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Can pelagic net heterotrophy account for carbon fluxes from eastern Canadian lakes?

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ABSTRACT

Lakes worldwide are commonly oversaturated with CO_2, however the source of this CO_2 oversaturation is not well understood. To examine the magnitude of the C flux to the atmosphere and determine if an excess of respiration (*R*) over gross primary production (GPP) is sufficient to account for this C flux, metabolic parameters and stable isotopes of dissolved O_2 and C were measured in 23 Québec lakes. All of the lakes sampled were oversaturated with CO_2 over the sampling period, on average 221 ± 25%. However, little evidence was found to conclude that this CO_2 oversaturation was the result of an excess of pelagic *R* over GPP. In lakes Croche and à l'Ours, where CO_2 flux, *R* and GPP were measured weekly, the annual difference between pelagic GPP and *R*, or net primary production (NPP), was not sufficient to account for the size of the CO_2 flux to the atmosphere. In Lac Croche average annual NPP was 14.4 mg C m^{-2} d^{-1} while the average annual flux of CO_2 to the atmosphere was 34 mg C m^{-2} d^{-1}. In Lac à l'Ours average annual NPP was -9.1 mg C m^{-2} d^{-1} while the average annual flux of CO_2 to the atmosphere was 55 mg C m^{-2} d^{-1}. In all of the lakes sampled, O_2 saturation averaged 104.0 ± 1.7% during the ice-free season and the isotopic composition of dissolved O_2 ($\delta^{18}O_{DO}$) was 22.9 ± 0.3‰, lower than atmospheric values and indicative of net autotrophy. Carbon evasion was not a function of *R*, nor did the isotopic signature of dissolved CO_2 in the lakes present evidence of excess *R* over GPP. External inputs of C must therefore subsidize the lake to explain the continued CO_2 oversaturation. The isotopic composition of dissolved inorganic C ($\delta^{13}C_{DIC}$) indicates that the CO_2 oversaturation cannot be attributed to in situ aerobic respiration. $\delta^{13}C_{DIC}$ reveals a source of excess C enriched in ^{13}C, which may be accounted for by anaerobic sediment respiration or groundwater inputs followed by kinetic isotope fractionation during degassing under open system conditions.

1. Introduction

Lakes, rivers and streams worldwide are commonly oversaturated in CO_2 resulting in a net flux of CO_2 from freshwater aquatic systems to the atmosphere (Cole et al., 1994; Kling et al., 1991; Sobek et al., 2005). Cole et al. (1994) found that 87% of 1835 lakes distributed worldwide were supersaturated with respect to atmospheric CO_2. Sobek et al. (2005) evaluated data from 4902 lakes and found that 93% were supersaturated in CO_2. Despite this general trend, there is much controversy surrounding C cycling in lakes and sources of CO_2 oversaturation in lakes have not been well quantified.

Biogeochemical process both in the watershed and in the lake influence C fluxes in lakes. Dissolved inorganic C, DIC, and dissolved organic C, DOC, can be transported into a lake through stream flow, overland flow, and subsurface flow (Myrbo and Shapley, 2006; Bade et al., 2004). Respiration of organic matter, aerobic and anaerobic, also occurs in both benthic and littoral sediments, thereby increasing concentrations of DIC (Kortelainen et al., 2006; Algesten et al., 2005; den Heyer and Kalff, 1998). Within a lake's water column, gross primary production, GPP, consumes inorganic C and produces organic C, while respiration, *R*, breaks down organic C and produces inorganic C. Thus, the difference between GPP and *R*, or net primary productivity, NPP, will influence the degree of CO_2 saturation. Exchange with the atmosphere can also influence the concentration of CO_2 in a lake. When undersaturated, atmospheric CO_2 will dissolve into the surface layers and when oversaturated, CO_2 will degas. Photooxidation of organic matter in the water column can also increase concentrations of DIC (Ma and Green, 2004).

