

# Temporal variation in methane emissions in a shallow lake at a southern mid latitude during high and low rainfall periods

Victoria S. Fusé · M. Eugenia Priano ·  
Karen E. Williams · José I. Gere · Sergio A. Guzmán ·  
Roberto Gratton · M. Paula Juliarena

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**Abstract** The global methane (CH<sub>4</sub>) emission of lakes is estimated at between 6 and 16 % of total natural CH<sub>4</sub> emissions. However, these values have a high uncertainty due to the wide variety of lakes with important differences in their morphological, biological, and physicochemical parameters and the relatively scarce data from southern mid-latitude lakes. For these reasons, we studied CH<sub>4</sub> fluxes and CH<sub>4</sub> dissolved in water in a typical shallow lake in the Pampean Wetland, Argentina, during four periods of consecutive years (April 2011–March 2015) preceded by different rainfall conditions. Other water physicochemical parameters were measured and meteorological data were reported. We identified three different states of the lake throughout the study as the result of the irregular alternation between high and low rainfall periods, with similar water temperature values but with important variations in dissolved oxygen, chemical oxygen demand, water turbidity, electric conductivity, and water level. As a consequence, marked seasonal and interannual variations

occurred in CH<sub>4</sub> dissolved in water and CH<sub>4</sub> fluxes from the lake. These temporal variations were best reflected by water temperature and depth of the Secchi disk, as a water turbidity estimation, which had a significant double correlation with CH<sub>4</sub> dissolved in water. The mean CH<sub>4</sub> fluxes values were 0.22 and 4.09 mg/m<sup>2</sup>/h for periods with low and high water turbidity, respectively. This work suggests that water temperature and turbidity measurements could serve as indicator parameters of the state of the lake and, therefore, of its behavior as either a CH<sub>4</sub> source or sink.

**Keywords** Greenhouse gases · Shallow lake · Methane production/fluxes · Methane dissolved in water · Water turbidity · Lake ecology

## Abbreviations

AT	air temperature
COD	chemical oxygen demand
EC	water electrical conductivity normalized to 25 °C
DO	dissolved oxygen
MF	methane diffusive fluxes
RF	total monthly rainfall
SPI-6	Standardized Precipitation Index for a 6-month timescale
WL	water level
WM	methane dissolved in water
WMe	methane dissolved in water that is in equilibrium with the atmospheric methane concentration
WT	surface water temperature
Z	depth of the Secchi disk

Roberto Gratton is deceased 7 November 2014

V. S. Fusé · M. E. Priano · M. P. Juliarena (✉)  
CIFICEN-UNCPBA-CICPBA-CONICET - Centro de  
investigaciones en Física e Ingeniería del Centro de la Provincia de  
Buenos Aires, Pinto 399, 7000 Tandil, Argentina  
e-mail: pjuliarena@exa.unicen.edu.ar

J. I. Gere · R. Gratton  
CONICET - Consejo Nacional de Investigaciones Científicas y  
Tecnológicas, Av. Rivadavia 1917, C1033AAJ CABA, Argentina

K. E. Williams · S. A. Guzmán  
UNCPBA - Universidad Nacional del Centro de la Provincia de  
Buenos Aires, Pinto 399, 7000 Tandil, Argentina

## Introduction

Methane (CH<sub>4</sub>) is an important greenhouse gas whose present atmospheric concentration has more than doubled pre-industrial values (Forster et al. 2007). The anthropogenic CH<sub>4</sub> emissions (between 264 and 428 Tg/year) altogether double the emissions from natural sources (between 145 and 260 Tg/year) (Denman et al. 2007). However, there is considerable interannual variation in atmospheric CH<sub>4</sub>. Such fluctuations have been assigned to changes in natural fluxes (Bousquet et al. 2006).

Wetlands are the main natural source and type of aquatic ecosystem emitting biogenic CH<sub>4</sub> with a global emission estimated at between 100 and 231 Tg/year (Denman et al. 2007). However, studies on emissions from water-related ecosystems other than wetlands are less frequent. CH<sub>4</sub> fluxes from lakes are comparable to those from wetlands (Ortiz-Llorente and Alvarez-Cobelas 2012). The global CH<sub>4</sub> emission of these ecosystems is estimated at between 4 and 48 Tg/year equivalent to 6 and 16 % of total natural CH<sub>4</sub> emissions (Bastviken et al. 2004).

CH<sub>4</sub> emission is the balance of two counteracting microbiological processes: production of CH<sub>4</sub> in anoxic conditions (methanogenesis) and the consumption or oxidation of the CH<sub>4</sub> generated (methanotrophy) (Borrel et al. 2011). Besides, there are at least three CH<sub>4</sub> emission pathways that determine the rate of CH<sub>4</sub> release from the sediment into the atmosphere: ebullition flux, diffusive flux, and flux through aquatic vegetation (Bastviken et al. 2004). These processes are regulated by many environmental physicochemical factors such as sediment and water temperature, oxygen availability, organic matter availability and composition, sediment and water chemistry, and factors such as water depth and lake size (Le Mer and Roger 2001). These parameters are sensitive to climatic factors (air temperature, precipitations, winds, etc.) and therefore, have significant seasonal and interannual variations (Vincent 2010). Consequently, many studies show that CH<sub>4</sub> emission from lakes follow rather regular annual cycles (Deborde et al. 2010; Gondwe and Masamba 2014), which are, however, greatly affected by year-to-year fluctuations (Li et al. 2015; Ringeval et al. 2010).

There are many studies which have reported CH<sub>4</sub> fluxes in lakes in different climatic regions, but most of them are located in the Northern Hemisphere (Ortiz-Llorente and Alvarez-Cobelas 2012). In particular, there are no studies of CH<sub>4</sub> fluxes in shallow lakes of the Pampean Wetland (central-east of Argentina).

