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Rainfall leads to increased *p*CO_2 in Brazilian Coastal Lakes

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Abstract

The variation of surface partial pressure of CO_2 (pCO_2), pH, salinity and dissolved organic carbon (DOC) in 12 coastal Brazilian lakes was examined following periods of contrasting rainfall. It was tested the hypothesis of a positive relationship of rainfall and the associated transport of terrestrial carbon with pCO_2 in tropical lakes. High rainfall was followed by a large, almost 10 fold increase in pCO_2 and a one unit decrease in pH in the lakes, whereas no consistent changes in DOC were observed. CO_2 emissions to the atmosphere from the Brazilian coastal lakes studied here were enhanced, on average, almost 10 fold, from $28.5\pm6.0\,\mathrm{mmol\,m^{-2}\,d^{-1}}$ in drier periods to $245.3.1\pm51.5\,\mathrm{mmol\,m^{-2}\,d^{-1}}$ following heavy rain. Hence, precipitation and subsequent ventilation of groundwater CO_2 in lakes might provide an important conduit to deliver CO_2 resulting from soil respiration to the atmosphere.

1 Introduction

Although they occupy a small fraction of the landscape (2 to 4%, Downing et al., 2006), inland aquatic ecosystems can affect regional carbon balances, as their net carbon fluxes tend to be much greater per unit area than across the surrounding land (Cole et al., 2007). The disproportionate role of lakes in the carbon balance of landscapes derives from their role as recipients of a substantial fraction of the carbon produced within the watershed (Lennon, 2004; Sobek et al., 2005), and transported to lakes through surface runoff and groundwater flow, which are intensified following rainfall events (Schindler, 1978).

Terrestrial organic carbon, though relatively refractory (Hopkinson et al., 1998), plays an important role in lakes, where it partially supports aquatic food webs (Pace et al., 2004), metabolism (Cole et al., 2000) and contribute to the prevalent carbon dioxide (CO_2) supersaturation of lake waters (Sobek et al., 2005). Allochthonous inputs of CO_2 can also contribute to maintain the high partial pressure of carbon dioxide (pCO_2)

above equilibrium with the atmosphere in aquatic ecosystems (Raymond and Cole, 2003). CO_2 enrichments in lake waters may follow closely the precipitation pattern (Rantakari and Kortelainen, 2005), possibly reflecting the corresponding inputs of surface and groundwater waters containing high concentrations of terrestrial organic and inorganic carbon (cf. review in Cole et al., 2007).

Tropical coastal lakes in Brazil are typically small, shallow, and broadly distributed in watersheds with important components of Restinga, the terrestrial vegetation from Atlantic Tropical Forest that colonizes extensive areas of sand plain along the shoreline. This vegetation is a major source of carbon to these lakes, which are often highly colored (Amado et al., 2007). Recent analyses have shown Brazilian lakes to be highly supersaturated in CO_2 (Marotta et al., 2009), supported by high inputs of terrestrial-derived carbon to these lakes. Groundwater plays an important role in the water budget and inputs of materials to Brazilian coastal lakes, a role that can be intensified by high rainfall, due to low water retention by the sandy soils in their watershed (Farjalla et al., 2002). Indeed, $p\mathrm{CO}_2$ in Brazilian coastal lakes have been shown to vary greatly and synchronously over time (Marotta et al., 2009), suggesting weather-control of this property. However, the role of rainfall in accounting for variability in CO_2 in these ecosystems has not yet been tested.

We examined here the variation of surface $p\mathrm{CO}_2$, pH, salinity and DOC in a series of coastal Brazilian lakes to test the hypothesis of a positive relationship of rainfall, and the associated transport of terrestrial carbon, with $p\mathrm{CO}_2$ in tropical lakes.

