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Do invasive quagga mussels alter CO₂ dynamics in the Laurentian Great Lakes?

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The Laurentian Great Lakes have experienced unprecedented ecological and environmental changes, especially after the introduction of invasive quagga mussel (*Dreissena rostriformis bugensis*). While impacts on ecological functions have been widely recognized, the response of carbon dynamics to invasive species remains largely unknown. We report new CO₂ data showing significant increases in pCO₂ (up to 800 μatm in Lake Michigan) and CO₂ emission fluxes in most of the Great Lakes compared to those prior to or during the early stage of the colonization of invasive quagga mussels. The increased CO₂ supersaturation is most prominent in Lakes Huron and Michigan, followed by Lakes Ontario and Erie, but no evident change was observed in Lake Superior. This trend mirrors the infestation extent of invasive quagga mussels in the Great Lakes and is consistent with the decline in primary production and increase in water clarity observed pre- and post-*Dreissena* introduction, revealing a close linkage between invasive species and carbon dynamics. The Great Lakes have become a significant CO₂ source to the atmosphere, emitting $>7.7 \pm 1.0$ Tg-C annually, which is higher than the organic carbon burial rate in global inland-seas and attesting to the significant role of the Laurentian Great Lakes in regional/global CO₂ budget and cycling.

Levels of carbon dioxide (CO₂) not only can serve as an indicator of autotrophic or heterotrophic nature of an aquatic environment¹, but also can be an important parameter to elucidate calcification and potential pH changes in a water body^{2–4}. Due to increasing human consumption of fossil fuels and other anthropogenic activities, atmospheric CO₂ level has increased from 280 μatm in the 1800s to levels above 400 μatm in 2015⁵. As the most important greenhouse gas on earth, inventory and fluxes of CO₂ across different reservoirs and its role in the global carbon cycle and thus climate and environmental changes have been the focus of many recent research programs^{6–8}.

Unlike the open ocean which contains abundant dissolved inorganic carbon (DIC, usually >2000 μmol/kg) and typically serves as a sink of CO₂^{7,9–11}, lakes and inland waters could serve as a source of CO₂ to the atmosphere^{12–14} and may play an essential role to the local, regional and even global carbon cycles and climate. Recently, carbon cycling and magnitude of CO₂ fluxes across the air-water interface in lakes and inland waters have received increasing attention^{15–18}, although studies on carbon dynamics in the Great Lakes remain scarce^{17,19}.

The Laurentian Great Lakes are the largest freshwater system on Earth and receive vast amounts of organic and inorganic carbon from surrounding terrestrial ecosystems. Over the past decades, the Great Lakes have experienced significant ecological and environmental changes due to the introduction of invasive species, notoriously nonindigenous quagga mussels (*Dreissena rostriformis bugensis*), leading to a decrease in primary production and increasing water clarity in the Great Lakes^{20–25}. In addition to impacts on foodweb structure and ecological functions, changes in biogeochemical cycles of nutrients have also been documented^{26–28}. However, specific changes in carbon dynamics, as well as the impacts and biogeochemical consequences after the colonization of invasive quagga mussels in the Laurentian Great Lakes remain poorly understood. The direction and magnitude of air-lake CO₂ fluxes after *dreissena* introduction in the Great Lakes are largely unquantified, especially in Lakes Michigan, Huron and Ontario^{17,29–31}.

To examine the response of carbon dynamics to the introduction of invasive quagga mussels and linkages between invasive species and changes in biogeochemical cycling, open lake water samples were collected from all of the Laurentian Great Lakes, including Lake Superior, Lake Michigan, Lake Huron, Lake Erie and Lake Ontario,

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Figure 1. Sampling locations in the Laurentian Great Lakes during August 2013 (The map is created from Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2015) and edited on Microsoft PowerPoint 14.5.8 (<https://products.office.com/en-us/home>)).

during August 2013 (Fig. 1). Furthermore, seasonal water samples were also collected from Lake Michigan between 2013 and 2015. In addition to water isotopic composition ($\delta^2\text{H}$ and $\delta^{18}\text{O}$), total alkalinity (TA), dissolved inorganic carbon (DIC), and pH were measured prior to the evaluation of the partial pressure of CO_2 ($p\text{CO}_2$) and air-water CO_2 fluxes.

Results

Variations in pH, TA and DIC in the Great Lakes. The Laurentian Great Lakes can be characterized as a high-pH and high-carbonate ecosystem although Lake Superior had a relatively lower pH and carbonate abundance compared to the other Great Lakes (Fig. 2 and Table 1). For example, pH values in Great Lakes waters were typically higher than 8 except for two sampling sites in Lake Superior (Table 1). Lakes Michigan, Erie and Ontario had higher pH values, averaging 8.22 ± 0.04 , 8.19 ± 0.08 and 8.20 ± 0.04 , respectively, followed by Lake Huron (8.07 ± 0.06) and Lake Superior (7.98 ± 0.05).