The Pampean Region is a temperate and plain zone, sparsely populated, with extensive livestock farms (Huarte et al. 2010). Shallow lakes in this region, as in the study area, are located in basins originated by deposition and erosion (Diovisalvi et al. 2015). In a great part of the region, the drainage is either endorheic or arheic and therefore, the lakes are basically the result of a hydrological balance between precipitation and evaporation (Bohn et al. 2016). In Buenos Aires Province (around 55 % of the Pampean region surface), the number of shallow lakes is on the order of 300,000, including both permanent and non-permanent water bodies (Diovisalvi et al. 2015). Generally, these lakes are naturally eutrophic or hypertrophic, with highly variable water residence time and salinity (Quirós and Drago 1999). As a consequence, many other water physicochemical properties, such as turbidity, electrical conductivity, dissolved oxygen, organic matter among others, undergo considerable changes in response to water level fluctuations and to changes in water retention time (Sánchez et al. 2015).

We should consider the changing nature of the Pampean lakes and how this characteristic affects CH<sub>4</sub> production and consumption. With the aim of identifying an easily measured parameter that could allow us to estimate whether the lake behaves either as a CH<sub>4</sub> source or a sink in long time periods, the present work reports measurements of CH<sub>4</sub> dissolved in water and CH<sub>4</sub> fluxes in “La Barrancosa,” a particular seepage lake of the Pampean Wetland. This lake was selected because of its central location in the wetland and intermediate area, and we therefore assume that it is representative of most of the water bodies of the wetland. The results correspond to fieldwork carried out across four periods of consecutive years (April 2011–March 2015) preceded by different rainfall conditions. Correlations of CH<sub>4</sub> dissolved in water and CH<sub>4</sub> fluxes with some water and meteorological parameters were explored.

## Materials and methods

### The study site

Lake “La Barrancosa” (37° 20' S, 60° 7' W, elevation 245 MAMSL) is a seepage lake located near the small town of Benito Juárez (~15,000 inhabitants), Buenos Aires Province, Argentina, in a thinly populated region with extensive livestock farms. It is a natural lake with

limited runoff and no stream outlet (Iriondo 2004). It belongs to the upper section of the Tapalqué stream basin (the area of the basin is 1750.5 Km<sup>2</sup> and its perimeter is 200.5 Km).

The average area of the lake was about 1.9 Km<sup>2</sup> (Dukat 2008) and the water level in the center varied between 1.2 and 3.7 m throughout the study. In general, the lake is alkaline, oligohaline, and with a high degree of eutrophication associated with the high content of total phosphorus and chlorophyll-a, as well as its lack of transparency (Díaz and Colasurdo 2008).

The climate in the region is temperate with a mean annual temperature of 15.0 °C. The mean monthly air temperature ranges from 5.0 to 31.0 °C (Weather Station of Benito Juárez). The rainfall pattern is irregular with marked interannual fluctuations. The annual average rainfall is around 893.1 mm, with a monthly average of 76.3 mm (period 1995–2014, Weather Station of Benito Juárez).

Fieldwork was carried out across four annual periods of consecutive years. Each period spanned from April through March of the following year (period 1, April 2011–March 2012; period 2, April 2012–March 2013; period 3, April 2013–March 2014; and period 4, April 2014–March 2015). In the first year (2011), fieldwork was carried out in all seasons, every 3 months. After June 2012, the interval between fieldwork studies was reduced to one study every 2 months to determine CH<sub>4</sub> fluxes more frequently. In each season, at least three fieldwork studies were performed to determine CH<sub>4</sub> dissolved in water and some water parameters associated.

### Methane flux

Methane diffusive fluxes at the water-air interface (MF) were determined by means of a couple of floating static chambers (Matthews et al. 2003) at the center of the lake (Gondwe and Masamba 2014) and used at the same time. PVC tube (16 cm in diameter) constituted the chamber bodies, whose headspace was limited at the bottom by the water surface and at the top by a removable lid. The headspace height, measured case by case, was about 20 cm.

The removable PVC lids were fitted with a valve to allow air samples to be withdrawn. A little fan attached inside the lids provided air mixing during the operation without appreciable perturbation of the water surface (Schrier-Uijl et al. 2011).

After the chamber closure, four air samples were extracted every 20 min during an hour (Matthews et al. 2003) between 10.30 and 14.30 h (Schrier-Uijl et al. 2011). Gas samples were collected with 25-ml syringes fit with three-way stopcocks, previously cleaned with pure N<sub>2</sub> and stored at a pressure slightly above 1 bar.

Within 6 h after sample collection, gas samples were injected into the gas chromatograph (GC Agilent 7890A) to measure CH<sub>4</sub> concentration. The GC was equipped with a FID and a 1.8-m Porapak Q (80/100 mesh) column. Oven, injector, and detector temperatures were respectively 50, 250, and 250 °C. Carrier gas (He) flow was 30 ml/min. H<sub>2</sub> and O<sub>2</sub> flows were 30 and 400 ml/min, respectively.

Finally, MF were calculated using linear regression of the CH<sub>4</sub> concentration in the headspace versus time. They were then converted to mg/m<sup>2</sup>/h considering the measured headspace volumes and temperatures. All regressions with  $R^2 > 0.85$  were considered valid experimental points (Matthews et al. 2003).

### Methane dissolved in water

In each fieldwork study, six 25-ml water samples were collected near the surface (Ojala et al. 2011) from the center of the lake (Gondwe and Masamba 2014) at the same time of floating static chamber operation. Water samples were stored in 50-ml glass flasks sealed with rubber septums, previously evacuated and filled twice with pure N<sub>2</sub>. The samples were preserved with 0.5 ml of ZnCl<sub>2</sub> 4 M to inhibit biological activity, and kept under refrigeration (Fonseca et al. 2004) until processing within 24 h. In the laboratory, at a room temperature of 20 °C, an air sample of the gaseous phase was withdrawn from each flask headspace and injected into the GC to measure CH<sub>4</sub> concentration. The CH<sub>4</sub> dissolved in water sample (WM) was calculated using Henry's law and following the EPA guideline for gases dissolved in water (U.S. EPA Region 1 2002).

