreases when the lake became more trophic.

3. 3. 3. Unsaturated FAs

Monounsaturated *n*-$C_{16:1}$ and *n*-$C_{18:1}$ n-FAs are major components of freshwater algae and are widely observed in lacustrine sediments (Meyers and Ishiwatari, 1993). They are more susceptible to diagenetic degradation than their saturated counterparts; hence the ratios of $C_{16:1}/C_{16:0}$ and $C_{18:1}/C_{18:0}$ reflect the preservation of the reactive organic molecules in the sediments (Meyers, 2003).

n-$C_{16:1}$ and *n*-$C_{18:1}$ fatty acids constitute an important portion of the fatty acids throughout our sediment core. Fig.4-2 shows that the ratios of $C_{16:1}/C_{16:0}$ and $C_{18:1}/C_{18:0}$ both decrease with depth in the sediment, suggesting that the unsaturated fatty acids are preferentially degraded by microbial utilization compared to the saturated ones. Overall, the $C_{18:1}/C_{18:0}$ ratios, ranging between 0.14-0.52, show larger values (except at the sediment surface) and decrease more slowly with the burial depth compared to $C_{16:1}/C_{16:0}$, which falls in the range between 0.06-0.57. The $C_{16:1}/C_{16:0}$ ratio drops rapidly in the upper ~20cms, below which it shows relatively constant values. The $C_{18:1}/C_{18:0}$ ratios, however, have an decreasing trend in the upper ~60cm while showing two high peaks at 28-29cm (recovery stage) and 51-52cm (rapid eutrophication stage) respectively. Both ratios, however, show the largest values near the sediment surface ($C_{16:1}/C_{16:0}$ ratio at 1-

2cm and $C_{16:1}/C_{16:0}$ ratio at 2-3cm) and the smallest values at the bottom of the sediment core (i.e. 101-102cm, the deepest sediment horizon where the FAs measured).

3. 3.4. PCA (Principle Component Analysis) Multivariate statistical analysis

PCA analysis was done on the concentrations (ug g^{-1} TOC) of all OLs between C_{12} and C_{30} including br-OLs and all FAs between C_{10} and C_{28} including monounsaturated and br- FAs to identify the differences in the biomarkers among the sediments at different eutrophic stages. For the group of OLs, PC1, PC2 and PC3 account for 67.37%, 8.90% and 6.63% of the variance of the data, respectively. For FAs, PC1 account for 44.55%, PC2 22.67% and PC3 14.35% of the variance in the data. The PC1 vs PC2 plots for OLs and FAs are shown in Fig.4-4. The coefficients of PC1 and PC2 of the samples were summarized in Table 4-1.

The sediment samples group according to their eutrophic status, while the surface sediments (i.e. 1-2cm and 2-3cm), which belong to the recovery period, are labeled out due to their distinct characteristics. PC1 in both analyses represents the amounts of the biomarker production associated with the lake eutrophic status (Fig.4-5). The samples during the slow eutrophication all have relatively low loadings of the variance on PC1 and those during the rapid eutrophication have highest loadings on PC1. The samples from the recovery period after rapid eutrophication are intermediate. PC2 for the OLs separate the samples from the rapid eutrophication period from other samples (Fig.4-5). This PC2 represents the relative importance of short-chain and long-chain components because it has positive coefficients for many short-chain OLs, with largest values for C_{12} and C_{14} and negative coefficients for many long-chain OLs. The more positive loadings on PC2 reflect the relatively high importance of short-chain components, suggesting more contributions from aquatic sources when the lake is more eutrophic. PC2 for the FAs, on the other hand, seems to represent the degree of diagenetic alterations of this group of biomarkers (Fig.4-5). The surface sediment (1.5cm and 2.5cm) samples are separated with high PC2 loadings because they are less altered by post-burial diagenesis.

Overall, the PCA analysis shows that primary productivity was the major factor in determining the variance of both FAs and OLs from the different trophic states. The variance of OLs is also controlled by the variations of relative contributions of aquatic

and terrigenous sources whereas the diagenetic alterations mainly determine the variance of FAs.

4. Discussion

4.1. Sedimentary sources

4.1.1. Sources of hydrocarbons

Although the occurrence of alkanes with even-over-odd predominance in geological samples is uncommon, it has been reported in marine and freshwater sediments with a variety of ages and depositional conditions, and in some of the cases, the concomitant appearance of a series of alkenes was also observed (Grimalt and Albaigés, 1987). A variety of biological sources, including planktonic inputs, microbial reworking of algal detritus, recent biogenesis of fatty acids or other lipid materials and direct microbial inputs have been suggested to account for this distribution (Nishimura and Baker, 1986; Elias et al., 1997), but there were some debates regarding this topic. For example, Dastillung and Corbet (1978) found *n*-alkanes with even numbered predominance under anoxic environments and suggested they are formed by the reduction of FAs (Grimalt and Albaigés, 1987). However, this hypothesis was questioned by several later studies showing the occurrence of these alkanes in some oxic environment and the distributions of n-alkanes that are not analogous to the corresponding n-FA distributions (Nishimura and Baker, 1986; Grimalt and Albaigés, 1987). Alternatively, direct biogenic contributions from algae, bacteria, fungi and yeast have been attributed to these alkanes (Grimalt and Albaigés, 1987; Solevic et al., 2002).

Despite alkenes having multiple natural sources, none of the commonly observed ones are likely the sources for the alkenes in our sediment core. Short-chain alkenes ($<C_{22}$) are biosynthesized by many algae and zooplankton and long-chain ones ($\geq$22) originate from higher plants (Gelpi et al., 1968). Nevertheless, these alkenes in the sediment samples are generally predominantly odd-numbered (Grimalt and Albaigés, 1987; Elloumin et al., 2008), contrasting to the even numbered predominance of alkenes in our samples. The most commonly observed alkenes in the sediments are those from microalgae, including *n*-$C_{21:6}$, *n*-$C_{17:1}$, and C_{25} and C_{30} isoprenoid alkenes, which each generally occur as an abundant single component in the HC distributions (Volkman et al., 1990) and hence are unlikely to be the sources for the alkenes appearing in the series

from $C_{16:1}$ to $C_{22:1}$ in our sediment samples. Contamination from chemical analysis in the laboratory are also excluded as the possible source because we did not find the occurrence of alkenes in other sediment samples that were analyzed at the same time as the samples described in this study.

Significantly, the co-occurrence of these two uncommon patterns of the HC distributions in our sediment core, i.e. the alkanes with even-numbered predominance and the even-numbered *n*-alkenes at high abundance, has been reported in two previous cases. The first case is from diatomaceous oozes from a freshwater lake located in the Cerdanya Basin (South of Pyrenees), where *n*-alkenes and *n*-alkanes in the C_{14}-C_{20} range with a strong even-to-odd predominance were reported, and microorganisms were suggested as the potential sources for this distribution (Grimalt and Albaigés, 1987). The second case is in oil-polluted sediments. Ekpo et al. (2005) reported the occurrence of even numbered *n*-alkanes (*n*-C_{12} to *n*-C_{26}) and *n*-alkenes (*n*-$C_{14:1}$ to *n*-$C_{26:1}$) in the surface sediments from Calabar River, SE Niger Delta, Nigeria. They believed that this uncommon hydrocarbon distribution pattern was attributed to the inputs from microorganisms inhabiting an oil-polluted environment. Hence, microorganisms were attributed to these unusual hydrocarbon distributions in both cases. The similarity between the hydrocarbon distribution in these two previous cases and our study is remarkable, suggesting microorganisms are likely also the source for the HC distributions in the Lake Erie core. Especially given that many potential oil-contaminations sources exist in the watershed of Lake Erie, including oil and gas wells constructed at the Canadian side of the Lake Erie shore, oil inputs from runoffs (especially the Cuyahoga River, which was so full of floating oil that it caught fire several times before the 1970s) and oil spills from small boat engines and shipping activities, the microorganisms living in an oil-polluted environment are probably the sources for the curious hydrocarbons in our sediment.

The validity of our data is supported by a previous study of the upstream Great Lakes, where Lake Erie receives its inflows. In Lake Superior, Michigan and Huron, even numbered alkanes have also been observed in the extractable lipid fractions of sediment samples collected from sediment traps (Parrish et al., 1992). Although only the molecular distributions of alkanes in the 10m sediment traps were examined, it is quite possible that this pattern of the dominance with even-numbered n-alkanes survive sinking

to the bottom of the lake since no previous studies have shown the preferential degradation of even numbered alkanes compared to their odd-numbered analogues. This study provided the evidence that the alkanes with even-numbered dominance in Great Lakes were mainly from the microorganisms inhabiting the water columns. Indeed, many studies have shown that some microorganisms including nonphotosynthetic-nutritional, unicellular, sporulating algae and many other types of dinoflagellates, have the ability to biosynthesize even numbered alkanes utilizing crude oil hydrocarbons in oil polluted groundwater (Śolević et al., 2003; Jovančićević et al., 2005). The activities of these microorganisms increase when they are in direct contact with the oil pollutants in the aqueous environment under anaerobic conditions (Šolević et al., 2003). Hence, it is quite possible that these microorganisms contributed to the unusual distributions of the hydrocarbons in our sediment core when Lake Erie was significantly affected by the oil contaminants from oil drilling, fishing activities and oil spills, etc. Although the Šolević et al.'s (2003) study was conducted under anaerobic conditions, the aforementioned sediment trap studies in the Upper Great Lakes (Parrish et al., 1992) suggest that the production of even- numbered alkanes may not require anaerobic environment.

Additionally, the carbon numbered distributions in all three groups of biomarkers may supply further evidence for the activities of microorganisms living under an oil-contaminated environment. First, the unusual distribution of HCs (i.e. the predominance of even-chain numbered alkanes and alkenes) only appear in short chain alkanes ($\leq$C22) in this study, which is consistent with the knowledge concerning the fate of oil contaminants in the environment, i.e. no microorganisms can be responsible for the generation of longer n-alkane homologues (Jovančićević et al., 2005). Second, the increases in even-numbered n-FAs and n-OLs with short chains ($<C_{20}$) have also been attributed by the utilization of oil contaminants by *Pyrrophyta*, the nonphotyosynthetic-nutritional, unicellular, sporulating algae (Šolević et al., 2003; Jovančićević et al.,2005). Despite the short-chain FAs and OLs having universal sources, their high amounts throughout our whole sedimentary core, especially C_{14} for OLs and C_{16} for FAs, may be an indicator of intense utilization of oil contaminants by the microorganisms in Lake Erie.

Moreover, the compound-specific $\delta^{13}C$ values of n-alkanes may also provide evidence of the unusual sources for n-alkanes in Lake Erie. Ostrom et al (1998) found

the normal molecular distributions of n-alkanes from the sediment cores in Lake Erie, i.e. *n*-alkanes with odd-over-even predominance, which disagrees with this study. However, their $\delta^{13}C$ analysis of the n-alkanes suggested that there were contributions from uncharacterized sources to the n-alkanes preserved in the EB of Lake Erie. The downcore variations of $\delta^{13}C$ values of short-chain n-alkanes, which are expected to provide a better indicator of the trophic state of the lake because they are not influenced by terrigenous inputs, do not record the changes in trophic status that the $\delta^{13}C$ of bulk organic matter did. The contribution of isotopically unique n-alkanes from unknown sources was suggested as one of the most possible causes for this contradiction. Our conclusion that microorganisms living under an oil contaminated environment contribute a significant part of the hydrocarbons may help to explain the discrepancies between the $\delta^{13}C$ values of n-alkanes with the changes of aquatic productivity in Lake Erie.

The biggest challenge to explain the uncommon HC distributions in our core arises from the contradictions between this study and the two previous studies by Bourbonniere and Meyers (1996) and Ostrom et al. (1998), both of which show a common HC distribution (i.e. *n*-alkanes with odd-over-even predominance) from the sediments deposited in the EB of Lake Erie. Because the intensities of the utilization of oil contaminants by the microorganism depends on the extent of their contact with the oil contaminants (Šolević et al., 2003; Jovančićević et al., 2005), our sediment core may be affected by oil contamination to a greater extent compared to the two aforementioned studies due to differences in the sampling locations and sampling ages. The postulated closer contact with oil contaminants in our samples promoted activities of the microorganism that can utilize oil contaminants and generate hydrocarbons with different patterns. However, this explanation is not completely tenable given that lacustrine sediments generally contain information about the integrative processes occurring in the water column and the sampling location is usually not expected to produce such significant differences in sediment cores. Moreover, although other studies have proved the generation of even-chain numbered alkanes by microorganisms inhabiting an oil-polluted environment, only the two cases we mentioned earlier showed the co-occurrence of even-numbered dominance of alkenes and alkanes. Without compound-specific

isotopic analysis of the alkanes and alkenes, we can not be certain that they are from the same source.

In conclusion, the unusual distributions of hydrocarbons in this study most likely are from the intense activities of microorganisms due to their close contact with the anthropogenic oil contaminants. Further analysis of compound-specific isotopes are needed to confirm our speculations.

4.1.2. Terrigenous vs aquatic sources

Short-chain compounds are less resistant to post-burial diagenesis than their long-chain counterparts because they are more easily utilized by microbial reworking (Meyers and Ishiwatari, 1993). Thus, post-burial diagenesis would tend to increase the TAR_{OL} values and introduce a biased interpretation for the sedimentary sources. The TAR_{OL} values have lower values deeper in the sediment core than near the surface, suggesting that post-burial diagenesis does not dominate their temporal variations and hence the signals from changes in the relative proportions of the sedimentary sources between terrigenous and aquatic origins are preserved.

The gradual increases in TAR_{OL} ratios with the progress of the slow eutrophication may reflect the progressively larger inputs of land-derived OLs delivery to the Lake Erie. This pattern reflects increased land runoff from paved roads, disturbed soils, and wastewater as results of the increasing urbanization of the watershed. This factor also increased aquatic inputs to the sedimentary organic matter as it provided more nutrient supplies and stimulated aquatic productivity. The increasing TAR_{OL} ratio, however, suggests that the OL inputs from the increased aquatic sources were surpassed by the increased terrigenous inputs. This trend was reversed during the stage of rapid eutrophication, when the TAR_{OL} showed slight decreases, suggesting that aquatic productivity reached its maximum and produced aquatic OLs that were able to exceed the increases in terrigenous OLs. The long-chain OLs show maximum contributions relative to short-chains during recovery period, perhaps reflecting, on one hand, the decreases of aquatic OLs due to the reduced aquatic productivity as the result of the restrictions on anthropogenic P inputs. On the other hand, all proxies including TOC, δ^{13}Corg and biomarker concentrations show that aquatic productivity level during the eutrophication recovery, although showing an overall decreasing trend, did not decrease to the levels

that existed before the rapid eutrophication. Hence, the high TAR_{OL} values reflect that the amounts of the land-derived runoff during the progress of eutrophication recovery, although containing low P contents, were still higher than those before rapid eutrophication.

Although the major sedimentary sources for OLs shifted between aquatic and terrigenous sources at different trophic status, TAR_{FA} shows that aquatic FAs were the most important sedimentary source and that the terrigenous FAs constituted only a minor fraction throughout the whole depositional period. The high inputs of aquatic short-chain FAs may result from the high primary productivity during the cultural eutrophication over the last century. The TAR_{FA} values in our study show similar values and temporal patterns as those obtained from the sediment core from Lake Erie by Bourbonniere and Meyers (1996), verifying the reliability of our data.

The differences in sedimentary sources for OLs and FAs are further illustrated by PCA analysis, which indicate that the relative importance between short and long chain components plays a significant role in the variance of the OLs while it is not important in the FAs (Fig.4-3). Previous studies also showed that the relative importance between terrigenous and aquatic sources differs for different biomarkers preserved in sediments. For example, Muri et al. (2004) made an observation similar to our study in the sediments of the western basin of Lake Bled, NW Slovenia, where long-chain n-OLs show a prevalence among total *n*-OLs while FAs and HCs are both dominated by their short-chain components. Given the eutrophic status of Lake Bled and the low C/N ratios (average= 7.5), they concluded that the major sedimentary source for the TOC is autochthonous, which is consistent with the molecular distributions of *n*-FAs and *n*-alkanes but is different with n-OLs. Likewise, the TAR ratios calculated for alkanes show significant contributions from terrigenous sources, whereas FAs from aquatic origins dominate the whole core in Lake Erie sediments from the 1920s to the 1980s (Bourbonniere and Meyers, 1996). This difference was attributed to the selective degradation and other diagenetic alterations that have more effects on the FAs than alkanes and hence, overprint the source signatures of the FAs (Bourbonniere and Meyers, 1996).