2 Material and methods

2.1 Study area

This region is characterized by warm temperatures, ranging from a minimum monthly average temperature of 20.7 °C in July to a maximum of 26.2 °C in February (INMET, 1992). The mean minimum and maximum rainfall are typically observed in August

(38 mm) and December (182 mm; INMET, 1992), with high inter-annual variation (Carmouze et al., 1991).

The 12 studied lakes (Fig. 1) are situated in the National Park of Restinga de Jurubatiba, one of the most important protected areas for coastal lakes of Brazil. This conservation area shows many small lakes separated from the sea by a sandbar along the shoreline, which is open only by episodic events, like high rainfall resulting in increased lake depth, extreme sea action or human-induced interventions.

The studied lakes are small (area below 5 km^2; Table 1), shallow (maximum depth varying from 0.8 to 4.0 m), affected by saltwater intrusions resulting in brackish-saline waters (salinity range from 2 to 33), and relatively close among them (along 40 km of shoreline between 22°00′ and 22°23′ S and 41°15′ and 41°45′ W; Fig. 1). Most part of lakes of this region is not fed by surface freshwater inputs. Rainfall is an important dynamic controlling depth mainly by groundwater inputs, which contribute to become lake waters often terrestrial DOC-enriched and dark (Suzuki et al., 1998). These lakes show important terrestrial acidic organic inputs from highly CO_2 supersaturated groundwaters (18.154%; Suzuki et al., 1998).

2.2 Study design

The general sampling strategy involved a combination of sampling events of serial measurements along 24 h cycles to characterise daily variability in pCO_2 between 2003 and 2006 at periods preceded by contrasting weekly-accumulated rainfall. In Carapebus Lake, the sampling effort was more intense, with pCO_2, pH, salinity and temperature analyzed 9 times in two consecutive daily cycles (06:00 p.m., 06:00 a.m., 10:00 a.m., 02:00 p.m., 06:00 p.m. the following day) and only once for DOC concentrations in each sampling events ($N=6$ samplings events between 2003 and 2004). Two sampling stations, characterized by a similar oligo-mesotrophic status during this period (about 0.8 $\mu mol\,L^{-1}$ of total phosphorus and 5 $\mu g\,L^{-1}$ of chlorophyll-*a* concentrations), were analyzed in this lake. A station colonized by submerged aquatic plants (macrophyte covered), mainly *Potamogetum stenostachys* with a standing crop of 1430±200 $g\,m^{-2}$;

mean±SE ($N = 21$ quadrats between 2004 January and July), and a station devoid of macrophytes (open waters). Moreover, 11 additional coastal lakes were sampled in the National Park of Restinga de Jurubatiba. These lakes also show similar trophic status between oligo and mesotrophic (total phosphorus below 1.1 μmol L^{-1}, Table 1). In these lakes, pCO$_2$, pH, salinity and temperature were simultaneously analyzed 4 times in one daily cycle (06:00 p.m., 06:00 a.m., 12:00 a.m. and 06:00 p.m. the following day) and only once per daily cycle for DOC concentrations, in each of two sampling events, both in 2006.

2.3 Analytical methods and pCO$_2$ calculations

Surface water samples were immediately analyzed for pH and alkalinity. Temperature and salinity were measured in situ with a calibrated Thermosalinometer YSI-30. At the laboratory, pre-filtered (0.7 μm, Whatman GF/F) water samples were acidified to pH<2.0 and analyzed for DOC concentrations using high-temperature catalytic oxidation on a Shimadzu TOC-5000 Analyzer. CO$_2$ concentrations and dissolved inorganic carbon concentrations (DIC) were calculated from pH and alkalinity (Gran titration) measurements after correction for temperature, altitude and ionic strength as Cole et al. (1994). pCO$_2$ was calculated from Henry's law, considering the division between CO$_2$ concentration and Henry's constant for this gas at a given temperature and salinity (Weiss, 1974).

