

## Radiocarbon and stable carbon isotopic insights into provenance and cycling of carbon in Lake Superior

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### *Abstract*

This study applies radiocarbon and stable carbon isotopic distributions to investigate carbon sources and cycling within Lake Superior. We report the radiocarbon ( $\Delta^{14}\text{C}$ ) and stable carbon isotope ( $\delta^{13}\text{C}$ ) values and the carbon concentrations within dissolved organic carbon (DOC), particulate organic carbon (POC), and dissolved inorganic carbon (DIC) in the lake's western basin water column. Samples were taken during spring mixing and late-summer thermal stratification over a 2-yr period (2007–2009). Distinct processes operating in the surface (photosynthesis) and deep waters (sediment resuspension and pore-water intrusion) control the relative contribution of modern and ancient DOC and POC in the water column. The terrigenous carbon input to the open lake POC varied from  $13\% \pm 4\%$  during late summer stratification to  $9\% \pm 3\%$  during spring mixing, with most of the terrestrial carbon being  $^{14}\text{C}$ -enriched (modern). The DIC reservoir cycles rapidly, with a bulk  $\Delta^{14}\text{C}_{\text{DIC}}$  value that records atmospheric radiocarbon levels from 3 yr prior to sampling. The DOC pool recycles on a longer time scale than does the DIC, with a DOC residence time of  $\leq 60$  yr. The suspended POC was in most cases older than co-occurring DOC, most likely as a result of resuspension of lake sediments.

The biogeochemical cycling of carbon (C) in aquatic ecosystems has gained increased attention in the past few decades as a result of global climate changes encompassing increases in atmospheric  $\text{CO}_2$ , potential hydrologic accelerations, and additional attendant ecosystem changes. As a result of their proximity to terrestrial environments and the associated delivery of allochthonous organic carbon (OC), inland aquatic systems can function simultaneously as both sinks and sources of atmospheric  $\text{CO}_2$  (Cole et al. 2007). Multiple biogeochemical processes, such as carbonate buffering, heterotrophic respiration, and sedimentary sequestration of OC, allow inland aquatic systems such as Lake Superior to outgas  $\text{CO}_2$  to the atmosphere while concurrently burying OC at depth (Kritzberg et al. 2005; Urban et al. 2005). The bioavailability and cycling of carbon is also important in within-ecosystem processes, as inorganic carbon is a basic building block for autotrophy and because labile OC provides necessary carbon and energy sources for heterotrophy.

The in situ biological and chemical transformations of OC in aquatic systems are largely dependent on its source, physical packaging (e.g., mineral associations), and prior diagenetic alterations in both the water column and surface sediments (Kaiser et al. 2004). However, the sources and processing of OC are poorly constrained in many ocean, river, and lake systems, even though delineating these is critical to understanding their transformation pathways

and ultimate fate. For instance, even though considerable evidence exists for transport of terrestrial OC to the oceans (Opsahl and Benner 1997), rivers (Raymond and Cole 2003), and lakes (Cole and Caraco 2001), the fate of terrestrial OC in these ecosystems is not well known.

Natural abundance stable and/or radiocarbon isotopes have been useful for studying OC sources and carbon cycling in the oceans (Druffel et al. 1992; Bauer et al. 2002), estuaries (Peterson et al. 1994), rivers (Raymond and Bauer 2001; Kaiser et al. 2004), and lakes (Karlsson et al. 2007; McCallister and del Giorgio 2008). The decadal-scale resolution added by the spike in  $\Delta^{14}\text{C}$  resulting from 1950s aboveground nuclear testing has been employed to study C cycling and turnover in both terrestrial and aquatic environments (McCallister et al. 2004; Trumbore 2009) and has provided an additional timescale to that offered by radioactive decay methods. While such studies of 'modern' processes in aquatic ecosystems have yielded insight into C transformation and cycling, to date there has not been a radiocarbon study investigating carbon cycling in any of the great lakes of the world, including the Laurentian Great Lakes of North America (Cotner et al. 2004). Therefore, this study (a time series from an open-lake [OL] station and a nearshore site in Lake Superior) was designed to assess sources, ages, and relative reactivity of particulate and dissolved OC (POC and DOC, respectively) in a temperate and relatively pristine large lake and to compare the stable-carbon and radiocarbon isotopic composition of lake OC with that of co-occurring dissolved inorganic carbon (DIC).

Lake Superior is the Earth's largest freshwater lake by surface area ( $8.2 \times 10^{10}$  m<sup>2</sup>), with maximum and mean depths of, respectively, 406 m and 150 m (Urban et al.

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2005). The lake is biogeochemically similar to open-ocean locations as a result of its oligotrophic nature, low terrestrial nutrient loading, and the dominance of its microbial food web on carbon cycling (Cotner et al. 2004). However, unlike the oceans, Lake Superior is dimictic; thus, there is density-driven complete vertical mixing of the water column in spring and early winter each year, which homogenizes the water column. The dimictic nature of Lake Superior provides a unique opportunity to study how organic matter (OM) from different allochthonous and autochthonous sources can vary in processing and reactivity on short timescales (annual to decadal), an aspect of OM dynamics that is not amenable to in situ study in the oceans since exchange of OM between surface and deep waters generally occurs over very long timescales (McNichol and Aluwihare 2007).

## Methods

**Sampling**—Multiple cruises were undertaken on the R/V *Blue Heron* to sample the thermally stratified water column in August or September 2007, 2008, and 2009 and the isothermal (mixed) water column in May or June 2008 and 2009.

Water samples were collected from an OL site ( $47^{\circ}19.20'N$ ,  $89^{\circ}49.49'W$ ), chosen to take advantage of data from a National Oceanic and Atmospheric Administration buoy (National Data Buoy Center Sta. 45006), from sediment trap moorings within 1–2 km of the site, and from a nearshore site (site Baptism River [BR]:  $47^{\circ}19.95'N$ ,  $91^{\circ}11.51'W$ ) just offshore of the Baptism River in the western arm of Lake Superior (Fig. 1). At the offshore site (total water depth approximately 165 m), three water depths were sampled each time: the surface (5 m), the depth of the summer deep chlorophyll maximum (DCM) (30 m), and the deep hypolimnion (127 m). The nearshore site (total water depth  $\sim 21$  m) was sampled only at 5 m.

Water samples were collected via Niskin bottles mounted on a Seabird model 911 plus conductivity, temperature, and depth rosette equipped with fluorometer, transmissometer, dissolved oxygen sensor, photosynthetically active radiation sensor, pH meter, and altimeter. DIC samples were taken directly from the Niskin bottles by rinsing three times with sample and then overflowing 2 volumes of the unfiltered water into previously acid-cleaned and combusted ( $450^{\circ}C$  for 4 h) 500-mL amber Pyrex bottles. Note that these are technically total inorganic carbon samples, but Lake Superior water does not contain measurable particulate inorganic carbon. After removing a known and consistent headspace, the samples were immediately preserved with saturated mercuric chloride solution, sealed airtight with glass stoppers coated with Apiezon grease, and stored at room temperature in the dark.

Water samples for POC and DOC were filtered through pre-combusted Whatman GF/F glass-fiber filters ( $450^{\circ}C$  for 4 h;  $0.7\text{-}\mu\text{m}$  nominal pore size) via nitrogen-pressurized stainless-steel canisters. For each DOC sample for radiocarbon analysis, approximately 1 liter of the resulting filtrate was collected into an acid-leached and combusted glass bottle. For each DOC concentration measurement,

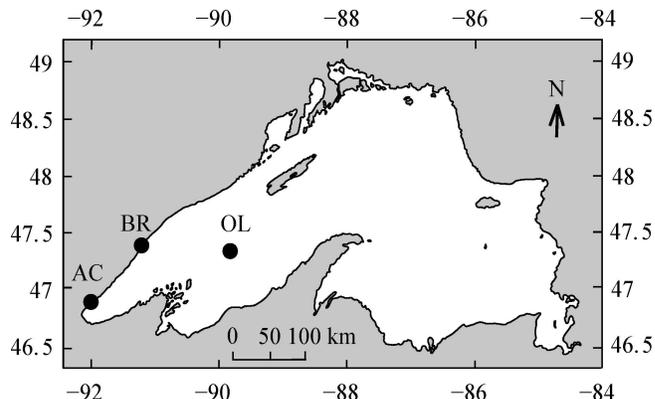


Fig. 1. Map showing sampling sites: Open-Lake Superior (OL), Baptism River (BR), and Amity Creek (AC).

approximately 40 mL of the filtrate was collected into an amber glass vial (previously acid leached and combusted). Both types of DOC samples were preserved by acidifying to pH 2 (using  $6\text{ mol L}^{-1}$  HCl, American Chemical Society [ACS] Plus grade) and were stored refrigerated. After  $\sim 10$  liters of lake water had passed through a GF/F filter, the filter and retained particulate matter was removed from the stainless-steel holder, folded, placed in previously combusted aluminum foil, and stored frozen until analysis.

To ensure that our sampling techniques are appropriately clean, a large-volume ultrapure water (Millipore Milli-Q Plus) blank was processed by filtering through the canister setup. This large-volume blank consisted of  $> 100$  liters of Milli-Q water (note that this is 10 times the volume of lake water filtered for POC samples) and was designed to provide enough carbon for a radiocarbon measurement.

Sediment cores from the OL site were taken in October 2008 and in June and August 2009 using an Ocean Instruments multi-corer. Upon recovery, the overlying water was collected via acid-cleaned syringe to just above the flocculant layer, and sediments (with the flocculant layer included in the first section) were sectioned at 2-cm resolution, with the depth 'slices' placed in pre-combusted glass jars and stored refrigerated for the duration of the cruise. Upon return to shore, within 9 d of coring, the overlying water DOC and sedimentary pore-water DOC from each depth slice were obtained by centrifuging and filtering the supernatant through pre-combusted glass-fiber filters. These pore-water DOC samples were then acidified to pH 2 and stored refrigerated until analysis.

Mesozooplankton samples were collected at site OL via vertical net tows (using a  $300\text{-}\mu\text{m}$  mesh net) from 50 m to the water surface. Sampling was done at night, thus taking advantage of zooplankton diurnal migration patterns and maximizing biomass collection for radiocarbon analysis. The biomass was rinsed with lake water into the cod end of the net and concentrated onto glass-fiber filters (pre-combusted GF/F filters,  $0.7\text{-}\mu\text{m}$  pore size), which were placed in combusted aluminum foil and stored frozen.

Amity Creek was sampled just above its confluence with the Lester River in June and September 2008 during storm-

flow and base-flow conditions, respectively. Amity Creek drains a small, primarily forested watershed in the western arm of Lake Superior. It flows into the Lester River less than 0.5 km before that river enters western Lake Superior and is conveniently located near the Large Lakes Observatory. Base-flow samples were taken as grab samples using acid-cleaned carboys, while storm-flow samples were taken using a Sigma 900 autosampler holding 24 acid-cleaned sample containers, with sampling triggered by stage height changes, as determined by a pressure sensor. Whole water samples were removed from the autosampler within 24 h of the storm event. Both base-flow and storm-flow samples were filtered through previously combusted GF/F filters to isolate POC vs. DOC. The base-flow DIC sample was collected by overflowing 2 volumes of the unfiltered water into previously acid-cleaned and combusted amber Pyrex bottles. After removal of a known headspace, the sample was preserved with saturated mercuric chloride solution, air-tight sealed, and stored at room temperature in the dark until analysis.

In September 2009, corn leaves (*Zea mays*) were collected from the watershed of western Lake Superior in order to determine the radiocarbon content of atmospheric CO<sub>2</sub>. The sampling site was chosen to minimize fossil contamination (i.e., by avoiding highways). The collected leaves were stored in perforated paper envelopes and refrigerated.

All sampling activities were carried out carefully to avoid <sup>14</sup>C contamination. Powder-free nitrile gloves were used during sampling. Plastic tubing (silicone, Teflon, and polypropylene) was rigorously cleaned with dilute HCl and rinsed with ~ 10 liters of distilled water. All other plasticware was cleaned with soap and distilled water, leached with 10% (by volume) HCl in water, and then rinsed with distilled water. Glassware was cleaned in the same manner, followed by combustion at 450°C for > 4 h. The R/V *Blue Heron* was free of <sup>14</sup>C contamination during a radiocarbon swipe test at the beginning of the project. Subsequent <sup>14</sup>C tracer work has been limited to a radiation van loaded and unloaded from the boat specifically for tracer work.

*Concentration measurements*—DOC concentrations were measured via high-temperature catalytic combustion on a Shimadzu total organic carbon Shimadzu TOC-VCSH analyzer, except for 2007 samples, which were analyzed by heated persulfate oxidation on an Oceanography International Corporation Analytical 1030 W TOC analyzer. Aliquots of the acidified DOC were bubbled with high-grade CO<sub>2</sub>-free air for 3.3 min to remove all inorganic carbon; 50 μL was then combusted at 680°C, and the evolved CO<sub>2</sub> was measured by a non-dispersive infrared (NDIR) detector. The TOC analyzer was calibrated using potassium hydrogen phthalate (KHP), and additional KHP standards were interspersed and analyzed along with the samples to assess instrumental performance. For each sample, three injections were performed. If the standard deviation was not ≤ 2.5%, two more injections were performed, and the closest three of the five injections were averaged to yield sample concentration (Minor and Stephens 2008).

