

1 **Methane sources in the waters of Lake Michigan and Lake Superior as revealed by**  
2 **natural radiocarbon measurements**

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10 **Key Points: (140 characters for each sentence)**

- 11 • The sources of methane dissolved in the waters of Lakes Michigan and Superior,  
12 components of the Great Lake system, were investigated.
- 13 • Natural radiocarbon measurements of methane indicate that the methane source in both  
14 lakes was largely from the atmosphere.
- 15 • In-situ aerobic methanogenesis, groundwater inputs, and nuclear power plants also appear  
16 to contribute to the methane source.

17

18

19 **Abstract**

20         The methane dynamics in the waters of Lakes Michigan and Superior, components of the  
21 North American Great Lake system, were investigated using measurements of methane  
22 concentration and natural radiocarbon ( $^{14}\text{C-CH}_4$ ) dissolved in these lake waters. All  $^{14}\text{C-CH}_4$   
23 measurements were above modern levels regardless of location and depth with a range of 117-  
24 145 percent modern carbon (pMC). Methane concentrations in the deep basin of both lakes were  
25 low, ranging from 3.3-4.3 nM, with minimal vertical variation. However, the concentrations of  
26  $\text{CH}_4$  increased toward coastal areas in both lakes, possibly due to higher groundwater inputs and  
27 aerobic methanogenesis associated with primary productivity. Except for one site,  $^{14}\text{C-CH}_4$   
28 dissolved in the waters of Lake Michigan was greater than in Lake Superior by  $\sim 12$  pMC, a  
29 difference that was likely due to inputs of excess  $^{14}\text{CH}_4$  from nuclear power plants along the  
30 coast of Lake Michigan.

31 **Plain Language Summary**

32         Methane is a greenhouse gas whose concentration is increasing rapidly in the modern  
33 atmosphere, and freshwater lakes globally provide a significant source to the atmosphere. Here,  
34 we investigate the dynamics of methane dissolved in waters of the North American Great Lakes,  
35 one of the largest liquid freshwater environments on Earth. We found that methane dynamics in  
36 both Lakes Michigan and Superior are impacted by atmospheric input, in-situ aerobic  
37 methanogenesis, groundwater, and nuclear power plants, as well as rapid vertical mixing in the  
38 water column.

39

## 40 **1. Introduction**

41 Freshwater lakes are known to be a source of methane (CH<sub>4</sub>) to the atmosphere,  
42 accounting for 6-16% of natural CH<sub>4</sub> emissions (Bastviken et al., 2004; Borrel et al., 2011). This  
43 contribution is substantially higher than oceanic emissions (Rhee et al., 2009), an interesting  
44 conclusion given the much smaller surface area of lakes globally (Downing et al., 2006). Lakes  
45 are also projected to provide a positive feedback to warming climate with projected increases in  
46 stratification (McCormick, 1990), as well as CH<sub>4</sub> production, accumulation, and emission to the  
47 atmosphere (Tranvik et al., 2009; Walter et al., 2006).

48 The North American Great Lake system is globally the largest liquid freshwater  
49 environment by area, yet to date CH<sub>4</sub> and associated carbon dynamics across this system have  
50 received disproportionately minimal attention compared to other freshwater lake environments  
51 (Alin and Johnson, 2007). Townsend-Small et al. (2016) reported that Lake Erie is a net source  
52 of CH<sub>4</sub> to the atmosphere in late summer with both natural and anthropogenic sources combining  
53 to release  $1.3 \times 10^8$  g CH<sub>4</sub>-C per day; assuming these emissions are constant over the entire year,  
54 this extrapolates to 0.09% of the global CH<sub>4</sub> emissions from lakes ( $54 \times 10^{12}$  g C/year; Bastviken  
55 et al. 2011). Including other Laurentian Great Lakes in this emission estimate may further  
56 increase the known annual CH<sub>4</sub> emissions from this system.

57 A variety of different CH<sub>4</sub> sources and sinks are known to influence emissions from  
58 freshwater lake environments. Conventional CH<sub>4</sub> production in lakes is viewed to occur in  
59 anoxic sediments through the anaerobic degradation of organic matter (Bartlett et al., 1988; Rudd  
60 and Hamilton, 1978), and diffusion from these sediments increases the CH<sub>4</sub> concentration  
61 dissolved in bottom waters (Wik et al., 2016). An additional source of CH<sub>4</sub> has more recently  
62 been documented where CH<sub>4</sub> is produced within the oxygenated water column as a byproduct of  
63 phosphorus regeneration in phosphorus-limited oligotrophic lakes (Yao et al., 2016; Grossart et

64 al., 2011; Bogard et al., 2014). Both inputs from sediments and in-situ production processes are  
65 likely responsible for CH<sub>4</sub> supersaturation in lake water columns (Blees et al., 2015; Tang et al.,  
66 2014), leading to net CH<sub>4</sub> emissions to the atmosphere. However, not all CH<sub>4</sub> produced in  
67 freshwater lakes is emitted to the atmosphere since biological oxidation is substantial in both  
68 anaerobic and aerobic environments, removing 30-99% of CH<sub>4</sub> produced in freshwater lakes  
69 (Bastviken et al., 2008). Despite these known sources and sinks, the additional processes of  
70 ebullition, diffusion, and storage in sediments and the water column, and flux through aquatic  
71 vegetation, can influence precise regional and global estimates of atmospheric CH<sub>4</sub> emissions  
72 from freshwater lakes (Wik et al., 2016; Dean et al., 2018).

