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Development of Isotopic Proxies for Paleoenvironmental Interpretation: A Carbon Perspective (DIPPI-C)

Key Points:

- Geochemical proxies in five sediment cores from Lake Erie were compared
- Geochemical record was sensitive to coring location and corer type
- Multiple cores are necessary for reliable paleolimnological reconstruction

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Sensitivity of sediment geochemical proxies to coring location and corer type in a large lake: Implications for paleolimnological reconstruction

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Abstract We compared a suite of geochemical proxies in sediment cores collected in 1982, 1988, 1991, and 2003 from sites near the depocenter of Lake Erie to evaluate the reliability of paleoenvironmental reconstructions derived from lacustrine sediments. Our proxies included the concentrations and carbon isotopic compositions of organic and inorganic carbon (TOC, CaCO₃, $\delta^{13}\text{C}_{\text{org}}$, and $\delta^{13}\text{C}_{\text{CaCO}_3}$), augmented by organic C to total N ratios ($\text{C}_{\text{org}}:\text{N}_{\text{tot}}$), $\delta^{15}\text{N}$, and carbonate $\delta^{18}\text{O}$ values ($\delta^{18}\text{O}_{\text{CaCO}_3}$). The three coring sites were clustered within 12 km; two types of corers—a Box corer and a Benthos gravity corer—were used for the 1991 sampling campaign. The variance of most proxies was accounted for not only by temporal environmental changes but also by coring locations and corer type, indicating that sediment spatial heterogeneity and differences in sediment recovery due to the use of different corers also played a part in determining the geochemical compositions of these cores. The TOC, $\delta^{13}\text{C}_{\text{org}}$, and $\delta^{13}\text{C}_{\text{CaCO}_3}$ values showed decadal temporal patterns that were consistent between the multiple sampling campaigns. In contrast, the $\delta^{15}\text{N}$, $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$, CaCO₃, and $\delta^{18}\text{O}_{\text{CaCO}_3}$ exhibited across-core differences in their temporal variations, making it difficult to extract consistent environment information from different cores. Our findings suggest that in addition to temporal environmental changes, high-resolution paleolimnological reconstruction is sensitive to many factors that could include spatial sediment heterogeneity, discontinuous sedimentation processes, bioturbation, sediment dating uncertainty, and artifacts associated with analytical and coring procedures. Therefore, multiple-core sampling and analysis are important in reliably reconstructing environmental changes, particularly for large, heterogeneous lacustrine basins.

1. Introduction

Various kinds of information for reconstructing the environmental histories of lakes reside in the amounts and elemental and isotopic compositions of their sedimentary materials. The concentration of total organic carbon (TOC) is a proxy for organic matter delivery and burial, and its variation in sediment records has been widely employed to infer paleoproductivity changes in lakes [cf., Talbot *et al.*, 2006; Wu *et al.*, 2008; Balascio and Bradley, 2012]. Organic $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{org}}$) values have also been widely applied as another paleoproductivity proxy because phytoplankton preferentially remove ¹²C-enriched inorganic C dissolved in water and leave the remaining pool more enriched in ¹³C [e.g., Schelske and Hodell, 1991, 1995; Hollander *et al.*, 1992; Teranes and Bernasconi, 2005; Lu *et al.*, 2010a]. Proportions of algal-derived and land-derived organic matter in lake sediments can be roughly discriminated by the atomic ratios of organic carbon to total nitrogen ($\text{C}_{\text{org}}:\text{N}_{\text{tot}}$). The standard interpretation is that algae generally have atomic $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$ values smaller than ~10, whereas land plants commonly have ratios larger than ~20 [e.g., Meyers and Ishiwatari, 1993]. As such elevated $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$ values identify greater inputs of land-plant organic matter to lakes [cf., Meyers, 1994; Dean, 1999], but caution must be exercised because the value delineating aquatic versus terrestrial sources is not universally applicable (e.g., broccoli, a terrestrial plant, has $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$ range of ~6–13) [Brodie *et al.*, 2011b]. Additionally, $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$ values may be sensitive to postburial diagenesis and analytic procedure variation [e.g., Meyers and Ishiwatari, 1993; Brodie *et al.*, 2011a, 2011b].

In paleolimnological research, using a single lacustrine sediment core to reconstruct basin-scale environmental changes is not uncommon [e.g., Fedotov *et al.*, 2008; Finsinger *et al.*, 2008; Lu and Meyers, 2009; Lu

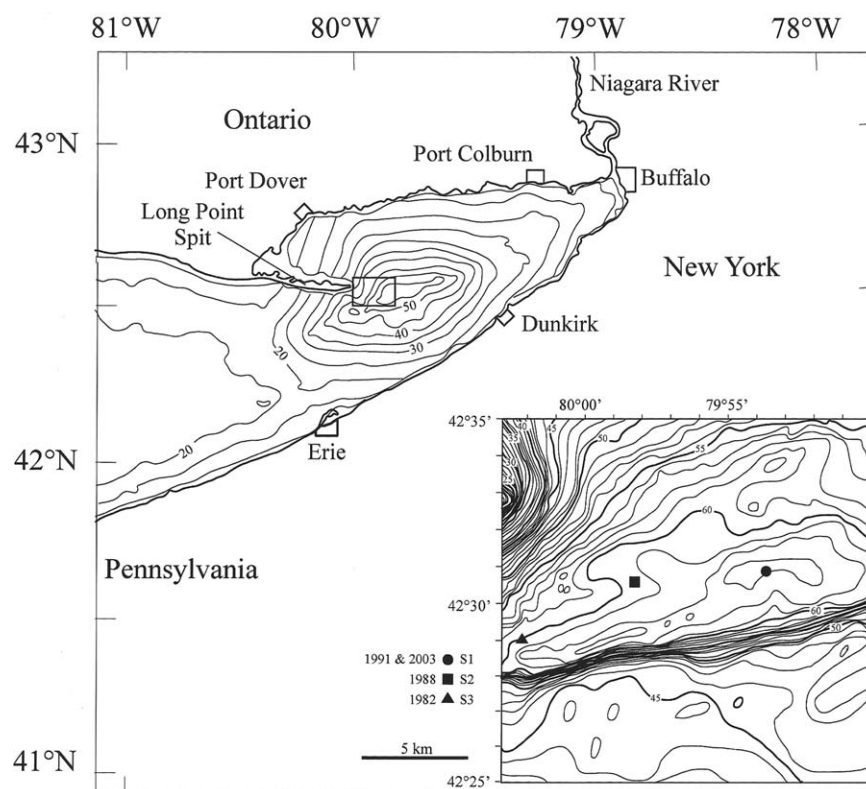


Figure 1. Lake Erie map showing our three coring sites S1, S2, and S3. The unit of bathymetric contours is meter.

et al., 2010a). This practice assumes that sediment spatial variability within the depocenter of a lake does not markedly affect geochemical proxies and thus does not influence the derived climatic and environmental interpretations; in other words, it is representative of the whole system. This assumption has been found to be consistent with independent evidence of environmental changes, such as the documented history of cultural eutrophication in Lake Erie [Schelske and Hodell, 1995; Lu *et al.*, 2010a] or global periods of deglaciation [Fedotov *et al.*, 2008]. However, as improved temporal resolution of paleolimnological reconstructions has become of greater interest in paleoclimatic studies, the single-core approach merits further evaluation. Spatial variability of sediments does not seem to be significant enough to affect environmental patterns at centennial or decadal scales [e.g., Chu *et al.*, 2006; Hambley and Lamoureux, 2006; Lu *et al.*, 2010a, 2010b], yet it may generate significant uncertainties for subdecadal, annual, and seasonal records of environmental changes.

Two studies using cores from varved Swedish lakes have evaluated the importance of spatial variability of sediments to paleolimnological reconstructions. Petterson *et al.* [1993] analyzed replicate cores from Lake Kassjön, which has a maximum depth of 12.2 m and an area of 0.23 km². These researchers, based on varve thickness and image analysis, found that the spatial variability of sediment accumulation is low and unlikely to affect records at annual or even seasonal resolutions. However, sediment variability is not necessarily reflecting the variability of geochemical proxies. In Lake Nylandssjön, a lake with maximum depth of ~17.5 m and surface area of 0.28 km², Gälman *et al.* [2008, 2009] analyzed a collection of ten freeze sediment cores sampled from 1979 to 2007. Combining water depth measurements and GPS coordinates, the cores were positioned in a relatively small area (~50 × 50 m) of the deep basin (C. Bigler, personal communication, 2013). Although these researchers reported that the geochemical proxies (TOC, TN, C_{org}:N_{totr}, δ¹³C_{org}, and δ¹⁵N) were affected by postdepositional diagenesis to varying extents, these proxies demonstrated largely consistent annual variations.

