

## Radiocarbon and stable-isotope geochemistry of organic and inorganic carbon in Lake Superior

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[1] We present a lake-wide investigation of Lake Superior carbon and organic matter biogeochemistry using radiocarbon, stable isotope, and carbon concentrations. Dissolved inorganic carbon (DIC) abundance in the lake was 121–122 Tg C, with offshore concentration and  $\delta^{13}\text{C}$  values being laterally homogenous and tightly coupled to the physical and thermal regime and biochemical processes. Offshore  $\Delta^{14}\text{C}$  of DIC (50–65‰) exhibited lateral homogeneity and was more  $^{14}\text{C}$  enriched than co-occurring atmospheric  $\text{CO}_2$  (~38‰); nearshore  $\Delta^{14}\text{C}$  of DIC (36–38‰) was similar to atmospheric  $\text{CO}_2$ . Dissolved organic carbon (DOC) abundance was 14.2–16.4 Tg C. DOC's concentration and  $\delta^{13}\text{C}$  were homogenous in June (mixed lake), but varied laterally during August (stratification) possibly due to spatial differences in lake productivity. Throughout sampling, DOC had modern radiocarbon values (14–58‰) indicating a semilabile nature with a turnover time of  $\leq 60$  years. Lake particulate organic carbon (POC, 0.9–1.3 Tg C) was consistently  $^{13}\text{C}$  depleted relative to DOC. The  $\delta^{15}\text{N}$  of epilimnetic particulate organic nitrogen shifted to more negative values during stratification possibly indicating greater use of nitrate (rather than ammonium) by phytoplankton in August. POC's radiocarbon was spatially heterogeneous ( $\Delta^{14}\text{C}$  range: 58‰ to –303‰), and generally  $^{14}\text{C}$  depleted relative to DOC and DIC. POC  $^{14}\text{C}$  depletion could not be accounted for by black carbon in the lake but, because of its spatial and temporal distribution, is attributed to sediment resuspension. The presence of old POC within the epilimnion of the open lake indicates possible benthic-pelagic coupling in the lake's organic carbon cycle; the ultimate fate of this old POC bears further investigation.

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### 1. Introduction

[2] Globally, lakes play important roles in the carbon cycle through carbon sequestration in sediments, and efflux of  $\text{CO}_2$  to the atmosphere [Cole *et al.*, 1994, 2007]. The importance of lakes as hot spots of carbon burial is shown by a comparison of average annual carbon burial rates in lakes (on a global basis) versus the ocean; lakes bury ~25–58% of the carbon that oceans do per year even though the combined surface area of lakes is less than 2% that of the ocean [Dean and Gorham, 1998; Cole *et al.*, 2007]. Because most lakes are net heterotrophic due to carbon subsidies from the surrounding landscape, they are also hot spots of carbon dioxide efflux, with an estimated potential global  $\text{CO}_2$  emission of 140 Tg  $\text{C y}^{-1}$ , roughly half the annual carbon

transport from rivers to the ocean [Cole *et al.*, 1994]. Large lakes such as Lake Superior (with surface areas  $>10,000 \text{ m}^2$ ) generally have a higher balance of autochthony to allochthony [Kelly *et al.*, 2001], but are also important in sending significant amounts of carbon (including terrestrially derived carbon) to the atmosphere [Alin and Johnson, 2007], and can influence regional and global climate both through this efflux and through the lakes' roles in heat exchange with the atmosphere. Despite the ecological and climatic importance of large lakes, both to their watershed regions and on a global scale, existing data on carbon cycling within them is sparse.

[3] Lake Superior, the earth's largest freshwater lake by surface area, is situated within the North American Precambrian Shield. The maximum and mean depths of the lake are, respectively, 406 m and 150 m [Urban *et al.*, 2005], and it is the coldest and deepest of the Laurentian Great Lakes system in the United States and Canada. The pelagic region of the lake is oligotrophic and compares well with open oceanic regions in terms of low organic carbon concentrations, little terrestrial influence, and the dominance of microbial food web in carbon processing [Cotner *et al.*, 2004]. Lake Superior therefore serves as an interesting

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“intermediate” system for comparison with both smaller lakes and larger oceanic systems. It is small enough to study at a basin wide level, which is logistically difficult with oceanic systems, but large enough to have biogeochemical similarities (low organic carbon concentrations, little terrestrial influence, and the dominance of microbial food web in carbon processing) to oceanic systems. However, unlike oceanic systems, the dimictic (that is, semiannual complete vertical mixing) nature of Lake Superior allows for studying reactions between carbon reservoirs on short time scales (annual-decadal); the view of such reactions in ocean systems is obscured by the long ventilation times and long thermohaline circulation cycles in the oceans. As compared to small lakes, Lake Superior provides a key reference point in the potential continuum of allochthony-to-autochthony ratios hypothesized to be a function of lake size or variables that covary with lake size [Kelly *et al.*, 2001].

[4] Lake Superior appears to be an important regional source of CO<sub>2</sub> to the atmosphere, with efflux estimates of 3–12 Tg C yr<sup>-1</sup> [Urban *et al.*, 2005; Alin and Johnson, 2007]. Current estimates of community respiration of 13–84 Tg C yr<sup>-1</sup> in the lake far exceed the known organic carbon inputs (2.4–9 Tg C yr<sup>-1</sup>) from atmospheric deposition, riverine flux and autochthonous primary production [Cotner *et al.*, 2004; Urban *et al.*, 2005]. This mismatch in organic carbon input and output terms represents a major gap in our present knowledge of the dynamics of the lake ecosystem [Sternner, 2010], and could be due to difficulty in constraining the magnitude of the various carbon fluxes, or could indicate that the organic carbon budget is not in equilibrium. In this study we apply radiocarbon and stable C and N isotopes to provide additional information on the lake’s C cycle.

[5] In the past few decades, radiocarbon (<sup>14</sup>C) has been useful in assessing the ages, reactivity and sources of carbon in surficial environments. <sup>14</sup>C, the radioisotope of carbon, has a half-life of 5730 years. Therefore, ancient organic material that is older than ~60,000 years or new organic material synthesized from an ancient inorganic carbon source would be <sup>14</sup>C dead, and will contain essentially no <sup>14</sup>C [Petsch *et al.*, 2001; McNichol and Aluwihare, 2007]. Aboveground nuclear testing in the 1950s added a “bomb spike” of radiocarbon to the Earth’s C cycle, thus extending radiocarbon usefulness to modern/decadal-level environmental processes (described in detail by McNichol and Aluwihare [2007]). Investigating the distribution of <sup>14</sup>C in the natural environment has provided valuable insights into the sources and fate of carbon in the ocean water column [Bauer and Druffel, 1998; McCarthy *et al.*, 2011; Pohlman *et al.*, 2011], marine sediments [Eglinton *et al.*, 1997; Goñi *et al.*, 1997], and the atmosphere [Hsueh *et al.*, 2007; Rose *et al.*, 2010]. Natural <sup>14</sup>C activity has also been useful in characterizing processes and/or sources of carbon in rivers [Raymond and Bauer, 2001], lakes [McCallister and del Giorgio, 2008], groundwater [Murphy *et al.*, 1989], rainwater [Raymond, 2005], and soils [Trumbore, 1997; Petsch *et al.*, 2001]. However, these studies have been limited to discrete observations or comparisons within small sample sets taken across space or time.

[6] Our objectives in the present study were to investigate lateral heterogeneity in the sources and biogeochemistry of carbon in Lake Superior using carbon concentration and

isotopic distributions, and the effect of thermal stratification on the dynamics of mean ages and/or reactivity and origins of organic carbon across the lake. The Lake Superior data set collected in this study thus represents the first lake-wide radiocarbon study in a large lake system and one of the few studies in any aquatic system to address temporal as well as spatial variations in the radiocarbon composition of the major water column carbon pools. We measured the natural abundance isotopic ( $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$ ) composition and concentrations of particulate organic carbon (POC), dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC) at nearshore and offshore sites in Lake Superior. Together, the POC, DOC, and DIC constitute the total carbon reservoir in the lake water column as the lake is undersaturated with respect to calcium carbonate. Due to the cost and effort currently associated with radiocarbon measurements, the spatial and temporal coverage here is limited to eight sampling sites visited twice and measured at two to three depths on each visit. While limited in spatial and temporal coverage, this sampling scheme represents one of the most extensive aquatic-system radiocarbon studies performed thus far. The resulting data reveals large-scale variations within Lake Superior’s carbon pools and an idea of the temporal variability that may occur in the system. Further, more detailed temporal and spatial sampling would considerably refine this initial isotopic view of the lake’s carbon cycle.

## 2. Methods

### 2.1. Sampling

[7] Cruises were undertaken on the R/V *Blue Heron* to sample the isothermal (mixed) water column in June 2009 and the thermally stratified water column in August 2009. Site locations, water depths, and sampling depths are given in Table 1 and Figure 1. At each of the open-lake (OL) sites, we sampled at 3 depths corresponding to the epilimnion or surface (5 m), the location of the summer deep chlorophyll maximum (DCM, 30–40 m), and the hypolimnion or deep water (127–340 m). At the nearshore (NS) sites, the depths were selected to reflect surface and underlying waters.

[8] At each site, we first obtained temperature, chlorophyll and depth profiles using a Seabird model 911 plus Conductivity, Temperature, and Depth (CTD) rosette equipped with fluorometer, transmissometer, dissolved oxygen sensor, and altimeter (see the auxiliary material).<sup>1</sup> Water samples were drawn from selected depths using 12.8 L Niskin bottles mounted on the CTD rosette. DIC samples were taken directly from the Niskin bottles via precleaned (10% HCl v/v, and ultra pure water [Millipore Milli-Q Plus]) silicone tubing into previously acid-cleaned and combusted (450°C for 4 h) 500 mL amber Pyrex bottles. The bottles for DIC were rinsed three times with sample and then overflowed with two volumes of the unfiltered water. After creating a 5 mL headspace, the samples were immediately preserved with saturated mercuric chloride solution, sealed airtight with glass stoppers coated with Apiezon grease (M), and stored at room temperature in the dark.

[9] Water samples for POC (the fraction that collects on a 0.7  $\mu\text{m}$ , GF/F glass fiber filter) and DOC (the fraction

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2011GB004132.

**Table 1.** Coordinates, Sampling, and Total Water Depths of Stations in Lake Superior

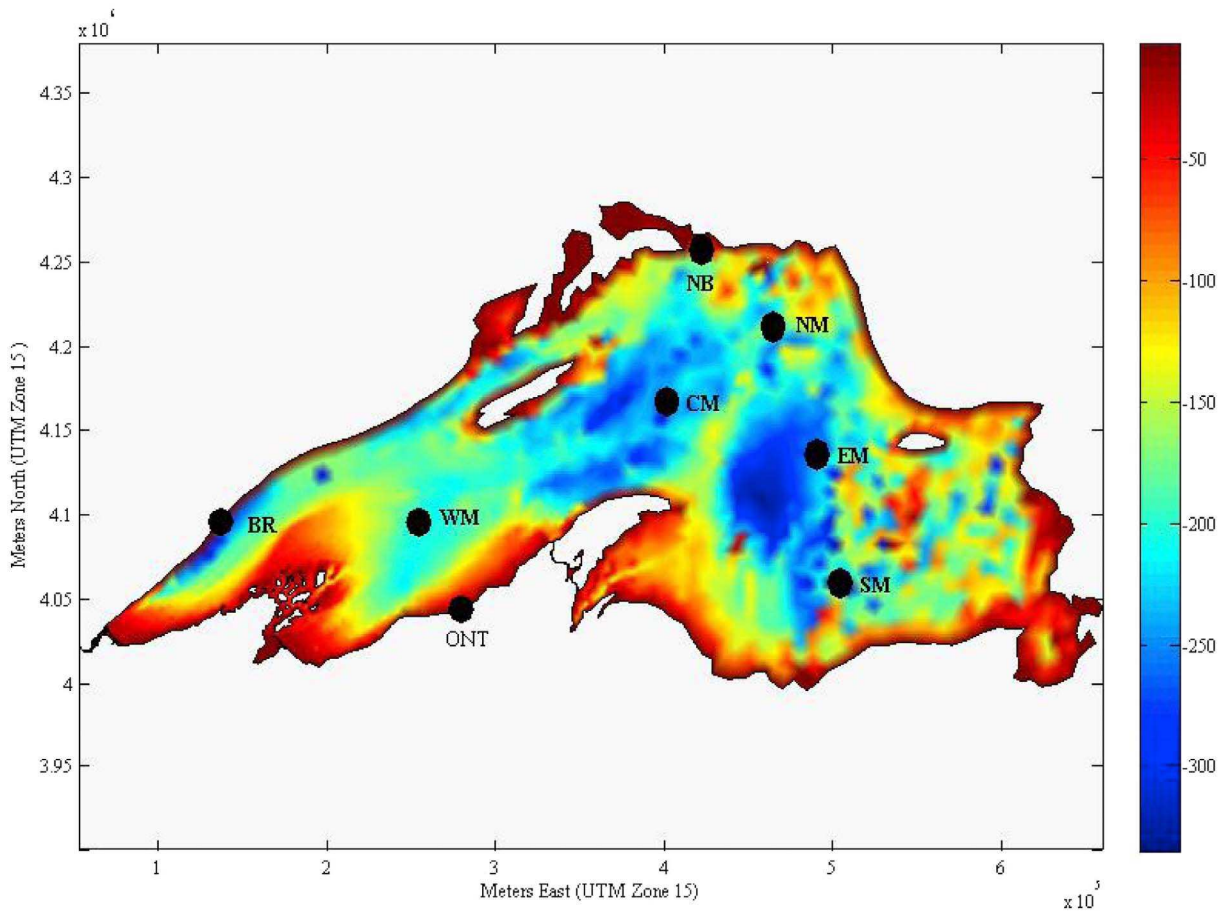
Site Name	Site Description	Latitude (deg and min N)	Longitude (deg and min W)	Depth Sampled (m)	Total Water Depth (m)
WM	Western mooring/site (Offshore)	47° 18.835	89° 51.078	5, 30, 127	171
CM	Central mooring (Offshore)	48° 01.916	87° 44.409	5, 30 (35), <sup>a</sup> 190	257
EM	Eastern mooring (Offshore)	47° 33.694	86° 38.739	5, 40, 210	242
SM	Southern mooring (Offshore)	46° 54.410	86° 36.017	5, 40, 340	398
NM	Northern mooring (Offshore)	48° 29.351	87° 3.802	5, 30, 150	216
BR	Baptism River mouth (Nearshore)	47° 20.056	91° 11.423	4 (2), <sup>a</sup> 14	20
ONT	Ontonagon River mouth (Nearshore)	46° 53.705	89° 20.401	4 (5), <sup>a</sup> 13	20
NB	Nipigon Bay (Nearshore)	48° 51.646	87° 45.344	4 (5), <sup>a</sup> 10, 50	62