Despite the fact that different groups of biomarkers can produce different TARs, previous studies have used biomarkers to evaluate the changes in terrigenous vs aquatic sedimentary sources (Meyers and Eadie, 1993). Consequently, the question of which biomarkers are more reliable in recording the sedimentary sources for organic matter is raised. The HCs are generally considered the most reliable molecules due to their high resistance to degradation (Meyers and Ishiwatari, 1993; Bourbonniere and Meyers, 1996). However, the hydrocarbons in this study from natural sources are disturbed by oil contamination as discussed earlier, and hence, they cannot be used to indicate the changes between terrigenous and aquatic sources. Similar situations probably will often be observed in many recent sediments that have also experienced increases of anthropogenic perturbations to the aquatic environment. It is often hard to generalize the reliability of FAs and OLs under an unknown environmental setting since their order of resistance to degradation varies under different environmental settings (Muri and Wakeham, 2006). C/N_{at} values and the documented environmental changes during the eutrophication in Lake Erie, however, provide us the necessary background to evaluate changes in the sedimentary organic matter sources. C/N_{at} values, falling in the range of aquatic sources throughout the depositional period, are consistent with the TAR_{FA}, showing that aquatic sources were prevalent in the whole sediment core. Even though aquatic sources were dominant, the relative proportions between terrigenous and aquatic sources were changing with the trophic status of Lake Erie, which is indicated by the temporal trends of C/N_{at} values. TAR_{FA} fails to represent this change whereas the TAR_{OL} shows good correspondence with the temporal patterns of C/N_{at} (see Fig.4-2) and reflects the changes in relative importance between terrigenous and aquatic inputs. Hence, it seems that while both TAR_{FA} and TAR_{OL} provide useful information about the sedimentary organic matter source, neither can be fully relied on to reflect the original depositional source signatures. Conversely, they only reflect the TARs for the specific biomarker groups preserved in the sediments, which can be significantly different from the original ratios between the terrigenous and aquatic depositional sources, depending on their resistance to post-burial diagenetic alterations. However, when used together,they may complement each other to provide a reliable estimate of the changes in sedimentary organic matter sources.

4.2. Diagenesis

The degree of the diagenetic alteration of organic matter preserved in our sediment core is mainly reflected by two components - the amounts of unsaturated fatty acids and the amounts of branched fatty acids and alcohols. PCA also shows that the degree of post-burial diagenesis is an important factor controlling the variance of the FAs. .

Diagenetic alteration by microbial biomass is most active at the sediment surface, as indicated by the high ratios of the Br-C_{15}/C_{14} for the FAs, which are promoted by two factors, the high availability of the labile organic mater that is easily utilized by microbial biomass, as indicated by the high ratios of the $C_{16:1}/C_{16:0}$ and $C_{18:1}/C_{18:0}$, and the easier access to free oxygen in the water column. We want to point out again that although Lake Erie was subjected to rapid eutrophication between the 1950s-1970s, the EB has never been reported to be anoxic or even suboxic. Hence, the microbial biomass living in the sediment surface always had easy access to the DO in the water column and could efficiently degrade organic matter.

Microbial activities decreased rapidly in the upper ~20cms, mainly due to the lack of the availability of free oxygen in the deeper sediments because the labile organic matter was still abundant for microbial utilization, as indicated by relatively high $C_{18:1}/C_{18:0}$ ratios. The more rapid decreases in $C_{16:1}/C_{16:0}$ than $C_{18:1}/C_{18:0}$ with burial depth suggests that $C_{16:1}$ was preferentially utilized by the microbial biomass relative to $C_{18:1}$, which has been observed by Nissenbaum (1972). Below ~20cm, while the microbial activity was not significant enough to produce measurable amounts of branched compounds, the apparent decreases in the $C_{18:1}/C_{18:0}$ until ~60cm suggests the existence of active diagenesis within 60 cm below the sediment surface.

The slight decreases of br-C_{15}/C_{14} for FAs with the progress of rapid eutrophication may also reflect a decrease in microbial activity. As mentioned earlier, the EB never had anoxia or suboxia in the bottom, hence, this decrease was most likely the result of decreased exposure time of organic matter to free oxygen due to the faster burial of organic matter.

Overall, the diagenetic history reconstructed by the FAs is straightforward, suggesting the availability of oxygen related with the burial rate and burial depth was the primary factor determining the preservation of organic matter in Lake Erie.

5. Conclusions

Based on a good understanding of the history of the environmental changes in the Lake Erie, we evaluated three groups of biomarkers (HCs, FAs, and OLs) in recording different aspects of the biogeochemical processes associated with these changes. The major conclusions of this study were:

1. The amounts of all three groups of biomarkers reflect the changes in aquatic productivity in the Lake Erie.
2. The uncommon molecular distributions of HCs most likely originated from microbial biomass, whose activities are promoted by the availability of anthropogenic oil contaminants as their main carbon source.
3. The ratios between terrigenous and aquatic sources are different for FAs and OL, and neither of these two ratios provides a completely reliable record of the ratios of the original sedimentary sources for the organic matter in the sediment. OLs reflect the history of the changes in relative proportions of the terrigenous and aquatic sources with the progress of the eutrophication, and FAs record the signals from the dominant aquatic sources.
4. The post-depositional diagenetic history is mainly reflected by the branched (i.e. *iso* and *anteiso* $C_{15:0}$) and unsaturated fatty acids (i.e. $C_{16:1}$ and $C_{18:1}$), whereas HCs and OLs show little variation with post-burial diagenesis.

Table 4-1 The coefficients of PCA analysis based on the fatty alcohols (OLs) and fatty acids (FAs) in the samples. The PCA analysis for OLs was done according to the concentrations of OLs (ug g^{-1} TOC) between C_{10} and C_{30} including branched OLs; The PCA analysis for FAs was done based on the concentrations of FAs (ug g^{-1} TOC) between C_{10} and C_{28} including branched and unsaturated FAs.

OLs:

Age	Depth	PC1	PC2
2002.9	1.5	-0.61108	-0.98144
2001.7	2.5	-0.71937	-1.04277
1996.6	7.5	0	0
1990.4	14.5	-0.26094	-0.7598
1984.5	21.5	0.40738	-0.67963
1983.6	22.5	-0.44032	-0.74763
1980.9	25.5	2.24003	-0.89831
1975.3	31.5	0.69117	-0.30898
1972.9	34.5	1.75938	-0.87808
1970.6	37.5	0.51041	1.85694
1965.2	44.5	1.12514	1.90338
1959.5	51.5	-0.25788	1.58426
1953.2	59.5	-0.4883	-0.24384
1947.8	65.5	-1.40189	-0.21042
1942.4	71.5	-0.84193	0.14858
1931	83.5	-0.99232	0.07371
1919.5	95.5	0.0533	0.22825
1913.3	101.5	-0.77277	0.95577

FAs:

Age	Depth	PC1	PC2
2002.9	1.5	0.32071	2.78163
2001.7	2.5	-0.53858	1.6202
1990.4	14.5	0.81056	0.33723
1984.5	21.5	-0.26528	-0.13237
1983.6	22.5	0.82899	-0.28164
1978.1	28.5	-0.54534	-0.65074
1972.9	34.5	0.54013	-0.62259
1970.6	37.5	0.6813	-0.62213
1965.2	44.5	1.3141	-0.49895
1959.5	51.5	1.31019	-0.56947
1953.2	59.5	-0.13829	-0.19202
1947.8	65.5	-1.07731	-0.13799
1919.5	95.5	-1.25774	-0.6999
1913.3	101.5	-1.98345	-0.33127

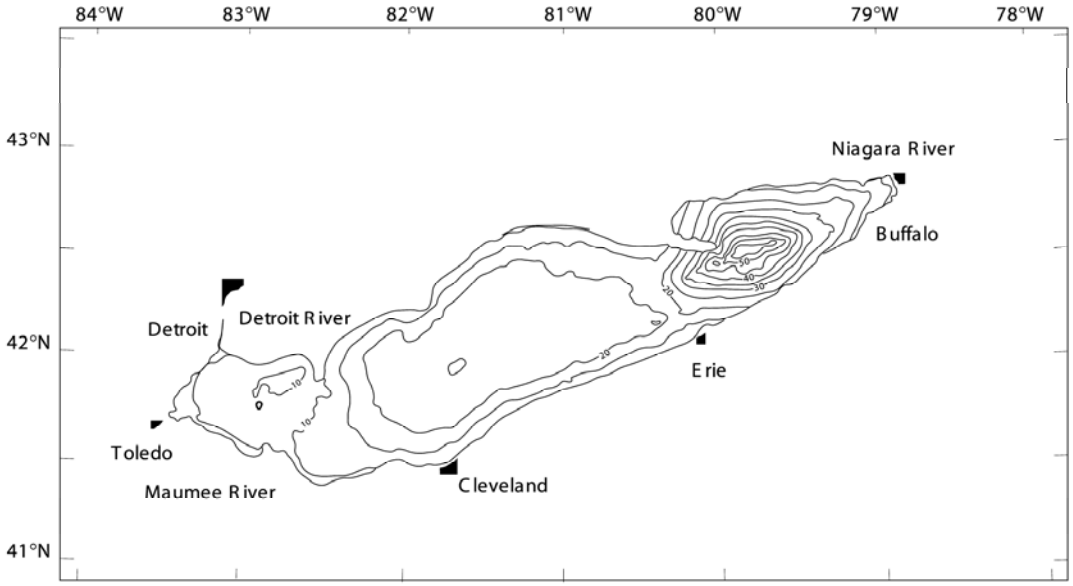

Fig.4-1 Map of Lake Erie. The star indicates the location of the sampling site, East Basin Reference Site.

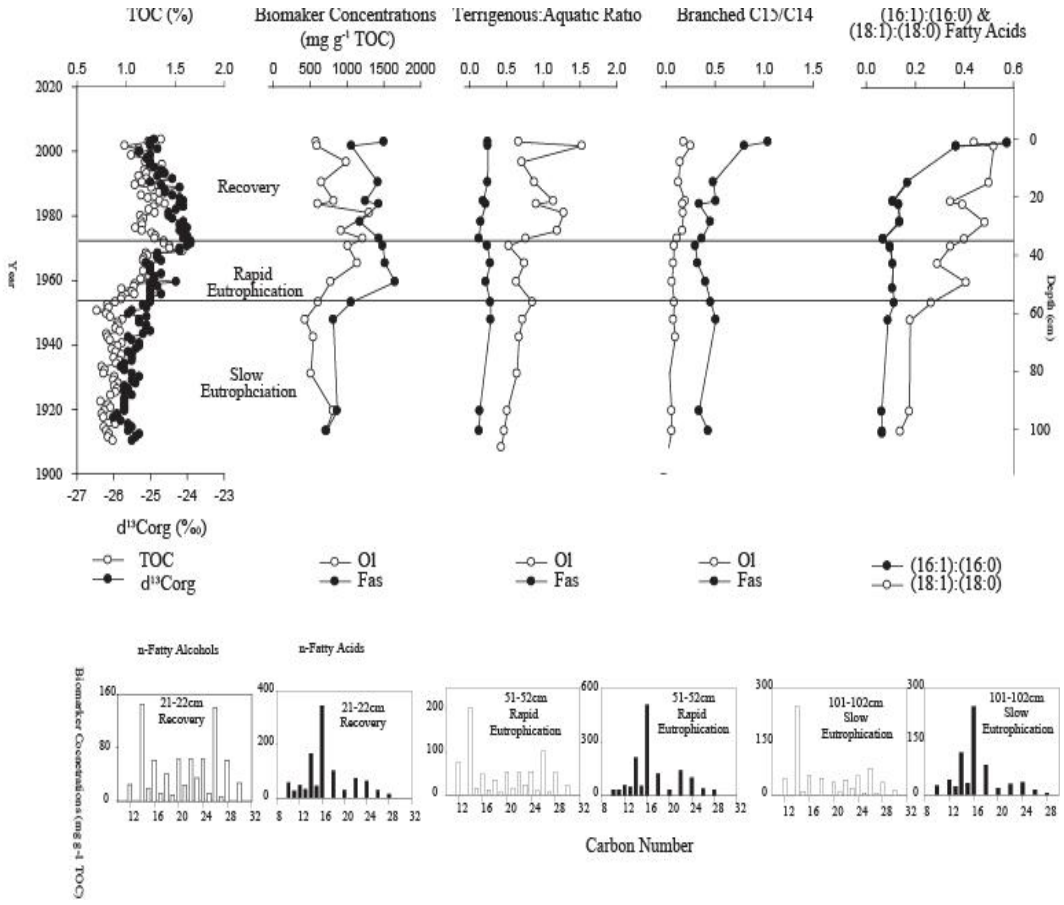

Fig. 4-2 The profiles of bulk and lipid paleoenvironmental proxies with the depositional time (in Calendar Year) and the depositonal depth. The eutrophication stages are marked according to variations of the proxies along with the documented and previously reconstructed eutrophication history (Hartman, 1973; Munawar and Munawar, 1991; Schelske and Hodell, 1995). The carbon chain length distribution of n-FAs and n-OLs at three different depths are presented to show typical distributions at each eutrophication development stage.

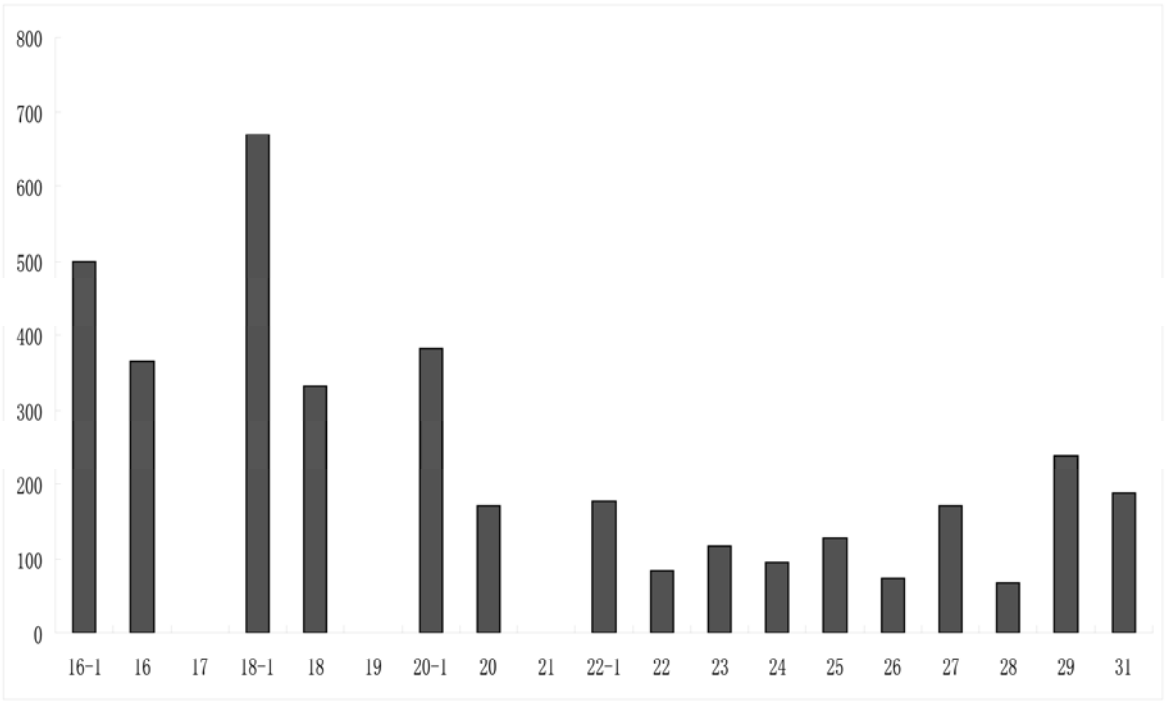

Fig. 4-3 Carbon number distributions of hydrocarbons at sediment samples from 50-51cm. The carbon number distribution for HCs was similar throughout the sediment core. The concentrations of C_{17}, C_{19} and C_{21} are too low to be quantitatively presented.