Concentrations of DIC and TA typically exceeded the threshold of $1000 \mu\text{mol}/\text{kg}$ except for Lake Superior (Table 1). Values of TA varied from 830 to $2200 \mu\text{mol}/\text{kg}$ for all the Great Lakes, with an average of $843 \pm 10 \mu\text{mol}/\text{kg}$ in Lake Superior, $2168 \pm 22 \mu\text{mol}/\text{kg}$ in Lake Michigan, $1600 \pm 59 \mu\text{mol}/\text{kg}$ in Lake Huron, $1872 \pm 22 \mu\text{mol}/\text{kg}$ in Lake Erie and $1815 \pm 19 \mu\text{mol}/\text{kg}$ in Lake Ontario (Table 1). Similarly, different DIC concentrations were observed among the five Great Lakes, showing the highest value in Lake Michigan (average of $2065 \pm 24 \mu\text{mol}/\text{kg}$) and lowest values in Lake Superior (average of $793 \pm 26 \mu\text{mol}/\text{kg}$). Generally, these DIC and TA values are higher than those in most freshwater systems (e.g., refs 32, 33 and 34) and comparable to those of global ocean basins³⁵ (especially data of Lake Michigan, Table 1S). Our data here are also similar to the long-term data from previous studies in the Great Lakes³⁶. High DIC and TA in Great Lakes waters are related to the spatial distribution of limestone and carbonate weathering in the Great Lakes basin. It is the high carbonate abundance that allows the thriving and rapid colonization of the mussel community in the Great Lakes³⁷, which in turn has “re-engineered” the lake ecosystem during the past decades^{22–25}.

The surface distribution (Fig. 2) showed that TA, pH and DIC concentration all increased consistently from the upper Great Lakes (i.e., Lake Superior) to Lake Huron and then to the lower Great Lakes (i.e., Lakes Erie and Ontario), similar to the increasing $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in surface waters along the Great Lakes. This is consistent with the general water transport pathway from the upper to the lower Great Lakes, suggesting an accumulative effect on water chemistry in the lower Great Lakes from surrounding riverine inputs³⁸. Among the five Great Lakes, Lake Michigan had notably high values for each of the measured parameters including pH, TA, DIC, and water isotopes (Fig. 2 and Table 1), which is related to its high abundance of limestone and the fact that it is a semi-closed basin which allows the accumulative effect of evaporation in Lake Michigan.

Variations in $p\text{CO}_2$ along the Great Lakes. As shown in Table 1 and Fig. 3, our results consistently showed an evident CO_2 supersaturation ($>398 \mu\text{atm}$) for all the Great Lakes, with the highest $p\text{CO}_2$ in Lake Michigan ($762 \pm 88 \mu\text{atm}$) and Lake Huron ($774 \pm 92 \mu\text{atm}$), followed by Lakes Erie ($725 \pm 126 \mu\text{atm}$) and Ontario ($647 \pm 47 \mu\text{atm}$). Even in Lake Superior, with the lowest TA and DIC abundance (both $<1000 \mu\text{mol}/\text{kg}$) and lowest $p\text{CO}_2$ values ($461 \pm 77 \mu\text{atm}$), CO_2 supersaturation was still evident (Fig. 3). This indicated that surface waters of all the Laurentian Great Lakes can be a net CO_2 source to the atmosphere, consistent with those observed for other global lakes^{16,18}.

Additionally, our seasonal $p\text{CO}_2$ data from Lake Michigan between 2013 and 2015 also showed a significant CO_2 supersaturation during all sampling seasons. For example, average $p\text{CO}_2$ was $762 \pm 88 \mu\text{atm}$ in August 2013, $699 \pm 17 \mu\text{atm}$ in May 2014, $769 \pm 124 \mu\text{atm}$ in October 2014, $815 \pm 48 \mu\text{atm}$ in October 2015, and $944 \pm 83 \mu\text{atm}$ in December 2015 (Fig. 4). Furthermore, CO_2 supersaturation existed throughout the whole water column of open Lake Michigan although $p\text{CO}_2$ values decreased slightly in the middle water column due to biological uptake (see examples of vertical profiles in October 2015, Fig. 4).

