

Inter- and intra-annual variations of $p\text{CO}_2$ and $p\text{O}_2$ in a freshwater subtropical coastal lake

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Received 14 January 2014; accepted 26 November 2014; published 18 February 2015

Abstract

Inland waters emit significant amounts of carbon dioxide to the atmosphere, but tropical and subtropical lakes are underrepresented in current assessments. Here we present results of a 6-year study of the dynamics of surface partial pressures of carbon dioxide and oxygen ($p\text{CO}_2$ and $p\text{O}_2$) in a subtropical lake, Lake Peri, Brazil, to determine how temperature, rainfall, and wind moderate surface concentrations. Both $p\text{CO}_2$ and $p\text{O}_2$ tended to increase during the transitions between seasons when rainfall increased, with $p\text{CO}_2$ averaging 2.5–3-fold higher than atmospheric values. Occasionally during autumn/winter, $p\text{CO}_2$ similarly increased and $p\text{O}_2$ decreased. We infer that the increases in both gases during the transition periods resulted from increasing inputs of allochthonous material into the lake. Those in winter resulted from near-bottom intrusions that intermittently reach the depth of measurement. In autumn/winter, $p\text{CO}_2$ was 3-fold higher (average 1700 μatm) compared to spring/summer (550 μatm), whereas changes in $p\text{O}_2$ did not have a clear seasonal pattern. Overall median net CO_2 evasion was 11 $\text{mg C m}^{-2} \text{d}^{-1}$. Variability in the extent of rainfall and the associated high intra- and inter-annual variability in CO_2 and CO_2 emissions are in part controlled by atmospheric processes related to the South American Monsoon System and to El Niño Southern Oscillation cycles.

Key words: carbon dioxide, $p\text{CO}_2$, $p\text{O}_2$, rainfall, South American Monsoon, subtropical lake, temperature, wind

Introduction

On a global scale, lakes emit to the atmosphere significant amounts of carbon dioxide (CO_2) produced by the degradation of organic matter (Cole et al. 1994, 2007, Marotta et al. 2009a). Lakes receive large inputs of organic substrates for CO_2 production from multiple sources, including terrestrial vegetation and soils (e.g., via runoff and leaching; Pace et al. 2004), and produce organic substrates via photosynthesis (e.g., aquatic plants and algae; Jonsson et al. 2001, Solomon et al. 2013). Direct inputs of mineralized carbon (C) from the

catchment areas are an additional source of CO_2 for lakes (Jones and Mulholland 1998, Marotta et al. 2010, Maberly et al. 2013). Despite potential prevalence of both autotrophic and heterotrophic processes, resulting respectively in CO_2 subsaturation and supersaturation (Cole et al. 2000), large terrestrial C inputs induce net heterotrophy and subsequent CO_2 outgassing in many of the world's lakes (Duarte and Prairie 2005, Aufdenkampe et al. 2011). Along a latitudinal gradient, inland waters in the tropics emit more CO_2 per area to the atmosphere than temperate and polar lakes (Marotta et al. 2009a), particularly in forested areas (Richey et al. 2002, Abril et

al. 2014). Subtropical lakes remain underrepresented in global comparisons.

Short- and long-term fluctuations in meteorological parameters can cause changes in the introduction of organic matter and its cycling in lakes. A positive relationship between temperature and degradation of organic matter (Gudas et al. 2010, Yvon-Durocher et al. 2010, Marotta et al. 2014), and subsequently CO₂ enrichments in inland waters (Marotta et al. 2009b), has been consistently reported in the literature. Rainfall events can promote substantial increases in terrestrial organic and inorganic C inputs into lakes from runoff and groundwater (Rantakari and Kortelainen 2005, Kritzberg et al. 2014). Wind and heat loss (cooling) may contribute to high partial pressure of CO₂ and outgassing from lakes through increasing turbulence of the water column (MacIntyre et al. 2010, Marotta et al. 2012). Thus, short-term changes in the partial pressure of O₂ and CO₂ (pO_2 and pCO_2) can be related to fluctuations in meteorological parameters.

Subtropical lakes, which are distributed between 23.4 and 30°S in Southern Brazil, are under the influence of the South American Monsoon, which is characterized by a variation in atmospheric circulation and rainfall distribution during warm and cold seasons (Carvalho et al. 2011, Silva and Kousky 2012, Jones and Carvalho 2013). The South American Monsoon can be intensified or weakened inter-annually by El Niño Southern Oscillation (ENSO) cycles that promote, in general, increasing rainfall events during El Niño and drought or rainfall deficits during La Niña in Southern Brazil (e.g., Ropelewski and Halpert 1987, Grimm 2003). It is not clear, however, whether pCO_2 and pO_2 in subtropical lakes respond to changes in temperature, wind, or rainfall, or whether their response varies intra- and inter-annually and with patterns moderated by ENSO cycles.

Here, our aim was to assess the intra-annual and long-term dynamics of surface pCO_2 and pO_2 in a subtropical lake, Lake Peri, situated on the south coast of Brazil, and its response to meteorological fluctuations in temperature, rainfall, and wind using 6 years of data. Our earlier work indicated that this low-nutrient freshwater lake experiences periodic upwelling of CO₂ in winter and increased dissolved organic C (DOC) due to exudates by cyanobacteria in summer (Fontes et al. 2013). The extent of inter-annual fluctuations and potential relationships with meteorological variables remains unclear. To address this question, we present meteorological data and monthly data on pCO_2 and pO_2 , pH, and chlorophyll *a* in surface waters between 2007 and 2012. Further, we illustrate the links between daily CO₂ fluxes and seasonality and atmospheric cycles.

Study site

Lake Peri is a small (surface area 5.7 km²), shallow (average depth 7 m; maximum depth 11 m) lake situated along the Brazilian coast near Florianópolis City (27°43'32"S, 48°30'36"W; Fig. 1). Its catchment area is 20.1 km² (Santos et al. 1989). This coastal lake is parallel to the sea and surrounded by 250–500 m of hills on 3 sides, and a sandbar ~3 km long and 0.5 km wide separates it from the sea to the east (Fig. 1). Its watershed of 20.3 km² is entirely located within a conservation area for the subtropical Atlantic Forest, the Municipal Park of Lake Peri created in 1981, and seawater exchange is negligible as indicated by the low-nutrient freshwaters that allow important recreational and water supply uses by the city of Florianópolis.