### Environmental parameters

Surface water temperature (WT), pH, dissolved oxygen (DO), and water electrical conductivity normalized to 25 °C (EC) were determined in the field by means of a portable multiparametric probe (Hanna 9828). Water level (WL) and depth of the Secchi disk (Z) (inversely related to water turbidity) were also measured.

In order to estimate the water organic content in the lake, water samples were collected for laboratory determinations of the chemical oxygen demand (COD) using the closed reflux titulometric method (APHA 1976), as this is a simple technique available in our laboratory. Samples were stored at 4 °C after adding H<sub>2</sub>SO<sub>4</sub> to obtain pH = 2, until processing in the laboratory within 7 days.

Air temperature (AT) and total monthly rainfall (RF) throughout the study were provided by the National Weather Service, Weather Station of Benito Juárez (located 40 Km from the study site).

#### Data analysis and statistics

Origin Lab 6.0 software was used to calculate the slopes of the linear regressions for CH<sub>4</sub> concentrations in the air samples sequentially withdrawn from each chamber and in all sets of WM and MF versus environmental parameters. Year-to-year differences of the means of the environmental parameters (ANOVA, *Fisher's LSD Test*) and correlations between magnitudes (*Pearson correlation*) were analyzed using Infostat Statistical Software.

Rainfall variability was determined by using the Standardized Precipitation Index (SPI) that calculates values between 4 and -4 (Wu et al. 2005). Higher values indicate greater than mean precipitation whereas lower values indicate less than mean precipitation. The calculation was based on a record of monthly precipitations for 20 years (April 1995–March 2015) provided by the National Weather Service, Weather Station of Benito Juárez. The SPI values for a 6-month timescale (SPI-6) were calculated using SPI SL 6 software. To calculate SPI values for periods either shorter or longer than 6 months, in situ precipitation data or a record for over 20 years, respectively, would be necessary (Wu et al. 2005).

To determine if the lake acts as a source or a sink of CH<sub>4</sub>, we compared WM with CH<sub>4</sub> dissolved in water that is in equilibrium with the atmospheric CH<sub>4</sub> concentration (WMe). WMe was calculated using Henry's law with the constant adjusted for WT (Wiesenburg and Guinasso 1979). This parameter is a function of the CH<sub>4</sub> concentration in the surrounding air, which has been taken equal to 1.7 ppmv (Huarte et al. 2010). Undersaturation (WM < WMe) indicates uptake of CH<sub>4</sub> into the water phase, while supersaturation (WM > WMe) suggests CH<sub>4</sub> release from the water phase to the atmosphere (Bange 2006).

## Results and discussion

### Environmental parameters

Figure 1a shows AT and RF and Fig. 1b shows the variation in the SPI-6 over the study period April 2011–March 2015.

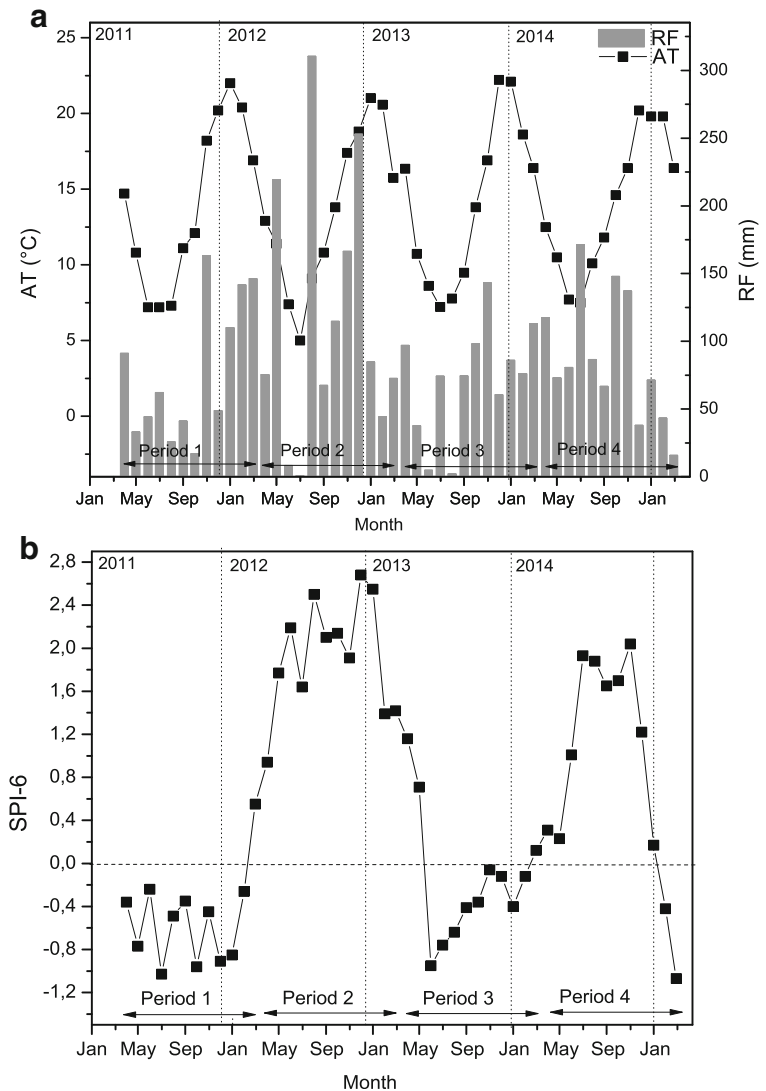
Across the four periods, the mean monthly AT ranged from 5.0 to 22.2 °C, with an average temperature value of 13.9 °C (Fig. 1a). AT varied seasonally, without statistically significant differences between the four periods (Fisher's LSD Test,  $p > 0.05$ ).

