Exogenously produced CO$_2$ doubles the CO$_2$ efflux from three north temperate lakes

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Abstract  It is well established that lakes are typically sources of CO$_2$ to the atmosphere. However, it remains unclear what portion of CO$_2$ efflux is from endogenously processed organic carbon or from exogenously produced CO$_2$ transported into lakes. We estimated high-frequency CO$_2$ and O$_2$ efflux from three north temperate lakes in summer to determine the proportion of the total CO$_2$ efflux that was exogenously produced. Two of the lakes were amended with nutrients to experimentally enhance endogenous CO$_2$ uptake. In the unfertilized lake, 50% of CO$_2$ efflux was from exogenous sources and hydrology had a large influence on efflux. In the fertilized lakes, endogenous CO$_2$ efflux was negative (into the lake) yet exogenous CO$_2$ made the lakes net sources of CO$_2$ to the atmosphere. Shifts in hydrologic regimes and nutrient loading have the potential to change whether small lakes act primarily as reactors or vents in the watershed.

1. Introduction

The majority of lakes are supersaturated in carbon dioxide (CO$_2$) [Cole et al., 1994; Sobek et al., 2005] and are a source of greenhouse gases to the atmosphere. The CO$_2$ emitted from lakes comes from two potential sources. The first is within-lake (endogenous) mineralization of aquatic and terrestrial organic matter. Terrestrial material dominates the organic matter pools in many north temperate lakes [Wilkinson et al., 2013], the mineralization of which can lead to respiration being higher than gross primary production and CO$_2$ supersaturation [del Giorgio et al., 1999; Jonsson et al., 2003; Duarte and Prairie, 2005]. The other major source of carbon emitted from lakes is advective (exogenous) input of CO$_2$ from soil respiration and mineral weathering within the catchment [Stiegl and Michmerhuizen, 1998; Finlay et al., 2010; McDonald et al., 2013]. Exogenous CO$_2$ dominates the carbon efflux from streams and rivers [Hotchkiss et al., 2015] and hydrologic modeling in larger lakes (>4 ha) has revealed that exogenous inputs of pCO$_2$ also drive CO$_2$ efflux from larger lakes [McDonald et al., 2013]. However, there is very little information about the proportional contribution of endogenous and exogenous carbon to CO$_2$ efflux from small lakes which are numerically dominant [Downing et al., 2006]. Partitioning the sources of CO$_2$ efflux is not only necessary for lake and watershed carbon budgets, but it also aids in understanding how CO$_2$ efflux may change with future climate conditions.

Partitioning the exogenous and endogenous contributions to total lake CO$_2$ efflux can be accomplished through measurements of inflows and outflows used in mass balance modeling [Stets et al., 2009; Knoll et al., 2013; Perkins et al., 2015], hydrologic modeling of groundwater and surface water movement [McDonald et al., 2013], or inference from point measurements of stoichiometric ratios of O$_2$ and CO$_2$ concentrations [Torgersen and Branco, 2008; Holgerson, 2015]. With the advent of affordable environmental sensor technology, researchers are able to collect high-frequency (on the order of minutes) dissolved oxygen (DO) data in lakes and rivers to assess endogenous carbon processing. Many environmental sensors also measure pH and temperature at a high frequency. In soft water lakes, pH, dissolved inorganic carbon (DIC) concentration, and temperature can be used to calculate high-frequency pCO$_2$ and subsequently, high-frequency CO$_2$ efflux. The high-frequency time series of O$_2$ and CO$_2$ efflux can then be stoichiometrically compared to assess endogenous and exogenous contributions to CO$_2$ efflux from lakes.