As the Swedish studies were done in small and shallow lakes with varved sediments, studies in large lake settings, where larger spatial sediment variability is expected, are necessary to complete our understanding

Table 1. Sampling Location, Coring Method, Sedimentation Rate, and the Length of the Study Cores^a

| NOAA Core Archive ID | Core Name | Water Depth (m) | Latitude and Longitude | Coring Location | Coring Method | LSR ^b (cm/yr) | MAR ^c (mg/cm ² /yr) | Core Length (cm) | Depositional Years | Navigation Techniques |
|----------------------|------------|-----------------|------------------------|-----------------|---------------|--------------------------|---|------------------|--------------------|---------------------------|
| LE-82-MS-BEN | 82-core | n.d. | 42°29.1'N, 80°2.3'W | S3 | Benthos | 1.26 | 682 | 24 | 1964.4–1982.3 | Long range navigation |
| LE88-EBRSII-BEN-1 | 88-core | 59 | 42°30.9'N, 79°58.6'W | S2 | Benthos | 1.71 | 1146 | 142 | 1899.6–1988.6 | Long range navigation |
| LE91-EBRS-BEN-1 | 91ben-core | 60 | 42°31.0'N, 79°53.6'W | S1 | Benthos | 0.61 | 393 | 64 | 1896.8–1960.6 | Long range navigation |
| LE91-EBRS-Box | 91box-core | 60 | 42°31.0'N, 79°53.6'W | S1 | Box | 1.71 | 663 | 61 | 1956.8–1991.4 | Long range navigation |
| LE03-EBRS-BEN-3 | 03-core | 60 | 42°31.0'N, 79°53.6'W | S1 | Benthos | 1.11 | 447 | 107 | 1909.2–2003.6 | Global positioning system |

^an.d.: not determined.^bLSR: linear sedimentation rate.^cMAR: net mass accumulation rate based on the STA model.

of how sediment variability may affect geochemical distributions in sediments as a function of lake depositional processes, which in turn can impact paleolimnological interpretations. In the present study, we compared a suite of geochemical proxies in the five sediment cores collected from Lake Erie, one of the Laurentian Great Lakes. The proxies included TOC, CaCO₃, $\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$, stable carbon and oxygen isotope composition of calcium carbonate ($\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{18}\text{O}_{\text{CaCO}_3}$), and $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$. Sediment cores were collected with a Benthos gravity corer in 1982, 1988, 1991, and 2003 at sites within 12 km of each other in the depositional center of Lake Erie. A second core was collected by a Box corer at the 1991 site. Our objective was to assess the reliability of high-resolution paleoenvironmental records derived from a single sediment core in this large lake. An important assumption is that though our sediment cores were not from exactly the same site or by the same corer, their proxies should provide consistent record of lacustrine environmental changes within the measured precision of the geochemical proxies and their interpretative thresholds (i.e., no added uncertainty). This assumption does not deny that proximate coring sites may be influenced by different local processes, but it is based on the general paleolimnological principle that environmental and climatic changes that occurred on broader scales, such as the whole lake basin or watershed, should not be masked by depositional processes occurring at much smaller spatial scales or by variability associated with coring. This assumption remains untested in high and ultrahigh resolution records.

2. Materials and Methods

2.1. Sampling Site

Lake Erie, although the smallest of the five Laurentian Great Lakes, is a large lake with a surface area of 25,700 km², a volume of 484 km³, and a maximum depth of 64 m [Quinn, 1992]. The lake receives the outflow of lakes Superior, Huron, and Michigan through Detroit River and drains into Lake Ontario through the Niagara River. Because Superior, Huron, and Michigan are much larger than Erie, this flow system creates a relatively short hydraulic residence time of 2.7 years in the lake [Quinn, 1992].

Lake Erie is bathymetrically divided into three basins. The shallow western basin contains only 5% of the total lake volume and, among the three basins, is closest to urban areas and thereby most strongly influenced by anthropogenic activities [Berner and Berner, 1996]. The central basin constitutes 63% of the total lake volume. Our study area is in the eastern basin, which is deeper than the other two basins and makes up 32% of the total lake volume [Hartman, 1973] (Figure 1). This basin is relatively less affected by anthropogenic activities because it is farthest from large cities and has a sufficiently large volume to render it relatively tolerant of pollutants [Berner and Berner, 1996].

The ecosystem of Lake Erie has experienced dramatic changes due to expansion of European settlement of its surroundings starting in the early nineteenth century. From ~1830 to ~1972, cultural eutrophication progressively increased and caused a series of environmental changes, including dramatic increases in aquatic productivity, depletions in dissolved oxygen (DO) in the central basin hypolimnion, and alterations in the compositions of biological communities [Leach, 1999; MacIsaac, 1999]. In 1972, regulations to limit anthropogenic P inputs were implemented jointly by the U.S. and Canadian governments, and thereafter aquatic

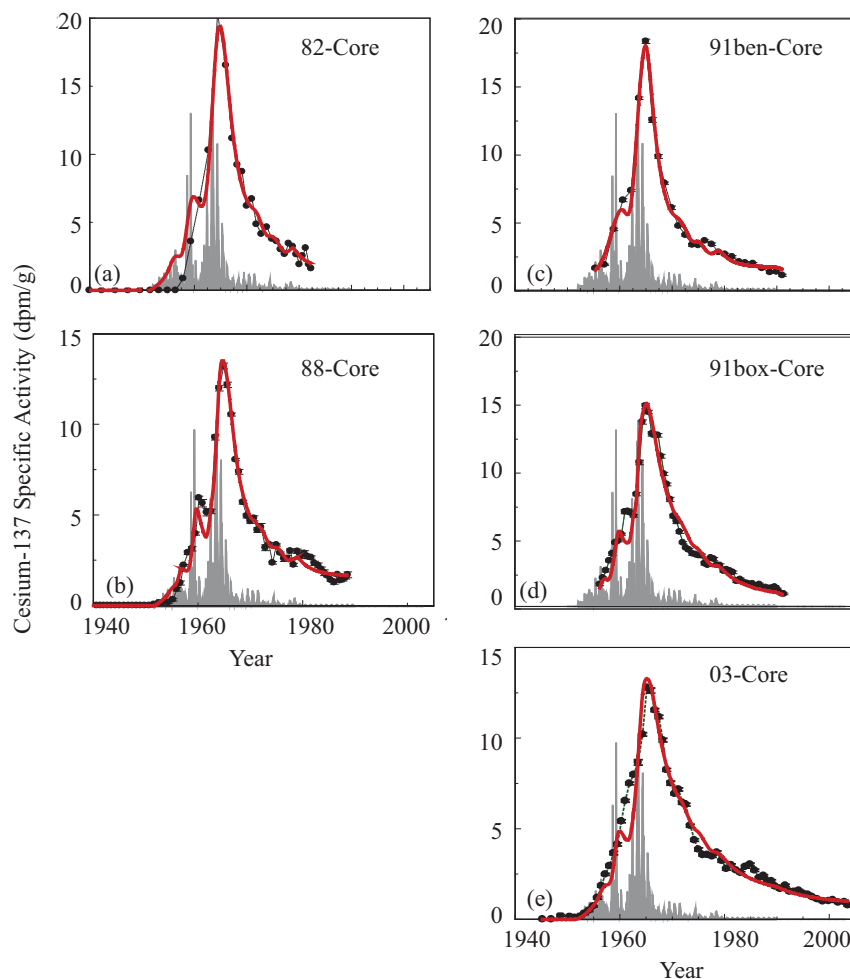


Figure 2. Cesium-137 profiles of the five sediment cores in the present study. The black, closed circles are the specific activity of ^{137}Cs in the sediments; the gray bars indicate monthly fall of our record for the Great Lakes region, and the red solid lines represent the smoothing results from the System Time Average (STA) model [Robbins *et al.*, 2000].

productivity began to decline, although the DO depletion in the central basin has not shown improvement [Hartman, 1973; Munawar *et al.*, 1999; Schloesser *et al.*, 2005]. In addition to the impacts of cultural eutrophication, the Lake Erie ecosystem has been altered by a succession of invasive species. In particular, Zebra mussels introduced from Russia (*Dreissena polymorpha*) displaced the native Chironomidae larvae as the dominant benthic fauna in the late 1980s and have subsequently been displaced by Quagga mussels (*Dreissena rostriformis*) introduced from the Ukraine [Mills *et al.*, 1996].

2.2. Core Sampling

The four coring sites are located near the deepest point of the eastern basin (Figure 1), which is the depositor for sediments of the entire lake. Four Benthos gravity cores were collected with respective lengths of 24 cm in 1982 (82-core), 142 cm in 1988 (88-core), 64 cm in 1991 (91ben-core; note only 40 cm of this core was analyzed for geochemical proxies) and 107 cm in 2003 (03-core) (Table 1). One box-core was also collected in 1991 (91box-core) with a length of 61 cm. The 91ben-core, 91box-core (collectively referred to as “91-cores” in some parts of the following text) and 03-core were collected at the same latitude and longitude, although different positioning system was used (Table 1). The 82-core and 88-core were respectively ~12 km and ~7 km southwest of the 91-cores and 03-core (Figure 1). All cores were cut into 1–2 cm intervals, packed into separate bags in the field, and transported to the NOAA Great Lakes Environmental Research Laboratory (Ann Arbor, Michigan, USA), where they were stored at -20°C until analysis.