From April 2011 to March 2015, a succession of dry and wet years was observed (Fig. 1a). Average total annual rainfall during the study period was 1060 mm, denoting marked year-to-year fluctuations. Period 2 (2012/2013) was particularly wet, with an average RF of 112.2 mm and a maximum of 310.6 mm in August 2012, whereas periods 1 and 3 were the driest ones, with an average RF of 76.9 and 61.8 mm, respectively. Despite this, there were no significant differences in total rainfall between the four periods (Fisher's LSD Test,  $p > 0.05$ ). Differences arise, however, when considering the previous precipitations. The mean SPI-6 values were -0.51, 1.94, -0.15, and 0.89 for periods 1, 2, 3, and 4, respectively. Period 2 showed the highest SPI-6 values, with significant differences from the other three (Fisher's LSD Test,  $p < 0.05$ ) (Fig. 1b). According to SPI-6 values, we can distinguish three different "states" of the lake throughout the study: state I, a relatively dry state (period 1); state II, a very wet state, immediately after heavy rainfall (period 2); and state III, one of normal to slightly wet conditions (periods 3 and 4) (Wu et al. 2005).

Table 1 shows mean values for WL and for the water physicochemical parameters measured in the lake for each study period. It also shows the results of the variance comparison of the mean values of the environmental parameters between the four periods using Fisher's LSD test.

Neither WT nor pH show statistically significant differences between the four periods (Fisher's LSD Test,  $p > 0.05$ ). The mean WT was 15.0 °C during the total study period, with a marked seasonal variation, significantly correlated with AT ( $R^2 = 0.7927$ ,  $p < 0.001$ ,  $N = 38$ ). pH remained almost constant throughout the study period. By contrast, the results of Fisher's LSD test did show statistically significant differences in the remaining environmental parameters over the four periods ( $p < 0.05$ ) (Table 1).

**Fig. 1** **a** Air temperature (*AT*), total monthly rainfall (*RF*). **b** Standardized precipitation index for a 6-month timescale (*SPI-6*) during the total study period (*arrows* show the extent of the four study periods)



**Table 1** Water physicochemical parameters: mean values, standard deviations, and number of measurements (*n*)

Parameter	Period 1 (2011/12)	Period 2 (2012/13)	Period 3 (2013/14)	Period 4 (2014/15)
WT (°C)	14.5 ± 6.6 ( <i>n</i> = 6) <sup>a</sup>	15.6 ± 6.5 ( <i>n</i> = 13) <sup>a</sup>	14.5 ± 5.4 ( <i>n</i> = 12) <sup>a</sup>	15.2 ± 7.3 ( <i>n</i> = 7) <sup>a</sup>
pH	9.5 ± 0.3 ( <i>n</i> = 5) <sup>a</sup>	9.2 ± 0.4 ( <i>n</i> = 5) <sup>a</sup>	9.7 ± 0.2 ( <i>n</i> = 2) <sup>a</sup>	9.6 ± 0.1 ( <i>n</i> = 3) <sup>a</sup>
WL (m)	1.3 ± 0.1 ( <i>n</i> = 3) <sup>a</sup>	2.9 ± 0.5 ( <i>n</i> = 13) <sup>b</sup>	3.1 ± 0.2 ( <i>n</i> = 12) <sup>bc</sup>	3.4 ± 0.3 ( <i>n</i> = 6) <sup>c</sup>
EC (μS/cm)	4601 ± 773 ( <i>n</i> = 5) <sup>b</sup>	2606 ± 250 ( <i>n</i> = 7) <sup>a</sup>	2242 ± 317 ( <i>n</i> = 3) <sup>a</sup>	2193 ± 270 ( <i>n</i> = 6) <sup>a</sup>
DO (%)	50.9 ± 6.3 ( <i>n</i> = 3) <sup>a</sup>	100.5 ± 20.5 ( <i>n</i> = 4) <sup>b</sup>	129.5 ± 8.5 ( <i>n</i> = 3) <sup>b</sup>	105.1 ± 25.4 ( <i>n</i> = 4) <sup>b</sup>
Z (cm)	20.3 ± 5.7 ( <i>n</i> = 3) <sup>a</sup>	45.0 ± 18.9 ( <i>n</i> = 10) <sup>b</sup>	24.4 ± 5.2 ( <i>n</i> = 11) <sup>a</sup>	20.2 ± 6.5 ( <i>n</i> = 6) <sup>a</sup>
COD (mg/l)	<i>nm</i>	111.1 ± 42.7 ( <i>n</i> = 4) <sup>a</sup>	206.9 ± 0.3 ( <i>n</i> = 4) <sup>b</sup>	209.9 ± 29.5 ( <i>n</i> = 7) <sup>b</sup>

*Superscript letters* show results for Fisher’s LSD Test at a significance value of *p* < 0.05

*nm* not measured, surface water temperature (*WT*), pH, water level (*WL*), water electrical conductivity (*EC*) normalized to 25 °C, dissolved oxygen (*DO*), depth of the Secchi disk (*Z*), and chemical oxygen demand (*COD*)

High rainfall during period 2 (2012/2013) was reflected in variations in WL, as shown by a considerable WL increase from one period to the next. Being a plain lake, a Pampean lake has a basin that is usually small in relation to its water mirror area (Quirós and Drago 1999). As a result, water retention in the lake and therefore its depth vary directly with the balance between rainfall and evapotranspiration during the drought/flood cycle (Guerra et al. 2015). However, WL is not significantly correlated with RF ( $R^2 = 0.04$ ,  $p > 0.05$ ,  $N = 15$ ), but correlation improves when considering the influence of the previous precipitation. We observed a statistically significant correlation between WL and SPI-6 ( $R^2 = 0.55$ ,  $p = 0.0015$ ,  $N = 15$ ). While some lakes with stream inlets show the effect of rainfall almost immediately, others, such as seepage lakes, do not reflect changes caused by precipitation for months (Iriondo 2004).