The main tributaries that flow into Lake Peri are Cachoeira Grande and Ribeirão Grande streams (Fig. 1A and B), and 2 other small creeks that also flow into the lake in the northern section. The Sangradouro River does not flow into the lake due to the presence of a small dam built where the lake and the river meet, allowing the river to flow directly to the ocean (Fig. 1). Cachoeira Grande is a third-order stream that drains an area of 1.66 km² and flows 1.17 km down to the lake, with a maximum elevation of 280 m (Lisboa et al. 2014), whereas the smaller Ribeirão Grande flows 1 km from an elevation of 120 m (Fig. 1). The organic matter (OM) budget estimated for Cachoeira Grande shows that on a monthly basis 70.5 g OM is laterally flushed into the stream, whereas just half, 32.4 g, comes from vertical input, with a benthic contribution of 115.5 g OM month⁻¹ (Lisboa et al. 2014). The authors conclude that rainfall was the main driver of OM variation in the stream, with higher lateral inputs of leaves and removal of benthic stocks during rainfall events (Lisboa et al. 2014).

Surface respiration rates are low but exceed primary production; waters are oligotrophic based on nutrient concentrations ranging from 10 to 27 µg L⁻¹ for total phosphorus (TP) and 400–1000 µg L⁻¹ for total nitrogen (TN), respectively, but meso-eutrophic for pelagic chlorophyll *a* (Chl-*a*), varying from 4 to 32 µg L⁻¹ (Hennemann and Petrucio 2011). DOC varies from 2.6 to 8.9 mg L⁻¹, reflecting the influence of different autochthonous and allochthonous sources throughout the year (Fontes et al. 2013). Aquatic macrophyte stands are reduced, and the dominance of cyanobacteria (*Cylindrospermopsis raciborskii*, a potential nitrogen-fixing bacterium) in the phytoplankton explains the low-nutrient, high-Chl-*a* paradox in Lake Peri waters (Tonetta et al. 2013).

Mean monthly air temperatures vary from 16.5 to 17 °C during the winter months of June to August and

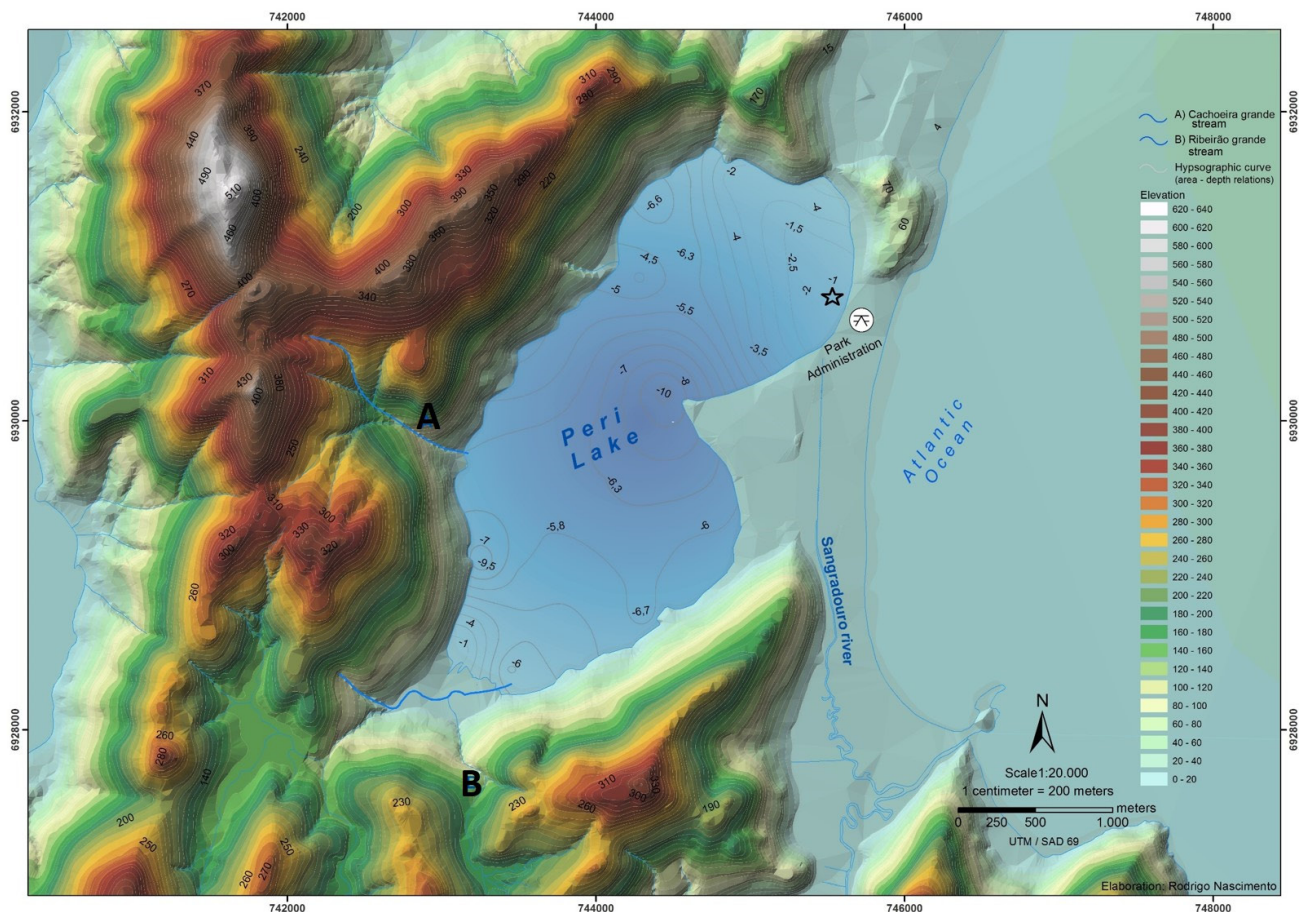


Fig. 1. Geographic location of the sampling station (star symbol), along with the bathymetry of the lake, hypsographic curve, and elevation of the coastal Lake Peri Park area. A = Cachoeira Grande stream, B = Ribeirão Grande stream.

between 23 and 24 °C during the summer months of December to February (1961–1991; Brazilian National Institute of Meteorology, <http://www.inmet.gov.br>). Rainfall occurs throughout the year (Hennemann and Petrucio 2011), with higher rainfall between January and March due to the influence of the South American Monsoon (Jones and Carvalho 2002, Vera et al. 2006). Annual precipitation for this area is on average ~900 mm (REDEMET Florianópolis – Rede de Meteorologia do Comando da Aeronáutica – aeroporto de Florianópolis/Hercilio Luz, SC).