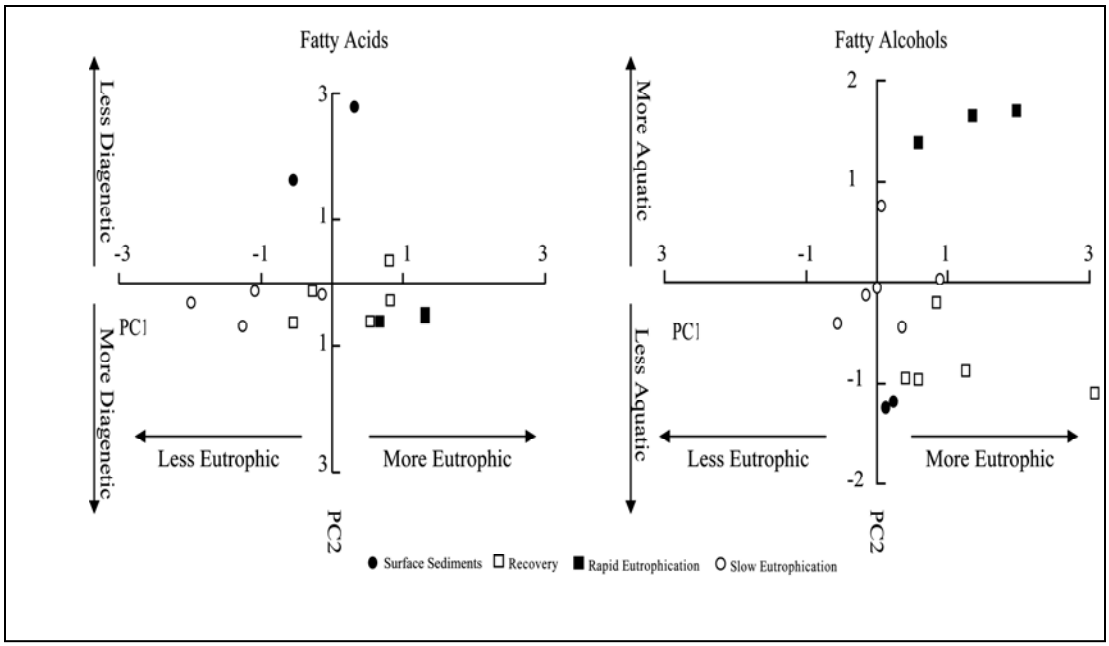

Fig. 4-4 The PC1 and PC2 plot based on the principal component analysis of FAs and OLs. The sediment samples are divided according to the eutrophication stages when they were deposited. The sediment samples in the upper 3cm were marked out because of their distinct PC loadings. Both PC1 in the FAs and OLs represent the productivity level. PC2 in the FAs overall represents the diagenetic alterations of the samples while the PC2 for OLs describes the changes in the sedimentary sources.

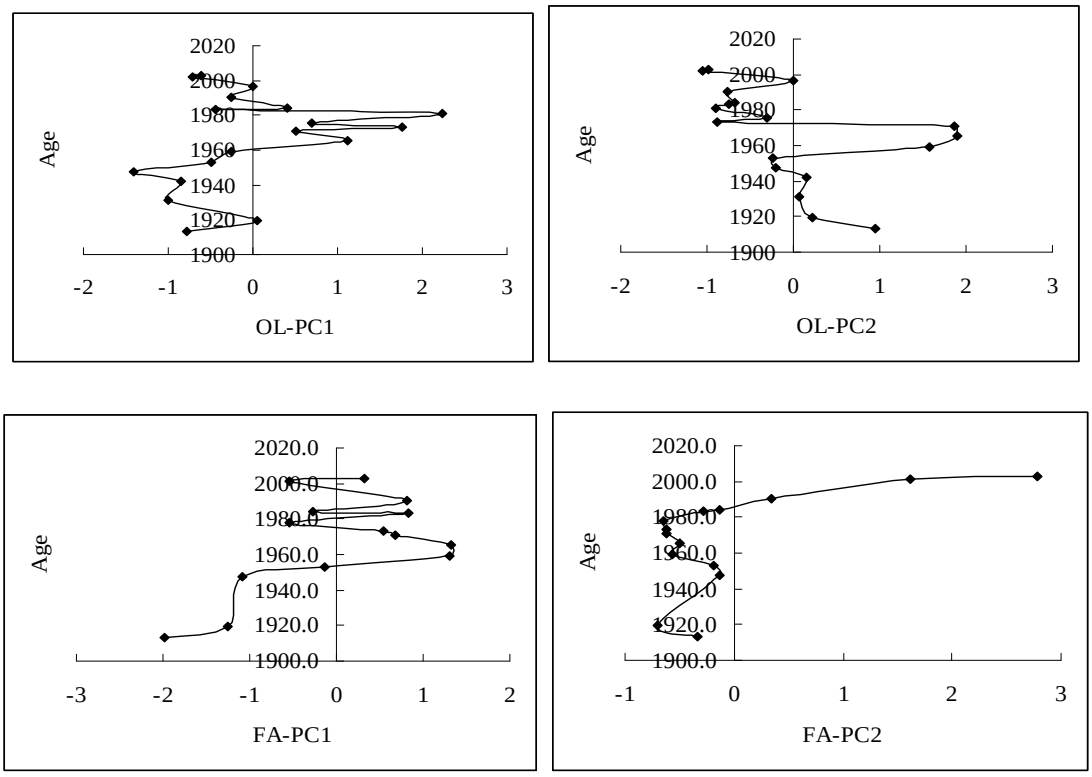

Fig. 4-5 The coefficients of PCA component analysis versus the age of the sediment samples. PC1 in both fatty alcohols (OLs) and fatty acids (FAs) represent the amounts of productivity. PC2 in OL indicate the variations of the sedimentary sources while PC2 in FA indicates the degrees of diagenetic alterations.

Reference

Berner, E. K., and R. A. Berner. 1996. Global environment: water, air, and geochemical cycles, Prentice-Hall Inc., New Jersey.

Bourbonniere, R. A., and P. A. Meyers. 1996. Sedimentary geolipid records of historical changes in the watersheds and productivities of Lakes Ontario and Erie. Limnology and Oceanography **41:** 352-359.

Countway, R. E., E. A. Canuel, and R. M. Dickhut. 2007. Sources of particulate organic matter in surface waters of the York River, VA estuary. Organic Geochemistry **38:** 365-379.

Dastillung, M., and B. Corbet. 1978. La géochimie organique des sédiments marins profonds.-I:Hydrocarbures saturés et insaturés des sédiments. In Canbaz, A., Pelet, R. (Ed.), Géochimie organique des sédiments marins profonds,Orgon II,Atlantique. N.E.Brésil, CNRS, Paris, pp. 293-323.

Ekpo, B. O., O. E. Oyo-Ita, and H. Wehner. 2005. Even-n-alkane/alkene predominances in surface sediments from the Calabar River, SE Niger Delta, Nigeria. Naturwissenschaften **92:** 341-346.

Elias, V. O., B. R. T. Simoneit, and J. N. Cardoso. 1997. Even n-alkane predominances on the Amazon shelf and a Northeast Pacific hydrothermal system. Naturwissenschaften **84:** 415-420.

Elloumi, J., W. Guermazi, H. Ayadi, A. Bouain, and L. Aleya. 2008. Detection of water and sediments pollution of an arid saltern (Sfax, Tunisia) by coupling the distribution of microorganisms with hydrocarbons. Water Air and Soil Pollution **187:** 157-171.

Gelpi, E., J. Oro, Schneide.Hj, and E. O. Bennett. 1968. Olefins Of High Molecular Weight In 2 Microscopic Algae. Science **161:** 700.

Grimalt, J., and J. Albaiges. 1987. Sources and occurrence of C12-C22 normal-alkane distributions with even carbon-number preference in sedimentary environments. Geochimica Et Cosmochimica Acta **51:** 1379-1384.

Hartman, W. L., 1973. Effects of exploitation, environmental changes, and new species on the fish habitats and resources of Lake Erie. Technique report no. 22, Great Lakes Fishery Commission, U. S. Bureau of Sport Fisheries and Wildlife, Biological Station, Sandusky, Ohi

Jovančićević, B., M. P. Antic, T. M. Solevic, M. V. Vrvic, A. Kronimus, and J. Schwarzbauer. 2005. Investigation of interactions between surface water and petroleum-type pollutants. Environmental Science and Pollution Research **12:** 205-212.

Leach, J H., 1999. Lake Erie: passages revisited. In: Munawar, M., Edsail., T., Munawar, I. F. (Ed.), State of Lake Ere: past, present and future. Backhuys Publishers, Leiden, The Netherlands, pp. 5-22.

Logan, G. A., and G. Eglinton. 1994. Biogeochemistry Of The Miocene Lacustrine Deposit, At Clarkia, Northern Idaho, USA. Organic Geochemistry **21:** 857-870.

MacIsaac, H. J. 1999. Biological invasions in Lake Erie: past, present and future. In: Munawar, M., Edsail., T., Munawar, I. F. (Ed.), State of Lake Ere: past, present and future. Backhuys Publishers, Leiden, The Netherlands, pp. 305-322.

Makarewicz, J.C., and P. Bertram. 1991. Evidence for the restoration of the Lake Erie ecosystem - water-quality, oxygen levels, and pelagic function appear to be improving. Bioscience **41**: 216-223.

Meyers, P.A., 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Organic Geochemistry **27**: 213-250.

Meyers, P.A., 2003. Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. Organic Geochemistry **34**: 261-289.

Meyers, P.A., and B.J. Eadie.1993. Sources, degradation and recycling of organic-matter associated with sinking particles in Lake Michigan. Organic Geochemistry **20**: 47-56.

Meyers, P.A., and R. Ishiwatari. 1993. lacustrine organic geochemistry - an overview of indicators of organic-matter sources and diagenesis in lake-sediments. Organic Geochemistry **20**: 867-900.

Meyers, P. A., M. J. Leenheer, B. J. Eadie, and S. J. Maule. 1984. Organic Geochemistry Of Suspended And Settling Particulate Matter In Lake-Michigan. Geochimica Et Cosmochimica Acta **48:** 443-452.

Mudge, S. M., and G. E. Norris. 1997. Lipid biomarkers in the Conwy Estuary (North Wales, UK): A comparison between fatty alcohols and sterols. Marine Chemistry **57:** 61-84.

Munawar, M., T. Edsail. and I. F. Munawar. 1999. State of Lake Ere: past, present and future. Backhuys Publishers, Leiden, The Netherlands.

Muri, G., and S.G. Wakeham. 2006. Organic matter and lipids in sediments of Lake Bled (NW Slovenia): Source and effect of anoxic and oxic depositional regimes. Organic Geochemistry **37**: 1664-1679.

Muri, G., S. G. Wakeham, T. K. Pease and J. Faganeli. 2004. Evaluation of lipid biomarkers as indicators of changes in organic matter delivery to sediments from Lake Planina, a remote mountain lake in NW Slovenia. Organic Geochemistry **35**: 1083-1093.

Nishimura, M. and E. W. Baker. 1986. Possible origin of n-alkanes with a remarkable even-to-odd predominance in recent marine-sediments. Geochimica Et Cosmochimica Acta **50**: 299-305.

Nissenbaum, A., M. J. Baedecker and I. R. Kaplan. 1972. Organic geochemistry of Dead Sea sediments. Geochimica Et Cosmochimica Acta **36**: 709–727.

Pond, K.L., Y.S. Huang, Y. Wang, and C.F. Kulpa. 2002. Hydrogen isotopic composition of individual n-alkanes as an intrinsic tracer for bioremediation and source identification of petroleum contamination. Environmental Science & Technology **36**: 724-728.

Ostrom, P.H., N.E. Ostrom, J. Henry, B.J. Eadie, P.A. Meyers and J.A. Robbins. 1998. Changes in the trophic state of Lake Erie: discordance between molecular delta C-13 and bulk delta C-13 sedimentary records. Chemical Geology **152**: 163-179.

Parrish, C.C., B.J. Eadie, W.S. Gardner and J.F. Cavaletto. 1992. Lipid class and alkane distribution in settling particles of the upper Laurentian Great Lakes. Organic Geochemistry **18**: 33-40.

Schelske, C.L. and D.A. Hodell. 1995. Using carbon isotopes of bulk sedimentary organic-matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. Limnology and Oceanography **40**: 918-929.

Šolević, T., B. Jovančićević, M. Vrvic, and H. Wehner. 2003. Oil pollutants in alluvial sediments - influence of the intensity of contact with ground waters on the effect of microorganisms. Journal of the Serbian Chemical Society **68**: 227-234.

Upsdell, B. L. 2005. The carbon and nitrogen composition of suspended particulate matter in Lake Erie, selected tributaries, and its outflow. M.S. thesis. Univ. of Waterloo.

Volkman, J.K., P. Kearney, and S. W. Jeffrey. 1990. A new source of 4-methyl sterols and 5-alpha(h)-stanols in sediments - prymnesiophyte microalgae of the genus pavlova. Organic Geochemistry **15**: 489-497.

Chapter V
Comparison of Organic Paleoenvironmental Records in Multiple Lake Erie Sediment Cores Sampled Years Apart

1. Introduction

Lacustrine sediments have attracted more scientific research interest recently because they provide high-resolution records of climatic and environmental change. Compared to ocean sediments recording global changes spanning thousands to millons of years, lacustrine sediments reflect regional environmental changes on continents occurring centennially, annually, seasonally and even monthly. Many paleolimnological studies have used a single lacustrine sediment core, the location of which may depend on sedimentation rate, accessibility and researchers' background knowledge, but generally the location chosen is the deepest point in a lake basin. Although spatial variability of sediments is expected, many paleolimnologists have assumed this variability is not significant enough to affect paleoenvironment interpretations and hence a single core can provide information representative of the lacustrine environment of the entire lake. This assumption is reasonably built on the validity of many previous studies in which the past environmental changes reconstructed from a single core correlated well with other paleoenvironmental records (e.g. archaeological evidence) or reconstructions (e.g. paleoclimate model analysis).

However, as increasing resolution of the paleolimnological records has become a strong focus in paleoclimatic studies, concerns about the accuracy of paleoenvironmental reconstructions have been raised because variability in sediment cores, that may not be significant enough to affect the climatic patterns at decadal scales, may generate significant uncertainty for seasonal and annual records of environmental change. A few studies have been undertaken attempting to resolve these concerns, which mainly lie in two aspects. First, is the geographic variability of sediment cores; for example, Petterson et al (1993) analyzed replicate cores from Lake Kassjön, Sweden, a lake with maximum

depth at 12.2m and an area of 0.23km^2, and found the spatial variability of sediment accumulation in varved sediments is very low at a resolution recording seasonal, annual and centennial changes. Nevertheless, they did stress that this low variability highly depends on the choice of the coring site, utilization of best available coring techniques, and care in the subsequent transportation and laboratory analysis. Second, is the temporal variability of sediment cores, i.e., the numbers of the years that the objective sediment horizons have been buried; for instance, Galman et al. (2008) used a collection of ten freeze cores of varved lake sediments sampled at different years from 1979 to 2007 from Lake Nylandssjön in Sweden, a lake with a maximum depth of 17.5m and a surface area of 0.95km^2, to examine possible carbon and nitrogen loss due to diagenetic processes in the bottom of the lake basin with aging of the sediment. They compared specific years in different cores and found a loss of 20% for carbon, 30% for nitrogen, and a consequent rise of C:N ratio within the first five years after deposition. This study confirmed the potential for bias related to the burial ages in paleoenvironment reconstructions because the post-burial processes may change sediment compositions as sediment ages.

Although these studies describe the spatial and temporal variability of sediment cores, none of them have fully explored its effects on paleoenvironmental records. For example, the two aforementioned studies, while briefly mentioning that the sediment variability may affect environmental records, did not specify how the environmental records were impacted. Moreover, the extents of the variability of sediment cores in affecting paleoenvironmental interpretations may differ with different lacustrine settings. As the few previous studies were done in small and shallow lakes, the study in large lake settings, where larger variability of the sediment cores is expected, are important in providing a complete understanding of this topic.

Herein, we compare a comprehensive set of paleoenvironmental proxies including total organic carbon (TOC) and calcium carbonate ($CaCO_3$) contents and their stable carbon isotope compositions ($\delta^{13}C_{org}$ and $\delta^{13}C_{caco3}$), C:N ratios (C:N), stable nitrogen compositions of total nitrogen ($\delta^{15}N$) and stable oxygen isotope compositions of $CaCO_3$ ($\delta^{18}O_{caco3}$) in four sediment cores sampled at 1982, 1988, 1991 and 2003 in Lake Erie, a lake with a surface area of ~26km^2 and a maximum depth of 64 m and that has undergone

rapid changes in its ecosystem over the last century because of intense human perturbations. Many previous studies regarding environmental changes in Lake Erie over the last century furnish us with a thorough background knowledge as a reference to evaluate the accuracy of the paleoenviromental proxies among the multiple cores. The main purpose of this study is to identify the differences in the paleoenvironmental proxies due to the spatial or temporal variability of the sediment cores and to evaluate the reliability of high–resolution paleoenvironmental reconstructions using a single sediment core in a large and complex lake setting. Along with previous studies focusing on small and shallow lakes, this study provides important references to paleolimnologsits in assessing reliability of single-core paleoenvironmental records under various lacustrine settings.