The relative contribution of each of these processes to CO_2 oversaturation in lakes is contested. For example, the importance of sediment respiration to CO_2 oversaturation is unclear. A recent study of 177 randomly selected Finnish lakes found that respiration in sediments was a major contributor to high CO_2 saturation (Kortelainen et al., 2006). Yet, a study of oligotrophic boreal lakes in Sweden found that water column respiration even in

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unproductive lakes was ~10-fold higher per lake unit area than sediment respiration and that sediments contributed little to the total production of CO_2 in summer months (Algesten et al., 2005).

The balance between GPP and R in lakes is also a highly debated subject. In Quebec lakes, the relative contribution of respiration of allochthonous organic matter to CO_2 oversaturation is confounded by widely varying observations in a narrow geographic region. Studies done in the Eastern Townships region of Quebec found that respiration exceeds photosynthesis in all but the most eutrophic ecosystems (del Giorgio and Peters, 1994; Prairie et al., 2002). On the other hand, Carignan et al. (2000) found that GPP exceeds R in the epilimnia of oligotrophic systems and proposed that allochthonous C metabolism is an insignificant source of CO_2 in 12 lakes in the Laurentian region of Quebec.

The primary goal of this study was to determine if an excess of R over GPP in the water column could account for the flux of CO_2 to the atmosphere. Net primary productivity was measured in the water column of two Quebec lakes on a weekly basis for one year using bottle incubation techniques and changes in concentrations of O_2 and CO_2. This NPP was compared with the flux of CO_2 to the atmosphere to determine if respiration in the water column was sufficient to account for the degree of CO_2 oversaturation. In addition, 21 lakes in 3 regions of Quebec we sampled during the ice-free season to assess whether the trends observed were specific to the two sampled lakes or occurred over a broader geographic range. Stable isotopes of C and dissolved O_2 were then used to confirm the assessments of lake metabolic balance and as tracers to help constrain the external sources of DIC.

Table 1
Morphometric properties of the 23 study lakes. Region (L = Laurentians, E = Eastern Townships, G = Gatineau Hills), n = number of times sampled, LA = lake area (km^2) WA = watershed area (km^2), Zm = mean depth (m).

Lake	Region	Location	n	LA	WA	Zm
Achigan	L	45°56'N, 74°00'W	6	5.31	96.5	12.7
d'Argent	E	45°29'N, 72°28'W	3	1.00	13.2	4.6
de la Blanche	L	46°08'N, 74°44'W	6	0.41	1.14	10.5
Bowker	E	45°42'N, 72°21'W	3	2.30	8.10	25.9
Brome	E	45°23'N, 72°49'W	3	14.5	185.7	5.8
Connelly	L	45°53'N, 73°58'W	5	1.24	24.4	7.8
Croche	L	45°58'N, 74°01'W	40	0.19	0.88	5.1
En Coeur	L	45°58'N, 74°01'W	5	0.47	1.6	3.4
Gervais	L	46°16'N, 74°41'W	6	0.97	8.8	24.4
La Pêche	G	45°59'N, 75°98'W	3	7.05	93.8	8.4
Montange Noire	L	46°12'N, 74°16'W	6	2.80	12.6	13.0
du Nord	L	46°03'N, 74°02'W	6	4.02	34.9	7.9
Orford	E	45°29'N, 72°27'W	3	1.30	10.6	17.7
Ouimet	L	46°10'N, 74°35'W	6	1.60	16.7	9.3
à l'Ours	L	45°58'N, 74°01'W	40	0.15	3.26	6.7
Phillippe	G	45°63'N, 76°18'W	3	1.72	18.4	6.6
Pin Rouge	L	45°57'N, 74°02'W	6	0.15	7.00	4.9
de la Rouge	L	46°07'N, 74°42'W	6	0.66	3.45	8.1
des Sables	L	46°01'N, 74°15'W	6	2.92	35.4	9.3
St. Joseph	L	45°96'N, 74°33'W	6	1.47	14.9	12.1
Tremblant	L	46°12'N, 74°35'W	6	9.56	129.3	36.5
à la Truite	L	46°01'N, 74°15'W	6	0.49	1.04	8.9
Waterloo	E	45°27'N, 74°68'W	3	1.50	31.6	2.9