Material and methods

Study design and chemical analysis

Water sampling was performed at one station (average 0.5 m deep) located in unvegetated margins of the eastern side of Lake Peri (Fig. 1). With this near-shore sampling, we assumed that due to cross-basin exchange our surface samples were representative of surface samples elsewhere in the lake. Only a few studies have been conducted on

horizontal dispersion in lakes (Peeters et al. 1996). In one lake slightly smaller than Lake Peri, during low winds, spatial heterogeneity of incoming storm water persisted for 10 days, but once winds reached moderate values, heterogeneity was lost within 1 day (Rueda and MacIntyre 2009). In our case, the response to incoming storm water from the rivers originating in the more mountainous regions to the west would likely be delayed. Temperature data from a pelagic station 7 m deep (Denise Tonetta, UFSC, unpublished data collected between May and end of July of 2014) indicate cooling of bottom waters from advection, suggesting that some of the river water is cooler than ambient and plunges below the surface. Thus, the frequency of vertical mixing events and rates of horizontal dispersion determine when storm water reached our study site. All water samples for each variable were collected in 3 L van Dorn bottles monthly for 6 years from March 2007 to December 2012 ($n = 70$) at the same morning hour (10:00 h) to avoid any bias from daily variations in our dataset. This study design allowed reporting intra- and inter-annual variability of $p\text{CO}_2$ and $p\text{O}_2$ in surface waters of Lake Peri.

Temperature, specific conductivity, pH, and dissolved oxygen (DO) were measured with calibrated probes (WTW – Multi350i), and Chl-*a* was extracted from AP40 Millipore glass filters with acetone after filtration of 500 mL of water (Lorenzen 1967, Strickland and Parsons 1972). CO₂ concentrations were estimated from measurements of pH and alkalinity (Stumm and Morgan 1996) with corrections for temperature, altitude, and ionic strength (Kling et al. 1991, Cole et al. 1994); *p*CO₂ and *p*O₂ were calculated from Henry's law with appropriate adjustments for the solubility of CO₂ and O₂ with respect to temperature and salinity (Weiss 1974, Garcia and Gordon 1992). Additionally, the respiration index (RI) was calculated as the log₁₀ (*p*CO₂/*p*O₂), as described by Brewer and Peltzer (2009) to define the physiological limits for animal respiration (e.g., practical limit for aerobic respiration, RI < 0.7). We calculated the flux (*F*) of CO₂ to the atmosphere as: $F = k(C_w - \alpha C_a)$, where *k* is the gas transfer coefficient; *C_w* and *C_a* are gas concentration in water and air, respectively; and α is the Ostwald solubility coefficient. We used the atmospheric CO₂ concentrations from 2007–2012 (Tans and Keeling 2014), local wind velocities (in m s⁻¹) measured during the week prior to sampling, and gas transfer coefficients calculated from wind speed following Cole and Caraco (1998) to estimate the daily net CO₂ flux from the surface waters of Lake Peri. Daily precipitation, air temperature, and wind speed and direction data were provided by the REDEMET-Florianopolis (Rede de Meteorologia do Comando da Aeronautica – aeroporto de Florianopolis/Hercilio Luz, SC), located 7 km from the lake. We computed the variability in the daily range of temperatures by computing the difference between the maximum and minimum temperature each day and then averaging over 30 days.

Statistical Analyses

Log-transformed data met the assumptions of parametric tests (Zar 1999), including normality (Kolmogorov-Smirnov, *p* > 0.05) and homogeneity of variances (Bartlett, *p* > 0.05). Correlations and differences in variables were analyzed (significance level at *p* < 0.05) using the t-test for 2 sampling groups and one-way analysis of variance (ANOVA) followed by Tukey-Kramer multiple comparison test. Univariate statistical tests and graphs were performed using PRISM v.4.0 (GraphPad Software, San Diego, CA). Multiple regression analyses were conducted for dependent variables *p*CO₂ and *p*O₂ (log-transformed) in SPSS Statistics 19.0 (IBM Corp., NY).

Results

Annually, air temperatures cycled between maxima in late summer (Mar) and minima in late winter (Jul/Aug; Fig. 2A); however, more intense differences in meteorological variables and metabolic gases were observed during the transition from autumn to winter and spring to summer (Fig. 2 and 3). Temperatures during autumn/winter were significantly lower than during spring/summer (21 vs. 25 °C, respectively; Fig. 4A; t-test, *p* < 0.05). Daily temperature variation was greater in winter than in summer (data not shown). As air temperatures reached their summer maximum, wind direction began to shift from predominately easterly to predominantly westerly (Fig. 2A and B). After air temperatures reached their minimum and began to increase again, wind directions shifted back from westerly to easterly. Wind speeds were lowest in autumn/winter and maximal in spring/summer (Fig. 2C, 4B, and 4C; t-test, *p* < 0.05). Rainfall was lowest in summer and winter and highest during the transitions from summer to autumn and winter to spring when winds were southerly (Fig. 2D). Differences in rainfall between autumn/winter and spring/summer were not significant (Fig. 4D; t-test, *p* > 0.05; Fig. 4A–C), although rainfall more frequently intensified at the onset of cooling and low winds (transition periods of years 2008, 2010, 2011, and 2012), consistent with monthly climatology for southern Brazil (Leibmann and Mechoso 2011). Persistent rainfall also occurred in mid-winter 2007, 2011, and mid-summer 2011. Consistent with La Niña conditions, spring/summer 2008/2009 was dry (Fig. 2D).

Although *p*O₂ values were usually undersaturated and *p*CO₂ values were supersaturated (Fig. 3A), these metabolic gases showed intense inter- and intra-annual variability (Fig. 3A and B). The inter-annual coefficient of variation for both gases was 12% for *p*O₂ and 119% for *p*CO₂, with peaks of high *p*CO₂ and low RI co-occurring with peaks in rainfall, especially during the transition periods of autumn/winter (e.g., 2011) or both autumn/winter and spring/summer (e.g., 2010, 2011, and 2012; Fig. 3A and D). Supersaturated *p*O₂ sometimes co-occurred with peaks in *p*CO₂, such as in autumn/winter 2007, with concentrations of dissolved oxygen reaching 12 mg L⁻¹, and at both transitions periods of autumn/winter and spring/summer in 2010, 2011, and 2012, with concentrations near 9 mg L⁻¹ (Fig. 3A, 2D). Significantly higher *p*CO₂ and lower RI values were observed in the autumn/winter period (*p* < 0.05; Fig. 4E and F); values of RI < 0.7 occurred only in autumn/winter (Fig. 4F). Values for *p*O₂ were variable, with no clear intra-annual pattern (Fig. 3A) and no significant difference between autumn/winter (t-test, *p* > 0.05; Fig. 4G). Peaks in CO₂ efflux to

the atmosphere were observed mainly in the transition periods of autumn/winter 2008, 2010, 2011, and 2012, with maximum in July 2011 (Fig. 3D), corresponding to minimum RI values. In comparison, negative CO_2 fluxes around -100 and $-150 \text{ mg C m}^{-2} \text{ d}^{-1}$ were common during spring/summer periods (Fig. 3D).