<sup>a</sup>Numbers in parentheses indicate August water sampling depth if it differed from the June value.

passing through GF/F glass fiber filter) were filtered through precombusted Whatman GF/F glass fiber filters (450°C for 4 h; 0.7  $\mu$ m nominal pore size) via nitrogen pressurized stainless steel canisters. For each DOC sample for radiocarbon analysis, approximately 1 L of the resulting filtrate was collected into an acid-washed and combusted glass bottle. Also, approximately 40 mL of the filtrate was collected into an amber glass vial (previously acid-leached and combusted) for DOC concentration measurement. All the DOC samples (both radiocarbon and concentration

samples) were preserved by acidifying to pH 2 using 6N HCl (American Chemical Society ACS Plus grade) and subsequent refrigeration. After a known volume (usually about 10 L) of lake water had passed through a GF/F filter, the filter with retained particulate matter was removed from the stainless steel holder, folded, placed in previously combusted aluminum foil and stored frozen until analysis.

[10] Considerable care was taken throughout sampling to avoid  $^{14}$ C contamination. Powder-free nitrile gloves were used during sampling. All plastic tubing (silicone, Teflon,



**Figure 1.** Bathymetry map of Lake Superior showing stations in the open lake, and nearshore sites. The open lake sites include western station/mooring (WM), central mooring (CM), northern mooring (NM), eastern mooring (EM), and southern mooring (SM). The nearshore sites are off Baptism River (BR), off Ontonagon River (ONT), and off Nipigon Bay (NB).

and polypropylene) was cleaned with 10% (v/v) HCl in water, and rinsed with ~10 L of distilled water. All other plastic ware was cleaned with soap and distilled water, leached with 10% (v/v) 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* and organic geochemistry lab spaces were swiped for possible radiocarbon contamination prior to and during this study and results from both scintillation counting and accelerator mass spectrometry showed no signs of the presence of radiocarbon label.

## 2.2. Measurement of Concentrations of DOC, DIC, POC, and PON

[11] Concentrations of DOC were measured by high temperature catalytic combustion on a Shimadzu Total Organic Carbon (TOC)-Vcsh analyzer. The TOC analyzer was calibrated with potassium hydrogen phthalate (KHP). Deep seawater from Florida Strait at 700 m (Batch-8 2008) reference waters obtained from the DOC Consensus Reference Program (Hansell laboratory, University of Miami, USA) and additional KHP standards were interspersed and analyzed along with the samples to assess instrumental performance. Our mean DOC value of the external reference sample was  $43.9 \pm 3.9 \mu\text{M}$  ( $n = 5$ ), and agrees with the consensus value of 41–43  $\mu\text{M}$ . For each sample, three injections were performed. If the standard deviation was not  $\leq 2.5\%$ , two more injections were performed and the closest three of the five injections were averaged to yield sample concentration [Minor and Stephens, 2008].

[12] 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%  $\text{H}_3\text{PO}_4$  (by weight) in a  $\text{CO}_2$ -free closed reaction vessel, and the  $\text{CO}_2$  evolved was measured by a nondispersive infrared (NDIR) gas detector as by Zigah *et al.* [2011]. Suspended particulate organic matter (POM) filters were freeze-dried and homogenized, fumigated with 12 N HCl (ACS Plus grade) overnight to remove carbonates, dried again at 60°C, and cooled in a desiccator. They were then loaded into tin capsules and analyzed for particulate organic carbon (POC) and particulate organic nitrogen (PON) concentrations on a Costech ECS 4010 elemental analyzer (EA) coupled to Finnigan Delta Plus XP isotope ratio mass spectrometer (IRMS). The EA was calibrated with acetanilide (Costech Analytical Technologies Inc., Valencia, CA, USA) and caffeine (SigmaUltra; Wheaton Science Products, NJ, USA) reference standard materials, and carbon and nitrogen contents were quantified using the IRMS. Typical instrumental precisions for POC and PON measurements were, respectively, 0.2% and 0.4% of the measured concentrations.

## 2.3. Black Carbon Determinations

[13] The black carbon (BC) content of suspended POC was measured via the thermal oxidation method as described by Gustafsson *et al.* [1997, 2001]. Briefly, freeze-dried and homogenized POC filters and NIST Urban Dust standard reference material (NIST SRM 1649a) were loaded into silver cups, placed in a heating block, and set in a combustion oven at 375°C for 24 h. The carbon percent was then

measured on a Costech ECS 4010 elemental analyzer (EA) as in POC analysis. Our thermal oxidation method yielded a measured value of TOC of  $0.1778 \pm 0.0001 \text{ g C g}^{-1}$  dry weight solid and BC of  $0.0273 \pm 0.0001 \text{ g C g}^{-1}$  dry weight solid for the NIST SRM 1649a, similar to reported values of total organic carbon (TOC) of  $0.176 \pm 0.004 \text{ g C g}^{-1}$  dry weight solid and BC of  $0.014 \pm 0.001 \text{ g C g}^{-1}$  dry weight solid [Reddy *et al.*, 2002; Gustafsson *et al.*, 2001].

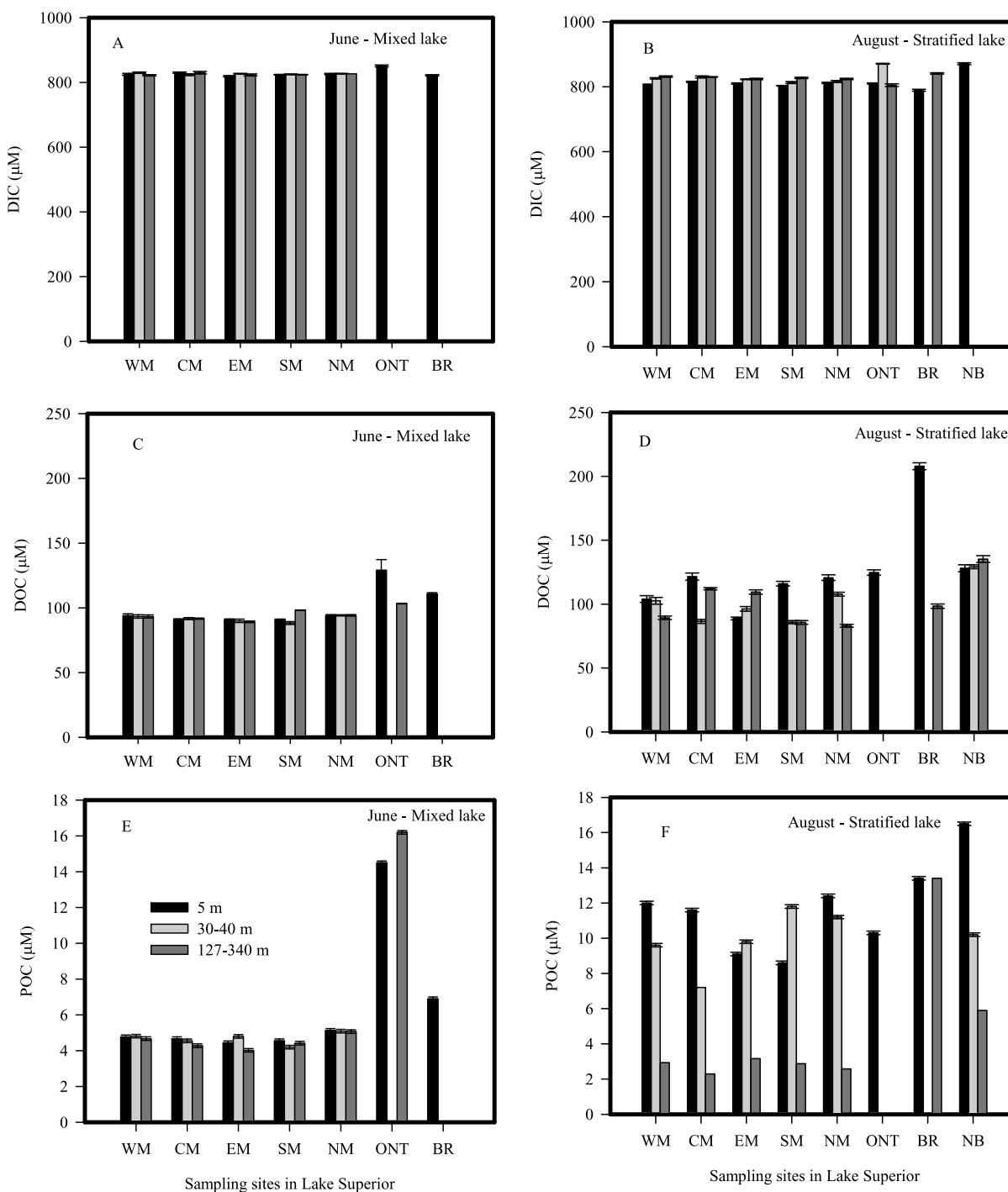
## 2.4. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ Measurements

[14] Stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of samples (DOC, DIC, and POC) were determined at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) at the Woods Hole Oceanographic Institution (WHOI) using an Optima IRMS to measure subsamples of the purified  $\text{CO}_2$  of DOC, DIC, and POC intended for radiocarbon analyses. Stable nitrogen isotope ratios ( $\delta^{15}\text{N}$ ) and some additional  $\delta^{13}\text{C}$  values in POM samples were measured at the Large Lakes Observatory (LLO) using a Finnigan Delta Plus XP IRMS with Conflo III interface (Thermo Fisher Scientific Inc., Waltham, MA) coupled to Costech ECS 4010 EA. The instrument was calibrated with certified reference materials (low organic soil B-2153, sorghum flour B-2159; from Elemental Microanalysis Ltd., Okehampton, Devon, UK) and in-house standards (acetanilide, caffeine, and urea) that have been calibrated against NIST reference standards (NBS 19, NBS 8540, and NBS 8542 for carbon, and NBS 8547, NS 8548, and NBS 8549 for nitrogen). Typical instrumental precision of  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  based on analyses of multiple external standards were 0.17‰ and 0.2‰, respectively. The stable isotope ratios ( $^{13}\text{C}:^{12}\text{C}$  and  $^{15}\text{N}:^{14}\text{N}$ ) are reported as  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , respectively, which are the per mil difference relative to Pee Dee Belemnite carbonate and atmospheric air standards. The  $\delta$  notation is calculated as:  $\delta\text{Q} = [\text{R}_{\text{sample}}/\text{R}_{\text{standard}} - 1] \times 1000$ , where Q is either  $^{13}\text{C}$  or  $^{15}\text{N}$ , and R is either  $^{13}\text{C}:^{12}\text{C}$  or  $^{15}\text{N}:^{14}\text{N}$ .

## 2.5. $\Delta^{14}\text{C}$ Measurements

[15] Radiocarbon ( $\Delta^{14}\text{C}$ ) measurements were performed at NOSAMS. DOC samples were ultraviolet (UV) irradiated using a protocol based upon work by Beaupre *et al.* [2007] but using three hours of oxidation instead of four. The evolved  $\text{CO}_2$  was trapped in a vacuum line, purified cryogenically and reduced to graphite with  $\text{H}_2$  over Fe catalyst. POC samples were freeze-dried, fumigated with 12 N HCl (ACS Plus grade) for 24 h to remove carbonates, redried at 60°C, and combusted to  $\text{CO}_2$  in a modified Carlo Erba NA1500 elemental analyzer. The evolved  $\text{CO}_2$  was separated cryogenically and reduced to graphite. DIC samples were directly hydrolyzed with  $\text{H}_3\text{PO}_4$ , and the resulting  $\text{CO}_2$  was stripped with nitrogen gas and trapped, cryogenically cleaned, and reduced to graphite as by Zigah *et al.* [2011].