Not only WL, but also DO and Z increased from period 1 to period 2, whereas the opposite occurred for EC. A linear inverse correlation of EC with WL leads to  $R^2 = 0.8237$ ,  $p < 0.001$ ,  $N = 18$ . In period 1, RF and SPI-6 were low (Fig. 1a, b), which indicates that evaporation plays an important role in determining WL (Guerra et al. 2015) and then EC (Cirelli and Miretzky 2004). In period 2, the decrease of EC values reflects the effect of precipitations on the increment of WL (e.g., dilution by increase in inflow water) (Torremorell et al. 2007). Fresh water entrance from high precipitations and strong winds increase DO, sometimes over saturation level, whereas in extremely dry periods DO takes very low values (Schrier-Uijl et al. 2011). A linear inverse correlation of EC with

DO leads to  $R^2 = 0.5882$ ,  $p = 0.0014$ ,  $N = 14$ , and both parameters are influenced by rainfall.

After period 2, EC, WL, and DO remained constant despite slight variations (lower than 18 %) in relation to their respective mean values 2383  $\mu\text{S}/\text{cm}$ , 3.0 m, and 110.1 % (means for periods 2, 3, and 4). However, COD increased and Z decreased, with a statistically significant correlation between both parameters ( $R^2 = 0.8459$ ,  $p < 0.001$ ,  $N = 14$ ). Whereas low Z values were obtained in period 1, which was predominantly dry, a major increase was observed in the wet period (period 2). When precipitation finally ceased in periods 3 and 4, values were nearly as low as those recorded in the first period. These variations were reflected in the significant correlation between Z and SPI-6 ( $R^2 = 0.38$ ,  $p < 0.001$ ,  $N = 30$ ).

#### Seasonal variations of methane dissolved in water and methane fluxes

Table 2 shows mean values for WM and MF from the lake for the four seasons during the study period April 2011–March 2015. Increases in  $\text{CH}_4$  concentration in the static chamber due to ebullition were not observed (Matthews et al. 2003; Marani and Alvalá 2007).

Statistically significant differences were observed for MF between summer and winter/spring (Fisher's LSD Test,  $p < 0.05$ ). MF from the lake ranged from  $<0.007 \text{ mg}/\text{m}^2/\text{h}$  (limit of detection) to  $16.628 \text{ mg}/\text{m}^2/\text{h}$  (Table 2). The MF of the lake remained low in spring, fall, and winter with a marked increase in summer. The same behavior was reported for WM; the mean WM ranged from 0.228 mg/l in summer to 0.036 mg/l in winter

**Table 2** Seasonal variations of  $\text{CH}_4$  dissolved in water (WM) and  $\text{CH}_4$  fluxes (MF): statistical parameters

Statistical parameters	WM (mg/l)				MF (mg/m <sup>2</sup> /h)			
	Fall	Winter	Spring	Summer	Fall	Winter	Spring	Summer
Mean	0.118	0.036	0.141	0.228	0.504	0.025	0.324	7.852
SD	0.122	0.016	0.118	0.222	0.594	0.032	0.432	7.186
Min	0.021	<0.001	0.009	0.039	0.101	<0.007	<0.007	0.097
Max	0.307	0.055	0.418	0.737	1.188	0.065	0.360	16.628
N	7	7	12	9	3	3	4	7
CV (%)	103.7	45.7	83.9	97.3	118.1	124.9	133.3	91.5
Fisher's LSD Test ( $p < 0.05$ )	AB	A	AB	B	AB	A	A	B

Mean, SD standard deviation, Min minimum, Max maximum, N number of fieldwork studies, CV coefficient of variation and results of Fisher's LSD test at a level of significance of  $p < 0.05$  (mean values with same letters have not statistically significant differences)

(Table 2), with statistically significant differences in WM between both seasons.

Lakes usually show a CH<sub>4</sub> emission peak in summer, with CH<sub>4</sub> fluxes near zero or even zero during winter, with rapid shift between both seasons (Ortiz-Llorente and Alvarez-Cobelas 2012), as it was observed in La Barrancosa. Generally, the temporal variability of CH<sub>4</sub> emissions from lakes is related to temperature when measured over long time spans (Kankaala et al. 2004; Gondwe and Masamba 2014). Sediment and water temperature are considered a determinant of CH<sub>4</sub> production (methanogenesis) and consumption (methanotrophy) (Le Mer and Roger 2001). Low temperature may limit CH<sub>4</sub> production either by restricting the growth rate of methanogenic microorganisms or by limiting substrate production (Borrel et al. 2011). Based on the seasonal variations in WM and MF presented in Table 2, dependence of such parameters and WT was analyzed. We obtained a statistically significant correlation between WM and MF with WT ( $R^2 = 0.2195, p = 0.004, N = 36$  and  $R^2 = 0.2308, p = 0.051, N = 17$ , respectively). Nevertheless, CV of WM and MF were really high (sometimes >100 %) as a result of considerable year-to-year variations in WM and MF over the study period April 2011–March 2015 (Table 3), that could be a consequence of the irregular RF regime (Fig. 1a).

Interannual variations of methane dissolved in water and methane fluxes

Table 3 shows mean values for WM and MF from the lake for the four periods during the total study period April 2011–March 2015.

MF and WM show a common trend, with marked variations from one period to the next (Table 3) and with a significant correlation between both parameters ( $R^2 = 0.5143, p = 0.0012, N = 17$ ).

