Carbon Dioxide Supersaturation in the Surface Waters of Lakes

Jonathan J. Cole, Nina F. Caraco, George W. Kling, and Timothy K. Kratz

Copyright © 1994 by the American Association for the Advancement of Science
Carbon Dioxide Supersaturation in the Surface Waters of Lakes

Jonathan J. Cole, Nina F. Caraco, George W. Kling, Timothy K. Kratz

Data on the partial pressure of carbon dioxide (CO₂) in the surface waters from a large number of lakes (1835) with a worldwide distribution show that only a small proportion of the 4665 samples analyzed (less than 10 percent) were within ±20 percent of equilibrium with the atmosphere and that most samples (87 percent) were supersaturated. The mean partial pressure of CO₂ averaged 1036 microbaromespheres, about three times the value in the overlying atmosphere, indicating that lakes are sources rather than sinks of atmospheric CO₂. On a global scale, the potential efflux of CO₂ from lakes (about 0.14 x 10¹³ grams of carbon per year) is about half as large as riverine transport of organic plus inorganic carbon to the ocean. Lakes are a small but potentially important conduit for carbon from terrestrial sources to the atmospheric sink.

Processes that add and remove CO₂ occur simultaneously in the surface waters of lakes. Lakes can thus act either as sources or as sinks for CO₂. Earlier studies have shown that Arctic lakes are strongly supersaturated in CO₂, and therefore are sources to the overlying atmosphere (1, 2). In the Arctic the transport of tundra organic matter to surface waters leads to CO₂ supersaturation (1, 2). Other regions that lack the vast soil carbon storage of the Arctic may behave differently. In fact, detailed studies on a limited number of temperate and boreal lakes have suggested that these lakes are net sinks for atmospheric CO₂ (3), but no comprehensive analysis exists. We report data from lakes with a worldwide distribution that show that boreal, temperate, and tropical lakes are typically supersaturated with CO₂ and thus are net sources to the atmosphere.

Data were obtained both from the literature and from our own direct measurements of the partial pressure of CO₂ (P₁CO₂). The value of P₁CO₂ was calculated from pH and dissolved inorganic carbon (DIC) or acid-neutralizing capacity (ANC) with corrections for other physical and chemical variables (4). For the direct measurement of P₁CO₂, we collected water from 0.1 to 0.27 m below the surface into a theromally insulated 2-liter glass bottle and equilibrated it with 50 ml of ambient air (5). Gas chromatography was used to measure CO₂ on the equilibrated head space. Simultaneously ambient air 1 m above the lake surface was collected for the measurement of atmospheric CO₂.

The lakes analyzed range in size from 8.2 x 10⁶ ha (Lake Superior) to 0.4 ha, span latitudes from 69°S to 62°N, and include both hard and soft waters (Table 1). For each data set there are differences in the type of measurements made, the intensity of those measurements over time, and geographic location (Table 1). For these reasons we discuss the data in terms of a series of individual data sets.

Of the 37 lakes (190 samples) where direct measurements of P₁CO₂ were made, 16 lakes (43%) were supersaturated at all samplings. Data for a persistently supersaturated lake are shown in Fig. 1. The mean measured P₁CO₂ for the 37 lakes was 801 ± 67 μatm (mean ± standard error), about 2.2 times the measured atmospheric value (2). Only 7% of the samples were within ±20% of atmospheric equilibrium (2A). In the larger data sets for which P₁CO₂ was calculated, we also see a consistent tendency toward supersaturation. For the 1612 lakes sampled in autumn (eastern lakes survey) (6) (Fig. 2B), mean P₁CO₂ was 1031 ± 19.4 μatm or three times the atmospheric equilibrium value. Relatively few lakes (6.6%) were within ±20% of the atmospheric equilibrium value.