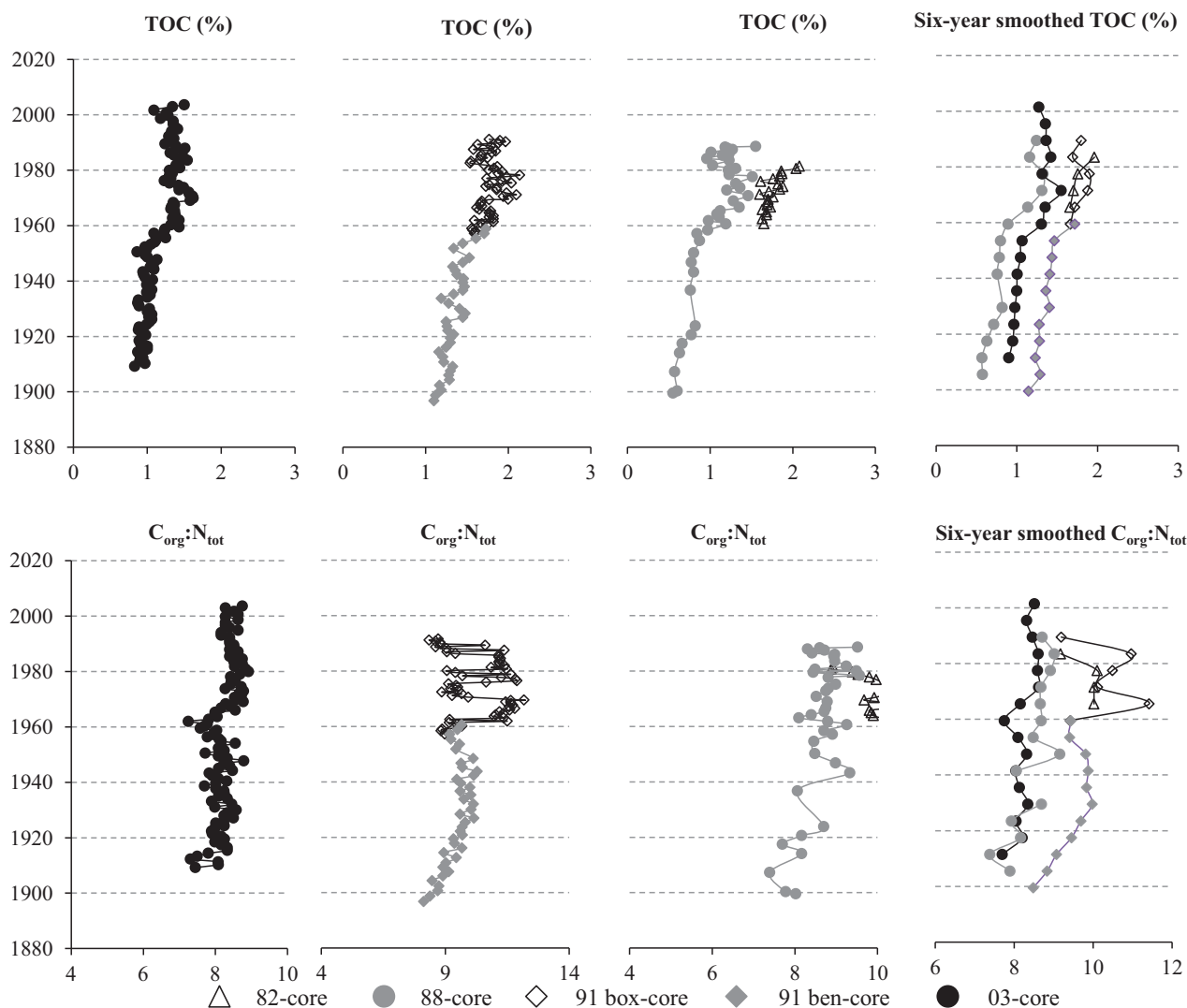


Figure 3. The temporal profiles of total organic carbon concentration (TOC) and $C_{org}:N_{tot}$ ratios of the sediment cores from Lake Erie.

2.3. Methods

Age determination of each core follows the 1963 spike ^{137}Cs -dating method and the system time averaging (STA) model described in *Robbins et al.* [2000] and *Schloesser et al.* [2014]. Cesium-137-specific activity of each core (Figure 2) was measured on a carefully calibrated gamma counting system with a counting error of less than 3%. In the Great Lakes region, monthly deposition of ^{137}Cs fallout was well documented for ~30 years [*Robbins, 1985; Schloesser et al., 2014*], which showed a spike in 1963 and dropped off rapidly beyond 1970. The STA model assumes that ^{137}Cs in sediments was delivered from a well-mixed reservoir primarily loaded by atmospheric fall out with little contribution from watershed tributaries, yielding sediment mass accumulation rates comparable to that from the ^{210}Pb profiles in our sediment cores (i.e., 82-core: 0.682 g/sq cm/yr from STA model versus 0.659 ± 0.032 g/sq cm/yr from ^{210}Pb exponential model; 91ben-core: 0.393 g/sq cm/yr from STA model versus 0.449 ± 0.021 g/sq cm/yr from ^{210}Pb exponential model; 03-core: 0.447 g/sq cm/yr from STA model versus 0.555 ± 0.046 g/sq cm/yr from ^{210}Pb exponential model; the ^{210}Pb data were not obtained for the 88-core and 91box-core). The uncertainty of the age assignment from ^{137}Cs was determined from the mean residence time of particles in the sediment mixed layer, i.e., the full width at half maximum of ^{137}Cs profiles, which was 5.39, 5.13, 4.88, 6.91, and 8.64 years for

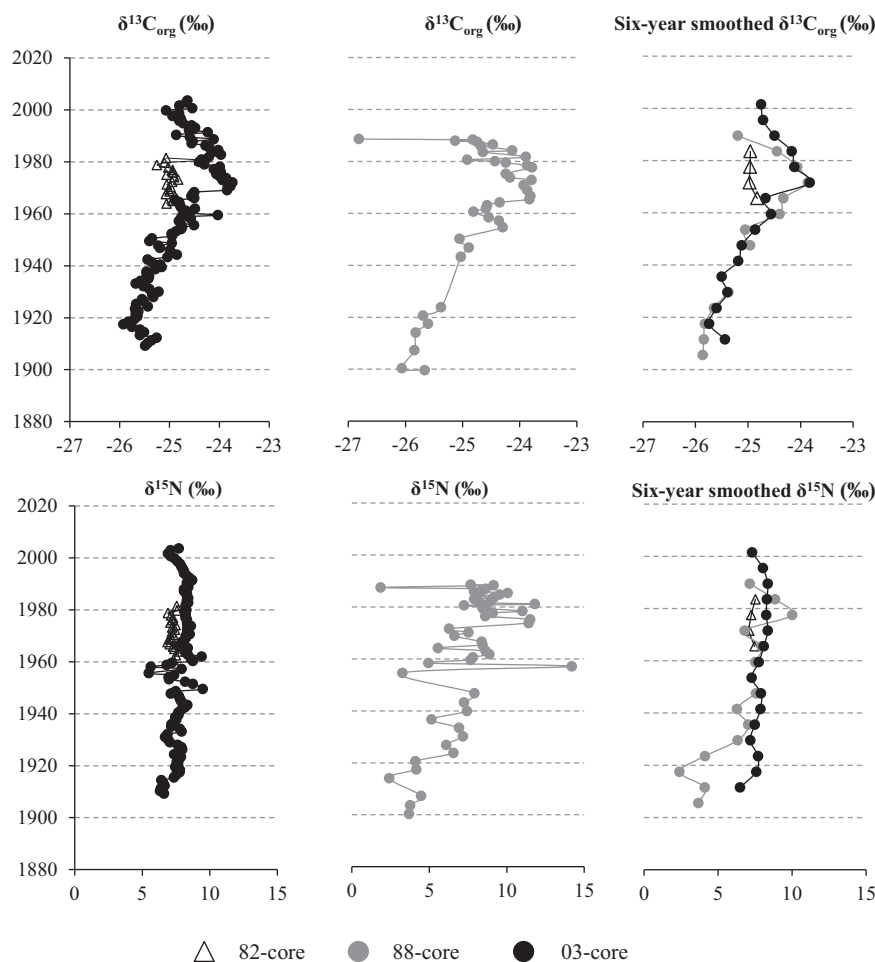


Figure 4. The temporal profiles of stable carbon isotope of organic carbon ($\delta^{13}C_{org}$) and stable nitrogen isotope of total nitrogen ($\delta^{15}N$) of the sediment cores from Lake Erie.

82-core, 88-core, 91box-core, 91ben-core, and 03-core, respectively, yielding a mean uncertainty of 6.19 ± 1.41 years.

Sediment samples were freeze dried and ground to fine powders. $CaCO_3$ concentration was measured by the carbonate bomb technique [Müller and Gastner, 1971; Dunn, 1979], where a specified mass of freeze-dried sediments reacted with 3M hydrochloric acid and the resulting CO_2 was proportional to the $CaCO_3$ content in the sediment. Pure $CaCO_3$ was used to establish daily, 5 point calibration curve of mass of $CaCO_3$ versus CO_2 generated from the reaction. Duplicate samples were run daily, and the relative standard deviation of $CaCO_3$ concentration for duplicate samples was within 9%. The acid treatment used in $CaCO_3$ measurement yielded carbonate-free samples, which were thoroughly rinsed by deionized water, dried, and then submitted to the Environmental Isotope Laboratory at the University of Arizona (USA) for the analyses of TOC (wt %), total nitrogen (TN, wt %), $\delta^{13}C_{org}$ (‰), and $\delta^{15}N$ (‰), which were done using the elemental analysis-isotope ratio mass spectrometry (EA-IRMS) flow through system. Precision is $\pm 0.1\text{‰}$ for $\delta^{13}C_{org}$ and $\pm 0.2\text{‰}$ for $\delta^{15}N$ relative to certified standards.

