

Late Glacial and Holocene Paleolimnology of two temperate lakes inferred from sediment organic $\delta^{13}\text{C}$ chronology

N A LOVAN and R V KRISHNAMURTHY

*Department of Geology, Western Michigan University, Kalamazoo, Michigan, USA.
email: lovan1NA@mail.cmich.edu*

The stable carbon isotope ($\delta^{13}\text{C}$) and elemental C/N ratios in Total Organic Carbon (TOC) extracted from radiometrically dated cores from two Midwestern USA lakes were determined to investigate the factors that control these values in temperate lakes. The range of $\delta^{13}\text{C}$ values (-26 to -32‰) and C/N ratios (mean value ~ 10.8) are typical of values reported for other temperate lake organic matter in this region. In the core from Lake Winnebago, Wisconsin, a negative correlation was seen between the TOC and $\delta^{13}\text{C}$, which can be interpreted in terms of a re-mixing and consumption of sedimented organic carbon along with rapid equilibration throughout the water column. No correlation was seen between the TOC and $\delta^{13}\text{C}$ in the record from Ladd Lake, Ohio, implying that in this latter lake productivity alone was not a singular process controlling the isotope ratio. Here, it is suggested that equilibrium conditions are maintained such that the DIC of the water is never depleted of aqueous CO_2 during high organic production and the resulting $\delta^{13}\text{C}$ of the organic carbon lacks correlation with the TOC. Further, in this lake a fine resolution analysis was carried out which indicated a possible anthropogenic influence on the isotope ratio around times when human settlement (~ 300 yrs ago) and enhanced agricultural practices (~ 80 yrs ago) were significant. The study shows that carbon isotope studies are useful in paleolimnologic investigations.

1. Introduction

The stable carbon isotope ratios ($\delta^{13}\text{C}$) of sediment bulk organic matter have been used in discussions of lacustrine carbon cycling to explain variations in lacustrine productivity and atmospheric CO_2 levels (Arthur *et al* 1985; Jasper and Hayes 1990; Hollander and McKenzie 1991; Schelske and Hodell 1991 and 1995). The use of C/N ratio was suggested by Nakai (1972) and coworkers to constrain and assist the interpretation of the source of organic carbon in lake sediments (C/N of lower aquatic organisms < 10 , while terrestrial plants yield values from 70 to 200). This technique has been successfully applied by numerous others (Krishnamurthy *et al* 1986; Talbot and Johannessen 1992; Meyers and Horie 1993; Meyers 1994). The dissolved inorganic carbon (DIC) in lacustrine environments provides the carbon source for lake organic carbon. Lacustrine DIC is controlled

by the DIC of waters that recharge the lake, CO_2 exchange with the atmosphere, and photosynthesis and respiration of the organic matter in the lake. Thus, the $\delta^{13}\text{C}$ of lacustrine organic carbon can be dictated by water temperature, atmospheric CO_2 concentration, lake productivity and contribution from terrestrial sources. Jasper and Hayes (1990) and Rau *et al* (1991) have argued that atmospheric CO_2 is a determinant of the ultimate isotopic carbon ratio of sedimentary organic matter. This study examines the isotopic carbon signal from sediment organic carbon in two Midwestern USA lakes.

2. Study Area

Samples used in this study came from radiometrically dated cores raised from Ladd Lake ($44^\circ 09' \text{N}$; $88^\circ 10' \text{W}$) in northwestern Ohio and Lake Winnebago

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(44° 09' N; 88° 10' W) in east central Wisconsin (figure 1). Many, if not most, of the Midwestern USA lakes were formed in glacial drift as kettle or pro-glacial lakes related to the last glacial advance of the specific area. The oldest dates, 14,680 radiocarbon years before the present (^{14}C yr BP) for the Ladd Lake core and 12,050 ^{14}C yr BP for the Lake Winnebago core, are consistent with geological observations in both areas that these lakes formed at the termination of the last glacial period in response to a melting and retreating ice mass (uncalibrated radiocarbon dates are used throughout this paper).

Ladd Lake is located on the outer edge of the Fort Wayne moraine. The predominant local landform is the lake plain formed by a series of pro-glacial lakes ancestral to Lake Erie that filled the Lake Erie basin. The ice free date for Ladd Lake corresponds to ~14,500 to 14,000 ^{14}C yr BP (Shane, personal communication). Lewis and Anderson (1992) reported that the ice was out of Ohio and the Lake Erie Basin by 14,100 radio-

carbon years BP. The various glacial levels of Lake Erie do not affect Ladd Lake directly as it is outside the maximum Erie basin of Lake Maumee. Shane (1987, 1991) suggested that modern south to north climatic gradients were not established until about 11,000 years ago, being several thousand years after the area was free of glacial ice.

Lake Winnebago is a 747 km² lake (45 km × 16.6 km), having an average and very uniform depth of 5.3 meters (Smith 1997). The contemporary lake is a remnant of the larger glacial Lake Oshkosh that occupied the lake basin during the Two Rivers-Younger Dryas advance 11 to 8 k ^{14}C yr BP (Thwaites 1943; McKee and Laudon 1972; Smith 1997). During the Two Rivers oscillation the Green Bay lobe of the Laurentide ice sheet re-advanced over Two Creeks-age forests (12.5–11 kyr BP) to a position along the northern end of contemporary Lake Winnebago. Here, it deposited a low moraine that now forms the retaining dam of the lake and marks the terminal