[16] In all cases, the graphite produced was analyzed by accelerator 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 nineteenth 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

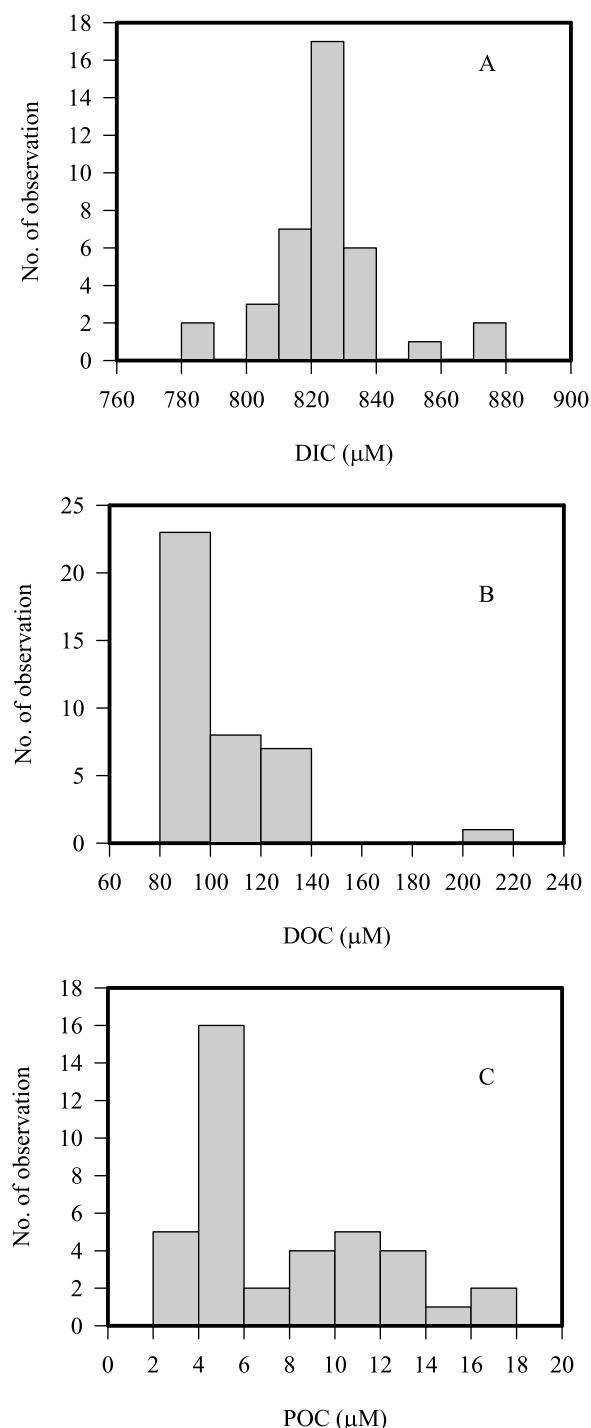


**Figure 2.** Site-specific distributions of the isothermal lake concentrations of (a) DIC, (c) DOC, (e) POC, and stratified lake concentrations of (b) DIC, (d) DOC, (f) POC. Isothermal samples were collected during June 2009, and stratified samples taken during August 2009. The depth labels in the plot are for offshore samples. The equivalent nearshore depths are 2–4 m for the surface, 10 m at NB sites, the only nearshore site with middepth value, and 13–50 m for deep samples.

Polach [1977]. Instrumental precision of the  $\Delta^{14}\text{C}$  analysis is based on the error of standards or multiple analyses on a target and were 2–5‰ for DIC, 2–5‰ for DOC, and 3–11‰ for POC.

[17] Because of the challenges inherent in sampling for and analyzing natural-abundance radiocarbon, we performed

radiocarbon analysis on POC and DOC method blanks. The POC method blank was obtained by filtering >100 L of Milli-Q water through precombusted GF/F filters using our canister setup. This large volume is ten times the volume of lake water filtered for POC samples and was designed to provide enough carbon for a radiocarbon measurement. For



**Figure 3.** Frequency distribution of (a) DIC, (b) DOC, and (c) POC in Lake Superior. These show most frequently seen values during both stratified and isothermal conditions.

comparison, we also measured carbon content of a clean GF/F filter. A 1 L portion of the GF/F filtrate was collected as the DOC method blank. Details concerning the POC blank are described by Zigah *et al.* [2011] and we report both uncorrected (measured) and blank-corrected  $\Delta^{14}\text{C}_{\text{POC}}$  values. The POC-blank  $\Delta^{14}\text{C}$  value does not affect basic depth and locational trends in the samples discussed here. We have since analyzed the DOC method blank, which

generated  $8.6 \mu\text{mol C L}^{-1}$ . Just as in the POC method blank [Zigah *et al.*, 2011] the DOC method blank carbon would also include contributions from the MilliQ water as well as the filtration apparatus, and would thus contribute  $<9.8\%$  of the carbon in the least concentrated DOC sample. As the DOC method blank's  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  values were  $-386 \pm 3\text{‰}$  and  $-30.4\text{‰}$ , respectively, blank-corrected DOC samples would be shifted by  $\sim 38\%$  toward more  $^{14}\text{C}$ -enriched values. We report both uncorrected (measured) and blank-corrected values of  $\Delta^{14}\text{C}_{\text{DOC}}$  here as we cannot isolate the MilliQ water contribution (which is not relevant when lake water is filtered) from the filter apparatus contribution, and suspect that much of the carbon in the DOC blank actually originated from the starting MilliQ water. Again, as with POC [Zigah *et al.*, 2011], depth and locational trends remain the same in blank-corrected versus uncorrected samples.

## 2.6. Statistical Analyses

[18] We used STATISTICA (StatSoft, Tulsa, Oklahoma, USA) or Excel (Microsoft, USA) in all analyses. The relationships between delta values and concentrations of the different carbon pools were assessed with correlation analyses in which we report Pearson's correlation coefficient ( $R$ ), the probability ( $P$ ) and the number of samples ( $n$ ). Statistical significance was tested at the 95% confidence level, thus  $\alpha = 0.05$ . We checked all data for normality, and those that were not normally distributed (POC and PON concentrations and  $\delta^{13}\text{C}_{\text{DIC}}$ ) were log transformed before analysis. DIC and DOC concentrations, and translated (thus a constant added to remove negative values) values of  $\Delta^{14}\text{C}$  POC remained skewed even after log transformation and were not used for statistical analysis. In order to improve statistical power in all analysis, sample sizes less than 30 ( $n < 30$ ) were not used for significance testing.

## 3. Results

### 3.1. Concentrations of Carbon Species, Particulate Nitrogen, and Particulate Black Carbon

[19] The DIC concentration in the lake ranged from 789 to 871  $\mu\text{M}$  (Figures 2a and 2b) with the most frequently observed values ranging from 820 to 830  $\mu\text{M}$  (Figure 3a). DOC and POC concentrations ranged from 89 to 208  $\mu\text{M}$  (Figures 2c and 2d) and 2.3 to 16.5  $\mu\text{M}$  (Figures 2e and 2f), respectively, and their frequency distributions show that 80 to 100  $\mu\text{M}$  DOC (Figure 3b), and 4 to 6  $\mu\text{M}$  POC (Figure 3c), were the most commonly observed values. The Lake Superior water column undergoes physical homogenization twice each year, during late spring and early winter. Concentrations of DIC, DOC, POC, and PON during spring mixing in June were uniform vertically (i.e., with depth) and, in general, laterally across the lake, although the nearshore sites (BR and ONT) were higher in concentrations in all the carbon species than the offshore sites (Figures 2a–2f and Table 2). In August when the lake is thermally stratified, the offshore DIC concentration increased with depth from an average of 815  $\mu\text{M}$  in the epilimnion to 826  $\mu\text{M}$  in the deep hypolimnion (Figure 2b). Epilimnetic DOC concentrations were higher during stratification in August than in June as would be expected in the warmer and more productive stratified surface waters. DOC concentrations were also

**Table 2.** Concentrations and Isotopic Compositions of DIC, DOC, and POM From Multiple Open Lake and Nearshore Sites in the Isothermal (Well Mixed) Water Column of Lake Superior in June 2009<sup>a</sup>

Station <sup>b</sup>	Depth (m)	DIC			DOC				POC				PON		POM
		$\mu\text{M}$	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	$\mu\text{M}$	$\delta^{13}\text{C}$ (‰)	Measured $\Delta^{14}\text{C}$ (‰)	Blank- Corrected $\Delta^{14}\text{C}$ (‰)	$\mu\text{M}$	$\delta^{13}\text{C}$ (‰)	Measured $\Delta^{14}\text{C}$ (‰)	Blank- Corrected $\Delta^{14}\text{C}$ (‰)	$\mu\text{M}$	$\delta^{15}\text{N}$ (‰)	Molar C:N
<i>Isothermal</i>															
WM - OL	5	825 ± 3	0.4	56 ± 4	94.0 ± 1.3	−26.5	49 ± 4	93 ± 4	4.77 ± 0.03	−29.2	21 ± 4	50 ± 5	0.66	1.7	7.2 ± 0.7
CM - OL	5	830 ± 2	0.3	61 ± 4	90.8 ± 0.8	−25.9	58 ± 4	104 ± 4	4.67 ± 0.03	−29.9	−55 ± 4	−45 ± 5	0.59	0.1	7.9 ± 0.8
EM - OL	5	819 ± 2	0.4	59 ± 5	90.8 ± 0.7	−26.3	42 ± 4	86 ± 4	4.44 ± 0.02	−30.3	−24 ± 3	−4 ± 4	0.56	0.1	7.9 ± 0.7
SM - OL	5	824 ± 1	0.4	62 ± 3	90.8 ± 0.6	−26	25 ± 5	68 ± 5	4.56 ± 0.03	−29.8	34 ± 5	68 ± 6	0.57	0.4	8.0 ± 0.8
NM - OL	5	826 ± 2	0.5	52 ± 2	94.2 ± 0.6	−26.5	22 ± 4	63 ± 4	5.13 ± 0.03	−29.9	34 ± 3	64 ± 4	0.74	0.7	7.0 ± 0.6
ONT - NS	4	851 ± 3	ND <sup>c</sup>	38 ± 2	129.2 ± 8.2	ND <sup>c</sup>	−10 ± 3	17 ± 3	14.47 ± 0.08	−29.3	16 ± 3	24 ± 3	1.57	−0.6	9.1 ± 0.8
BR - NS	4	822 ± 2	ND <sup>c</sup>	54 ± 4	110.8 ± 0.9	ND <sup>c</sup>	38 ± 4	74 ± 4	6.85 ± 0.04	−30.6	14 ± 4	32 ± 5	0.72	1.1	9.5 ± 0.9
WM - OL	30	830 ± 2	0.3	60 ± 4	93.3 ± 1.3	−26.4	40 ± 5	83 ± 5	4.81 ± 0.03	−29.4	−12 ± 4	8 ± 5	0.57	1.2	8.4 ± 0.8
CM - OL	30	824 ± 3	0.4	64 ± 4	91.7 ± 0.8	−26.3	36 ± 4	79 ± 4	4.55 ± 0.03	−29.6	25 ± 3	56 ± 4	0.64	1	7.1 ± 0.7
EM - OL	40	827 ± 1	0.3	54 ± 4	90.0 ± 1.4	−26.3	39 ± 4	84 ± 4	4.80 ± 0.03	−29.8	−303 ± 3	−354 ± 4	0.61	0.3	7.8 ± 0.8
SM - OL	30	825 ± 1	0.4	56 ± 3	88.3 ± 1.1	−26.4	40 ± 4	86 ± 4	4.20 ± 0.02	ND	−16 ± 4	8 ± 5	0.55	−1	7.7 ± 0.6
NM - OL	30	827 ± 1	0.5	61 ± 4	94.2 ± 0.5	−26.3	58 ± 4	102 ± 4	5.09 ± 0.03	−29.4	10 ± 4	34 ± 5	0.70	0	7.3 ± 0.7
WM - OL	127	822 ± 2	0.3	58 ± 3	93.3 ± 1.2	−26.7	42 ± 4	85 ± 4	4.67 ± 0.03	−29.9	12 ± 4	39 ± 5	0.62	1.6	7.5 ± 0.7
CM - OL	190	830 ± 4	0.4	63 ± 4	91.7 ± 0.5	−26.6	35 ± 4	78 ± 4	4.28 ± 0.02	−29.1	−107 ± 4	−112 ± 5	0.56	1.2	7.6 ± 0.7
EM - OL	210	823 ± 3	0.3	58 ± 2	89.2 ± 0.7	−26	30 ± 4	74 ± 4	4.02 ± 0.02	−29	−172 ± 3	−196 ± 4	0.48	3.7	8.4 ± 0.7
SM - OL	340	824 ± 1	0.4	56 ± 4	98.3 ± 0.1	−26.6	52 ± 3	93 ± 3	4.42 ± 0.02	−30	1 ± 5	27 ± 6	0.59	0.4	7.5 ± 0.7
NM - OL	150	827 ± 0	0.5	60 ± 4	94.2 ± 0.6	−26.5	47 ± 3	90 ± 3	5.07 ± 0.03	−29.6	12 ± 3	36 ± 4	0.65	0.4	7.9 ± 0.7
ONT - NS	13	ND	ND	ND	103.3 ± 0.2	ND	50 ± 4	89 ± 4	16.21 ± 0.09	ND	36 ± 4	44 ± 4	1.75	−1.7	9.2 ± 0.8

<sup>a</sup>Precision of radiocarbon is based on analyses of multiple external standards, and those of concentrations are based on multiple sample analyses.

<sup>b</sup>OL refers to open lake samples; and NS means nearshore samples.

<sup>c</sup>Not determined, either because sample was not collected, not measured, or was lost during processing in the field or lab.