Both $\delta^{13}C_{CaCO_3}$ and $\delta^{18}O_{CaCO_3}$ were determined using a Finnigan Element high resolution-mass spectrometer at the Keck Elemental Geochemistry Laboratory at the University of Michigan (USA). Precision is $\pm 0.08\text{‰}$ for $\delta^{13}C_{CaCO_3}$ and $\pm 0.1\text{‰}$ for $\delta^{18}O_{CaCO_3}$ relative to certified standards. Suess effect corrections were applied to the $\delta^{13}C_{org}$ and $\delta^{13}C_{CaCO_3}$ values to compensate for the atmospheric carbon isotopic shifts caused by fossil fuel combustion [Schelske and Hodell, 1995; Verburg, 2007]. Briefly, 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.,

Table 2. Spearman Correlation of the Paleolimnological Proxies of the Sediment Intervals of Corresponding Depositional Years at 1 and 6 Year Resolution Between the 03-Core and the Other Cores^a

| Proxy | Resolution | 03-Core Versus 91Ben-Core | 03-Core Versus 91Box-Core | 03-Core Versus 88-Core | 03-Core Versus 82-Core |
|------------------------|------------|---------------------------------|---------------------------------|---------------------------------|-------------------------------|
| TOC | 1 year | $r = 0.75, P < 0.001^*, n = 32$ | $r = -0.34, P = 0.1, n = 24$ | $r = 0.70, P < 0.001^*, n = 28$ | $r = 0.05, P = 0.84, n = 21$ |
| | 6 years | $r = 0.97, P < 0.001^*, n = 9$ | $r = 0.26, P = 0.62, n = 6$ | $r = 0.91, P < 0.001^*, n = 13$ | $r = 0, P = 1, n = 4$ |
| CaCO ₃ | 1 year | $r = 0.15, P = 0.42, n = 31$ | $r = 0.09, P = 0.62, n = 35$ | n.d. | $r = 0.05, P = 0.82, n = 20$ |
| | 6 years | $r = 0.32, P = 0.41, n = 9$ | $r = -0.14, P = 0.79, n = 6$ | n.d. | $r = 0.4, P = 0.6, n = 4$ |
| C:N _a | 1 year | $r = 0.32, P = 0.08, n = 32$ | $r = 0.14, P = 0.42, n = 36$ | $r = 0.38, P = 0.05^*, n = 27$ | $r = -0.31, P = 0.18, n = 21$ |
| | 6 years | $r = 0.7, P = 0.008^*, n = 9$ | $r = 0.14, P = 0.79, n = 6$ | $r = 0.70, P = 0.008^*, n = 13$ | $r = 0, P = 1, n = 4$ |
| $\delta^{13}C_{org}$ | 1 year | n.d. | n.d. | $r = 0.63, P < 0.001^*, n = 31$ | $r = -0.15, P = 0.53, n = 21$ |
| | 6 years | n.d. | n.d. | $r = 0.86, P < 0.001^*, n = 12$ | $r = -1, P = 4, n = 4$ |
| $\delta^{13}C_{CaCO3}$ | 1 year | n.d. | $r = 0.89, P < 0.001^*, n = 36$ | n.d. | n.d. |
| | 6 years | n.d. | $r = 1, P < 0.001^*, n = 6$ | n.d. | n.d. |
| $\delta^{15}N$ | 1 year | n.d. | n.d. | $r = 0.6, P < 0.001^*, n = 37$ | $r = 0.26, P = 0.25, n = 21$ |
| | 6 years | n.d. | n.d. | $r = 0.62, P = 0.03^*, n = 13$ | $r = -0.4, P = 0.6, n = 13$ |
| $\delta^{18}O_{CaCO3}$ | 1 year | n.d. | $r = 0.08, P = 0.66, n = 36$ | n.d. | n.d. |
| | 6 years | n.d. | $r = -0.26, P = 0.62, n = 6$ | n.d. | n.d. |

^aAsterisk indicates that correlation is significant at a level of 0.05. n.d. = not determined, because data were not collected.

1999] were used to simulate the $\delta^{13}C$ values of CO₂ in the air at a specific year as a function of calendar year as follows.

$$\delta^{13}C_{CO_2} = 5.6129E3 - 8.9296 * \text{year} + 4.7308E(-3) * [(\text{year})^2] - 8.3563E(-7) * [(\text{year})^3] \quad (1)$$

The Suess correction factor was calculated by subtracting the simulated $\delta^{13}C$ values of atmospheric CO₂ at a specific year from the average $\delta^{13}C$ value of preindustrial atmospheric CO₂ (i.e., -6.49‰). Each measured $\delta^{13}C_{org}$ and $\delta^{13}C_{CaCO3}$ of the sediment samples was adjusted by the yearly correction factor to obtain the respective $\delta^{13}C_{org}$ and $\delta^{13}C_{CaCO3}$ values used in the present study.

2.4. Statistical Analysis

For all statistical analyses, paleoenvironmental proxies including TOC, C_{org}:N_{tot}, CaCO₃, $\delta^{13}C_{org}$, $\delta^{15}N$, $\delta^{13}C_{CaCO3}$, and $\delta^{18}O_{CaCO3}$ and the year in which the 1–2 cm sediment interval was deposited based on ¹³⁷Cs (referred to as “depositional year” hereinafter) were numerical variables. “Core location,” which included the three sampling locations, i.e., S1, S2, and S3 (Figure 1), and “corer type,” which comprises two values, i.e., Box for 91box-core and Benthos for all the other cores (Table 1), were set as categorical variables. The significant level, α , was set at 0.05.

CART (Classification and Regression Trees) analysis was applied to our data set in order to understand main variables explaining variations in the geochemical proxies. CART requires no implicit assumption regarding data distribution and underlying relationships between predictor and dependent variables and hence is

Table 3. Comparison of the Paleolimnological Proxies Across the Study Cores^a

| Core | TOC (%) | CaCO ₃ (%) | C _{org} :N _{tot} | $\delta^{13}C_{org}$ (‰) | $\delta^{13}C_{CaCO3}$ (‰) | $\delta^{15}N$ (‰) | $\delta^{18}O_{CaCO3}$ (‰) |
|----------------------------|---|--|---------------------------------------|---|---|---|---|
| 82-core | 1.76 ± 0.03 n = 22 | 21.23 ± 0.27 n = 22 | 8.49 ± 0.08 n = 22 | -24.93 ± 0.04 n = 22 | n.d. | 7.31 ± 0.06 n = 22 | n.d. |
| 88-core | 1.05 ± 0.04 n = 40 | n.d. | 7.47 ± 0.09 n = 40 | -24.80 ± 0.23 n = 40 | n.d. | 7.63 ± 0.36 n = 40 | n.d. |
| 91box-core | 1.77 ± 0.03 n = 60 | 5.44 ± 0.12 n = 60 | 8.80 ± 0.13 n = 60 | n.d. | 0.79 ± 0.03 n = 60 | n.d. | -5.58 ± 0.03 n = 60 |
| 91ben-core | 1.36 ± 0.03 n = 39 | 7.51 ± 0.33 n = 40 | 8.10 ± 0.07 n = 39 | n.d. | n.d. | n.d. | n.d. |
| 03-core | 1.19 ± 0.01 n = 106 | 11.93 ± 0.21 n = 102 | 7.07 ± 0.03 n = 106 | -24.85 ± 0.06 n = 106 | 0.76 ± 0.03 n = 105 | 7.86 ± 0.09 n = 106 | -5.81 ± 0.01 n = 104 |
| CART analysis ^b | Depositional year = 1955 (R ² = 0.74) | Core location (R ² = 0.80) | Corer type (R ² = 0.64) | Depositional year = 1951 (R ² = 0.71) | Depositional year = 1978 (R ² = 0.87) | Depositional year = 1921 (R ² = 0.14) | Depositional year = 1956 (R ² = 0.59) |

^aThe values of all the proxies are expressed as mean ± SE (standard error) and n represents sample size; n.d. = not determined.

^bThe primary factor accounting for the main variance based on CART; R² = the percentage of variance being explained by all splits of the CART tree.