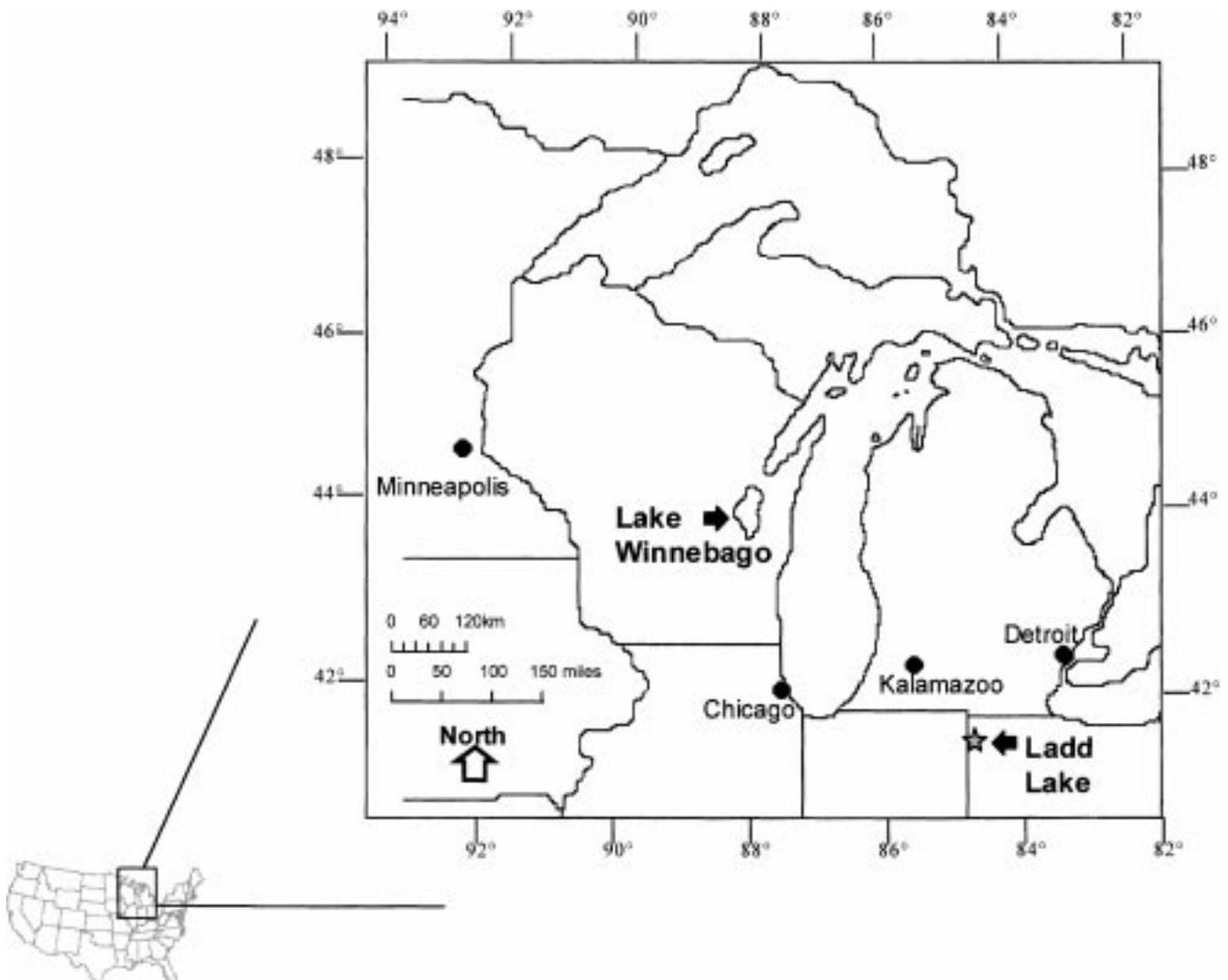


Figure 1. Map showing the Midwestern United States and the location of Ladd Lake in northwestern Ohio and Lake Winnebago in east-central Wisconsin (exploded view).

position of the last glacial re-advance in the area (Smith 1997). A 23-meter drop in lake-level, to near modern levels, has been documented by mapping the elevations of raised paleo-shorelines and outlets (Weidman 1911; Thwaites 1943). Groundwater provides a major source of recharge to the lake (Smith, personal communication). The lake is seasonally ice covered at which time the groundwater charges the lake with dissolved solids (420 ppm in late winter) emanating from the carbonate bedrock (Olcott 1966) and carbonate-rich glacial drift aquifers. Olcott (1966) reports a seasonal variation in the pH of the lake water with winter pH values of 7.4 compared to summer pH values of 8.4 indicating that the lake is a HCO_3^- -dominated system.

3. Sample collection and radiocarbon chronology

The 12-meter Ladd Lake core was raised in November, 1986, by the University of Minnesota Limnologic Research Center using a 5 cm diameter Wright-Livingston piston sampler. Samples were extracted in 1995 for isotopic analysis using washed and modified (blunt cut) plastic 3, 6 and/or 10 cc syringes then extruded using the syringe plunger. Approximately 3 to 5 grams of sediment was collected for each sample. Individual samples were collected at 4 to 5 cm intervals over the length of the core. Approximately 300 samples were removed and 137 were processed for use in this study. Workers from Lawrence University in Appleton, Wisconsin, raised several vibracores from the north-central portion of Lake Winnebago during the summer of 1995. Sixty sediment samples from core LW7, a single 3-meter core, were extracted and provided for stable isotope study. Sediment samples were extracted using an acid-washed plastic utensil then individually placed into separate new, acid-washed and pre-labeled 20 ml vials.

Six radiocarbon dates were obtained from each core. Radiocarbon dates for the Ladd Lake core were obtained from bulk sediment organic matter in samples collected from select intervals over the length of the core. Dates were generated by the Illinois State Geological Survey for the University of Minnesota Limnologic Research Center (UMLRC). Sample pretreatment included use of acid to remove carbonates and KOH to remove humics. Radiocarbon dates obtained for the Lake Winnebago samples are from the CO_2 gas evolved from sediment organic matter by combustion of the carbonate free organic fraction. AMS dating analysis was performed for Western Michigan University at Purdue University's Prime Laboratory for Rare Isotope Measurement.

Plotted as core depth versus ^{14}C yr BP, the sedimentation rate for the Ladd Lake and Lake Winne-

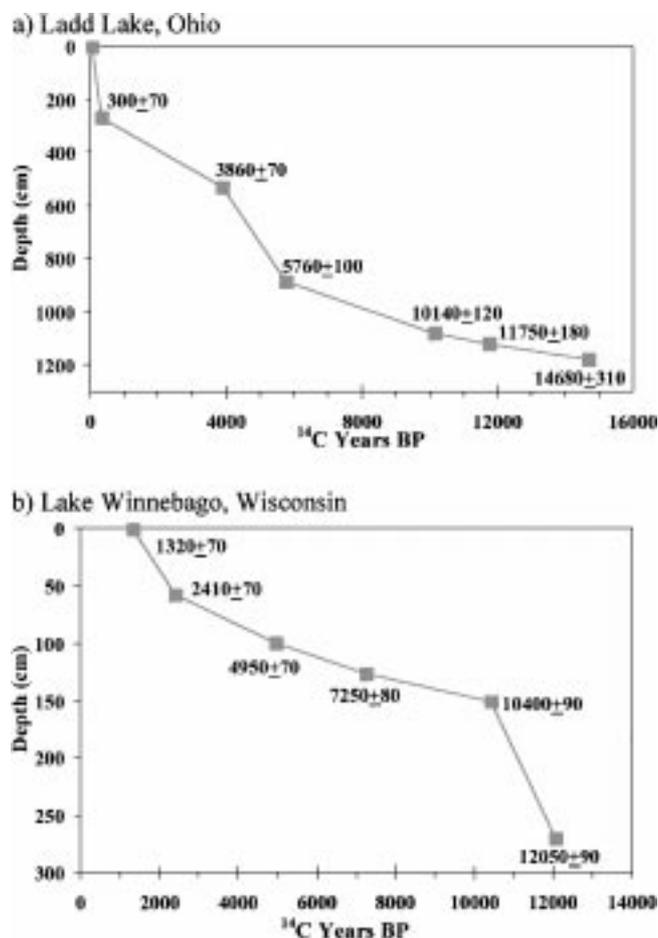


Figure 2. Sedimentation rates for Ladd Lake (a) and Lake Winnebago (b) plotted as a function of core depth versus radiocarbon age.