2. Materials and Methods

2.1. Study site

Lake Erie (Fig.5-1) is centered at latitude 42°15'N and longitude 81°15' W. It was formed from the melting of the glaciers during last glacial maximum. It is 388 km long, 92 km wide and has a surface area of 25,690 km^2 and the volume of 484 km3. The lake receives the outflow of Lake Superior, Huron and Michigan mainly through Detroit River and drains into Lake Ontario through the Niagara River. Lake Erie water is bicarbonate rich and has a pH averaging 8.3. The region has short and humid summers and long winters with some snow. The maximum surface water temperature generally occurs in early August at an average of about 24ºC.

Lake Erie is bathymetrically divided into three basins. The shallow western basin, containing 5% of the lake's total volume, is close to large urban areas and rivers that bring pollutants into the lakes and therefore is the most vulnerable to anthropogenic impacts among the three basins. The central basin constitutes 63% of the total lake's volume and is the only basin showing summer anoxia since ~1930s as the result of the development of cultural eutrophication (Hartman, 1973; Schloesser et al. 2005). The deep eastern basin has the maximum depth of 64m among the three basins and makes up 32% of the total lake volume. The eastern basin is least affected by human activities because it is the deepest and farthest from pollution sources. Both the eastern and central basins thermally stratify while the western basin does not.

Lake Erie underwent dramatic changes in its ecosystem over the last century because of human perturbations. Aquatic productivity rose gradually from 1900 to 1970 because of increased nutrient loadings from anthropogenic activities. The most dramatic increase occurred at 1950-1970, when the phosphorus (P) inputs increased rapidly with the rapid industrialization and urbanization of the surrounding regions. A series of changes occurred including the deteriorations of water quality, the depletions of dissolved oxygen (DO) in hypoliminion in the central basin, and the collapse of commercial fisheries, etc.. Because of the limitations of anthropogenic P inputs established by the U.S. and Canadian governments in the early 1970s, the productivity began to decline thereafter while the DO depletions in the central basin strangely have not improved (Hartman, 1973; Munawar et al., 1999; Schloesser et al. 2005). Lake Erie has also been significantly affected by invasive species, among which two non-native species of mussel, *Dreissena polymorpha* (commonly known as the zebra mussel) and *D. bugensis* (commonly known as the quagga mussel) proliferated within Lake Erie in the late 1980s and attracted most scientific concern because of their significant effects on the native biota and the entire lacustrine ecosystem (Upsdell, 2005).

Our sampling site is the East Basin Reference Site, which is located at the center of the eastern basin and is the deepest point of the entire lake basin (Fig.5-1). Three benthos cores were collected with respective lengths of 142cms in 1988, 64cm in 1991 and 106cms in 2003. Two box cores were collected in 1981 and 1991 with a respective length of 24cm and 60cm. The locations of the cores were determined mainly by the water depth of 60 m, combined with the longitudes and latitudes (Table 5-1). These cores were approximately but not from exactly the same location because significant variations in water depth occur in the lake basin at different time periods and different navigation systems were used in arriving the coring site (i.e. LORAN for the 1982,1988 and 1991 core and GPS for the 2003core). All cores were cut into 1cm intervals, packed into separate bags in the field and stored in the freezer after they were transported into the Great Lakes Environmental Research Laboratory, Ann Arbor, MI.

2.2. Analyses

Age determination for the 1982, 1988, 1991 and the 2003 core were based on the identification of the 1963 bomb spike in the ^{137}Cs profile data, which was measured on a

carefully calibrated gamma counting system with a counting error of less than 3%. The ages of the 1-cm core sections were established assuming a constant sedimentation rate of each core. The linear sedimentation rate and mean bulk mass accumulation rates of these four cores are listed at Table5-1.

Samples were freeze dried and ground to a fine powder. Calcium carbonate concentrations of each sample were measured by the carbonate bomb technique, which yielded a carbonate-free residue suitable for the analysis of organic carbon (TOC) and its stable carbon compositions ($\delta^{13}C_{org}$). Analysis of TOC (%), total nitrogen (TN, %), $\delta^{13}C_{org}$ and $\delta^{15}N$ was done at the elemental analysis-isotope ratio mass spectrometry (EA-IRMS) flow through system of the Laboratory of Isotope Geochemistry at the University of Arizona. Stable oxygen isotopes of $CaCO_3$ were measured at Finnigan Element high resolution ICP-mass spectrometers at the Keck Elemental Geochemistry Laboratory at University of Michigan. $\delta^{13}C_{org}$, $\delta^{15}N$ and $\delta^{13}C_{org}$ values were reported in standard per mille (‰) delta notation relative to the Peedee Belemnite, atmospheric N_2, and Standard Mean Ocean Water (SMOW) respectively.

Suess Effect corrections were applied to the $\delta^{13}C_{org}$ to compensate for the atmospheric carbon isotopic shifts caused by fossil fuel combustion as recommended by Schelske and Hodell (1995). The $\delta^{13}C$ values of CO_2 obtained from the measurement of $\delta^{13}C$ ratios in air extracted from Antarctic ice core and firn samples (Francey et al. 1999) were used to simulate the $\delta^{13}C$ values of CO_2 in the air at a specific year as a function of calendar year as the follows.

$\delta^{13}C_{co2}$= 5612.9-8.9296* Year +0.0047308*(Year)^2-0.00000083563*(Year)^3 (1)

The Suess correction factor was calculated by subtracting the simulated $\delta^{13}C$ values of atmospheric CO_2 at a specific year from the average $\delta^{13}C$ value of pre-industrial atmospheric CO_2 (i.e. –6.49‰). Each measured $\delta^{13}C_{org}$ of the sediment samples was subtracted by the correction factor to obtain the $\delta^{13}C_{org}$ used in this study.

Because the 1988 and the 1991 box core lacks the measurements of $CaCO_3$ concentrations, TOC concentrations used in this study were not adjusted to a whole-sediment basis from the measured $CaCO_3$ concentrations for a better comparison among the different cores.

3. Results and Discussion

3.1. Comparisons of paleoenvironmental proxies from different cores

We compare paleoenvironmental proxies at specific years in different cores to evaluate if the reliability of these proxies is affected by the spatial and temporal variability of the sediment cores. If the proxies in the sediment within the upper 5cm below the surface showed abnormal values, we disregarded them in paleoenvironmental reconstructions due to the active diagenesis in these sediment horizons.

Different paleoenvironmental proxies show different aspects of the environmental changes. TOC contents and $\delta^{13}C_{org}$ values in the sediments of Lake Erie are reliable proxies for paleoproductivity (Schelske and Hodell, 1995; Lu and Meyers, 2008 submitted). $\delta^{13}C_{caco3}$ values display divergent trends from that of $\delta^{13}C_{org}$, tracing carbon cycles affected by many other environmental factors besides primary productivity (Lu and Meyers, 2008, submitted). $CaCO_3$ contents are an indictor of the internal carbon cycles between the epiliminion and the hypoliminion/sediment in Lake Erie. C:N values are a reflector of the changes in sedimentary organic matter sources, while the $\delta^{15}N$ values reflect the many processes affecting N cycles in Lake Erie including denitrification, external N inputs and invasive species (Lu et al., 2008 submitted). Finally, $\delta^{18}O_{CaCO3}$ values record temperature changes in Lake Erie by showing a good correlation with the documented water temperature changes.

As shown in Fig.5-2 and Fig.5-3, all paleoenvironmental proxies show consistent long-term temporal patterns among the different cores, while they can be quite different in year-to-year changes. We use TOC contents as the example to illustrate this point.

TOC contents in the 1988, 1991box, 1991 benthos and 2003 core display similar trends, that reflect the changes in lacustrine productivity corresponding with the documented and reconstructed eutrophication development history in Lake Erie, including a gradual increase from ~1900 to ~1950, a rapid increase between early 1950s to early 1970s, and an apparent decrease from ~1970s to present (Hartman, 1973; Schelske and Hodell, 1995) (See Fig.5-2). The 1982 core shows somewhat similar temporal patterns with the other cores in its 20cm deposition, but it is too short to indicate a clear temporal pattern. The roughly consistent temporal patterns of TOC among different cores insure a reliable reconstruction of past productivity changes over a decade scale independent of the years represented and locations of the sediment cores. However,

the small-scale year-to-year difference in TOC contents was not the same among different cores (e.g. TOC contents increase from ~1972 to ~1973 in the 1982 core while decreasing in the 2003 core), questioning the reliability of reconstructing annual changes in the climatic records.

This study suggests sediment cores with high sedimentation rates, while providing an opportunity to recod climatic records with high resolution, perhaps should not be used in reflecting changes at a resolution equal to the sedimentation rate because the small-scale changes in paleoenvironmental proxies are affected by the variability of the sediment cores. Our observation disagrees with the study in Lake Nylandssjön in Sweden (Galman et al., 2008), where the ten cores collected at different years showed the same patterns in year-to-year changes in total carbon and total nitrogen concentrations. We shall discuss the reasons for this disagreement in the following section.

3.2. Causes for the differences in paleoenvironmental proxies among the cores

Besides the differences shown in the annual changes in paleoenvironmental proxies, the paleoenvironmental proxies may also show different values among different sediment cores. For example, the TOC values in the 1982 and 1991 cores are consistently larger than those in the 1988 and 2003 cores. Although these differences are not significant enough to generate biases for long-term paleoenvironmental interpretations, clarification of the causes for these differences is important for understanding the factors determining the compositions of paleoenvironmental proxies in the sediment core and making reliable interpretations for high-resolution environmental records.

The sediment cores in this study differ mainly in two factors: the temporal variability, i.e. the number of years the sediment was buried, and spatial variability, i.e. the locations where the sediment were cored. The temporal variability is caused by the post-burial *in situ* diagenesis related with the aging of sediment. Many studies have shown that *in situ* diagenesis of the sediment is most dramatic within the upper 2-3cms below the surface and can be reasonably ignored in the deeper sediments, where the lack of the free oxygen and the consolidations of the sediments prevented apparent changes of sediment compositions (e.g. Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993). We compared paleoenvironmental proxies in the sediment horizons deposited within the

upper 10cms below the surface among different cores to examine if *in situ* diagenesis was the main cause for the differences in the values of paleoenvironmental proxies. As shown in Fig.5-4 and Fig.5-5, paleoenvironmental proxies in the sediment horizons at the same depths show about as much difference as those at the same ages, suggesting that the *in situ* diagnesis associated with the burial depth does not account for the differences in the values of paleoenvironmental proxies among different cores. Using TOC contents to illustrate this conclusion, if different extents of *in situ* diagenetic alterations due to the different numbers of years for which the sediment horizon was buried accounted for the TOC differences among different cores, the TOC differences in the sediment horizons at the same depth would be apparently smaller than those in the horizons with the same age. The lack of such an observation suggests that in situ diagenesis does not play a significant role in making differences in TOC contents preserved in the sediment. Similar patterns also appear in other paleoenvironmental proxies that show apparently different values in different cores, including $CaCO_3$, C:N and $\delta^{13}C_{org}$. As a matter of fact, some proxies, such as $\delta^{13}C_{caco3}$, show similar values when compared at the same age (Fig.5-3), but more different values at the same depositional depth (Fig.5-5), further suggesting that the burial depth of the sediment was not important in accounting for these differences. This study agrees with many previous studies suggesting in-situ diagenesis can be reasonably disregarded for paleoenvironmental interpretations (Meyers and Ishiwatari, 1993).

Alternatively, spatial variability of the cores arising from uneven distributions of the sediments causes the differences in the initial compositions of the sediment, most probably mainly accounting for the differences in paleoenvrionmental proxies among the difference cores. It has long been recognized that sediment distribution is not even over most lake beds and at least ten potential mechanisms have been proved to affect sediment distributions in a small lake (Hilton et al., 1986). These ten mechanisms include riverine delta sedimentation, riverine plume sedimentation, continuous complete mixing, intermittent complete mixing, epilimnetic intermittent complete mixing, peripheral wave attack, random distribution of sediment, current erosion/redeposition, slumping and sliding on slopes, and organic degradation (Hilton et al., 1986). Our cores are located at the center of the deepest part of the lake basin and hence have a slight chance to be

affected by the rivers, slumping or sliding on slopes while other mechanisms can potentially contribute to the observed differences among different cores. However, some factors may affect sediment distribution in bottom of the lakes. For example, seiches can reach the bottom of the lake and redistribute sediment there. Additionally, more variable factors affect sediment distribution in large lakes.

In a comparison with the two previous studies by Petterson et al (1993) and Galman et al (2008), both of which indicated minor influences of spatial variability of sediment cores, this study does not show completely contradicting evidence as the long-term temporal patterns of the proxies are consistent among different cores, but does show a greater importance of spatial variability of sediment cores in affecting annual environmental records in larger lakes. This difference is not surprising given that higher spatial variability is expected in large lakes. Like the two aforementioned studies, the water depth has also been used as the most important standard for the choice of coring site in this study (Table 1). Unlike the small lakes, however, in which the water level show slight changes over years, Lake Erie showed significant fluctuations in water level over the last century, mainly due to the changes in precipitation and evaporation balance but also affected by man-made changes such as water diversion, control structures, land-use alterations and increased human consumption (Bishop, 1990). For example, Lake Erie water level fell approximate 1m from 1996 to 2000 (Dusini, 2005). Such significant fluctuations of water levels not only increase the uncertainties of our coring locations, but may also cause the changes in fluid forces applied to the lake bed, resulting in the resuspension of previously deposited sediment (Dusini, 2005). Hence, this study suggests that the spatial variability of sediment cores may be greater in larger lakes and produce more variability in the environmental records preserved in sediments, potentially biasing the high-resolution paleoenvironmental interpretations.

3.3. In-situ diagenetic alterations of paleoenvironmental proxies

The in-situ digenetic processes occurring in the bottom of the lake basin have been observed to cause the loss of carbon and nitrogen and shifts in other paleoenvironmental proxies, the direction of which is still debatable (Macko et al., 1987; Bada et al, 1989; Lehmann et al., 2002; Galman et al, 2008). If we assume the shifts occurring in the upper 2-5cms of the sediment cores were mainly caused by *in situ*

diagenesis, we may compare the effects of *in-situ* diagenesis on paleoenvironmental proxies in the different cores. Our assumption is reasonably built on many previous paleoenvironmental studies showing that *in situ* diagenesis is most intense within 5 years after deposition (e.g. Galman et al, 2008) and after which, the sediment composition is relative stable.

Alike many previous studies, carbon and nitrogen loss was observed within the upper several centimeters of all four cores, where a large fraction of the organic material is remineralized and recycled to the lake water. The relative loss rates of carbon and nitrogen differed in different cores while the relative carbon loss is higher than nitrogen in the upper 2cms of all four cores. The carbon versus nitrogen loss in the upper 2cms for different cores is: 2.2% vs 0.74% in the 1982 core, 23.7% vs. 15.8% in the 1988 core, 31.1% vs 28.1% in the 1991core and 10.7% vs. 5.6% in the 2003 core. As a result, the C:N values for all four cores decrease in the upper 2cms due to the preferential recycling of C relative to N (Fig.5-4). This result contradicts some studies showing that the increases in C:N values during early diagenesis are due to the preferential degradation of nitrogen rich compounds (Emery and Rittenberg, 1952; Gehman, 1962; Lehmann et al., 2002; Galman et al., 2008;) but agrees with those exhibiting the increases in C:N values, which are explained by the microbial recycling of carbon and stabilization of inorganic nitrogen in the sediment (Meyers and Ishiwatari, 1993). Given that those studies that show preferential degradation of N generally used sediments with relatively high N contents, we speculate that the preferential loss of N versus C may more likely occur in the N-rich sediments but may be otherwise in sediment containing low N contents.

While TOC, TN and C:N values showed shifts at the same direction due to the *in-situ* diagnesis, other paleoenvrionmental proxies showed shifts of different magnitudes and directions in the upper two centimeters, suggesting high uncertainties in the diagenetic effects on these paleoenviromental proxies. Our observation suggests that various diagenetic shifts are associated with different paleoenviromental proxies, explaining why previous studies show contradicting results regarding diagenetic alterations of paleoenvironmental proxies. Some studies have associated the direction of the diagenetic shifts with the oxic conditions and even suggested the potential of using the diagenetic shifts to reconstruct the past oxic conditions (Libes and Deuser, 1988).

