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Determining the high variability of *p*CO_2 and *p*O_2 in the littoral zone of a subtropical coastal lake

Determinando a alta variabilidade da *p*CO_2 e *p*O_2 na zona litorânea de uma lagoa costeira subtropical

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Abstract: The aquatic metabolism comprises production and mineralization of organic matter through biological processes, such as primary production and respiration that can be estimated by gases concentration in the water column. **Aim:** The study aimed to assess the temporal variability of *p*CO_2 and *p*O_2 in the littoral zone of a subtropical coastal lake. Our hypotheses are i) high variability in meteorological conditions, such as temperature and light, drive the high variability in *p*CO_2 and *p*O_2, and ii) the lake is permanently heterotrophic due to the low phosphorus concentration. **Methods:** We estimated *p*CO_2 from pH-alkalinity method, and *p*O_2 from dissolved oxygen concentration and water temperature measured in free-water during 24 hours in the autumn, winter, spring and summer. **Results:** Our findings showed that limnological variables had low temporal variability, while the meteorological variables and *p*CO_2 presented a high coefficient of variation, which is representative of each climatic season. In autumn and winter, it was recorded that the lake was supersaturated in CO_2 relative to the atmosphere, while in spring and summer CO_2 concentration was below the concentration found in the atmosphere. Over 24 hours, *p*CO_2 also showed high variability, with autumn presenting higher concentration during the night when compared to daytime. Water temperature and chlorophyll *a* were negatively correlated with *p*CO_2, while *p*O_2 was positively correlated with wind and light. **Conclusion:** Agreeing with our first hypothesis, *p*CO_2 showed an expressive temporal variation in a subtropical lake associated to the high variability in meteorological conditions. On the other hand, our second hypothesis was not confirmed, since Peri Lake exported CO_2 to the atmosphere in some periods and in others, CO_2 was removed from the atmosphere.

Keywords: subtropical, temporal variation, aquatic metabolism, meteorological conditions, seasonality.

Resumo: O metabolismo aquático envolve os processos de produção e mineralização da matéria orgânica através de processos biológicos, tais como produção primária e respiração, que podem ser estimados através da concentração de gases na coluna d'água. **Objetivo:** O objetivo do presente estudo foi determinar a variabilidade temporal da *p*CO_2 e da *p*O_2 na zona litorânea de uma lagoa costeira subtropical, tendo como hipótese que i) a alta variabilidade nas condições meteorológicas, tais como temperatura e luz, direcionam a elevada variabilidade na *p*CO_2 e *p*O_2 e que ii) o ambiente é permanentemente heterotrófico devido à baixa concentração de fósforo. **Métodos:** Nós estimamos a *p*CO_2 através do método pH-alcalinidade, e a *p*O_2 a partir da concentração de oxigênio dissolvido e temperatura da água, medidos em água livre, durante 24 horas, no outono, inverno, primavera e verão. **Resultados:** Nossos resultados mostraram que as variáveis limnológicas amostradas apresentaram baixa variabilidade temporal, porém as variáveis meteorológicas e a *p*CO_2 apresentaram elevado coeficiente de variação, refletindo a variação em cada estação amostrada. No outono e no inverno foi registrado que o ambiente foi supersaturado em CO_2 em relação à atmosfera, enquanto na primavera e no verão a concentração de CO_2 foi abaixo da concentração encontrada na atmosfera. Ao longo de 24 horas, a *p*CO_2 também se apresentou variável, sendo que no outono ocorreu maior *p*CO_2 durante a noite que durante o dia. A *p*CO_2 foi correlacionada negativamente com a temperature da água e a concentração de clorofila *a*, enquanto que a *p*O_2 foi positivamente correlacionada com o vento e a luz. **Conclusão:** De acordo com a nossa primeira hipótese, a pCO_2 apresentou expressiva variação temporal na zona litorânea de um lago costeiro subtropical, juntamente com a alta variabilidade das condições meteorológicas. Entretanto, nossa segunda hipótese não foi confirmada uma vez que em alguns períodos ocorreu um balanço líquido de liberação de CO_2 para a atmosfera, enquanto em outros períodos ocorreu absorção de CO_2 da atmosfera.

Palavras-chave: subtropical, variação temporal, metabolismo aquático, condições meteorológicas, sazonalidade.