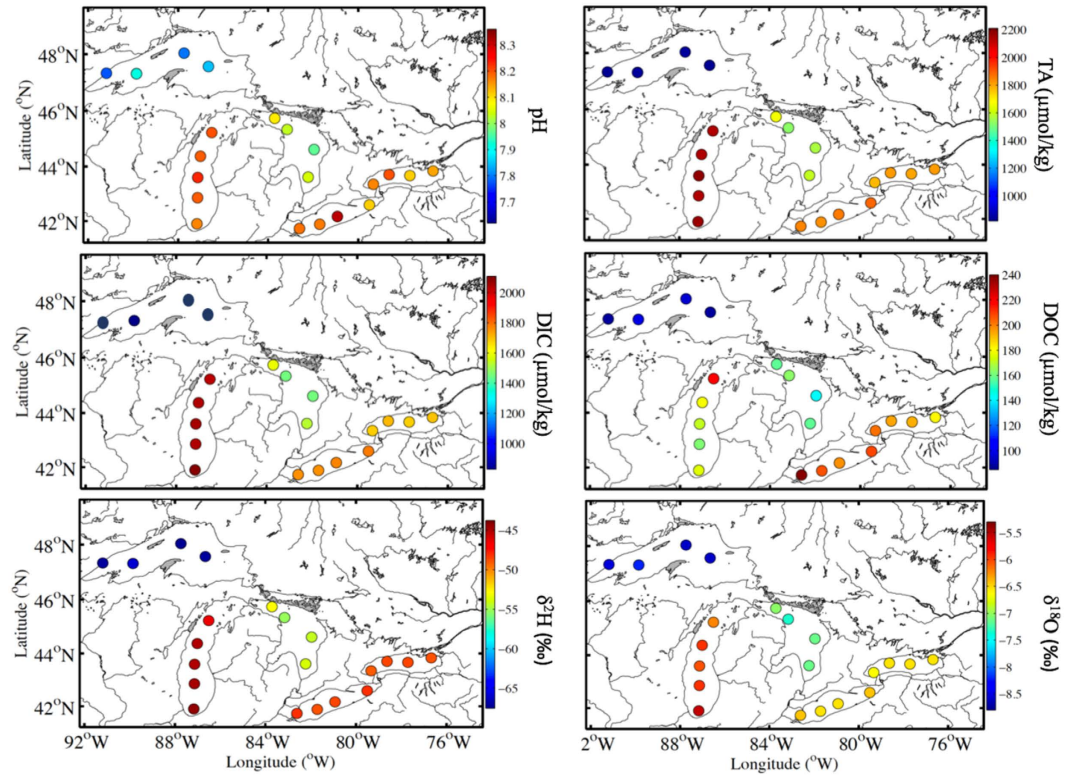


Figure 2. Spatial distributions of surface water pH, total alkalinity (TA), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) and water isotope composition ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) in the Laurentian Great Lakes during the summer of 2013. The figure is created from MATLAB R2013 (http://www.mathworks.com/products/matlab/index.html?s_tid=gn_loc_drop) and modified by Microsoft PowerPoint 14.5.8 (<https://products.office.com/en-us/home>).

Discussion

The invasive species, especially filter feeders including zebra and quagga mussels, have been shown to strongly affect the foodweb structure and biogeochemical cycles of nutrients after their introduction to the Great Lakes^{21–25}. Thus, the equilibrium and interaction of CO_2 between lake and atmosphere may have been altered during the past decades, particularly after quagga mussels became predominant. As shown in Fig. 3, the $p\text{CO}_2$ values in the Great Lakes observed in 2013 are significantly higher than the median values of $p\text{CO}_2$ observed during the same sampling season between 1983–2006^{17,30,39} (Table 1), especially for Lakes Michigan ($p < 0.001$), Huron ($p < 0.001$), Erie ($p = 0.004$) and Ontario ($p = 0.035$). Compared to the increase in atmospheric CO_2 levels from 1983 to 2013 ($\sim 60 \mu\text{atm}$), the increase in $p\text{CO}_2$ in the water column of the Great Lakes was considerably larger. Taking Lakes Michigan and Huron as examples, during 1983–2006, the average $\Delta p\text{CO}_2$ value, the difference in $p\text{CO}_2$ between atmosphere (averaging $\sim 362 \mu\text{atm}$ during that time periods) and lake waters, was about 118 and 22 μatm for Lakes Michigan and Huron^{30,39}, respectively. In comparison, $\Delta p\text{CO}_2$ values in these two lakes during summer 2013 reached a new high of $\sim 400 \mu\text{atm}$, averaging 365 ± 89 and $377 \pm 92 \mu\text{atm}$ for Lake Michigan and Lake Huron, respectively (Table 1), showing an increase of 4 times in $\Delta p\text{CO}_2$ values in August between 1983–2006 and 2013 (Fig. 3). For Lakes Erie and Ontario, the increase in $p\text{CO}_2$ values between 1983–2006 and 2013 was also significant, although large errors existed in historical CO_2 data^{30,39} for the shallower lakes with high primary production and anthropogenic influences including seasonal hypoxia and algal bloom, especially in Lake Erie^{40,41}.

