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# Large $CO_2$ disequilibria in tropical lakes

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[1] On the basis of a broad compilation of data on $p\mathrm{CO}_2$ in surface waters, we show tropical lakes to be, on average, far more supersaturated and variable in $CO_2$ (geometric mean ± SE $p\mathrm{CO}_2 = 1804 \pm 35$ $\mu$atm) than temperate lakes ($1070 \pm 6$ $\mu$atm). There was a significant negative relationship between $p\mathrm{CO}_2$ and latitude, resulting in an average decrease of $p\mathrm{CO}_2$ by 2.8 ± 0.5% per degree latitude. In addition, we found a general positive relationship between $p\mathrm{CO}_2$ and water temperature across lakes involving an average increase (±SE) in 6.7 ± 0.8% per °C. A conservative annual efflux from global lakes to the atmosphere was reestimated to 0.44 Gt C. Our results show tropical lakes maintain large $CO_2$ disequilibria with the atmosphere, playing a disproportionate and variable role in the flux of $CO_2$ between lakes and the atmosphere, thereby being a significant component of the global C cycle.

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## 1. Introduction

[2] Increasing recognition of the role of lakes as conduits of $CO_2$ to the atmosphere has prompted a series of global surveys of $p\mathrm{CO}_2$ in lake surface waters encompassing an increasing number of lakes across the world [*Cole et al.*, 1994; *Sobek et al.*, 2005]. Although the broadest analysis in the published literature [*Sobek et al.*, 2005] includes almost 5000 lakes (4902 lakes), tropical lakes remain severely underrepresented ($\leq$3% of lakes) in these data sets, because of a paucity of reported observations on lake $p\mathrm{CO}_2$ at low latitudes. Yet, tropical lakes can show persistence of $CO_2$ supersaturation even along the day or year [*Marotta et al.*, 2009] and support intense metabolism [*Richey et al.*, 2002], enhanced by their warm temperatures [*Brown et al.*, 2004] and the high production of the tropical forests and grasslands in their watersheds [*Luyssaert et al.*, 2007]. Terrestrial organic inputs play an important role in supporting aquatic heterotrophy and, hence, $CO_2$ supersaturation in lakes, as supported by the general relationship between dissolved organic carbon (DOC) and $p\mathrm{CO}_2$ in lakes [*Cole et al.*, 2007; *Sobek et al.*, 2005]. Indeed, warm temperatures have been often reported to affect the $CO_2$ balance in natural environments, increasing $CO_2$ fluxes [*Cornelissen et al.*, 2007; *Knorr et al.*, 2005; *Rastetter et al.*, 2005; *Shaver et al.*, 2006; *Wang et al.*, 1999]. Yet, the global lake $p\mathrm{CO}_2$ surveys conducted thus far report no significant relationship between the $p\mathrm{CO}_2$ of lake waters and either latitude or water temperature [*Cole et al.*, 1994; *Sobek et al.*, 2005]. However, these results may derive from the limitations of these surveys to assess these relationships due to the underrepresentation of tropical lakes in the data sets, rather than from an intrinsic absence of such relationships.

[3] Here we test the relationship between the $p\mathrm{CO}_2$ of lake waters and latitude and water temperature. In order to do so, we substantially expanded the observational basis on $p\mathrm{CO}_2$ in the surface waters of tropical lakes by combining our own survey in Brazil with estimates for tropical lakes elsewhere derived from the published literature (see section 2 and Data Sets S1 and S2).[5] We then combined these data with the data set of *Sobek et al.* [2005], the most thorough data set on $p\mathrm{CO}_2$ available. The resulting data set comprised data on $p\mathrm{CO}_2$ for 5190 lakes across all continents and encompassing a broad range of $p\mathrm{CO}_2$ (3 to 71,394 $\mu$atm), latitude (0° to 79°), and water temperature (0.7 to 33.5°C).