2. Methods

2.1. Study site

To examine the annual atmospheric flux of CO_2 and net primary productivity, two Quebec lakes, Croche and à l'Ours, were sampled on a weekly basis between May 2002 and March 2003, excluding two weeks in November when the lakes were not yet completely frozen. Both are located on the Canadian Shield, approximately 60 km NE of Montreal. Lake Croche is a small, pristine oligotrophic clearwater lake with low total P (TP), total N (TN) and DOC concentrations (3.8 mg m^{-3}, 211 mg m^{-3} and 4600 mg m^{-3}, respectively; Carignan et al., 1998). Macrophytes are virtually absent, but epilithic and epipelic communities are well developed. Lake à l'Ours is a mesotrophic lake with higher TP and DOC concentrations (14 mg m^{-3} and 8900 mg m^{-3}) due to its larger drainage ratio and to the presence of wetlands in its watershed. Its watershed is more developed, with 22 cottages on its shores.

To determine if the C dynamics observed in lakes Croche and à l'Ours applied over a wider geographic area, 21 lakes in three regions of Québec, were also sampled between May and October of 2003 (Table 1). Most of these lakes stratify and are ice covered between November and April. Fourteen of these lakes are in the Laurentian hills located NW of Montreal on the Canadian Shield, and were sampled monthly. There are no carbonates in the watersheds of these lakes. Two lakes are in the Gatineau Hills, north of Ottawa, also on the Canadian Shield. Five lakes in the Eastern Townships, SE of Montreal, are situated on sedimentary rocks of the St. Lawrence lowlands and metamorphic schist terrains. The Gatineau Hills and the Eastern Townships lakes were sampled in the spring, summer and fall of 2003.

2.2. Carbon dioxide concentrations and atmospheric fluxes

In lakes Croche and à l'Ours CO_2 concentrations were measured at 1-m intervals throughout the water column on a weekly basis between May 2002 and March 2003. Samples were taken in 60 mL syringes, transported to the laboratory and their temperature allowed to equilibrate with cool water. Thirty mL of sample was equilibrated with 30 mL CO_2-free gas and the CO_2 concentration of the resultant gas measured with a LI-COR LI-820 CO_2 analyzer. Henry's law was then used to calculate the concentration of dissolved CO_2 in the water samples. Alkalinity, pH and total dissolved solids (TDS) were measured for each isotope sample in the field with a Hach field chemistry kit (Loveland, CO). The pCO_2 calculated from alkalinity, pH and temperature (Clarke and Fritz, 1997) agreed with CO_2 concentrations measured from the LI-COR CO_2 analyzer to within ±10%.

In the 21 lakes sampled in 2003, a 4-L Van Dorn Bottle was used to collect samples for DIC analysis from the middle of the mixed layer. Samples were poisoned with $HgCl_2$, stored in 40 mL amber glass bottles with silicon/teflon septa, refrigerated at 4 °C, and analyzed within a maximum of 4 months after collection using an OI Analytical "TIC–TOC" Analyzer. Alkalinity, pH and TDS were measured as described above. Concentrations of CO_2 were calculated from DIC and pH measurements and the degree of CO_2 saturation (CO_{2sat}) was then calculated with respect to temperature and pressure.

Evasion from the lakes sampled over the ice-free season was estimated using the flux equation:

$$F = k(C_{\text{water}} - C_{\text{equilibrium}}) \qquad (1)$$

where F is the evasion flux, C_{water} is the concentration of CO_2 in the water, $C_{\text{equilibrium}}$ is the concentration of dissolved CO_2 in equilibrium with atmospheric CO_2 that depends on temperature and pressure, and k is the gas transfer velocity (Carignan, 1998). Cole and Caraco (1998) used SF_6 to measure the atmospheric exchange of CO_2 in a small oligotrophic lake and found that the gas transfer velocity, k, of CO_2 normalized to a Schmidt number of 600 (0.636 ± 0.29 m d^{-1}), was independent of wind at low wind speeds. Wind speed at Lake Croche averaged 1.79 ± 0.05 m s^{-1} during the ice-free season, and the above k is therefore applicable to the lakes in the present study. Temperature dependency relationships in Wanninkhof (1992) were used to determine appropriate Schmidt numbers, and the relationship