**Table 3.** Concentrations and Isotopic Compositions of DIC, DOC, and POM From Multiple Open Lake and Nearshore Sites in the Thermally Stratified Water Column of Lake Superior in August 2009<sup>a</sup>

Station <sup>b</sup>	Depth (m)	DIC			DOC				POC				PON		POM
		$\mu\text{M}$	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	$\mu\text{M}$	$\delta^{13}\text{C}$ (‰)	Measured $\Delta^{14}\text{C}$ (‰)	Blank- Corrected $\Delta^{14}\text{C}$ (‰)	$\mu\text{M}$	$\delta^{13}\text{C}$ (‰)	Measured $\Delta^{14}\text{C}$ (‰)	Blank- Corrected $\Delta^{14}\text{C}$ (‰)	$\mu\text{M}$	$\delta^{15}\text{N}$ (‰)	Molar C:N
Stratified Epilimnion															
WM - OL	5	808 ± 0	1.3	61 ± 3	104.0 ± 2.6	−26.1	51 ± 3	90 ± 3	11.96 ± 0.06	−27.8	33 ± 4	44 ± 4	1.42	−2.8	8.4 ± 0.7
CM - OL	5	815 ± 2	1	62 ± 3	121.6 ± 2.8	−26	50 ± 4	82 ± 4	11.61 ± 0.06	−29.1	39 ± 3	51 ± 3	1.40	−2.3	8.3 ± 0.7
EM - OL	5	810 ± 2	0.9	59 ± 4	88.8 ± 1.0	−26	54 ± 3	101 ± 3	9.09 ± 0.05	−29.2	38 ± 4	53 ± 4	1.20	−3.9	7.6 ± 0.6
SM - OL	5	803 ± 1	1.1	54 ± 4	116.0 ± 1.8	−26	27 ± 4	60 ± 4	8.59 ± 0.05	−28.1	−24 ± 3	−15 ± 3	1.02	−2.9	8.4 ± 0.7
NM - OL	5	812 ± 2	0.9	50 ± 3	120.7 ± 2.2	−26.1	21 ± 3	52 ± 3	12.39 ± 0.07	−28.9	22 ± 3	31 ± 3	1.46	−2.9	8.5 ± 0.7
ONT - NS	5	810 ± 2	1	56 ± 4	124.7 ± 2.1	−28.3	ND <sup>c</sup>	ND <sup>c</sup>	10.33 ± 0.06	−27.2	ND	ND	1.25	−3.7	8.3 ± 0.7
BR - NS	2	789 ± 3	0.9	60 ± 4	208.0 ± 2.7	−26.5	74 ± 4	94 ± 4	13.40 ± 0.07	−28.3	7 ± 3	15 ± 3	1.60	−2.7	8.4 ± 0.7
NB - NS	5	871 ± 3	0.2	36 ± 3	128.1 ± 2.7	−26.5	39 ± 4	69 ± 4	16.50 ± 0.09	−28	−19 ± 4	−14 ± 4	2.09	−2	7.9 ± 0.7
DCM <sup>d</sup>															
WM - OL	30	826 ± 2	0.6	59 ± 3	102.6 ± 2.6	−26	46 ± 3	85 ± 3	9.61 ± 0.05	−29.7	30 ± 3	44 ± 3	1.25	−1.4	7.7 ± 0.6
CM - OL	35	830 ± 3	0.4	59 ± 5	86.5 ± 1.6	−26.1	50 ± 3	97 ± 3	7.23 ± 0.04	−30.5	40 ± 3	61 ± 3	0.88	−1.4	8.2 ± 0.7
EM - OL	40	823 ± 1	0.5	60 ± 3	96.3 ± 1.8	−26.3	44 ± 4	86 ± 4	9.82 ± 0.05	−34.9	58 ± 11	75 ± 12	1.18	−1.6	8.3 ± 0.7
SM - OL	30	813 ± 3	0.6	65 ± 4	85.9 ± 1.2	−26	41 ± 3	88 ± 3	11.76 ± 0.06	−31	29 ± 3	40 ± 3	1.41	−1.7	8.3 ± 0.7
NM - OL	30	816 ± 3	0.6	56 ± 4	107.8 ± 1.5	−25.9	40 ± 5	76 ± 5	11.21 ± 0.06	−29.5	16 ± 4	26 ± 4	1.30	−1.6	8.6 ± 0.7
NB - NS	10	871 ± 1	ND	ND	129.3 ± 1.5	−26	52 ± 4	83 ± 4	10.20 ± 0.06	−29	3 ± 3	13 ± 3	1.29	−1.5	7.9 ± 0.7
Hypolimnion															
WM - OL	127	831 ± 2	0.2	52 ± 5	89.3 ± 1.3	−25	14 ± 4	56 ± 4	2.93 ± 0.02	−29.5	−17 ± 3	20 ± 4	0.34	3.1	8.7 ± 0.7
CM - OL	190	830 ± 1	0.2	55 ± 4	112.1 ± 0.9	−23.7	24 ± 4	58 ± 4	2.29 ± 0.01	−29	−29 ± 3	18 ± 5	0.25	0.9	9.2 ± 0.8
EM - OL	210	824 ± 2	0.3	63 ± 4	109.5 ± 1.7	−25.9	46 ± 4	82 ± 4	3.16 ± 0.02	−29.3	−20 ± 4	13 ± 6	0.37	−1.4	8.6 ± 0.7
SM - OL	340	827 ± 2	0.1	61 ± 4	85.7 ± 1.4	−26.1	44 ± 3	92 ± 3	2.88 ± 0.02	−32.3	−145 ± 11	−170 ± 16	0.32	−0.1	8.9 ± 0.7
NM - OL	150	824 ± 2	0.2	65 ± 4	83.1 ± 1.2	−26.1	44 ± 4	94 ± 4	2.58 ± 0.01	−28.6	−0 ± 4	55 ± 6	0.33	0.9	7.8 ± 0.7
BR - NS	14	805 ± 4	1	57 ± 3	98.4 ± 1.7	−26	39 ± 3	79 ± 3	13.38 ± 0.07	−28	28 ± 3	37 ± 3	1.60	−2.1	8.4 ± 0.7
NB - NS	50	841 ± 2	−0.1	54 ± 3	135.3 ± 2.6	−26	39 ± 3	68 ± 3	5.94 ± 0.03	−29.8	16 ± 4	37 ± 5	0.76	−2.8	7.8 ± 0.7

<sup>a</sup>Precision of radiocarbon is based on analyses of multiple external standards, and those of concentrations are based on multiple sample analyses.<sup>b</sup>OL refers to open lake samples, and NS means nearshore samples.<sup>c</sup>Not determined either because sample was not collected, was not measured, or was lost during processing in the field or lab.<sup>d</sup>DCM is depth of deep chlorophyll maximum during summer thermal stratification.



**Table 4.** Black carbon (BC) Content of Suspended POC From June (Isothermal Condition) Sampling in the Water Column of Lake Superior

Station	Depth (m)	BC <sup>a</sup> ( $\mu\text{M}$ )	POC ( $\mu\text{M}$ )	BC/POC (mole percent)
EM - OL	5	0.17	4.44	3.9
EM - OL	40	0.43	4.80	8.9
EM - OL	210	0.23	4.02	5.6
CM - OL	5	0.21	4.67	4.5
CM - OL	190	0.18	4.28	4.1
SM - OL	30	0.20	4.20	4.8
WM - OL	30	0.20	4.81	4.1

<sup>a</sup>BC was measured via thermal oxidation at 375°C for 24 h.

higher (124–208  $\mu\text{M}$ ) at the nearshore sites (BR, ONT, NB) than the offshore sites (89–122  $\mu\text{M}$ ) during stratification (Figure 2d). Of the offshore sites, the highest epilimnetic DOC concentration during stratification was observed in the central province (CM) of the lake. With the exception of the EM site, DOC concentration decreased with depth at the offshore sites during stratification (Figure 2d and Table 3).

[20] POC and PON concentrations declined with depth during stratification at the offshore sites (Table 3). The POM C:N values in the open lake shifted by  $\sim 0.7$  units from a mean of 7.7 (range 7.2–8.4,  $n = 14$  pairs) in the isothermal lake in June to a mean of 8.4 (range 7.6 to 9.2,  $n = 14$  pairs) during stratification in August (Tables 2 and 3). Black carbon concentrations within a subset of suspended POC samples from the isothermal water column in June ranged from 0.17 to 0.43  $\mu\text{M}$  (mean  $0.23 \pm 0.09$ ,  $n = 7$ ) corresponding to mole percent black carbon (BC/POC) of 3.9–8.9% (mean  $5.1 \pm 1.8\%$ ) (Table 4).

### 3.2. Vertical and Lateral Variations of Stable Carbon and Nitrogen Isotopes

[21] The  $\delta^{13}\text{C}_{\text{DIC}}$  was tightly coupled to the mixing/thermal regime of the lake. During physical homogenization (isothermal condition) in June, the  $\delta^{13}\text{C}_{\text{DIC}}$  values, like DIC concentrations, were spatially (by depth and laterally) uniform, with a mean of  $0.4 \pm 0.1\%$  (Figure 4a). However, in the warmer productive surface layer during thermal stratification in August, the  $\delta^{13}\text{C}_{\text{DIC}}$  in the epilimnion averaged  $1.0 \pm 0.2\%$  ( $n = 5$ ), and decreased vertically to an average hypolimnetic  $\delta^{13}\text{C}_{\text{DIC}}$  of  $0.2 \pm 0.1\%$  ( $n = 5$ ) (Figure 4b). In the offshore lake, the WM site had the largest shift toward more positive ( $^{13}\text{C}$  enriched) values in epilimnetic  $\delta^{13}\text{C}_{\text{DIC}}$  after transition from isothermal to stratified conditions.  $\delta^{13}\text{C}_{\text{DIC}}$  was positively and significantly correlated to POC concentration ( $R = 0.74$ ,  $P < 0.0001$ ,  $n = 34$ ), and negatively and significantly correlated to  $\delta^{15}\text{N}_{\text{PON}}$  ( $R = 0.68$ ,  $P < 0.0001$ ,  $n = 34$ ).

[22] The  $\delta^{13}\text{C}_{\text{DOC}}$  values were not coupled to the physical and/or thermal regime of the lake, and did not exhibit considerable vertical or lateral variation. The apparent DCM and epilimnetic  $^{13}\text{C}$  enrichment of approximately 0.2‰ relative to hypolimnetic  $\delta^{13}\text{C}_{\text{DOC}}$  in June and August is within the precision of  $\delta^{13}\text{C}$  measurement, except at CM in August where the epilimnion was  $^{13}\text{C}$  enriched by 2.3‰ relative to the hypolimnion. The surface-to-deep water integrated mean value of  $\delta^{13}\text{C}_{\text{DOC}}$  in the offshore region of the lake was  $-26.3 \pm 0.2\%$  in June and  $-25.8 \pm 0.4\%$  in August

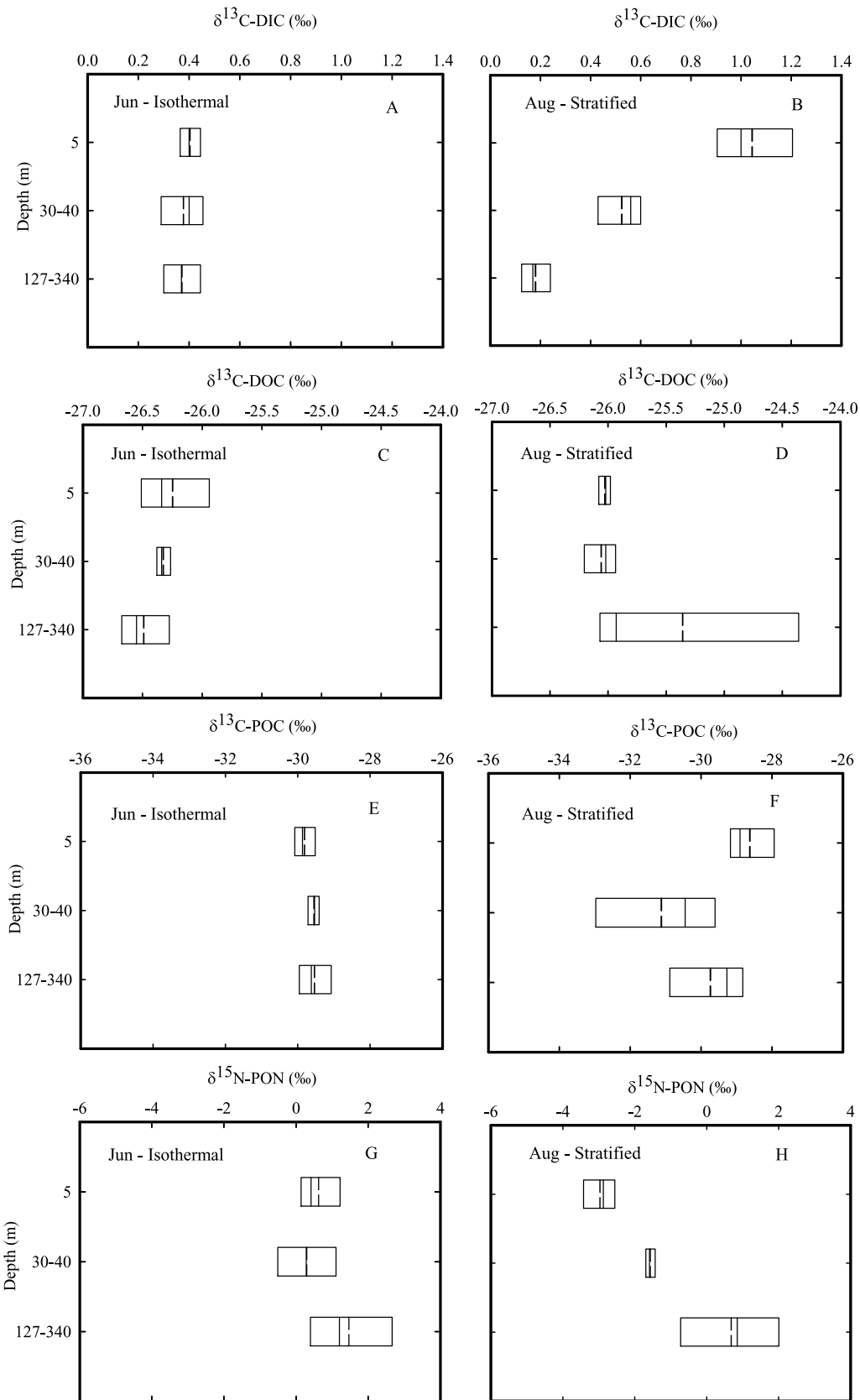
(Figures 4c and 4d). On the other hand, the  $\delta^{13}\text{C}_{\text{POC}}$  in the epilimnion was responsive to physical regime. Epilimnetic  $\delta^{13}\text{C}_{\text{POC}}$  in the isothermal lake shifted by  $1.5 \pm 0.6\%$  toward more  $^{13}\text{C}$ -enriched values during stratification (Figures 4e and 4f). There was a lateral gradient in the difference in epilimnetic  $\delta^{13}\text{C}_{\text{POC}}$  between stratified and isothermal conditions ( $\Delta\delta^{13}\text{C}_{\text{POC}}$ ).  $\Delta\delta^{13}\text{C}_{\text{POC}}$ , which is defined here as the stratified  $\delta^{13}\text{C}_{\text{POC}}$  minus isothermal  $\delta^{13}\text{C}_{\text{POC}}$ , was higher ( $\sim 2.2\%$ ) at the nearshore sites (BR and ONT). In the offshore sites, the western and southern provinces shifted most, with a  $\Delta\delta^{13}\text{C}_{\text{POC}}$  of 1.4‰ and 1.7‰, respectively (Figures 4e and 4f).