## 2. Material and Methods

[4] We conducted a survey of water temperature, DOC, and $p\mathrm{CO}_2$ in surface waters of tropical lakes across Brazil ($n$ = 86) and used them, along with data from tropical lakes elsewhere derived from published papers and theses ($n$ = 133) and previous global assessments ($n$ = 148 from *Sobek et al.* [2005]) to produce a database on these properties for a total of 367 tropical lakes. The data set encompassed broad ranges of lake types, including shallow and deep lakes and saline lakes. We then combined these data with that on 4791 nontropical lakes from *Sobek et al.* [2005] and *Alin and Johnson* [2007] and 32 subtropical lakes from our own

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[5] Auxiliary materials are available at ftp://ftp.agu.org/apend/gb/2008gb003434.

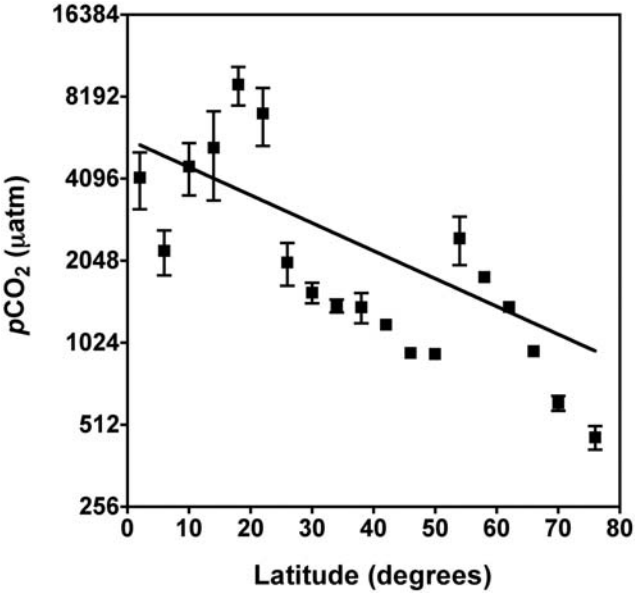

**Figure 1.** The relationship between the average (±SE) $p\text{CO}_2$ of lakes, grouped by 4° latitude bins, and latitude. The solid line represents the fitted regression equation $p\text{CO}_2$ ($\mu$atm) = 5518.3 $e^{0.028\pm0.005\text{Latitude (degrees)}}$; $R^2 = 0.62$; $F = 27.52$; $p < 0.0001$.

survey in southern Brazil. Details about bibliographic sources are in the supplementary data set. The vast majority (95%) of the $p\text{CO}_2$ data in the current analysis, including all of the data on Brazilian lakes contributed here, were derived using the same method, namely, calculations based on pH and alkalinity. Differences among methods are therefore not expected to contribute much to the variance in the data. In addition, *Sobek et al.* [2005] already concluded that differences in methods had little bearing on the variance in $p\text{CO}_2$ in their data set.

[5] In our survey, 119 Brazilian lakes were sampled between 2005 and 2007. Surface lake water was gently sampled to avoid bubbles. Samples were immediately analyzed for pH and alkalinity, and $p\text{CO}_2$ was calculated following *Weiss* [1974]. Temperature and salinity were measured in situ with a calibrated Thermosalinometer YSI-30. At the laboratory, prefiltered (0.7 $\mu$m, Whatman GF/F) water samples preacidified to pH < 2.0 were analyzed for DOC concentrations by high-temperature catalytic oxidation using a TOC-5000 Shimadzu Analyzer. $CO_2$ concentrations in surface waters were derived from direct measurements using calibrated infrared gas analyzers or calculated from pH and alkalinity (Gran titration) measurements after correction for temperature, altitude, and ionic strength following *Cole et al.* [1994]. Air-water carbon fluxes ($F_{CO2}$) were estimated as $F_{CO2} = \alpha K ([CO_2]_{water} - [CO_2]_{sat})$, where $\alpha$ is the chemical enhancement factor calculated as by *Wanninkhof and Knox* [1996]; $K$ is the piston velocity (cm h$^{-1}$), calculated from wind velocity following *Cole and Caraco* [1998], assuming either the conservative wind velocity equal to 0.5 m s$^{-1}$ [*Cole et al.*, 1994] or the global mean value recently estimated by *Archer and Jacobson* [2005], 3.28 m s$^{-1}$; $[CO_2]_{water}$ is the $CO_2$ concentration ($\mu$mol L$^{-1}$) in the water; and $[CO_2]_{sat}$ is the $CO_2$ concentration ($\mu$mol L$^{-1}$) of the water at equilibrium with the overlying atmosphere calculated from Henry's law [*Weiss*, 1974], considering a $p\text{CO}_2$ in equilibrium of 380 $\mu$atm.