bago cores are shown in figure 2(a) and 2(b), respectively. Depths shown on the Ladd Lake core were zeroed by subtracting the water column depth from the core depth (the water surface was considered 0 cm; the top of core starts at 930 cm and the base of core at 2132 cm). The radiocarbon date at 264–270 cm in the Ladd Lake core is taken just below the so-called European settlement horizon and dates to ~ 300 ^{14}C yr BP (Shane 1991). The dates from the 521–529 cm interval (3860 ^{14}C yr BP) and the 877–885 cm interval (5760 ^{14}C yr BP) are generally correct. However, it should be noted that the basal three dates from the Ladd Lake core are considered generally correct but are thought potentially off by a few hundred years. The error arises due to hard water effects, slow sedimentation rates through these intervals, and the several centimeter span of bulk sample used for the radiocarbon analysis. Dates assigned to intervals below the oldest radiocarbon interval were based on use of the previous up core sedimentation rate and should be used with a modest degree of caution. Dates younger than 300 years in the Ladd Lake core were based on extrapolation to the surface (designated as zero).

Similar problems in the Lake Winnebago core were avoided by analysis of CO₂ gas from organic matter extracted at a discrete depth interval. Dates for individual samples were estimated by using a linear sedimentation rate between radiocarbon dated intervals. The age of the topmost Lake Winnebago sample is 1320 yr BP based on the radiocarbon chronology determined. This result is most likely due to the loss of the first few centimeters during core recovery. A living clam sample, collected from the lake's surface sediment, gave a "modern" radiocarbon age suggesting very little hard water effect. Dates for samples separated by less than 140 years (i.e. twice the standard deviation reported for the radiocarbon dates) were averaged.

4. Experimental methods

Sediment samples were first digested in concentrated HCl (38%) to remove carbonates. Three sequential digestions at 80°C for 3–5 hours each were performed. Samples were then rinsed to pH neutral and freeze dried. Sediment organic matter was further concentrated using a newly developed microwave digestion procedure (Lovan 1998). Aliquots of carbonate free residues were digested in HF:HCl [mixed as a 1:1 (v:v) solution from concentrated HF (48%) and HCl (38%)] within sealed containers under microwave conditions (120°C and ~35 PSI) to remove silicates. The prime purpose for this later digestion was the removal of hydrogen bearing silicates in preparation for isotopic analysis of hydrogen in the residual organic matter. Analysis of the carbon from these HF:HCl residues was undertaken as a secondary study and is noted here.

Carbon isotope ratios ($\delta^{13}\text{C}$) of the organic matter were obtained from the Ladd Lake and Lake Winnebago samples. Isotopic analysis of organic carbon ($\delta^{13}\text{C}$) was accomplished by combustion of insoluble HCl and HF:HCl residues in the presence of CuO at 900°C for 3 hours. Their gaseous CO₂, H₂O and N₂ combustion by-products were cryogenically separated and measured. Percent organic carbon and the atomic carbon to nitrogen (C/N) ratios were determined for both the carbonate free residue (HCl-residue) and the HF:HCl residues. The C/N ratios of the carbonate free fraction were used to constrain the interpretation of the organic carbon data. The $\delta^{13}\text{C}$ of the CO₂ gas were determined for both residual materials only in a pilot series of 42 samples from Ladd Lake. Isotopic analysis was accomplished using a Micromass-Optima isotope ratio mass spectrometer. All isotopic ratio data are expressed in the delta notation per mil where:

$$\delta\text{‰} = [(R_{\text{sample}}/R_{\text{standard}}) - 1]10^3$$

where R is ¹⁸O/¹⁶O, D/H, ¹³C/¹²C etc. Carbon isotope ratios are reported relative to the PDB Standard (calibrated using NBS-19) with a precision of $\pm 0.1\text{‰}$.

5. Results and Discussion

5.1 Background and preliminary findings

In general, lakes respond quickly to environmental pressures. Because of the limited size of their reservoir, the isotopic signals resulting from environmental perturbations are amplified (McKenzie 1985). The main sources of organic carbon in a lake are the submerged plants (i.e. macrophytes and plankton) living in the lake that take their isotopic signal from the lake DIC. Thus, the $\delta^{13}\text{C}$ of lake organic matter can be related to climatically induced changes in the trophic state of the lake.

Francey and Farquhar (1982) and Farquhar *et al* (1989) modeled the physical and enzymatic basis of carbon isotope discrimination during photosynthesis. This model equation, in its simplest form, is given by $\delta^{13}\text{C}_p = \delta^{13}\text{C}_{\text{air}} - a - (b - a) (C_i/C_a)$ where $\delta^{13}\text{C}_p$ is the isotope ratio of the fixed carbon (photosynthate); $\delta^{13}\text{C}_{\text{air}}$ is the isotope ratio of the source carbon (i.e. atmospheric carbon); a is the fractionation due to diffusion of CO₂ in the leaf (4.4‰); b is the fractionation due to fixation of CO₂ via enzyme action (~27‰ for C₃ plants); C_i is the concentration of CO₂ in the leaf intercellular space; C_a is the concentration of CO₂ in the atmosphere. Smith and Epstein (1971) subdivided photosynthetic plants into two large categories based on their $\delta^{13}\text{C}$ values. Most terrestrial plants range from -24 to -34‰, while the $\delta^{13}\text{C}$ of aquatic plants, tropical grasses, corn, and desert and salt marsh plants vary from -6 to -19‰. An intermediate group is formed by algae and lichen with $\delta^{13}\text{C}$ values from -12 to -23‰. Organic matter in Holocene sediment has $\delta^{13}\text{C}$ values ranging from -10 to -30‰ (Eckelman *et al* 1962; Shultz and Calder 1976; Meyers *et al* 1984; Krishnamurthy *et al* 1986; Meyers and Eadie 1993). Most aquatic plants fix CO₂ by the normal C₃ pathways with diffusion taking place in the aqueous phase (Farquhar *et al* 1989). When disequilibrium conditions exist (i.e. during high productivity) a depletion of the CO₂ available for plant photosynthesis can result and bicarbonate is used as the carbon source. This leads to more enriched $\delta^{13}\text{C}$ values. Measured $\delta^{13}\text{C}$ values for aquatic plants range between -11 and -39‰.