DIC samples were also analyzed on the Shimadzu TOC-VCSH analyzer. In this case, the analyzer was calibrated using primary standard-grade sodium carbonate and ACS reagent grade sodium bicarbonate. The inorganic carbon in the sample was volatilized with 25% ACS grade H<sub>3</sub>PO<sub>4</sub> (by weight) in a CO<sub>2</sub>-free closed reaction vessel, and the CO<sub>2</sub> evolved was measured by the NDIR gas detector.

Suspended particulate organic matter (POM) samples were either freeze-dried or oven-dried to constant weight at 60°C and homogenized, fumigated with 12 mol L<sup>-1</sup> HCl (ACS Plus grade) overnight to remove carbonates, dried again, and cooled in a dessicator. They were then loaded into tin capsules and analyzed for POC and particulate organic nitrogen (PON) concentrations on a Costech ESC 4010 elemental analyzer.

*Radiocarbon and stable carbon isotope measurements*—All isotope measurements were performed at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) at the Woods Hole Oceanographic Institution, with the exception of the corn leaves sample, which was measured at the Keck Carbon Cycle AMS Facility (KCCAMS) at the University of California, Irvine. Most water-column and pore-water DOC samples were processed for radiocarbon measurement at NOSAMS by ultraviolet (UV) oxidation using a protocol based upon the work of Beaupre et al. (2007), but we oxidized for 3 h rather than 4 h. DOC samples from September 2007 were freeze-dried before combustion to CO<sub>2</sub>. With both approaches, the evolved CO<sub>2</sub> was trapped in a vacuum line, purified cryogenically, and reduced to graphite with H<sub>2</sub> over iron catalyst. A subsample of the purified CO<sub>2</sub> was collected for δ<sup>13</sup>C-DOC measurement.

Suspended POC and mesozooplankton biomass were oven-dried to constant weight at 60°C, fumigated with 12 mol L<sup>-1</sup> HCl (ACS Plus grade) for 24 h to remove carbonates, re-dried, and combusted to CO<sub>2</sub> in a modified Carlo Erba NA1500 elemental analyzer. The evolved CO<sub>2</sub> was separated from the carrier gas, cryogenically trapped, and stored in a modular manifold and was then reduced to graphite. A subsample of the purified CO<sub>2</sub> was taken for δ<sup>13</sup>C-POC measurement.

DIC samples were directly hydrolyzed with H<sub>3</sub>PO<sub>4</sub>, and the resulting CO<sub>2</sub> was stripped with nitrogen gas and trapped. The evolved CO<sub>2</sub> was cleaned cryogenically and reduced to graphite. A portion of the cleaned CO<sub>2</sub> was taken for δ<sup>13</sup>C-DIC measurement.

The radiocarbon content of atmospheric CO<sub>2</sub> was determined at KCCAMS using the protocol of Hsueh et al. (2007). The corn leaves sample was cleaned with ~ 5 liters (in five separate rinses) of Milli-Q water to remove extraneous particles on the leaves and dried to a constant weight for ~ 30 h at 60°C. The dried sample was homogenized, combusted to CO<sub>2</sub>, and graphitized as outlined in Santos et al. (2004). A subsample of the CO<sub>2</sub> from the corn leaves was taken for δ<sup>13</sup>C analysis at KCCAMS using a gas bench coupled to a Finnigan Delta Plus Isotope Ratio Mass Spectrometer.

In all cases, the graphite produced was compacted onto an aluminum cartridge target and analyzed by accelerator

Table 1. Concentrations of bulk DOC (< GF/F, approximately < 0.7  $\mu\text{m}$ ), DIC, POC, PON, and particulate C:N within the water column of Lake Superior covering thermally stratified and isothermal water conditions. Molar C:N of POM is based on the ratio of organic C to organic N. For this and later tables, R1 and R2 refer to replicates 1 and 2 from the same sample site and depth. Errors for DOC and DIC are based upon replicate injections, and errors for POC and PON are based upon analyses of multiple external standards. nd = not determined, either because sample was not collected or because sample was not measured.

Date and depth	DIC ( $\mu\text{mol C L}^{-1}$ )	DOC ( $\mu\text{mol C L}^{-1}$ )	POC ( $\mu\text{mol C L}^{-1}$ )	PON ( $\mu\text{mol N L}^{-1}$ )	POM molar C:N
Sep 07—stratified					
OL 5 m	nd	129.3 $\pm$ 4.9	8.7 $\pm$ 0.2	0.99 $\pm$ 0.04	8.8 $\pm$ 0.4
OL 30 m	nd	143.0 $\pm$ 4.0	10.6 $\pm$ 0.2	1.30 $\pm$ 0.06	8.2 $\pm$ 0.4
OL 127 m R1	nd	113.8 $\pm$ 5.0	2.5 $\pm$ 0.1	0.29 $\pm$ 0.01	8.8 $\pm$ 0.4
OL 127 m R2	nd	115.3 $\pm$ 4.8	3.1 $\pm$ 0.1	0.35 $\pm$ 0.02	8.9 $\pm$ 0.4
BR 5 m	nd	nd	nd	nd	nd
May 08—isothermal					
OL 5 m	819 $\pm$ 4	82.0 $\pm$ 2.1	6.4 $\pm$ 0.1	0.80 $\pm$ 0.02	8.0 $\pm$ 0.3
OL 30 m	815 $\pm$ 3	81.1 $\pm$ 2.0	7.7 $\pm$ 0.2	0.94 $\pm$ 0.02	8.2 $\pm$ 0.3
OL 127 m	809 $\pm$ 2	80.2 $\pm$ 0.6	6.5 $\pm$ 0.1	0.76 $\pm$ 0.02	8.5 $\pm$ 0.3
BR 5 m	813 $\pm$ 2	83.0 $\pm$ 0.8	9.2 $\pm$ 0.2	1.14 $\pm$ 0.03	8.1 $\pm$ 0.3
Sep 08—stratified					
OL 5 m	802 $\pm$ 3	102.4 $\pm$ 1.9	15.86 $\pm$ 0.05	1.70 $\pm$ 0.04	9.3 $\pm$ 0.2
OL 30 m	821 $\pm$ 3	92.5 $\pm$ 1.1	11.93 $\pm$ 0.04	1.56 $\pm$ 0.03	7.7 $\pm$ 0.2
OL 127 m	830 $\pm$ 3	92.8 $\pm$ 1.5	4.42 $\pm$ 0.01	0.49 $\pm$ 0.01	9.1 $\pm$ 0.2
BR 5 m	806 $\pm$ 3	106.3 $\pm$ 1.1	11.48 $\pm$ 0.04	1.44 $\pm$ 0.03	7.9 $\pm$ 0.2
Jun 09—isothermal					
OL 5 m	825 $\pm$ 3	94.2 $\pm$ 1.3	4.80 $\pm$ 0.03	0.66 $\pm$ 0.002	7.26 $\pm$ 0.04
OL 30 m	830 $\pm$ 2	93.3 $\pm$ 1.3	4.80 $\pm$ 0.03	0.57 $\pm$ 0.002	8.4 $\pm$ 0.1
OL 127 m	822 $\pm$ 2	93.3 $\pm$ 1.2	4.70 $\pm$ 0.03	0.62 $\pm$ 0.002	7.5 $\pm$ 0.1
BR 5 m	822 $\pm$ 2	110.8 $\pm$ 0.9	6.85 $\pm$ 0.04	0.72 $\pm$ 0.002	9.5 $\pm$ 0.1
Aug 09—stratified					
OL 5 m	807.5 $\pm$ 0.4	104.0 $\pm$ 1.9	12.0 $\pm$ 0.1	1.42 $\pm$ 0.002	8.4 $\pm$ 0.1
OL 30 m	826 $\pm$ 2	102.6 $\pm$ 2.6	9.6 $\pm$ 0.1	1.25 $\pm$ 0.002	7.69 $\pm$ 0.04
OL 127 m	831 $\pm$ 2	89.3 $\pm$ 1.3	2.93 $\pm$ 0.02	0.34 $\pm$ 0.001	8.7 $\pm$ 0.1
BR 5 m	789 $\pm$ 3	98.4 $\pm$ 2.7	13.4 $\pm$ 0.1	1.60 $\pm$ 0.003	8.4 $\pm$ 0.1

mass spectrometry (AMS), along with primary and secondary standards and combustion and graphitization process blanks. Radiocarbon values are reported as  $\Delta^{14}\text{C}$ , the part-per-thousand deviation of the sample's  $^{14}\text{C}:^{12}\text{C}$  ratio relative to a 19th-century wood standard that has been corrected to the activity it would have had in 1950 and a  $\delta^{13}\text{C}$  of  $-25\text{‰}$ .  $\Delta^{14}\text{C}$  was corrected for fractionation using  $\delta^{13}\text{C}$  of samples according to the convention of Stuiver and Polach (1977). Instrumental precision of  $\Delta^{14}\text{C}$  analysis was based on error of standards or multiple analyses on a target and ranged from 2‰ to 10‰. Total measurement uncertainties for  $\Delta^{14}\text{C}$  analyses based on measurement of duplicate natural samples were 6‰ for  $\Delta^{14}\text{C}$ -DIC and 16‰ for  $\Delta^{14}\text{C}$ -POC.

Combusting our large-volume blank POC sample generated 94.75  $\mu\text{mol}$  of C (or < 0.95  $\mu\text{mol C L}^{-1}$ ), enough carbon for a radiocarbon analysis, although this carbon would also include contributions from the Milli-Q water as well as the filtration apparatus. The  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values of the large-volume blank POC sample were  $-95\text{‰} \pm 3\text{‰}$  and  $-27.3\text{‰}$ , respectively. For additional comparison, combusting a clean GF/F filter generated 2.19  $\mu\text{mol}$  of C. While this GF/F blank did not provide sufficient carbon for a radiocarbon analysis, it may be

more representative of the amount of blank carbon in our samples, as it is not subject to the addition of carbon from 100 liters of Milli-Q water. Using this GF/F filter blank and our lowest concentration POC sample, our processing techniques contribute 9% or less to the carbon identified in POC samples. Estimates of blank carbon in our samples based upon the large-volume blank ranged from 6.0% to 37.7% of the carbon identified in our POC samples, and the resulting radiocarbon correction would shift samples an average of 23‰ (with a standard deviation of 15‰) toward more  $^{14}\text{C}$ -enriched values. Basic depth and locational trends remained similar in the blank-adjusted and measured  $\Delta^{14}\text{C}$  values but the extent of the depth variations is less strong in the blank-adjusted samples; note that blank adjustment more strongly affects the radiocarbon values in the deep-water, low-POC samples. Because we cannot be sure of the applicability of our blank carbon and radiocarbon values (as they contain carbon from the Milli-Q water as well from the processing apparatus), we discuss measured POC  $\Delta^{14}\text{C}$  values in the text that follows. The radiocarbon blank issue should be most severe with the POC samples (relative to DIC, DOC, and mesozooplankton samples), as they are by far the lowest in carbon concentration (*see* Table 1).

Stable carbon isotope ratios of samples (DOC, DIC, and POC) were measured at NOSAMS using an Optima stable isotope ratio mass spectrometer. Instrumental precision of  $\delta^{13}\text{C}$  analysis was 0.15‰, and total measurement average deviation based on analyses of duplicate natural samples was 0.15‰ and 0.48‰, respectively, for  $\delta^{13}\text{C}$ -DIC and  $\delta^{13}\text{C}$ -POC (Table 2). All stable carbon isotope ratios ( $^{13}\text{C}:^{12}\text{C}$ ) are reported as  $\delta^{13}\text{C}$ , which is the per-mil difference relative to Pee Dee Belemnite carbonate. The  $\delta$  notation is calculated as follows:  $\delta\text{Q} = [\text{R}_{\text{sample}}/\text{R}_{\text{standard}} - 1] \times 1000$ , where Q is  $^{13}\text{C}$  and R is  $^{13}\text{C}:^{12}\text{C}$ . The  $\delta^{13}\text{C}$ -POC values are reported here as measured without correction using the large-volume blank data.

*Proportion of pre-aged contents of POC ( $\text{POC}_p$ ) and DOC ( $\text{DOC}_p$ )*— $\text{POC}_p$  was estimated using a binary (pre-aged and modern) isotopic mixing model. The model is presented below, accounting for isotopic mass balance (Eq. 1) and conservation of mass (Eq. 2):

$$\Delta^{14}\text{C} \times [\text{POC}] = \Delta^{14}\text{C}_m \times [\text{POC}_m] + \Delta^{14}\text{C}_p \times [\text{POC}_p] \quad (1)$$

$$[\text{POC}] = [\text{POC}_m] + [\text{POC}_p] \quad (2)$$

where the subscripts “m” and “p” refer to modern and pre-aged, respectively. We used the  $\Delta^{14}\text{C}_{\text{DIC}}$  in the surface water as modern  $\Delta^{14}\text{C}$  (and assigned this value to POM derived from recent photosynthesis, based on Druffel et al. [1996] and Repeta and Aluwihare [2006]). As a conservative estimate, the pre-aged end-member was assigned a  $\Delta^{14}\text{C}$  value of  $-24\text{‰}$  (173 yr B.P.), equivalent to the hydrologic residence time (the average number of years that water stays in the lake based on volume divided by average net outflow rates) of the lake. Using our measured suspended  $\Delta^{14}\text{C}_{\text{POC}}$  values and POC concentrations, we calculated  $\text{POC}_p$  within bulk suspended POM at each depth. For comparison (as a sensitivity analysis), we also calculated  $\text{POC}_p$  using our large-volume blank-adjusted values for  $\Delta^{14}\text{C}_{\text{POC}}$ .  $\text{DOC}_p$  was calculated similarly, using measured [DOC] and  $\Delta^{14}\text{C}$  and the same estimates for  $\Delta^{14}\text{C}_m$  and  $\Delta^{14}\text{C}_p$  as in the  $\text{POC}_p$  calculation.