Significantly lower values of pH occurred in autumn/winter (t-test, $p < 0.05$; Fig. 4H). Higher values of Chl-*a* occurred at the end of summer and lower values in winter

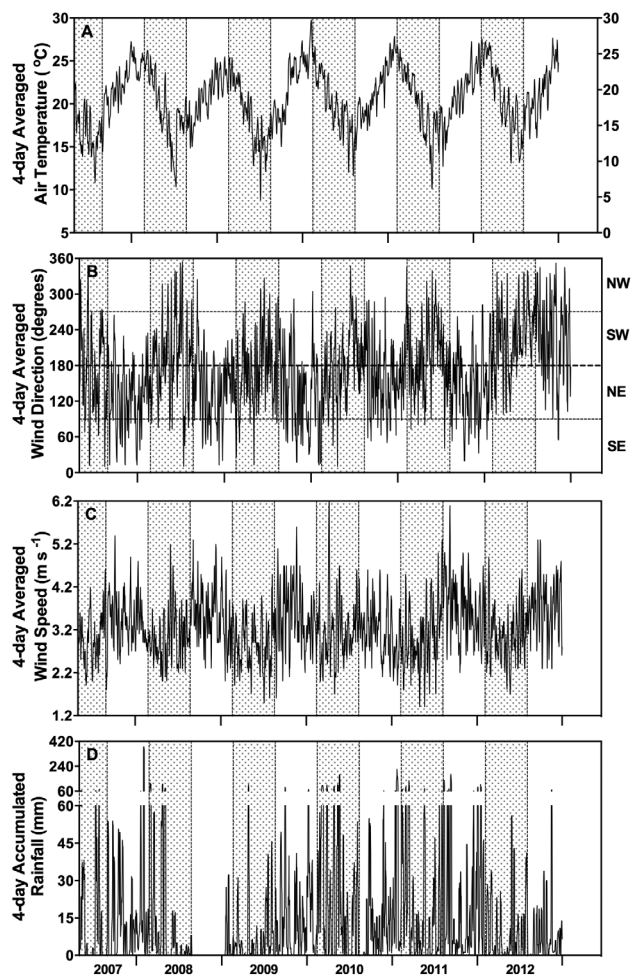


Fig. 2. (A) 4-day averaged fluctuations in air temperature, (B) wind direction, (C) wind speed, and (D) accumulated rainfall measured continuously over 70 months from March 2007 to December 2012 at the meteorological station near Lake Peri (see methods for details on the data source). The dotted frame in all panels indicates the period of decline in temperature during autumn/winter (Mar-Aug). The dashed lines bordering this time period correspond closely to the transition periods in wind direction, when winds shift from easterly ($<180^\circ$) to westerly ($>180^\circ$) or the converse (panel B). Dashed lines in panel B show the limits of 90° , 180° , and 270° for wind direction, where 180° marks the separation between eastern ($<180^\circ$) and western ($>180^\circ$) winds, and NE = $0-90^\circ$; SE = $90-180^\circ$; SW = $180-270^\circ$; and NW = $270-360^\circ$.

(Fig. 3C), although seasonally there were no significant differences (t-test, $p > 0.05$; Fig. 4I). Water temperature and Chl-*a* were positively correlated (Pearson $r = 0.25$; $p < 0.05$). Conductivity values indicated the waters were fresh, despite the lake being adjacent to the Atlantic Ocean. Fluctuations were small, with an increase to $140 \mu\text{S cm}^{-1}$ in late winter 2010 concurrent with increases in both $p\text{CO}_2$ and $p\text{O}_2$ and a pronounced decrease in early summer 2012 (Figs. 3A and B).

Results of multiple regression analysis showed the average daily air temperature variability significantly correlated with $p\text{CO}_2$ variability ($p < 0.05$), whereas

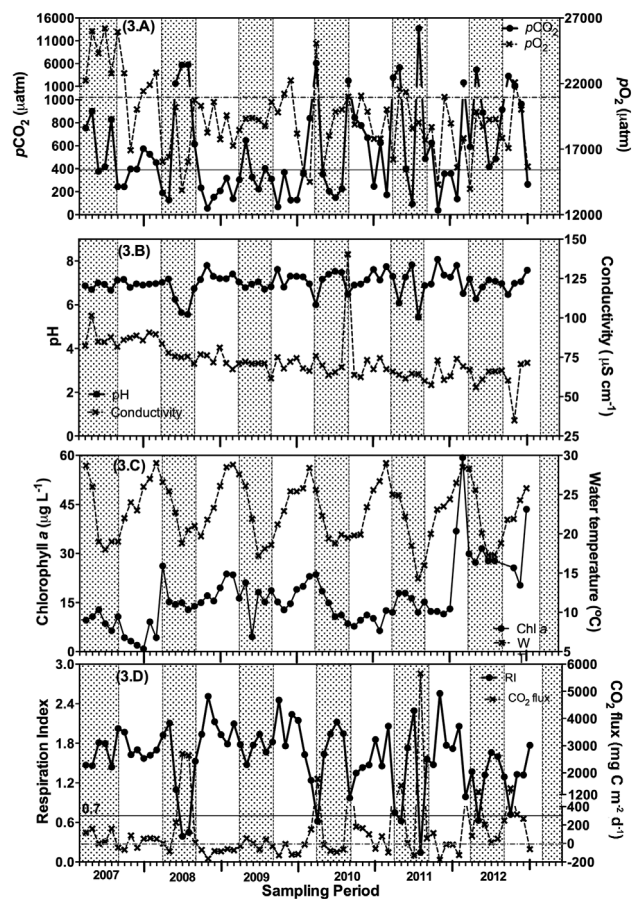


Fig. 3. Monthly fluctuations in (A) $p\text{CO}_2$ and $p\text{O}_2$; (B) pH and conductivity; (C) water temperature and chlorophyll *a*; and (D) respiration index and CO_2 fluxes (in $\text{mg C m}^{-2} \text{ d}^{-1}$). Note break in panel D y-axis to capture high CO_2 fluxes during storm events in surface waters of Lake Peri over 70 months from March 2007 to December 2012. The dotted frames in all panels indicate the decline in temperature during autumn/winter (Mar-Aug). The dash-dot line in (A) represents the $p\text{O}_2$ in atmospheric equilibrium ($20000 \mu\text{atm}$). The solid line in (A) represents the $p\text{CO}_2$ in atmospheric equilibrium (an average value for the 6 years of $390 \mu\text{atm}$, according to Tans and Keeling 2014), and the solid line in (D) shows the critical limit for RI to major aquatic organisms (Brewer and Peltzer 2009).

Table 1. Stepwise (forward) multiple regression model for $\log p\text{CO}_2$ (dependent variable), showing the variables that better explained the model (4-day accumulated rainfall, daily air temperature range, chlorophyll *a*, and $\log p\text{O}_2$). $n = 68$; adjusted $R^2 = 0.12$. Beta = standardized coefficient; B = unstandardized coefficient; t = t-test; p-value = significance level.