Moreover, our seasonal CO_2 data and its vertical distribution in Lake Michigan (Fig. 4) further demonstrated the increased CO_2 supersaturation in the water column. For example, $p\text{CO}_2$ in Lake Michigan during October 2015 ranged from $\sim 600 \mu\text{atm}$ in subsurface waters to $\sim 770 \mu\text{atm}$ in deeper waters (Fig. 4). Elevated $p\text{CO}_2$ in deeper waters resulted from the decomposition of organic matter and decreased biological uptake also implied a potential higher CO_2 emission flux from lake waters when the CO_2 -enriched deeper water is upwelled to surface during winter mixing seasons⁴². Furthermore, our seasonal data clearly show a consistent increase in $p\text{CO}_2$ from summer to fall and then to winter, reaching as high as $944 \pm 83 \mu\text{atm}$ during December 2015; an increase by $\sim 30\%$ compared to other seasons (Fig. 4). Thus, the $p\text{CO}_2$ data obtained during summer 2013 (Fig. 3) might represent the lower limit of CO_2 supersaturation in the Great Lakes, although other factors could have an influence, such as partial ice-cover during winter.

In contrast to Lake Michigan and other lower Great Lakes, the increase in $p\text{CO}_2$ in Lake Superior during summer between 1983–2006^{17,30} and 2013 does not seem to be significant ($p = 0.665$, Fig. 3, Table 1). Nevertheless, increased CO_2 supersaturation in Lake Michigan and other lower Great Lakes coincides with the distribution and density of invasive quagga mussels among all the Great Lakes. For example, high quagga mussel densities

Station ID	pH	Ca (mg/L)	Mg (mg/L)	TA ($\mu\text{mol/kg}$)	DIC ($\mu\text{mol/kg}$)	DIC- $p\text{CO}_2$ (μatm)	DIC- F_{CO_2} (mmol-C/m ² /d)	TA- $p\text{CO}_2$ (μatm)	TA- F_{CO_2} (mmol-C/m ² /d)
Lake Superior									
LS-1	8.00	13.9	2.15	850	831	474	2.20	496	2.83
LS-2	7.94	13.8	2.54	850	785	519	3.48	576	5.10
LS-3	8.05	13.9	2.34	840	780	350	-1.32	386	-0.30
LS-4	7.95	13.8	2.25	830	775	502	3.00	551	4.39
AVG	7.98 \pm 0.05	13.8 \pm 0.1	2.32 \pm 0.17	843 \pm 10	793 \pm 26	461 \pm 77	1.84 \pm 2.17	502 \pm 84	3.01 \pm 2.40
1983–2006 ³⁰						500 \pm 100			
1996–2006 ¹⁷						370 \pm 66			
Lake Michigan									
LM-1	8.16	32.5	4.61	2180	2107	906	14.48	945	15.59
LM-2	8.21	33.4	3.20	2150	2054	780	10.90	822	12.09
LM-3	8.26	33.4	3.48	2200	2066	691	8.37	739	9.73
LM-4	8.22	32.3	3.02	2160	2053	739	9.73	783	10.98
LM-5	8.25	31.5	2.57	2150	2046	693	8.43	733	9.56
AVG	8.22 \pm 0.04	32.6 \pm 0.8	3.38 \pm 0.77	2168 \pm 22	2065 \pm 24	762 \pm 88	10.38 \pm 2.52	805 \pm 86	11.59 \pm 2.46
1983–2006 ³⁰						480 \pm 66			
Lake Huron									
LH-1	8.15	26.7	3.04	1680	1605	667	7.69	706	8.79
LH-2	8.07	26.1	2.92	1540	1464	733	9.56	782	10.95
LH-3	8.00	25.5	2.80	1580	1467	875	13.60	961	16.04
LH-4	8.06	32.8	2.96	1600	1540	819	12.01	864	13.28
AVG	8.07 \pm 0.06	27.8 \pm 3.4	2.93 \pm 0.10	1600 \pm 59	1519 \pm 67	774 \pm 92	10.71 \pm 2.61	828 \pm 109	12.27 \pm 3.11
1983–2006 ³⁰						450 \pm 330			
1999 ³⁹						317 \pm 55			
Lake Erie									
LE-1	8.17	31.6	2.76	1860	1771	753	10.13	797	11.38
LE-2	8.16	—	—	1850	1767	768	10.56	810	11.75
LE-3	8.31	25.8	2.42	1880	1784	544	4.19	574	5.04
LE-4	8.12	32.0	2.73	1900	1797	837	12.52	895	14.16
AVG	8.19 \pm 0.08	29.8 \pm 3.5	2.64 \pm 0.19	1872 \pm 22	1780 \pm 14	725 \pm 126	9.35 \pm 3.59	769 \pm 137	10.58 \pm 3.89
1983–2006 ³⁰						400 \pm 380			
1999 ³⁹						400 \pm 194			
Lake Ontario									
LO-1	8.20	32.0	2.64	1790	1694	640	6.92	682	8.11
LO-2	8.24	32.7	2.60	1830	1721	588	5.44	629	6.61
LO-3	8.16	31.9	2.64	1810	1695	700	8.62	755	10.19
LO-4	8.19	32.1	2.64	1830	1710	662	7.54	715	9.05
AVG	8.20 \pm 0.04	32.2 \pm 0.4	2.63 \pm 0.02	1815 \pm 19	1705 \pm 13	647 \pm 47	7.13 \pm 1.33	695 \pm 53	8.49 \pm 1.51
1983–2006 ³⁰						420 \pm 200			
All Great Lakes during 2013									
	8.14 \pm 0.11	27.4 \pm 7.4	2.82 \pm 0.53	1683 \pm 461	1596 \pm 442	678 \pm 142	8.00 \pm 4.02	724 \pm 148	9.30 \pm 4.20