1. Introduction

Lakes are recognized for their substantial role in global carbon cycle. They are extremely active sites for transport, transformation and storage of considerable amounts of carbon received from the terrestrial environment (Tranvik et al., 2009). In this way, primary production and respiration are the most important biological processes responsible for production and mineralization of organic matter and involve CO_2 uptake by primary producers, releasing O_2, which is, in turn, used by heterotrophic organisms that release CO_2 (Cole et al., 2000). The net balance between production and mineralization result in an environment considered as a carbon source or sink.

The trophic status is one of the most important variables related to metabolic processes. The majority of the oligotrophic aquatic environments are typically heterotrophic, which means respiration is higher than primary production, making lakes important sources of CO_2 to the atmosphere. On the other hand, when the primary production is higher than respiration, the environment is considered autotrophic, thus CO_2 is removed from atmosphere and carbon can be stored as organic carbon (Cole et al., 1994, 2007). Therefore, changes in nutrient concentrations can influence biological processes and consequently, the ecosystem net balance.

Other variables have been related to extent and magnitude of temporal variability in metabolic processes. Variations in irradiance, temperature, and organic matter affect aquatic organisms and their metabolisms, driving the net ecosystem production and shifting between autotrophic and heterotrophic phases during the course of a day or year (Staehr et al., 2010; Marotta et al., 2010). However, the intensity of these metabolic processes can vary between temperate and tropical/subtropical lakes (Amado et al., 2013), both daily and seasonally, since temperature and light are highly variable in boreal and temperate regions compared to tropical areas (Barbosa, 1997).

The diel variation, especially in temperature and radiation, affect the photosynthetic rates of the community and act indirectly on the regulation of other metabolic processes. Petrucio and Barbosa (2004) demonstrated that bacterioplankton production may vary widely over the course of the day even in tropical lakes. On the other hand, Sadro et al. (2011) reported higher respiration rates occurring at dusk and in the first part of the night, coupled directly to the diel production of organic carbon. Although changes in temporal patterns have been studied for several decades, much less is known about the diel changes in aquatic metabolism (Staehr and Sand-Jensen 2007; Marotta et al., 2012).

Aiming to determine the temporal variability (diel and seasonal) of pCO_2 and pO_2 in the littoral zone of a subtropical coastal lake, and to infer about the aquatic metabolism, we estimated pCO_2, and pO_2 in free-water, during 24 hours in four periods (autumn, winter, spring and summer). Our hypotheses are i) subtropical lakes will show high diel and seasonal variability in pCO_2 and pO_2, and ii) the low phosphorus concentration of the lake drive to a permanently net heterotrophic condition.

2. Material and Methods

2.1. Study site

Peri Lake is a freshwater coastal lake, with a surface area of 5.07 km^2, average and maximum depths of 4.2 m and 11.0 m, respectively, located in the southeast of Santa Catarina Island (27°44’S and 48°31’W), Brazil, into a environmental protected area. Spatial homogeneity of nutrients and chlorophyll *a*, elevated densities of the cyanobacteria *Cylindrospermopsis raciborskii* (Woloszinska) Seenayya and Subba-Raju, and low phosphorus concentration have been observed in the lake (Hennemann and Petrucio 2011; Tonetta et al., 2013). The system has two main tributaries (Cachoeira Grande and Ribeirão Grande Streams) and it is the largest source of drinking water in Santa Catarina Island (Figure 1).