Data on rainfall was obtained from Brazilian Aerospace Technical Center (CTA, São José dos Campos). Rainfall data were aggregated as the cumulative rainfall in the week preceding each sampling event, encompassing the time scale for time lags between rainfall events and hydrological inputs. The weekly time scale is also more fitted with changes in lake metabolism (Staehr and Sand-Jensen, 2007).

Log-transformed data showed significant Gaussian distribution (Kolmogorov-Smirnov, $p < 0.05$), homogeneity of variances (Bartlett, $p > 0.05$) and significant pairing (F test, $p < 0.05$). Hence, sampling events were compared using paired parametric tests with a significance of $p < 0.05$ (Zar, 1996). We used paired t-test to compare two data sets or repeated measures one-way ANOVA followed by Tukey-Kramer test for multiple comparisons. All statistics were calculated using the software Graphpad Prism 4.0. Daily means of $p\mathrm{CO}_2$ were calculated in each sampling event and lake ($N = 2$ in Carapebus Lake and $N = 1$ in other lakes).

3 Results

There was considerable daily variability in $p\mathrm{CO}_2$ and pH (coefficient of variation=68 and 42%, respectively), which was almost as large as variation across lakes for sampling events with contrasting weekly-accumulated precipitation (coefficient of variation=75 and 72%, respectively). However, the daily range between minimum and maximum in $p\mathrm{CO}_2$ and pH were much larger, increasing from 3.5 to 50 fold and from 0.5 to 8 fold, respectively, following rainy periods in all studied lakes, except in Carapebus lakes where the daily range in pH was similar. The mean increase in maximum daily values of $p\mathrm{CO}_2$ was about 6 fold (paired t-test, $p < 0.0001$) following higher weekly-accumulated precipitation, an enrichment consistently higher than shown by minimum daily values of $p\mathrm{CO}_2$ (about 85%; $p < 0.05$, paired t-test).

The increase in weekly-accumulated rainfall at Carapebus Lake (Fig. 2) was coupled to great $p\mathrm{CO}_2$ enrichments (about 11 fold in the macrophyte covered station and 4 fold in the open water station), two-fold higher DOC concentrations, decrease of 50% in salinity and a reduction in pH by 1.0 unit (Tukey-Kramer and paired t-test, $p < 0.05$; Fig. 2 and Table 2). Indeed, there were strong positive relationships of lake $p\mathrm{CO}_2$ and DOC with respect to weekly-accumulated rainfall, which was negatively correlated with pH and salinity, in both Carapebus Lake stations (linear regression, $p < 0.05$; Fig. 3). Higher rainfall also homogenised $p\mathrm{CO}_2$ within Carapebus lake, as the high intra-ecosystem heterogeneity for $p\mathrm{CO}_2$ ($p\mathrm{CO}_2$ about 4 times higher in the open water compared to the station with submerged macrophytes) was reduced to a non-significant difference following intense rain.

A pattern toward strong increase in pCO_2 and decrease in pH with increasing rainfall was also evident considering all remaining lakes sampled, with pCO_2 increasing by 300 to 1500% and pH decreasing from 0.1 to 1.1 unities under rainier conditions (Table 2). Lake pCO_2 and pH showed significant relation within, and combining, both sampling events (linear regression, $p < 0.05$; Fig. 4). In contrast, changes in DOC concentrations comparing rainier and drier sampling events did not follow the same trend among lakes simultaneously sampled (Table 2). Even relationships between pCO_2 and DOC within each, and combining both, sampling events for these lakes were not significant (linear regression, $p > 0.05$; Fig. 4).

Salinity fluctuations between both sampling events were also non synchronic in these lakes, probably by hydrological differences in the balance between sea water inflow and terrestrial freshwater inputs. Salinity was not a significant predictor for pCO_2 among these lakes (linear regression, $p > 0.05$; Fig. 4). Despite this uncoupling between rainfall and salinity among lakes, ones with higher decline in salinity (like Peri-peri1 and Robalo) showed higher pCO_2 enrichments in the rainier with respect to drier period (Table 2). Indeed, pCO_2 changes observed between both drier and rainier sampling events in the 11 lakes sampled simultaneously showed a significant relationship with variations in salinity and pH (positive and negative, respectively), but not with fluctuations in DOC (Table 2 and Fig. 5, linear regression, significant $p < 0.05$).