The percent organic content and the C/N ratios of the Ladd Lake and Lake Winnebago cores are shown in figures 3(a–d). Figure 3(a) shows the Ladd Lake percent organic carbon content from both the HCl and HF:HCl residues. Historically, literary reference to percent organic carbon data has been presented with respect to the HCl (carbonate free) residue. Here, these data show a mid-core increase to roughly 25% organic carbon with the basal and surface portions of the core having as low as 2% organic carbon. The general scatter of the HCl-percent organic carbon data over the length of the core and the similarity in

the surface and basal percent organic content suggests that no diagenetic effects have altered the sediment mass in the Ladd Lake core. An apparent concentration of the sediment organic matter during the HF:HCl digestion is graphically evidenced by the higher percent organic content of the HF:HCl residues. These values mirror the temporal change seen in the HCl residues.

Although generally lower in % organic content, the Lake Winnebago HCl and HF:HCl residues (figure 3c) again show mirrored temporal variation. Percent organic carbon in the HCl residues show a generally increasing trend from the base of the core upwards ranging from ~1% to ~9%. Basal marsh peat samples exhibited individual % organic carbon contents > 60%. These samples (at ~12,000 ¹⁴C yr BP) sit stratigraphically above a basal clay-till. Subsequent regression analysis omits these lower units from analysis using only the lacustrine samples above the marsh peat.

Atomic carbon to nitrogen (C/N) ratios from both the HCl and the HF:HCl residues for the Ladd Lake

and Lake Winnebago samples are shown in figure 3(b) and 3(d), respectively. The C/N ratios of the organic carbon in the HCl-residues reflect mean values of ~10.7 at Ladd Lake and 10.9 for Lake Winnebago. Values near and below 10 are indicative of lacustrine origins for the residual organic matter (Meyers and Ishiwatari 1993). The general positive shift in the HF:HCl values from both cores compared to their corresponding C/N ratios in the HCl-residues is due to loss of nitrogen. One potential source for nitrogen in the residual organic matter is protein (Meyers and Ishiwatari 1993). These data may suggest that N₂ may have been lost from the protein portion of the organic matter during the successive acid digestions.

Figure 4(a) shows the $\delta^{13}\text{C}$ from both the HCl and the HF:HCl residues in the pilot series of 42 samples from Ladd Lake. The $\delta^{13}\text{C}$ in the HCl-residues range from -26.2‰ to -32.8‰. The $\delta^{13}\text{C}$ of the HF:HCl-residues closely mimic those of the HCl-residues. Interestingly, the $\delta^{13}\text{C}$ of organic matter reported

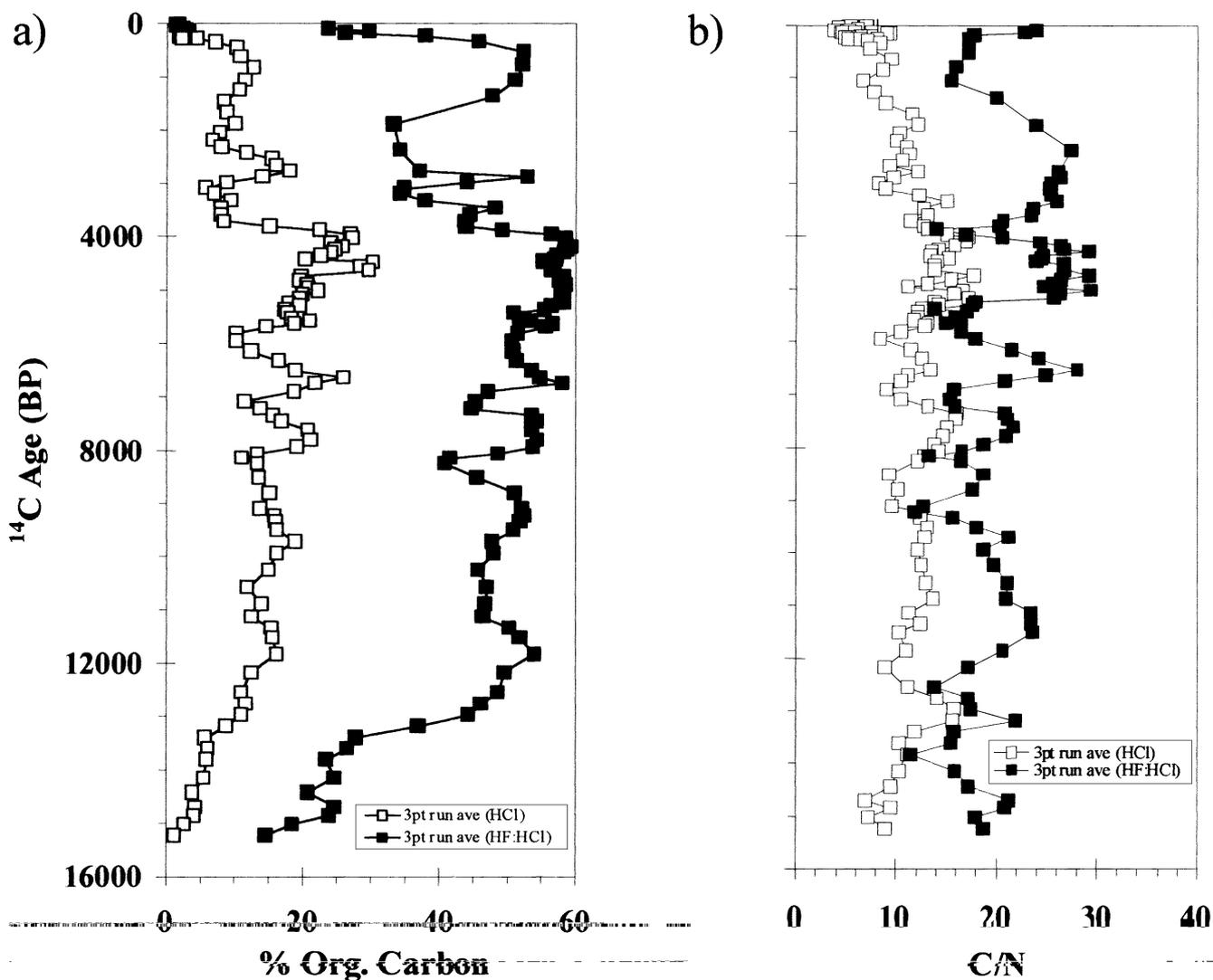


Figure 3(a-b). (Continued)