[6] Despite our efforts to balance the data set across latitudinal bands, the data set is still dominated by temperate lakes, which may bias the relationship between log $p\text{CO}_2$ and temperature or latitude, as the regression equation must intersect the coordinate given by the mean log $p\text{CO}_2$ and the mean temperature. We avoided this bias by also binning the data by temperature or latitudinal ranges, thereby giving equal weight to the average $p\text{CO}_2$ at different water temperatures or latitudes, independent of the number of observations at a certain latitude or temperature. Simple and multiple regressions (significance $p < 0.05$) were performed to assess significant relationships among log $p\text{CO}_2$, latitude, and temperature. Our choice of 2°C temperature bins and 4° latitudinal bins in these analyses depended on the need to have a minimum number of observations per bin to deliver robust mean log $p\text{CO}_2$ estimates, which was not achieved when binning the data by narrower temperature or latitude intervals.

[7] In addition, differences of $p\text{CO}_2$ between tropical (0–24° of latitude), temperate (24–66°), and polar (>66°) lakes were assessed by Kruskall-Wallis followed by Dunn's posttest (significance $p < 0.05$), as transformed data sets did not reach the normality (Kolmogorov-Smirnov, significance $p < 0.05$) and homogeneity of variance (Bartlett, significance $p < 0.05$) assumptions. Changes in range of $p\text{CO}_2$ in lake surface waters with increasing temperature were tested by fitting the relationship between the 97% and 3% quartiles of the distribution of $p\text{CO}_2$ and water temperature using quantile regression. Quantile regression may be viewed as an extension of classical least squares estimation of conditional mean models to the estimation of an ensemble of models for several conditional quantile functions, considering the median as the central parameter [*Koenker*, 2005]. Statistical analyses were performed using Graphpad Prism 4.0 for simple regressions, JMP 5.0 for multiple regression analyses, and *R* for quantile regression.

## 3. Results and Discussion

[8] Most (87%) tropical lakes were supersaturated with $CO_2$, acting as sources to the atmosphere, comparable to that for nontropical lakes (92%). However, the geometric mean (±SE) of $p\text{CO}_2$ for tropical lakes (1804 ± 35 $\mu$atm) was significantly higher (Dunn's posttest, $p < 0.001$) than those for polar (494 ± 8 $\mu$atm) and temperate (1070 ± 6 $\mu$atm) lakes. There was a significant negative relationship between the $p\text{CO}_2$ and latitude (Figure 1), indicating a decrease by 2.8 ± 0.5% of $p\text{CO}_2$ per degree latitude, on average, from tropical to polar lakes. Closer examination of the results showed that the highest $p\text{CO}_2$ is attained in lakes located around 16 to 20° latitude, which average $p\text{CO}_2$ exceed by more than 20 times that in polar lakes (Figure 1). Although lake $p\text{CO}_2$ has been reported to increase with DOC concentrations [*Sobek et al.*, 2005], the decline in $p\text{CO}_2$ with increasing latitude was independent of any possible changes in DOC, as there was no significant relationship between DOC and latitude ($p > 0.05$). On the other hand, the average $p\text{CO}_2$ of lakes increased significantly with increasing water temperature (Figure 2), at