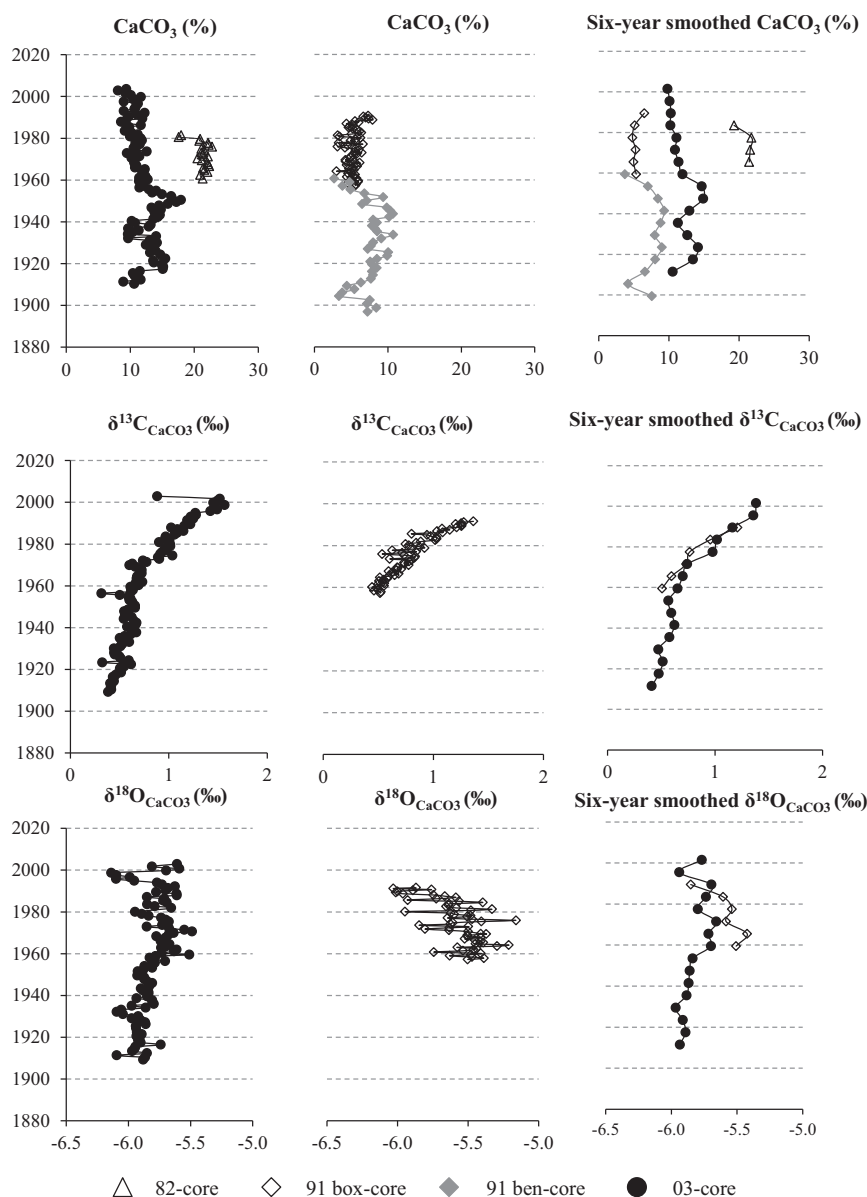


Figure 5. The temporal profiles of total calcium carbonate concentration (CaCO_3), stable C isotope of calcium carbonate ($\delta^{13}\text{C}_{\text{CaCO}_3}$), and stable O isotope of calcium carbonate ($\delta^{18}\text{O}_{\text{CaCO}_3}$) of the sediment cores from Lake Erie.

more flexible and robust than ANCOVA (analysis of covariance) in dealing with unbalanced data set with non-linear relations, high-order interactions, and missing values [De'ath and Fabricius, 2000]. CART analysis was conducted in R with the package "rpart" and produced trees explaining variations of a single response variable through repeatedly splitting the data into more homogenous groups, using the combinations of explanatory variables. Each geochemical proxy was set as a single response variable for each CART tree, and explanatory variables included "depositional year," "corer type," and "core location." CART trees were pruned to minimize the cross-validated prediction error, following the method described in Everitt and Hothorn [2010].

Nonparametric Spearman rank correlation was conducted to assess across-core correlations between the geochemical proxies from the sediment intervals of the same or similar "depositional year." Additionally, the correlation between the mean values of the sediment intervals over every 6 years was assessed to reduce bias arising from sediment dating uncertainty (6.19 ± 1.41 years). Outliers (>3 sigma) were removed before averaging the values over each 6 year interval, and missing data were disregarded.

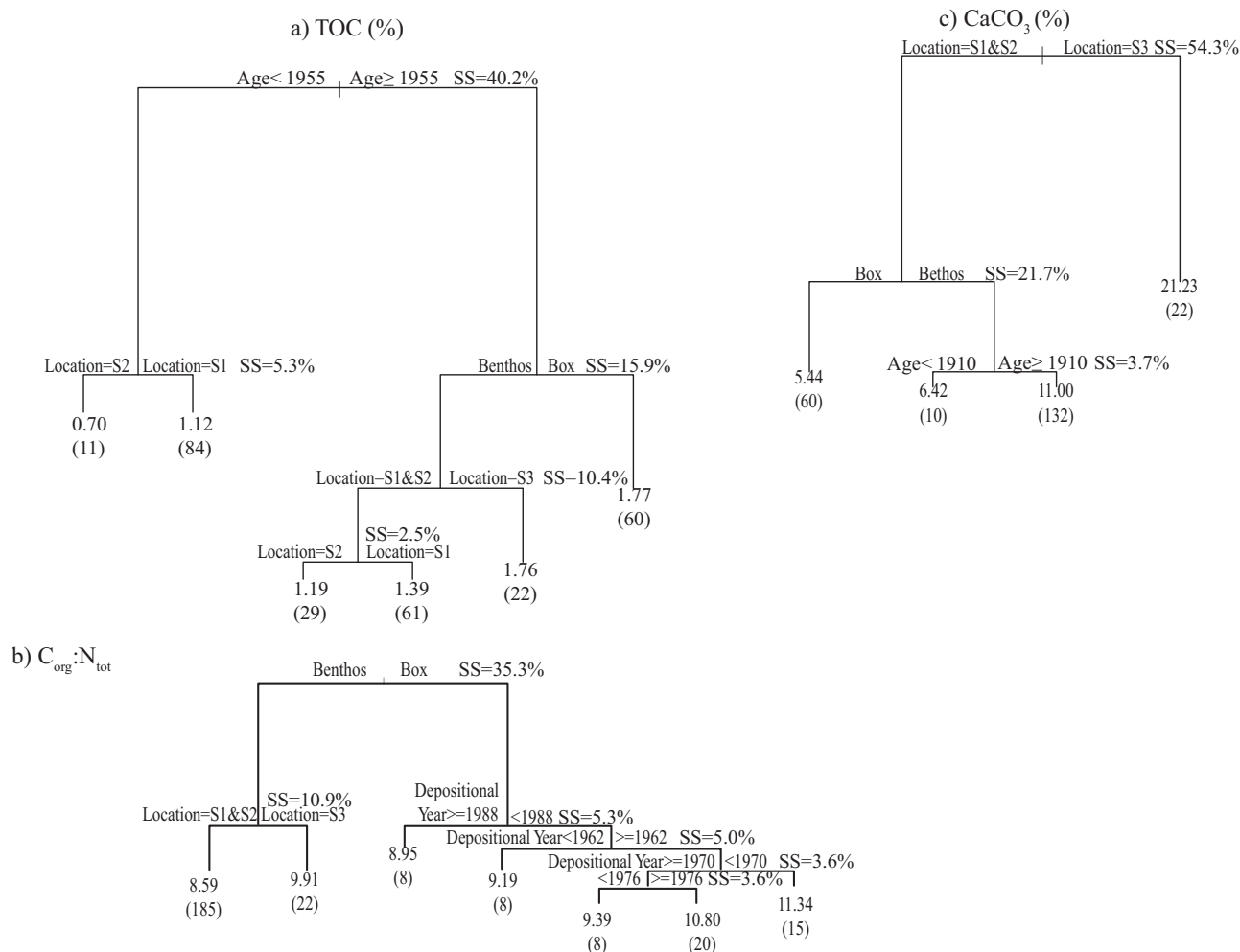


Figure 6. Regression trees explaining the variations of (a) TOC, (b) $C_{org}:N_{tot}$ ratios, and (c) $CaCO_3$ in terms of three variables: “corer type (Benthos, Box),” “core location (S1, S2, and S3),” and “depositional year (the calendar year of deposition of each sediment interval based on ^{137}Cs dating).” The vertical depth of each split is proportional to the total sum of square (ss) of the variance explained. The mean values of each split group are listed at the bottom of the plot and the sample size for each split group is shown in bracket.

3. Results and Discussion

3.1. Comparison of the Geochemical Proxies and Derived Paleolimnological Records of the Different Cores

A common means for extracting paleoenvironmental information from sediment cores in paleolimnological studies is to assess the down-core variation of geochemical proxies, assuming these variations are caused by broad-scale environmental and climatic changes unmasked by core-core variability associated with local heterogeneity in depositional processes and coring processes [Meyers, 1994; Lu et al., 2010a, 2010b]. Therefore, we compared down-core profiles of the proxies to assess whether consistent environmental changes can be reconstructed. Because paleoenvironmental interpretations of TOC concentrations, $\delta^{13}C_{org}$, $\delta^{13}C_{CaCO_3}$, $C_{org}:N_{tot}$, and $\delta^{15}N$ of the 03-core have been presented and discussed in Lu and Meyers [2009] and Lu et al. [2010a, 2010b], below we do not elaborate on how the interpretations of each proxy were derived and instead focus on comparisons between the five cores. The 03-core was used as the reference core because it has the most continuous and complete proxy record.