Because of thermal mixing, autumn may be a time of elevated P₁CO₂ in surface waters. Nevertheless, a similar pattern of supersaturation was seen for 69 lakes from all over the world with full seasonal data for the entire ice-free season (Fig. 2C). For lakes with ANC-based data, calculated mean P₁CO₂ averaged 1122 μatm; for lakes with DIC-based data, calculated mean P₁CO₂ was 1039 μatm. Both of these values are well above atmospheric equilibrium (7) and similar to that from the lakes sampled only in autumn (Fig. 2B). For 34 of these 69 lakes, 100% of the samples were supersaturated, and for every lake the time-weighted average was above the atmospheric value.

The 60 lakes (179 samples) sampled only during summer stratification, a time of lower-than-average P₁CO₂, were also supersaturated. The distribution is broader and the mean lower (680 ± 65 μatm) than for the other data sets (Fig. 2D). For these samples also, 100% of the samples were the atmosphere; few samples (11%) were within ±20% of atmospheric equilibrium (Fig. 2E).

For the lakes for which we both directly measured and calculated P₁CO₂, we found relatively good agreement between measured and calculated values (8), but such agreement...
may not be universal. Electrode-based measurements of pH in lakes with high concentrations of dissolved organic carbon may be biased low by about 0.2 pH unit, which would lead to overestimates of $P_{\text{CO}_2}$ (9). Recalculating our data with the assumption that the reported pH was in error by 0.2 pH unit lowers the mean $P_{\text{CO}_2}$ to 797 μatm but still leads to the conclusion that lakes are generally supersaturated in $\text{CO}_2$.

Whether $P_{\text{CO}_2}$ in the surface waters of lakes is measured directly or calculated from other chemical measurements, most of the lakes that we surveyed were out of equilibrium with the atmosphere and were supersaturated. Only 7% of the samples in the combined data set were within ±20% of equilibrium with the atmosphere, and 87% were supersaturated. Our analysis suggests that the surface water of lakes is rarely at equilibrium with the atmosphere. Furthermore, lakes showed an enormous range of $\text{CO}_2$ concentrations, from 175-fold below to 57-fold above atmospheric equilibrium at the extremes and 3.1-fold below to 1.6-fold above equilibrium for the means of the upper and lower 10% of the samples.

Lakes from boreal, temperate, and tropical regions appear to be similar to those of the Arctic in overall $\text{CO}_2$ supersaturation. The mean $P_{\text{CO}_2}$ from the surface waters of Arctic lakes averaged 1162 ± 132 μatm (1, 4), which compares closely to the mean $P_{\text{CO}_2}$ of 1036 μatm for lakes from other regions. The Arctic lakes also show a small percentage (8%) of samples within ±20% of atmospheric equilibrium and a large range in $P_{\text{CO}_2}$ from 93 to 2758 μatm (1, 4).

Analyzing our data set by broad regions, we see supersaturation of comparable magnitude within each region. Lakes from boreal (non-Arctic) Sweden, for example, have a mean $P_{\text{CO}_2}$ of 1469 ± 38 μatm; South American lakes, 1520 ± 101 μatm; non-Arctic lakes from North America, 1087 ± 23 μatm; and lakes from somewhat higher, tropical Africa, 1296 ± 429 μatm.

In the specific case of Arctic tundra lakes, the large accumulation of organic matter in the tundra and its respiration in soil or lake water is a probable explanation for the excess $\text{CO}_2$ (1, 4). Our data suggest that the phenomenon of excess $\text{CO}_2$ in lake water is quite general and occurs in other regions without these accumulations. Lakes must either import excess $\text{CO}_2$ (derived from plant-root or soil respiration) in inflowing ground or surface waters or produce internally more $\text{CO}_2$ than they consume (that is, ecosystem respiration exceeds ecosystem primary production). If excess respiration within the lake is the cause, the organic matter that supports this process must come either from previously deposited lake sediments or from new inputs from the catchment. Either model would be at odds with published carbon budgets for some lakes (10), but both agree with some recent

![Fig. 2. Frequency diagram (by numbers of samples) for calculated $P_{\text{CO}_2}$ in the surface waters of lakes from five different, nonoverlapping data sets: (A) direct measurements, (B) autumn survey, (C) full seasonal data, (D) summer survey, and (E) tropical Africa. Only values from the ice-free season are shown. Relative saturation (RS) is the degree of supersaturation (hatched bars) or undersaturation (solid bars) relative to atmospheric equilibrium. For supersaturation, $RS = P_{\text{CO}_2(\text{water})}/P_{\text{CO}_2(\text{air})}$.