Table 1. Surface water pH, total alkalinity (TA) and dissolved inorganic carbon (DIC), as well as partial pressure of CO₂ ($p\text{CO}_2$) and air-lake CO₂ fluxes (F_{CO_2}) from the Laurentian Great Lakes based on TA-pH and DIC-pH data, respectively. LS, LM, LH, LE and LO denote Lakes Superior, Michigan, Huron, Erie and Ontario, respectively. AVG denotes averaged values with standard deviation for each lake. Data of $p\text{CO}_2$ between 1983 and 2006 are taken from refs 17, 30 and 39.

(e.g., >19,000-mussels/m²) have been reported for Lake Michigan^{22,25,27,43}, but a very low density for Lake Superior. Although zebra mussels arrived into the Great Lakes before quagga mussels, they have much weaker filter ability, and changes in foodweb structure and ecological function were more evident only after quagga mussels became predominant^{25,44–46}. In addition, quagga mussels did not start blanketing offshore regions of the Great Lakes, such as Lake Michigan until 2005^{25,44}. Therefore, CO₂ data collected during 1983–2006^{17,30,39} can be considered representative of the time period prior to or during the early stage of the colonization of invasive quagga mussels in the Great Lakes. Linking the spatiotemporal variations of quagga mussel population with the changes in the extent of CO₂ supersaturation during summer sampling time, we hypothesized that increasing CO₂ supersaturation in the Great Lakes during the past decade has been induced by the colonization of invasive quagga mussels and the subsequent biogeochemical response to that colonization.

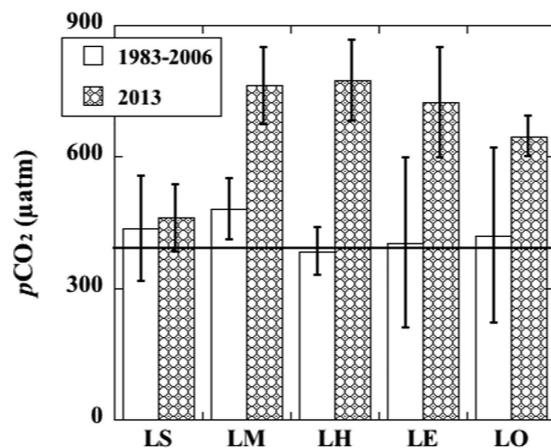


Figure 3. The averaged partial pressure of CO₂ ($p\text{CO}_2$) in the Laurentian Great Lakes during summer months from 1983–2006 and 2013. LS, LM, LH, LE and LO denote Lakes Superior, Michigan, Huron, Erie and Ontario, respectively. The horizontal line represents the averaged atmospheric $p\text{CO}_2$ value in 2013 (398 μatm , from NOAA at <http://www.esrl.noaa.gov/gmd/>). Data from 1983–2006 are calculated from surface water pH and alkalinity obtained from the EPA's biannual Great Lakes surveillance program, which begin from 1983 except for Lake Superior beginning from 1992 (see Urban and Desai (2009)³⁰). The $p\text{CO}_2$ values for Lakes Superior, Huron and Erie were derived from the averaged values from previous studies^{17,30,39}, excluding outlier data points.

Possible pathways and mechanisms to support our hypothesis include (1) decreasing primary production in the Great Lakes after the introduction of invasive quagga mussels^{20–23,47,48}; (2) increase in water clarity²⁴ which enables the light penetration into deeper waters and consequently enhances the photo-degradation of natural organic matter in the water column; and (3) metabolic processes of vast quantities of invasive quagga mussels blanketing lake floor^{27,49}, although other processes, such as changes in sediment-water processes, coastal erosion and water chemistry after the colonization of quagga mussels, are also important. All these changes are inter-correlated and are the result of the colonization of invasive quagga mussels and all these processes would directly or indirectly favor the accumulation and release of CO₂ in the water column, resulting in increased CO₂ abundance in the Great Lakes, especially those heavily infested with quagga mussels (e.g., Lake Michigan²⁵). The close coupling between invasive species and carbon dynamics elucidated here in the Great Lakes clearly shows how small invasive quagga mussels could have caused basin-scale changes in carbon dynamics and biogeochemical cycling.