[23] The  $\delta^{15}\text{N}_{\text{PON}}$  was sensitive to the physical regime of the lake. Epilimnetic  $\delta^{15}\text{N}_{\text{PON}}$  shifted from  $^{15}\text{N}$ -enriched values (range  $-0.6\%$  to 1.7‰; mean 0.5‰) in the isothermal lake in June to  $^{15}\text{N}$ -depleted values (range  $-3.9\%$  to  $-2.3\%$ ; mean  $-3.0\%$ ) in the stratified lake in August (Figures 4g and 4h). An interesting, although not surprising, observation was the consistent  $^{15}\text{N}$  enrichment of PON with depth in all the offshore sites of the lake during stratification (Figure 4h and Table 3). In addition to the high sensitivity of  $\delta^{15}\text{N}_{\text{PON}}$  to the physical regime of the lake,  $\delta^{15}\text{N}_{\text{PON}}$  showed significant and negative correlations with concentrations of POC ( $R = -0.71$ ,  $P < 0.0001$ ,  $n = 39$ ), and PON ( $R = -0.71$ ,  $P < 0.0001$ ,  $n = 39$ ).

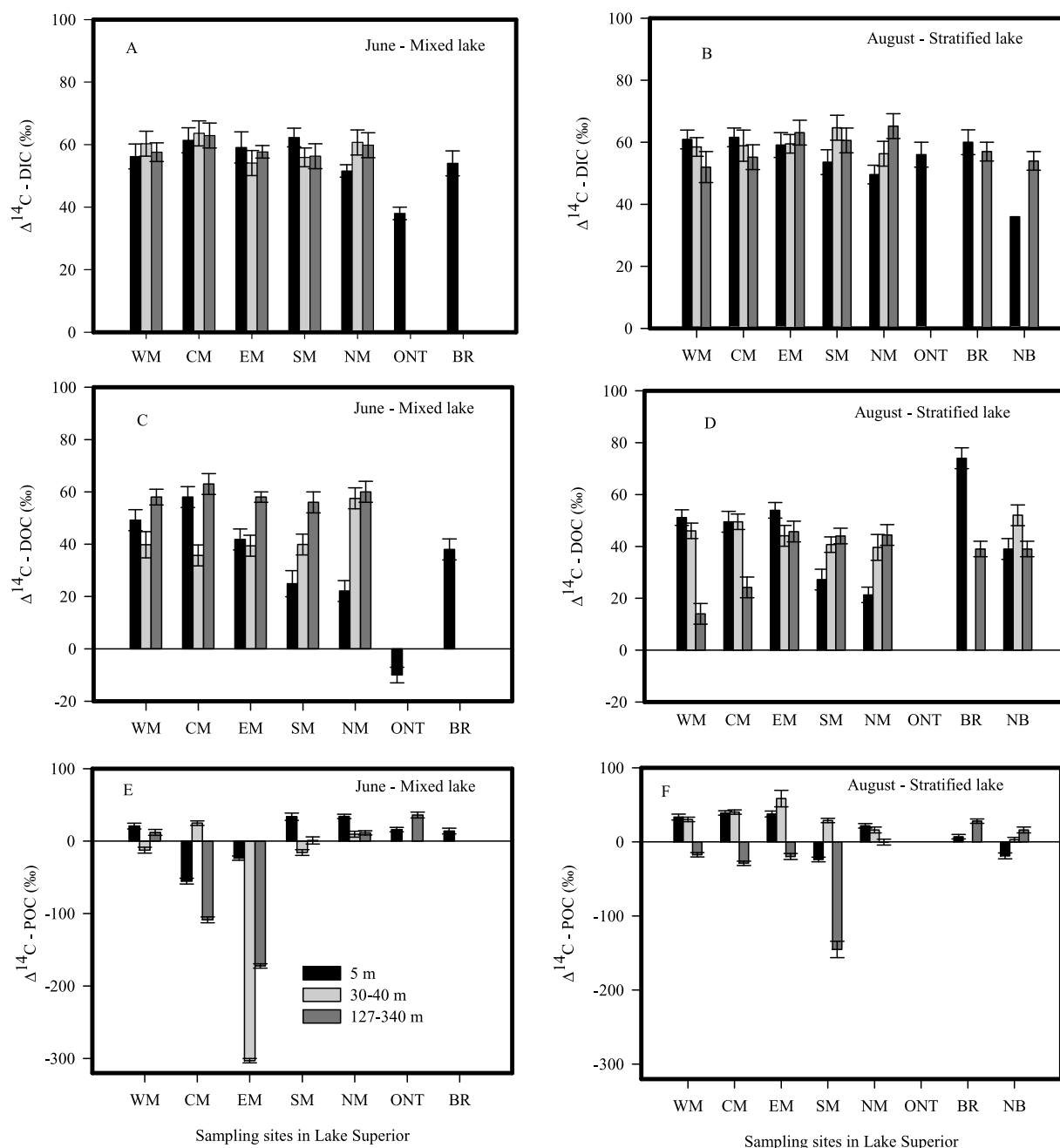
### 3.3. Distributions of $\Delta^{14}\text{C}$ of DIC, DOC and POC

[24] The  $\Delta^{14}\text{C}_{\text{DIC}}$  in the surface-to-deep offshore sites averaged 59‰ (range 52‰ to 63‰,  $n = 15$ ) in June, and 59‰ (range 50‰ to 65‰,  $n = 15$ ) in August (Figures 5a and 5b). Distribution of  $\Delta^{14}\text{C}_{\text{DIC}}$  with depth, and with season (isothermal versus stratified) was spatially homogeneous at the current precision of accelerator mass spectrometry (AMS) of 2–7‰ [Turnbull *et al.*, 2006; McNichol and Aluwihare, 2007]. At the nearshore sites,  $\Delta^{14}\text{C}_{\text{DIC}}$  ranged from 38‰ off the Ontonagon river (ONT site) to 54‰ off the Baptism river (BR) in June, and averaged 53‰ (range 36‰ to 60‰,  $n = 5$ ) in August (Figures 5a and 5b).

[25] Uncorrected  $\Delta^{14}\text{C}_{\text{DOC}}$  in the offshore provinces of the lake was similar to or somewhat  $^{14}\text{C}$  depleted relative to concurrent DIC, with a mean  $\Delta^{14}\text{C}_{\text{DOC}}$  of 41‰ (range 22‰ to 58‰,  $n = 15$ ) in June, and mean of 40‰ (range 14‰ to 54‰,  $n = 15$ ) in August (Figures 8a–8d). Blank-corrected  $\Delta^{14}\text{C}_{\text{DOC}}$ , which may be overcorrected if MilliQ water carbon is a significant portion of the blank as we suspect, was consistently higher than concurrent  $\Delta^{14}\text{C}_{\text{DIC}}$ , and ranged from 63 to 104‰ ( $n = 15$ ) in June and 52–101‰ ( $n = 15$ ) in August (Tables 2 and 3). An interesting observation in the open lake was the approximately 28 to 30‰ (18–49‰ for blank-corrected values; Figures 5c and 5d)  $^{14}\text{C}$  depletion of the epilimnetic DOC from southern, eastern, and northern regions (SM, EM, and NM) in June and SM and NM regions of the lake in August, compared to the corresponding epilimnetic DOC from the other offshore regions of the lake (Figures 5c and 5d and Tables 2 and 3). A depth gradient was observed at the western, central, and eastern provinces of the lake during stratification in August (both for measured, i.e., uncorrected, and blank-corrected  $\Delta^{14}\text{C}_{\text{DOC}}$ ), with the epilimnetic DOC being  $^{14}\text{C}$  enriched relative to the hypolimnetic DOC (Figure 5d and Table 3). However, an intriguing contrast was observed at the southern and northern provinces of the lake (based on both measured



**Figure 4.** Depth profiles of mean values of all sites during isothermal lake condition in June of (a)  $\delta^{13}\text{C}_{\text{DIC}}$ , (c)  $\delta^{13}\text{C}_{\text{DOC}}$ , (e)  $\delta^{13}\text{C}_{\text{POC}}$ , and (g)  $\delta^{15}\text{N}_{\text{PON}}$  and during stratified lake condition in August of (b)  $\delta^{13}\text{C}_{\text{DIC}}$ , (d)  $\delta^{13}\text{C}_{\text{DOC}}$ , (f)  $\delta^{13}\text{C}_{\text{POC}}$ , and (h)  $\delta^{15}\text{N}_{\text{PON}}$ . Box represents the 25th and 75th percentiles, the solid line within the box represents the median value, and the dash line within the box is mean value.

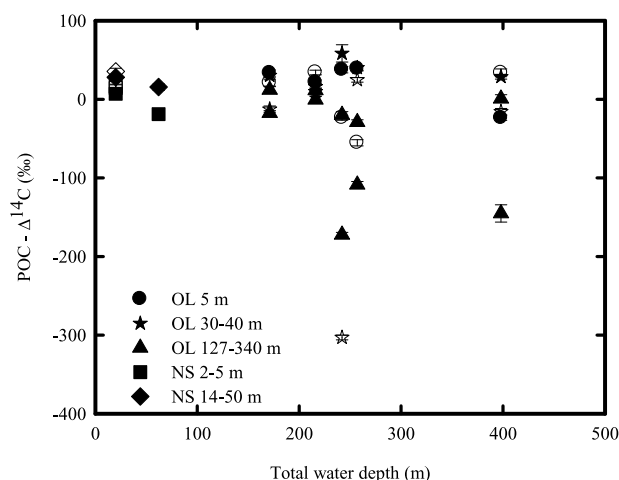


**Figure 5.** Site-specific distribution of the isothermal lake measured  $\Delta^{14}\text{C}$  values of (a) DIC, (c) DOC, (e) POC, and stratified lake  $\Delta^{14}\text{C}$  values of (b) DIC, (d) DOC, (f) POC. The depth labels in the plot are for offshore samples. The equivalent nearshore depths are 2–4 m for the surface, 10 m at NB sites, the only nearshore site with middepth value, and 13–50 m for deep samples.

and blank-corrected  $\Delta^{14}\text{C}_{\text{DOC}}$ ), where the hypolimnetic DOC was  $^{14}\text{C}$  enriched compared to the epilimnetic DOC (Figure 5d and Table 3). At the nearshore sites (BR and ONT), measured  $\Delta^{14}\text{C}_{\text{DOC}}$  was more variable, ranging from  $-10\text{‰}$  to  $74\text{‰}$  (mean  $40\text{‰}$ ,  $n = 8$ ) (Figures 5c and 5d), with blank-corrected values ranging from 17 to  $94\text{‰}$  (Tables 2 and 3). The most  $^{14}\text{C}$ -depleted offshore DOC was seen in the deep water at the western province (measured  $\Delta^{14}\text{C} = 14\text{‰}$ ) during stratification in August (Figure 5d), and the most depleted (and actually prebomb) nearshore DOC was observed at the ONT site (measured

$\Delta^{14}\text{C} = -10\text{‰}$ ) in June (Figure 5c). These values are shifted to more  $^{14}\text{C}$ -enriched values when blank corrected as shown in Tables 2 and 3.