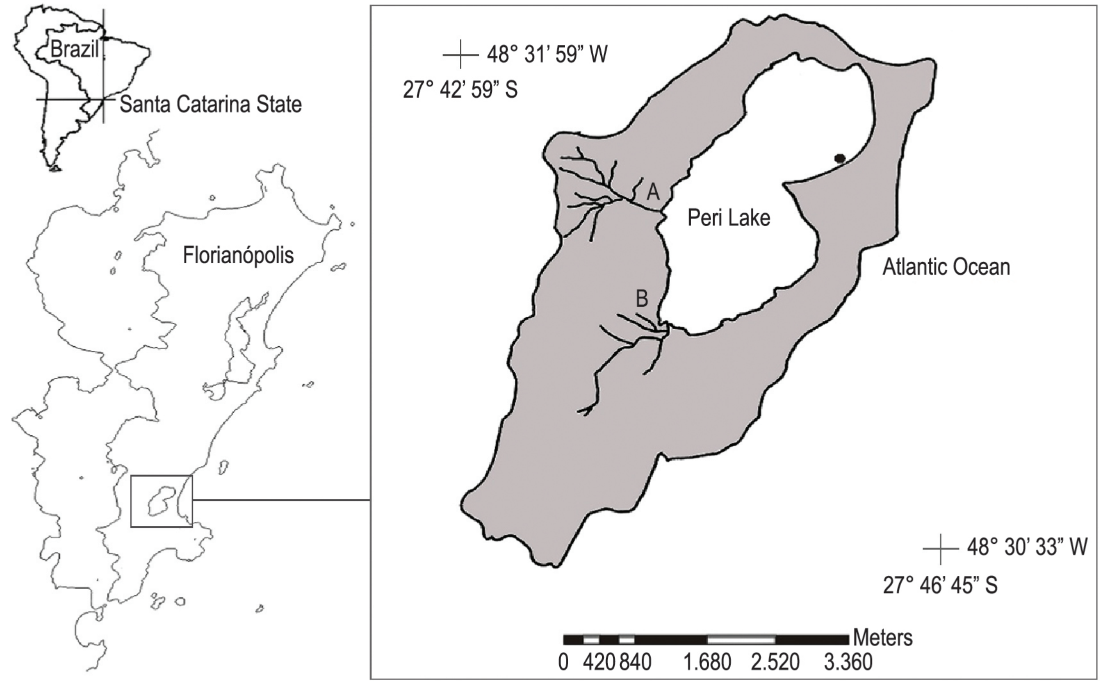

Figure 1. Location of the Peri Lake, in Santa Catarina Island, Brazil, showing the site sampled (littoral black dot). Letter A indicates Cachoeira Grande Stream and letter B indicates Ribeirão Grande Stream. Adapted from Hennemann and Petrucio (2011).

2.2. Environmental variables

All variables were sampled at the following hours of one day cycle: 9:00, 12:00, 15:00, 18:00, 24:00, 6:00 and 9:00 h in four different periods of the year: autumn (May 23, 2010), winter (August 1, 2010), spring (September 30, 2010) and summer (January 13, 2011). Since the lake has spatial homogeneity concerning nutrients and chlorophyll *a*, water samples were taken in the subsurface of the littoral zone in the northeast portion of Peri Lake for determination of water temperature and dissolved oxygen with a multiparameter probe (YSI-85). pH was determined using a Digimed pH meter (DM-22) and alkalinity determined by Gran's titration, immediately after sampling. For chlorophyll *a* analysis, 500 mL of water was filtered (0.7 µm, Millipore AP40 glass fibre) and kept frozen at –20°C, followed by extraction using 90% acetone (Lorenzen, 1967). The light – photosynthetically active radiation (PAR) was measured at the subsurface in the water column using a radiometer (Li-cor 250A) with a spherical sensor, and wind speed was estimated using an anemometer (Instrutherm TAD 500). Precipitation records were obtained from the Santa Catarina Environmental Resources and Hydrometeorology Information Centre (EPAGRI/CIRAM). The complete values of nutrient concentration can be accessed in Tonetta et al. (2013).

2.3. pCO_2 and pO_2

CO_2 concentrations were estimated in subsurface waters, determined from pH and alkalinity measurements (Stumm and Morgan, 1996) with correction for temperature, altitude, and ionic strength (Cole et al., 1994). pCO_2 and pO_2 were determined from the Henry's law with appropriated adjustments for temperature and salinity for CO_2 (Weiss, 1974) and O_2 solubility (Garcia and Gordon, 1992). CO_2 saturation was calculated considering the equilibrium with atmosphere of 393 µatm in May/2010, 388 µatm in August/2010, 387 µatm in September/2010 and 391 µatm in January/2011 (Data from Mauna Loa Observatory at http://www.esrl.noaa.gov/gmd/ccgg/trends/; Tans (2013)). O_2 saturation was considered in equilibrium with the atmosphere at 22,000 µatm.

2.4. Statistical analysis

The coefficient of variation was calculated for all variables to estimate the variability along the day and among periods. This coefficient gives a relative measure of variability and is not sensitive to extreme values (Melack, 1979). Pearson correlation coefficients were used to identify significant correlations between pCO_2 and pO_2 and environmental variables. Variables were log (x+1) transformed and analysis was conducted in the software Statistica 7 (StatSoft®).