The increase in $p\text{CO}_2$ levels after the colonization of invasive quagga mussels in the Great Lakes evidently exceeded the increase in average atmospheric CO₂ level from 1983 to 2013 ($\sim 60 \mu\text{atm}$). Thus, enhanced CO₂ emission fluxes from lake waters to the atmosphere can be expected. Based on these summer $p\text{CO}_2$ data, the daily CO₂ emission fluxes ranged from 8.37 to 14.48 mmol-C/m²/d with an average of 10.38 ± 2.52 mmol-C/m²/d for Lake Michigan and ranged from 7.69 to 13.60 mmol-C/m²/d, averaging 10.71 ± 2.61 mmol-C/m²/d for Lake Huron (Fig. 5 and Table 1). These CO₂ emission fluxes were 3 to 4 times higher than those in Lakes Michigan and Huron at the same sampling time during 1983–2006, based on their differences in $\Delta p\text{CO}_2$ values. Lakes Erie and Ontario had CO₂ emission fluxes of 9.35 ± 3.59 mmol-C/m²/d and 7.13 ± 1.33 mmol-C/m²/d respectively, while an emission flux of 1.84 ± 2.17 mmol-C/m²/d was estimated for Lake Superior. Overall, the emission fluxes of CO₂ in all five Great Lakes follow the order of Huron \geq Michigan $>$ Erie $>$ Ontario $>$ Superior during summer 2013 (Fig. 5 and Table 1), distinct from the order of Superior $>$ Michigan $>$ Huron $>$ Ontario $>$ Erie observed prior to or during the early stage of quagga mussel colonization^{30,50} and further attests to the strong impact of invasive species on carbon cycles in the Laurentian Great Lakes.

Although CO₂ emission fluxes from the Great Lakes were comparable to or lower than those from small lakes (e.g., refs 51, 52 and 53), the large surface areas still made the Great Lakes a strong CO₂ source to the atmosphere. We estimated the lake-wide integrated CO₂ fluxes for each Great Lake and those estimated flux values are 1.5×10^8 mol-C/d for Lake Superior, 6.0×10^8 mol-C/d for Lake Michigan, 6.4×10^8 mol-C/d for Lake Huron, 2.4×10^8 mol-C/d for Lake Erie, and 1.4×10^8 mol-C/d for Lake Ontario (Fig. 5). Collectively, up to $(7.7 \pm 1.0) \times 10^{12}$ g-C/yr or 7.7 ± 1.0 g-C/yr in the form of CO₂ can be released to the atmosphere from the Laurentian Great Lakes, which is comparable to the annual DIC flux to the ocean from the Mississippi River and many other world rivers^{54,55}. This annual CO₂ emission flux from the Laurentian Great Lakes is also higher than the annual organic carbon burial rate in all inland seas^{16,56}, and makes up 1% of the annual CO₂ emission from global deforestation⁵⁷. It should be noted that our estimated CO₂ emission flux could be the lower limit since it was calculated from summer sampling when $p\text{CO}_2$ levels were lower relative to winter seasons⁴² (e.g., Fig. 4). Consequently, the Laurentian Great Lakes certainly serve as a significant CO₂ source to the atmosphere especially after the colonization of invasive species, and play an essential role in regional and global CO₂ budgets and cycling. This is a paradox in that the Great Lakes with similar carbonate abundance and pH as those in global oceans, should be expected to absorb CO₂ from the atmosphere and become acidified in the face of the