[26] In most cases, POC samples were more  $^{14}\text{C}$  depleted than co-occurring DOC samples. Measured  $\Delta^{14}\text{C}$  of POC in the isothermal open lake varied widely between  $34\text{‰}$  ( $68\text{‰}$  for blank-corrected values) and  $-303\text{‰}$  ( $-354\text{‰}$  for blank-corrected values), corresponding to ‘modern’ and 2840 yrs B.P. (3453 yrs B.P. for blank-corrected values), respectively (Figure 5e and Table 2). Variation in  $\Delta^{14}\text{C}$  was similarly wide in open lake POC from August, with measured



**Figure 6.** Distributions of  $\Delta^{14}\text{C}$  POC in the water column as a function of total water depth at the various stations. Old POC samples and variability of POC ages appear to increase in the deep basins of the lake. Filled symbols are stratified lake data and open symbols are for isothermal data.

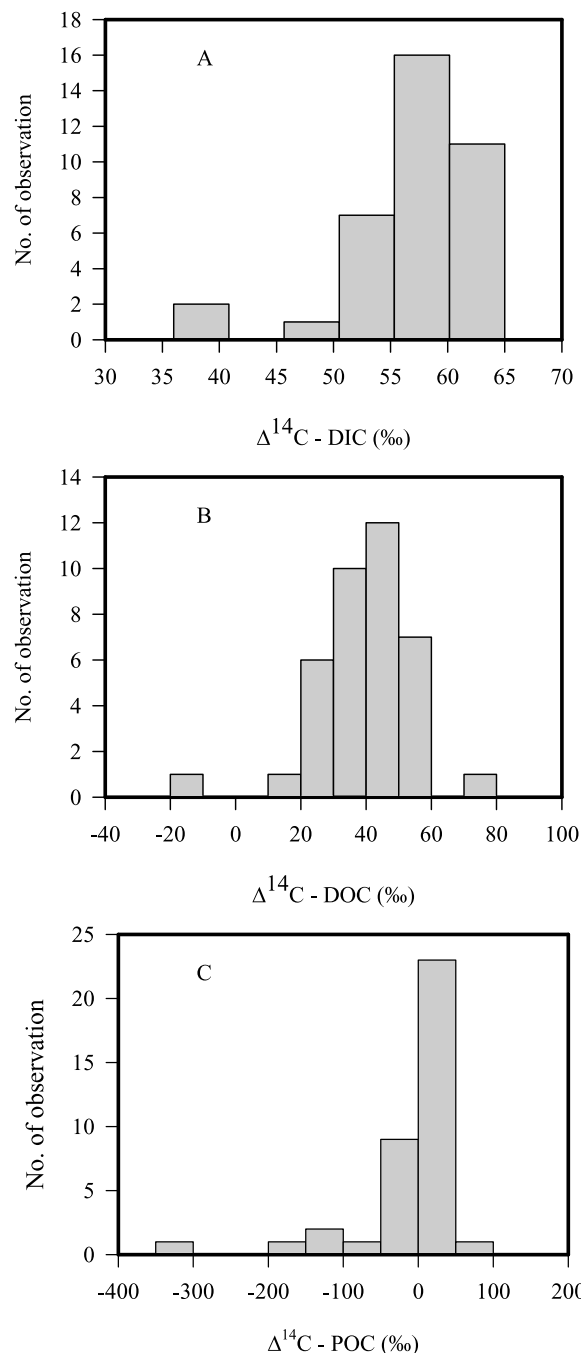
and blank-corrected values, respectively, from 58 to 75‰ (modern) to  $-145\text{‰}$  to  $-170\text{‰}$  (1200–1440 yrs B.P.) (Figure 5f and Table 3). While  $^{14}\text{C}$  depletion was seen across both surface and deep POC samples during isothermal conditions in June, the  $^{14}\text{C}$ -depleted samples were mostly limited to deepwater POC during stratification in August (Figures 5e and 5f). The measured  $\Delta^{14}\text{C}_{\text{POC}}$  from the near-shore regions of the lake averaged 13‰ (range  $-19\text{‰}$  to  $36\text{‰}$ ,  $n = 8$ ) (Figures 5e and 5f). The oldest offshore POC ( $\Delta^{14}\text{C} = -303\text{‰}$  to  $-354\text{‰}$ ; 2840–3453 yrs B.P. at EM in June, and  $-145\text{‰}$  to  $-170\text{‰}$ ; 1200–1440 yrs B.P. at SM in August) were seen in the deepest basins of the lake (Figure 6). Nearshore POC showed much less  $^{14}\text{C}$  depletion, with the most depleted nearshore sample (NB) having  $\Delta^{14}\text{C} = -19\text{‰}$  to  $-14\text{‰}$  (56–95 yrs B.P.). Although a considerable number of the open-lake POC samples were old, most ( $\sim 70\%$ ) of the POC samples from the lake had a modern (post 1950)  $^{14}\text{C}$  signal (measured  $\Delta^{14}\text{C}$  of 0–50‰, Figure 7c).

## 4. Discussion

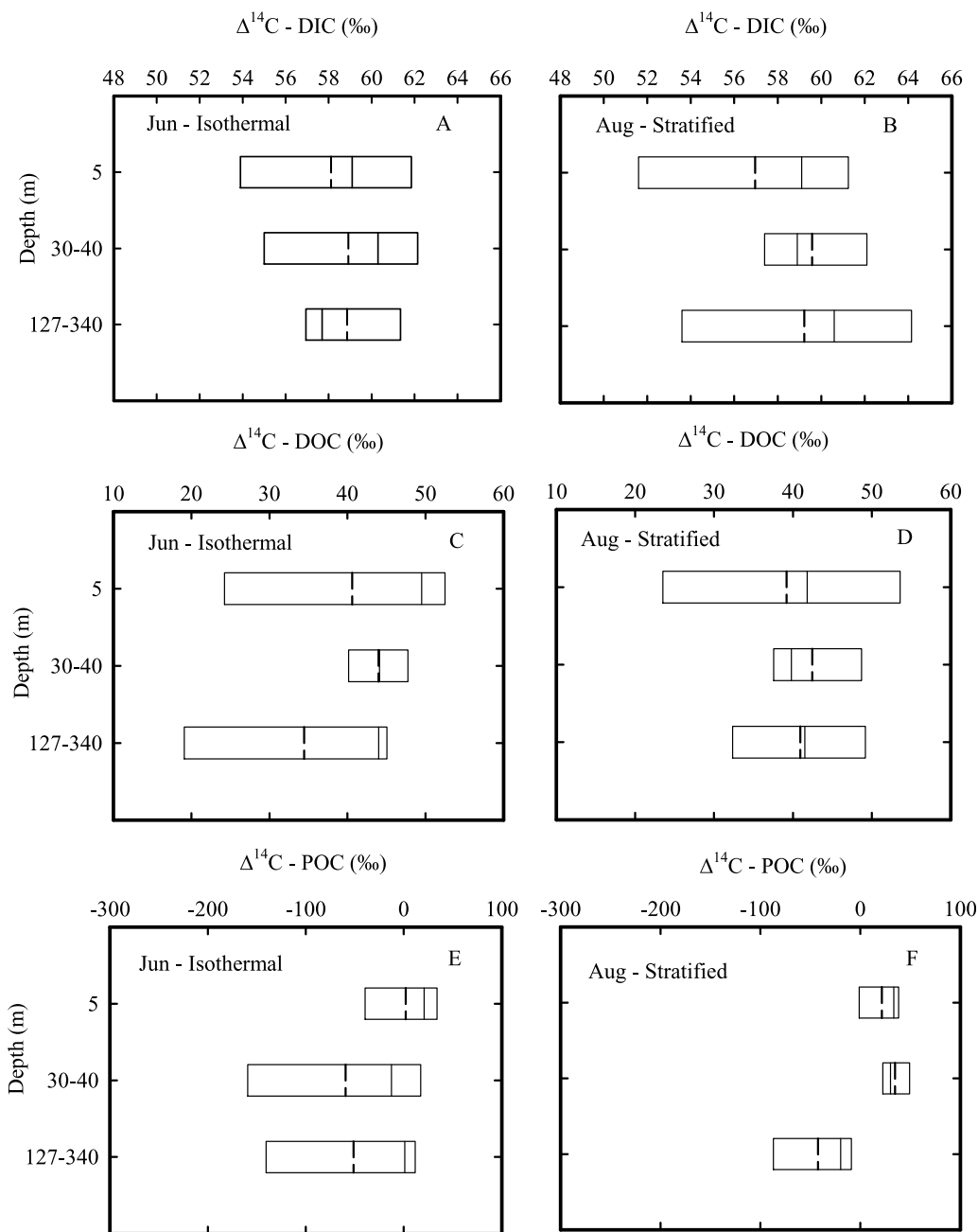
### 4.1. Physical Regime and the Distribution of DIC Concentration and Isotopes

[27] In general, DIC concentrations and  $\delta^{13}\text{C}$  in the open lake appear laterally homogenous with no significant localized influence (Figures 2a, 2b, 4a, and 4b) and with their dynamics modulated by, and tightly coupled to the physical homogenization of the water column in June (isothermal conditions). Photosynthesis and respiration appear responsible for the open-lake depth trends in August, where the epilimnion is lower in DIC concentrations and has a higher  $\delta^{13}\text{C}_{\text{DIC}}$ , due to photosynthetic depletion and fractionation of the DIC pool (coupled with lower DIC solubility in warmer waters), while the hypolimnion shows higher DIC concentrations and lower  $\delta^{13}\text{C}_{\text{DIC}}$ , indicating the effects of increased remineralization of organic carbon at depth [Velinsky and Fogel, 1999; Zigah et al., 2011]. The largest

shift of  $\delta^{13}\text{C}_{\text{DIC}}$  between isothermal and stratified conditions was observed in the epilimnion at the western province (WM) and could be due to the higher primary productivity reported for this region of the lake relative to the central lake and eastern basin [McManus et al., 2003; Cotner et al., 2004]. The general homogeneity of  $\Delta^{14}\text{C}_{\text{DIC}}$  across the entire open lake is consistent with the lake's large surface area, spatially well mixed water column, and the absence of significant localized groundwater input or input of  $^{14}\text{C}$ -dead



**Figure 7.** Frequency plots of  $\Delta^{14}\text{C}$  values of (a) DIC, (b) DOC, and (c) POC in Lake Superior showing mostly seen ranges during both stratified and isothermal seasons. Note that  $\Delta^{14}\text{C}$  of DOC and POC are the measured values.



**Figure 8.** Depth profiles of site-combined-mean values during isothermal condition of (a)  $\Delta^{14}\text{C}_{\text{DIC}}$ , (c)  $\Delta^{14}\text{C}_{\text{DOC}}$ , and (e)  $\Delta^{14}\text{C}_{\text{POC}}$ , and during stratified condition of (b)  $\Delta^{14}\text{C}_{\text{DIC}}$ , (d)  $\Delta^{14}\text{C}_{\text{DOC}}$ , (f)  $\Delta^{14}\text{C}_{\text{POC}}$ . The  $\Delta^{14}\text{C}$  are the measured values. Box represents the 25th and 75th percentiles, the solid line within the box represents the median value, and the dash line within the box is the mean value.

carbon from dolomite or carbonate. Values of  $\Delta^{14}\text{C}_{\text{DIC}}$  (50–65‰) in the open lake were higher than that of co-occurring atmospheric  $\text{CO}_2$  ( $38 \pm 2\text{‰}$ ) [Zigah *et al.*, 2011] as determined from the  $\Delta^{14}\text{C}$  content of leaves of a local corn plant collected the same year [after Hsueh *et al.*, 2007]. This offset is most likely due to the time of exchange for the in-lake DIC pool with the atmosphere, which is affected by water column stratification, ice cover, and the extent of water column mixing [Hesshaimer *et al.*, 1994; Abbott and Stanford, 1996; Huguen *et al.*, 2004; Urban *et al.*, 2005; Alin and Johnson, 2007]. In the nearshore regions, the

low values of  $\Delta^{14}\text{C}_{\text{DIC}}$  observed off the Ontonagon ( $\Delta^{14}\text{C}_{\text{DIC}} = 38\text{‰}$ ) in June and in Nipigon Bay ( $\Delta^{14}\text{C}_{\text{DIC}} = 36\text{‰}$ ) in August were similar to the atmospheric  $\Delta^{14}\text{C}$ , and suggest mineralization of recent terrestrially derived OM (such as leaf material) and/or quicker equilibration of these shallower nearshore sites with the overlying atmosphere.

#### 4.2. DOC Biogeochemistry

[28] Vertical distributions of DOC concentration and  $\delta^{13}\text{C}_{\text{DOC}}$  in June, which were homogeneous (Figure 2c), are

consistent with the physical regime of the lake, which exhibits complete water column mixing at this time of the year. However, the lateral similarities in concentration and stable isotope composition in June are a bit more surprising as modeling studies have shown exchange between basins on the order of months to years (V. Bennington, personal communication, 2011; P. Cheng, personal communication, 2010) and differ from  $\Delta^{14}\text{C}_{\text{DOC}}$  results indicated below, perhaps because radiocarbon presents a larger dynamic range ( $\Delta^{14}\text{C}$ ,  $-1000\text{‰}$  to  $+200\text{‰}$ ) and is therefore more sensitive to variations in the carbon cycle than are concentrations or  $\delta^{13}\text{C}$  values ( $\delta^{13}\text{C}$  for organic carbon range from  $-32$  to  $-12\text{‰}$ ) [Petsch *et al.*, 2001; Wakeham *et al.*, 2006].