3.1.1. Paleoproductivity: TOC and $\delta^{13}C_{org}$

Although the year-to-year variation can be quite different, the 91ben-core and the 88-core exhibited temporal changes in TOC and $\delta^{13}C_{org}$ largely consistent with those of the 03-core, and the across-core consistency is more apparent from the 6 year smoothed profiles (Figures 3 and 4). This consistency is further

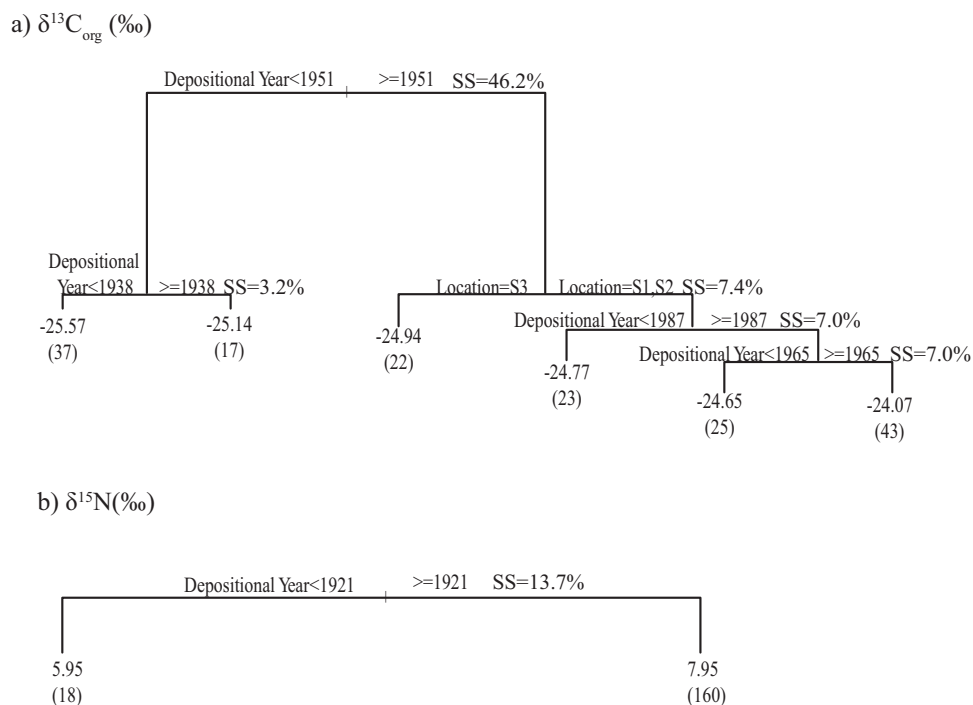


Figure 7. Regression trees explaining the variations of (a) $\delta^{13}\text{C}_{\text{org}}$ and (b) $\delta^{15}\text{N}$ in terms of two variables: “core location (S1, S2, and S3)” and “depositional year (the calendar year of deposition of each sediment interval based on ^{137}Cs dating).” The vertical depth of each split is proportional to the total sum of square (ss) of the variance explained. The mean values of each split group are listed at the bottom of the plot and the sample size for each split group is shown in bracket.

supported by the significant correlations of TOC and $\delta^{13}\text{C}_{\text{org}}$ between the 91ben-core versus the 03-core as well as between the 88-core versus the 03-core (Table 2) for both annual and 6 year smoothed values. The three cores showed increases in TOC and $\delta^{13}\text{C}$ values from 1950s to 1970s (Figures 3 and 4), recording a rapid increase in lacustrine productivity from the 1950s to 1970s [e.g., Schelske and Hodell, 1995; Lu *et al.*, 2010a]. TOC and $\delta^{13}\text{C}$ values decreased thereafter, reflecting that the productivity reached a maximum in the early 1970s and thereafter declined because of the joint phosphorous regulation effort enacted by the US and Canadian governments (Figures 3 and 4). This paleoproductivity pattern agrees with documented and reconstructed eutrophication histories of Lake Erie [e.g., Hartman, 1973; Schelske and Hodell, 1995; Munawar *et al.*, 1999], indicating that TOC and $\delta^{13}\text{C}_{\text{org}}$ of the three cores recorded changes in lacustrine productivity on a decadal scale.

In contrast, it is difficult to extract the same paleoproductivity pattern from the TOC and $\delta^{13}\text{C}_{\text{org}}$ of the 82-core and the 91box-core (Figure 3), which may be partly due that these two cores were too short to demonstrate the decadal patterns described above. Correspondingly, the values of TOC and $\delta^{13}\text{C}_{\text{org}}$ of the 82-core and the 91box-core did not correlate with the values of the 03-core for both annual and 6 year scales (Table 2), perhaps also resulting from the temporal records of the 82-core and the 91box-core being too short and thus containing a too small sample size to demonstrate significant correlations with the 03-core.

3.1.2. Sources of Organic Matter: $\delta^{13}\text{C}_{\text{org}}$ and $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$

The absolute values of $\delta^{13}\text{C}_{\text{org}}$ and $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$ ratios may be diagnostic of the sources of lacustrine organic matter [Meyers, 1994; Routh *et al.*, 2004]. While the $\delta^{13}\text{C}_{\text{org}}$ values of the 82-core were more negative than those of the 88-core and 03-core (Table 3), all $\delta^{13}\text{C}_{\text{org}}$ values fell in the range from -26.8 to -21.5 ‰, which was a common range for C_3 land plants, soil organic matter, freshwater algae, and petroleum organics [Faure and Mensing, 2005; Ogrinc *et al.*, 2008; Lu *et al.*, 2013]. Therefore, the across-core differences in the values of $\delta^{13}\text{C}_{\text{org}}$ did not influence our interpretation of the sources of organic matter. Similarly, while the five cores showed different values of $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$ (Figure 3), they all fell between 7.3 and 12.2 (Table 3), a range indicating that the primary source of the organic matter in the sediments was aquatic organism, which fits with the eutrophic status of Lake Erie.

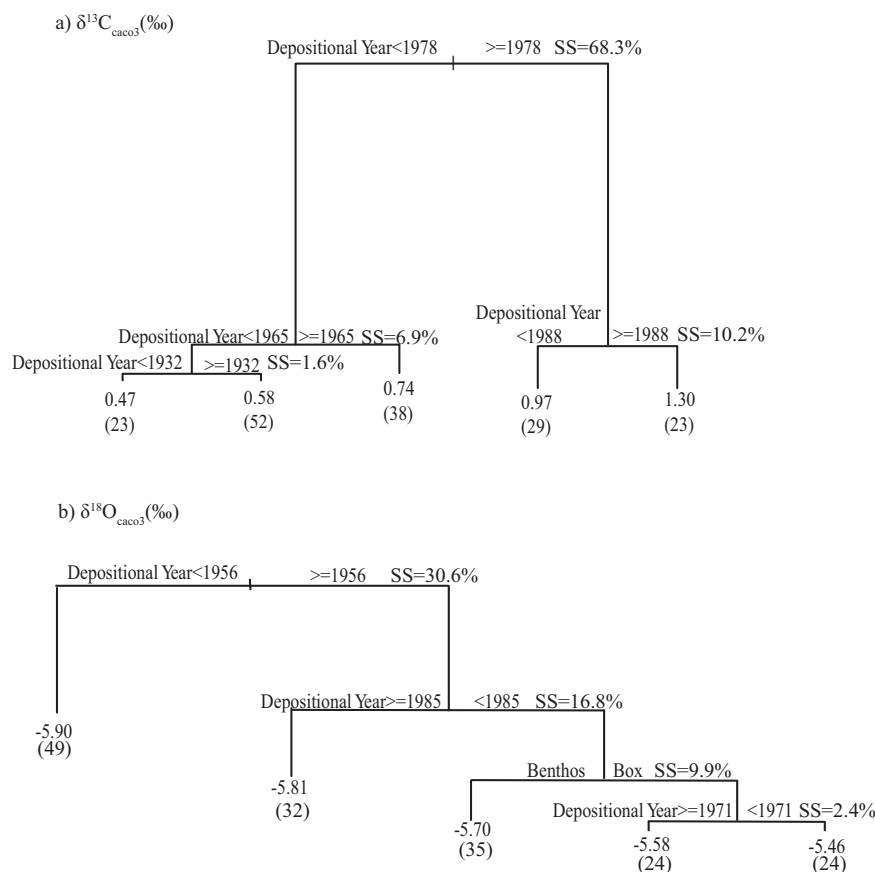


Figure 8. Regression trees explaining the variations of (a) $\delta^{13}\text{C}_{\text{CaCO}_3}$ and (b) $\delta^{18}\text{O}_{\text{CaCO}_3}$ in terms of two variables: “core method (Benthos, Box)” and “depositional year (the calendar year of deposition of each sediment interval based on ^{137}Cs dating).” The vertical depth of each split is proportional to the total sum of square (ss) of the variance explained. The mean values of each split group are listed at the bottom of the plot and the sample size for each split group is shown in bracket.

The temporal variation in $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$ values have been used to reconstruct changes in the relative contributions of terrestrial versus aquatic organic matter [Meyers and Ishiwatari, 1993; Meyers, 1994]. While significant correlations of $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$ were found between the 03-core versus the 88-core and between the 03-core versus the 91ben-core at the 6 year scale (Table 2), it was difficult to identify concordant trends of these three cores from the visual observation of their temporal profiles (Figure 3). Similar to $\delta^{13}\text{C}_{\text{org}}$ and TOC, the $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$ values of the 82-core and 91box-core did not correlate with the values of the 03-core, and the temporal patterns of the three cores did not correspond (Table 2 and Figure 2). The dissimilar temporal patterns of these cores may lead to different interpretations of historical variation in the sources of sedimentary organic matter.