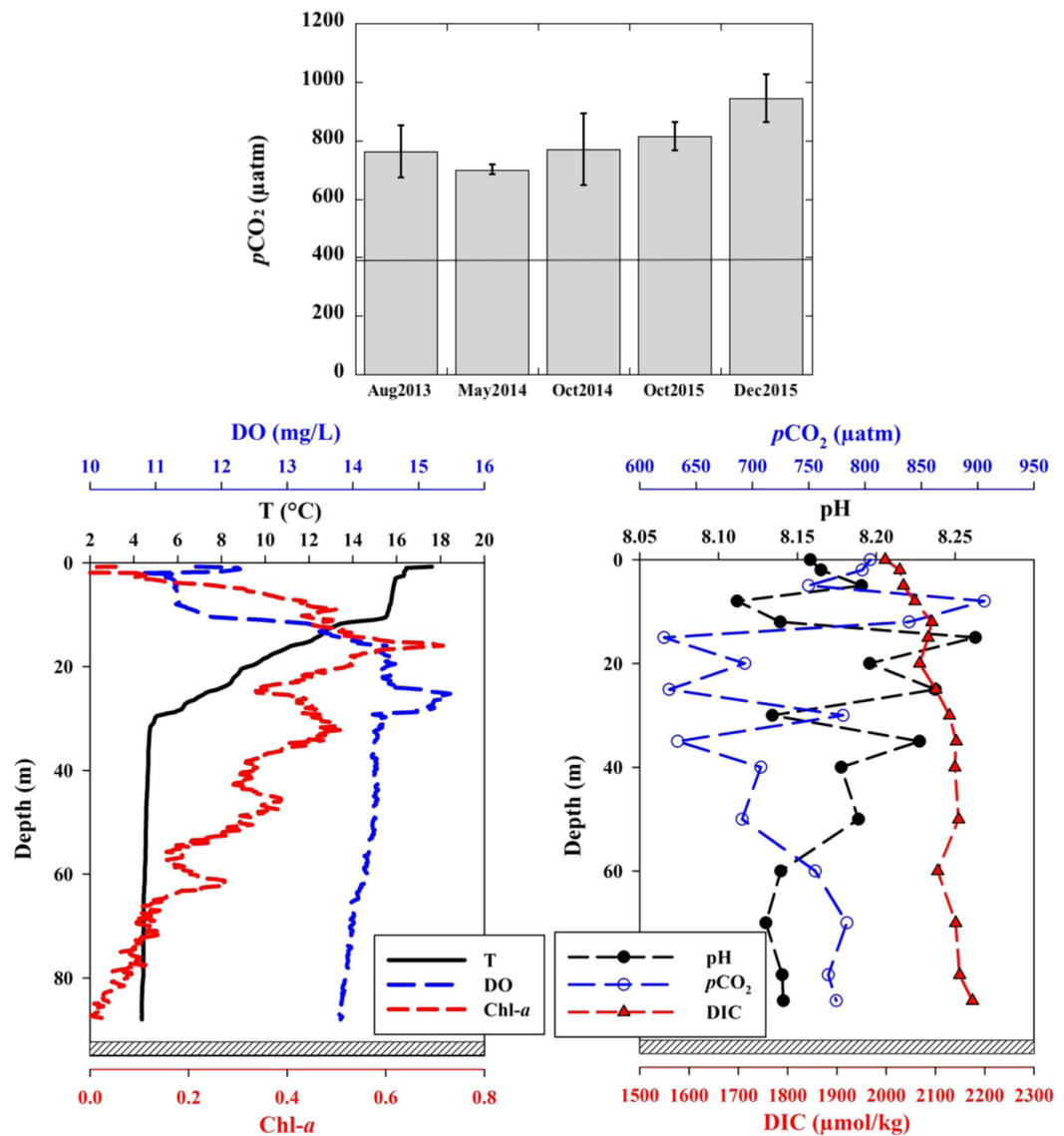


Figure 4. Seasonal variations in partial pressure of CO_2 ($p\text{CO}_2$) in surface waters of Lake Michigan (upper panel) between 2013 and 2015 and the vertical profiles of $p\text{CO}_2$ and other hydrological data (pH, dissolved inorganic carbon, DIC) in open Lake Michigan during October 2015 (lower panels). The horizontal line represents the averaged atmospheric $p\text{CO}_2$ value ($398 \mu\text{atm}$) during 2013–2015.

accelerating rise of atmospheric CO_2 ⁵⁸. However, the Great Lakes have responded actively to the changing ecosystem and are making a positive feedback to climate change, with decreased whiting events (or CaCO_3 saturation/precipitation) during summer²⁴, increased CO_2 supersaturation and emission fluxes after the introduction of invasive quagga mussels and resultant decrease in primary production, enhanced degradation of natural organic matter due to increased water clarity, and direct CO_2 release from quagga mussel respiration^{27,49}.

Materials and Methods

Sampling. During August 2013, surface water samples were collected from open lake stations on all of the Great Lakes: including Lake Superior, Lake Michigan, Lake Huron, Lake Erie and Lake Ontario (LS, LM, LH, LE and LO). Specific sample locations are shown in Fig. 1 and Table 1. Additionally, seasonal transect sampling, including a vertical profile at an open lake station ($43^{\circ}11.5362'N$; $87^{\circ}39.9566'W$, 104 m depth), was also conducted in open Lake Michigan during 2013 to 2015. Detailed sampling locations can be found in ref. 28. Surface water samples were taken from a hull-mounted, all-Teflon and stainless steel, high-speed pumping system (2 m depth). Hydrographic parameters were recorded with a Hydrolab Datasonde 5A and coordinated with ship's positioning systems, such as temperature ($^{\circ}\text{C}$) and chlorophyll-*a* fluorescence (V). Vertical profiles of hydrographic characteristics (SeaBird SBE 25Plus) and Niskin bottle-collected water samples were taken in open Lake Michigan at the offshore station. After collection, samples were saved for pH and total alkalinity (TA) and water isotopes,