During the second period, WM concentrations were lower, whereas the highest were recorded during the fourth period, with statistically significant differences in WM between both periods (Fisher’s LSD Test,  $p < 0.05$ ). Period 1 and period 3 presented intermediate WM values compared with periods 2 and 4. The same behavior was reported for MF; the lowest MF were measured during the second period, whereas the highest were recorded during the fourth period. The MF values for each period show great variability, with high SD values associated to seasonal changes. As a consequence, MF values did not show statistically significant differences between periods (Fisher’s LSD Test,  $p > 0.05$ ).

Environmental parameters that influence over methane emissions and methane dissolved in the lake

The net CH<sub>4</sub> flux from lakes results from diverse environmental variables that influence, in a complex manner, its production, consumption, and transport (Le Mer and Roger 2001). The alternation between high and low rainfall periods, characteristic of the Pampean region (Diovisalvi et al. 2015) produces changes in water physicochemical parameters and in the morphology of lakes (Bohn et al. 2016; Guerra et al. 2015; Sánchez et al. 2015; Torremorell et al. 2007). This leads to marked variations among states in CH<sub>4</sub> emissions and CH<sub>4</sub> dissolved in water from the lake (Bange et al. 2010; Gondwe and Masamba 2014) as it was observed in this

**Table 3** Interannual variations of CH<sub>4</sub> dissolved in water (WM) and CH<sub>4</sub> fluxes (MF): statistical parameters

Statistical parameter	WM (mg/l)				MF (mg/m <sup>2</sup> /h)			
	Period 1 (2011/12)	Period 2 (2012/13)	Period 3 (2013/14)	Period 4 (2014/15)	Period 1 (2011/12)	Period 2 (2012/13)	Period 3 (2013/14)	Period 4 (2014/15)
Mean	0.186	0.059	0.131	0.225	1.609	0.166	5.641	6.444
SD	0.123	0.038	0.143	0.250	2.916	0.256	9.266	7.974
Min	<0.001	0.009	0.008	0.024	<0.007	<0.007	0.223	0.065
Max	0.306	0.156	0.418	0.737	6.746	0.544	16.340	16.628
N	6	12	11	7	5	4	3	5
Fisher’s LSD Test ( $p < 0.05$ )	AB	A	AB	B	A	A	A	A

Mean, SD standard deviation, Min minimum, Max maximum, N number of fieldwork studies, and results of Fisher’s LSD test at a level of significance of  $p < 0.05$  (mean values with same letters have not statistically significant differences)

study. Below, we compare the three states the lake went through (defined previously according to SPI-6 values) and analyze the main variations. As WM determination was more frequent and well correlated with MF, it is better to analyze the variability of this parameter as an indicator of CH<sub>4</sub> production and CH<sub>4</sub> consumption balance during the total study period.

### *State I vs. state II*

The effect of high rainfall during state II was reflected in the dilution of salt contents and a saturation of DO. Besides, WL increased from state I to state II. Values for WM and MF were extremely low in the second period compared with the first one (Table 3). The notable increase in WL from period 1 to period 2, in which also DO levels were higher (Table 1) probably increased CH<sub>4</sub> oxidation in the water column (Schrier-Uijl et al. 2011), decreasing WM and consequently MF (Lopes et al. 2011). This is because the transport pathway rich in oxygen is longer (Bastviken et al. 2004). Besides, the increase in WL resulting from high rainfall is likely to promote the dilution of biodegradable organic matter (Zhou et al. 2015), therefore decreasing CH<sub>4</sub> production (Yang 1998). In addition, high DO concentrations completely inhibit methanogens (Borrel et al. 2011). Based on these interannual variations, a simple lineal correlation between WM (or MF) and WT is inadequate to explain the variation in MF. It is necessary to introduce at least a second parameter to account for the change in the status of the lake, for instance EC, which is easily measured. We studied a double linear dependence of WM on WT and EC. This results in a significant correlation with  $R^2 = 0.85$ ,  $p_{WT} < 0.005$ ,  $p_{CE} < 0.005$ ,  $N = 12$ . The inclusion of DO as a third variable did not improve the statistical significance of the correlations because in our case DO was well correlated with EC.

### *State II vs. state III*

The effect of high rainfall during state II was reflected in the dilution of the water organic content, whereas high COD values were obtained when high precipitation finally ceased in state III. WM and MF were markedly higher in the third state, compared with the second one. Once anaerobiosis is established, organic substrate is considered the major limiting factor for CH<sub>4</sub> production (Le Mer and Roger 2001). Higher values of organic

matter as a substrate in the lake increase the availability of substrates. This, in turn, can increase CH<sub>4</sub> production and may minimize the competition for electron donors between methanogenesis and other anaerobic processes (Borrel et al. 2011). Based on this, a double dependence of WM on WT and COD was explored, which resulted in a good correlation with  $R^2 = 0.42$ ,  $p_{WT} = 0.0133$ ,  $p_{COD} = 0.085$ ,  $N = 15$ . The inclusion of Z as a third variable did not improve the statistical significance of the correlations because in our case Z was well correlated with COD.

Studies carried out on other lakes in the world showed a statistically significant linear correlation between the water biological oxygen demand (BOD) and its chemical oxygen demand (COD) as well as between organic matter and CH<sub>4</sub> production in sediments (Yang 1998). Although COD values do not correspond to BOD values, they may be helpful in comparing conditions in a water body at one time with those at another time (Hem 1985), as we did in this work.

### All periods

In both transitions (from state I to state II, and from state II to state III), Z was the parameter that best reflected the influence of rainfall and, therefore, the lake dynamics (Table 1). The trophic state of the Pampean lakes, similar in size to La Barrancosa, is dependent on local precipitation and the use of its surrounding land (Bohn et al. 2016). As a result, two different water states have been previously reported for these lakes: “turbid” and “clear,” both a consequence of the different relative weight of precipitation and evaporation over the water balance in the watershed (Cano et al. 2016; Sánchez et al. 2015; Torremorell et al. 2007).