For undersaturation, $RS = -P_{\text{CO}_2(\text{air})}/P_{\text{CO}_2(\text{water})}$.

On this scale, water with twice the $P_{\text{CO}_2}$ of the atmosphere has a value of 2; water with half the value of the atmosphere has a value of −2. The vertical dotted line represents equilibrium with the atmosphere (RS = 1.0), and the open bars represent the samples in near equilibrium with the atmosphere (±20% of equilibrium). See Table 1 for characteristics of the data sets.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Data set</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lakes (n)</td>
<td>Direct $P_{\text{CO}_2}$ measurements</td>
<td>305</td>
<td>1012</td>
<td>60</td>
<td>60</td>
<td>59</td>
</tr>
<tr>
<td>Samples (n)</td>
<td></td>
<td>301</td>
<td>1012</td>
<td>60</td>
<td>60</td>
<td>59</td>
</tr>
<tr>
<td>Latitude (range)</td>
<td></td>
<td>44°25'S–41°21'N</td>
<td>47°13'N–27°14'N</td>
<td>62°00'N–50°43'S</td>
<td>44°56'N–28°00'N</td>
<td>72°00'S–21°47'S</td>
</tr>
<tr>
<td>Area (km²)</td>
<td></td>
<td>1.6 x 10⁵–5.8 x 10⁶</td>
<td>1.8–9.358²</td>
<td>6.5 x 10⁵–1.2 x 10⁶</td>
<td>0.4–9.275</td>
<td>1.6–9.900</td>
</tr>
<tr>
<td>pH (range)</td>
<td></td>
<td>4.5–8.5</td>
<td>3.8–9.4</td>
<td>4.2–9.6</td>
<td>4.9–9.3</td>
<td>6.0–9.9</td>
</tr>
<tr>
<td>DIC (μM) (range)</td>
<td></td>
<td>4.9–2.500</td>
<td>13.3–4.077</td>
<td>6.0–4.800</td>
<td>11–3.578</td>
<td>43–145,790</td>
</tr>
<tr>
<td>$P_{\text{CO}_2}$ (μatm) (range)</td>
<td></td>
<td>801</td>
<td>1031</td>
<td>1064</td>
<td>690</td>
<td>2590</td>
</tr>
<tr>
<td>$P_{\text{CO}_2}$ (μatm) (range)</td>
<td></td>
<td>107–4,128</td>
<td>20–6,789</td>
<td>1–7.845</td>
<td>5–7.991</td>
<td>32–20,249</td>
</tr>
<tr>
<td>Batches of $P_{\text{CO}_2}$ estimate</td>
<td></td>
<td>Direct measurement</td>
<td>Each once in autumn</td>
<td>Ph, DIC</td>
<td>Ph, DIC</td>
<td>Ph, DIC</td>
</tr>
<tr>
<td>Sampling intensity</td>
<td></td>
<td>Weekly to quarterly</td>
<td>Each once in autumn</td>
<td>Ph, DIC</td>
<td>Ph, DIC</td>
<td>Ph, DIC</td>
</tr>
<tr>
<td>Source</td>
<td></td>
<td>This study</td>
<td>(5)</td>
<td>(17)</td>
<td>(16)</td>
<td>(18)</td>
</tr>
</tbody>
</table>
reassessments of the balance between pelagic production and respiration in lakes (11). Our data suggest that the transport of carbon from land to water is an important control on the carbon budget in most lakes.