Using high-frequency time series of CO$_2$ and O$_2$ concentrations, we evaluated the contribution of endogenous and exogenous sources to total CO$_2$ efflux during the summer in three north temperate lakes. In order to understand the role that eutrophication plays in endogenous CO$_2$ contributions to total efflux, two of the lakes were amended with nutrients in order to predictably manipulate the endogenous CO$_2$ signal without changing the
Michigan, USA (Table 1), with a water residence time of approximately 1 year. The groundwater input to see-
page lakes in this area is on average 57% of the total annual water input [Cole and Pace, 1998]. Beginning on
day of year (DoY) 153 in 2014, ammonium nitrate (NH₄NO₃) and phosphoric acid (H₃PO₄) were dissolved in
lake water and added daily to Peter and Tuesday Lakes at a molar N:P ratio of 15:1 and a phosphorous loading
rate of 3 mg m⁻² d⁻¹. The nutrients were distributed into the epilimnion of the lakes in the propeller wash of
an underway electric motor. Paul Lake served as a reference with no nutrient amendment.

High-frequency measurements (every 5 min) of DO, pH, and temperature were made using a Hydrolab DS SX
(OTT Hydromet, Loveland, Colorado, USA) deployed at 0.75 m in each lake. Brief gaps in the data record were
interpolated in R (version 3.1.30) [R Core Development Team, 2015] using a maximum likelihood multivariate
autoregressive state-space model (MARSS package version 3.9) [Holmes et al., 2015] with a simultaneous data
record taken with a YSI 6600 V2-4 multiparameter sonde (YSI Incorporated, Yellow Springs, Ohio, USA). The
MARSS-interpolated pH time series was then calibrated with the weekly manual measurements of surface
water pH using the more accurate long equilibration technique of Stauffer [1990].

Water temperature, pCO₂, and dissolved inorganic carbon (DIC) samples were taken weekly at the surface of
each lake. For DIC concentration, 10 mL of water were acidified with 200 μL of 2N H₂SO₄ and combined with
20 mL of helium in a gas tight syringe and equilibrated through vigorous shaking. The 0.5 mL sample loop
was flushed with 10 mL of headspace and automatically injected into a Shimadzu GC-8A gas chromatograph
with a 2 m column, packed with Porapak-Q, and connected to a thermal conductivity detector. Air samples
for the atmospheric concentration of CO₂ were taken weekly at 1.5 m above the surface on the aether side
of the boat. Samples of surface water pCO₂ were taken from 60 mL of atmospheric headspace equilibrated
with surface water in a 2 L container. Staff gauge height was recorded daily in each lake to track changes
in lake level (ΔL) which was compared to the daily change in mean CO₂ efflux (ΔCO₂) in each lake.

### 2.2. CO₂ and O₂ Efflux Calculation

Acid neutralizing capacity (ANC) was calculated weekly for each lake using the weekly measurements of DIC,
pH, and temperature (see supporting information for details). We used ANC as it is not altered by gains or
losses of CO₂. The weekly ANC time series was interpolated to a 5 min time scale to match the other high-
frequency observations (see SI for details). The interpolated ANC time series, high-frequency pH, and tem-
perature were used to calculate high-frequency pCO₂. It is common for calculated pCO₂ to be greater than
measured pCO₂ [Abril et al., 2015]; therefore, the difference between the weekly measured pCO₂ and calcu-
lated pCO₂ values was used to calibrate the calculated pCO₂ time series. The DO concentration was measured
directly by the sonde at the same frequency.

Efflux of CO₂ and O₂ (Fₓ; movement of gas from the lake to the atmosphere) was calculated using the follow-
ing equation

\[ F_{Xt} = \left( X_{surf} - X_{eq} \right) \times k_{Xt} \times k_{Xt} \tag{1} \]

where \( X_{surf} \) is the concentration of the gas (CO₂ or O₂) in the surface waters at time \( t \) and \( X_{eq} \) is the
atmospheric concentration of the gas. For CO₂, the atmospheric concentration was the average of weekly
measurements on each lake taken during the 99 day sampling period (\( n = 43 \)). For O₂, the atmospheric con-
centration was calculated using the R package LakeMetabolizer (version 1.3.1) [Winslow et al., 2015]. \( k_{(X)} \) is