	Beta	SE of Beta	B	SE of B	t(63)	p-value
Intercept			-5.871	4.493	-1.307	0.196
Temperature range ($^{\circ}\text{C}$)	0.433	0.129	0.064	0.019	3.352	0.001*
4-day rainfall (mm)	0.238	0.132	0.006	0.003	1.802	0.075
Chlorophyll <i>a</i> ($\mu\text{g/L}$)	0.251	0.133	0.013	0.007	1.890	0.063
$\log p\text{O}_2$	0.229	0.130	1.812	1.027	1.764	0.083

* significant p-value < 0.05

$n = 68$; $R = 0.410$; $R^2 = 0.168$; adjusted $R^2 = 0.115$; $F(4,63) = 3.190$; $p < 0.019$; SE (standard deviation) of estimate: 0.473

Table 2. Stepwise (forward) multiple regression model for $\log p\text{O}_2$ (dependent variable), showing the variables that better explained the model (4-day accumulated rainfall, wind direction, water temperature, and chlorophyll *a*). $n = 68$; adjusted $R^2 = 0.28$. Beta = standardized coefficient; B = unstandardized coefficient; t = t-test; p-value = significance level.

	Beta	SE of Beta	B	SE of B	t(63)	p-level
Intercept			4.420	0.047	94.068	0.000*
Chlorophyll <i>a</i> ($\mu\text{g L}^{-1}$)	-0.302	0.113	-0.002	0.001	-2.663	0.010*
Wind Direction ($^{\circ}$)	-0.312	0.113	0.000	0.000	-2.771	0.007*
4-day rainfall (mm)	-0.208	0.109	-0.001	0.000	-1.907	0.061
Water temperature ($^{\circ}\text{C}$)	-0.168	0.114	-0.003	0.002	-1.472	0.146

* significant p-value < 0.05

$n = 68$; $R = 0.5266$; $R^2 = 0.2773$; adjusted $R^2 = 0.2315$; $F(4,63) = 6.0450$; $p < 0.00035$; SE of estimate: 0.05565

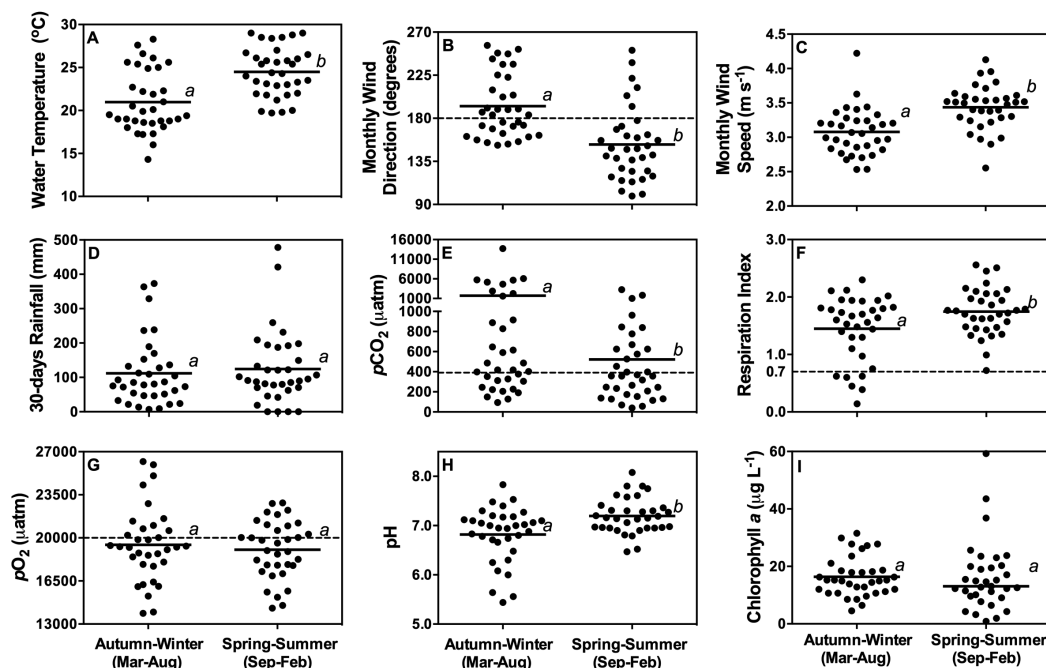


Fig. 4. Comparisons of (A) water temperature, (B) wind direction, (C) wind speed, (D) 30-day precipitation, (E) $p\text{CO}_2$, (F) RI, (G) $p\text{O}_2$, (H) pH, and (I) chlorophyll *a* during autumn/winter and spring/summer months in Lake Peri. Solid lines are the averages, and different letters indicate significant differences between these periods (t-test, $p < 0.05$). Dashed line in panel B shows the limit of 180° for wind direction, where 180° marks the separation between eastern ($<180^{\circ}$) and western ($>180^{\circ}$) winds. In subsequent panels, dashed lines represent $p\text{CO}_2$ and $p\text{O}_2$ in atmospheric equilibrium and the critical limit for RI for major aquatic organisms (Brewer and Peltzer 2009) at (F) $390 \mu\text{atm}$; (G) $20000 \mu\text{atm}$; and (I) 0.7, respectively.

rainfall ($p = 0.07$), Chl-*a* ($p = 0.06$), and $\log p\text{O}_2$ ($p = 0.08$), were not significant (Table 1). Because variability in air temperature was most pronounced and rainfall was often highest in transition periods such as late winter, we inferred that the variability in air temperature reflects synoptic or larger-scale climate variability. Among the variables used in the multiple regression analyses for $p\text{O}_2$, Chl-*a* and wind direction were significant, both with a negative relation to $\log p\text{O}_2$ ($p < 0.05$). Rainfall ($p = 0.061$) and water temperature ($p = 0.146$) were not significant (Table 2).

Discussion

Values of $p\text{O}_2$ and $p\text{CO}_2$ in surface waters of Lake Peri showed large inter- and intra-annual variations. Overall net heterotrophy was revealed by the $p\text{O}_2$ predominantly below and $p\text{CO}_2$ above atmospheric equilibrium in our 6-year study. Inter-annual variability in both O_2 and CO_2 was mainly due to rainfall events, which tended to intensify during the transition between seasons when temperature variability also increased. We observed 2 different patterns with respect to the dissolved gases. In the first, elevated $p\text{O}_2$ and $p\text{CO}_2$ covaried, and in the second, $p\text{CO}_2$ increases were associated with corresponding decreases in $p\text{O}_2$.

Increases in $p\text{O}_2$ co-occurred with $p\text{CO}_2$ increasing above saturation during the transition periods between autumn/winter and spring/summer 2007, 2010, 2011, and 2012. Increased precipitation also tended to occur at those times. In many cases, $p\text{O}_2$ was near saturation, as expected with well-mixed incoming water. Rainfall would have increased lateral transfer of CO_2 (Marotta et al. 2010, Maberly et al. 2013) and caused lateral inputs of coarse particulate organic matter into Cachoeira Grande stream, one of the main streams in the Lake Peri catchment area, and the removal of benthic stocks (Lisboa et al. 2014). Consequently, stormflows are a source of allochthonous organic material into the western area of the lake and a cause of heterotrophy similar to observations in other aquatic ecosystems (Cole et al. 1994, 2000, Duarte and Prairie 2005, Trolle et al. 2012).