73         Measurements of the natural isotopic content of CH<sub>4</sub> have been used to help constrain  
74 CH<sub>4</sub> sources and sinks. The stable carbon and hydrogen isotopic contents of CH<sub>4</sub> are the most  
75 widely used measurements, however, the interpretation of this stable isotopic data can be  
76 complicated due to multiple sources containing similar isotopic values and isotopic  
77 fractionations caused by both anaerobic and aerobic CH<sub>4</sub> oxidation (Whiticar, 1999). The  
78 combination of these isotopic effects can lead to variations in measured CH<sub>4</sub> stable isotopic  
79 values both regionally and temporally. Thus, the application and interpretation of stable isotopes  
80 to determine CH<sub>4</sub> dynamics is most informative when the endmembers of different sources and  
81 the associated isotopic fractionation processes are known (e.g. Kessler and Reeburgh 2005;  
82 Valentine et al. 2001; Leonte et al., 2017 and 2018). While measured less frequently, natural  
83 radiocarbon measurements of CH<sub>4</sub> (<sup>14</sup>C-CH<sub>4</sub>) are uninfluenced by fractionation processes, such  
84 as oxidation, since measured <sup>14</sup>C isotopic values are conventionally normalized to <sup>13</sup>C (Stuiver  
85 and Polach, 1977). This measurement is particularly useful when trying to determine the source  
86 of CH<sub>4</sub> in an environment with both fossil (e.g. hydrocarbon seeps) and modern (e.g. aerobic

87 methanogenesis) endmembers (e.g. Kessler and Reeburgh, 2005; Kessler et al., 2005; Sparrow et  
88 al., 2017). Fossil CH<sub>4</sub> generally refers to a source of carbon that is older than approximately ten  
89 <sup>14</sup>C half-lives, leaving analytically undetectable quantities of <sup>14</sup>C, and is equivalent to 0 percent  
90 Modern Carbon (pMC; Stuiver and Polach, 1977). In addition, atmospheric <sup>14</sup>C-CH<sub>4</sub> levels are  
91 currently supersaturated relative to natural <sup>14</sup>C production with values of ~ 135 pMC due to the  
92 addition of <sup>14</sup>CH<sub>4</sub> from nuclear reactors (Eisma et al., 1995; Lassey et al., 2007; Townsend-small  
93 et al., 2012; Sparrow et al., 2018). Thus, radiocarbon isotopic values, together with conventional  
94 stable isotopes of CH<sub>4</sub>, can precisely constrain the age of CH<sub>4</sub> in aquatic environments and help  
95 determine the source (e.g., Kessler and Reeburgh, 2005; Kessler et al., 2005, 2008; Sparrow and  
96 Kessler, 2017; Sparrow et al., 2018).

97         In this study, we investigated the radio- and stable-carbon isotopic signatures, together  
98 with the concentrations of CH<sub>4</sub> dissolved in the waters of Lakes Michigan and Superior to  
99 constrain the dominant sources of CH<sub>4</sub> into the waters of these two Great Lakes. This study  
100 provides critical information on CH<sub>4</sub> sources in these environments which can be used to help  
101 extrapolate CH<sub>4</sub> emissions across this massive freshwater system.