3. Results

3.1. Environmental variables

Water temperature was higher in summer and lower in winter, whereas dissolved oxygen showed an opposite pattern (Figure 2c, e). Summer also recorded the highest values of PAR at the water subsurface, whereas in autumn and winter they were similar (Figure 2a). Chlorophyll *a* was higher in spring and summer (Figure 2f) and the pH was also higher in spring and summer (Figure 2d). Mean wind speed in the 24h period was higher in winter, reaching 11 m s^{-1} (Figure 2b), while mean precipitation, for seven days previously each period sampled, ranged from 0.1 mm day^{-1} in the winter to 16.8 mm day^{-1} in the autumn, with 9.5 mm day^{-1} and 3.0 mm day^{-1} in spring and summer, respectively. Meteorological variables, e.g. wind and PAR showed high variability, 39 and 52%, respectively; while limnological variables in Figure 2 showed variability lower than 10%.

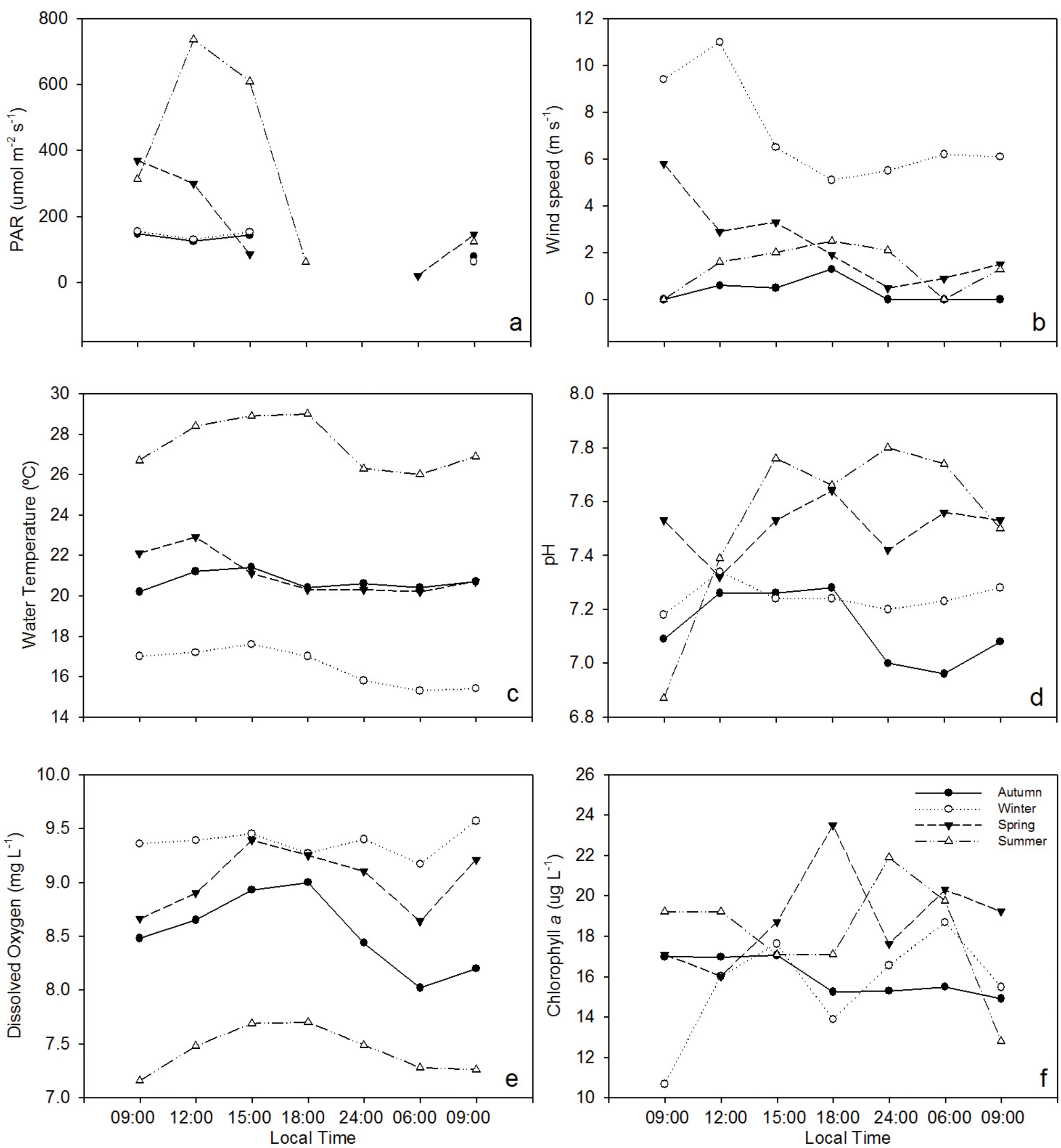

Figure 2. Diel and seasonal variation in environmental conditions in Peri Lake during the sampled period in autumn (May 23, 2010), winter (August 1, 2010), spring (September 30, 2010) and summer (January 13, 2011).