4 Discussion

Most of the lakes examined had waters supersaturated in CO_2, acting therefore as sources to the atmosphere in all sampling fields, suggesting high allochthonous carbon inputs to these aquatic ecosystems. Only two lakes showed daily mean pCO_2 below atmospheric equilibrium (about 380 μatm). The lowest values of pCO_2 were observed in the station colonized by submerged macrophytes in Carapebus Lake, confirming the role of submerged vegetation as CO_2 sinks in natural waters (Krause-Jensen and Sand-Jensen, 1998).

Increased weekly-accumulated precipitation prompted large changes in pCO_2 and a broad amplitude of daily cycles. The strong increase in mean and maximum values much higher than in minimum ones caused diel variations greatly increased under higher weekly rainfall. This result confirmed not only the coupling between intense rainfall delivered CO_2 to the lakes, as reported elsewhere (Rantakari and Kortelainen, 2005), but also the intense metabolism of tropical inland waters (Richey et al., 2002), responsible for the amplitude of diel CO_2 changes in lakes (Staehr and Sand-Jensen, 2007).

The positive relationship of pCO_2 with DOC, and negative with pH and salinity, following higher weekly accumulated rainfall in both Carapebus Lake stations confirmed the well recognized role of terrestrial freshwater inputs in subsiding net heterotrophy in lake waters (Cole et al., 1994, 2007). In the study region, pCO_2 values in groundwaters can reach up to 70 000 μatm or about 180 times higher than the equilibrium with the atmosphere (Suzuki et al., 1998). Groundwater inputs have been shown to be important drivers of changes in coastal tropical lakes elsewhere (Herrera-Silveira, 1996), and are a major source of humic organic acids (Farjalla et al., 2002) and CO_2 (Suzuki et al., 1998) into studied lakes. Both humic acids and CO_2 contribute to acidification natural waters (Jones and Mulholland, 1998), and might further also explain the general reduction in pH with increasing rainfall observed in lakes here.

In line with results in Carapebus Lake, large pCO_2 enrichments were also coupled to decreases in pH and salinity between drier and rainier sampling events in the 11 lakes simultaneously sampled. In contrast, the lack of significant relationships between variation rates in pCO_2 and DOC in these lakes indicated that strong pCO_2 enrichments with increasing rainfall may not be always accompanied by an increase in DOC. The significant relationship between lake DOC and pCO_2 observed in many regions around the world and at global scale (cf. review in Sobek et al., 2005) was also not confirmed in lakes simultaneously sampled here, even with the absence of marked differences of trophic status contributing to differences in DOC from primary producers among them. This suggests that pCO_2 enhancements following rainfall was not driven by increased inputs, and subsequent respiration, of DOC from the watershed, a common driver of net heterotrophy in coastal waters (Ram et al., 2003) and lake CO_2 supersaturation elsewhere (Sobek et al., 2005).