## 102 **2 Materials and Methods**

### 103 ***2.1. Study Site***

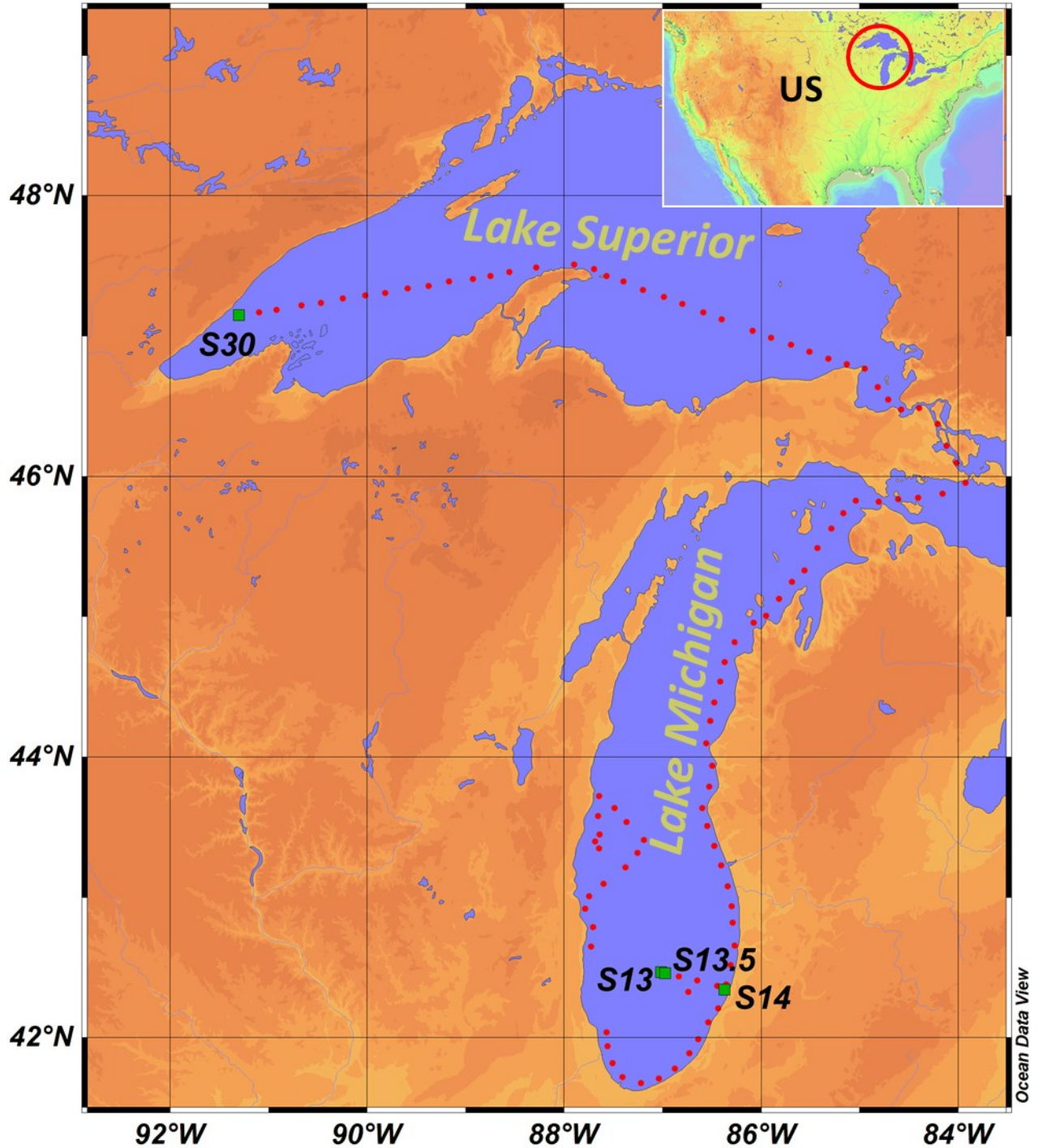
104         The North American Great Lake system is one of the largest freshwater bodies by total  
105 area and volume, containing about 21% of Earth's surface liquid freshwater  
106 (<https://www.epa.gov/greatlakes>). Due to their massive size, the Great Lakes have sea-like  
107 characteristics with waves, strong currents, and distant horizons, and as such, they have long  
108 been referred to as inland seas. Geologically, the Great Lakes were formed at the end of the last  
109 glacial period approximately 14,000 years ago as ice retreated and the basins filled with

110 meltwater (Larson and Schaetzl, 2001). Lake Superior is the largest by volume among the Great  
111 Lakes with a water residence time of ~ 193 years (Quinn, 1992); it is an oligotrophic lake with  
112 relatively low anthropogenic impact since most of the watersheds are forested with little  
113 agriculture activities due to cool climate and poor soils (Dove and Chapar 2015). Lake Michigan  
114 is the second-largest of the Great Lakes by volume and is connected to Lake Huron to the  
115 northeast. The flushing time of water in Lake Michigan is about 60 years (Quinn, 1992).  
116 Although Lake Michigan hosts highly populated cities along the coast including Chicago,  
117 Milwaukee, Green Bay, Gary, and Muskegon, the lake is classified as oligotrophic (Dove and  
118 Chapra, 2015). Recently, the waters of Lake Michigan have been experiencing significant  
119 changes in carbon dynamics as an invasive species, quagga mussels, consume primary  
120 producers, leading to higher water clarity and increasing pCO<sub>2</sub> in the water column (Lin and  
121 Guo, 2016). Groundwater inputs associated with Paleozoic bedrock are known to influence the  
122 hydrology of Lake Michigan as areas of saline water bodies near the land surface of the Lower  
123 Peninsula of Michigan (Lampe, 2009; Wahrer et al, 1996).

## 124 ***2.2. Determination of concentration and isotopic signature of methane***

125 Sample collections were conducted in Lakes Michigan and Superior during June 14-20,  
126 2017 using the research vessel R/V *Blue Heron* (Figure 1). In this sampling campaign, water  
127 samples were collected for CH<sub>4</sub> concentration and natural isotopic values ( $\delta^{13}\text{C-CH}_4$  and  $^{14}\text{C-}$   
128 CH<sub>4</sub>) together with ancillary sensor measurements of temperature, specific conductivity,  
129 dissolved oxygen (DO), and chlorophyll *a*. In addition to the surface water collections, water  
130 column profiles were also collected in two deep water sites (i.e., S13 in Lake Michigan and S31  
131 in Lake Superior) to investigate CH<sub>4</sub> distributions in the water column. Detailed methods and  
132 procedures for the determination of CH<sub>4</sub> concentrations and isotopic values can be found in

133 Leonte et al (2017) and Sparrow and Kessler (2017), respectively. Briefly, discrete bottle  
134 samples were collected for dissolved CH<sub>4</sub> concentration analysis in both the surface waters and  
135 the vertical water column.