3.2. *p*CO_2 and *p*O_2

Figure 3 shows the diel and seasonal variability of *p*CO_2 and *p*O_2. Along the 24 hours, *p*O_2 showed a similar pattern in all periods sampled, with a maximum *p*O_2 at 15:00 h (in summer the *p*O_2 increased until 18:00 h, Figure 3b). For *p*CO_2 no clear pattern was observed, and high variability was recorded (29%), with some periods of *p*CO_2 decrease during the day and increase during the night (Figure 3a). The variation in both gases showed that, in general, *p*CO_2 is undersaturated in spring and summer, suggesting a CO_2 uptake from the atmosphere, while in autumn and winter, *p*CO_2 values suggest a release from the lake to the atmosphere. On the other hand, *p*O_2 was always below saturation level and showed low variability (3%).

In autumn and some periods of summer, we observed an inverse relationship between *p*CO_2 and *p*O_2, as expected, since the biological production of a gas requires the consumption of another. In other periods, this relationship was not clear. In general, *p*CO_2 and *p*O_2 maintained a negative relationship, although it was not statistically significant ($r = -0.36$, $p > 0.05$; Table 1). The strong correlation between *p*O_2 and DO is because this variable was used to calculate the O_2 partial pressure; the same is valid to pH relative to *p*CO_2. Water temperature and chlorophyll *a* were also negatively correlated with *p*CO_2, while *p*O_2 was positively correlated with wind and PAR (Table 1).

4. Discussion

Our data was recorded in only four days along 2010-2011, but it was possible to observe important environmental variations, especially meteorological ones (e.g. wind, PAR and precipitation), and their influence in the metabolism of a subtropical environment. Even though the limnological variables seem not to be directly influenced by wind and PAR, due to the low variability recorded, *p*CO_2 showed a high variability, in accordance with the variability of biological process. Thus, we confirmed our first hypothesis, since high variability of *p*CO_2 over the course of both the day and the year was recorded.

The variation observed in *p*O_2 along 24 hours was similar in all periods sampled, increasing along the morning showing maximum values in mid-afternoon, and decreasing at night. This

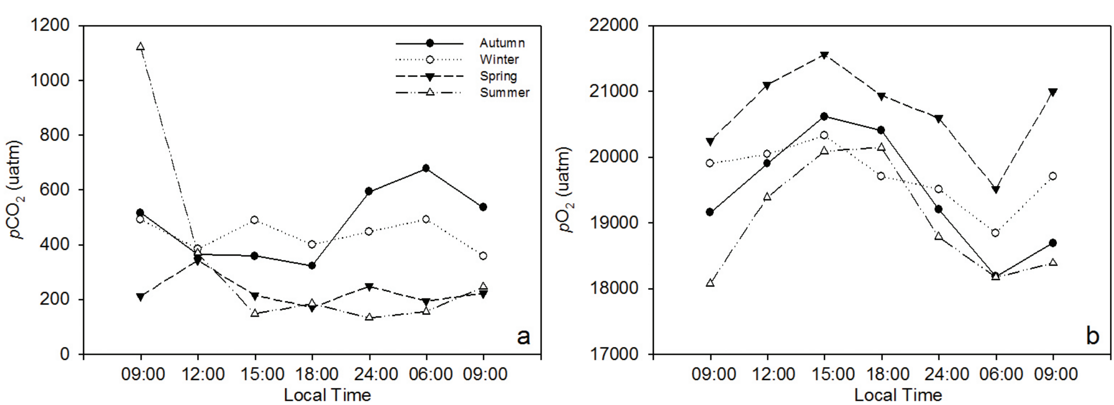

Figure 3. Diel and seasonal variation in *p*CO_2 (a) and *p*O_2 (b) in Peri Lake during the sampled period in autumn (May 23, 2010), winter (August 1, 2010), spring (September 30, 2010) and summer (January 13, 2011).