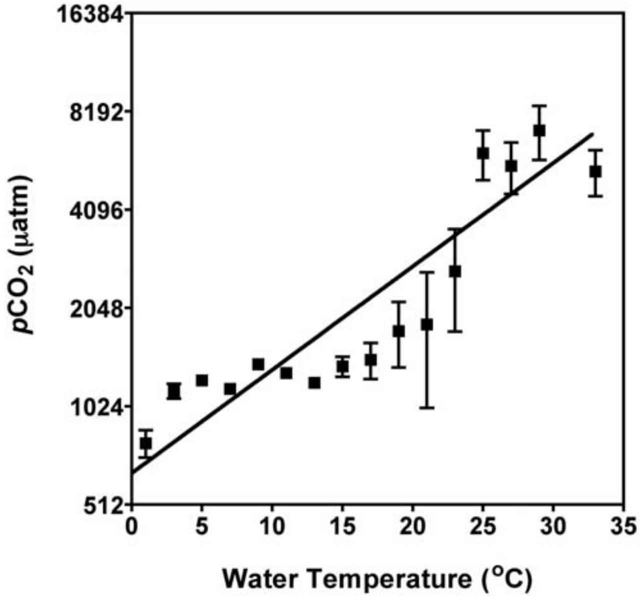

**Figure 2.** The relationship between the average (±SE) $pCO_2$ of lakes, grouped by 2°C temperature bins, and water temperature. The solid line represents the fitted regression equation $pCO_2$ (μatm) = 682.6 $e^{0.066 \pm 0.008 \mathrm{Temperature}\ (^\circ\mathrm{C})}$; $R^2 = 0.82$; $F = 4.44$; $p < 0.0001$.

a mean (±SE) rate of 6.7 ± 0.8% of $pCO_2$ per degree Celsius (Figure 2). This significant relationship between temperature and $pCO_2$ was observed (linear regression, $p < 0.05$) also when the data was binned by 1, 3, 4, or 5°C, or when raw data were used. Multiple regression analysis showed that these relationships were not redundant, with differences in latitude and temperature both being statistically significant ($p < 0.001$).

[9] A closer examination of the distribution of $pCO_2$ with water temperature also showed that the range of $pCO_2$ increased significantly with increasing water temperature (quantile regression, $p < 0.01$, Figure 3), suggesting that the relationship between $pCO_2$ and water temperature is a complex one, probably driven by the effect of temperature on lake metabolism, which may enhance both net heterotrophy, leading to high $pCO_2$, and net autotrophy, leading to low $pCO_2$ depending on lake conditions. The higher range in lake $pCO_2$ with increasing temperature is consistent with a higher range in $CO_2$ under warm conditions previously reported in forests [*Luyssaert et al.*, 2007] and soils [*Raich and Schlesinger*, 1992]. Whereas these patterns do not allow inferences on the underlying mechanisms, the increasing range of variability in lake $pCO_2$ with water temperature suggests the participation of a number of processes, including enhanced metabolic activity, both autotrophic [*Alin and Johnson*, 2007] and heterotrophic [*Davidson and Janssens*, 2006], under warmer conditions, as expected from metabolic theory [*Brown et al.*, 2004]. The strongly higher and more variable $CO_2$ supersaturation in tropical lakes than ones at higher latitudes reported here confirmed earlier results derived for tropical African lakes included in the seminal paper of *Cole et al.* [1994].

[10] Therefore, our results show a fundamental difference in $pCO_2$ in lake waters with latitude. No significant relationship between $pCO_2$ and temperature ($p > 0.05$) was observed when the data set of *Sobek et al.* [2005] was reanalyzed using the same aggregation of lakes by temperature "bins" as used here. This confirms that previous reports of no latitudinal pattern in $pCO_2$ and an independence of $pCO_2$ on water temperature in the previous analysis by *Sobek et al.* [2005] were derived from a poor representation of tropical lakes in the data sets rather than the specific approach used to examine the relationship.