### Table 1. Mean (± Standard Deviation) of Limnological Variables in the Three Study Lakes (See Supporting Information for Sampling Details)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Unit</th>
<th>Paul</th>
<th>Peter</th>
<th>Tuesday</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area</td>
<td>ha</td>
<td>1.9</td>
<td>2.5</td>
<td>0.9</td>
</tr>
<tr>
<td>Max depth</td>
<td>m</td>
<td>12</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>DOC mg L⁻¹</td>
<td></td>
<td>4.3 ± 0.4</td>
<td>8.3 ± 7.3</td>
<td>12.3 ± 4.7</td>
</tr>
<tr>
<td>Color m⁻¹</td>
<td></td>
<td>1.3 ± 0.2</td>
<td>2.2 ± 0.3</td>
<td>5.3 ± 1.0</td>
</tr>
<tr>
<td>pH n.a.</td>
<td></td>
<td>6.4 ± 0.3</td>
<td>6.6 ± 0.3</td>
<td>5.8 ± 0.4</td>
</tr>
<tr>
<td>DIC μmol L⁻¹</td>
<td></td>
<td>111.1 ± 8.1</td>
<td>90.5 ± 28.2</td>
<td>46.6 ± 12.7</td>
</tr>
<tr>
<td>TN μmol L⁻¹</td>
<td></td>
<td>13.7 ± 1.7</td>
<td>23.7 ± 6.1</td>
<td>25.0 ± 1.8</td>
</tr>
<tr>
<td>TP μmol L⁻¹</td>
<td></td>
<td>0.4 ± 0.1</td>
<td>0.5 ± 0.4</td>
<td>0.7 ± 0.3</td>
</tr>
</tbody>
</table>
| Chlorophyll a μg L⁻¹ | | 2.1 ± 0.7 | 5.8 ± 2.7 | 11.0 ± 4.5 | exogenous CO₂ signal. The goal was
to determine to what degree lakes act
as reactors (releasing endogen-
ously produced CO₂) and vents to
the atmosphere (releasing exogen-
ously produced CO₂).

### 2. Methods

#### 2.1. Study Lakes and Sampling

Peter, Paul, and Tuesday Lakes are small (<3 ha), soft water seepage lakes located in Gogebic County,
the Henry’s law constant for the gas at time \( t \) and \( kX(0) \) is the piston velocity (m\(^{-1}\)) for each gas. The piston velocity was fixed at the \( k_{600} \) values reported in Cole et al. [2010], measured in the study lakes and adjusted to be gas and temperature specific based on the high-frequency temperature data [Wanninkhof, 1992].

### 2.3. Estimating Endogenous and Exogenous CO\(_2\) Efflux

Instances of O\(_2\) efflux are periods of positive net ecosystem production (NEP) in the lake even if CO\(_2\) efflux is also occurring. Under the assumption that aerobic respiration consumes 1 mole of O\(_2\) for every mole of CO\(_2\) produced [Mattson and Likens, 1993], O\(_2\) influx (the inverse of efflux) is equal to the expected CO\(_2\) efflux if only endogenous, aerobic production of CO\(_2\) was contributing to efflux from the lakes. Any CO\(_2\) efflux greater than the O\(_2\) influx is therefore assumed to be exogenously produced CO\(_2\) or anaerobically produced endogenous CO\(_2\) from methanogenesis, sulfate reduction, or denitrification.