Table 1. Spearman correlation of selected variables in Peri Lake along the period sampled. N= 28. Values with an asterisk are significant at p<0.05.

	pCO_2	*p*O_2	WT	pH	DO	Chla	Wind	PAR
pCO_2	1.00							
pO_2	–0.36	1.00						
WT	–0.39*	–0.18	1.00					
pH	–0.98*	0.31	0.43*	1.00				
DO	0.12	0.66*	–0.86*	–0.17	1.00			
Chla	–0.40*	0.09	0.28	0.44*	–0.16	1.00		
Wind	–0.12	0.40*	–0.48*	0.20	0.56*	–0.22	1.00	
PAR	0.07	0.22	0.31	0.00	–0.12	–0.16	0.13	1.00

WT: water temperature; DO: dissolved oxygen; Chla: chlorophyll *a*.

diel variation follows the variation in water temperature, pH and PAR availability, and these variables are associated with photosynthesis (Boehrer and Schultze, 2008; Kosten et al., 2010). Even tough photosynthesis varies along the day, the heterotrophic bacterioplankton also changes in a diel cycle (Fontes et al., 2013), related to environmental condition, thus influencing the variability of the pCO_2, as observed and recorded in tropical lakes (Marotta et al., 2012).

Opposite to pO_2, the pCO_2 had no clear diel pattern, even though we found a negative correlation between water temperature, chlorophyll *a* and pCO_2. Although biological activity is important on regulating CO_2 and O_2 gases, physical forces, such as solar radiation, heat loss and wind, will also influence the turbulence of the water column and depth of the surface mixed layer, which will act over the gas exchanges in the lake-air interface (Read et al., 2012). Since the correlation between pCO_2 and pO_2 was weak, other processes may be contributing to CO_2 and O_2 saturation in the water column, such as organic matter photooxidation, intrusion of supersaturated groundwater, and wind action (Kling et al., 2001).

We are aware that lakes generally present differences between pelagic and littoral zones, and that shallow areas are more influenced by benthic processes than pelagic zones (Staehr et al., 2012; They et al., 2013). However, our aim here was the temporal variability specifically in the littoral zone, since no spatial variation of pCO_2 and pO_2 in nutrients and chlorophyll *a* was recorded in Peri Lake (Hennemann and Petrucio, 2011).

The known characteristics of the Peri Lake, such as low phosphorus concentration, Cyanobacteria dominance, nutrient and light limitation (Tonetta et al., 2013) suggest a persistent heterotrophic condition (Cole et al., 1994). However, the high water temperature and PAR in summer favored autotrophic instead of heterotrophic activities, increasing pH and resulting in lower pCO_2 in the water compared to the atmosphere. The autumn and winter may be considered as having high heterotrophic biological activity, since pH was low and higher pCO_2 in the water than in the atmosphere was recorded. Thus, our second hypothesis was not confirmed, since there were shifts between autotrophic and heterotrophic periods. This high variability in pCO_2 is similar to the one observed in tropical lakes (Marotta et al., 2009).

Besides PAR and wind were positively correlated with pO_2, precipitation also influenced the biological processes, increasing pCO_2. The highest precipitation was recorded in autumn, what promoted organic matter inputs and decreased water transparency, consequently lowering photosynthesis and resulting in high heterotrophic activity and the highest pCO_2 in this period. Precipitation is a common variable leading the aquatic metabolism to net heterotrophy (Lennon, 2004), even in tropical lakes (Marotta et al., 2010).

Transitions between autotrophy and heterotrophy are mostly known to be controlled by changes in limnological variables, especially phosphorus, dissolved organic carbon, light attenuation, and by living organisms inhabiting the system (Loebl et al., 2007; Hagerthey et al., 2010; Montero et al., 2011). Even though tropical lakes have been pointed out to act as important CO_2 sources to the atmosphere (Marotta et al., 2009), our findings demonstrate the importance of meteorological variables driving limnological conditions. Consequently, shifts in aquatic metabolism along the year are found, as has been recorded in other subtropical (Carmouze et al., 1991; Thomaz et al., 2001) and temperate lakes (Staehr et al., 2010).

Whether the entire lake ecosystem is net autotrophic or heterotrophic on a yearly basis remains unclear, and sampling in short-term can improve our understanding about carbon cycling in this environment. However, this high variability illustrates that subtropical lakes can be very dynamic concerning the carbon cycle, where in some periods, Peri Lake is a source of CO_2 to the atmosphere, while in others; it stores the CO_2 as organic carbon. Thus, in Peri Lake the meteorological conditions were strongly responsible for changes in pCO_2 and pO_2, through their influence on terrestrial inputs of nutrients and carbon into aquatic ecosystems and light availability.

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