For this reason, we studied a double linear dependence of WM on WT and Z and found a moderate correlation, statistically significant, with  $R^2 = 0.30$ ,  $p_{WT} = 0.0023$ ,  $p_Z = 0.0389$ ,  $N = 30$ . Studies in other temperate shallow lakes show that a higher trophic status was positively correlated with CH<sub>4</sub> emissions (Furlanetto et al. 2012; Schrier-Uijl et al. 2011). Besides, we observed a very good correlation between COD y Z (reported previously in section “Environmental parameters”), and it is therefore likely that decreasing the organic matter and nutrients will reduce CH<sub>4</sub> emissions as it is suggested in Schrier-Uijl et al. (2011).

Figure 2 shows WM vs. WT for two ranges of Z  $22.5 \pm 5.8$  and  $45.0 \pm 18.9$  cm, with statistically



significant differences between both ranges (Fisher's LSD Test,  $p < 0.05$ ), whose correlation leads to  $R^2 = 0.4296$ ,  $p = 0.003$ ,  $N = 26$  and  $R^2 = 0.5790$ ,  $p = 0.0106$ ,  $N = 10$ , respectively. WM shows statistically significant differences between both periods (Fisher's LSD Test,  $p < 0.05$ ). Figure 2 also shows WMe values for each WT.

The correlation between WM with WT improves when considering the differences in Z between the two periods, reflecting again the influence of temperature on methanogenesis and methanotrophy. See that with equivalent WT, in periods when Z was low, WM was relatively higher than when Z was high. During periods with high Z, WM was very close to WMe and in some cases even lower, regardless of the temperature; whereas in periods with low Z, WM was much higher than WMe for temperatures above 10 °C and its value was very sensitive to the latter parameter. According to Bange (2006),  $WM > WMe$  suggests CH<sub>4</sub> release from the water phase to the atmosphere. Therefore, in our case, the lake behaved mainly as a CH<sub>4</sub> source during the study period, with large differences in fluxes between both states. When Z was low, the WT interval in which the lake behaved as a CH<sub>4</sub> source was longer than when Z was high (Fig. 2).

The mean and maximum MF values were 4.086 and 16.628 mg/m<sup>2</sup>/h respectively for periods with low Z values (high water turbidity and low SPI-6). During the period with high Z values (low water turbidity and high SPI-6), the MF values were one order of magnitude

lower than in other periods, with a mean and maximum MF of 0.216 and 0.544 mg/m<sup>2</sup>/h, respectively.

MF values during the second period were lower than those reported for shallow lakes from other temperate regions of the world (Deborde et al. 2010; Ortiz-Llorente and Alvarez-Cobelas 2012) whereas MF values obtained in other periods were comparable to those recorded in the literature (Ortiz-Llorente and Alvarez-Cobelas 2012).

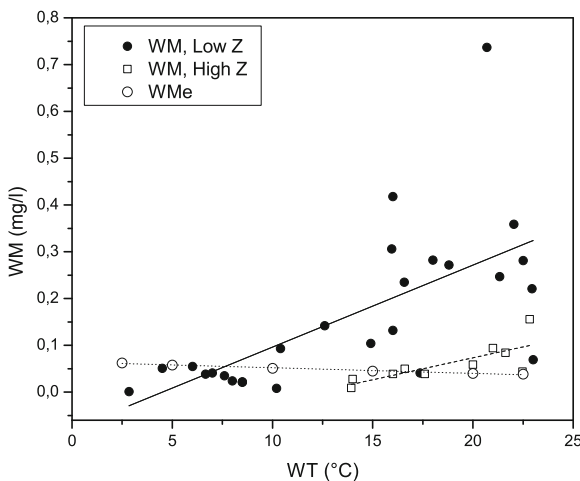
Just like the marked MF variations observed in La Barrancosa between periods, we could expect that drought/flood cycles, characteristic of this region, promote such changes in other lakes on the wetland (Claps et al. 2004; Diovisalvi et al. 2015; Sánchez et al. 2015). From the differences in WM and MF between two periods with low and high Z in the lake, it follows that the water turbidity could serve as an indicator parameter of the state of the lake and, therefore, of its behavior as either a CH<sub>4</sub> source or sink (Bange et al. 2010). Besides, according to seasonal variations, the WT is also an important factor to estimate the temporal behavior of CH<sub>4</sub> emission. These parameters are easily measurable, and they can be monitored in situ or using satellite techniques (Canziani et al. 2008; Wan et al. 2002).

### Conclusion

For the first time, CH<sub>4</sub> concentration in water and CH<sub>4</sub> fluxes were measured in a lake of the Pampean Wetland. We observed marked differences in water physicochemical parameters which affected CH<sub>4</sub> dissolved in water and CH<sub>4</sub> fluxes during a 4-year period with different previous rainfall.

Due to the temporary nature of the Pampean lakes, the physicochemical and biological parameters exhibit relatively large variation in short time periods; therefore, studies limited to short periods cannot record long-term dynamics. We should consider the changing nature of these water bodies and how this characteristic affects CH<sub>4</sub> production and consumption.