136

137 *Figure 1 Map of sampling locations in Lakes Michigan and Superior. Green-rectangles represent sites where dissolved methane*  
138 *samples were collected for natural radiocarbon and stable isotope analyses. Red-dots indicate where discrete dissolved methane*  
139 *concentration samples were collected in surface waters.*

140 The vessel's scientific surface water supply system was used to sample surface waters while

141 Niskin bottles connected to the rosette sampler were used for the water column collections. A



142 comparison of surface water samples collected using both the scientific surface water supply  
143 system and the Niskin bottles showed insignificant differences. Immediately after the water  
144 samples were collected, a 10 mL headspace of ultra-high purity air was injected via displacement  
145 and 100  $\mu$ l of supersaturated  $\text{HgCl}_2$  solution were added as a preservative. The samples were  
146 stored isothermally in an incubator at 4°C for at least 12 hours while dissolved gases came into  
147 equilibrium with the headspace. Concentration of  $\text{CH}_4$  in the headspace was then determined on  
148 the ship with an Agilent 6850 gas chromatograph with a flame ionization detector (GC-FID) and  
149 was used along with the solubility of  $\text{CH}_4$  and the volumes of the headspace and water to  
150 determine the initial dissolved concentration.

151 Samples for natural  $^{14}\text{C}$ - $\text{CH}_4$  dissolved in lake waters were also collected. Due to the low  
152 concentration of  $\text{CH}_4$  dissolved in these waters (3.3-4.3 nM) and the typical sample size for an  
153 analysis via Accelerator Mass Spectrometry (ca. 20  $\mu$ moles of C),  $\text{CH}_4$  needed to be extracted  
154 from several thousand liters of lake water per sample. A previously published procedure was  
155 employed to perform this task in an efficient manner (Sparrow and Kessler, 2017). In brief, a  
156 high-performance discharge pump was used to pump water onto the vessel at a rate of  
157 approximately 200 liters per minute and the water was sequentially filtered to remove particles  
158 (100, 50, and 10  $\mu$ m) prior to flowing through two gas-permeable membranes (Liqui-Cel, 3M).  
159 A vacuum was applied to the outside of the gas-permeable membrane, extracting the dissolved  
160 gases, and the degassed water was continuously returned overboard. The extracted gas was then  
161 compressed into a small 1.6 L gas cylinder and returned to the land-based laboratory for further  
162 sample processing and analysis. To adequately flush all water and gas handling equipment and  
163 collect sufficient quantities of  $\text{CH}_4$ , up to 35,000 L of water were processed per sample. Deeper  
164 waters, up to almost 300 m, were sampled for this analysis by connecting multiple hoses together

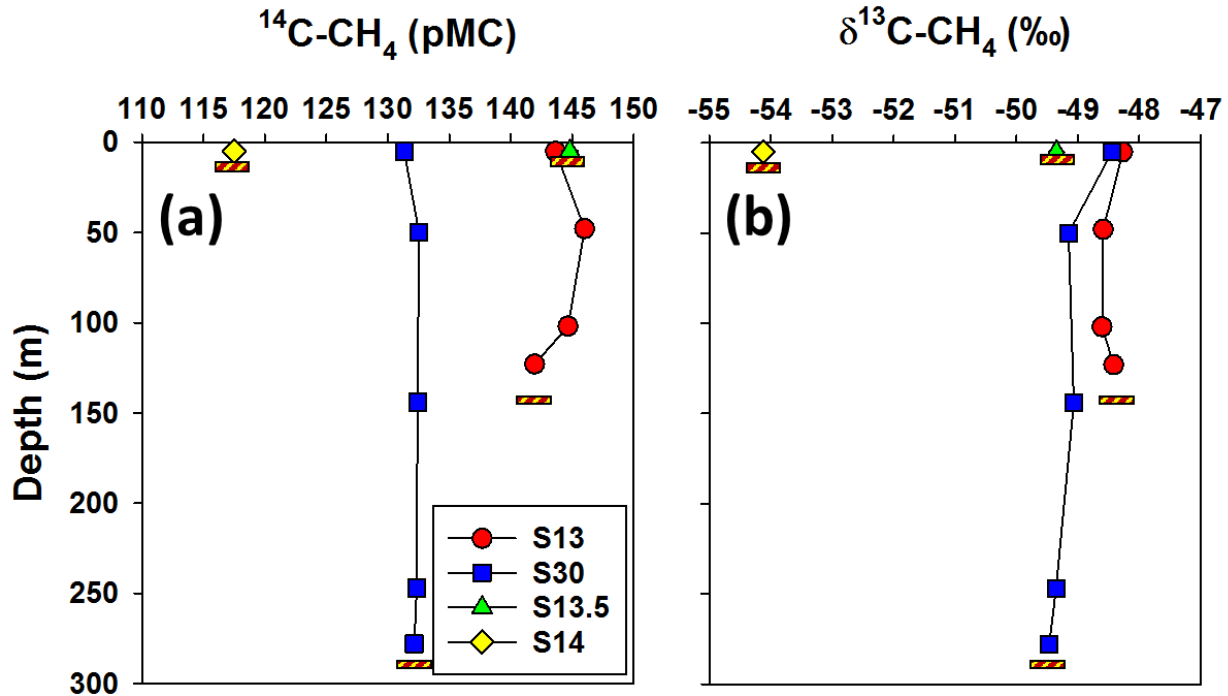
165 (each 10 m in length and 7.62 cm in diameter) and attaching them to the winch wire to reach the  
166 desired depth. In the Kessler laboratory at the University of Rochester, the CH<sub>4</sub> in the gas sample  
167 was purified and combusted into CO<sub>2</sub> and H<sub>2</sub>O. This CO<sub>2</sub> was then stored in acid-cleaned and  
168 pre-combusted Pyrex tubes prior to analysis for <sup>14</sup>C-CH<sub>4</sub> and δ<sup>13</sup>C-CH<sub>4</sub> via Accelerator Mass  
169 Spectrometry (AMS) and Isotope Ratio Mass Spectrometry, respectively, at the Keck Carbon  
170 Cycle AMS facility at UC Irvine. Lastly, multiple radiocarbon blank and standard analyses were  
171 also conducted showing minimal sample contamination and were used in the interpretation of the  
172 results (Supplementary Figure 1). Full details of the procedures, including experimental  
173 validations, can be found in Sparrow and Kessler (2017).