Peaks of $p\text{CO}_2$ and $p\text{O}_2$ were inversely related, and RI decreased mid-winter in 2008 and 2011. In general, increased $p\text{CO}_2$ and decreased $p\text{O}_2$ are expected after mixing events in stratified lakes. Lake Peri, however, is weakly stratified in winter with diurnal stratification and nocturnal mixing. Cool water intermittently occurs near the bottom and sometimes rises higher in the water column (Denise Tonetta, UFSC, unpublished data collected between May and end of July 2014). The cool bottom water is indicative of advection, either from cool

incoming stream waters or gravity currents from differential cooling. If the residence time of the incoming water is long enough, it could become enriched in CO_2 produced by sediment respiration (Ferland et al. 2014). The high biomass and abundance of heterotrophic bacterioplankton in Lake Peri in winter (Fontes et al. 2013) reinforces the hypothesis that the CO_2 may be produced within the lake with concomitant O_2 consumption. Thus, CO_2 enrichment in lake surface waters could result either from entrainment due to nocturnal mixing or continued advection, such that the incoming waters filled the basin to the depth of our sampling. The $p\text{CO}_2$ in surface waters was, on average, almost 3-fold higher than atmospheric equilibrium; thus, increased rainfall correlates with high $p\text{CO}_2$, and $p\text{O}_2$ concentrations depend on the pathways and residence time of stream inflows.

Values of $p\text{CO}_2$ are expected to increase in shallow tropical lakes as temperatures rise due to increased respiration rates, particularly in the sediments (Cardoso et al. 2014, Marotta et al. 2014). Levels of $p\text{CO}_2$ in surface waters of Peri Lake, however, did not increase with air temperature but instead depended on variability in daily air temperatures (Table 1). In summer, the day to night differences in air temperatures were less than those observed in winter. The few days with high variability were likely due to cloud cover. Oxygen concentrations increased in summer, and undersaturation of $p\text{CO}_2$ was common. Variability in air temperature was greater in winter and during seasonal transitions. Increased concentrations of CO_2 resulted from either cooling with entrainment of deeper waters or rainfall intermittently bringing CO_2 into surface waters. Thus, we infer that the relation between variability in air temperature and $p\text{CO}_2$ is indicative of seasonal differences in meteorology.

Chl-*a* concentrations increased from winter through the end of summer (Fig. 3C), were independent of rainfall, and covaried with oxygen concentrations (Table 2). The relation with oxygen is weak, in part because the hydrodynamics associated with incoming stormwaters moderate oxygen concentrations and in part because Chl-*a* is not indicative of community structure. Different species have different growth rates that moderate $p\text{CO}_2$ and $p\text{O}_2$. The phytoplankton community in Lake Peri is dominated by cyanobacteria throughout the year (>80% of the phytoplankton community), with *Cylindrospermopsis raciborskii* the most abundant species (82 000 individuals mL^{-1} ; Tonetta et al. 2013). The Chl-*a* concentrations reported in this study are high, and for many lakes, decomposition of phytoplankton that settles to the lower water column would lead to decreased oxygen and increased CO_2 in the hypolimnion. The time series temperature data available indicate Lake Peri is weakly

stratified in summer (Denise Tonetta, UFSC, unpublished data collected between May and end of July 2014). Thus, similar to other shallow tropical waterbodies (Talling and Lemoalle 1998, MacIntyre et al. 2002), the lower water column is likely to vent frequently, preventing accumulation of CO₂ and depletion of oxygen. Thus, despite high chlorophyll concentrations, the relation between Chl-*a* and *p*O₂ is weak due to the multiple factors influencing oxygen concentrations. These complexities indicate whole-lake metabolism studies would be difficult to perform in weakly stratified lakes similar to Lake Peri with high inflows of rainwater.

The variability of weather systems influencing Lake Peri may result from the sub-seasonal shifts of the South American Convergence Zone, which moderates rainfall (Jones and Carvalho 2002, Carvalho et al. 2004), and El Niño Southern Oscillation (ENSO) cycles (Kayano and Sansigolo 2009). Increases in rainfall frequently began when air temperatures were maximal or had just begun their seasonal decrease. In some years, high rainfall events were also recorded in winter, demonstrating high inter-annual variability of precipitation.

La Niña years are characterized by droughts in the South of Brazil, and El Niño years such as 2010 have high rainfall (Kayano and Sansigolo 2009). In typical years the annual accumulated precipitation is ~900 mm, but during El Niño years it is ~2100 mm. Our results showed that spring/summer 2008/2009 was dry and 2010/2011 was rainy. During a dry year, the contributions of lateral transfer of carbon into the lake are smaller. As the 2009 data illustrate, the reduced loading led to undersaturated annual average *p*CO₂ (280 ± 158 μatm). In contrast, in other years, *p*CO₂ was on average supersaturated. Additionally, the annual variation of both gases was smaller in 2009. Measures of *p*CO₂ and *p*O₂ had coefficients of variation of 54% and 6%, respectively. Thus, the variability in rainfall and of both magnitude and variability in *p*CO₂ and *p*O₂ was moderated by the South American Monsoon and ENSO cycles.

Shifts between supersaturation and undersaturation of metabolic gases in Lake Peri waters were comparable with the variations previously reported in long-term and intra-annual (Marotta et al. 2009b, 2010) surveys at low latitudes. The average *p*CO₂ of 1100 μatm calculated for the littoral zone of Lake Peri is similar to the *p*CO₂ previously predicted for temperate lakes but below those of tropical lakes (Marotta et al. 2009a).

The net daily CO₂ flux from the surface waters of Lake Peri to the atmosphere was positive, median (25/75% interquartile range) 11 mg C m⁻² d⁻¹ (-5/160 mg C m⁻² d⁻¹). On average, this flux is small in comparison to those of lakes in the Amazon floodplain (Rudorff et al.

2011). Underestimates could result from our use of a conservative approach to compute fluxes instead of some of the newer equations (Rudorff et al. 2011, Heiskanen et al. 2014, Tedford et al. 2014). Similarly, we assumed our nearshore measurements were representative of the entire lake and could be biased low if we undersampled the high concentrations of CO₂ that were mixed to the surface offshore during cooling events or introduced from the mountain streams in the western basin. Notably, fluxes during events were similar and sometimes exceeded average fluxes in Rudorff et al. (2011; wind-based model); however, when rainy conditions did not prevail, fluxes were considerably lower, and the lake alternated between being a source or a sink for CO₂.