*Proportion of terrigenous content of POC ( $\text{POC}_T$ )*— $\text{POC}_T$  was estimated using a binary (terrigenous and autochthonous) mixing model as follows:

$$\text{C} : \text{N}_{\text{POM}} = f \times \text{C} : \text{N}_{\text{Terr}} + (1-f) \times \text{C} : \text{N}_{\text{Auto}} \quad (3)$$

where  $f$  is the fraction of terrigenous OC in the suspended POC,  $(1-f)$  is the fraction of autochthonous OC in the suspended POC, and the subscripts “Terr” and “Auto” refer to terrigenous and autochthonous, respectively. We used a molar carbon : nitrogen (C : N) ratio of 6.6 (based on the Redfield ratio [Redfield et al. 1963]) as representative of autochthonous OM sources. While we were unable to find values for the C : N ratio within Lake Superior phytoplankton, the range of ratios found within POM from Lake Superior (4.6–14.2; Sterner 2010) indicates that the Redfield ratio is a good first approximation. We applied a molar C : N ratio of 21 (Hoffman et al. 2010) for the terrigenous end-member.

Table 2. The  $\delta^{13}\text{C}$  compositions within the DIC, DOC, and POC in the water column of Lake Superior. Instrumental precision based on analyses of multiple external standards was 0.15‰. nd = not determined, either because sample was not collected or because sample was not measured.

Date and depth	DIC- $\delta^{13}\text{C}$ (‰)	POC- $\delta^{13}\text{C}$ (‰)	DOC- $\delta^{13}\text{C}$ (‰)
Sep 07—stratified			
OL 5 m	1.2	-27.2	-19.1*
OL 30 m	0.9	-29.5	-22.1*
OL 127 m R1	0.3	-29.5	-19.3*
OL 127 m R2	0.4	-30.0	-25.3*
BR 5 m	1.2	-28.1	nd
May 08—isothermal			
OL 5 m	0.2	-30.3	-26.4*
OL 30 m	0.5	-30.9	-25.7*
OL 127 m	0.5	-30.3	-27.5*
BR 5 m	0.5	-30.6	-25.4
Sep 08—stratified			
OL 5 m	1.5	-26.7	-25.6
OL 30 m	0.6	-29.4	-25.9
OL 127 m	0.2	-28.7	nd
BR 5 m	1.2	-27.4	-28.9*
Jun 09—isothermal			
OL 5 m	0.4	-29.2	-26.5
OL 30 m	0.3	-29.4	-26.4
OL 127 m	0.3	-29.9	-26.7
BR 5 m	0.3	-30.1	-26.1
Aug 09—stratified			
OL 5 m	1.3	-27.8	-26.1
OL 30 m	0.6	-29.7	-26.0
OL 127 m	0.2	-29.5	-25.8
BR 5 m	0.9	-28.3	-26.5

\* Based on measurement of freeze-dried DOC samples.

## Results

*Concentration of carbon pools*—The concentrations of DOC, POC, and PON showed temporal (seasonal) and spatial (lateral and depth profile) variations (Table 1). At the OL site, two distinct seasonal depth profiles of DOC, POC, and PON are distinguishable: one during thermal stratification and the other during isothermal or mixed conditions.

During isothermal conditions, the nearshore site (BR) exhibited slightly higher DOC concentrations than did the surface waters at the offshore site (OL) (Table 1). Similarly, the POC and PON concentrations were higher at BR than in the surface waters of OL (Table 1). At site OL, the concentrations in the isothermal condition were low and invariant across depth, with water-column surface-to-deep-water averages (and standard deviations) of  $81.1 (\pm 0.9) \mu\text{mol L}^{-1}$  of DOC,  $6.9 (\pm 0.7) \mu\text{mol L}^{-1}$  of POC, and  $0.8 (\pm 0.1) \mu\text{mol L}^{-1}$  of PON in May 2008 and  $93.6 (\pm 0.5) \mu\text{mol L}^{-1}$  of DOC,  $4.8 (\pm 0.1) \mu\text{mol L}^{-1}$  of POC, and  $0.6 (\pm 0.1) \mu\text{mol L}^{-1}$  of PON in June 2009 (Table 1).

During stratification, DOC concentrations at BR ( $107 \mu\text{mol L}^{-1}$  and  $98 \mu\text{mol L}^{-1}$ , respectively, in September 2008

and August 2009) were similar to the values at surface OL ( $102 \mu\text{mol L}^{-1}$  in September 2008 and  $104 \mu\text{mol L}^{-1}$  in August 2009) (Table 1). POC values at BR ( $11.5 \mu\text{mol L}^{-1}$  and  $13.4 \mu\text{mol L}^{-1}$ ) during the stratified period were similar to those seen in surface ( $15.9 \mu\text{mol L}^{-1}$  and  $12.0 \mu\text{mol L}^{-1}$ ) and chlorophyll maximum waters ( $11.9 \mu\text{mol L}^{-1}$  and  $9.6 \mu\text{mol L}^{-1}$ ) at the OL site (Table 1). For all samplings, surface concentrations of DOC, POC, and PON at site OL were higher during stratification than during isothermal periods (Table 1).

DIC concentrations in the water column at OL did not vary much with depth during isothermal conditions. The DIC values ranged from  $809 \mu\text{mol L}^{-1}$  to  $819 \mu\text{mol L}^{-1}$  in May 2008 and from  $822 \mu\text{mol L}^{-1}$  to  $830 \mu\text{mol L}^{-1}$  in June 2009 (Table 1). In the stratified months, DIC concentration increased with depth, from  $802 \mu\text{mol L}^{-1}$  at the surface to  $830 \mu\text{mol L}^{-1}$  in the deep waters in September 2008 and from  $807.5 \mu\text{mol L}^{-1}$  to  $831 \mu\text{mol L}^{-1}$  in August 2009 (Table 1).

The molar C:N ratios of suspended POM ( $\text{C:N}_{\text{POM}}$ ) in the lake from 2007 to 2009 did not exhibit consistent variation with depth or season (Table 1). Overall, the  $\text{C:N}_{\text{POM}}$  values in the lake ranged from 7.3 to 9.3 and from 7.1 to 9.5, respectively, at the OL and BR sites.

*Stable isotopic composition*—The  $\delta^{13}\text{C}$  of DIC ( $\delta^{13}\text{C}_{\text{DIC}}$ ) values were  $^{13}\text{C}$ -depleted progressively with depth at site OL during the stratified period. The  $\delta^{13}\text{C}_{\text{DIC}}$  values decreased from 1.2‰, 1.5‰, and 1.3‰ (average of  $1.3\text{‰} \pm 0.1\text{‰}$ ) in the surface waters to 0.4‰, 0.2‰, and 0.2‰ (average of  $0.2\text{‰} \pm 0.1\text{‰}$ ) in the deep waters, respectively, in September 2007, September 2008, and August 2009 (Table 2; Fig. 2). In the isothermal water column in spring,  $\delta^{13}\text{C}_{\text{DIC}}$  values at site OL were similar in both surface waters (0.2‰ in May 2008 and 0.4‰ in June 2009) and deep waters (0.5‰ in May 2008 and 0.3‰ in June 2009), giving water-column averages of  $0.4\text{‰} \pm 0.1\text{‰}$  in May 2008 and  $0.3\text{‰} \pm 0.1\text{‰}$  in June 2009. The  $\delta^{13}\text{C}_{\text{DIC}}$  at BR was more  $^{13}\text{C}$ -enriched in late summer (1.2‰, 1.2‰, and 0.9‰, respectively, in September 2007, September 2008, and August 2009) than in spring (0.5‰ and 0.3‰, respectively, in May 2008 and June 2009) (Table 2). The  $\delta^{13}\text{C}_{\text{DIC}}$  at BR was similar to that of surface OL samples during the stratified seasons and was similar to all OL samples during the isothermal samplings.

The distribution of  $\delta^{13}\text{C}_{\text{POC}}$  at site OL changed markedly with depth during the stratified seasons. Stratified-season  $\delta^{13}\text{C}_{\text{POC}}$  values at OL ranged from  $-27.8\text{‰}$  to  $-26.7\text{‰}$  in the surface waters, from  $-29.7\text{‰}$  to  $-29.4\text{‰}$  in the DCM, and from  $-29.8\text{‰}$  to  $-29.5\text{‰}$  in the deep waters (Table 2). In September 2008 and August 2009, the most  $^{13}\text{C}$ -depleted  $\delta^{13}\text{C}_{\text{POC}}$  values were observed in the DCM (Table 2). During spring isothermal condition, the  $\delta^{13}\text{C}_{\text{POC}}$  values were nearly invariant with depth, averaging  $-30.5\text{‰} \pm 0.4\text{‰}$  in May 2008 and  $-29.5\text{‰} \pm 0.3\text{‰}$  in June 2009 (Table 2). POC from the surface waters in the isothermal period exhibit more  $^{13}\text{C}$ -depleted values than did the corresponding stratified-period surface samples. Our data show a positive correlation between  $\delta^{13}\text{C}_{\text{POC}}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  ( $R^2 = 0.641$ ,  $p < 0.001$ ,  $n = 21$ ), with the relationship

strongly driven by stratified samples, especially those from surface water (at both BR and OL sites) and the DCM (Fig. 3).

The  $\delta^{13}\text{C}_{\text{DOC}}$  varied from  $-27.5\text{‰}$  to  $-25.7\text{‰}$  in the well-mixed lake at site OL in May 2008 and June 2009 (Table 2). In the stratified lake, the September 2007 DOC samples, which were freeze-dried, were more  $^{13}\text{C}$ -enriched (surface to deep water ranged from  $-25.3\text{‰}$  to  $-19.1\text{‰}$ ) than the samples from September 2008 (ranged from  $-25.9\text{‰}$  to  $-25.6\text{‰}$ ) and August 2009 (ranged from  $-26.1\text{‰}$  to  $-25.8\text{‰}$ ). Our data show no distinct  $\delta^{13}\text{C}_{\text{DOC}}$  depth profiles during the stratified period, in contrast to  $\delta^{13}\text{C}_{\text{POC}}$  (Table 2). The  $\delta^{13}\text{C}_{\text{DOC}}$  values at the BR site ( $-28.9\text{‰}$  in September 2008 and  $-26.5\text{‰}$  in August 2009) are more  $^{13}\text{C}$ -depleted relative to the corresponding values in the surface waters at OL ( $-25.6\text{‰}$  and  $-26.1\text{‰}$ ; Table 2).

*The  $\Delta^{14}\text{C}$  signatures of carbon pools*—The  $\Delta^{14}\text{C}$  value of atmospheric  $\text{CO}_2$  ( $\Delta^{14}\text{C}_{\text{Atm CO}_2}$ ) in the Lake Superior watershed, as integrated in the leaves of an annual plant (corn), was  $38\text{‰} \pm 2\text{‰}$  in September 2009. Hsueh et al. (2007) reported a  $\Delta^{14}\text{C}$  value of  $65\text{‰} \pm 2\text{‰}$  for corn leaves collected at the western basin of the lake in summer 2004, implying that the mean annual decline rate of  $\Delta^{14}\text{C}_{\text{Atm CO}_2}$  had been  $4.5\text{--}6.0\text{‰ yr}^{-1}$  over the past 5 yr. The  $\Delta^{14}\text{C}_{\text{DIC}}$  values in the surface waters at site OL during the stratified period were 83‰, 69‰, and 61‰, respectively, in 2007, 2008, and 2009 (Table 3; Fig. 4), revealing a mean  $\Delta^{14}\text{C}$  decline rate of  $\sim 11\text{‰ yr}^{-1}$ . The  $\Delta^{14}\text{C}_{\text{DIC}}$  values in the deep waters at OL showed a similar decline, from 74‰ in 2007 to 52‰ in 2009. There were no significant variations in  $\Delta^{14}\text{C}_{\text{DIC}}$  as a function of depth within the current precision of AMS ( $2\text{--}7\text{‰}$ ; Turnbull et al. 2006; McNichol and Aluwihare 2007), implying thorough mixing between the surface and deep-water DIC.