### 174 **3. Results and Discussion**

#### 175 ***3.1. Natural Radiocarbon of CH<sub>4</sub> Dissolved in the Water Column***

176 Natural radiocarbon values of CH<sub>4</sub> dissolved in both lake waters ranged from 117 to 145  
177 pMC (Figure 2, and Supplementary Table 1). The average <sup>14</sup>C-CH<sub>4</sub> values in Lake Michigan  
178 were significantly greater than Lake Superior (ca. 142 ± 1.5 pMC, n= 5 vs. 132 ± 0.5 pMC, n=5),  
179 except at site S14 in Lake Michigan (see below). Atmospheric values of <sup>14</sup>C-CH<sub>4</sub> range from  
180 135-136 pMC, values that are above the modern radiocarbon values for CO<sub>2</sub> in the atmosphere  
181 (ca. 103 pMC) due to thermonuclear weapons and nuclear power generation (Figure 3; Eisma et  
182 al., 1995; Lassey et al., 2007; Sparrow et al., 2018; Townsend-small et al., 2012; Wahlen et al.,  
183 1989; Kessler et al., 2008). Thus, <sup>14</sup>C-CH<sub>4</sub> in the surface waters of Lake Michigan are  
184 considerably higher than the atmosphere, whereas values in Lake Superior appear closer to  
185 equilibrium with the modern atmosphere. Along the Lake Michigan coast are five active nuclear  
186 power plants and an additional four are within 120 km from the coast (Supplementary Figure 2).

187 Thus, the higher  $^{14}\text{C-CH}_4$  in Lake Michigan water is likely the influence of these nuclear power  
 188 plants and the subsequent introduction of power plant-derived  $\text{CH}_4$  into the lake waters.



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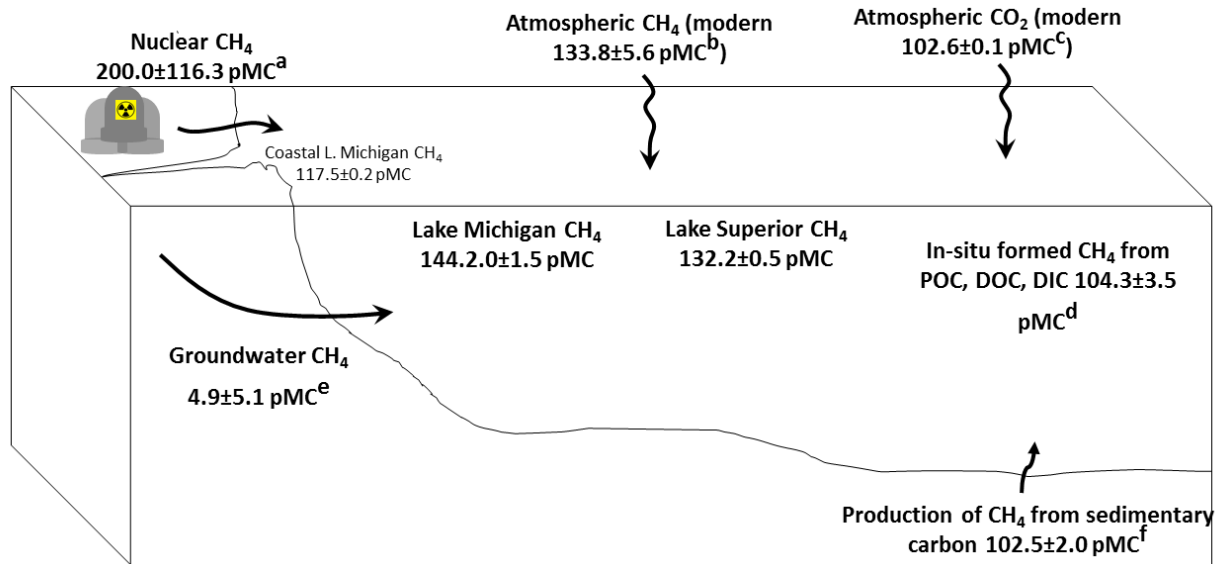
190 *Figure 2 Vertical profiles of methane (a) radiocarbon ( $^{14}\text{C-CH}_4$ ) and (b) stable ( $\delta^{13}\text{C-CH}_4$ ) isotope values in Lake Michigan and*  
 191 *Superior. S13, S13.5 and S14 are in Lake Michigan, and S30 is in Lake Superior. The horizontal bars represent the depth of the*  
 192 *water column*

193

194 Unlike Lake Michigan, Lake Superior does not have active nuclear power plants along  
 195 the coast or in the watershed (Supplementary Figure 2), likely explaining the lower values of  
 196  $^{14}\text{C-CH}_4$  in this environment compared to Lake Michigan. Nonetheless, the water column  $^{14}\text{C-}$   
 197  $\text{CH}_4$  values are greater than the  $^{14}\text{C}$  contents of any other C pool in the water column (particulate  
 198 organic carbon, dissolved organic carbon, and dissolved inorganic carbon; avg.  $\sim 104.3 \pm 3.5$   
 199 pMC,  $n=63$ ; Figure 3) (Zigah et al., 2011), suggesting that in-situ production via aerobic  
 200 methanogenesis has minimal influence on the dissolved  $\text{CH}_4$  isotopic signatures. The similarity  
 201 of the  $^{14}\text{C-CH}_4$  values between the contemporary atmosphere and dissolved in the waters of Lake  
 202 Superior instead suggest that the atmosphere is the dominant source of  $\text{CH}_4$  to this environment.