Variability in *p*CO₂ and *p*O₂ and the extent of net heterotrophy are linked to seasonality and rainfall in a subtropical lake, which in turn are moderated by the position of the South American Convergence Zone and phase of ENSO cycles. Thus, we link climate conditions with physical–chemical and metabolic responses. Values of *p*CO₂ undergo large fluctuations, with values intermittently in excess of saturation during seasonal transitions in normal and El Niño years with their higher rainfall. Values below saturation occur during La Niña conditions and at other times when rainfall is lower. Recognition that variability in dissolved oxygen and CO₂ and the flux of CO₂ in Lake Peri are, in part, moderated by larger scale climate drivers indicates that efforts to link variability in concentrations and fluxes of dissolved gases to climate will be fruitful in other locations and will enable more accurate scaling up of greenhouse gas emissions in the context of global change.

Acknowledgements

We thank Danilo Funke (FLORAM/ Lake Peri Municipal Park), Alex Pires De Oliveira Nuñer (LAPAD – UFSC), undergraduate and graduate students from the Laboratório de Aguas Continentais – UFSC, and Ms. Rodrigo Nascimento for making and editing the map of Lake Peri area. We also thank J.M. Melack for critically reading the manuscript, and Dr. Leila Carvalho and Dr. Charles Jones for their valuable comments on the dynamics of the South American Monsoon system and its effects on the subtropics. We also thank the 2 anonymous reviewers for their contributions. Funding was provided by CNPq – Brazil (Conselho Nacional de Desenvolvimento Científico e Tecnológico; Universal Process: 473572/2008-7) to MMP, CAPES Foundation, Ministry of Education of Brazil, process n. 10307-12-5 to MLF, and from the US NSF Division of Environmental Biology grant DEB-0919603 to SM.

References

- Abril G, Martinez J-M, Artigas LF, Moreira-Turcq P, Benedetti MF, Vidal L, Meziane T, Kim J-H, Bernardes MC, Savoye N, et al. 2014. Amazon River carbon dioxide outgassing fuelled by wetlands. *Nature*. 505(7483):395–398.
- Aufdenkampe AK, Mayorga E, Raymond PA, Melack JM, Doney SC, Alin SR, Aalto RE, Yoo K. 2011. Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. *Front Ecol Environ*. 9(1):53–60.
- Brewer PG, Peltzer ET. 2009. Limits to marine life. *Science*. 324(5925):347–348.
- Cardoso SJ, Enrich-Prast A, Pace ML, Roland F. 2014. Do models of organic carbon mineralization extrapolate to warmer tropical sediments? *Limnol Oceanogr-Methods*. 59(1):48–54.
- Carvalho L, Jones C, Liebmann B. 2004. The South Atlantic Convergence Zone: intensity, form, persistence, and relationships with intraseasonal to interannual activity and extreme rainfall. *J Climate*. 17:88–108.
- Carvalho LMV, Jones C, Silva AE, Liebmann B, Dias PLS. 2011. The South American Monsoon System and the 1970s climate transition. *Int J Climatol*. 31:1248–1256.
- Cole JJ, Caraco NF, Kling GW, Kratz TK. 1994. Carbon-dioxide supersaturation in the surface waters of lakes. *Science*. 265(5178):1568–1570.
- Cole JJ, Caraco NF. 1998. Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF_6 . *Limnol Oceanogr*. 43:647–656.
- Cole JJ, Pace ML, Carpenter SR, Kitchell JF. 2000. Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations. *Limnol Oceanogr*. 45(8):1718–1730.
- Cole JJ, Prairie YT, Caraco NF, McDowell WH, Tranvik LJ, Striegl RG, Duarte CM, Kortelainen P, Downing JA, Middelburg JJ, Melack JM. 2007. Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems*. 10(1):171–184.
- Duarte CM, Prairie YT. 2005. Prevalence of heterotrophy and atmospheric CO_2 emissions from aquatic ecosystems. *Ecosystems*. 8:862–870.
- Ferland ME, Prairie YT, Teodoru C, del Giorgio PA. 2014. Linking organic carbon sedimentation, burial efficiency, and long-term accumulation in boreal lakes. *J Geophys Res-Biogeosci*. 119(5):2013JG002345.
- Fontes MLS, Dalpaz L, Tonetta D, Antônio RV, Petrucio M. 2013. Dynamics of planktonic prokaryotes and dissolved carbon in a subtropical coastal lake. *Front Microbiol*. 4:71.
- Garcia HE, Gordon LI. 1992. Oxygen solubility in seawater - better fitting equations. *Limnol Oceanogr*. 37(6):1307–1312.
- Grimm AM. 2003. The El Niño impact on the summer monsoon in Brazil: regional processes versus remote influences. *J Climate*. 16:263–280.
- Gudasz C, Bastviken D, Steger K, Premke K, Sobek S, Tranvik LJ. 2010. Temperature-controlled organic carbon mineralization in lake sediments. *Nature*. 466(7305):478–481.
- Heiskanen JJ, Mammarella I, Haapanala S, Pumpanen J, Vesala T, MacIntyre S, Ojala A. 2014. Effects of cooling and internal wave motions on gas transfer coefficients in a boreal lake. *Tellus B*. 66:22827.
- Hennemann MC, Petrucio MM. 2011. Spatial and temporal dynamic of trophic relevant parameters in a subtropical coastal lagoon in Brazil. *Environ Monit Assess*. 181:347–361.
- Jones C, Carvalho LMV. 2002. Active and break phases in the South American Monsoon System. *J Climate*. 15:905–914.
- Jones C, Carvalho LMV. 2013. Climate change in the South American Monsoon System: present climate and CMIP5 projections. *J Climate*. 26:6660–6678.
- Jonsson A, Meili M, Bergström A-K, Jansson M. 2001. Whole-lake mineralization of allochthonous and autochthonous organic carbon in a large humic lake (Ortrasket, N. Sweden). *Limnol Oceanogr*. 46(7):1691–1700.
- Kayano M, Sansigolo C. 2009. Interannual to decadal variations of precipitation and daily maximum and daily minimum temperatures in southern Brazil. *Theor Appl Climatol*. 97(1–2):81–90.
- Kling GW, Kipphut GW, Miller MC. 1991. Arctic lakes and streams as gas conduits to the atmosphere: implications for tundra carbon budgets. *Science*. 251(4991):298–301.
- Kritzbeg ES, Graneli W, Bjork J, Bronmark C, Hallgren P, Nicolle A, Persson A, Hansson L-A. 2014. Warming and browning of lakes: consequences for pelagic carbon metabolism and sediment delivery. *Freshwater Biol*. 59(2):325–336.
- Leibmann B, Mechoso CR. 2011. The South American Monsoon System. Chapter 9. In: Chang C-P et al., editors. *The global monsoon system: research and forecast*. World Scientific. p. 137–157.
- Lisboa LK, Silva ALL, Siegloch AE, Goncalves JFJ, Petrucio MM. 2014. Temporal dynamics of allochthonous coarse particulate organic matter in a subtropical Atlantic Rainforest Brazilian stream. *Mar Freshw Res*. MF14068.
- Lorenzen CJ. 1967. Determination of chlorophyll and phaeo-pigments – spectrophotometric equations. *Limnol Oceanogr*. 12(2):343–346.
- Maberly SC, Barker PA, Stott AW, De Ville MM. 2013. Catchment productivity controls CO_2 emissions from lakes. *Nature Climate Change*. 3(4):391–394.
- MacIntyre S, Jonsson A, Jansson M, Aberg J, Turney DE, Miller SD. 2010. Buoyancy flux, turbulence, and the gas transfer coefficient in a stratified lake. *Geophys Res Lett*. 37(24):L24604.
- MacIntyre S, Romero JR, Kling GW. 2002. Spatio-temporal variability in surface deepening and lateral advection in an embayment of Lake Victoria, East Africa. *Limnol Oceanogr*. 47:656–671.
- Marotta H, Duarte CM, Sobek S, Enrich-Prast A. 2009a. Large CO_2 disequilibria in tropical lakes. *Global Biogeochem Cy*. 23(4):GB4022.
- Marotta H, Duarte CM, Pinho L, Enrich-Prast A. 2010. Rainfall leads to increased $p\text{CO}_2$ in Brazilian coastal lakes. *Biogeosciences*. 7:1607–1614.
- Marotta H, Fontes ML, Petrucio MM. 2012. Natural events of anoxia and low respiration index in oligotrophic lakes of the Atlantic Tropical Forest. *Biogeosciences*. 9:2879–2887.

