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 ρCO₂ (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 ± 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.
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 (δ²H and δ¹⁸O), total alkalinity (TA), dissolved inorganic carbon (DIC), and pH were measured prior to the evaluation of the partial pressure of CO₂ (pCO₂) and air-water CO₂ 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 μmol/kg except for Lake Superior (Table 1). Values of TA varied from 830 to 2200 μmol/kg for all the Great Lakes, with an average of 843 ± 10 μmol/kg in Lake Superior, 2168 ± 22 μmol/kg in Lake Michigan, 1600 ± 59 μmol/kg in Lake Huron, 1872 ± 22 μmol/kg in Lake Erie and 1815 ± 19 μmol/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 ± 24 μmol/kg) and lowest values in Lake Superior (average of 793 ± 26 μmol/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 Lakes16,18. 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 decades22–25.

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 δ²H and δ¹⁸O 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 inputs18. 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 pCO₂ along the Great Lakes. As shown in Table 1 and Fig. 3, our results consistently showed an evident CO₂ supersaturation (>398 μatm) for all the Great Lakes, with the highest pCO₂ in Lake Michigan (762 ± 88 μatm) and Lake Huron (774 ± 92 μatm), followed by Lakes Erie (725 ± 126 μatm) and Ontario (647 ± 47 μatm). Even in Lake Superior, with the lowest TA and DIC abundance (both <1000 μmol/kg) and lowest pCO₂ values (461 ± 77 μatm), CO₂ supersaturation was still evident (Fig. 3). This indicated that surface waters of all the Laurentian Great Lakes can be a net CO₂ source to the atmosphere, consistent with those observed for other global lakes16,18.

Additionally, our seasonal pCO₂ data from Lake Michigan between 2013 and 2015 also showed a significant CO₂ supersaturation during all sampling seasons. For example, average pCO₂ was 762 ± 88 μatm in August 2013, 699 ± 17 μatm in May 2014, 769 ± 124 μatm in October 2014, 815 ± 48 μatm in October 2015, and 944 ± 83 μatm in December 2015 (Fig. 4). Furthermore, CO₂ supersaturation existed throughout the whole water column of open Lake Michigan although pCO₂ values decreased slightly in the middle water column due to biological uptake (see examples of vertical profiles in October 2015, Fig. 4).
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 Lakes21–25. 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 pCO$_2$ values in the Great Lakes observed in 2013 are significantly higher than the median values of pCO$_2$ observed during the same sampling season between 1983–200617,30,39 (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 ($\sim 60 \mu$atm), the increase in pCO$_2$ in the water column of the Great Lakes was considerably larger. Taking Lakes Michigan and Huron as examples, during 1983–2006, the average $\Delta$pCO$_2$ value, the difference in pCO$_2$ between atmosphere (averaging $\sim 362 \mu$tm during that time periods) and lake waters, was about 118 and 22 $\mu$atm for Lakes Michigan and Huron17,30,39, respectively. In comparison, $\Delta$pCO$_2$ values in these two lakes during summer 2013 reached a new high of $\sim 400 \mu$atm, averaging 365 ± 89 and 377 ± 92 $\mu$atm for Lake Michigan and Lake Huron, respectively (Table 1), showing an increase of 4 times in $\Delta$pCO$_2$ values in August between 1983–2006 and 2013 (Fig. 3). For Lakes Erie and Ontario, the increase in pCO$_2$ values between 1983–2006 and 2013 was also significant, although large errors existed in historical CO$_2$ data30,39 for the shallower lakes with high primary production and anthropogenic influences including seasonal hypoxia and algal bloom, especially in Lake Erie40,41.

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, pCO$_2$ in Lake Michigan during October 2015 ranged from $\sim 600 \mu$atm in subsurface waters to $\sim 770 \mu$atm in deeper waters (Fig. 4). Elevated pCO$_2$ 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 pCO$_2$ from summer to fall and then to winter, reaching as high as 944 ± 83 $\mu$atm during December 2015; an increase by $\sim 30\%$ compared to other seasons (Fig. 4). Thus, the pCO$_2$ 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 pCO$_2$ in Lake Superior during summer between 1983–200617,30 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
(e.g., > 19,000-mussels/m³) have been reported for Lake Michigan\textsuperscript{12,25,27,33}, 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\textsuperscript{10,11,15,16}. In addition, quagga mussels did not start blanketing offshore regions of the Great Lakes, such as Lake Michigan until 2005\textsuperscript{13,14}. Therefore, CO\textsubscript{2} data collected during 1983–2006\textsuperscript{17,20,21,30,39} 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 CO\textsubscript{2} supersaturation during summer sampling time, we hypothesized that increasing CO\textsubscript{2} 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.