The  $\Delta^{14}\text{C}$  values of POC at site OL varied as a function of depth (Fig. 2; Table 3). POC in the surface waters during stratification (61‰, 48‰, and 33‰, respectively, in September 2007, September 2008, and August 2009) was more  $^{14}\text{C}$ -enriched than was corresponding deep-water POC (12‰, 10‰, and  $-17\text{‰}$ , respectively, in September 2007, September 2008, and August 2009) and was closer to co-occurring  $\Delta^{14}\text{C}_{\text{DIC}}$  levels (Table 3). The  $\Delta^{14}\text{C}$  values of deep-water POC were  $^{14}\text{C}$ -depleted to a greater extent than the co-occurring DIC in the stratified lake. The decline rate of surface-water  $\Delta^{14}\text{C}_{\text{POC}}$  in the stratified lake from 2007 to 2009 ( $\sim 14\text{‰ yr}^{-1}$ ) was similar to that of  $\Delta^{14}\text{C}_{\text{DIC}}$ . Correlation analysis indicates a positive linear relationship between the  $\Delta^{14}\text{C}$  in POC and DIC at site OL, with 41% (based on coefficient of determination,  $R^2$  of 0.41) of  $\Delta^{14}\text{C}_{\text{POC}}$  variation predicted by  $\Delta^{14}\text{C}_{\text{DIC}}$ .

Measured  $\Delta^{14}\text{C}_{\text{POC}}$  values were generally more  $^{14}\text{C}$ -depleted than  $\Delta^{14}\text{C}_{\text{DOC}}$ . Exceptions include one deep-water sample in September 2007 in which the DOC was more  $^{14}\text{C}$ -depleted ( $-77\text{‰}$ ) and two samples from the May 2008 isothermal sampling, in which the DOC and POC were not significantly different in  $\Delta^{14}\text{C}$ . (Large-volume blank-adjusted  $\Delta^{14}\text{C}_{\text{POC}}$  values were closer to those of  $\Delta^{14}\text{C}_{\text{DOC}}$ , but the blank-adjusted  $\Delta^{14}\text{C}_{\text{POC}}$  remained  $^{14}\text{C}$ -depleted relative to the corresponding measured  $\Delta^{14}\text{C}_{\text{DOC}}$  values in many of

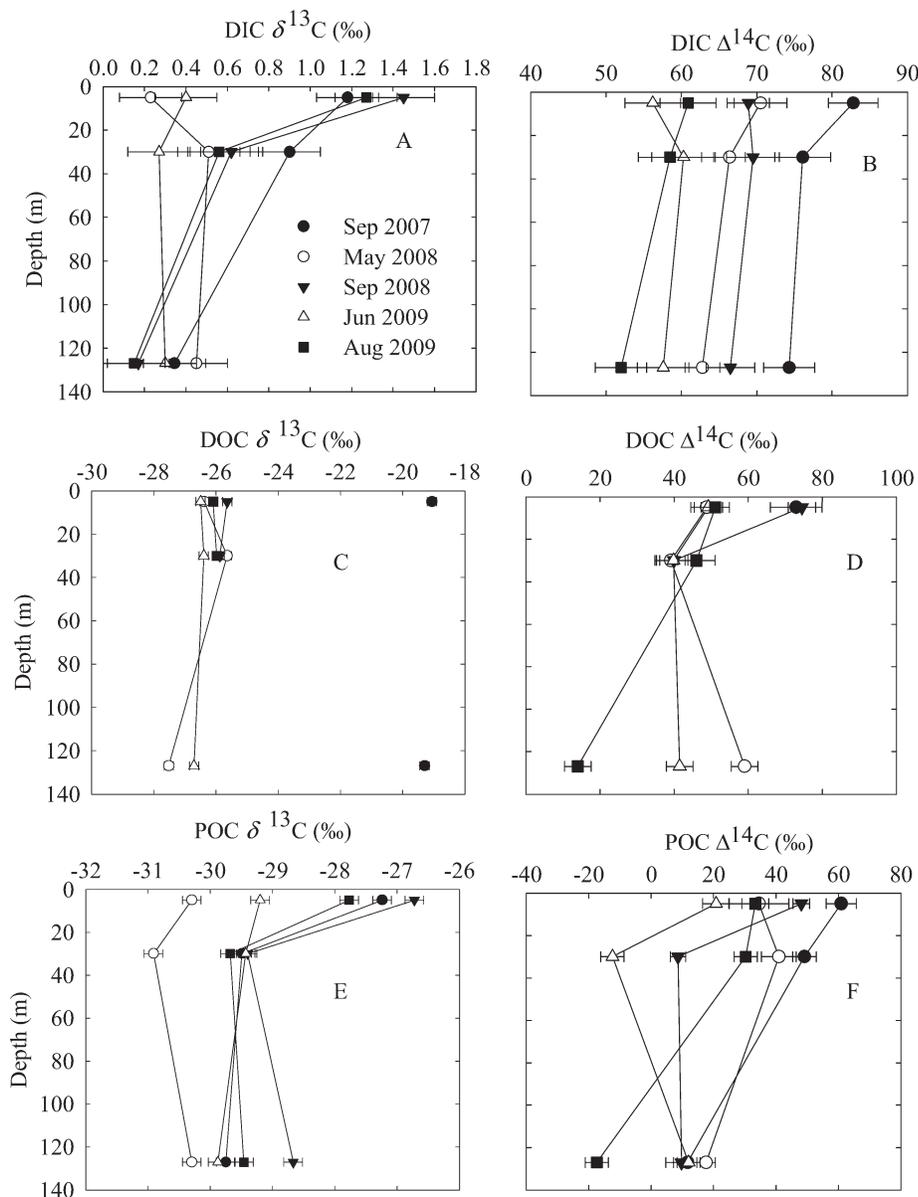


Fig. 2. The depth profiles of  $\delta^{13}\text{C}$  within (A) DIC, (C) DOC, and (E) POC and depth profiles of  $\Delta^{14}\text{C}$  within (B) DIC, (D) DOC, and (F) POC in the water column of Lake Superior. The data from May 2008 and June 2009 are for the isothermal (mixed) condition, whereas September 2007, September 2008, and August 2009 data are for a thermally stratified water column, as noted in Table 1. Instrumental error bars are based on analyses of standards or multiple analyses on a target for  $\Delta^{14}\text{C}$  and analyses of multiple external standards for  $\delta^{13}\text{C}$ .

the samples). The DOC was more  $^{14}\text{C}$ -enriched (51–73‰) in the surface waters and  $^{14}\text{C}$ -depleted in the deep waters (–77‰ to 14‰) during the stratified periods in 2007 to 2009 (Table 3).

Correlation between  $\Delta^{14}\text{C}_{\text{DOC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  indicated a positive relationship, with  $\sim 52\%$  ( $R^2 = 0.52$ ) of the  $\Delta^{14}\text{C}$  variation in DOC accounted for by DIC when the anomalous deep-water  $\Delta^{14}\text{C}_{\text{DOC}}$  value of –77‰ was excluded. The DOC in the surface waters at OL during stratification in September 2008 and August 2009 was more  $^{14}\text{C}$ -depleted compared to DOC from the nearshore BR site (Table 3).

*Sedimentary pore-water DOC*—At site OL, concentrations of DOC were somewhat higher in the surficial sediments (0–2 cm) in June 2009 ( $108 \mu\text{mol L}^{-1}$ ) and much higher in August 2009 ( $395 \mu\text{mol L}^{-1}$ ) than in the immediately overlying water in direct contact with the sediments ( $102 \mu\text{mol L}^{-1}$  in June 2009 and  $118 \mu\text{mol L}^{-1}$  in August 2009) (Table 4). The pore-water DOC from surficial sediments (0–2 cm) was considerably depleted in  $^{14}\text{C}$  relative to the water column in the lake. The  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values of the pore-water DOC (0–2 cm) were, respectively, –302‰ and –35.6‰ in June 2009 and –158‰ and –33.3‰ in August 2009 (Table 4).

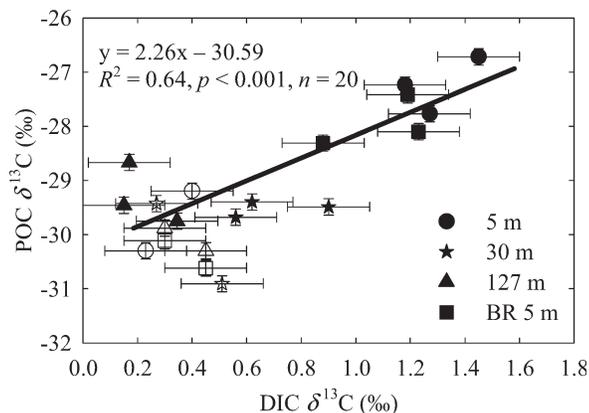


Fig. 3. Plot of  $\delta^{13}\text{C}$  in POC vs. DIC. Linear regression shows strong relationship. As is the case for all subsequent plots, the filled symbols are for stratified lake data, and the open symbols are for isothermal data.

*Amity Creek*—We determined the concentrations and isotopic compositions of Amity Creek carbon coming into the lake in order to assess its varying nature and, thus, potential allochthonous inputs from North Shore streams into western Lake Superior. Amity Creek DOC concentrations were  $489 \mu\text{mol L}^{-1}$  during base flow in September

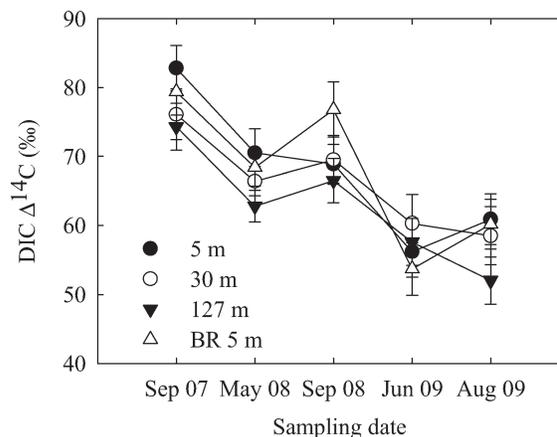


Fig. 4. The  $\Delta^{14}\text{C}$  within lake water DIC showing decline over time.

2008 and as high as  $885 \mu\text{mol L}^{-1}$  at the same sampling location during a storm event in June 2008 (Table 5). Base-flow DIC concentration at the creek was  $2421 \mu\text{mol L}^{-1}$ , and DIC was the largest carbon pool at this sampling time.

The  $\delta^{13}\text{C}$  composition of DOC in the creek ( $-28.6\text{‰}$  to  $-28.1\text{‰}$ ) did not vary much as a function of flow rate (Table 5). In contrast, the  $\Delta^{14}\text{C}$  of DOC was  $^{14}\text{C}$ -enriched

Table 3.  $\Delta^{14}\text{C}$  within bulk DIC, DOC, and POC in the water column of Lake Superior. The precisions are based on error of standards or of multiple analyses on a target. The values in parentheses represent radiocarbon ages in B.P. years; all other values are modern (post-1950). nd = not determined, either because sample was not collected or because sample was not measured.

Date and depth	DIC- $\Delta^{14}\text{C}$ (‰)	POC- $\Delta^{14}\text{C}$ (‰)	DOC- $\Delta^{14}\text{C}$ (‰)
Sep 07—stratified			
OL 5 m	$83 \pm 3$	$61 \pm 5$	$73 \pm 7^*$
OL 30 m	$76 \pm 4$	$49 \pm 4$	nd
OL 127 m R1	$74 \pm 3$	$12 \pm 7$	$-77 \pm 7^*(585 \pm 60)$
OL 127 m R2	$80 \pm 3$	$28 \pm 6$	nd
BR 5 m	$79 \pm 3$	$31 \pm 4$	nd
May 08—isothermal			
OL 5 m	$71 \pm 4$	$35 \pm 10$	$49 \pm 4^*$
OL 30 m	$66 \pm 2$	$41 \pm 6$	$39 \pm 4^*$
OL 127 m	$63 \pm 2$	$18 \pm 3$	$59 \pm 4^*$
BR 5 m	$68 \pm 3$	$40 \pm 5$	$43 \pm 4$
Sep 08—stratified			
OL 5 m	$69 \pm 3$	$48 \pm 3$	$75 \pm 4$
OL 30 m	$70 \pm 4$	$9 \pm 3$	$40 \pm 4$
OL 127 m	$67 \pm 3$	$10 \pm 3$	nd
BR 5 m	$77 \pm 4$	$53 \pm 3$	$78 \pm 4$
Jun 09—isothermal			
OL 5 m	$56 \pm 4$	$21 \pm 4$	$49 \pm 4$
OL 30 m	$60 \pm 4$	$-12 \pm 4(45 \pm 30)$	$40 \pm 5$
OL 127 m	$58 \pm 3$	$12 \pm 4$	$42 \pm 4$
BR 5 m	$54 \pm 4$	$14 \pm 4$	$38 \pm 4$
Aug 09—stratified			
OL 5 m	$61 \pm 4$	$33 \pm 4$	$51 \pm 4$
OL 30 m	$59 \pm 4$	$30 \pm 4$	$46 \pm 5$
OL 127 m	$52 \pm 3$	$-17 \pm 4(85 \pm 25)$	$14 \pm 4$
BR 5 m	$60 \pm 4$	$7 \pm 3$	$74 \pm 4$

\* Based on measurement of freeze-dried DOC samples.

Table 4. Sedimentary pore-water DOC concentrations and surface pore-water DOC isotopic compositions in Lake Superior. Isotopic compositions were determined on only 0–2-cm sediment slices (which include unconsolidated material; i.e., the flocculant layer) from October 2008, June 2009, and August 2009. DOC errors are based on multiple injections, and isotopic errors are based on instrumental precision. OW = refers to water overlying the sediments and collected within the multicore tube. nd = not determined, either because sample was not collected or because sample was not measured.