203 While modern CH<sub>4</sub> in the surface waters of both lakes is less surprising due to direct  
204 interaction with the atmosphere, elevated values of <sup>14</sup>C-CH<sub>4</sub> at the bottom of the water column in  
205 both lakes were somewhat unexpected (Figure 2). These results suggest that emissions of CH<sub>4</sub>  
206 from the lake floor into the water column, be those emissions of fossil or modern CH<sub>4</sub>, are  
207 negligible. More specifically, Silliman et al. (1996) and Meyers (2003) reported that the age of  
208 organic matter in Great Lake sediments was widely distributed (e.g. sediment <sup>14</sup>C ages equal ~  
209 400 yrs at surficial 40 cm sediment in Lake Huron, and about 5700 yrs at 113-119 cm and >  
210 20000 yrs at 763-769 cm in Lake Ontario's sediments). In addition, Zigah et al. (2011) reported  
211 that water column particulate organic carbon (POC) in Lake Superior has modern <sup>14</sup>C contents  
212 (102.5±2.0 pMC, n=21), meaning that CH<sub>4</sub> generated after this POC is deposited on the lake  
213 floor is not a significant source to the water column. One additional argument against the  
214 sediments being significant sources of CH<sub>4</sub> to the bottom waters follows the study by Remsen et  
215 al. (1989), which found a rapid depletion of CH<sub>4</sub> in the surface (~ 2 cm) sediments of Lake  
216 Superior; this study concluded that the CH<sub>4</sub> depletion was due to oxidation under the oxic  
217 conditions near the sediment-water interface. Similarly, since the dissolved oxygen concentration  
218 we measured in bottom waters from both lakes is > 90% saturation (Supplementary Figure 3),  
219 the sediment-water interface is likely oxic, diminishing the diffusive sedimentary fluxes.  
220 However, we note that our measurements of <sup>14</sup>C-CH<sub>4</sub> and dissolved oxygen investigated waters  
221 approximately 5 m above the actual sediment-water interface, and thus, waters closer to the lake  
222 floor may display older <sup>14</sup>C-CH<sub>4</sub> reflecting sedimentary diffusive fluxes. Overall, the observed  
223 <sup>14</sup>C-CH<sub>4</sub> throughout the water column suggests that the source of CH<sub>4</sub> in these lake waters is  
224 largely the atmosphere, with influences from nuclear power plants in Lake Michigan, which is

225 then mixed vertically in the water column; and any influence from sediments into the deeper  
 226 waters is likely restricted to only a few meters above the lake floor.



227

228 *Figure 3 Schematic diagrams representing  $^{14}\text{C}$ - $\text{CH}_4$  endmembers of nuclear powerplants, atmosphere, in-situ production, and*  
 229 *groundwater. The  $^{14}\text{C}$ - $\text{CH}_4$  values of Lake Michigan and Superior are also shown. a: Easemen et al. 1995, b: Townsend-small et*  
 230 *al., 2012; Lassey et al. 2007; Sparrow et al. 2018, c: Sparrow et al. 2018, d: Zigah et al. 2011; e: Aravena and Wassenaar, 1993,*  
 231 *and f: Zigah et al. 2011.*

232

233 In Lake Michigan, surface water of S14 showed the lowest  $^{14}\text{C}$ - $\text{CH}_4$  (117 pMC), while  
 234 the other two sites in this lake displayed much higher values ( $142.2 \pm 0.8$  pMC,  $n=2$ ) (Figure 2).  
 235 The S14 station is the shallowest ( $\sim 10$  m) and closest (ca. 4 km) site to the coast and nuclear  
 236 power plants in our Lake Michigan sampling locations (Supplementary Figure 2), thus we  
 237 expected the opposite, that this site would display the highest  $^{14}\text{C}$ - $\text{CH}_4$ . We suspect that this site  
 238 has an additional source of  $\text{CH}_4$  that does not appear in the other sites. First, this suspicion is  
 239 supported by the  $\delta^{13}\text{C}$ - $\text{CH}_4$  at the S14, which is about  $-6$  ‰ lighter than the other sites (Figure 2).  
 240 Second, the concentration of  $\text{CH}_4$  at this surface station was 20 nM, the highest among the  
 241 samples collected in Lake Michigan (Figure 2). Third, we suspect that the additional  $\text{CH}_4$  source  
 242 is likely a combination of aerobic methanogenesis and groundwater discharge. Typically,