We estimated anaerobically produced endogenous CO\(_2\) from previous studies. The ebulliative flux of methane, which ranges between 0.27 and 1.02 mmol C m\(^{-2}\) d\(^{-1}\) in these lakes [Bastviken et al., 2004], is an additional source of DIC without a concomitant loss of O\(_2\). The daily flux of methane from epilimnion sediments (calculated from hypsographic curves) must be accounted for as a source of anaerobic, endogenous carbon processing. The occurrence of methanogenesis is indicative of a depletion of other anaerobic anions such as nitrate and sulfate in the sediment. Thus, the production of DIC from denitrification and sulfate reduction is temporary. These sources of DIC can be accounted for by calculating the difference in spring and fall concentrations of nitrate (measured directly,
plus the 63.8 mmol m\(^{-2}\) of nitrate added to Peter and Tuesday Lakes), assuming that exchange is occurring between the sediments and water column to a depth of 10 cm and applying the molar conversions for DIC production from sulfate and nitrate reduction (2 mol and 1.25 mol, respectively) [Mattson and Likens, 1993]. The springtime epilimnetic concentrations of sulfate in the three lakes were taken from Houser [2001] and the fall concentrations were assumed to be zero. The calculated DIC from nitrate and sulfate reduction (DIC\(_{NO_3^-}\) and DIC\(_{SO_4^{2-}}\), respectively) was then added to the sum of the O\(_2\) influx and the sum of the ebulliative methane influx to calculate the endogenously produced CO\(_2\) efflux CO\(_2\)endo as follows

\[
CO_{2\text{endo}} = \sum O_2 \text{ influx} + \sum CH_4 \text{ Flux} + DIC_{NO_3^-} + DIC_{SO_4^{2-}}
\]

for the entire 99 day data record in each lake. The total exogenous CO\(_2\) efflux (CO\(_2\)exo) was then calculated as

\[
CO_{2\text{exo}} = \frac{\sum CO_2 \text{ Flux}}{CO_{2\text{endo}}}
\]

where CO\(_2\)exo can be either positive (efflux from the lake to the atmosphere) or negative (influx to the lake).

3. Results

3.1. Patterns of Gas Efflux

The measured and calculated pCO\(_2\) values are in strong agreement after calibration (Figure 1) with \(R^2 = 0.99\) in a regression between measured and calibrated pCO\(_2\) (Figure S1 in the supporting information). Surface water pCO\(_2\) in all three lakes was substantially higher than the atmosphere (389 ± 44.6 ppmv) for large periods of the data record (Figure 1). On average, all three lakes were net sources of CO\(_2\) to the atmosphere even though there were brief periods of CO\(_2\) influx (Figure 2). Over the course of the summer, the unfertilized system, Paul Lake, had the highest average (± SD) CO\(_2\) efflux (8.0 ± 3.3 mmol m\(^{-2}\) d\(^{-1}\)) followed by the fertilized lakes Tuesday (4.0 ± 3.5 mmol m\(^{-2}\) d\(^{-1}\)) and Peter (2.0 ± 4.9 mmol m\(^{-2}\) d\(^{-1}\); Figure 2). Conversely, Paul Lake had the lowest average O\(_2\) efflux (3.7 ± 5.0 mmol m\(^{-2}\) d\(^{-1}\)) followed by Peter Lake (5.3 ± 7.2 mmol m\(^{-2}\) d\(^{-1}\)) and Tuesday Lake (6.5 ± 7.9 mmol m\(^{-2}\) d\(^{-1}\)).

A phytoplankton bloom composed largely of Anabaena spp. peaked on DoY 225 in Peter Lake. This bloom coincided with the peak daily average O\(_2\) efflux (18.8 mmol m\(^{-2}\) d\(^{-1}\); DoY 220) and the minimum daily average CO\(_2\) efflux (−8.2 mmol m\(^{-2}\) d\(^{-1}\); DoY 220). Similarly, in Tuesday Lake, there was a Chrysochromulina spp. bloom peaking on DoY 234 which coincided with the only period of intermittent negative daily average CO\(_2\) efflux in the lake (DoY 231–234), although there was not a peak in O\(_2\) efflux at this time. In Paul Lake, 13% of the days had a positive NEP (O\(_2\) efflux > 0), the majority of which were during the spring bloom period. In the fertilized lakes NEP was usually positive, with 78% and 88% of the days having a positive O\(_2\) efflux in Peter and Tuesday Lakes, respectively. The range in \(\Delta L\) in all lakes was −5.6 cm to +5.1 cm. In all three lakes there

\[\text{Figure 3.} \text{ The high-frequency (lighter points) and daily mean (darker points) of CO}_2\text{ efflux and the O}_2\text{ influx for (a) Paul, (b) Peter, and (c) Tuesday Lakes. The dashed line is the 1:1 line.} \]
was a positive relationship between daily $\Delta_{LL}$ and $\Delta_{CO2}$ (linear regression by lake, $p$ value $<0.05$ for all regressions) such that when lake level increased CO$_2$ efflux also significantly increased.