Depth (cm)	$\mu\text{mol C L}^{-1}$	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)
Oct 08			
OW	nd	nd	nd
1–2	93±1	nd	nd
2–3	145±2	nd	nd
3–4	355±2	nd	nd
Jun 09			
OW	102±2	nd	nd
0–2	108±2	−35.6±0.2	−302±5
2–4	301±3	nd	nd
Aug 09			
OW	118±1	nd	nd
0–2	395±4	−33.3±0.2	−158±5

with flow rate, increasing from −13‰ during base flow in September 2008 to 62‰ during storm flow in June 2008. The  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  values were −10.9‰ and 21‰, respectively, during base flow in September 2008 (Table 5). The DIC was  $^{14}\text{C}$ -depleted by ~ 18‰ relative to the  $\Delta^{14}\text{C}$  value of atmospheric  $\text{CO}_2$ . The POC pool was more  $^{14}\text{C}$ -depleted than creek DOC during the June 2008 storm event.

*Mesozooplankton*—The  $\delta^{13}\text{C}$  values of mesozooplankton biomass ( $\delta^{13}\text{C}_{\text{Zoop}}$ ) were −29.7‰ and −31.0‰ in June and August 2009, respectively (Table 6). The  $\Delta^{14}\text{C}_{\text{Zoop}}$  values (57‰ and 62‰; Table 6) were nearly the same as  $\Delta^{14}\text{C}_{\text{DIC}}$  values (56‰ and 61‰) in June and August 2009, but more  $^{14}\text{C}$ -enriched than co-occurring POC.

*Pre-aged and terrigenous carbon compositions*—Based upon our mixing model and measured  $\Delta^{14}\text{C}_{\text{POC}}$  values, the proportion of pre-aged materials in the surface-water POC samples during stratification was 20%, 22%, and 32%, respectively, in September 2007, September 2008, and

August 2009. These values increased, respectively, to 66%, 63%, and 92% in the deep-water POC (Table 7). Using large-volume blank-adjusted  $\Delta^{14}\text{C}_{\text{POC}}$  values shifts the pre-aged proportion in both surface-water and deep-water POC during stratification and increases the scatter, with surface-water values of 3%, 13%, and 22% and deep-water values of 6%, 33%, and 65%. The proportions of pre-aged materials at BR, based upon measured values, were 17% in September 2008 and 63% in August 2009 (Table 7), and based upon large-volume blank-corrected values, proportions were 3% and 35%, respectively.

For the DOC, during stratification the pre-aged content increased from 9% (September 2007) and 11% (August 2009) in the surface water to values ranging from 55% (August 2009) to 74% (September 2008) in the deep water (Table 7).

The DOC in the isothermal water column showed a similar proportion of pre-aged carbon throughout the water column at site OL (Table 7), consistent with what would be expected from water-column mixing. The pre-aged proportion of POC showed a less strong relationship with depth during isothermal conditions but was higher in surface waters in comparison to the stratified periods.

The contribution of terrestrial carbon to the POC pool at site BR from four samplings from September 2008 to August 2009 ranged from 0.9 to 1.6  $\mu\text{mol C L}^{-1}$  (Table 7) and was consistently higher relative to the samples from OL, as would be expected as a result of the proximity to shore (Table 7). However, this did not necessarily translate into a higher proportion of terrigenous carbon because of the correspondingly high aquatic primary productivity at site BR. The terrestrial carbon concentrations at OL during stratification decreased with depth in the water column, although the percentage of POC considered terrestrial increased from the DCM to the deep water. The averages of concentrations of terrestrial carbon from the three stratified samplings in September 2007, September 2008, and August 2009 were  $2.0 \pm 0.9 \mu\text{mol C L}^{-1}$  (16% ± 3%) in the surface-water POC,  $0.9 \pm 0.2 \mu\text{mol C L}^{-1}$  (9% ± 2%) in the DCM, and  $0.5 \pm 0.2 \mu\text{mol C L}^{-1}$  (16% ± 1%) in the deep-water POC (Table 7). Our calculated water-column (surface-to-deep-water) average values for terrigenous carbon subsidy to the OL POC was 13% ± 4% during late-summer stratification for the three stratified periods (August 2007, September 2008, and August 2009) and 9% ± 3% during the two spring mixing periods (May 2008 and June 2009). There was a positive relationship

Table 5.  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  and concentration of DIC, DOC, and POC in Amity Creek. DIC and DOC concentration errors are based upon replicate injections, and POC concentration error is based on analyses of multiple external standards. Values in parentheses represent radiocarbon ages in B.P. years.

Carbon pool	Date	Water height (cm)	$\mu\text{mol C L}^{-1}$	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)
Base-flow DIC	13 Sep 2008	~41	2421±4	−10.9	21±3
Base-flow DOC	13 Sep 2008	~41	489±8	−28.5	−13±4(45±35)
Storm-flow DOC	12 Jun 2008	53	825±8	−28.1	51±4
Storm-flow DOC	12 Jun 2008	98	885±8	−28.6	62±4
Storm-flow POC	12 Jun 2008	53	352±1	−27.3	11±2

Table 6.  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  within pelagic mesozooplankton. The surface POC and DIC values from Table 3 are included here for comparison to mesozooplankton values in order to assess food sources for mesozooplankton biomass production.

	Jun 2009		Aug 2009	
	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)
Surface POC	-29.2	21±4	-27.8	33±4
Zooplankton	-29.7	57±4	-31.0	62±4
Surface DIC	0.4	56±4	1.3	61±4

between estimated terrestrial carbon input and  $\Delta^{14}\text{C}_{\text{POC}}$  at the OL site ( $R^2 = 0.31$ ,  $p < 0.01$ ,  $n = 15$ ) (Fig. 5C).

## Discussion

*Concentration trends of DOC, POC, PON, and DIC*—The somewhat higher DOC and POC concentrations at the nearshore site (BR) relative to the offshore site (OL) in May or June are due most likely to a combination of allochthonous OM inputs, the effects of terrestrially derived nutrient loading on autochthonous primary productivity (Urban et al. 2005), and the effects of nearshore increases in water temperature on productivity.

The OL DOC concentrations agree well with previously reported ranges (Table 8). During thermal stratification, the increase in DOC concentration in the surface waters at OL relative to that in the isothermal condition is possibly due to increased exudation from phytoplankton cells and release from sloppy feeding by zooplankton. The considerably lower concentrations of DOC, POC, and PON in the deep, cold waters during stratification conceivably reflect a background level of soluble and particulate OM that persists in the water column across seasons.

DOC concentration in the lake has been fluctuating seasonally and within season (monthly) over the past four decades (Table 8). In addition to temporal changes, DOC concentration is likely to differ spatially within the lake as a result of water mass movement and changes in biogeochemical processes. The lake has not yet been sampled at fine enough resolution to determine spatial patchiness in DOC concentrations resulting from currents, eddies, and other mesoscale phenomena. In addition, most carbon concentration measurements have been performed on samples obtained during fair weather conditions conducive for sampling from a research vessel. Over the past few decades, lake DOC shows concentrations oscillating within a range of 80–210  $\mu\text{mol L}^{-1}$  (Table 8). An interesting observation in our data set was a sudden, significant decline (~ 36%) in DOC concentration between September 2007 and May 2008. This is consistent with values reported by Sterner (2010), indicating a similar decline of ~ 32% of DOC values between July 2007 and July 2008. Sterner (2010) also reported an ~ 40% decline in DOC concentration over just a period of 4 months (April 2008 to July 2008) (Table 8). These rapid declines in the largest OC pool in the lake are very intriguing and are likely driven by within-lake biogeochemical processes rather than lake

Table 7. Results of binary models showing relative contribution of pre-aged and modern carbon to water-column POC and DOC and contribution of terrigenous carbon to POC in Lake Superior.  $F_p$  and  $F_m$  are fractions in % of pre-aged and modern components, respectively. Average values of DOC and POC replicates (R1 and R2) from 127 m in 2007 were used in the model.\*

Date and depth	POC		DOC		Terrigenous POC	
	$F_p$	$F_m$	$F_p$	$F_m$	$\mu\text{mol C L}^{-1}$	%
	Sep 07—stratified					
OL 5 m	20	80	9	91	1.3	15
OL 30 m	31	69	77	23	1.2	11
OL 127 m	66	34	*	*	0.5	16
BR 5 m	**	**	**	**	**	**
May 08—isothermal						
OL 5 m	38	62	23	77	0.6	10
OL 30 m	31	69	33	67	0.8	11
OL 127 m	56	44	12	88	0.9	13
BR 5 m	33	67	29	71	0.9	10
Sep 08—stratified						
OL 5 m	22	78	*	*	3.0	19
OL 30 m	65	35	31	69	0.9	7
OL 127 m	63	37	74	26	0.8	17
BR 5 m	17	83	*	*	1.1	9
Jun 09—isothermal						
OL 5 m	44	56	9	91	0.2	4
OL 30 m	85	15	20	80	0.6	13
OL 127 m	55	45	18	82	0.3	6
BR 5 m	52	48	22	78	1.4	20
Aug 09—stratified						
OL 5 m	32	68	11	89	1.5	13
OL 30 m	36	64	17	83	0.7	8
OL 127 m	92	8	55	45	0.4	15
BR 5 m	63	37	*	*	1.6	12

\* Indicates model could not calculate components; \*\* indicates not calculated, either because sample was not collected or was not measured.

water-level changes. They could be a key reason for the imbalanced carbon budgets reported by Cotner et al. (2004) and Urban et al. (2005), since the DOC pool is likely to be poorly constrained by snapshot data.

The POC concentrations are consistent with values ( $\leq 18 \mu\text{mol L}^{-1}$ ) in Lake Superior over the past four decades and appear to show seasonal variation, with low values in spring (Table 8). The PON concentrations are significantly lower than DOC and POC and consistent with values reported by Sterner (2010), but slightly higher than the values of 0.1–0.4  $\mu\text{mol L}^{-1}$  reported by Ostrom et al. (1998). The increased surface concentration of POC and PON at OL is potentially a result of increased algal, bacterial, and zooplankton production (Velinsky and Fogel 1999). Historically, the POC concentrations in the lake are quite variable, but they may have declined slightly in the past few decades (Table 8).

Our DIC concentrations are within the range (733–965  $\mu\text{mol L}^{-1}$ ; Table 8) seen in the lake over the past four

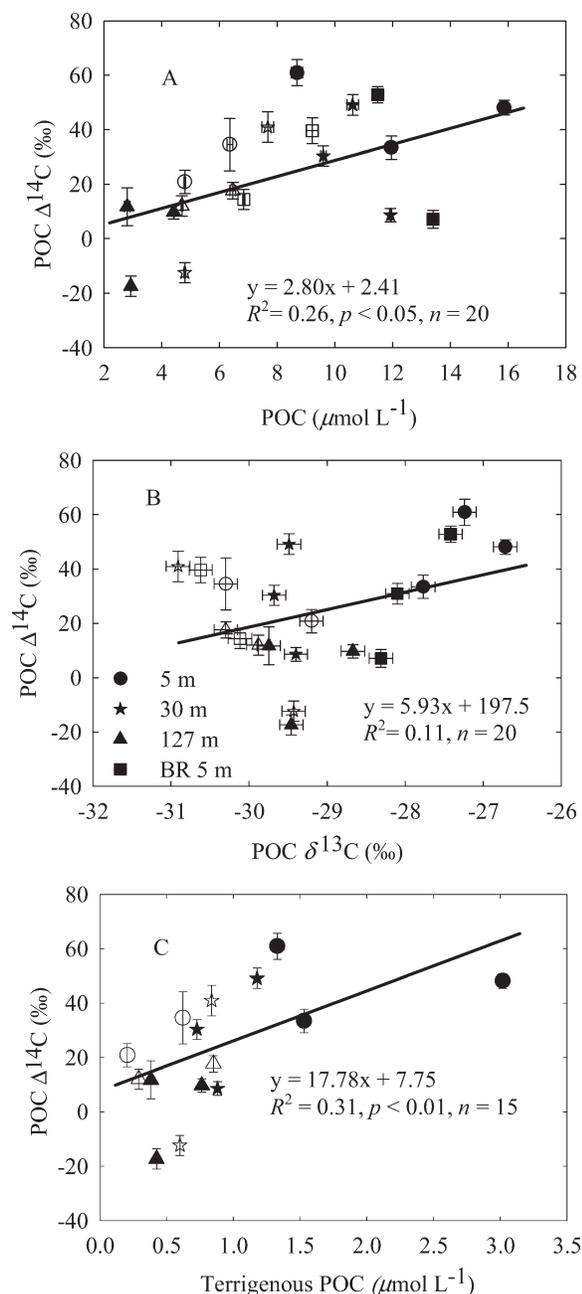


Fig. 5. The relationship between (A)  $\Delta^{14}\text{C}$  and concentration, (B)  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$ , and (C)  $\Delta^{14}\text{C}$  and suspended terrigenous POC during thermal stratification (estimated based upon C:N ratios, as described in the text) across sampling depths (5–127 m) in the water column of Lake Superior. The plots show clustering of POC based on potential sources.

decades. Reported DIC values in the past four decades exhibited some seasonal variation but have been generally steady (Table 8). In our study (Table 1), DIC concentrations were higher in the surface waters during isothermal conditions, likely as a result of (1) lower primary productivity, (2) increased surface-water exchange with the atmosphere (Cole et al. 1994), and (3) higher  $\text{CO}_2$  solubility at low temperatures. During stratified conditions (Table 1), we see an increase in DIC with depth, probably

as a result of utilization of surface DIC for photosynthesis, mineralization of sinking particulate matter, and the increased solubility of  $\text{CO}_2$  in the cooler deep waters.