243 shallow sites in water bodies have higher CH<sub>4</sub> concentrations due to groundwater discharge  
244 and/or higher rates of aerobic methanogenesis associated with higher rates of primary production  
245 (Dulaiova et al., 2010; Lecher et al., 2016). Zigah et al (2011) reported that the <sup>14</sup>C contents in  
246 carbon pools from Lake Superior's water ranged from 102-106 pMC, thus, CH<sub>4</sub> produced  
247 aerobically from this carbon could potentially diminish the higher <sup>14</sup>C-CH<sub>4</sub> values seen  
248 elsewhere in this lake. Chlorophyll concentrations were slightly higher in the southeastern side of  
249 Lake Michigan near S14 relative to the central basin (Supplementary Figure 4), suggesting that  
250 the aerobically produced CH<sub>4</sub> from the byproducts of primary production may contribute to this  
251 <sup>14</sup>C-CH<sub>4</sub> signal. Aravena and Wassenaar (1993) investigated C-isotopes in groundwater collected  
252 from aquifer wells in southern Ontario, Canada, north of Lake Ontario, and reported that <sup>14</sup>C-  
253 CH<sub>4</sub> ranged from 0.5 to 16.7 pMC (avg. 4.9±5.0, n=16). Additional groundwater measurements  
254 in the Eastern Ontario aquifer ranged from 1.1 to 26.5 pMC, with an average of ~ 11.2±8.6 pMC,  
255 n=20 (Lemieux et al., 2019). This suggests that groundwater discharge could lead to a significant  
256 reduction in the dissolved <sup>14</sup>C-CH<sub>4</sub> in the lake water when mixed with ambient water containing  
257 elevated <sup>14</sup>C-CH<sub>4</sub>. In ground waters from the southern shore of Lake Michigan, specific  
258 conductivity and pH were measured to be typically in the ranges of 165-852 µS/cm and 5.7-8.0,  
259 respectively (Shedlock et al., 1993). Our measurements show a higher specific conductivity and  
260 lower pH in the region of S14 relative to the other surface waters in the more central lake  
261 (Supplementary Figure 3 and 4), in agreement with potential groundwater contributions to these  
262 areas. Finally, a report from the USGS also indicated that the development of surficial aquifers is  
263 greater in the eastern side of Lake Michigan relative to the west (see, Fig 26 in Olcott et al.,  
264 1992). Thus, the measurements of relatively older <sup>14</sup>C-CH<sub>4</sub>, higher specific conductivity, lower  
265 pH, and higher chlorophyll in some sites along the eastern coast of Lake Michigan are likely

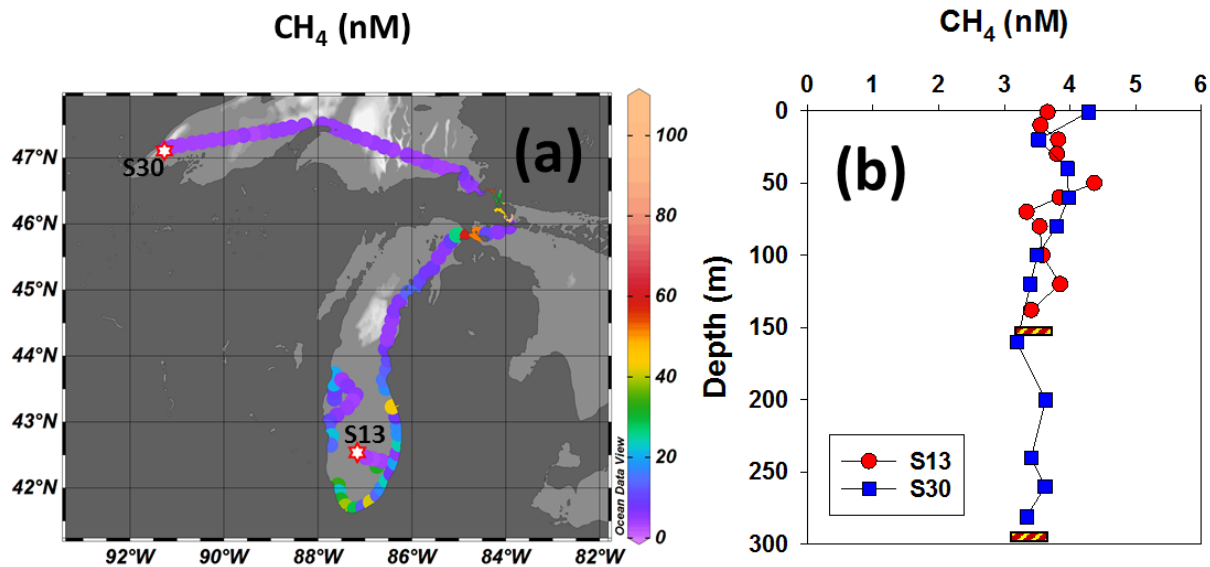
266 reflecting contributions from both active groundwater discharge and aerobic methanogenesis,  
267 displaying important components of the coastal CH<sub>4</sub> system in the waters of Lake Michigan, and  
268 possibly Lake Superior (e.g., Hofmann et al., 2010; Heilweil et al., 2015).