### 3.2. Endogenous and Exogenous CO$_2$ Efflux

The daily average influx of O$_2$ was less than the efflux of CO$_2$ 86% of the time in Paul, 85% in Peter, and 95% in Tuesday (Figure 3). The endogenous contribution to the total CO$_2$ efflux was negative in the two fertilized lakes ($-547.4$ mmol m$^{-2}$ in Tuesday Lake and $-413.3$ mmol m$^{-2}$ in Peter Lake) and the positive in Paul Lake ($394.9$ mmol m$^{-2}$; Figure 4). However, the net CO$_2$ efflux was positive in all three lakes due to exogenous CO$_2$ contributions. The exogenous contribution to the total CO$_2$ efflux ranged from $400.4$ mmol m$^{-2}$ in Paul Lake to $938.3$ mmol m$^{-2}$ in Tuesday Lake. The percent contribution of exogenous CO$_2$ to net CO$_2$ efflux was 50% in Paul Lake and 100% in the fertilized lakes. The negative endogenous CO$_2$ efflux in the fertilized lakes lowered the net CO$_2$ efflux.

### 4. Discussion

The exogenous contribution to total CO$_2$ efflux more than doubled the total CO$_2$ efflux in Paul Lake and caused the fertilized lakes to be net sources of CO$_2$ to the atmosphere instead of sinks. Considering the hydrologic residence times of these lakes [Cole and Pace, 1998] and the calculated exogenous CO$_2$ efflux, incoming ground water would need to have $pCO_2$ concentrations of approximately 1000 μmol L$^{-1}$ to support the estimate. Average groundwater $pCO_2$ from an area near the study lakes ranged from 0.8 to 955 μmol L$^{-1}$ with maximum measurements of 2080 μmol L$^{-1}$ [Crawford et al., 2014]. This indicates that the estimated input of $pCO_2$ from groundwater is within the range of possibility. Based on the significant but weak relationships between daily mean CO$_2$ efflux and changes in lake level, there was evidence that changes in groundwater input to the lake may play a role in the within lake variability in CO$_2$ efflux over the course of the summer. Increases in lake level from precipitation can indicate pulses of exogenous CO$_2$ input into the lake [Vachon and del Giorgio, 2014]. In each lake, an increase in $\Delta_{LL}$ from one day to the next coincided with an increase in CO$_2$ efflux. However, the correlation was weak and without examination on a finer scale with precipitation data should be interpreted cautiously.

As expected, the fertilization of Peter and Tuesday Lakes influenced the endogenous CO$_2$ efflux making it negative. The fertilization not only provided a check on the modeling method used in this study by modifying the endogenous signal, the results are also consistent with previous metabolism estimates in the two fertilized lakes. In previous years, both lakes have had either negative or near-zero NEP [Van de Bogert et al., 2007, 2012; Coloso et al., 2011a, 2011b], which would correspond to a small or negative endogenous CO$_2$ efflux. In a previous fertilization of Peter Lake in 2002, NEP was highly positive as it was in this study [Carpenter et al., 2005]. However, while endogenous CO$_2$ efflux was negative in 2014, the internal processing was still overwhelmed by the net exogenous inputs and made both fertilized lakes net sources of CO$_2$ to the atmosphere, a phenomenon which has been reported in other north temperate lakes [Stets et al., 2009].