[29] Heterogeneity in DOC concentration during stratified conditions in August (Figure 2d) is most likely due to differences in productivity in the epilimnion and heterotrophy in the deeper waters. The western province of the lake has been shown to have higher primary production relative to other parts of the lake [McManus *et al.*, 2003; Cotner *et al.*, 2004], consistent with the relatively higher DOC concentration at WM relative to EM, and with the trends in DIC concentration and isotopic composition discussed in the previous section. Site CM can be impacted by the Keweenaw current [Zhu *et al.*, 2001] and sites SM and NM by the generally cyclonic gyre circulation in the eastern basin [Bennington *et al.*, 2010] thus these locations are affected by water from nearshore regions, with its higher concentrations of land-derived material, nutrients, and warmer summer temperatures, the latter two of which could enhance primary productivity in August. The  $\delta^{13}\text{C}$  of DOC in most cases exhibited no significant variation laterally or vertically in August within the instrumental precision of  $0.2\text{‰}$  (Table 3), possibly because water column mixing (twice per year) and lateral flow distributes it more quickly than biogeochemical processes can inflict a fingerprint upon it. The  $^{13}\text{C}$  enrichment with depth seen at CM and WM during stratification could be due to diagenetic alterations or remineralization in the water column [Vahatalo and Wetzel, 2008].

[30] Throughout the lake, both nearshore and offshore, the bulk  $\Delta^{14}\text{C}_{\text{DOC}}$  (both measured and blank corrected) was modern (postbomb) with the exception of site ONT in June (Figures 5c and 5d). The  $^{14}\text{C}$  depletion of the surface DOC at NM, EM, and SM sites during spring mixing in June (relative to WM and CM sites) may be due in part to the current structure of Lake Superior (as described by Bennington *et al.* [2010]), where sites NM and SM, and to some extent EM, are in the flow paths of the generally cyclonic flow in that region of the lake and would be affected by nearshore-derived organic matter entrained into these currents, especially in winter and spring. In summer, sites NM and SM are likely to remain affected by this cyclonic flow and nearshore organic matter transported in it, while site EM is less impacted and shows epilimnetic  $\Delta^{14}\text{C}_{\text{DOC}}$  values similar to the central and western lake sites (Figure 5d). Another process/mechanism that could explain the  $^{14}\text{C}$  depletion of epilimnetic DOC seen at SM and NM sites is photoproduction of DOC from POC as observed in several natural systems [Komada and Reimers, 2001; Koelmans and Prevo, 2003; Kieber *et al.*, 2006; Butman *et al.*, 2007; Mayer *et al.*, 2006, 2009; Shank *et al.*, 2011]. Also, OC in rainwater could be a source of  $^{14}\text{C}$  depletion of DOC in the epilimnion as the lake is considerably influenced by its

“airshed” due to its large surface area [Cotner *et al.*, 2004]. Old rainwater OC has been observed in Woods Hole, MA and New Haven, CT in USA ( $\Delta^{14}\text{C} = -653\text{‰}$ , 8567 yrs B.P [Raymond, 2005]) but  $\Delta^{14}\text{C}$  of rainwater over Lake Superior is not available. We expect the influence of photoproduced DOC and rainwater DOC to be widespread across the lake rather than being localized at NM and SM as was seen in the lake, hence the likely cause of the surface water DOC  $^{14}\text{C}$  depletion is nearshore old DOC transported by currents as discussed above.

[31] During the stratified period, DOM at the WM, CM, and EM sites shows depletion in  $^{14}\text{C}$  with depth in the water column suggesting some input of old DOC to the hypolimnetic waters at these sites. Pore water-derived DOC could potentially be the source of this old POC. Also, lateral deep water current could transport old DOC from the nearshore region to the offshore sites, especially at the CM site which is close to the nearshore ONT site.

[32] Although DOC in groundwater could also be considerably  $^{14}\text{C}$  depleted [Murphy *et al.*, 1989], groundwater is not a significant source of deep water in Lake Superior, and likely has very little influence on the lake DOC. This is also confirmed by the absence of considerable  $^{14}\text{C}$  depletion in our hypolimnetic  $\Delta^{14}\text{C}_{\text{DIC}}$  as the presence of groundwater should also affect lake DIC. In general, the bulk DOC pool appears semilabile throughout the lake because of the post-bomb  $\Delta^{14}\text{C}$  values indicating DOC turnover times of  $\leq 60$  years. Using our DOC pool size (calculated from concentration data and lake volume as  $14.2\text{--}16.4\text{ Tg C}$ ) and the DOC influx rate of  $0.7\text{--}1.3\text{ Tg C yr}^{-1}$  reported by Cotner *et al.* [2004] puts the DOC residence time at 11–23 years, whereas the DOC influx rate of  $0.1\text{ Tg C yr}^{-1}$  reported by Urban *et al.* [2005] gives a DOC residence time of 16–41 years. These turnover times are consistent with previous estimates of approximately one to four decades [Cotner *et al.*, 2004; Urban *et al.*, 2005] based upon carbon budget approaches.

### 4.3. Dynamics of C and N Concentrations and Stable Isotope Ratios Within POM

[33] Higher epilimnetic POC and PON values observed during stratification (Table 3) could be due to increased algal, bacterial and zooplankton production [Velinsky and Fogel, 1999]. The lakewide C:N values of POM agree with previously reported values (C:N values of 4.6–14.3) [Guildford and Hecky, 2000; Urban *et al.*, 2004; Sterner, 2010; Zigah *et al.*, 2011]. The positive shift in the POM C:N values during stratification implies a disproportionately higher increase in organic carbon relative to organic nitrogen (or preferential mineralization of PON) most likely due to shifts in algal and/or bacterial communities and their biomass production versus remineralization demands.

[34] Increased aquatic in situ primary production in the warmer epilimnetic waters most likely yielded the observed shift in  $\delta^{13}\text{C}_{\text{POC}}$  toward more  $^{13}\text{C}$ -enriched values during stratification (Figure 4d) [Keough *et al.*, 1996, 1998; Sierszen *et al.*, 2006]. Just as in  $\delta^{13}\text{C}_{\text{DIC}}$ , the largest shift in  $\delta^{13}\text{C}_{\text{POC}}$ , occurring at the western province during stratification (Table 3), was likely due to higher primary productivity in the western arm relative to the central and eastern lake [McManus *et al.*, 2003; Cotner *et al.*, 2004]. Our  $\delta^{15}\text{N}_{\text{PON}}$  values are consistent with previously reported values in the lake of  $-1.0\text{‰}$  to  $3.0\text{‰}$  in May–June, and  $-4\text{‰}$  to  $1\text{‰}$  in

August–September [Pang and Nriagu, 1977; Keough et al., 1996; Ostrom et al., 1998; Harvey and Kitchell, 2000; Sierszen et al., 2006; Kumar et al., 2011]. The shift in  $\delta^{15}\text{N}_{\text{PON}}$  to more  $^{15}\text{N}$ -depleted values during stratification is likely due to utilization of more nitrate relative to ammonium by phytoplankton. Nitrate ( $\text{NO}_3^-$ ) is the most abundant inorganic nitrogen (N) species in the lake ( $\sim 25 \mu\text{M}$ ) [Sterner et al., 2007; Sterner, 2010] with  $^{15}\text{N}$ -depleted values of nitrogen isotopes ( $-2.3 \pm 0.3\text{‰}$ ) [Finlay et al., 2007]. On the other hand, ammonium ( $\text{NH}_4^+$ ) concentration in the lake is low ( $\sim 0.2 \mu\text{M}$ ) [Sterner, 2010] but constitutes a disproportionately larger ( $\sim 75\%$ ) portion of the total N uptake by plankton [Kumar et al., 2008], and has comparatively  $^{15}\text{N}$ -enriched values ( $\delta^{15}\text{N}$  of  $2.7\text{‰}$ ) [Kumar et al., 2011]. Therefore, the  $^{15}\text{N}$ -depleted values of PON during stratification in August indicate greater relative uptake of  $\text{NO}_3^-$  in the productive surface waters perhaps due to decreases (via microbial utilization or conversion to oxidized form, thus nitrate) in the available ammonium or a shift in the phytoplankton species composition [Kumar et al., 2011]. The  $^{15}\text{N}$  enrichment of PON with depth during stratification is due to the combination of less nitrate utilization in the less productive colder deeper waters, and also the preferential release of  $^{14}\text{N}$  from remineralization of sinking POM [Kumar et al., 2011].

#### 4.4. New Insights Into OC Budget of Lake Superior

[35] The current OC budget for Lake Superior is thought to be out of balance with estimated community respiration far exceeding total inputs of OC from primary production and allochthonous sources. Cotner et al. [2004] reported total OC input of  $6\text{--}9.23 \text{ Tg C yr}^{-1}$  (inclusive of atmospheric deposition, riverine loading, and phytoplankton primary production), and total OC output of  $13.48\text{--}40.5 \text{ Tg C yr}^{-1}$ , mainly from respiration. Urban et al. [2005] reported total OC input of  $2.4\text{--}7.7 \text{ Tg C yr}^{-1}$  (inclusive of shoreline erosion in addition to the input terms in the earlier estimate), and total OC output of  $13.2\text{--}83.1 \text{ Tg C yr}^{-1}$ . The mismatch in the input and output OC terms has been attributed to poor constraint on the respiration and/or OC pool sizes (because of poor spatial and temporal coverage in existing data, mostly nearshore biased), or could result from the lake's OC budget not being in equilibrium.

[36] Based on our data on the abundances of OC, we determine that the lake's DOC pool is  $14.2\text{--}16.4 \text{ Tg C}$  (compared to its DIC pool of  $121\text{--}122 \text{ Tg C}$ ), and its POC pool is  $0.9\text{--}1.3 \text{ Tg C}$ . Our values are slightly lower than, but generally comparable to, the DOC and POC pools of  $15\text{--}19 \text{ Tg C}$  and  $1.2\text{--}2.5 \text{ Tg C}$  estimated by Cotner et al. [2004], and  $\sim 17 \text{ Tg C}$  and  $\sim 1 \text{ Tg C}$ , respectively, given by Urban et al. [2005]. Recent work by Sterner [2010] constrains the total phytoplankton production in the lake at  $9.73 \text{ Tg C yr}^{-1}$ . Using this new primary production and the OC flux estimates of Cotner et al. [2004] puts the total OC inputs at  $10.43\text{--}10.76 \text{ Tg C yr}^{-1}$ . Similarly, recalculating using the other input terms of Urban et al. [2005] with the new primary production and pool estimates gives OC input of  $10.13\text{--}10.73 \text{ Tg C yr}^{-1}$ . These values are just slightly lower than the lower limit of the respiration estimate ( $13 \text{ Tg C yr}^{-1}$ ) by both Cotner et al. [2004] and Urban et al. [2005] and considerably lower than their upper limits ( $39\text{--}81 \text{ Tg C yr}^{-1}$ ).

[37] In an effort to constrain the respiration estimate in the lake, Strom [2007] used changes in deep water oxygen and nitrate levels at multiple offshore and nearshore sites from 2003 to 2006 and reported an annual lake-wide community respiration of  $\sim 4 \text{ Tg C yr}^{-1}$ . Also, Bennington [2010], using a modeling approach, reported a modeled lake-wide community respiration of  $5.8 \text{ Tg C yr}^{-1}$  based on data from the year 1999. These revised respiration estimates imply that poor constraint (thus, overestimation) on the lake-wide community respiration could have been the cause of the apparent imbalance in the lake's OC budget as reported previously by Cotner et al. [2004] and Urban et al. [2005]. We initially hoped that spatial and temporal variations within the radiocarbon in lake DIC could provide further insight into these respiration values. However, due to the large amount of carbon in the DIC pool and the magnitude of atmospheric exchange processes, radiocarbon measurements on DIC do not provide sufficient resolution to further constrain the lake's respiration. It is worth noting that winter time OC abundances, primary production, and community respiration are still unconstrained because portions of the lake show incomplete ice coverage making sampling more challenging by ice or water. Therefore winter time and higher spatial scale community respiration in the lake would be needed to close the OC budget of the lake.

#### 4.5. Putative Origins of POC

[38] The depletion of  $\Delta^{14}\text{C}$  values of POC compared to DOC shows a spatial decoupling of the processes modulating their dynamics and radiocarbon content. The  $^{14}\text{C}$  ages of POC in the lake (Figures 5e and 5f) suggest that they are affected by an old C source (considerably prebomb) in the water column in June and especially in the deep waters in August. Potential sources of lake POC include autochthonous production, terrestrial organic matter, dry and wet atmospheric deposition, and sedimentary particulate matter. In the paragraphs below, we will discuss these sources in detail to determine their relative importance in Lake Superior.

[39] If the majority of the POC were derived from that year's autochthonous production, it would have  $\Delta^{14}\text{C}$  values tracking lake  $\Delta^{14}\text{C}_{\text{DIC}}$  since the inorganic carbon is incorporated during biosynthesis [McCarthy et al., 2011]. The  $^{14}\text{C}$  depletion of POC compared to DIC implies that a variable portion of the POC in the lake is not derived from recent within-lake production. Lake Superior is less influenced by organic carbon from terrestrial origin than most lake systems, due in large part to its low watershed-to-lake-surface area ratio [Cotner et al., 2004], with current estimates of terrestrial organic carbon inputs at  $\sim 10\%$  of total annual organic carbon influxes [Maier and Swain, 1978; Urban et al., 2005; Cotner et al., 2004; Zigah et al., 2011].  $\Delta^{14}\text{C}$  values of POC from most of the nearshore sites were not considerably  $^{14}\text{C}$  depleted (Figures 5e and 5f) and stormflow data from a Lake Superior tributary (Amity Creek, Duluth, MN) also shows moderate  $\Delta^{14}\text{C}_{\text{POC}}$  ( $\Delta^{14}\text{C} = 11.1\text{‰}$ ) [Zigah et al., 2011]. Thus both existing carbon budgets and isotopic data discount terrestrial influence as the likely cause of the  $^{14}\text{C}$  depletion of open lake POC samples.