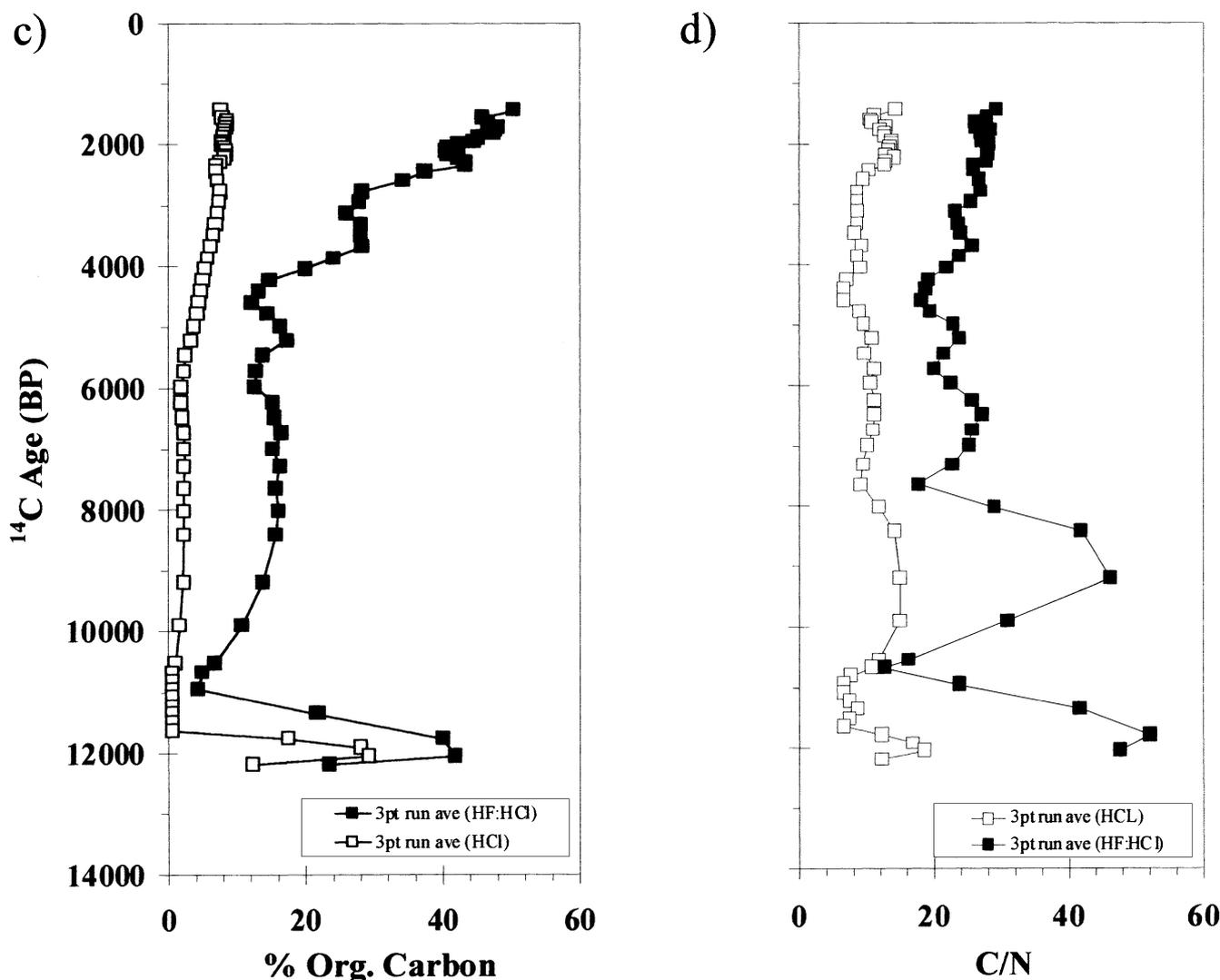


Figure 3. Ladd Lake percent organic carbon (a) and (b) atomic carbon to nitrogen ratios, C/N, plus Lake Winnebago percent organic carbon (c) and C/N ratios (d) for insoluble sediment organic matter in both the HCl and HF:HCl residues plotted vs. ^{14}C Age as years Before Present (BP).

from both the HCl residues and the HF:HCl residues are consistent with values reported in organic matter from Holocene sediment in other studies (Eckelman *et al* 1962; Shultz and Calder 1976; Meyers *et al* 1984; Krishnamurthy *et al* 1986; Meyers and Eadie 1993). This similarity in $\delta^{13}\text{C}$ values from the respective insoluble residues with a lack of correlation on regression of the $\delta^{13}\text{C}$ vs. the % organic carbon within their respective residual materials (figures 4(b) and 4(c)) may indicate very little destruction of the organic carbon during the successive acid digestions. If this is true, future work using the HF:HCl residues for isotopic hydrogen studies in bulk organic matter may be able to rely on cryogenically separated CO_2 from the combustion by-products in corresponding carbon studies. That aside, regression of the difference in the $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{HCl}} - \delta^{13}\text{C}_{\text{HF:HCl}}$) with respect to the % organic carbon content showed no correlation for either the HF:HCl residues ($R^2 = 0.028$, $n = 42$) or the HCl residues ($R^2 = 0.012$, $n = 42$). Because the

$\delta^{13}\text{C}$ of the HCl and HF:HCl residues were similar, the remainder of the discussion will focus only on the $\delta^{13}\text{C}_{\text{HCl}}$.

5.2 $\delta^{13}\text{C}_{\text{HCl}}$ from sediment organic carbon

The $\delta^{13}\text{C}_{\text{HCl}}$ from the whole core analysis of the Ladd Lake organic carbon is shown in figure 5. Isotopic values range from -25.4‰ to -32.8‰ . The $\delta^{13}\text{C}_{\text{HCl}}$ from organic carbon in the Lake Winnebago core range from -31.0 to -28.5‰ (figure 6). Carbon isotopic values from both cores are consistent with values reported from $\delta^{13}\text{C}$ of lacustrine organic carbon in other Midwestern USA studies. Regression of the Ladd Lake $\delta^{13}\text{C}_{\text{HCl}}$ with respect to % organic carbon (TOC) content (figure 5) shows a lack of correlation ($R^2 = 0.054$, $n = 137$). This lack of correlation may suggest that the $\delta^{13}\text{C}$ of the organic matter from Ladd Lake is not singularly controlled by productivity in the lake. Conversely, regression of the $\delta^{13}\text{C}_{\text{HCl}}$ vs.