[11] The conclusion that tropical aquatic ecosystems can support large $CO_2$ exchanges is consistent with reports that the Amazon flooded area, including wetlands and rivers, acts as a major source of $CO_2$ to the atmosphere, releasing, on average, 830 g C $m^{-2}$ $a^{-1}$ [*Richey et al.*, 2002]. Assuming similar, and conservative, gas diffusion coefficients calculated from a wind velocity of 0.5 m $s^{-1}$ in temperate and tropical lakes (see section 2 for calculation details), the differences in $pCO_2$ with latitude implies that tropical lakes release to the atmosphere about 600 and 80% more $CO_2$ in median per unit area (176 g C $m^{-2}$ $a^{-1}$) than polar (28 g C $m^{-2}$ $a^{-1}$) and temperate lakes (99 g C $m^{-2}$ $a^{-1}$), respectively. Hence, present estimates of the release of $pCO_2$ from lakes to the atmosphere need be revised upward to include the larger flux from tropical lakes.

[12] We used the product of the median $CO_2$ flux above described for tropical, temperate, and polar lakes and the distribution of lake area for each of these regions extracted

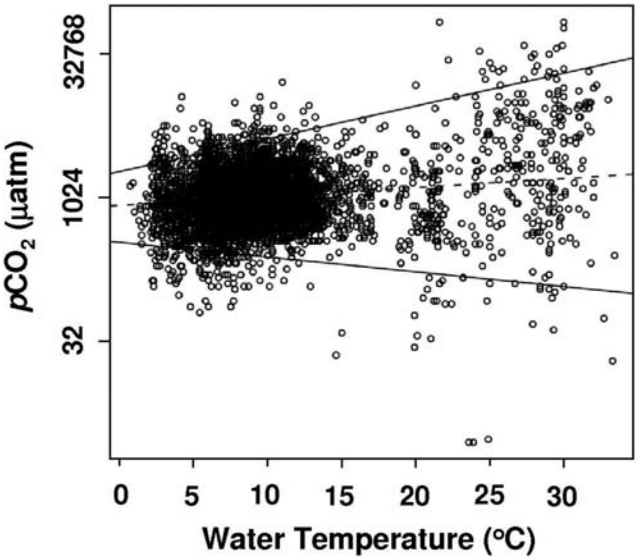

**Figure 3.** The relationship between the $pCO_2$ of individual lakes and water temperature. The solid lines represent the fitted regression for the upper 97% quartile (log2 $pCO_2$ = 0.114 ± 0.013 × Temperature + 10.90 ± 0.12, $p < 0.0001$) and the lower 3% quartile (log2 $pCO_2$ = −0.052 ± 0.015 × Temperature + 8.46 ± 0.14, $p < 0.001$) of the distribution of $pCO_2$ with increasing temperature. The dashed line represents the fitted regression for the median or 50% quartile (log2 $pCO_2$ = 0.030 ± 0.005 × Temperature + 9.74 ± 0.04, $p < 0.0001$).

following *Downing et al.* [2006] and a conservative piston velocity of 0.5 m $d^{-1}$ (to allow comparison with the estimates of *Cole et al.* [1994]) to recalculate the global annual $CO_2$ efflux from lakes to the atmosphere at 0.44 Gt C. This estimate exceeds the flux reported earlier for rivers, reservoirs, or estuaries and is comparable in size to the global export of organic carbon from rivers to the ocean [*Cole et al.*, 2007]. Use of the reported mean global wind velocity of 3.28 m $s^{-1}$ over land [*Archer and Jacobson*, 2005] to derive a less conservative piston velocity, and recalculation of $CO_2$ efflux for each lake in the data set according to *Cole and Caraco* [1998], will raise this estimate to 0.86 Gt C $a^{-1}$, which confirms the notion that lakes are significant sources of $CO_2$ to the atmosphere [*Cole et al.*, 2007]. We conclude that future attempts to further assess the role of lakes in global carbon cycle must explicitly address the high and variable rates of tropical lakes to achieve a reliable global representation of the processes examined.

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