This study questions the validity of this association by showing uncertain diagenetic shifts in cores that were all deposited under oxic conditions, which is documented by the lack of DO depletions in Eastern Basin.

4. Conclusions

This is the first study evaluating the potential effects of temporal and spatial variability on the reliability of organic geochemical paleoenviromental proxies in a large lake setting. The temporal patterns of paleoenvironmental proxies are consistent in the multiple cores, providing strong evidence of the reliability of long-term paleoenvironmental reconstructions utilizing a single core. However, the year-to-year differences in proxies differ among the different cores, questioning the reliability of a single-core study in reconstructing high-resolution paleoenvironmental changes. Moreover, different absolute values appear in the paleoenvironmental proxies among the different cores. These differences are mainly attributed to spatial variability of the sediment cores. Compared to the two previous studies that strengthen the values of a single core in faithfully reflecting annual environmental changes studies in much smaller lakes (i.e. Petterson et al., 1993 and Galman et al., 2008), this study shows that spatial variability of sediment cores in larger lakes may be great enough to affect the accuracy of paleoenvironmental reconstructions at a high resolution. *In situ* diagenesis, although perhaps safely disregarded for paleoenvironmental reconstructions, affects paleoenvironmental proxies differently among the different cores, verifying the uncertainties of alterations of paleoenvironmental proxies related to *in situ* diagenesis and questioning those studies attempting to relate the nature of diagenetic shifts to environmental conditions.

Table 5-1 Details of cores collected at Lake Erie Eastern Basin Reference Site.

Sampling Year (Cal. Yr.)	Water Depth (m)	Latitude	Longitude	Core Type	Mean Bulk MAR ($mg/cm^2/yr$)	Linear Sedimentation Rate (cm/yr)
1982	NA	42° 29.1' N	80° 2.3' W	Box	NA	1.1
1988	59	42° 30.9' N	79° 58.6' W	Benthos	1089	1.7
1991	60	42° 31.0' N	79° 53.6' W	Benthos	390	1.0
1991	60	42° 31.0' N	79° 53.6' W	Box	667	1.6
2003	60	42° 31.0' N	79° 53.6' W	Benthos	435	1.1

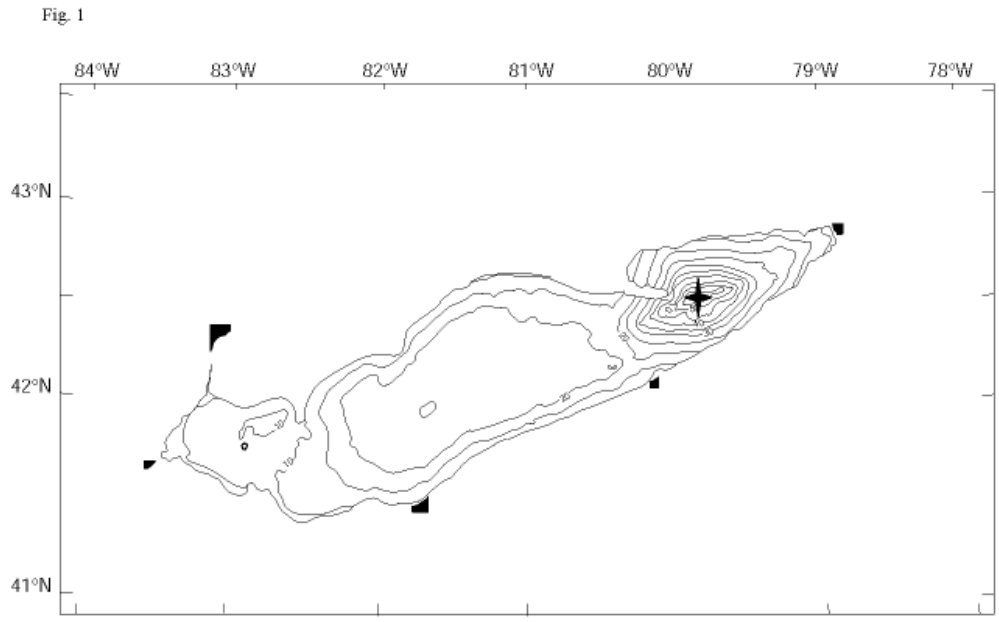

Fig.5-1 Map of Lake Erie. The star indicates the location of the sampling site, Eastern Basin Reference Site.

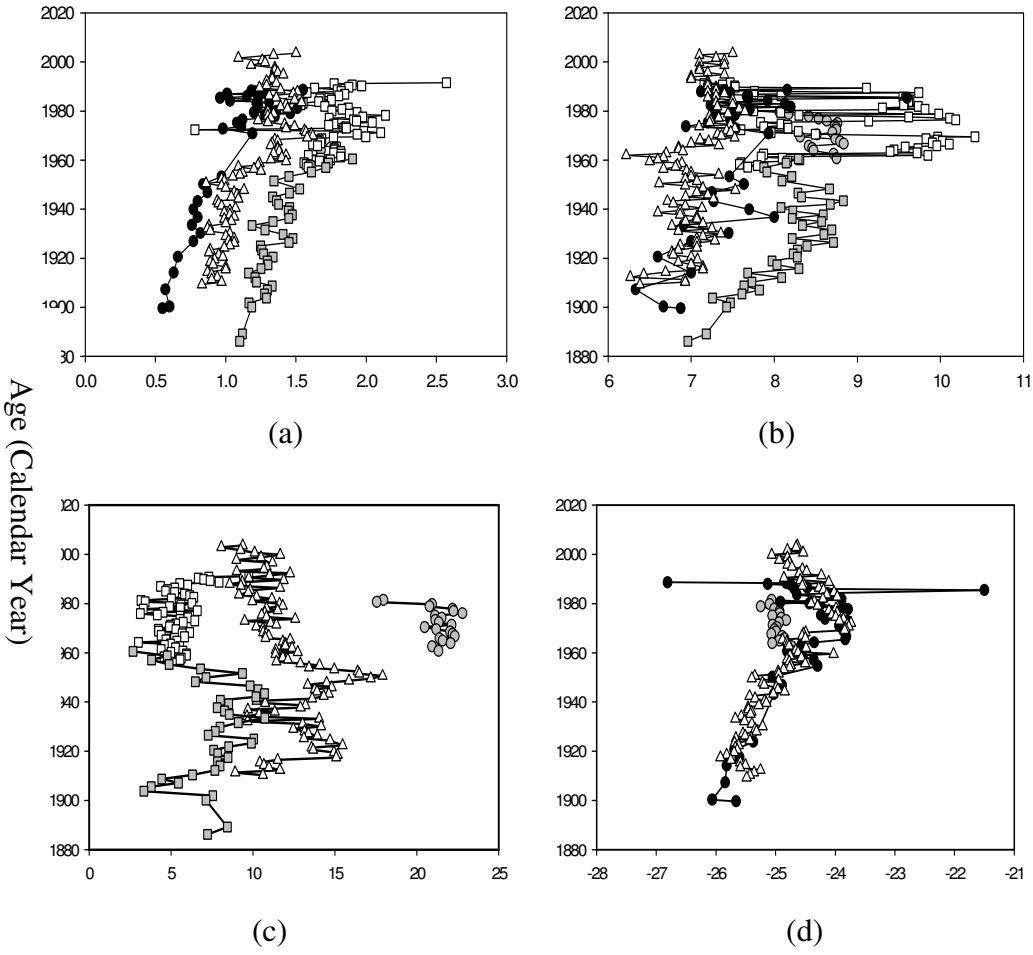

Fig. 5-2 Comparisons of paleoenvironmental proxies in multiple cores based on corresponding ages. Grey circles represent the 1982 core, black circles are the 1988 core, open squares 1991box core, grey squares 1991 benthos core and open triangles the 2003 core. The paleoenvironmental proxies are (a) TOC (%), (b) C:N, (c) $CaCO_3$ (%) and (d) $\delta\,^{13}$Corg (‰).

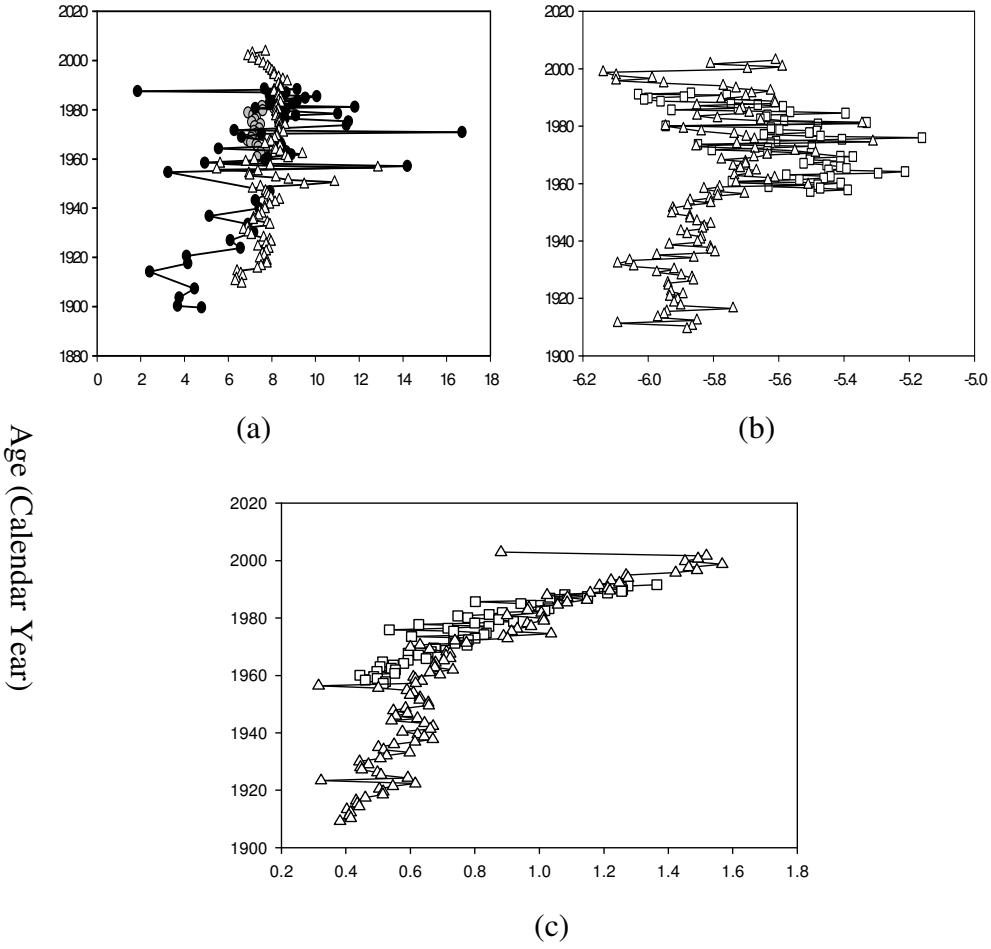

Fig. 5-3 Comparisons of paleoenvironmental proxies in multiple cores based on corresponding ages. Grey circles represent the 1982 core, black circles are the 1988 core, open squares 1991box core, grey squares 1991 benthos core and open triangles the 2003 core. The paleoenvironmental proxies are (a) $\delta^{15}N$ (‰), (b) $\delta^{18}O_{caco3}$ (‰) (c) $\delta^{13}C_{caco3}$(‰).

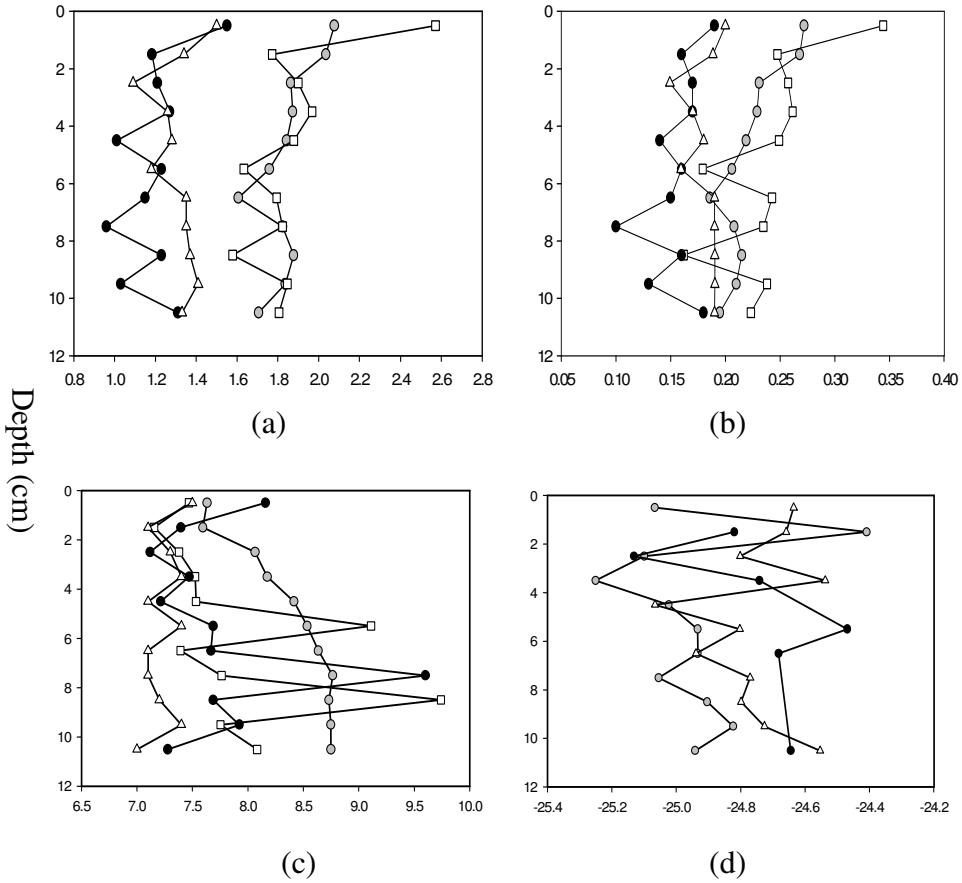

Fig. 5-4 Comparisons of paleoenvironmental proxies in multiple cores based on corresponding depths. Grey circles represent the 1982 core, black circles are the 1988 core, open squares 1991box core and open triangles the 2003 core. The paleoenvironmental proxies are (a) TOC (%), (b) TN (%), (c) C:N, and (d) $\delta^{13}C_{org}$ (‰).

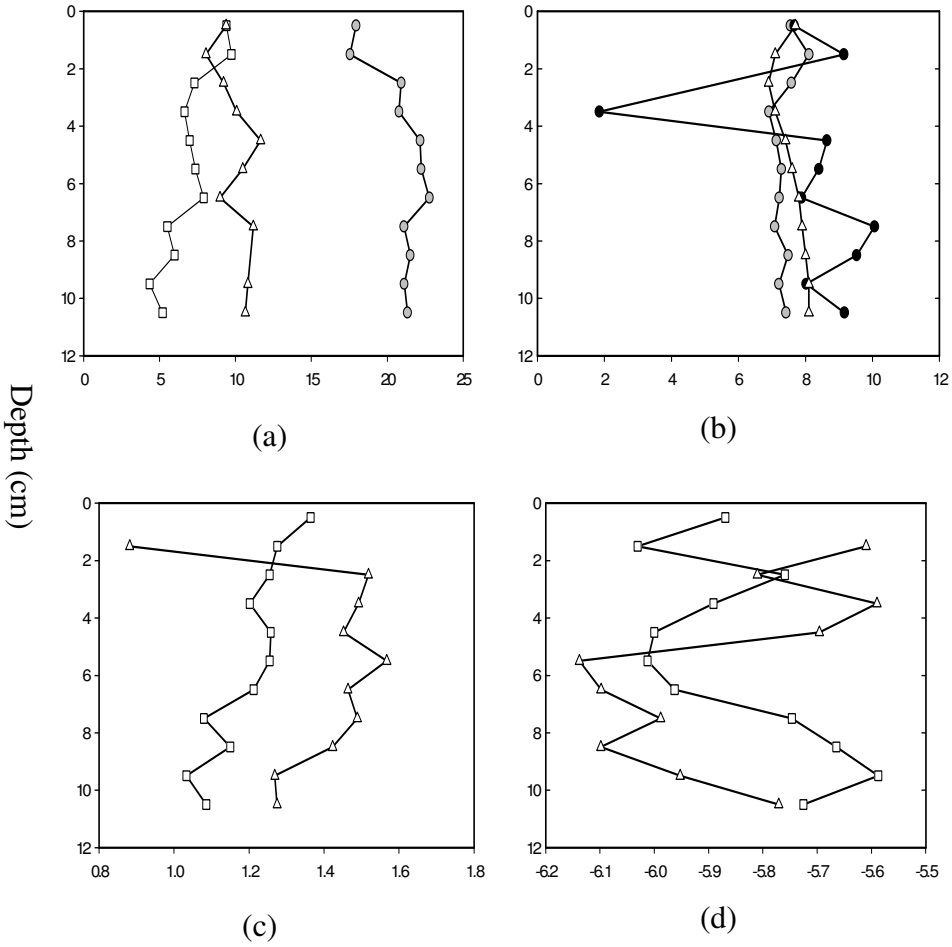

Fig. 5-5 Comparisons of paleoenvironmental proxies in multiple cores based on corresponding depths. Grey circles represent the 1982 core, black circles are the 1988 core, open squares 1991box core and open triangles the 2003 core. The paleoenvironmental proxies are (a) $CaCO_3$ (%), (b) $\delta^{15}N$(‰) (c) $\delta^{13}C_{caco3}$ (‰) , and (d)$\delta^{18}O_{caco3}$ (‰).