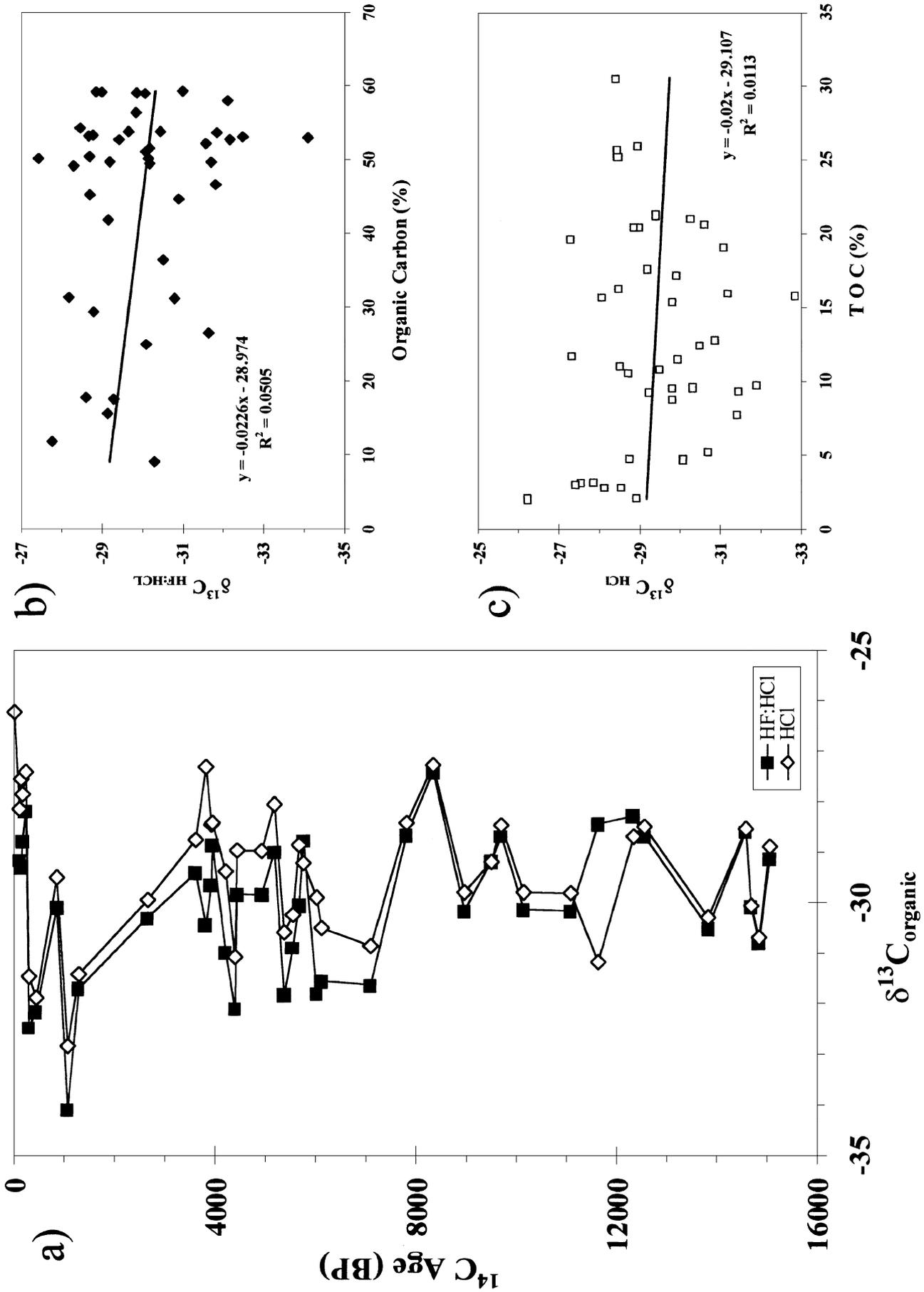


Figure 4. Ladd Lake Pilot Group $\delta^{13}\text{C}$ vs. ^{14}C years BP (a) and regression of $\delta^{13}\text{C}$ vs. per cent organic carbon for both the HCl and HF:HCl residual organic material (b and c).

TOC of the Lake Winnebago core indicates a negative correlation with $R^2 = 0.6$.

When CO_2 dissolves in water to form carbonic acid and its ions, isotopic exchange reactions enrich HCO_3^- in ^{13}C relative to the CO_2 . If isotopic equilibrium is maintained between the atmospheric CO_2 and the lake, the $\delta^{13}\text{C}$ of the lake organic matter reflects this equilibrium value via the aqueous CO_2 . However, when a lake goes into a state of enhanced photosynthesis, disequilibrium conditions exist and the production zone is depleted in dissolved CO_2 resulting in uptake of the isotopically heavier bicarbonate. Therefore, an increase of productivity in a stratified lake should be reflected by an increase in the $\delta^{13}\text{C}$ of the organic carbon that is produced in the surface water and subsequently sedimented. While the Ladd Lake core shows a low correlation coefficient for TOC vs. $\delta^{13}\text{C}$, its % organic content (TOC) is generally higher than that of the Lake Winnebago core. If high organic content were controlled by periods of high productivity, a positive covariance would be expected between the % organic carbon and the $\delta^{13}\text{C}$. Where negative covariance is evidenced with a high correlation coefficient, such as that seen in the Lake Winnebago core, a longer period of lake stratification may be implied wherein relatively little of the production is sedimented (Lean *et al* 1987; Schelske and Hodell 1991). If, however, equilibrium conditions are maintained such that the DIC of the water is never depleted of aqueous CO_2 during high organic production, the resulting $\delta^{13}\text{C}$ of the organic carbon should lack correlation with the % organic matter. This latter seems evident in the Ladd Lake core. However, unpublished water temperature data taken from 1 and 4-meter depths in Lake Winnebago suggest that thermal stratification in this large and uniformly shallow lake is evidenced only during the winter months of January, February and March. Lack of stratification during the warmer, ice-free months may be effected by persistent westerly winds that create wind driven lake-circulation, preventing thermal stratification and allowing rapid equilibrium throughout the shallow water column. Re-mixing and consumption of sedimented organic carbon and rapid equilibration may account for the negative correlation while very little of the net production is sedimented at Lake Winnebago.

5.3 Anthropogenic influence?

Figure 7 shows a plot of the $\delta^{13}\text{C}_{\text{HCl}}$ over the most recent 500 years where a fine resolution analysis was carried out for the Ladd Lake samples. Interestingly, regression of the $\delta^{13}\text{C}_{\text{HCl}}$ vs. % organic carbon for the 300 year period since European settlement shows a negative correlation with $R^2 = 0.58$ ($n = 33$) while the whole core regression shows an $R^2 = 0.054$. Within this 300 year interval, two phases are indicated where

the $\delta^{13}\text{C}_{\text{Organic}}$ show rapid positive shifts in value. The shift beginning at ~ 300 years ago corresponds to the time of settlement and land clearing while the positive shift from ~ 80 years ago to the present corresponds to more modern and intensified agricultural practices. During these periods, increased nutrient supply to the lake may have afforded greater productivity. The positive shifts in $\delta^{13}\text{C}$ would represent periods of increased productivity wherein the available CO_2 becomes depleted and photosynthesis continues while consuming the isotopically heavier bicarbonate. If high organic content were controlled by periods of high productivity, a positive covariance would be expected between the % organic carbon and the $\delta^{13}\text{C}$ signature. The negative correlation may indicate longer periods of thermal stratification of the lake wherein primary production is restricted mainly to the mixed layer (Lean *et al* 1987) and during which time relatively little of the production is sedimented (Schelske and Hodell 1991). Thus the higher % organic content mid core in Ladd Lake may reflect primary production early in the seasonal cycle when fixed carbon goes unused in the water column and is sedimented (Gardner *et al* 1985) whereas the trend in the most recent 300 years from the Ladd Lake core may reflect greater productivity during a period of longer seasonal stratification when relatively little of the production is sedimented.