We can use the frequency distribution of $P_{CO_2}$ to estimate the potential contribution of $CO_2$ from lakes to the atmosphere. We assume an evasion coefficient of 0.5 m day$^{-1}$ for all lakes, and for undersaturated lakes an enhancement factor of 3 (12). Globally, lakes (an area of 2.2 x 10$^{12}$ m$^2$) could contribute CO$_2$ to the atmosphere in the amount of 0.14 x 10$^{11}$ g of carbon per year. This flux is slightly less than half as great as the total export of organic plus inorganic carbon from rivers to the sea (13), is larger than recent estimates of total organic carbon burial in lake sediments (0.06 x 10$^{11}$ g (14)), and is comparable to organic carbon burial in reservoirs (0.2 x 10$^{11}$ g (15)). Lakes have longer hydrologic residence times than do flowing waters, which may allow for both the degassing of CO$_2$ derived from soil respiration and for increased respiration of organic materials derived from the catchment.

REFERENCES AND NOTES

4. G. W. Kling, G. W. Kipphut, M. C. Miller, Hydrobiology 240, 23 (1992), and references therein. In all cases adjustments were made for temperature, air, and volcanic inputs. Where complete chemical data were not available, we estimated ionic strengths from conductivity (J. N. Butler, Carbon Cycle Equilib. and Their Applications, Lewis, Detroit, 1962). Where complete chemical data were available, we also corrected for the effects of specific ion complexation on the activity of biocarbonate and carbonates, using MINEQL version 2.3.9 (W. D. Schindler and D. C. McKown, MINEQL: User's Manual [Proctor and Gamble, Cincinnati, CA, 1981] for most data sets and PHREEQ [J. L. Parkhurst, D. O. Thornstev, L. N. Hummer, U.S. Geol. Surv. Water Res. Inv. 36–36, (1992)] for the lakes of the North Temperate Lakes Long-Term Ecological Research (LTER) program.
7. During the calculation of $P_{CO_2}$ from pH and ANC, we may overestimate the presence of noncarbonate ANC. This effect is strongest at low values of ANC. We exclude from our ANC-based calculations samples with ANC below 40 mg/L to minimize this effect.
8. We found a strong, unexplained relation between $P_{CO_2}$ directly measured versus calculated from pH and DIC. A linear regression of measured versus calculated $P_{CO_2}$ (N = 330 samples) has an r$^2$ of 0.90 and a slope of 1.00 ± 0.01.
12. Evasion of CO$_2$ from supersaturated water was calculated as:

\[ \text{Flux} = D \cdot \frac{\partial[P_{CO_2}]}{\partial z} \]

where $D$ is Henry's constant, $z$ is the depth expressed as a function of the surface boundary layer. An evaporation coefficient of 0.5 m day$^{-1}$ would be equivalent to 300 µm at 22°C for $z = 200$ µm at 10°C and is within published values for lakes. In undersaturated water, atmospheric CO$_2$ may react chemically with hydroxyl or carbonate ions more rapidly than it would diffuse passively (S. Emerson, Limnol. Oceanogr. 28, 743 (1973). We used an enhancement factor of 3 to calculate flux into undersaturated waters.

17. References for seasonal data for the 69 lakes are too numerous to list and are available upon request.
19. We thank G. Defalco, K. Postak, C. Bowser, and D. Armstrong for assistance with the computations and S. Pach, G. Likens, and G. Kipphut for thoughtful discussions throughout this work. We thank C. Sandgren, R. A. G. Fahnestock, C. Driscoll, C. Ellis-Clark, M. Miel, S. Norum, and J. K. Brewer for providing published and unpublished data. We thank D. Rugg, D. Mason, and E. Monroy for making the $P_{CO_2}$ measurements at Mirror Lake and G. Likens, P. Lillers, A. Stearns, R. Miller, P. Raymond, J. F. Reid, and P. Truel for $P_{CO_2}$ measurements at other sites. Financial support was provided by the National Science Foundation (NSF DEB 911775, 9031456, 9317068, 9011900, 0019187). This is a contribution to the Institute of Ecosystem Studies, the Hubbard Brook Ecosystem Study, and the North Temperate Lakes LTER program.

29 April 1994; accepted 27 July 1994.