Therefore, the results presented demonstrate a large role for rainfall, and subsequent groundwater inputs, in generating variability in $p\mathrm{CO}_2$ in the Brazilian coastal lakes studied, with a large increase in $p\mathrm{CO}_2$, and a decline in pH, following higher rainfall. Whereas groundwater contributes relatively small amounts of CO_2 to the atmosphere directly (Cole et al., 2007), the ventilation of the high CO_2 concentrations in groundwater when entering lakes may support intense fluxes. We also calculated the CO_2 emissions to the atmosphere from these lakes, using diffusion calculations as Cole and Caraco (1998), the $p\mathrm{CO}_2$ value in equilibrium with the atmosphere of 380 μatm and the mean global wind velocity reported over land of 3.28 $\mathrm{m\,s^{-1}}$ (Archer and Jacobson, 2005). Air-water CO_2 emissions from Brazilian coastal lakes studied here were enhanced, on average, almost 10 fold, from an average (±SE) of 28.5±6.0 $\mathrm{mmol\,C\,m^{-2}\,d^{-1}}$ in drier periods to 245.3±51.5 $\mathrm{mmol\,C\,m^{-2}\,d^{-1}}$ following heavy rain. Hence, it suggests that precipitation and subsequent ventilation of groundwater CO_2 at the lake-atmosphere interface may provide a conduit to deliver CO_2 resulting from soil respiration to the atmosphere.

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Table 1. General characteristics of the studied lakes.

Lakes	Total P* (μmol L^{-1})	Coloration* (at 430 nm)	Area (km^2)
Garças	0.4–0.5	0.026–0.089	0.42
Peri-peri 1	0.7–0.9	0.036–0.040	0.14
Peri-peri 2	0.8–1.0	0.080–0.138	0.83
Maria Menina	0.5–0.7	0.019–0.089	0.24
Robalo	0.4–0.6	0.014–0.026	0.85
Preta	0.2–0.7	0.217–0.307	2.19
Pires	0.4–1.0	0.071–0.075	0.92
Catingosa	0.5–0.7	0.013–0.049	0.09
Visgueiro	0.3–1.0	0.021–0.037	1.18
Casa Velha	0.2–0.5	0.044–0.068	0.54
Barrinha	0.8–1.1	0.049–0.087	0.24
Carapebus	0.6–1.1	0.009–0.028	4.33

* Range considering the sampling events in each lake.

Table 2. Daily-Integrated values of $p\text{CO}_2$, DOC, pH and salinity in higher and lower weekly-accumulated precipitation events for each studied lake.

Lakes	7-days precipitation (mm)	$p\text{CO}_2$ (μatm)	DOC (mg L^{-1})	pH	Salinity (US)
Garças	*1.2*	871	17.7	8.4	33.2
	38.7	4419	23.0	7.8	32.2
	Variation Rate*	*5.07*	*1.30*	*−0.6*	*0.97*
Peri-peri 1	*1.2*	552	18.8	8.5	25.7
	38.7	8389	34.8	7.4	12.9
	Variation Rate*	*15.20*	*1.30*	*−1.1*	*0.50*
Peri-peri 2	*1.2*	1927	38.0	7.8	10.6
	38.7	6644	43.8	7.7	14.0
	Variation Rate*	*3.45*	*1.15*	*−0.1*	*1.32*
Maria Menina	**1.2**	1889	35.9	8.0	18.1
	38.7	6387	42.7	7.7	15.8
	Variation Rate*	*3.38*	*1.19*	*0.3*	*0.87*
Robalo	*1.2*	1611	43.0	8.3	25.8
	38.7	13 736	38.3	7.6	20.0
	Variation Rate*	*8.53*	*0.89*	*−0.7*	*0.77*
Preta	*1.2*	2115	39.0	7.6	3.3
	38.7	5950	42.0	7.3	4.5
	Variation Rate*	*2.81*	*1.08*	*−0.3*	*1.36*
Pires	*1.2*	1564	35.5	8.0	7.0
	38.7	5505	34.5	7.5	3.5
	Variation Rate*	*3.52*	*0.97*	*−0.5*	*0.50*
Catingosa	*1.2*	3446	Nc	7.8	20.6
	38.7	20 037	40.1	7.1	20.5
	Variation Rate*	*5.81*	–	*−0.7*	*0.99*
Visgueiro	*1.2*	2643	37.6	8.0	21.8
	38.7	16 672	37.8	7.2	22.1
	Variation Rate*	*6.31*	*1.01*	*−0.8*	*1.01*

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Table 2. Continued.