6. Conclusions

In this study, the organic matter extracted from lake sediment was analyzed for $\delta^{13}\text{C}$ in two Midwestern United States lake cores. Total organic carbon (% organic carbon) was calculated and the atomic C/N ratios were used to constrain the interpretation of the isotopic carbon data. The range of $\delta^{13}\text{C}$ values and C/N ratios from both lakes are typical of values reported for other temperate lake organic matter in this region. Regression of the TOC vs. $\delta^{13}\text{C}$ for both cores shows that sedimented organic carbon from Lake Winnebago in Wisconsin reflects more negative $\delta^{13}\text{C}$ with higher % organic carbon. No correlation was seen in the record from Ladd Lake core implying that productivity alone was not controlling the isotope ratio. Where negative covariance is evidenced a longer period of lake stratification may be implied wherein relatively little of the production is sedimented (Schelske and Hodell 1991). Alternatively, a re-mixing and consumption of sedimented organic carbon and rapid equilibration throughout the water column may account for the negative correlation while very little of the net production is sedimented at Lake Winnebago. In the Ladd Lake core, a fine resolution analysis was carried out which indicated a possible anthropogenic influence on the isotope ratio around time periods when human settlement

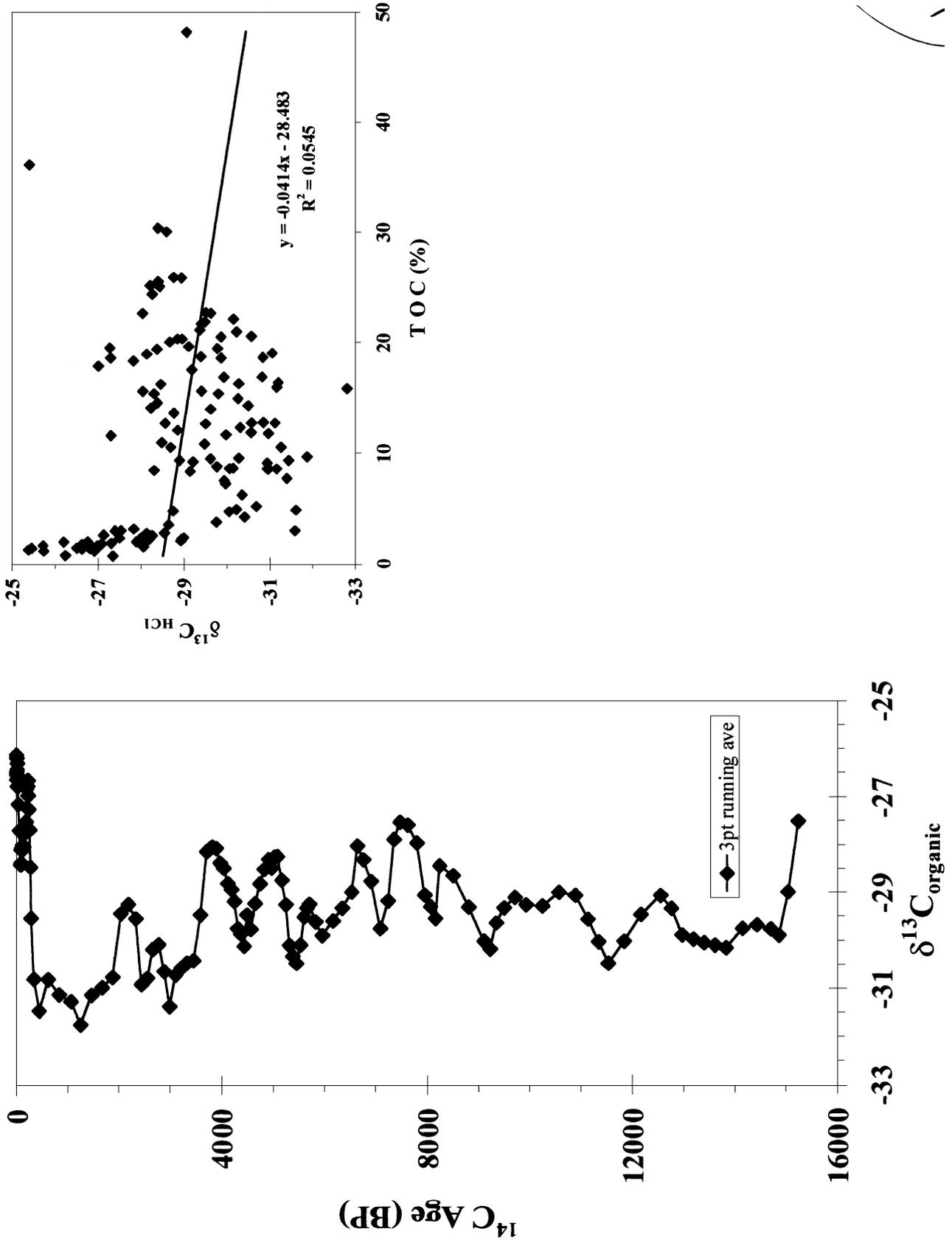


Figure 5. Ladd Lake $\delta^{13}\text{C}_{\text{Organic}}$ vs. ^{14}C Age and regression of $\delta^{13}\text{C}$ vs. total organic carbon for the HCl residual organic material.