The C:N values of suspended POM (Table 1) are consistent with previously reported values in the lake. Halfon (1984) reported an average C:N value of 8.4 for suspended POM at various depths ( $\leq 100$  m); Guildford and Hecky (2000) reported a C:N range of 7.2–12.7 (mean of 10.3) for suspended POM; and Urban et al. (2004a,b) reported a value of  $8.5 \pm 0.3$  for suspended POM in the upper 25 m off the Keweenaw Peninsula region of Lake Superior. The C:N values of suspended POM from 2 to 80 m deep in the water column (C:N values of 7.8–14.3) reported by Sterner (2010) for 2007–2008 are in agreement with our values, but the values reported for 2006 (4.6–7.9; Sterner 2010) are considerably lower than our values. The lower C:N values in 2006 seen by Sterner (2010) could be due to varying internal processes within the lake or considerably lower terrestrial influence on POM during that year.

Our C:N<sub>POM</sub> values do not reflect purely terrigenous plants (C:N > 20) or solely phytoplankton (C:N  $\sim$  6.6; Redfield et al. 1963) sources of OM. They are consistent with a composite of the two, with the algal proportion being predominant (Meyers 2003), and they are also at the lower range of C:N found in cool biome soils (Aitkenhead and McDowell 2000). In comparison with open oceanic systems, our C:N values are higher than values reported for suspended POM in the equatorial Pacific Ocean (5.7; Pena et al. 1991) and the equatorial Atlantic Ocean (6.1; Herbrand and Le Bouteiller 1981), probably as a result of greater riverine inputs (and their concomitant inputs of terrestrially derived material) relative to water volume.

*Stable isotopic composition of inorganic and OC pools*—Our  $\delta^{13}\text{C}_{\text{DIC}}$  values are in general agreement with other reported values (–4‰ to 0‰) in the lake (Keough et al. 1996; Hoffman et al. 2010). The  $\delta^{13}\text{C}_{\text{DIC}}$  values at site OL during stratified conditions are consistent with depletion of  $^{12}\text{C}$  due to photosynthetic fractionation in surface waters and subsequent respiration of sinking OM, which releases  $^{12}\text{C}$ -enriched  $\text{CO}_2$  into deep waters (Velinsky and Fogel 1999). Similarity in surface and deep  $\delta^{13}\text{C}_{\text{DIC}}$  values at site OL during isothermal conditions in spring is due to homogenization of the water column from vertical mixing.

The  $\delta^{13}\text{C}_{\text{POC}}$  values in the lake during the stratified season are consistent with values previously observed in far western coastal Lake Superior (Hoffman et al. 2010). The  $\delta^{13}\text{C}_{\text{POC}}$  values in the surface water (–27.8‰ to –26.7‰) during stratification are similar to the  $\delta^{13}\text{C}$  of primary producers (–27.9‰ to –26.7‰ for diatoms and –26.7‰ to –26.3‰ for chrysophytes; Keough et al. 1996, 1998) in the lake. Sierszen et al. (2006) also reported that small-sized plankton (110–253  $\mu\text{m}$ ) in the lake had  $\delta^{13}\text{C}$  values of –28.7‰ to –26.9‰, whereas  $\delta^{13}\text{C}$  of large-sized plankton ( $> 183 \mu\text{m}$ ) was  $-28.2 \pm 1.2\text{‰}$ . These values are similar to the  $\delta^{13}\text{C}_{\text{POC}}$  values in the surface water of the lake during the stratified season. In the stratified lake in September 2008 and August 2009, the lowest  $\delta^{13}\text{C}_{\text{POC}}$  value was observed in the DCM, similar to observations in the

Table 8. Reported concentrations of DIC, DOC, and POC in offshore Lake Superior water column over the past four decades. Although not exhaustive, this is detailed enough to reflect the historical trends in the lake. These are reported averages, and the values in parentheses represent reported ranges. For multiple depths, the order of the values represents their corresponding concentrations.

Date of sample collection	Depth (m)	No. of samples (n)	DIC ( $\mu\text{mol C L}^{-1}$ )	DOC ( $\mu\text{mol C L}^{-1}$ )	POC ( $\mu\text{mol C L}^{-1}$ )	Reference
May–Nov 1973	$\leq 100$	120			4–16	Halfon 1984
Mar 1975	$< 1$	9	733(683–825)	92(83–208)		Maier and Swain 1978
Jun–Sep 1983	5–10	4, 8; DOC, POC		210(158–317)	9–34	Baker and Eisenreich 1985
Jul–Aug 1986	5–10	9, 5; DOC, POC		133(94–178)	18(10–27)	Baker and Eisenreich 1989
1990		6			16.1	Hecky et al. 1993
Spring 1993					6	Anderson et al. 1998
Jun 1994	5–220	16			1–3	Ostrom et al. 1998
May–Jul 1998	3	460, 293; DOC, POC		116	7	Urban et al. 2005
Aug 1999	1–24	3	965	107		Ma and Green 2004
Sep 1999	20, 30, 240	6		112, 113, 98		Biddanda and Cotner 2003
May–Oct 1999				127		Urban et al. 2005
May–Oct 2000				123		Urban et al. 2005
Jul 2002	5, 30, 200	1			13, 21, 13	Cotner et al. 2004
Aug 2006	5, 30, 80	1	804, 775, 794	108, 103, 107	7, 18, 6	Sterner 2010
Sep 2006	5	6		210		Minor and Stephens 2008
Jul 2007	5, 30, 80	1	773, 788, 773	125, 118, 128	10, 11, 6	Sterner 2010
Sep 2007	5, 30, 127	9		129, 143, 115	9, 11, 3	This study
Nov 2007	5, 30, 80	1	812, 813, 822	168, 118, 140	7, 7, 4	Sterner 2010
Apr 2008	5, 30, 80	1	791, 788, 779	163, 135, 126	2, 2, 2	Sterner 2010
May 2008	5, 30, 127	9	819, 815, 809	82, 81, 80	6, 8, 7	This study
Jul 2008	5, 30, 80	1	803, 808, 813	88, 84, 81	12, 4, 4	Sterner 2010
Sep 2008	5, 30, 127	9	802, 821, 830	102, 93, 93	16, 12, 4	This study
Jun 2009	5, 30, 127	6	825, 830, 822	94, 93, 93	5, 5, 5	This study
Aug 2009	5, 30, 127	6	808, 826, 831	104, 103, 89	12, 10, 3	This study

Northeast Pacific Ocean (Bianchi et al. 1998; Druffel et al. 1998).

The  $^{13}\text{C}$ -depletion of POC with depth observed in Lake Superior is consistent with observations in the Middle Atlantic Bight shelf and slope in July–August 1996 (Bauer et al. 2002), but contrasts with  $^{13}\text{C}$ -enrichment of POC with depth observed in the Northeast Pacific in September 1994 and June 1995 (Druffel et al. 1998). These shifts in  $\delta^{13}\text{C}$  between depths in Lake Superior are most likely due to slower algal growth rates in the colder subsurface depths (Karlsson et al. 2003; Marty and Planas 2008). Other potential causes could be shifts in photoautotrophic community composition (Falkowski 1991; Velinsky and Fogel 1999); incorporation of dissolved  $\text{CO}_2$  vs. bicarbonate by different algal species (Laws and Bidigare 1997); variation in temperature, light intensity, and nutrients (Freeman and Hayes 1992; Burkhardt et al. 1999; Hayes 2001); variation in cell geometry (Popp et al. 1998); or a shift in the sources of particles to the deep waters vs. surface waters.

The  $^{13}\text{C}$ -depletion of POC values in the isothermal periods in May 2008 and June 2009 relative to the following stratified-period samples (September 2008 and August 2009) is consistent with low temperature ( $\sim 4^\circ\text{C}$ ) and

reduced phytoplankton growth rates in the colder spring samplings. The trends in Fig. 2E are consistent with autochthonous processes as a primary driver of POC stable isotope composition. The portion of the  $\delta^{13}\text{C}_{\text{POC}}$  signature that is not correlated to  $\delta^{13}\text{C}_{\text{DIC}}$  (Fig. 3) indicates that additional processes may be affecting the  $\delta^{13}\text{C}_{\text{POC}}$  signal in the surface and in the deep waters; one process likely to be significant is sedimentary resuspension, as discussed below.

The  $\delta^{13}\text{C}_{\text{DOC}}$  values are consistent with  $\delta^{13}\text{C}$  values of phytoplankton in the lake (Keough et al. 1996, 1998; Sierszen et al. 2006). The variation in  $\delta^{13}\text{C}_{\text{DOC}}$  in the stratified lake is limited to the freeze-dried samples from September 2007. These were more  $^{13}\text{C}$ -enriched than were the DOC samples from September 2008 and August 2009, which were not freeze-dried and combusted but rather were UV-oxidized in their liquid state. It is not clear whether this  $^{13}\text{C}$ -enrichment is due to unique sources, in-lake variability, or the freeze-drying process. The consistent  $^{13}\text{C}$ -enrichment of DOC (both freeze-dried samples and wet-oxidized ones) relative to POC may indicate that POC and DOC are differently sourced (Raymond and Hopkinson 2003) and/or that the DOC pool was relatively more subjected to photodegradation (Opsahl and Zepp 2001; Vahatalo and Wetzel 2008), or a combination of these factors.

*The  $\Delta^{14}\text{C}$  within atmospheric  $\text{CO}_2$ , water-column DIC, and water-column POC*—Our data show a consistent  $^{14}\text{C}$ -depletion of atmospheric  $\text{CO}_2$  relative to surface DIC from 2007 to 2009; this is due to positioning on the tailing portion of the bomb spike (cf, fig. 5 in McNichol and Aluwihare 2007). The absence of a reservoir effect in the lake implies that the hard water effect is negligible. In other words, there is little to no  $^{14}\text{C}$ -depletion of the DIC pool relative to atmospheric  $\text{CO}_2$  due to addition of radioactively inert ( $^{14}\text{C}$ -dead or old) carbon from limestone and/or dolomite in the sediments or rocks in the lake basin. This absence of a reservoir effect is consistent with the lake's large surface area, the absence of significant limestone and dolomite deposits in its drainage basin, and the biannual vertical mixing of the lake water column.

The offset between radiocarbon values in DIC and atmospheric  $\text{CO}_2$  indicates that the DIC pool is not in equilibrium with atmospheric  $^{14}\text{CO}_2$ . Potential causes of this include (1) a reduction in the rate of exchange between water-column DIC and atmospheric  $\text{CO}_2$  during periods (April and November; Urban et al. 2005) when the lake is supersaturated with  $\text{pCO}_2$  and effluxes  $\text{CO}_2$  to the atmosphere instead of taking in atmospheric  $^{14}\text{CO}_2$  (Abbott and Stanford 1996), (2) a reduction in exchange between lake DIC and atmospheric  $^{14}\text{CO}_2$  during winter ice cover (December to May), and (3) a relatively long residence time of lake DIC. We determined the residence time to be  $\sim 3$  yr (calculated using the DIC pool,  $\sim 125$  Tg C, divided by a lake-atmospheric  $\text{CO}_2$  exchange flux,  $F_{\text{CO}_2}$ , of  $50$  Tg C  $\text{yr}^{-1}$ ; Alin and Johnson 2007). Our  $\Delta^{14}\text{C}_{\text{DIC}}$  values are consistent with this concentration-and-flux-based estimate showing  $^{14}\text{C}$ -enrichment by  $\sim 20\%$  relative to the  $\Delta^{14}\text{C}_{\text{Atm CO}_2}$  in 2009.

The similarity in decline rate of  $\Delta^{14}\text{C}_{\text{POC}}$ , and  $\Delta^{14}\text{C}_{\text{DIC}}$  values in the surface waters during stratified conditions, in conjunction with our C:N data, and  $\delta^{13}\text{C}$  trends for both POC and DIC imply that much of the POC in the stratified surface waters is derived from recent photosynthesis in the lake. However, contrary to the surface waters,  $\Delta^{14}\text{C}$  values of deep-water POC were  $^{14}\text{C}$ -depleted to a greater extent than the co-occurring DIC in the lake during stratification, consistent with inputs of older POC from sediment resuspension and with selective diagenetic remineralization or solubilization of younger POC. Ageing during vertical transport alone (i.e., as a function of the time of sinking) cannot account for the  $\Delta^{14}\text{C}$  depth gradient.

The positive correlation observed between  $\Delta^{14}\text{C}$  in POC and DIC could most likely be due to aquatic photosynthetic depletion of DIC and the subsequent homogenization of fixed DIC throughout the water column via particle sinking and the semi-annual water-column overturn. The remainder of the POC  $\Delta^{14}\text{C}$  signal that is not explained by DIC is most likely a function of inputs from the surrounding watershed, sediment resuspension events, and the presence of trace black carbon from forest fires and fossil fuel combustion.