Lakes	7-days precipitation (mm)	pCO_2 (μatm)	DOC (mg L^{-1})	pH	Salinity (US)
Casa Velha	*1.2*	361	41.2	8.7	5.0
	38.7	1153	40.9	8.3	7.0
	Variation Rate*	*3.19*	*0.99*	*−0.4*	*1.40*
Barrinha	*1.2*	1167	42.9	8.2	4.9
	38.7	2684	43.1	7.8	6.5
	Variation Rate*	*2.30*	*1.00*	*−0.4*	*1.32*
CAR_ Macrophytes	*0.0–6.7*	386	9.1	7.9	*6.0*
	34.6–67.6	4203	17.9	6.8	2.2
	Variation Rate*	*10.90*	*1.98*	*−1.1*	*0.37*
CAR_ Open	*0.0–6.7*	1609	8.1	7.4	6.2
	34.6–67.6	5905	16.6	6.6	2.4
	Variation Rate*	*3.67*	*2.05*	*−0.8*	*0.39*

nc – not collected.

[*] Variation Rate was expressed by ratio Rainier:Drier sampling events for changes in pCO_2, DOC and salinity, and by difference between both for fluctuations in pH.

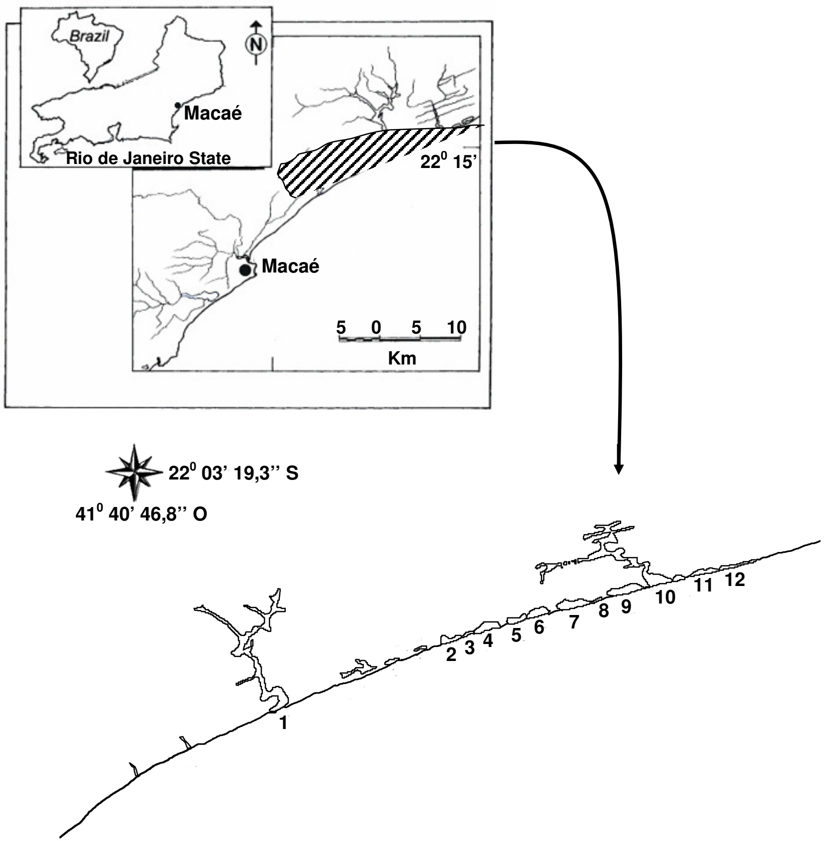

Fig. 1. Localization of the studied lakes (1) Carapebus, (2) Garças, (3) Piri-piri 1, (4) Peri-peri 2, (5) Maria Menina, (6) Robalo, (7) Visgueiro, (8) Catingosa, (9) Pires, (10) Preta, (11) Barrinha and (12) Casa Velha.