3.1.3. Nitrogen Sources and Processes: $\delta^{15}\text{N}$ Values

The $\delta^{15}\text{N}$ values in the 82-core, the 88-core, and the 03-core varied from 6.9‰ to 8.1‰, 1.9‰ to 16.7‰, and 5.5‰ to 12.9‰, respectively. It is difficult to assess how these core-core differences influence paleolimnological interpretations because the ambiguity of $\delta^{15}\text{N}$ as an indicator of sources and processes controlling sedimentary N. A variety of potential sources have $\delta^{15}\text{N}$ values falling in the observed range (e.g., soil N: 0 to +12‰; fertilizers: -6 to +7‰; rain: -13 to +2‰; phytoplankton: +6 to +9‰) [Heaton, 1986; Hodell and Schelske, 1998; Faure and Mensing, 2005; Wu et al., 2008], and several processes may further alter $\delta^{15}\text{N}$ values (e.g., denitrification and nitrogen fixation) [e.g., Altabet and Francois, 1994; Altabet et al., 1995; Wu et al., 2007; Gälman et al., 2009]. Related to this, it was also difficult to extract paleolimnological information from the variations of $\delta^{15}\text{N}$ values in the study cores. The $\delta^{15}\text{N}$ values of the 88-core versus the 03-core showed significant correlations for annual and 6 year scale (Table 2), while these correlations were not apparent from the temporal profiles of $\delta^{15}\text{N}$ (Figure 4). No significant correlation was found between the 82-core

versus the 03-core (Table 2). As a result, it is difficult to obtain reliable paleolimnological records of N sources and processed based on a single core. *Lu et al.* [2010b] compared the 88-core and the 03-core and attributed to their temporal variations to increasing inputs of N-fertilizers and denitrification, but these interpretations were made possible only by the prior knowledge of the history of fertilizer inputs and dissolved oxygen contents for the Lake Erie [Bertram, 1993; Burns *et al.*, 2005; Lu *et al.*, 2010b], which was often unavailable for many lake basins and for reconstructing preinstrumental environmental changes.

3.1.4. Calcium Carbonate Proxies

In Lake Erie, CaCO_3 in sediments can be detrital, i.e., derived from erosion of glacial till and limestone/dolomite outcrops on the northern shores [Krissek and Ausich, 1997], or authigenic, e.g., a significant amount of CaCO_3 precipitates out of water and causes "whiting events" [Strong and Eadie, 1978] (photos can be seen in <http://earthobservatory.nasa.gov/NaturalHazards/view.php?id=9487>) because of higher temperatures that reduce the solubility of CaCO_3 and elevated productivity that draws down the concentration of dissolved CO_2 . No significant correlation for CaCO_3 was found among the four cores (Table 2), which was echoed by dissimilar trends in the temporal patterns of the four cores (Figure 5), indicating that CaCO_3 is not appropriate for reconstructing any basin or watershed-scale temperature or aquatic productivity.

The $\delta^{13}\text{C}_{\text{CaCO}_3}$ of 03-core and 91box-core showed significant correlations and consistent variation patterns (Table 2 and Figure 5). This observation, given these two cores were from the same location but collected with different corers, indicates that $\delta^{13}\text{C}_{\text{CaCO}_3}$ values were not much influenced by sediment variability arising from corer types. Both cores showed a gradual increase in $\delta^{13}\text{C}_{\text{CaCO}_3}$ from 1955 to 1992, which has been interpreted to reflect increasing lacustrine productivity between the 1950s and the 1970s and a combined result of lacustrine productivity and temperature variations thereafter [Lu *et al.*, 2010a].

In contrast, the temporal variations of $\delta^{18}\text{O}_{\text{CaCO}_3}$ differed between the 91box-core and the 03-core (Table 2 and Figure 5), indicating that $\delta^{18}\text{O}_{\text{CaCO}_3}$ was sensitive to the variability associated with the corer type. Since $\delta^{18}\text{O}_{\text{CaCO}_3}$ may be influenced by multiple hydrological parameters such as precipitation and evaporation budget, temperature, and atmospheric $\delta^{18}\text{O}$ [Li *et al.*, 1997; Zhang *et al.*, 2009; Jonsson *et al.*, 2010], the interpretation of $\delta^{18}\text{O}_{\text{CaCO}_3}$ as an indicator of hydrological processes often has to be substantiated from independent evidence. In our cores, no correlation was found between the precipitation record in nearby Erie, PA (~20–45 km from our core sites) and the $\delta^{18}\text{O}_{\text{CaCO}_3}$ values (for the 91box-core: $r = -0.28$, $P = 0.1$; for the 03-core: $r = 0.16$, $P = 0.1$) or between annual air temperatures in Erie and the $\delta^{18}\text{O}_{\text{CaCO}_3}$ values (for the 03-core: $r = -0.28$, $P = 0.007$; for the 91box-core: $r = -0.36$, $P = 0.03$) (precipitation and air temperature data from US Department of Agriculture Weather Bureau). Another consideration is that $\delta^{18}\text{O}_{\text{CaCO}_3}$ potentially records water temperatures because of the temperature-dependent fractionation between lake water and $\delta^{18}\text{O}_{\text{CaCO}_3}$ [Epstein *et al.*, 1953; Craig, 1965]. As most of the authigenic CaCO_3 in Lake Erie is formed in late April–early May, we assessed the correspondence of water temperature record in the Eastern Basin of Lake Erie (available from 1983 to 1993; K. W. Klewin, personal communication) to the sedimentary $\delta^{18}\text{O}_{\text{CaCO}_3}$ record. Their temporal patterns were not correspondent, and the values showed no correlation (03-core: $r = -0.02$, $P = 0.97$; 91box-core: $r = -0.25$, $P = 0.48$). Therefore, $\delta^{18}\text{O}_{\text{CaCO}_3}$ in Lake Erie is not a straightforward geochemical proxy for paleolimnological reconstructions, which, along with the influences of corer types on $\delta^{18}\text{O}_{\text{CaCO}_3}$, highlights the complexity and undependability of extracting environmental information from $\delta^{18}\text{O}_{\text{CaCO}_3}$ of sediments from this lake.

3.2. Factors Contributing to Core-Core Differences in the Geochemical Proxies

CART tree analysis, by including "depositional year," "core location," and "corer type" as exploratory variables, collectively assessed the influences of temporal environmental changes, coring location, and corer type on the proxies (Figures 6–8). For CART trees, the primary split represents the variable accounting for the highest total sum of square (ss) of the variance of the geochemical proxies. Different proxies had different variables accounting for the highest total ss: "corer type" for C_{org} : N_{tot} , "core location" for CaCO_3 , and "depositional year" for TOC, $\delta^{13}\text{C}_{\text{org}}$, $\delta^{13}\text{C}_{\text{CaCO}_3}$, $\delta^{15}\text{N}$, and $\delta^{18}\text{O}_{\text{CaCO}_3}$ (Table 3 and Figures 6–8). From the perspective of paleolimnological interpretations, we prefer proxies that are primarily controlled by "depositional year," which is representative of temporal variations usually associated with changes in lacustrine environments. However, it is important to note that our data sets were limited that the influence of "core location" was not assessed for $\delta^{13}\text{C}_{\text{CaCO}_3}$ and $\delta^{18}\text{O}_{\text{CaCO}_3}$ and the influence of "corer type" was not assessed

for $\delta^{13}\text{C}_{\text{org}}$. Additionally, “core location” and “corer type” accounted for part of the variance for most geochemical proxies (Figures 6–8), demonstrating that across-core differences of some sediment intervals may be more important than the relative differences between sample horizons of different depositional years within one core, contrasting to the fundamental paleolimnological assumption that environmental changes are the major factor driving the variation of geochemical proxies in lacustrine sediment. We discuss below how each factor may influence geochemical composition of sediment cores and, consequently, the across-core differences we observed.

3.2.1. Core Location

The significance of “core location” in explaining the variance of geochemical proxies may arise from greater sediment spatial heterogeneity in Lake Erie than anticipated. The locations of the 82-core (S2) and the 88-core (S3) were west of the site for the two 91-cores and the 03-core (S1) (Figure 1), and the former two cores had overall higher total mass accumulation rates than the latter three cores (Table 1). In Lake Erie, sediment in the eastern basin originates primarily in the central basin and is a mixture of bottom material resuspended during storms and of material from shoreline erosion along the north coast that is then transported into the eastern basin [Lick *et al.*, 1994; Hawley and Eadie, 2007]. For example, satellite photos show plumes of fine-grained materials being transported south of Long Point into the eastern basin (<http://coastwatch.glerl.noaa.gov/modis/modis.cgi/modis?region=e&page=1>) (see Long Point in Figure 1). The higher mass accumulation rates measured closer to Long Point in the present study thus may reflect the difference in distance to the original source of the suspended load, since the coarser material will not be transported as far as the finer fraction prior to deposition. Similarly, many previous studies in Lake Erie have also reported various linear sedimentation rates for the sediment cores from the eastern basin [Robbins, 1982; Eadie and Robbins, 1987; Robbins *et al.*, 1989]. This sediment heterogeneity well explained CaCO_3 content being the proxy most sensitive to “core location” (Figure 6) because it could greatly influence the delivery of detrital CaCO_3 to the coring locations. Additionally, authigenic carbonate production and preservation were regulated by multiple in situ variables including temperature, pH, ion concentrations, and oxic levels. These variables can be influenced by various physical and biological processes such as water stratification and mixing, aquatic productivity, and bioturbation, and these processes are highly heterogeneous in Lake Erie [e.g., Hartman, 1973; Burns, 1985; Richards and Baker, 1993; Munawar *et al.*, 1999; Ludsin *et al.*, 2001; Rockwell *et al.*, 2005; Hawley and Eadie, 2007; Dusini, 2005]. As such the sensitivity of CaCO_3 to “core locations” can be attributed to the high spatial heterogeneity of sediment and water column conditions in this large lake.