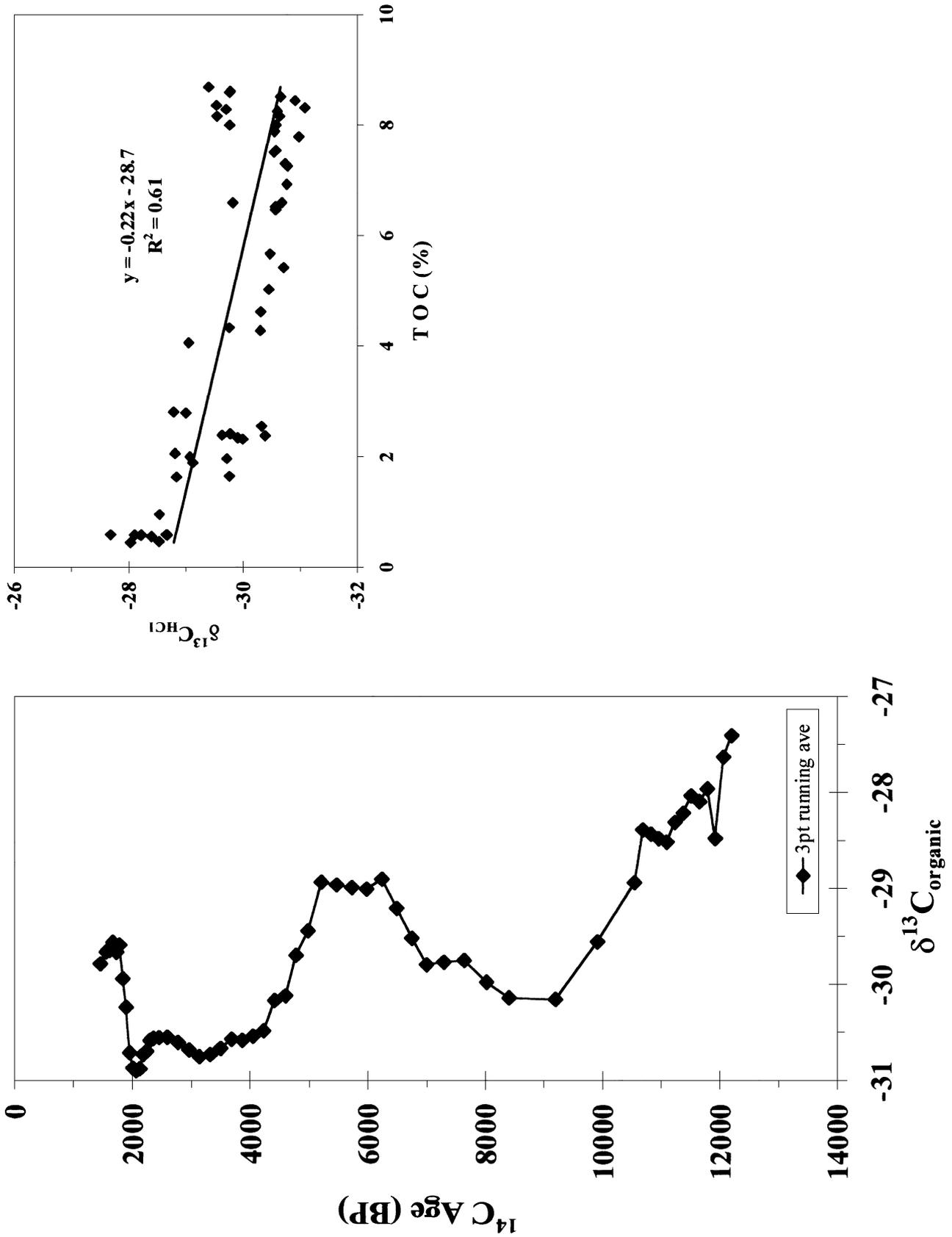


Figure 6. Lake Winnebago $\delta^{13}\text{C}_{\text{Organic}}$ vs. ^{14}C Age and regression of $\delta^{13}\text{C}$ vs. total organic carbon for the HCl residual organic material.

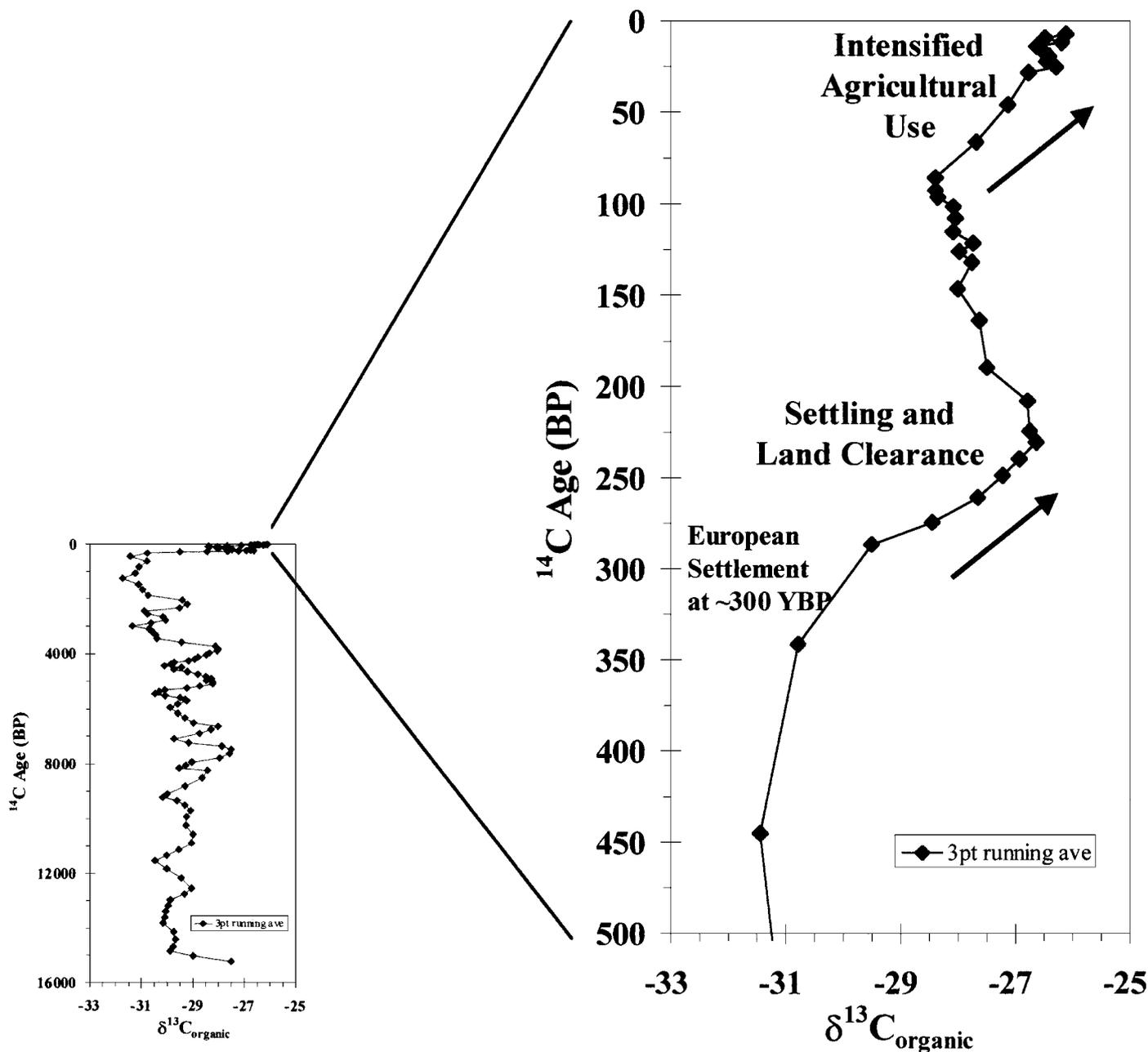


Figure 7. Plot of the $\delta^{13}C_{HCl}$ over the most recent 500 years (exploded view) from the Ladd Lake samples.

(~300 yrs ago) and enhanced agricultural practices (~80 yrs ago) were significant. The study shows that carbon isotope studies are useful in paleolimnologic investigations.

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