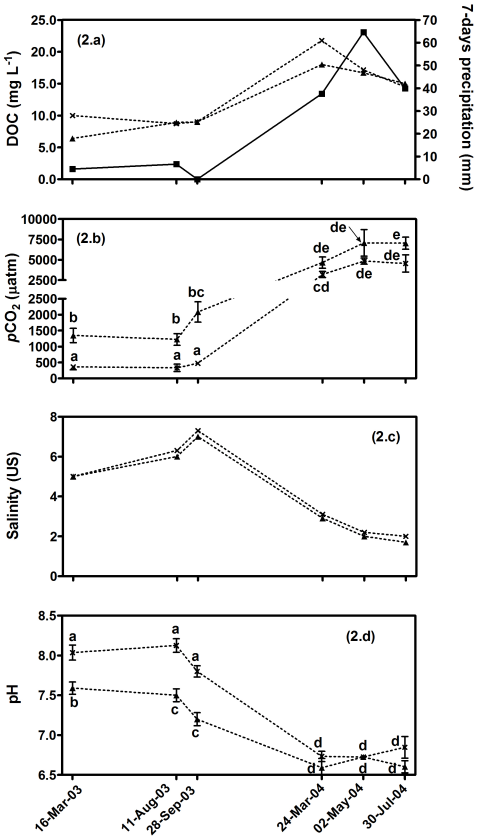

Fig. 2. Accumulated precipitation in the week preceding the sampling (full squares) and average DOC concentrations **(a)**, $p\text{CO}_2$ **(b)**, salinity **(c)** and pH **(d)** in open waters (triangles) and macrophyte-covered (crosses) waters of Carapebus Lake along the studied period. Bars indicate standard errors and at least a letter shared by different dates indicates no significant differences (Tukey-Kramer, $p < 0.05$) for pH and $p\text{CO}_2$ among stations and sampling events.

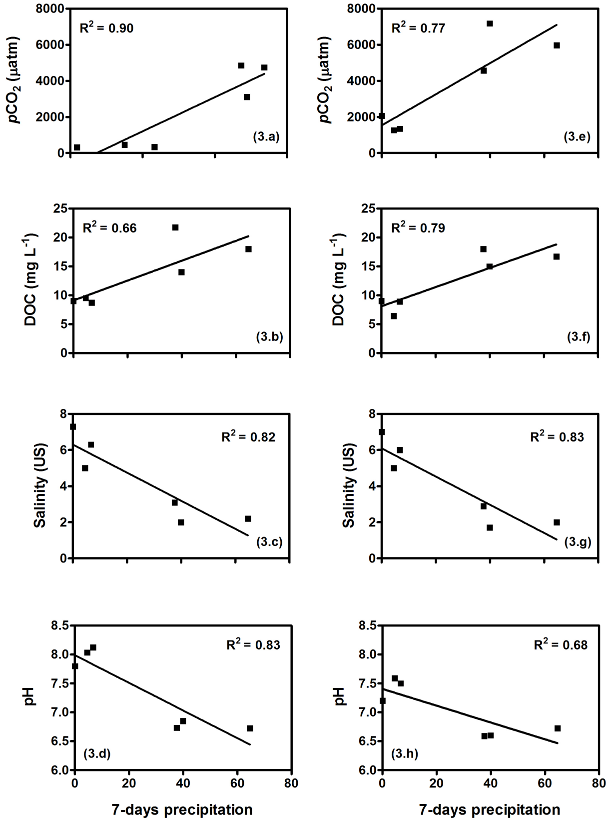

Fig. 3. The relationships between mean $p\mathrm{CO}_2$, DOC, salinity and pH with accumulated precipitation in the week preceding the sampling in the macrophyte covered (**a, b, c** and **d**) and open water (**e, f, g** and **h**) stations of Carapebus Lake. Solid lines represent significant linear regressions ($p < 0.05$).