Table 1. Surface water pH, total alkalinity (TA) and dissolved inorganic carbon (DIC), as well as partial pressure of CO\textsubscript{2} (pCO\textsubscript{2}) and air-lake CO\textsubscript{2} fluxes (FCO\textsubscript{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 pCO\textsubscript{2} between 1983 and 2006 are taken from refs 17, 30 and 39.
Ontario had CO2 emission fluxes of 9.35 ± 3.59 mmol-C/m²/d and 7.13 ± 3.33 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 Erie, and 1.4 ± 1.0 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 rivers54,55. This annual CO2 emission flux from the Laurentian Great Lakes is also higher than the annual organic carbon burial rate in all inland seas16,36, and makes up 1% of the annual CO2 emission flux to the ocean from the Laurentian Great Lakes, which is comparable to the annual DIC flux to the ocean from the Mississippi River and many other world rivers54,55.

Possible pathways and mechanisms to support our hypothesis include (1) decreasing primary production in the Great Lakes after the introduction of invasive quagga mussels20–23,47,48, (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 floor27,49, 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 pCO2 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 (~60 μatm). Thus, enhanced CO2 emission fluxes from lake waters to the atmosphere can be expected. Based on these summer pCO2 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 ∆pCO2 values. Lakes Erie and Ontario had CO2 emission fluxes of 9.35 ± 3.59 mmol-C/m²/d and 7.13 ± 3.33 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 > 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 colonization30,50 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 × 10⁴ mol-C/d for Lake Superior, 6.0 × 10⁴ mol-C/d for Lake Michigan, 6.4 × 10⁴ mol-C/d for Lake Huron, 2.4 × 10⁴ mol-C/d for Lake Erie, and 1.4 × 10⁴ mol-C/d for Lake Ontario (Fig. 5). Collectively, up to (7.7 ± 1.0) × 10¹² 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 rivers54,55. This annual CO2 emission flux from the Laurentian Great Lakes is also higher than the annual organic carbon burial rate in all inland seas16,36, 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 pCO2 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
accelerating rise of atmospheric CO2. 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 CaCO3 saturation/precipitation) during summer, increased CO2 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 CO2 release from quagga mussel respiration.

**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°11.5362′N; 87°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 (°C) and chlorophyll-α 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,
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 method. 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 concentrations. Community consensus seawater reference from the University of Miami for DOC and the certified reference seawater (CRS) from the Scripps Institution of Oceanography for DIC, 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 procedure, 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 μmol/kg.

**Calculations of pCO₂ and flux of CO₂.** pCO₂ was calculated using the CO₂ program and measured pH and DIC concentrations or TA under the freshwater option. The CO₂ fluxes (F) were calculated based on the one-dimension flux model:

$$F = k K_o (p_{CO_2\text{-water}} - p_{CO_2\text{-air}}) = k K_o \Delta pCO_2$$

where k (cm/h) is the gas transfer velocity of CO₂, and the K₀ (mol/m²/atm) is the solubility coefficient of CO₂ at in situ temperature and salinity. Values of k and K₀ 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 pCO₂-water and pCO₂-air are the partial pressures of CO₂ (in μatm) in surface waters and air, respectively. The global annual averaged surface air pCO₂ for 2013 from NOAA (http://www.esrl.noaa.gov/gmd/) was used as the pCO₂-air value (398 μatm). When the difference in partial pressure of CO₂ between water and air (∆pCO₂) is higher than zero, the emission of CO₂ from surface waters to the atmosphere occurs. In contrast, a negative value of ∆pCO₂ indicates uptake of atmospheric CO₂ in surface waters.

**Uncertainties of pCO₂ and statistical analysis.** Both DIC-pH and TA-pH pairs were used to derive the pCO₂ values in lake waters. Uncertainties of pCO₂ derived from pH (±0.01) were estimated to be ±16 μatm. For the discussion on CO₂ fluxes, pCO₂ data derived from pH-DIC were used, while data derived from pH-TA were used to evaluate possible contribution from non-carbonate alkalinity. As shown in Table 1, pCO₂ values calculated from pH-TA pair were, on average, 48.8 ± 14.4 μatm higher than those derived from pH-DIC pair. In other words, overestimation of pCO₂ from non-carbonate alkalinity could be up to 6.5 ± 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 pCO₂ between different sample groups.

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