The positive endogenous CO$_2$ efflux in Paul Lake is also consistent with previous studies of its metabolic behavior. Paul Lake has had a negative summertime NEP over the past decade [Carpenter et al., 2005; Coloso et al., 2011a, 2011b; Batt et al., 2015] indicating that it is a consistent source of both endogenously and exogenously produced CO$_2$ to the atmosphere. Using high-frequency DO data in Paul Lake but only...
weekly pCO₂ measurements, Cole et al. [2000] concluded that CO₂ efflux was entirely endogenous. In this study, the once per week measurements of CO₂ missed the diel and day to day variability in pCO₂, illustrating the value of the continuous CO₂ approach used here. The large exogenous contribution to CO₂ efflux in Paul Lake estimated here is consistent with estimates for other lakes [Striegl and Michenerhuizen, 1998; Stets et al., 2009; McDonald et al., 2013; Weyhenmeyer et al., 2015] leading to an emerging consensus that exogenous CO₂ inputs contribute significantly to lake CO₂ efflux.

In order to calculate the exogenous and endogenous contributions to the total CO₂ efflux, a number of assumptions had to be made. The first assumption was that the stoichiometry of aerobic respiration was one mole of DIC produced for every mole of O₂ consumed [Mattson and Likens, 1993], which has also been found in other studies [Kelly et al., 1988; Matthews et al., 2008]. If the ratio of DIC produced to O₂ consumed is less than one, then the estimate of exogenous CO₂ contribution would be slightly lower. Similar assumptions were made concerning the stoichiometry of DIC produced during anaerobic metabolism [Mattson and Likens, 1993; Hedin et al., 1998]. However, the contribution of anaerobic metabolism to the endogenous CO₂ efflux was much smaller than aerobic metabolism and therefore uncertainty in the ratios used in this calculation has a minimal impact.

A second assumption was that accounting for epilimnetic anaerobic respiration using previous measurements of methane ebullition [Bastviken et al., 2004] and assuming that springtime concentrations of nitrate and sulfate accounted for the total availability of these electron acceptors. In Peter and Tuesday Lakes this was not the case for nitrate as it was added to the epilimnion daily. However, the total added mass of nitrate was included in the calculation, likely leading to an overestimate of anaerobic metabolism as some nitrate was incorporated into algal biomass instead of being denitrified. Additionally, with the continual nitrate amendment, sulfate reduction and methanogenesis may have been suppressed and, therefore, overaccounted for in the anaerobic metabolism calculation. Iron reduction was not estimated in the anaerobic metabolism calculation as measured iron concentrations in these lakes are low (1.5–6.6 μM; unpublished data) and only 0.25 moles of DIC are produced for every mole of iron reduced. Although the anaerobic metabolism processes were not directly measured and only constrained estimates, they are important to include as anaerobic metabolism can contribute significantly to CO₂ efflux [Mattson and Likens, 1993; Torgersen and Branco, 2008; Holgerson, 2015], although this was not the case in the lakes considered here.

A final assumption involved nonrespiratory oxygen consumption. While photodegradation would not affect the endogenous CO₂ efflux accounting, photolysis (the photochemical mineralization of dissolved organic matter without O₂ consumption) was not accounted for in the model. Photolysis of dissolved organic matter ranges from undetectable [Laurion and Mladenov, 2013] to 10% of planktonic respiration or greater [Bélanger et al., 2006; Granéli et al., 1996]. For more than 1000 lakes across Sweden, the average DIC production from photolysis was approximately 12% of total C emissions [Koehler et al., 2014]. If these rates held for the lakes in this study, that would reduce the estimated exogenous CO₂ contribution to the total CO₂ efflux but not alter the overall pattern of exogenous CO₂ contribution. Conversely, if the groundwater is undersaturated in O₂, the exogenous signal would be higher.

Recent research has demonstrated that CO₂ efflux from streams and rivers is dominated by exogenous CO₂ inputs [Hotchkiss et al., 2015], whereas for large lakes the endogenous contribution likely dominates due to longer hydraulic residence times. In small lakes (<0.025 km²) we found that hydrologic inputs of CO₂ more than double the CO₂ efflux from these inland water bodies, even in fertilized lakes. In the future, changes in precipitation and nutrient runoff could shift whether small lakes are primarily processors of organic carbon or vents of inorganic carbon to the atmosphere.

References