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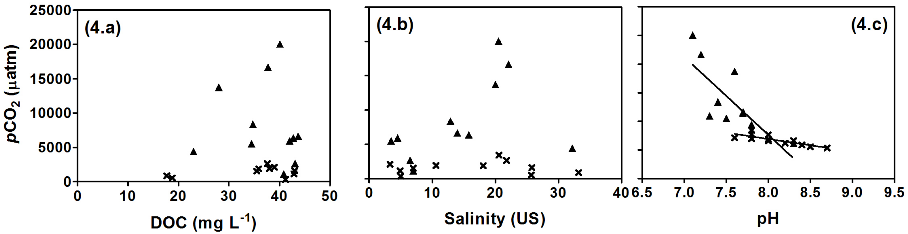

Fig. 4. The relationships of pCO_2 with **(a)** DOC, **(b)** salinity and **(c)** pH in 11 lakes sampled simultaneously within drier (crosses) and rainier (full triangles) sampling events. Only pH showed significant linear regressions ($p < 0.05$) with pCO_2 in each period ($pCO_2 = -2214$ pH + 19 620, $R^2 = 0.61$ for the drier one; $pCO_2 = -13\,640$ pH + 111 800, $R^2 = 0.66$ for the rainier one), and combining both ($pCO_2 = -9823$ pH + 82 090, $R^2 = 0.60$).

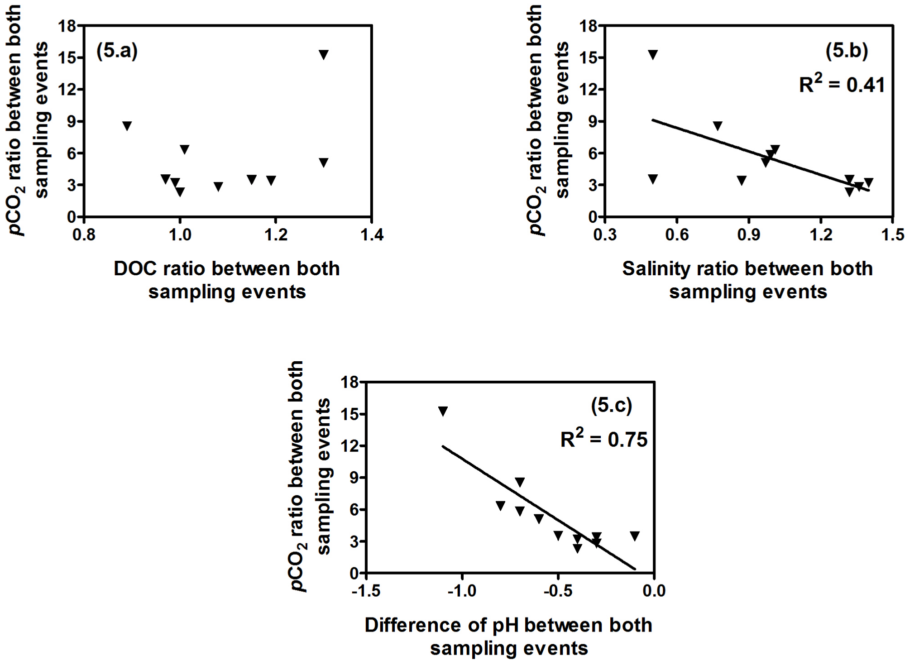

Fig. 5. The relationships of the variation rates, comparing the rainier sampling event to drier one, of pCO_2 **(a)** DOC, **(b)** salinity and **(c)** pH in the 11 lakes sampled simultaneously. Solid lines represent the significant fitted regression equations ($p < 0.05$) for changes in salinity (variation rate in $pCO_2 = -7.4$ variation rate in salinity $+12.8$, $R^2 = 0.41$) and pH (variation rate in $pCO_2 = -11.5$ variation rate in pH-0.8, $R^2 = 0.75$)