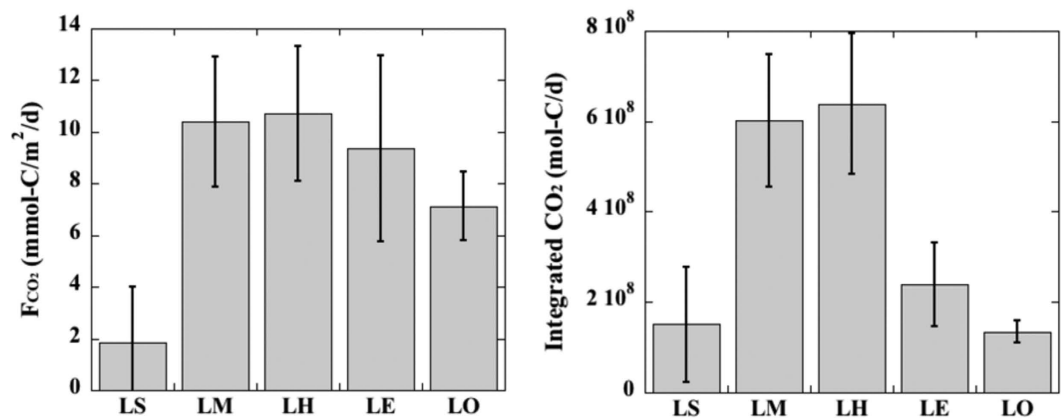


Figure 5. The averaged daily CO_2 emission fluxes (F_{CO_2}), and lake-wide integrated CO_2 emission fluxes in all Laurentian Great Lakes during the summer of 2013, derived from pH-dissolved inorganic carbon (pH-DIC) data pair. LS, LM, LH, LE and LO denote Lakes Superior, Michigan, Huron, Erie and Ontario.

and filtered through pre-rinsed syringe filters for the measurements of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC).

Analysis. Concentrations of DOC were measured on a Shimadzu TOC-L analyzer using the high temperature combustion method⁵⁹. Total dissolved carbon (TDC) was measured on the same TOC analyzer without acidification and sparging. The concentrations of DIC were calculated by the difference between TDC and DOC concentrations⁶⁰. Community consensus seawater reference from the University of Miami for DOC and the certified reference seawater (CRS) from the Scripps Institution of Oceanography for DIC⁵³, as well as working standards were measured as samples to ensure data quality. After calibration with three standard solutions (pH = 4.00, 7.00 and 10.00), the pH electrode (Sartorius PB-11) was used to measure the pH. The precision and accuracy of pH was ± 0.01 . Based on the Gran titration procedure⁶¹, the sample (~30 mL) for TA was titrated by the CRS-calibrated HCl solution (~0.02 M) to an endpoint pH of 4.5. The results of DIC, DOC and TA are all reported in $\mu\text{mol/kg}$. Stable hydrogen and oxygen isotopic composition (δ^2H and $\delta^{18}O$) of lake waters was measured on a Picarro cavity ring down spectrometer (L2130-i). Standard mean ocean water (Kona water) was used as a standard for both δ^2H and $\delta^{18}O$ with a precision of $\pm 0.02\%$.

Calculations of pCO_2 and flux of CO_2 . pCO_2 was calculated using the CO_2 program⁶² and measured pH and DIC concentrations or TA under the freshwater option. The CO_2 fluxes (F) were calculated based on the one-dimension flux model:

$$F = kK_o(pCO_{2\text{-water}} - pCO_{2\text{-air}}) = kK_o\Delta pCO_2$$

where k (cm/h) is the gas transfer velocity of CO_2 , and the K_o (mol/m³/atm) is the solubility coefficient of CO_2 at *in situ* temperature and salinity. Values of k and K_o were calculated based on the method of ref. 63 and ref. 64, respectively, and the monthly average wind speed in the study area was used for the calculation. The $pCO_{2\text{-water}}$ and $pCO_{2\text{-air}}$ are the partial pressures of CO_2 (in μatm) in surface waters and air, respectively. The global annual averaged surface air pCO_2 for 2013 from NOAA (<http://www.esrl.noaa.gov/gmd/>) was used as the $pCO_{2\text{-air}}$ value (398 μatm). When the difference in partial pressure of CO_2 between water and air (ΔpCO_2) is higher than zero, the emission of CO_2 from surface waters to the atmosphere occurs. In contrast, a negative value of ΔpCO_2 indicates uptake of atmospheric CO_2 in surface waters.

Uncertainties of pCO_2 and statistical analysis. Both DIC-pH and TA-pH pairs were used to derive the pCO_2 values in lake waters. Uncertainties of pCO_2 derived from pH (± 0.01) were estimated to be $\pm 16 \mu\text{atm}$. For the discussion on CO_2 fluxes, pCO_2 data derived from pH-DIC were used, while data derived from pH-TA were used to evaluate possible contribution from non-carbonate alkalinity⁶⁵. As shown in Table 1, pCO_2 values calculated from pH-TA pair were, on average, $48.8 \pm 14.4 \mu\text{atm}$ higher than those derived from pH-DIC pair. In other words, overestimation of pCO_2 from non-carbonate alkalinity could be up to $6.5 \pm 1.4\%$ in Great Lake waters even under the generally low DOC concentrations (Fig. 2). A one-way ANOVA analysis was performed to determine the significance of differences in pCO_2 between different sample groups.

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Author Contributions

L.G. conceived the project. P.L. analyzed the samples and performed data processing. P.L. and L.G. co-wrote the paper.

Additional Information

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