References

Bada, J. L., M. J. Schoeninger, and A. Schimmelmann. 1989. Isotopic fractionation during peptide-bond hydrolysis. Geochimica Et Cosmochimica Acta **53:** 3337-3341.

Bishop, C. T. 1990. Historical variation of water levels in lakes erie and michigan-huron. Journal of Great Lakes Research **16:** 406-425.

Dusini, D. S. 2005. The effect of Lake Erie water level variations on sediment resuspension. M.S. thesis, Ohio State University.

Emery, K. O., and S. C. Rittenberg. 1952. Early diagenesis of california basin sediments in relation to origin of oil. AAPG Bulletin-American Association of Petroleum Geologists **36:** 735-806

Francey, R. J. and others 1999. A 1000-year high precision record of delta C-13 in atmospheric CO2. Tellus Series B-Chemical and Physical Meteorology **51:** 170-193.

Galman, V., J. Rydberg, S. S. De-Luna, R. Bindler, and I. Renberg. 2008. Carbon and nitrogen loss rates during aging of lake sediment: Changes over 27 years studied in varved lake sediment. Limnology and Oceanography **53:** 1076-1082.

Gehman, H. M. 1962. Organic matter in limestones. Geochimica Et Cosmochimica Acta **26:** 885-897.

Hartman, W. L. 1973. Effects of exploitation, environmental changes, and new species on the fish habitats and resources of Lake Erie. Technique report no. 22, Great Lakes Fishery Commission, U. S. Bureau of Sport Fisheries and Wildlife, Biological Station, Sandusky, Ohio.

Hilton, J., J. P. Lishman, and P. V. Allen. 1986. The dominant processes of sediment distribution and focusing in a small, eutrophic, monomictic lake. Limnology and Oceanography **31:** 125-133.

Lehmann, M. F., S. M. Bernasconi, A. Barbieri, and J. A. Mckenzie. 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early sedimentary diagenesis. Geochimica Et Cosmochimica Acta **66:** 3573-3584.

Libes, S. M., and W. G. Deuser. 1988. The isotope geochemistry of particulate nitrogen in the peru upwelling area and the gulf of maine. Deep-Sea Research Part a-Oceanographic Research Papers **35:** 517-533.

Macko, S. A., M. L. Fogel, P. E. Hare, and T. C. Hoering. 1987. Isotopic fractionation of nitrogen and carbon in the synthesis of amino-acids by microorganisms. Chemical Geology **65:** 79-92.

Meyers, P. A., and B. J. Eadie. 1993. Sources, degradation and recycling of organic-matter associated with sinking particles in lake-michigan. Organic Geochemistry **20:** 47-56.

Meyers, P. A., and R. Ishiwatari. 1993. Lacustrine organic geochemistry - an overview of indicators of organic-matter sources and diagenesis in lake-sediments. Organic Geochemistry **20:** 867-900.

Munawar, M., T. Edsail, and I.F. Munawar I F (eds), 1999. State of Lake Ere: past, present and future. Backhuys Publishers. Leiden, The Netherlands.

Petterson, G., Renberg, I., Geladi, P., Lindberg, A., and Lindgren, F. 1993. Spatial uniformity of sediment accumulation in varved lake sediments in northern Sweden. Journal of Paleolimnology **9**: 195-205.

Schelske, C. L., and D. A. Hodell. 1995. Using carbon isotopes of bulk sedimentary organic matter to reconstruct the history of nutrient loading and eutrophication in Lake Erie. Limnol Oceanogr. **40**: 918-929.

Schloesser, D. W., R. G. Sticker, and T.B. Bridgeman. 2005. Potential oxygen demand of sediments from Lake Erie. J. Great Lakes Res. **31** (Suppl.2): 272-283.

Upsdell, B. L. 2005. The carbon and nitrogen composition of suspended particulate matter in Lake Erie, selected tributaries, and its outflow. M.S. thesis. Univ. of Waterloo.

Chapter VI

Conclusions

The major findings of the research described in this dissertation are summarized to answer the questions that have been the motivation for this study, and two unanswered questions that deserve special future attentions are elaborated. Finally, based on the questions and challenges encountered in this study, the general directions of future research are suggested.

Summaries in answering the original research questions

In response to recent concerns about the accuracy of organic geochemical proxies of sediments in high-resolution paleoenvironmental reconstruction, this study evaluates the reliabilities of commonly used proxies in recording past environmental changes by using Lake Erie as an interpretive reference, where environmental changes over the last century are well reconstructed and documented. As discussed in the introduction of this thesis (Chapter I), the questioning of the proxy reliabilities mainly focuses on two assumptions: (1) the proxies are exclusively related to certain sources or biogeochemical processes, and (2) the proxies are not significantly affected by post-burial diagenesis and thus reliably preserve information about original sedimentary sources and environment. By utilizing different approaches, this study not only examines both assumptions, but also suggests a new potential factor that may undermine the proxy reliabilities but has been neglected in previous studies. Major conclusions are summarized as follows.

First assumption: the specificity of organic geochemical proxies in representing a sedimentary source or a biogeochemical process

Among many sedimentary proxies we examined, some are the explicit and direct response of either a certain producer or a biogeochemical process. Such proxies include:

1. Stable carbon isotope compositions of bulk organic carbon ($\delta^{13}C_{org}$), total organic carbon concentrations (TOC), and the total concentrations of three groups of biomarker molecules including hydrocarbons (HCs), fatty acids (FAs) and fatty alcohols (OLs), which all show variations consistent with the documented changes in

aquatic productivity in Lake Erie, and can be considered direct and reliable proxies in recording primary productivity in the lakes.

2. Calcium carbonate concentrations ($CaCO_3$), which are inversely related to TOC concentrations and reflect carbon cycling processes between the epilimnion and hypolimnion/sediments.
3. The atomic C:N values ($C:N_{at}$) are reliable in recording the shifts in sedimentary sources between autochthonous and allochthonous sedimentary sources.
4. The ratios of unsaturated FAs to their saturated counterparts, represented by $C_{16:1}$:$C_{16:0}$ and $C_{18:1}$:$C_{18:0}$, and the ratio of branched (Br) FAs to their straight-chain analogues, represented by Br-C_{15}:n-C_{14}, reflect the extents of post-burial diagenesis, whichlargely depends on the availability of free oxygen.

In contrast, other proxies are affected by many producers or/and complex biogeochemical processes and hence are not explicit in recording information about past ecosystem. These proxies include:

1. Stable nitrogen isotopic compositions of total nitrogen ($\delta^{15}N$) are potentially affected by human nitrogen inputs, the denitrification process, aquatic productivity and the changes of nitrogen dynamics caused by establishment of invasive species. The significance of these different factors varies depending on the specific environmental conditions of lacustrine ecosystem.
2. Stable carbon isotopic compositions of calcium carbonate ($\delta^{13}C_{caco3}$) appear to be influenced by changes in primary productivity, temperature variations, phosphorus distributions in the epilimnion and hypolimnion at different seasons, and recycling of carbon in the epilimnion during thermally stratified periods, among which the one mainly determining $\delta^{13}C_{caco3}$ variations is not certain even with a thorough understanding of the environmental changes in Lake Erie.
3. Neither the carbon chain length distribution for FAs nor that for OLs provides a completely reliable record of the original sedimentary sources for organic matter preserved in sediments, although they are good indictors of sedimentary sources for FA and OL molecules respectively.

4. The unusual molecular distributions of HCs in Lake Erie cannot be used to indicate changes in the primary producers because they are overprinted by an unusual source, most likely microorganisms living in close contact with oil contaminants.

Our conclusions, on one hand, strengthen the values of some proxies in tracing sedimentary sources or/and biogeochemical processes, and on the other hand, demonstrate the complexities of some other proxies and warrant cautions when applying such proxies in reconstructing paleoenviroment.

Second assumption: the effects of post-burial diagenesis on high-resolution paleoenviromental interpretations

The organic geochemical proxies in sediment cores sampled at 1982, 1988, 1991 and 2003 show consistent temporal patterns but different values. Although the cores were sampled at approximately the same location, the spatial variability of the sediment cores accounts for the main differences in proxies among these four cores. Post-burial diagenesis, while generating carbon and nitrogen loss and high variability of some proxies, is not significant enough in affecting paleoenvironmental interpretations. The diagenetic alterations of the cores seem to affect proxies in different ways among different cores, verifying the uncertainties of post-burial alterations of proxies and questioning those studies attempting to speculate environmental conditions from the nature of diagenetic alterations.

A potential factor affecting the accuracy of the organic geochemical proxies: sediment variability

While the two most concerned issues regarding the reliabilities of proxies are addressed, spatial variability of sediment cores is suggested to have a significant potential in affecting the accuracy of paleoenvironmental reconstructions, especially those aiming at high-resolution records, but it has not attracted enough scientific concern in previous studies. The few studies of small lakes that have evaluated the spatial variability of sediment cores suggest their effects are minor in recording environmental changes. Conversely, this study shows that spatial variability of sediment cores in larger lakes, although is not large enough to bias the environmental reconstructions over decades, but it may affect the accuracy of reconstructions of annual environmental records. The

greater spatial variability of sediment cores may largely result from significant water level fluctuations and sediment distribution patterns.

It is important to note that caution needs to be exercised when applying the conclusions of this study in paleoenvrionmental reconstructions under different environmental settings in which the behaviors of proxies may vary and conclusions derived from this study may not be directly applicable.

Future research questions and directions

Two Interesting Questions

Among several interesting questions with open answers in this study, two specific questions deserve special future research efforts because their important implications in future research directions of paleolimnological studies.

The first question is "what are sources of the unusual HC distributions in sediments from Lake Erie". This question deserves further efforts because the observation, which is uncommon in other current studies, may represent a phenomenon that will be widely observed with increasing anthropogenic perturbations to the geosphere.

The validity of the speculation that microorganisms inhibiting an oil-polluted environment are the source for this uncommon HC distribution can be tested by compound-specific isotopic analysis. Since microorganisms may have different stable carbon isotopic compositions from the primary producers, i.e., algae and high plants, our speculations can be further strengthened if the analysis of even-chain numbered alkanes and alkenes differ from odd-chain numbered analogues. To fully confirm our speculations, the further analysis of $\delta^{13}C$ values of microorganism living under an oil-contaminated environment is required to examine if they match the $\delta^{13}C$ values of HCs in our sediment samples.

The second question is whether sediment cores with high sedimentation rates can be confidently used in constructing high-resolution environmental records, which has become a stronger focus of recent paleoenvironmental studies.

The multiple sediment cores used in this study, although having sedimentation rate as high as 1cm/year, do not guarantee a reliable reflection of year-to-year environmental changes. Especially in large lake settings, the annual environmental

changes may be strongly overprinted by uneven distributions of sediments. However, the limited numbers of studies addressing this question and the variability of environmental settings determines that a widely applicable conclusion cannot be drawn without further comparisons of multiple cores at more research sites with different environmental conditions. Until then, any convincible high-resolution reconstructions must either provide collateral evidence, e.g., paleontological and anthropogenic evidence, or analyze multiple cores to prove effects from variability of sediment distributions on organic geochemical proxies are negligible.

General future research directions

The two interesting questions point out potential future research directions.

Modern anthropogenic activities are so intensive and extensive that they have imprinted more biomarkers on the geosphere. The understandings of these biomarkers, however, are relatively limited compared to those from nature sources, given that many traditional paleoenvironmental studies focus on prehistorical environmental changes. Fortunately, technological advances in recent years have made it possible to analyze samples in very small quantities or those from the organisms and environmental settings that were unreachable in the past, which will help to identify novel anthropogenic biomarkers and yield much information about the effects of anthropogenic activities on the geosphere.

Applications of multiple-core analyses are warranted in reconstructing high-resolution environmental records in future studies, especially when evidence is lacking from other means, such as model analysis, documented historical data, anthropogenic and paleontological records.

Appendices

Appendix 1: Geochemistry data of the 2003 core

Depth	Year	$\delta^{18}O_{caco3}$	corrected $\delta^{13}C_{caco3}$	TOC (whole- sediment based))	Atomic C:N	corrected $\delta^{13}C_{org}$	$\delta^{15}N_{total}$	$CaCO_3$	ε-fractiona-tion
(cm)	(Cal.)	(‰)	(‰)	(%)		(‰)	(‰)	(%)	TOC-$CACO_3$
0.50	2003.56			1.36	8.75	-24.90	7.70	9.38	
1.50	2002.91	-5.61	0.59	1.23	8.28	-25.00	7.10	8.06	26.25
2.50	2001.69	-5.81	1.25	0.99	8.52	-25.00	6.90	9.23	26.92
3.50	2000.65	-5.59	1.24	1.13	8.63	-24.80	7.10	10.08	26.70
4.50	1999.82	-5.70	1.22	1.13	8.28	-25.30	7.40	11.66	27.21
5.50	1998.72	-6.14	1.35	1.06	8.63	-25.00	7.60	10.49	27.03
6.50	1997.64	-6.10	1.26	1.23	8.28	-25.10	7.80	8.98	27.04
7.50	1996.65	-5.99	1.30	1.20	8.28	-25.00	7.90	11.19	26.97
8.50	1995.77	-6.10	1.25	1.37	8.40	-25.00	8.00		26.92
9.50	1994.90	-5.95	1.11	1.26	8.63	-24.90	8.10	10.83	26.67
10.50	1994.02	-5.77	1.10	1.19	8.17	-24.70	8.10	10.66	26.45
11.50	1993.12	-5.73	1.08	1.21	8.17	-24.60	8.30	8.99	26.33
12.50	1992.24	-5.63	1.10	1.13	8.40	-24.80	8.50	12.25	26.56
13.50	1991.37	-5.68	1.07	1.21	8.40	-24.40	8.70	11.02	26.11
14.50	1990.41	-5.70	1.12	1.16	8.40	-25.00	8.30	9.74	26.79
15.50	1989.50	-5.78	1.14	1.09	8.52	-24.70	8.40	11.88	26.49
16.50	1988.69	-5.61	1.10	1.26	8.52	-24.20	8.40	9.34	25.93
17.50	1987.92	-5.61	0.99	1.38	8.40	-24.60	8.10	8.57	26.24
18.50	1987.15	-5.85	1.00	1.34	8.63	-24.60	8.10	9.26	26.25
19.50	1986.29	-5.71	1.07	1.16	8.52	-24.40	8.30	11.66	26.11
20.50	1985.44	-5.72	1.04	1.23	8.40	-24.20	8.30	9.82	25.87
21.50	1984.55	-5.69	1.02	1.35	8.75	-24.10	8.40	9.70	25.74
22.50	1983.59	-5.85	0.89	1.40	8.52	-24.20	8.30	9.13	25.71
23.50	1982.73	-5.79	0.88	1.28	8.75	-24.10	8.40	10.21	25.60
24.50	1981.85	-5.66	0.88	1.23	8.54	-24.30	8.23	11.16	25.81
25.50	1980.89	-5.34	0.76	1.30	8.84	-24.50	8.21	9.96	25.89
26.50	1979.96	-5.95	0.92	1.15	8.92	-24.50	8.28	11.62	26.06
27.50	1979.04	-5.89	0.92	1.18	8.69	-24.40	8.19	11.82	25.95