- Marotta H, Paiva LT, Petrucio MM. 2009b. Changes in thermal and oxygen stratification pattern coupled to persistence of CO₂ outgassing in shallow lakes of the surroundings of Atlantic Tropical Forest, Brazil. *Limnology*. 10(3):195–202.
- Marotta H, Pinho L, Gudaszc C, Bastviken D, Tranvik LJ, Enrich-Prast A. 2014. Greenhouse gas production in low-latitude lake sediments responds strongly to warming. *Nature Climate Change*. 4:467–470.
- Pace ML, Cole JJ, Carpenter SR, Kitchell JF, Hodgson JR, Van de Bogert MC, Bade DL, Kritzberg ES, Bastviken D. 2004. Whole-lake carbon-13 additions reveal terrestrial support of aquatic food webs. *Nature*. 427:240–243.
- Peeters F, Wuest A, Piepke G, Imboden DM. 1996. Horizontal mixing in lakes. *J Geophys Res*. 101:18361–18375.
- Rantakari M, Kortelainen P. 2005. Interannual variation and climatic regulation of the CO₂ emission from large boreal lakes. *Global Change Biol*. 11(8):1368–1380.
- Richey JE, Melack JM, Aufdenkampe AK, Ballester VM, Hess LL. 2002. Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO₂. *Nature*. 416:617–620.
- Ropelewski CF, Halpert MS. 1987. Global and regional scale precipitation patterns associated with the El Niño/Southern Oscillation. *Monthly Weather Rev*. 115:1606–1626.
- Rudorff CM, Melack JM, MacIntyre S, Barbosa CCF, Novo EMLM. 2011. Seasonal and spatial variability of CO₂ emission from a large floodplain lake in the lower Amazon. *J Geophys Res-Biogeosci*. 116(4):G04007.
- Rueda FR, MacIntyre S. 2009. Flowpaths and spatial heterogeneity of storm-river-water in small multi-basin lakes. *Limnol Oceanogr*. 54:2041–2057.
- Santos GF, Silva JTN, Mendoca M, Veado RW. 1989. Análise Ambiental da Lagoa do Peri. *Geosul*. 8:101–123.
- Silva VBS, Kousky VE. 2012. The South American Monsoon System: climatology and variability. In: Shih-Yu Wang, editor. *Modern climatology*. ISBN: 978-953-51-0095-9, InTech. Available from: <http://www.intechopen.com/books/modern-climatology/the-south-american-monsoon-system-climatology-and-variability>
- Solomon CT, Bruesewitz DA, Richardson DC, Rose KC, Van de Bogert MC, Hanson PC, Kratz TK, Larget B, Adrian R, Babin BL, et al. 2013. Ecosystem respiration: drivers of daily variability and background respiration in lakes around the globe. *Limnol Oceanogr*. 58(3):849–866.
- Strickland J, Parsons T. 1972. *A practical handbook of seawater analysis*, 2nd ed. Ottawa (Canada): Fish Res Board Can. p. 310.
- Stumm W, Morgan JJ. 1996. *Aquatic chemistry: chemical equilibria and rates in natural waters*. New York: Wiley-Interscience.
- Talling JF, Lemoalle J. 1998. *Ecological dynamics of tropical inland waters*. Cambridge (UK): Cambridge University Press.
- Tans P, Keeling R. 2014. NOAA/ESRL, available from: www.esrl.noaa.gov/gmd/ccgg/trends/; and Scripps Institution of Oceanography, available from: scrippsco2.ucsd.edu/
- Tedford EW, MacIntyre S, Miller SD, Czirkowsky MJ. 2014. Similarity scaling of turbulence in a small temperate lake during fall cooling. *J Geophys Res Oceans*. doi:10.1002/2014JC010135
- Tonetta D, Petrucio MM, Laudaes-Silva R. 2013. Temporal variation in phytoplankton community in a freshwater coastal lake of southern Brazil. *Acta Limnol Bras*. 25(1):99–110.
- Tonetta D, Laudaes-Silva R, Petrucio MM. Forthcoming Feb 2015. Planktonic production and respiration in a subtropical lake dominated by cyanobacteria. *Braz J Biol*.
- Trolle D, Staehr PA, Davidson TA, Bjerring R, Lauridsen TL, Søndergaard M, Jeppesen E. 2012. Seasonal dynamics of CO₂ flux across the surface of shallow temperate lakes. *Ecosystems*. 15:336–347.
- Vera C, Higgins W, Amador J, Ambrizzi T, Garreaud R, Gochis D, Gutzler D, Lettenmaier D, Marengo J, Mechoso CR, et al. 2006. Toward a unified view of the American Monsoon Systems. *J Climate*. 19(20):4977–5000.
- Weiss RF. 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar Chem*. 2:203–215.
- Yvon-Durocher G, Jones JI, Trimmer M, Woodward G, Montoya JM. 2010. Warming alters the metabolic balance of ecosystems. *Philos T Roy Soc B*. 365(1549):2117–2126.
- Zar JH. 1999. *Biostatistical analysis*. Upper Saddle River (NJ): Prentice-Hall. p. 664.