### 269 **3.2. Concentration of CH<sub>4</sub> Dissolved in the Water Column**

270 Along with radiocarbon analyses, CH<sub>4</sub> concentrations were also determined (Figure 4 and  
271 Supplementary Table 2)). Surface CH<sub>4</sub> concentrations ranged from 3.5 to 60 nM (Figure 4a) in  
272 these two lakes. Concentrations in Lakes Michigan and Superior were much lower than that in  
273 the neighboring lake, Lake Erie, where the concentrations ranged from 24.2 - 107.1 nM in the  
274 surface (Townsend-Small et al., 2016). This stark difference in concentrations is likely  
275 associated with active natural gas seeps, leaking natural gas pipelines, and the relatively shallow  
276 water column in Lake Erie (Townsend-Small et al., 2016). While no acoustic investigations were  
277 conducted to identify seep bubbles in Lakes Michigan and Superior (Sheikh et al., 2008), our  
278 natural <sup>14</sup>C-CH<sub>4</sub> measurements do not suggest that fossil seep CH<sub>4</sub> is a significant source to  
279 either the deep or surface waters in these lakes. However, our data does not exclude the  
280 possibility that some fossil CH<sub>4</sub> seeps may exist and have more localized influences on the CH<sub>4</sub>  
281 dynamics. Nonetheless, in Lakes Michigan and Superior, CH<sub>4</sub> concentrations in surface water  
282 from the deep basin of both lakes were 3.7 (at S13) and 4.3 (at S30) nM. These concentrations  
283 were approximately in equilibrium (or slight supersaturation) relative to the current (June 2017)  
284 global average atmospheric concentrations of 1842.9 ppb (or 3.2 nmol/kg at 15°C and 4.2  
285 nmol/kg at 4°C in Lake Michigan and Superior, respectively)  
286 ([https://www.esrl.noaa.gov/gmd/ccgg/trends\\_ch4/](https://www.esrl.noaa.gov/gmd/ccgg/trends_ch4/)). Production and supersaturation of CH<sub>4</sub> at the  
287 surface layer may be associated with regeneration of phosphate from methyl-phosphonate, which

288 is typically observed in oligotrophic lake waters (e.g., Yao et al., 2016; Grossart et al., 2011;  
 289 Bogard et al., 2014).

290 While both Lakes Michigan and Superior have similarly low CH<sub>4</sub> concentrations in the  
 291 center of these lakes, we observed localized CH<sub>4</sub> enrichment along the coast of Lake Michigan,  
 292 reaching up to 60 nM (Figure 4). This distribution of increasing CH<sub>4</sub> concentration toward the  
 293 coast is common, since shallow sites would likely have more primary production and associated  
 294 in-situ aerobic methanogenesis along with wave actions to enhance pore water exchange with the  
 295 water column (Borrel et al., 2011; Bastaviken et al., 2011, Hofmann et al., 2010; Heilweil et al.,  
 296 2015; Dulaiova et al., 2010; Lecher et al., 2016). In both lakes, chlorophyll distributions were  
 297 generally higher toward to the coast (Supplementary Figure 4), and there are many active  
 298 groundwater discharge sites especially along the coast of Lake Michigan (Olcott et al., 1992), as  
 299 is suggested in our conductivity and pH distributions.



300

301 *Figure 4 (a) Spatial and (b) vertical distributions of methane in Lake Michigan (S13) and Superior (S30). The horizontal bars*  
 302 *represent the depth of the water column.*

303



304 Vertical profiles of CH<sub>4</sub> concentration in the deep sites in both lakes displayed similarly  
305 low concentrations with a range of 3.0-4.5 nM (Figure 4). Though small, there appeared to be a  
306 slight decrease in CH<sub>4</sub> concentration from the surface towards the bottom, similar to the  
307 observations in other lakes such as Lake Baikal, Russia (Schmid et al., 2007) and Lower Lake  
308 Constance, Germany (see, Fig 2 in Hofmann, 2013), which is likely attributed to aerobic  
309 oxidation. However, in our study, bottom water CH<sub>4</sub> concentrations (~ 3.0 nM in both lakes)  
310 were slightly higher than the concentrations in bottom waters from the lakes mentioned above,  
311 but close to the surface values, suggestive of rapid vertical mixing in both lakes. Overall, CH<sub>4</sub>  
312 concentration distributions in Lakes Michigan and Superior are consistent with <sup>14</sup>C-CH<sub>4</sub>  
313 distributions, indicating that atmospheric input, in-situ aerobic methanogenesis, groundwater,  
314 and nuclear power plants are important sources of CH<sub>4</sub> to the water column.

#### 315 **4 Conclusions**

316 Radio- and stable-carbon isotopes and concentration of CH<sub>4</sub> dissolved in the waters of  
317 Lakes Michigan and Superior were determined to assess CH<sub>4</sub> sources to these environments. Key  
318 results include (1) that CH<sub>4</sub> is not fossil and (2) that all measurements of <sup>14</sup>C-CH<sub>4</sub> were above  
319 modern, suggesting significant inputs from atmospheric CH<sub>4</sub> (Lakes Michigan and Superior) and  
320 nuclear power plants (Lake Michigan). Interestingly, the site closest to a nuclear power plant  
321 displayed the lowest value of <sup>14</sup>C-CH<sub>4</sub>, likely displaying the influence of groundwater discharge  
322 and aerobic methanogenesis. Concentrations of CH<sub>4</sub> in the central basin of both lakes were  
323 similarly low, which is approximately in equilibrium with the atmosphere. However, CH<sub>4</sub>  
324 concentrations in the coastal regions of both lakes were higher than the central basin, and likely  
325 associated with in-situ aerobic methanogenesis and groundwater inputs. Overall, our study

326 provides fundamental information about CH<sub>4</sub> sources and <sup>14</sup>C-CH<sub>4</sub> dynamics in the Great Lakes  
 327 of Lakes Michigan and Superior.

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