28.50	1978.12	-5.84	0.84	1.16	8.43	-24.10	8.23	10.81	25.56
29.50	1977.17	-5.74	0.88	1.17	8.56	-24.20	8.19	11.50	25.70
30.50	1976.21	-5.70	0.87	1.10	8.44	-24.00	8.31	10.71	25.48
31.50	1975.35	-5.68	0.79	1.16	8.43	-24.20	8.33	10.52	25.61
32.50	1974.53	-5.31	0.90	1.27	8.72	-24.10	8.33	10.81	25.62
33.50	1973.72	-5.73	0.76	1.30	8.28	-24.00	8.60	12.57	25.37
34.50	1972.90	-5.85	0.77	1.29	8.78	-24.10	8.34	9.49	25.48
35.50	1972.09	-5.67	0.59	1.39	8.67	-23.90	8.34	11.08	25.09
36.50	1971.36	-5.55	0.63	1.39	8.72	-23.90	8.32	11.42	25.13
37.50	1970.65	-5.49	0.40	1.45	8.54	-24.00	8.52	10.18	25.00
38.50	1969.90	-5.64	0.26	1.45	8.59	-24.20	8.23	10.61	25.07
39.50	1969.12	-5.68	0.35	1.58	8.78	-24.20	8.22		25.16
40.50	1968.33	-5.78	0.46	1.21	8.29	-24.80	8.12	10.63	25.90
41.50	1967.59	-5.70	0.49	1.22	8.41	-24.80	7.92	10.80	25.93
42.50	1966.83	-5.70	0.48	1.18	8.17	-24.80	7.96	10.96	25.92
43.50	1966.01	-5.74	0.49	1.18	8.56	-24.70	7.68	10.76	25.83
44.50	1965.25	-5.72	0.47	1.20	7.99	-25.10	8.37	12.27	26.23
45.50	1964.50	-5.67	0.44	1.21	7.99	-25.00	8.15	11.82	26.09
46.50	1963.65	-5.69	0.44	1.22	8.05	-25.00	8.17	11.94	26.09
47.50	1962.78	-5.74	0.44	1.18	7.82	-25.00	8.38	11.97	26.09
48.50	1961.95	-5.61	0.49	1.25	7.25	-24.70	9.40	12.39	25.83
49.50	1961.09	-5.63	0.42	1.24	7.78	-24.90	8.62	11.39	25.97
50.50	1960.27	-5.73	0.46	1.15	7.70	-24.90	8.74	12.73	26.01
51.50	1959.51	-5.51	0.39	1.27	7.58	-24.30	7.19	11.37	25.30
52.50	1958.78	-5.78	0.39	1.09	8.04	-25.00	6.80	11.83	26.04
53.50	1958.04	-5.83	0.41	1.08	7.97	-24.80	5.63	11.82	25.85
54.50	1957.24	-5.79	0.40	0.96	7.95	-25.00	7.92	12.12	26.05
55.50	1956.41	-5.71	0.10	1.06	7.78	-25.00	12.85	11.42	25.74
56.50	1955.64	-5.79	0.30	1.09	8.10	-24.70	5.48	12.88	25.63
57.50	1954.86	-5.81	0.38	0.96	8.17	-25.00	7.36	14.05	26.03
58.50	1954.06	-5.87	0.40	0.95	8.56	-25.00	6.95	13.41	26.05
59.50	1953.20	-5.81	0.39	0.89	8.17	-25.00	6.98	14.96	26.04
60.50	1952.32	-5.88	0.44	0.81	8.08	-25.20	8.18	16.38	26.30
61.50	1951.46	-5.92	0.46	0.83	8.25	-25.10	8.75	16.48	26.22
62.50	1950.50	-5.92	0.49	0.71	7.72	-25.50	10.87	17.91	26.67
63.50	1949.53	-5.93	0.51	0.80	8.08	-25.60	9.48	17.19	26.80
64.50	1948.64	-5.87	0.46	0.84	8.33	-25.10	7.48	15.85	26.22
65.50	1947.76	-5.87	0.43	0.97	8.79	-25.30	7.11	14.48	26.40
66.50	1946.85	-5.85	0.46	0.92	8.24	-25.30	7.71	13.33	26.43

67.50	1945.94	-5.81	0.42	0.92	8.40	-25.10	7.78	14.80	26.18
68.50	1945.05	-5.83	0.48	0.90	8.09	-25.10	7.85	13.76	26.24
69.50	1944.22	-5.83	0.39	0.94	8.48	-25.00	7.96	13.89	26.04
70.50	1943.33	-5.90	0.49	0.80	7.83	-25.20	8.34	14.63	26.35
71.50	1942.35	-5.88	0.52	0.81	7.92	-25.60	8.15	14.31	26.81
72.50	1941.37	-5.84	0.51	0.84	8.08	-25.50	7.89	13.60	26.69
73.50	1940.43	-5.84	0.42	0.96	8.32	-25.30	7.67	10.21	26.39
74.50	1939.54	-5.85	0.50	0.92	8.01	-25.30	7.68	10.75	26.47
75.50	1938.65	-5.94	0.54	0.86	7.70	-25.40	7.44	13.19	26.62
76.50	1937.74	-5.81	0.56	0.90	8.01	-25.60	7.53	12.90	26.85
77.50	1936.85	-5.81	0.53	0.96	8.24	-25.50	7.39	9.68	26.71
78.50	1935.95	-5.80	0.48	0.88	8.25	-25.50	7.16	11.33	26.66
79.50	1935.04	-5.97	0.42	0.93	8.09	-25.50	7.15	10.36	26.60
80.50	1934.13	-5.86	0.43	0.90	8.33	-25.70	7.79	9.62	26.82
81.50	1933.15	-6.06	0.49	0.76	7.90	-25.80	7.91	14.04	26.99
82.50	1932.10	-6.09	0.40	0.79	8.46	-25.70	6.88	9.66	26.79
83.50	1931.03	-6.04	0.38	0.77	7.99	-25.50	6.70	13.02	26.56
84.50	1930.04	-5.92	0.32	0.88	8.58	-25.30	6.92	14.16	26.29
85.50	1929.00	-5.97	0.34	0.88	8.33	-25.50	7.06	12.45	26.52
86.50	1928.01	-5.90	0.34	0.92	8.24	-25.40	7.62	13.14	26.41
87.50	1927.13	-5.87	0.35	0.88	8.50	-25.70	7.90	13.37	26.74
88.50	1926.21	-5.86	0.41	0.91	8.24	-25.60	7.96	13.93	26.69
89.50	1925.27	-5.94	0.44	0.90	8.01	-25.70	7.73	13.09	26.83
90.50	1924.33	-5.94	0.54	0.84	8.25	-25.50	7.36	14.69	26.72
91.50	1923.36				7.99	-25.70	7.86		26.38
92.50	1922.37	-5.93	0.58	0.74	7.90	-25.70	7.74	15.46	26.97
93.50	1921.42	-5.89	0.51	0.82	7.92	-25.70	7.56	13.57	26.90
94.50	1920.49	-5.93	0.48	0.85	8.17	-25.70	7.65	13.67	26.87
95.50	1919.53	-5.91	0.49	0.78	8.26	-25.70	7.44	14.93	26.88
96.50	1918.50	-5.92	0.49	0.76	7.99	-25.90	7.78	15.16	27.09
97.50	1917.44	-5.90	0.44	0.77	8.17	-26.00	7.77	15.07	27.15
98.50	1916.41	-5.74	0.40	0.88	8.33	-25.80	7.51	11.50	26.89
99.50	1915.39	-5.94	0.41	0.90	8.33	-25.60	7.34	10.41	26.69
100.50	1914.37	-5.95	0.41	0.78	7.81	-25.50	6.41	10.66	26.59
101.50	1913.33	-5.97	0.36	0.80	7.50	-25.60	6.57	10.98	26.64
102.50	1912.29	-5.85	0.35	0.83	7.31	-25.30	6.66	11.64	26.32
103.50	1911.29	-6.09	0.33	0.82	8.08	-25.40	6.38	8.92	26.40
104.50	1910.27	-5.87	0.32	0.87	8.08	-25.50	6.32	10.60	26.50
105.50	1909.22	-5.88	0.27		7.45	-25.60	6.62		26.55

106.50	1908.24							10.56	

Appendix 2: Geochemistry Data for the Biomarker Molecules for the 2003 Core

Appendix 2-a: Hydrocarbons (HCs)

Depth (cm)	Concentrations of HCs (ug/g sediment)	Age (Cal. Year)
1.5	10.59335	2002.9
2.5	10.3532	2001.7
7.5	12.17849	1996.6
14.5	6.587495	1990.4
21.5	7.432115	1984.5
22.5	11.37555	1983.6
25.5	9.082344	1980.9
34.5	14.31692	1972.9
44.5	19.00709	1965.2
51.5	20.64407	1959.5
59.5	10.0184	1953.2
65.5	9.410446	1947.8
71.5	5.864517	1942.4
83.5	8.603399	1931
95.5	10.32578	1919.5
106.5	6.816466	1908.2

Appendix 2-b: Free Fatty Acids (FAs)
TAR= $(C_{24}+C_{26}+C_{28})/ (C_{12}+C_{14}+C_{16})$, br indicates branched.

Depth (cm)	Age (Cal. Year)	Concentrations of FAs (ug/g sediment)	TAR	Concentration of FAs (ug/g TOC)	C_{20-}/C_{20+}	brC_{15s}/C_{14}	$C_{16:1}/C_{16}$	$C_{18:1}/C_{18}$
1.5	2002.914	18.48532	0.248485	1502.872	5.819672	1.04	0.574257	0.44
2.5	2001.685	13.07789	0.248485	1063.243	5.180328	0.8	0.366337	0.52
14.5	1990.41	16.50497	0.247368	1422.843	3.987805	0.483871	0.168224	0.5
21.5	1984.545	16.90745	0.185393	1252.404	5.153846	0.509434	0.109091	0.34375
22.5	1983.589	20.06366	0.219048	1433.118	4.079545	0.341772	0.132075	0.392857
28.5	1978.121	13.66469	0.152318	1177.991	5.265306	0.454545	0.136364	0.483871
34.5	1972.899	18.55762	0.128492	1438.575	5.45283	0.367347	0.069565	0.4
37.5	1970.646	21.55723	0.242268	1486.706	4	0.3	0.098214	0.34375
44.5	1965.246	18.23141	0.282828	1519.284	3.755319	0.322581	0.108108	0.290323
51.5	1959.514	21.02557	0.22093	1655.557	3.789474	0.404255	0.107143	0.407407
59.5	1953.203	9.42884	0.284153	1059.42	3.451613	0.457627	0.114286	0.264706
65.5	1947.764	7.92999	0.289017	817.5247	3.759036	0.509434	0.089109	0.179487
95.5	1919.533	6.789984	0.139303	870.5107	6.64	0.338462	0.063158	0.176471
101.5	1913.327	5.783437	0.130682	722.9296	6.386364	0.431373	0.065421	0.138889

Appendix 2-c: Free-Fatty Alcohols (OLs)
TAR= (C_{24}+C_{26}+C_{28})/ (C_{12}+C_{14}+C_{16}), br indicates branched.

Depth (cm)	Age (Cal. Year)	Concentrations of OLs (ug/g sediment)	Concentration of OLs (ug/g TOC)	TAR	br-C15s/C14
1.5	2002.914	7.171789	582.1366	0.666667	0.181034
2.5	2001.685	5.886681	594.9965	1.529032	0.252632
7.5	1996.648	11.91025	993.3958	0.711765	0.145299
14.5	1990.41	7.623508	654.7148	0.881356	0.12931
21.5	1984.545	11.07891	823.4586	1.140541	0.198276
22.5	1983.589	8.496843	607.2116	0.906077	0.172414
25.5	1980.885	16.94128	1306.573	1.281481	0.176471
31.5	1975.348	10.71942	921.5413	1.191257	0.17
34.5	1972.899	15.74166	1216.204	0.766082	0.112069
37.5	1970.646	14.66463	1014.122	0.533333	0.08547
44.5	1965.246	13.72771	1142.196	0.747191	0.076923
51.5	1959.514	9.907459	781.6679	0.636872	0.0625
59.5	1953.203	5.461374	611.5969	0.855422	0.086207
65.5	1947.764	4.185526	433.1403	0.72093	0.076923
71.5	1942.354	4.442003	545.6629	0.674641	0.097015
83.5	1931.034	3.966201	512.375	0.644444	0.037313
95.5	1919.533	6.367427	813.6226	0.512658	0.059829
101.5	1913.327	5.7308	715.275	0.47205	0.06087
106.5	1908.241	4.269652		0.432749	0.02963

Appendix 2-d: Principal Component Analysis of Concentrations of Free Fatty Acids (FAs) and Free Fatty Alcohols (OLs) (ug/g TOC)
F represents Principle Component

Depth of Samples (cm)	F1-FA	F2-FA	F3-FA	Depth of Samples (cm)	F1-OL	F2-OL
1.5	0.32071	2.78163	0.32647	1.5	-0.61108	-0.98144
2.5	-0.53858	1.6202	0.12263	2.5	-0.71937	-1.04277
14.5	0.81056	0.33723	-0.59912	7.5	0	0
21.5	-0.26528	-0.13237	0.4656	14.5	-0.26094	-0.7598
22.5	0.82899	-0.28164	-0.83516	21.5	0.40738	-0.67963
28.5	-0.54534	-0.65074	2.20326	22.5	-0.44032	-0.74763
34.5	0.54013	-0.62259	1.1394	25.5	2.24003	-0.89831
37.5	0.6813	-0.62213	-0.18019	31.5	0.69117	-0.30898
44.5	1.3141	-0.49895	-1.05597	34.5	1.75938	-0.87808
51.5	1.31019	-0.56947	1.06335	37.5	0.51041	1.85694
59.5	-0.13829	-0.19202	-0.85251	44.5	1.12514	1.90338
65.5	-1.07731	-0.13799	-0.91852	51.5	-0.25788	1.58426
95.5	-1.25774	-0.6999	-1.21979	59.5	-0.4883	-0.24384
101.5	-1.98345	-0.33127	0.34055	65.5	-1.40189	-0.21042
				71.5	-0.84193	0.14858
				83.5	-0.99232	0.07371
				95.5	0.0533	0.22825
				101.5	-0.77277	0.95577

Appendix 3: Geochemistry Data for the 1982 Core

Depth (cm)	Age (Cal. Year)	TOC (%)	TOC whole-sediment based (%)	TN (%)	Weight C:N	$\delta^{15}N$ (‰)	$CaCO_3$ (%)	Corrected $\delta^{13}C_{org}$ (‰)
0.5	1981.50	2.08	1.70	0.27	7.63	7.55	17.95	-25.07
1.5	1980.60	2.04	1.68	0.27	7.59	8.10	17.55	-24.41
2.50	1979.70	1.86	1.47	0.23	8.06	7.58	20.93	-25.10
3.50	1978.80	1.87	1.48	0.23	8.17	6.91	20.78	-25.25
4.50	1977.80	1.84	1.43	0.22	8.42	7.13	22.17	-25.02
5.50	1976.90	1.76	1.37	0.21	8.53	7.28	22.24	-24.93
6.50	1976.00	1.61	1.24	0.19	8.63	7.22	22.78	-24.93
7.50	1975.00	1.82	1.44	0.21	8.76	7.08	21.10	-25.06
8.50	1974.10	1.88	1.47	0.22	8.73	7.48	21.52	-24.90
9.50	1973.20	1.84	1.45	0.21	8.75	7.21	21.12	-24.82
10.50	1972.30	1.71	1.34	0.20	8.75	7.42	21.34	-24.94
11.50	1971.30	1.60	1.25	0.18	8.70	7.18	22.12	-25.05
12.50	1970.40	1.76	1.40	0.21	8.51	7.31	20.48	-24.98
13.50	1969.50	1.70	1.34	0.21	8.31	7.11	21.19	-25.02
14.50	1968.60	1.70	1.32	0.19	8.74	7.06	22.03	-24.99
15.50	1967.60	1.69	1.31	0.19	8.79	6.88	22.19	-25.07
16.50	1966.70	1.73	1.35	0.20	8.84	7.03	22.32	-24.89
17.50	1965.80	1.63	1.28	0.19	8.42	7.28	21.37	-24.85
18.50	1964.90	1.68	1.32	0.20	8.46	7.37	21.57	-24.94
19.50	1963.90	1.68	1.31	0.20	8.47	7.72	22.05	-25.06
21.00	1962.50	1.63	1.29	0.19	8.72	7.49	20.93	-24.73
23.00	1960.70	1.65	1.30	0.19	8.75	7.32	21.32	-24.58