3.2.2. Corer Type

Relative to benthos cores, the 91 box-core showed overall higher data variability (Figures 3 and 5), indicating that sediment recovery was different in Box and Benthos corers. The influence of “corer type” on the geochemical proxies was also found in TOC, $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$ and $\delta^{13}\text{C}_{\text{CaCO}_3}$ (Figures 6 and 8). Benthos and Box corers collect sediments in different manners. The Benthos corer used in all of our coring campaigns is a gravity corer with a 6.6 cm bore and equipped with a top-end poppet valve instead of a bottom-end core-catcher. It is designed to collect soft sediments that typify lake beds with minimal disturbance and is driven into sediment by a 25 kg weight. Benthos cores typically experience some compression that varies with sediment texture and porosity (i.e., we cannot treat any two samples in the same manner). In addition, this type of corer may collect incomplete sediment records because of its hydraulic “bow wave” effect that displaces a portion of sediments instead of capturing them. Unlike a gravity corer, a Box corer we used in the 1991 campaign was lowered slowly to the sediment and then pressed into it. Box cores usually experience little distortion and are likely to collect relatively intact records, although they are commonly shorter than those of gravity cores. Additionally, coring may be influenced by the degree of sediment compaction. For example, Morton and White [1997] have noted that thinning, bypassing, and compaction of unconsolidated sediments during coring process can result in the loss or thinning of up to 67% of sediments recovered. Maier *et al.* [2013] also observed that core compaction led to varve thickness decreasing by 60% after 5 years and the compaction continued after 33 years (the study period) of deposition. Therefore, core recovery may differ between shallow, less consolidated sediments versus deep, more compact sediments. We cored samples at different times, when sediments of the same depositional years were subjected to different extents of compaction and thus likely showed differing degrees of susceptibility to coring recovery and procedures.

3.2.3. Temporal Environmental Changes

Lake Erie has experienced substantial environmental changes over the last century [e.g., Hartman, 1973; Burns, 1985; Richards and Baker, 1993; Munawar et al., 1999; Ludsin et al., 2001; Rockwell et al., 2005], which should be reflected by geochemical compositions of the sediments of different depositional years. From our comparison of down-core variations of the geochemical proxies, it has become clear that the temporal resolution of environmental changes that can be drawn from the geochemical proxies is much lower than the sedimentation rate. Using $\delta^{13}\text{C}_{\text{org}}$ as an example, we found that it was useful in reflecting productivity variations on decadal scales (e.g., 20 years of rapid increases in paleoproductivity) but not robust for annual environmental changes in spite of the >1 cm/yr of sedimentation rates in most of our cores (Table 1). The year-to-year variations of the same proxies varied greatly between the cores, with many short-term excursions appearing only in a single core (Figures 3–5). For example, the 88-core showed unusually high $\delta^{13}\text{C}_{\text{org}}$ values in surface sediment (0–1 cm) and low values for sediments between 7 and 8 cm (Figure 4). These values were not found in the 82-core and the 03-core at the same or similar depositional years, suggesting that they were not the result of broad-scale lacustrine environmental changes but were instead due to local processes or coring artifacts. Therefore, it is not recommended in Lake Erie to reconstruct environmental changes at a resolution comparable to sedimentation rates (i.e., annual changes in the present study) or based on discrete data points. Related to this, paleoenvironmental information may not be confidently obtained from sediment cores with temporal records that are too short to demonstrate decadal changes. The 82-core (~ 21 year record) and the 91box-core (~ 34 year record) failed to indicate the significant environmental transitions that happened over the about two decades associated with the rapid cultural eutrophication from ~ 1950 s to ~ 1970 s in Lake Erie.

One seemingly apparent point that can be ignored in paleolimnological research is that the temporal resolution of reconstructed environmental changes must be limited by sediment dating uncertainty. In the present study, the correlation coefficients (r values) increased from the annual to 6 year scales for most proxies (Table 2), suggesting that sediment age uncertainty introduced age-related variability to the geochemical proxies, and therefore the 6 year smoothed profiles are more appropriate for reconstructing environmental changes.

3.2.4. Other Influences

All the geochemical proxies have part of their variance accounted for by unknown factors (Table 3). Among all the proxies, $\delta^{15}\text{N}$ had the largest percentage of variance (86%) unexplained by CART trees. Analytical artifact could be a contributing factor to the variance of the geochemical proxies. As noted in several recent studies, the accuracy and precision of $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$, $\delta^{13}\text{C}_{\text{org}}$, and $\delta^{15}\text{N}$ values can depend, to a greater extent than anticipated, on laboratory preparation procedures including acid treatment, sample size, and sample nature [Brodie et al., 2011a, 2011b, 2011c]. In the present study, all samples were subjected to the same standard procedure, assuming sediments from different cores reacted similarly to the analytical procedures. However, acid treatment, which was applied to our samples, has recently been shown to influence $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$ and $\delta^{15}\text{N}$ values in nonsystematic ways that could significantly bias paleoenvironmental interpretations [Brodie et al., 2010, 2011a, 2011b]. Furthermore, the form of carbonate was not assessed prior to sample grinding, which may bias both organic and inorganic carbon concentrations (e.g., detrital dolomite is more resistant to acid dissolution than CaCO_3), and the isotopic values of carbonates, e.g., ostracods and endogenic micrite differ in their isotopic values [Ng'ang'a et al., 1998].

3.3. Lake Erie Versus Other Lakes

The inconsistent core-core variation in the proxies from Lake Erie is contrary to the sedimentary records in smaller, varved Lake Nylandssjön, where consistent year-to-year variation of geochemical proxies (TOC, TN, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$) were observed between ten cores collected over a 27 year period [Gälman et al., 2008, 2009]. This difference can be attributed to different sedimentary processes between Lake Erie and varved lakes. Varved sediment indicates relatively continuous sedimentation and little or no reworking of sediment after its initial deposition. In contrast, the sediment that accumulated in the eastern basin of Lake Erie is almost certainly influenced by infrequent but large storm events that occur at irregular intervals, based on a numerical model of sediment transport [Lick et al., 1994] and actual observations of sediment movement and deposition in the eastern basin [Hawley and Eadie, 2007]. Hence, much of sediment materials deposited in Lake Erie may be accounted by episodic storms, rather than continuous sedimentation process. Additionally, biological mixing after sediment deposition, which may influence geochemical compositions of the

sediments, was also widely observed but unevenly distributed in Lake Erie in time and space [Robbins, 1982; Eadie and Robbins, 1987]. For example, Robbins [1982] reported a core collected in 1978 at an unspecified site in the eastern basin showing evidence of substantial surface mixing in approximately the upper 10 cm, which was attributed to bioturbation by oligochaete worms.

Our findings of Lake Erie may be applicable to large, heterogeneous lakes where sediments are highly variable spatiotemporally. Johnson *et al.* [2012] collected ten sediment cores from an 8 km² area representative of deep offshore basins in Lake Superior and reported, among the coring sites, mass accumulation rates varied greatly between 50 g/m² yr and 180 g/m² yr. They attributed this variability as sediment redistribution by bottom currents over the complex morphology of the Lake Superior basin that is not uniform in space and time. They analyzed a series of geochemical proxies including total organic carbon and nitrogen, biogenic silica, and total and methyl mercury and found their concentrations displayed differences between $\pm 14\%$ and $\pm 50\%$ among the cores. As a result, these researchers drew a conclusion similar to ours, that is, a single core from any given area in the lake may not be appropriate to reflect the changes in environmental conditions that extend even a few hundred meters beyond the core site.

Lastly, lake Erie is also special in that its environmental changes over the last century have been relatively well documented [e.g., Hartman, 1973; Burns, 1985; Richards and Baker, 1993; Munawar *et al.*, 1999; Ludsin *et al.*, 2001; Rockwell *et al.*, 2005], which provides us with important background information for assessing the reliability of the proxy-derived reconstructions and identifying temporal patterns that are associated with environmental changes. Such information is particularly important for those proxies whose paleoenvironmental interpretations remain ambiguous and show high variability to unknown factors, such as $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{CaCO}_3}$ in Lake Erie sediments. When background information is not available, which is the case for most paleoenvironmental studies, multiple-core investigation would be more critical for identifying effective temporal patterns and to extract reliable paleolimnological information.

4. Conclusions

Our comparison of a suite of geochemical proxies from the five cores at or near the depocenter of the eastern basin in Lake Erie showed a complex pattern—the measured proxies varied between cores. TOC, $\delta^{13}\text{C}_{\text{org}}$, and $\delta^{13}\text{C}_{\text{CaCO}_3}$ were the only three proxies that showed apparent consistency between the sediment cores that are long enough to record decadal environmental changes. $\text{C}_{\text{org}}:\text{N}_{\text{tot}}$ and $\delta^{15}\text{N}$ showed significant correlations between different sediment cores, but these correlations were difficult to identify based on temporal profiles only, making it difficult to extract reliable environmental patterns recorded in these proxies if background knowledge of the study sites is unavailable. CaCO_3 and $\delta^{18}\text{O}_{\text{CaCO}_3}$ varied with coring location and/or corer type, making them unreliable proxies to reconstruct basin-scale environmental changes in Lake Erie. In addition to temporal environmental changes, the majority of the geochemical proxies were influenced to varying extents by sampling location, corer variability, and other unknown factors. As a result, using multiple sediment cores from proximate locations may be necessary for reliably reconstructing lacustrine environmental changes in this large, heterogeneous lake.

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