[40] The atmosphere could be of importance in the Lake Superior carbon budget because of the huge surface area of the lake compared to the watershed [Cotner et al., 2004];

however, organic carbon loading from the atmosphere to Lake Superior has not been directly studied. Estimates of atmospheric organic carbon input range from 0.3 to 4% [Urban *et al.*, 2005] to 6–34% [Cotner *et al.*, 2004] of the lake organic carbon and these estimates include both dissolved and particulate phases. Studies of rainwater at Wilmington, NC, USA have shown that unfiltered rainwater mostly consists of dissolved organic carbon (~98%) [Willey *et al.*, 2000]; therefore it is likely that only trace POC is derived from wet deposition. The eastern and central provinces of the lake fall within the downwind range of depositional influence of the Chicago, IL metropolitan area, and previous studies have noted inputs of hydrophobic organic contaminants (HOCs) and soot carbon (both of which are byproducts of industrial incineration processes) to this region of the lake from the Chicago urban area [Buckley *et al.*, 2004]. Soot carbon (also, black carbon) from industrial sources could be considerably  $^{14}\text{C}$  depleted [Reddy *et al.*, 2002] and could shift POC values toward the old  $^{14}\text{C}$  age ranges seen in our POC samples. However, our data shows that black carbon makes up only 4–9% of POC and was on average, significantly lower than the amount needed to explain the old ages of POC seen in the lake, assuming that all the measured black carbon was  $^{14}\text{C}$  dead ( $\Delta^{14}\text{C} = -1000\text{‰}$ ), i.e., from fossil fuels rather than wood and biomass combustion. This is a conservative assumption considering Lake Superior's location bordering boreal forest, the prevalence of wildfires in the region, and the low human population in the Lake Superior watershed.

[41] The lake's underlying sediments are another, and more likely, source of older particulate material in the lake. Both radioactive decay of organic  $^{14}\text{C}$  in sediments (not so significant in a relatively young lake such as Lake Superior, approximately 10,000 years old [Mothersill, 1988; Lowell *et al.*, 1999] and preferential diagenesis of more labile younger organic carbon can result in  $^{14}\text{C}$ -depleted (old) values of organic carbon in the sediments [McCarthy *et al.*, 2011; Eglinton *et al.*, 1997]. Lake Superior receives a considerable amount of eroded materials each year, and previous studies have documented resuspension events in different parts of the lake [Baker and Eisenreich, 1989; Hawley, 2000; Urban *et al.*, 2004; Zigah *et al.*, 2011]. Of the estimated 40 million metric tons of eroded materials from the U.S. coastline of the Great Lakes every year, about a quarter (5–11 million metric tons) goes into Lake Superior [Stortz *et al.*, 1976; Monteith and Sonzogni, 1976; Siebel *et al.*, 1976; Kemp *et al.*, 1978]. The southwestern shoreline of Lake Superior contains large (~3600 km<sup>2</sup>) deposits of glacial-lacustrine red clay which is susceptible to extensive erosion into the lake [Siebel *et al.*, 1976; Bahnick *et al.*, 1978]. By using Landsat Satellite data and measurements of suspended solids, particle sizes, and turbidity depth profiles, Stortz *et al.* [1976] reported substantial sedimentary inputs into the western Lake Superior water column, especially during winter storms, and high northeasterly winds. In a study off the Keweenaw Peninsula, Churchill *et al.* [2004] used a Benthic Acoustic Stress Sensor (BASS) array (which had current and pressure sensors) and an in situ particle sampler for collecting suspended particulate matter, both deployed just above the lake floor on a tripod stand, and reported that high bottom stress during autumn and winter results in sediment resuspension (even at 90 m

depth), and these resuspended materials tend to be carried offshore by the Keweenaw current which flows northeastward along the western shoreline of Keweenaw Peninsula. The Keweenaw current (a coastal jet) hence inputs these resuspended particulate materials into the eastern basin of Lake Superior.

[42] Similarly, using a submersible equipped with video, camera, and a sampler, Flood [1989] reported large arcuate depressions at 240 m and furrows at 90 m water depth sites in the central basins, consistent with observations from side-scan sonar [Flood and Johnson, 1984], and caused by extensive erosion and resuspension of sediments. Furthermore, Hawley [2000] also reported sedimentary resuspension and transport offshore in a study off the Keweenaw Peninsula. Urban *et al.* [2005] reported that much of the POC in Lake Superior was derived from sediment resuspension based on concentrations of total suspended particles (TSP), and the observed relationship between POC and TSP. Resuspended materials have also been seen in sediment traps collecting sinking POC in the Lake. For instance, between 10 and 30% of sinking POC just offshore of the Keweenaw Peninsula in Lake Superior has been reported to be derived from resuspended sediments [Urban *et al.*, 2004].

[43] In this study, coupling the considerable  $^{14}\text{C}$  depletion in POC with depth during stratification in August with the presence of old POC in samples from both surface and deep water during isothermal conditions is consistent with both water column diagenesis/OC-remineralization of freshly synthesized OC, and considerable sediment resuspension, where such resuspension is likely confined to the hypolimnion by density-driven stratification in August and present throughout the water column during isothermal periods. Our data indicates that resuspension affects open-lake sites as well. That open-water regions can be significantly impacted has been seen in marine systems as well; as much as 35% of sinking POC from several open-ocean sites has been reported to be derived from resuspended sediments [Hwang *et al.*, 2010].

#### 4.6. Spatial Heterogeneity of $\Delta^{14}\text{C}$ of POC (POC Ages) in Lake Superior

[44] POC ages varied widely across the lake, and with the physical regime of the lake (Figures 8e and 8f). Although at a coarse spatial resolution, our data show that POC ages appear to increase ( $^{14}\text{C}$  depleted) in the deepest basins (SM and EM) of the lake (Figure 6). Trends in the POC ages observed in Lake Superior are consistent with the widespread influence of resuspension on sinking POC as has previously been seen in several open oceanic sites with the oldest marine POC observed in the deepest basin [Hwang *et al.*, 2010]. In large aquatic systems such as Lake Superior and the oceans, several entrainment, lateral transport and redeposition events are required to deposit sediments in the deeper basins, and that could lead to very old ( $^{14}\text{C}$  depleted) fine particles being present in these regions. The eastern basin, which exhibits more  $^{14}\text{C}$  depletion in its POC samples, contains north-south trending troughs covered by up to 13–15 cm of soft sediments sitting on top of stiff postglacial sediments due to the high currents that flow through [Boyer and Hedrick, 1989; Watruss and Rausch, 2001] whereas the western basin, whose POC radiocarbon signatures are more uniform, is characterized by very low



relief with the exception of two deep troughs at the north-western shore, which have thick deposits of sediments spanning several thousand years [Wattrus and Rausch, 2001; Pearson, 2005].

[45] For the resuspended sediments to considerably influence the lake water as suggested by the old ages of POC, strong bottom currents, and/or strong storms are required. Strong storms occur on the lake during spring and fall when the prevailing winds are out of northeast and are strong enough to erode and entrain sediments [Wattrus and Rausch, 2001]. Previous studies have shown that the south shore is more susceptible to erosion than the north shore is [Johnson and Johnston, 1995] with coastal erosion of clays being about 5 times faster at the south shore [Wattrus and Rausch, 2001]. Surface water circulation in the lake is mostly cyclonic whereas the bottom/deep circulation pattern in the lake is not well constrained, although thought to be generally cyclonic, flowing northeastward along the south shore [Lam, 1978], suggesting that entrained sediments from the south shore would potentially influence the central and eastern regions, those exhibiting older radiocarbon POC values. Although bottom-current velocities have not been well studied in the lake, reported current speeds up to  $35 \text{ cm s}^{-1}$  at 150 m (middepth) and  $15 \text{ cm s}^{-1}$  at 10 m above the lake floor have been reported near Isle Royale [Carlson, 1982] and up to  $42 \text{ cm s}^{-1}$  off the Keweenaw Peninsula [Miller et al., 1977]. The Keweenaw current, a strong along-shelf coastal jet from the Keweenaw Peninsula toward the northeastward direction, periodically splits off toward the center of the lake [Zhu et al., 2001; Van Luven et al., 1999]. The velocities of the coastal jet and bottom currents discussed above are high enough to resuspend loose fine sediments in these regions, and to transport them around the central-southern-eastern regions of the lake, leading to the observed considerably aged POC samples at these regions of the lake.

#### 4.7. Implications of Resuspension for Ecosystem Dynamics and Biogeochemistry

[46] The fate of the old POC from resuspended sediments remains an open question. In somewhat smaller lakes (e.g., Lake Michigan), sediment resuspension has been reported to influence water column ecosystems [Eadie et al., 2002; Schallenberg and Burns, 2004]. While some studies reported that resuspended sediments increase net primary and winter heterotrophic productions, and community respiration [Cotner et al., 2000; Schallenberg and Burns, 2004; Johengen et al., 2008], others noted that the reduced light availability from resuspension events would decrease primary production during the spring season [Lohrenz et al., 2004].

[47] In Lake Superior, the DIC pool (121–122 Tg C) is about two orders of magnitude larger than the POC pool (0.9–1.3 Tg C), so mineralization or sinking of the old POC to DIC will have only trace effects on the concentration and isotopic values of the DIC. For instance, if all the POC at each site and depth is mineralized to DIC, the effect on the  $\Delta^{14}\text{C}$  of DIC at each site and depth (in both stratified and mixed lake) will be  $^{14}\text{C}$  depletion by only  $0.5 \pm 0.4\text{‰}$  (range: 0.02–2.06‰,  $n = 38$ ). Although this estimation is conservative as we do not expect all the old POC to be mineralized, the radiocarbon effect, nonetheless, is negligible as these values are below the precision of  $\Delta^{14}\text{C}$  of DIC of 2–5‰ in this study. Similarly, if all the POC at each site

and depth is photochemically and/or microbially degraded to DOC (again, a conservative estimate), the effect on  $\Delta^{14}\text{C}$  of DOC will be  $2.5 \pm 3.3\text{‰}$  (range: 0.04–17.34‰,  $n = 39$ ). While the POC effect on DOC radiocarbon values would be negligible ( $\leq 5\text{‰}$ ) in most cases, it would be substantial ( $\sim 17\text{‰}$ ) at the EM site (40 m depth) during mixed lake condition if all the POC was degraded to DOC.

[48] Therefore, in a further attempt to identify whether old POC acts as a reduced carbon or food subsidy to the Lake Superior ecosystem,  $\Delta^{14}\text{C}$  values of mesozooplankton from the lake were measured. Mesozooplankton biomass does not exhibit incorporation of the old carbon [Zigah et al., 2011; Zigah, 2012]. Therefore, old POC does not appear to be supporting zooplankton secondary production (and by extension, zooplanktivorous fish production) in the lake.

[49] As discussed above, carbon sources fueling respiration in the lake are not well constrained. If the lake's resuspended sediments do fuel part of this respiration, then the lake's response to yearly variations in primary productivity would be buffered. More detailed studies (including investigation of bacterial production and respiration) to constrain the degree of benthic-pelagic coupling in Lake Superior's carbon cycle should be undertaken.

## 5. Conclusions

[50] Our lakewide radiocarbon and stable carbon data, the first of its kind in a large-lake system, reveals that bulk DOC across the entire lake (western through eastern basins) had modern radiocarbon signatures and a turnover time of  $\leq 60$  years, indicating most of the DOC in the lake is semilabile. The semilability of DOC is in sharp contrast to the old DOC ages seen in oceanic systems. This may be due in part to different water residence times ( $\sim 170$  years for Lake Superior [Quinn, 1992] compared to  $\sim 1000$ – $1500$  years for the deep ocean [McNichol and Aluwihare, 2007]), but also results at least in part from the dimictic nature of the lake, which homogenizes the water column twice a year, bringing a portion of DOC from deep water up to the more reactive (both microbially and photochemically) surface waters much more often and at a higher proportion than can occur in the open ocean. Variations in DOC concentrations across the lake support the idea that high resolution data on respiration estimates are needed in order to have a quantitative understanding of the OC budget of the lake.

[51] Our POC data show lateral heterogeneity in the mean ages and sources of POC across Lake Superior. The oldest POC samples were mostly seen in the water column of the deepest basins (eastern and southern) in the lake. POM characteristics such as POC and PON concentrations,  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$ , and  $\Delta^{14}\text{C}$  were tightly coupled to the physical regime of the lake, with  $^{14}\text{C}$  depletion of POM with depth observed during stratification. The extent of  $^{14}\text{C}$  depletion of POM appears to be related to the total water depth. Black carbon appears to be only a trace portion of the POC, and cannot account for the old ages of POC seen in the lake. Our results support previous observations [e.g., Baker and Eisenreich, 1989; Hawley, 2000; Urban et al., 2004] that a variable and often substantial portion of POC in the lake, especially in the hypolimnetic waters and in the deeper basins, is derived from sediment resuspension. The ultimate fate of these resuspended materials should be further evaluated by

examining the  $^{14}\text{C}$  signatures within bacterial respiration and/or bacterial biomass, and the biomass of known benthic feeders within the zooplankton and fish communities.

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