Appendix 4: Geochemistry of the 1991 box core

Depth (cm)	Age (Cal. Year)	TOC (%)	TOC whole-sediment based (%)	TN (%)	Weight C:N	$CaCO_3$ (%)	$\delta^{18}O_{caco3}$ (‰)	Corrected $\delta^{13}C_{org}$ (‰)
0.5	1991.58	2.57	2.33	0.34	7.47	9.41	-5.87	1.36
1.5	1991.18	1.77	1.60	0.25	7.16	9.74	-6.03	1.28
2.5	1990.72	1.90	1.76	0.26	7.38	7.31	-5.76	1.25
3.5	1990.28	1.97	1.84	0.26	7.52	6.65	-5.89	1.20
4.5	1989.82	1.88	1.75	0.25	7.53	6.98	-6.00	1.26
5.5	1989.31	1.63	1.51	0.18	9.11	7.37	-6.01	1.25
6.5	1988.69	1.79	1.65	0.24	7.39	7.92	-5.96	1.21
7.5	1988.11	1.82	1.72	0.23	7.76	5.52	-5.75	1.08
8.5	1987.52	1.58	1.48	0.16	9.74	6.00	-5.66	1.15
9.5	1986.90	1.85	1.77	0.24	7.75	4.35	-5.59	1.03
10.5	1986.27	1.80	1.71	0.22	8.08	5.20	-5.73	1.09
11.5	1985.65	1.68	1.60	0.18	9.55	4.78	-5.93	0.80
12.5	1985.07	1.67	1.59	0.17	9.58	4.65	-5.57	0.94
13.5	1984.49	1.75	1.66	0.18	9.63	5.20	-5.40	0.97
14.5	1983.87	1.66	1.57	0.17	9.62	5.81	-5.64	1.03
15.5	1983.23	1.55	1.46	0.16	9.57	6.13	-5.64	1.03
16.5	1982.57	1.54	1.44	0.16	9.56	6.39	-5.66	1.02
17.5	1981.90	1.71	1.62	0.18	9.73	5.02	-5.58	0.89
18.5	1981.27	1.87	1.81	0.20	9.30	3.16	-5.33	0.84
19.5	1980.72	1.83	1.76	0.19	9.81	3.41	-5.48	0.75
20.5	1980.12	1.76	1.65	0.23	7.75	6.27	-5.95	0.78
21.5	1979.45	1.93	1.82	0.24	8.08	5.60	-5.62	0.87
22.5	1978.83	1.88	1.79	0.19	9.98	4.91	-5.60	0.92
23.5	1978.25	2.14	2.02	0.26	8.30	5.56	-5.48	0.80
24.5	1977.70	1.98	1.91	0.21	9.62	3.29	-5.51	0.63
25.5	1977.10	1.74	1.62	0.17	10.11	6.59	-5.65	0.84
26.5	1976.50	1.91	1.82	0.19	10.19	4.51	-5.47	0.72
27.5	1975.94	1.93	1.87	0.21	9.14	3.12	-5.16	0.53
28.5	1975.38	2.04	1.96	0.26	7.84	4.16	-5.41	0.73

29.5	1974.79	1.77	1.67	0.22	8.08	5.55	-5.61	0.84
30.5	1974.18	1.73	1.63	0.21	8.16	6.01	-5.63	0.83
31.5	1973.57	1.86	1.75	0.24	7.87	5.54	-5.85	0.60
32.5	1972.96	1.86	1.74	0.23	8.17	6.44	-5.50	0.80
33.5	1972.37	0.78	0.74	0.10	7.60	5.74	-5.63	0.78
34.5	1971.77	1.98	1.88	0.24	8.29	5.28	-5.81	0.73
35.5	1971.17	2.10	2.00	0.26	7.96	4.96	-5.64	0.74
36.5	1970.56	1.94	1.84	0.23	8.50	4.90	-5.50	0.78
37.5	1969.50	2.00	1.91	0.19	10.42	4.21	-5.41	0.67
38.5	1969.37	1.77	1.67	0.18	9.97	5.28	-5.37	0.68
39.5	1968.80	1.68	1.61	0.17	9.83	4.23	-5.50	0.71
40.5	1968.25	1.67	1.56	0.17	9.97	6.13	-5.50	0.67
41.5	1967.68	1.66	1.56	0.17	10.02	5.68	-5.41	0.59
42.5	1967.08	1.68	1.60	0.17	9.90	4.39	-5.52	0.63
43.5	1966.46	1.62	1.52	0.16	10.11	5.82	-5.45	0.69
44.5	1965.85	1.65	1.57	0.17	9.96	5.21	-5.41	0.65
45.5	1965.28	1.79	1.70	0.19	9.58	4.69	-5.39	0.59
46.5	1964.71	1.77	1.68	0.18	9.73	5.35	-5.45	0.51
47.5	1964.14	1.78	1.72	0.19	9.44	3.00	-5.21	0.58
48.5	1963.58	1.82	1.73	0.19	9.40	4.97	-5.30	0.55
49.5	1963.04	1.77	1.69	0.18	9.72	4.59	-5.58	0.51
50.5	1962.49	1.82	1.72	0.23	7.87	5.53	-5.44	0.54
51.5	1961.93	1.59	1.51	0.16	9.85	5.26	-5.46	0.55
52.5	1961.36	1.82	1.74	0.23	7.84	4.40	-5.54	0.50
53.5	1960.74	1.68	1.58	0.21	8.10	5.71	-5.74	0.55
54.5	1960.12	1.74	1.66	0.21	8.31	4.99	-5.41	0.44
55.5	1959.53	1.67	1.57	0.20	8.16	5.93	-5.48	0.49
56.5	1958.97	1.56	1.47	0.21	7.60	5.93	-5.63	0.50
57.5	1958.39	1.57	1.50	0.21	7.58	4.56	-5.47	0.46
58.5	1957.79	1.60	1.51	0.21	7.80	5.62	-5.39	0.52
59.5	1957.20	1.59	1.50	0.21	7.68	5.54	-5.50	0.52

Appendix 5: Geochemistry Data of the 1991 Benthos Core

Depth (cm)	Age (Cal. Year)	TOC (%)	TOC whole-sediment based (%)	TN (%)	Weight C:N	$CaCO_3$ (%)
2.68	1960.54	1.90	1.85	0.23	8.29	2.68
4.77	1958.77	1.73	1.65	0.21	8.14	4.77
3.81	1957.02	1.71	1.65	0.22	7.88	3.81
4.89	1955.23	1.61	1.53	0.20	7.91	4.89
6.80	1953.41	1.45	1.35	0.18	8.21	6.80
9.35	1951.61	1.34	1.22	0.17	8.09	9.35
7.13	1949.88					7.13
6.48	1948.24	1.53	1.43	0.18	8.67	6.48
9.83	1946.55	1.45	1.31	0.18	8.29	9.83
10.31	1944.98	1.33	1.20	0.16	8.33	10.31
10.69	1943.49	1.36	1.22	0.15	8.83	10.69
10.18	1942.06	1.38	1.24	0.16	8.67	10.18
7.99	1940.63	1.46	1.34	0.18	8.08	7.99
8.52	1939.24	1.45	1.32	0.18	8.22	8.52
7.81	1937.74	1.47	1.36	0.17	8.59	7.81
8.26	1936.33	1.45	1.33	0.18	8.22	8.26
8.54	1934.99	1.34	1.22	0.16	8.57	8.54
10.71	1933.42	1.19	1.06	0.14	8.34	10.71
9.10	1931.62	1.28	1.16	0.15	8.69	9.10
7.99	1929.73	1.41	1.30	0.16	8.60	7.99
7.69	1928.01	1.48	1.37	0.18	8.22	7.69
7.25	1926.54	1.45	1.35	0.17	8.71	7.25
10.05	1924.96	1.25	1.12	0.15	8.40	10.05
9.90	1923.28	1.26	1.13	0.15	8.28	9.90
8.51	1921.76	1.27	1.16	0.15	8.23	8.51
7.59	1920.39	1.34	1.23	0.16	8.28	7.59
7.84	1918.97	1.30	1.19	0.16	7.97	7.84
8.48	1917.35	1.30	1.19	0.16	8.03	8.48
7.83	1915.70	1.25	1.15	0.15	8.30	7.83
7.98	1913.98	1.16	1.07	0.15	7.68	7.98
7.68	1912.14	1.21	1.12	0.15	8.09	7.68

6.31	1910.33	1.22	1.14	0.16	7.73	6.31
4.42	1908.69	1.33	1.27	0.17	7.64	4.42
5.44	1907.09	1.30	1.23	0.17	7.82	5.44
3.78	1905.49	1.28	1.23	0.17	7.61	3.78
3.33	1903.76	1.29	1.25	0.18	7.26	3.33
7.54	1901.88	1.17	1.08	0.16	7.47	7.54
7.13	1900.10	1.19	1.10	0.16	7.43	7.13
8.43	1889.20	1.12	1.03	0.16	7.18	8.43
7.23	1886.20	1.10	1.02	0.16	6.96	7.23

Appendix 6: Geochemistry Data for the 1988 Core

Depth (cm)	Year (Cal. Year)	TOC (%)	TON (%)	Weight C:N	$\delta^{15}N$ (‰)	Corrected $\delta^{13}C$ org (‰)
0.50	1988.60	1.55	0.19	8.16	7.66	-26.81
1.50					8.50	
1.50					9.51	
1.50					9.85	
1.50					8.59	
1.50					9.31	
1.50	1988.30	1.18	0.16	7.40	9.15	-24.82
2.50	1987.90	1.21	0.17	7.12		-25.13
3.50	1987.50	1.27	0.17	7.47	1.85	-24.74
4.50	1987.00	1.01	0.14	7.21	8.64	
5.50	1986.50	1.23	0.16	7.69	8.40	-24.47
6.50						
6.50	1986.00	1.15	0.15	7.67	7.88	-24.68
7.50	1985.40	0.96	0.10	9.60	10.06	-21.50
8.50	1984.80	1.23	0.16	7.69	9.53	
9.50						
9.50	1984.20	1.03	0.13	7.92	8.02	-24.13
10.50	1983.60	1.31	0.18	7.28	9.16	-24.64
11.50	1983.00	1.22	0.15	8.13	7.90	
12.50	1982.30	1.23	0.17	7.24	8.96	
13.50	1981.70	1.23	0.15	8.20	8.23	-23.89
14.50	1981.10	1.51	0.20	7.55	11.80	
15.50	1980.60	1.31	0.17	7.71	7.24	-24.92
16.50	1980.00	1.36	0.18	7.56	8.64	-24.43
17.50	1979.50	1.20	0.16	7.50	8.44	-24.24
18.50	1979.00	1.46	0.20	7.30		
19.50	1978.40	1.28	0.17	7.53	11.01	-23.87
20.50	1977.70	1.35	0.18	7.50	9.09	-23.79
21.50	1977.10					
22.50	1976.50	1.12	0.15	7.47	8.61	
23.50	1975.80					

24.50	1975.20	1.08	0.15	7.20	11.50	-24.24
25.50	1974.50					
26.50	1973.80	1.11	0.16	6.94	11.41	-24.17
27.50	1973.30					
28.50	1972.80	0.98	0.13	7.54		-23.79
29.50	1972.20					
30.50	1971.60				6.27	
31.50	1970.80	1.19	0.15	7.93	16.70	-23.93
32.50	1970.20				7.52	
33.50	1969.60					
34.50	1968.90				6.61	-23.87
35.50	1968.30					
36.50	1967.80					
37.50	1967.30					
38.50	1966.60				8.38	-23.81
39.50	1966.00					
40.50	1965.40				8.44	-23.83
41.50	1964.80					
42.50	1964.20				5.55	-24.35
43.50	1963.70					
44.50	1963.10				8.64	-24.57
45.50	1962.50					
46.50	1961.80				8.88	-24.59
47.50	1961.10					
48.50	1960.60				7.81	-24.81
49.50	1960.10					
50.50	1959.60				7.67	
51.50	1958.90					
52.50	1958.40				4.93	-24.54
53.50	1957.70					
54.50	1957.10				14.20	-24.36
55.50	1956.50					
56.50	1955.90					
57.50	1955.20					
58.50	1954.60				3.25	-24.30
59.50	1953.90					
60.50	1953.30	0.97	0.13	7.46		
61.50	1952.60					
62.50	1951.90					

63.50	1951.40					
64.50	1950.80					
65.50	1950.20	0.84	0.11	7.64		-25.05
66.50	1949.50					
67.50	1948.80					
68.50	1948.20					
69.50	1947.50					
70.50	1946.80	0.87	0.12	7.25	7.91	-24.89
71.50	1946.20					
72.50	1945.60					
73.50	1944.80					
74.50	1944.00					
75.50	1943.20	0.80	0.11	7.27	7.24	-25.03
76.50	1942.50					
77.50	1941.90					
78.50	1941.10					
79.50	1940.50					
80.50	1939.90	0.77	0.10	7.70	7.42	
81.50	1939.20					
82.50	1938.50					
83.50	1937.90					
84.50	1937.30					
85.50	1936.70	0.80	0.10	8.00	5.13	-31.89
86.50	1936.10					
87.50	1935.50					
88.50	1934.90					
89.50	1934.20					
90.50	1933.50	0.76	0.11	6.91	6.91	
91.50	1932.80					
92.50	1932.10					
93.50	1931.50					
94.50	1930.80					
95.50	1930.20	0.82	0.11	7.45	7.17	
96.50	1929.60					
97.50	1928.90					
98.50	1928.30					
99.50	1927.60					
100.50	1926.90	0.77	0.11	7.00	6.09	
101.50	1926.30					

102.50	1925.60					
103.50	1925.00					
104.50	1924.40					
105.50	1923.80				6.56	-25.37
106.50	1923.20					
107.50	1922.60					
108.50	1922.00					
109.50	1921.30					
110.50	1920.60	0.66	0.10	6.60	4.09	-25.69
111.50	1920.00					
112.50	1919.40					
113.50	1918.70					
114.50	1918.00					
115.50	1917.50				4.15	-25.60
116.50	1916.90					
117.50	1916.20					
118.50	1915.50					
119.50	1914.80					
120.50	1914.10	0.63	0.09	7.00	2.40	-25.82
121.50	1913.50					
122.50	1912.80					
123.50	1912.10					
124.50	1911.40					
125.50	1910.80					
126.50	1910.10					
127.50	1909.40					
128.50	1908.70					
129.50	1908.00					
130.50	1907.30	0.57	0.09	6.33	4.46	-25.84
131.50	1906.50					
132.50	1905.80					
133.50	1905.10					
134.50	1904.30					
135.50	1903.60				3.75	
136.50	1903.00					
137.50	1902.40					
138.50	1901.70					
139.50	1901.00					
140.50					4.06	

140.50	1900.30	0.60	0.09	6.67	3.68	-26.06
141.50	1899.60	0.55	0.08	6.88	4.78	-25.66
141.50					2.76	

Appendix 7: Experimental Methods for Biomarker Extraction

1. All glassware will be heated at 550ºC for 12 hrs before they are used. A batch of samples includes 6 samples, 1 duplicate sample and 1 blank. Weigh samples between 2-3 g and dump them into flask. Add 50mL DCM: Methanol (V:V=2:1) in each flask. Use aluminum foil to seal the flask before ultrasonic extraction for 1 hr.
2. The samples are filtered into a pear-shaped bulbs. Rinse the samples with DCM twice, then rinse the filter with DCM twice.
3. The samples are rotary evaporated in pear-shaped bulbs to remove solvent until the volume reaches at about 1.5 ML.
4. The samples are transferred into a 12ML centrifuge tubes with DCM.
5. Blow the solvent with N_2 to about 0.5ML and add 3 ML Hexane. Blow the solvent again to 0.5ML and add 3ML Hexane.
6. Blow the solvent to 0.5ML again before adding 3 ML KOH with Methanol (6%, Wt/Wt) in samples in the centrifuge tubes. Boil the samples for 5 minutes into a 1000ML beaker with water into it on a hot plate.
7. After the samples cool down, use Hexane (3ML) to extract three times. Put the upper layer into a glass vial, which is saved as neutral fraction.
8. Use 3M HCl to acidify the lower layer to PH=2, then use Hexane (3ML) to extract upper layer 3 times into a glass vial, which is saved as acid fraction.
9. Standard, 50 ul of 1.2 mg 5α-cholestane/ 25 ML DCM, 50 ul of 2.6mg Tridecyl Alcohol/ 25 ML DCM, is added into neutral fraction. Acid standard, 50ul of 1.1mg Heptadecanoic acid/ 25 ML Hexane, is added into acid fraction.
10. For neutral fraction, add 50ul BSTFA and heat it at 50ºC for 30 minutes. For acid fraction, add 2mL BF_3-Methanol and heat at 100ºC for 30 minutes.

11. After the samples cool down, blow dry the samples with N_2 and transfer them into small vials before Gas chromatography/ Mass spectrometer analysis.