The general  $^{14}\text{C}$ -depletion in POC relative to DOC, whose  $\Delta^{14}\text{C}$  values are closer to those of the DIC pool, indicates a different combination of sources (Raymond and Hopkinson 2003) and a smaller proportional contribution

of fresh primary production (both allochthonous and autochthonous) to the POC relative to the DOC in the lake. Our observations contrast with observations in most open oceans, where the DOC pool is consistently much older than the suspended POC (Druffel et al. 1992; Druffel and Bauer 2000), but they agree with those from smaller lakes (S. L. McCallister unpubl.). This contrast is likely due to the extent of fluvial influence (in which land-derived DOM from the past 50 yr of terrestrial primary production will be labeled with bomb radiocarbon) and the physical homogenization of the water column in the spring and early winter. Enhanced particle resuspension in the lake, with its shorter water column and vigorous storm events, could also contribute to older POC values in the subsurface water column.

The depth gradient in  $\Delta^{14}\text{C}_{\text{DOC}}$  during the stratified period as a result of  $^{14}\text{C}$ -enrichment in the surface waters and  $^{14}\text{C}$ -depletion in deep waters is possibly due to input of  $^{14}\text{C}$ -enriched DOC from photosynthesis in the surface water and to an influx of  $^{14}\text{C}$ -depleted DOC from sedimentary pore water into the overlying deep water.

*Comparison of  $\Delta^{14}\text{C}$  within water-column DOC and POC and pore-water DOC*—The DOC in the surface waters at OL during stratification in September 2008 and August 2009 was more  $^{14}\text{C}$ -depleted compared to DOC from the BR site. This difference is most likely due to larger modern DOC input at site BR, resulting from enhanced photosynthesis driven by greater nutrient concentrations and higher temperatures.

$\Delta^{14}\text{C}_{\text{DOC}}$  values were relatively less variable (39–59‰) during vertical mixing in May 2008 and June 2009, reflecting the  $\Delta^{14}\text{C}$  signal of a composite DOC pool derived from mixing of  $^{14}\text{C}$ -enriched (51–75‰) DOC in the surface water and  $^{14}\text{C}$ -depleted (–77‰ to 14‰) DOC in the deep water. It is interesting to note that mean  $\Delta^{14}\text{C}$  within the composite DOC pool ( $46\% \pm 8\%$ ) during spring mixing was  $^{14}\text{C}$ -depleted by  $\sim 20\%$  relative to mean  $\Delta^{14}\text{C}_{\text{DOC}}$  in the surface water during stratification, but it was  $^{14}\text{C}$ -enriched by  $\sim 77\%$  relative to mean  $\Delta^{14}\text{C}_{\text{DOC}}$  in the deep waters during stratification. This indicates a stronger role for semi-reactive DOC and a tighter coupling between DOC inputs and removal in Lake Superior compared to most open ocean systems, where the pre-aged non-reactive DOC dominates the bulk  $\Delta^{14}\text{C}_{\text{DOC}}$  signal (Druffel et al. 1992; Druffel and Bauer 2000). This is not surprising considering the highly varying water residence times ( $\sim 173$  yr for Lake Superior vs.  $\sim 1000$ – $1500$  yr for the deep ocean [Urban et al. 2005; McNichol and Aluwihare 2007]) and ventilation ages (months in Lake Superior vs.  $\sim 1000$  yr in the ocean) in the two systems.

Our Lake Superior pore-water DOC concentrations ( $93$ – $395$   $\mu\text{mol C L}^{-1}$ ) are lower than reported values for surface sediments in Lake Michigan ( $900$   $\mu\text{mol L}^{-1}$ ; O'Loughlin and Chin 2004) and Lake Ontario ( $2600$   $\mu\text{mol L}^{-1}$ ; Roy and Knowles 1994). This is not surprising, since Lake Michigan and Lake Ontario are both more terrestrially influenced and autochthonously productive and have higher sedimentation rates than does Lake Superior (Cotner et al. 2004). The difference in concentration

between overlying water and pore water (0–2 cm) at site OL in Lake Superior indicates diffusion of pore-water DOC into the overlying water column (Alperin et al. 1994; Burdige 2002).

The  $^{14}\text{C}$ - and  $^{13}\text{C}$ -enrichment of pore-water DOC in August relative to June is probably due to enhanced fluxes of  $^{14}\text{C}$ - and  $^{13}\text{C}$ -enriched POM sinking to the sediment–water interface from the surface water in August and to a lower concentration-gradient-induced flux from the deeper pore waters. The  $^{14}\text{C}$ -depletion in the pore water relative to the overlying water column is likely due to old carbon and/or preferentially preserved refractory components (e.g., bound and free lipids and lignocelluloses; Burdige 2007) diffusing from the deeper sediments into the surficial layers.

*The  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  distributions in carbon from Amity Creek*—Our DOC concentrations are within the range of reported values (230–3000  $\mu\text{mol L}^{-1}$ ) for streams and rivers entering Lake Superior (Maier and Swain 1978; Urban et al. 2005). DOC constitutes approximately 17% of the total carbon exported by Amity Creek during base-flow conditions (compared to 83% from DIC and only trace POC).

Observed  $\delta^{13}\text{C}_{\text{DOC}}$  values in Amity Creek are consistent with OM from terrestrial and riverine C3 plants and do not vary as a function of flow or discharge rate. Our  $\Delta^{14}\text{C}$  values show that pre-aged DOC ( $45 \pm 35$  yr B.P.) is drained from the watershed during low flow conditions. This pre-aged DOC could be from groundwater DOM, OM derived from fixation of groundwater DIC, incorporation of OM fixed prior to the 1950s (perhaps from deeper soil layers), or addition of fossil-derived carbon. The DOC during storm flows was  $^{14}\text{C}$ -enriched, indicating that most of this DOC originated from recent photosynthesis and most likely came from the uppermost soil layers. The  $^{14}\text{C}$ -depletion of POC relative to co-occurring DOC during peak flows is consistent with observations in northeast U.S. rivers (e.g., Hudson, Delaware, and Parker Rivers) (Raymond et al. 2004) and in temperate estuaries (Raymond and Bauer 2001; Raymond and Hopkinson 2003). The observed POC-DOC  $\Delta^{14}\text{C}$  offset indicates that a larger proportion of the POC is derived from older particulates stored in the watershed soil and rock or within the streambed for longer periods (Raymond and Hopkinson 2003), from pre-bomb woody material, or from some addition of fossil-derived particulate black carbon incorporated into the soils (Penner et al. 1993; Masiello and Druffel 1998).

The  $\delta^{13}\text{C}_{\text{DIC}}$  value observed in Amity Creek is consistent with reported values of  $\delta^{13}\text{C}_{\text{DIC}}$  in Bluff Creek ( $-11.9\%$ ; Keough et al. 1998) and Bear Creek ( $-12.9\%$ ; Keough et al. 1998), which are wetland tributaries in the western Lake Superior watershed. The important sources and processes controlling the isotopic signal of DIC in the stream are exchange with atmospheric  $\text{CO}_2$  ( $\delta^{13}\text{C} = -7.8\%$ ; Freeman and Hayes 1992),  $\text{CO}_2$  from soil respiration ( $\delta^{13}\text{C} = -29.0\%$  to  $-25.0\%$ ; Raymond and Hopkinson 2003), groundwater input, proportion of  $\text{CO}_{2(\text{aq})}$  vis-à-vis  $\text{HCO}_3^-$  ( $\delta^{13}\text{C} = 1.0\%$ ; Laws and Bidigare 1997) species, and DIC influx from soil ( $\delta^{13}\text{C} \sim -12.0\%$ ), especially during spring snowmelt or ice-out (Striegl et al. 2001). For our stream

site, DIC in equilibrium with atmospheric  $\text{CO}_2$  would be relatively  $^{13}\text{C}$ -enriched ( $-1.0\%$  to  $1.0\%$ ), whereas  $\text{CO}_2$  produced from soil respiration would be  $^{13}\text{C}$ -depleted by  $14\%$  to  $18\%$  relative to our observed value of  $\sim -11\%$ . A binary mixing model using the  $\delta^{13}\text{C}$  of atmospherically fixed aqueous  $\text{CO}_2$  and soil respiration  $\text{CO}_2$  as end-members indicates that OM decomposition could contribute from 38% to 43% of the total stream DIC.

The  $^{14}\text{C}$ -depletion of DIC relative to the  $\Delta^{14}\text{C}$  value of atmospheric  $\text{CO}_2$  implies some  $\text{CO}_2$  input from old (i.e., pre-bomb) inorganic carbon or OC in the watershed or groundwater input. As there is no limestone in this region, we applied a mixing model using the  $\Delta^{14}\text{C}$  of atmospheric  $\text{CO}_2$  and soil respiration  $\text{CO}_2$  as end-members, assuming the old OM respired had a  $\Delta^{14}\text{C}$  value that is the same as the pre-aged base-flow DOC ( $\Delta^{14}\text{C} = -13\%$ ). This calculation indicates that approximately 34% of the DIC originated from soil respiration. This estimate, much less well constrained as a result of variable radiocarbon ages within soil OM fractions and soil horizons (Crow et al. 2009; Koarashi et al. 2009), and the estimate from  $\delta^{13}\text{C}$  values both indicate that around 34–43% of the stream DIC is from soil respiration.

*$\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  composition of mesozooplankton*—The  $^{13}\text{C}$ -depletion of  $\delta^{13}\text{C}_{\text{Zoop}}$  relative to  $\delta^{13}\text{C}_{\text{POC}}$  in August 2009 (as compared to their similarity in June 2009),  $^{14}\text{C}$ -enrichment of  $\Delta^{14}\text{C}_{\text{Zoop}}$  relative to co-occurring  $\Delta^{14}\text{C}_{\text{POC}}$  (a trend that holds true for both measured and large-volume blank-adjusted  $\Delta^{14}\text{C}_{\text{POC}}$  values), and the similarity of  $\Delta^{14}\text{C}_{\text{Zoop}}$  and  $\Delta^{14}\text{C}_{\text{DIC}}$  values in June and August 2009 (Table 6) indicate that the abundance of phytoplankton in the surface water during stratification affords the mesozooplankton the chance to avoid organic detritus and to selectively feed on living plankton (Marty and Planas 2008). Since suspended POC consists of a mixture of living plankton and detrital materials, such as fecal material, crustacean molts, and fine particles (Banse 1977), selective feeding on living planktonic organisms yields  $\Delta^{14}\text{C}_{\text{Zoop}}$  similar to  $\Delta^{14}\text{C}_{\text{DIC}}$ . Our  $\delta^{13}\text{C}_{\text{Zoop}}$  and  $\Delta^{14}\text{C}_{\text{Zoop}}$  values in Lake Superior also indicate that the isotopic composition of POC in the surface waters of the lake cannot be reliably used as a proxy for the isotopic composition of algae or phytoplankton and that the ratio of algal carbon to total POC should be included in mixing models (McCallister and del Giorgio 2008).

*Sources of POC in Lake Superior as revealed by  $\Delta^{14}\text{C}$ ,  $\delta^{13}\text{C}$ , and molar C:N ratios*—Suspended POM in Lake Superior appears to result from a combination of autochthonous primary productivity, sedimentary resuspension, and terrestrial OM inputs. The net heterotrophy of temperate oligotrophic Lake Superior, as indicated by  $\text{CO}_2$  efflux estimates (McManus et al. 2003; Russ et al. 2004), indicates a significant spatial or temporal subsidy of either terrigenous or sedimentary OM into the lake water column.

Most of the  $^{14}\text{C}$ -depleted (old) carbon in the POC pool is potentially sourced from either older terrestrial OM or from the lake sediments, whereas the  $^{14}\text{C}$ -enriched (fresh

labile) portion of POC appears to come from fresh algae based on the difference in surface-water and deep-water  $\Delta^{14}\text{C}_{\text{POC}}$  values.

In order to tease apart the possible sources of the suspended POC, we correlated measured  $\Delta^{14}\text{C}_{\text{POC}}$  and POC concentrations (Fig. 5A) for all depths and seasons. Our data show that the  $\Delta^{14}\text{C}_{\text{POC}}$  values are more  $^{14}\text{C}$ -depleted ( $\leq 15\%$ ) at lower ( $< 4 \mu\text{mol L}^{-1}$ ) POC concentrations. Two departures from this trend were the June 2009 OL sample from 30-m depth (the depth of the DCM during August–September) and the August 2009 BR sample; both were  $^{14}\text{C}$ -depleted ( $-12\%$  and  $7\%$ , respectively) at higher POC concentration. These samples most likely contained resuspended organic particles from the sediment. In general, deep-water POM was  $^{14}\text{C}$ -depleted relative to other POM samples. The surface-water POM, with contributions from fresh algae, zooplankton, and bacterial matter, was  $^{14}\text{C}$ -enriched, whereas the POM from the DCM depth reflected an intermediate isotopic signal relative to the deep and surface waters.

A cross-plot of measured  $\Delta^{14}\text{C}_{\text{POC}}$  and  $\delta^{13}\text{C}_{\text{POC}}$  clusters the POC (Fig. 5B), separating surface-water samples from the stratified season, based upon less  $^{13}\text{C}$ -depleted POC (most likely due to a drawdown of available inorganic carbon as a result of increased primary production) and more modern  $\Delta^{14}\text{C}$  values, again recording the DIC signal. Deep-water samples from the stratified period are more depleted in both  $^{13}\text{C}$  and  $^{14}\text{C}$ , indicating the effects of diagenesis and perhaps sediment resuspension, while DCM depth samples showed similar  $\Delta^{14}\text{C}$  to surface samples but more  $^{13}\text{C}$ -depleted signatures, perhaps as a result of low algal growth rates in the cooler, deeper DCM. Samples during the isothermal period are, in general, more depleted in  $^{13}\text{C}$  than are those from stratified periods, and they have variable  $\Delta^{14}\text{C}$  that does not appear to be correlated with depth. We interpret this as showing the effects of detrital inputs and sediment resuspension throughout the dynamic, mixed water column.

Our estimates of the proportion of terrigenous carbon to the suspended POC pool are consistent with values obtained from the branched and isoprenoid tetraether (BIT) index of suspended POC at the same sampling site and depths in Lake Superior (M. Woltering et al. unpubl.). The BIT index is a measure of the ratio of aquatic vs. terrestrial glycerol dialkyl glycerol tetraether membrane lipids and is generally used to determine relative amounts of terrigenous OC in paleo-climate (e.g., past-temperature) reconstructions (Hopmans et al. 2004). The high percentage of terrestrial OC observed in the stratified deep waters is reflective of low algal production in the deep waters. The observed positive relationship between estimated terrestrial carbon input and  $\Delta^{14}\text{C}_{\text{POC}}$  (Fig. 5C) indicates that most of the terrestrial carbon subsidies to the POC pool are  $^{14}\text{C}$ -enriched (modern).

*Sources of DOC in Lake Superior as revealed by  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$* —For DOC, the potential sources in Lake Superior are phytoplankton exudation or zooplankton sloppy feeding, desorption from sinking POC, terrestrial inputs from the watershed, and pore-water fluxes from the

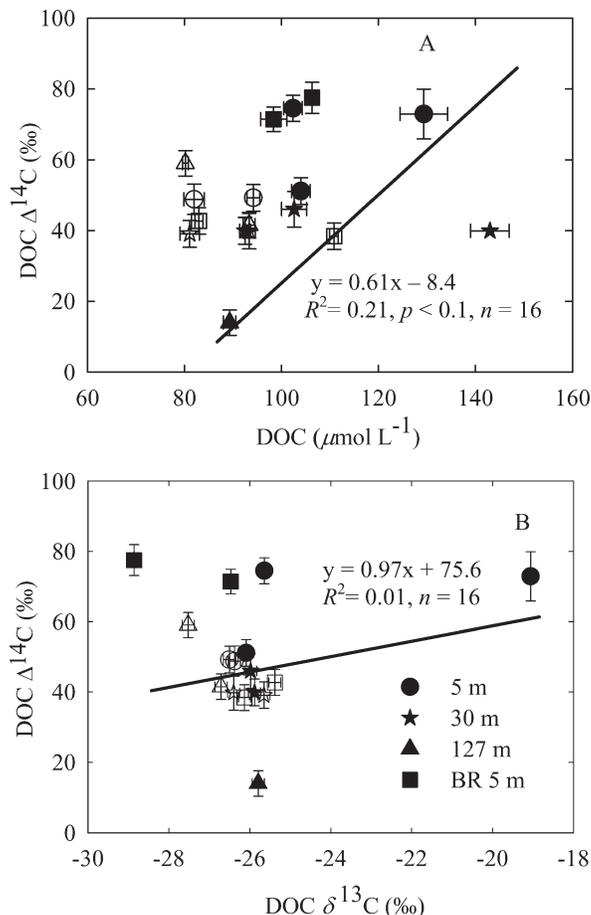


Fig. 6. Plot of  $\Delta^{14}\text{C}$  as a function of (A) concentration and (B)  $\delta^{13}\text{C}$  within bulk DOC in the water column of Lake Superior. Note that the anomalously  $^{14}\text{C}$ -depleted deep DOC sample ( $\Delta^{14}\text{C}$  of  $-77\%$ ) from 2007 was excluded.

sediment. A plot of water-column  $\Delta^{14}\text{C}_{\text{DOC}}$  vs. DOC concentration (Fig. 6A) isolated the stratified-period deep water from the other samples, with this sample exhibiting lower concentration and radiocarbon composition than the other stratified-period samples. The isotopic compositions of DOC in the isothermal water column were intermediate relative to the stratified deep water vs. surface water. Concentrations of DOC during the isothermal period were similar to those in the hypolimnion during stratification. A plot of  $\Delta^{14}\text{C}_{\text{DOC}}$  vs.  $\delta^{13}\text{C}_{\text{DOC}}$  (Fig. 6B) again isolated the stratified deep-water DOC from the remaining DOC pool (primarily due to radiocarbon ‘age’). This separation indicates an older source of DOC to the deep water column, consistent with pore-water DOC inputs.

In most cases, pre-aged OC was a considerably higher proportion of the suspended POC than it was in concurrent DOC. This indicates that in Lake Superior, the DOC, which is the largest OC pool in the lake, has more modern, and potentially biogeochemically labile, components, which is consistent with the results of previous studies that identified DOC as critical to both bacterial productivity and respiration in the lake (McManus et al. 2003; Cotner et al. 2004). This observation contrasts with ocean systems

(McNichol and Aluwihare 2007), where the bulk DOC pool is dominated by pre-aged OC, but is consistent with river systems (Raymond and Bauer 2001; Raymond et al. 2004), where the bulk POC pool is dominated by pre-aged OC.

*Biogeochemical carbon cycling insights from  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$* —The  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  values for DIC in the lake were, as expected,  $^{14}\text{C}$ -enriched relative to the OM pools, with  $\Delta^{14}\text{C}_{\text{DIC}}$  values showing slightly more bomb radiocarbon relative to atmospheric  $\Delta^{14}\text{C}$  at each sampling time. The DIC reservoir appears to cycle rapidly in the lake, on the order of every 3–5 yr. The depth gradient of  $\Delta^{14}\text{C}_{\text{DIC}}$  minus  $\Delta^{14}\text{C}_{\text{DOC}}$  ( $\Delta\Delta^{14}\text{C}_{\text{DIC-DOC}}$ ) (Fig. 7A) indicates that the DOC pool cycles on a longer timescale than does the DIC pool.

The oldest bulk DOC we measured in the lake water column (excluding the anomalous pre-aging in September 2007, which was not replicated in our later samplings) was modern (post-1950), which puts the residence time of the bulk DOC pool at  $\leq 60$  yr. This is in general agreement with estimated DOC turnover rates of  $\sim 8$  yr recorded by Urban et al. (2005) and 26–36 yr reported by Cotner et al. (2004), based on input and export carbon fluxes and the size of the DOC pool. Variations in DOC radiocarbon content with depth and time of year indicate, unsurprisingly, that bulk DOC consists of multiple pools of varying lability and that the most refractory component appears to cycle within the water column for some decades.

The oldest POC we measured in the western basin of the lake was aged ( $85 \pm 25$  v.p. yr) to about half the hydrologic residence time of the lake, though blank adjustment (if appropriate) shifts these values to slightly post-bomb (indicating incorporation of carbon from within the last 60 yr). The depth gradient of  $\Delta\Delta^{14}\text{C}_{\text{DIC-POC}}$  ( $\Delta^{14}\text{C}_{\text{DIC}}$  minus measured  $\Delta^{14}\text{C}_{\text{POC}}$ ) (Fig. 7B) in the thermally stratified lake indicates that the suspended POC pool recycles slowly relative to water-column mixing and on a somewhat longer timescale than does the bulk DOC. This contrasts with observations in open Atlantic and north-central Pacific Oceans, in which the suspended POC pool cycled on much shorter timescales (years to decades) relative to the DOC pool (centuries to millennia; Druffel and Williams 1990; Bauer et al. 2001).

The observed differences in Lake Superior POC vs. DOC cycling relative to the oceans are probably due in large part to the difference in water-column physical parameters in these two systems, in which the lake exhibits mixing of the entire water column twice a year. Thus, in the lake system, sediment resuspension is more likely to sporadically affect surface and mid-layer waters as well as the deep water column (adding to suspended POC age), while DOC is mixed into the photochemically and microbially active surface water semi-annually (thus enhancing water-column DOC removal and keeping the bulk DOC pool semi-labile).

It is worth noting that water-column bulk POC and bulk DOC contain a variety of biochemical compounds (carbohydrates, proteins, lipids, and nucleic acids) that reflect multiple sources and different pathways of production and decomposition (Hwang and Druffel 2003; Roland et al. 2008). In ocean waters, compound classes isolated from

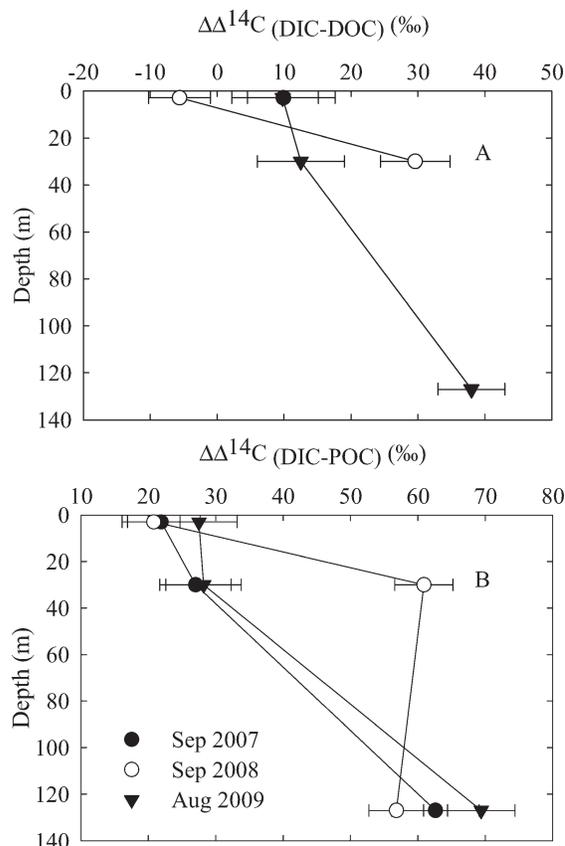


Fig. 7. The depth gradient of (A)  $\Delta\Delta^{14}\text{C}_{\text{DIC-DOC}}$  ( $\Delta^{14}\text{C}_{\text{DIC}}$  minus  $\Delta^{14}\text{C}_{\text{DOC}}$ ) and (B)  $\Delta\Delta^{14}\text{C}_{\text{DIC-POC}}$  ( $\Delta^{14}\text{C}_{\text{DIC}}$  minus  $\Delta^{14}\text{C}_{\text{POC}}$ ). These give an indication of relative recycling time and potential deep source (sedimentary input) of organic carbon in the lake. Note that the anomalously  $^{14}\text{C}$ -depleted deep DOC sample ( $\Delta^{14}\text{C}$  of  $-77\text{‰}$ ) from 2007 was excluded.

bulk POC and ultrafiltered DOC have exhibited radiocarbon ages that are both younger and older than those of the original bulk organic material (Hwang and Druffel 2003; Loh et al. 2004; Roland et al. 2008). Analyzing the  $\Delta^{14}\text{C}$  in compound-class samples from Lake Superior would enable more robust interpretations of the various sources and biogeochemical processes.

*Implications of future anthropogenic increases in carbon and nutrients in Lake Superior*—Increasing anthropogenic effects, such as nutrient and allochthonous carbon loading from surface run-off and sewage discharge, and increasing atmospheric  $\text{CO}_2$  within the Laurentian Great Lakes region could play important roles in shifting the dynamics of the carbon cycle in Lake Superior. The relatively pristine and oligotrophic nature of the lake puts its ecosystem under great threat from increased nutrient loading. Lake Superior is generally considered to be phosphorus (P) limited, with considerable excess nitrogen available (Cotner et al. 2004; Sterner et al. 2004). Increased P loading from run-off and human sewage, which has high P levels (Caraco 1995), could lead to eutrophication (Cotner et al. 2004). The current ratio of DOC to POC could be significantly shifted by increasing POC levels from enhanced productivity, and

the role of the microbial loop in carbon processing could thus be diminished by eutrophication.

The global carbon cycle has been linked to changes in climate, and the Laurentian Great Lakes are no exception (Nicholls 1999; Sousounis and Grover 2002). Water temperatures and wind speeds in Lake Superior have increased in the past decade, and ice coverage has decreased during the same period in the lake (Austin and Colman 2007; Bennington et al. 2010). The increase in water temperature coupled with longer duration of the stratified season could increase the role of microbial processes in converting recently synthesized POC into DOC (Jiao et al. 2010). Increasing air temperature could also further accelerate microbial turnover rates of DOC, and decreased ice cover along with longer stratified periods could enhance photodegradation of DOC. Wind speed increases may also play a role in a changing carbon cycle by leading to increases in mixed layer depths.

This is the first study coupling radiocarbon and stable-carbon isotopes, carbon concentrations, and C:N ratios to provide an understanding of the water-column carbon cycle of a great lake system. Both temporal (stratified vs. mixed water-column) and spatial (depth in open lake and nearshore vs. offshore) variations were important in constraining sources and processes. Such comprehensive approaches in multiple aquatic systems (with increased spatial and temporal resolution) should provide researchers with a deeper understanding of the basic parameters at work in the aquatic portion of the global carbon cycle.

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