In the lake La Barrancosa, marked seasonal variations occurred in CH<sub>4</sub> water concentration and CH<sub>4</sub> fluxes from the lake, associated with the influence of temperature on microbiological activity in the CH<sub>4</sub> production and CH<sub>4</sub> consumption. Such variations were deeply perturbed by year-to-year variations in water physicochemical parameters resulting from precipitation in the watershed. In this case, the rainfall regime had strong influence on net CH<sub>4</sub>



**Fig. 2** CH<sub>4</sub> dissolved in water that is in equilibrium with the atmospheric CH<sub>4</sub> concentration (WMe) and CH<sub>4</sub> concentrations in water (WM) vs. water temperature (WT) for two ranges of depth of the Secchi disk (Z)

flux. In particular, high CH<sub>4</sub> concentration in water and CH<sub>4</sub> fluxes were recorded during warm seasons after a long dry period. A double linear dependence of CH<sub>4</sub> dissolved in water on water temperature and depth of the Secchi disk fits well the results. The latter is used as an indicator of water state, organic matter availability, and therefore, the influence of rainfall upon the seepage lake.

The significant variation in CH<sub>4</sub> fluxes and CH<sub>4</sub> dissolved in water observed in the lake La Barrancosa are likely to occur at regional level in other lakes of the Pampean Wetland where high and low rainfall typically alternate causing physicochemical and morphological changes. For this reason, an important aspect of this study is the identification of a statistically significant relationship between CH<sub>4</sub> dissolved in water, water temperature, and turbidity in a lake, easily measurable parameters, that could serve to determine the different water states and therefore whether the lake acts as a CH<sub>4</sub> source or sink. It would be necessary to assess whether this relationship is repeated in other lakes of the region in order to evaluate similar effect of meteorological conditions on the water states. This would allow for the estimation of the natural CH<sub>4</sub> emission from the Pampean Wetland.

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#### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

## References

- APHA (1976). *Standard methods for the examination of water and wastewater*. Washington DC: American Public Health Association.
- Bange, H. W. (2006). Nitrous oxide and methane in European coastal waters. *Estuarine, Coastal and Shelf Science*. doi:10.1016/j.ecss.2006.05.042.
- Bange, H., Bergmann, K., Hansen, H. P., Kock, A., Koppe, R., Malien, F., & Ostrau, C. (2010). Dissolved methane during hypoxic events at the Boknis Eck time series station (Eckernförde Bay, SW Baltic Sea). *Biogeosciences*. doi:10.5194/bg-7-1279-2010.
- Bastviken, D., Cole, J., Pace, M., & Tranvik, L. (2004). Methane emissions from lakes: dependence of lake characteristics, two regional assessments, and a global estimate. *Global Biogeochemical Cycles*. doi:10.1029/2004GB002238.
- Bohn, V. Y., Delgado, A. L., Piccolo, M. C., & Perillo, G. M. (2016). Assessment of climate variability and land use effect on shallow lakes in temperate plains of Argentina. *Environmental Earth Sciences*. doi:10.1007/s12665-016-5569-6.
- Borel, G., Jézéquel, D., Biderre-Petit, C., Morel-Desrosiers, N., Morel, J. P., Peyret, P., Fonty, G., & Lehours, A. C. (2011). Production and consumption of methane in freshwater lake ecosystems. *Research in Microbiology*. doi:10.1016/j.resmic.2011.06.004.
- Bousquet, P., Ciais, P., Miller, J. B., Dlugokencky, E. J., Hauglustaine, D. A., Prigent, C., et al. (2006). Contribution of anthropogenic and natural sources to atmospheric methane variability. *Nature*. doi:10.1038/nature05132.
- Cano, M. G., Casco, M. A., & Claps, M. C. (2016). Epipelonal dynamics in a shallow lake through a turbid-and a clear-water regime. *Journal of Limnology*. doi:10.4081/jlimnol.2016.1340.
- Canziani, G., Ferrati, R., Marinelli, C., & Dukatz, F. (2008). Artificial neural networks and remote sensing in the analysis of the highly variable pampean shallow lakes. *Mathematical Biosciences and Engineering*. doi:10.3934/mbe.2008.5.691.
- Cirelli, A. F., & Miretzky, P. (2004). Ionic relations: a tool for studying hydrogeochemical processes in Pampean shallow lakes (Buenos Aires, Argentina). *Quaternary International*. doi:10.1016/S1040-6182(03)00046-6.
- Claps, M. C., Gabellone, N. A., & Benítez, H. H. (2004). Zooplankton biomass in an eutrophic shallow lake (Buenos Aires, Argentina): spatio-temporal variations. *Annales de Limnologie - International Journal of Limnology*. doi:10.1051/limn/2004018.
- Deborde, J., Anschutz, P., Guérin, F., Poirier, D., Marty, D., Boucher, G., Thouzeau, G., Canton, M., & Abril, G. (2010). Methane sources, sinks and fluxes in a temperate tidal lagoon: the Arcachon lagoon (SW France). *Estuarine, Coastal and Shelf Science*. doi:10.1016/j.ecss.2010.07.013.
- Denman, K. L., Brasseur, G., Chidthaisong, A., Ciais, P., Cox, P. M., Dickinson, R. E., Hauglustaine, D., Heinze, C., Holland, E., Jacob, D., Lohmann, U., Ramachandran, S., da Silva Dias, P. L., Wofsy, S. C., & Zhang, X. (2007). Couplings between changes in the climate system and biogeochemistry. In S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, & H. L. Miller (Eds.), *Climate change 2007: the physical science basis. Contribution of working group I to the fourth assessment report of the inter-governmental panel on climate change* (pp. 499–587). Cambridge: Cambridge University Press.
- Díaz, O., & Colasurdo, V. (2008). Capítulo III: El agua revela sus secretos. Química de las lagunas pampeanas. In F. Grosman (Ed.), *Especios en la llanura. Nuestras lagunas de la región pampeana* (pp. 119–127). Buenos Aires: Universidad Nacional del Centro de la Provincia de Buenos Aires.
- Diovisalvi, N., Bohn, V. Y., Piccolo, M. C., Perillo, G. M., Baigún, C., & Zagarese, H. E. (2015). Shallow lakes from the Central Plains of Argentina: an overview and worldwide comparative

- analysis of their basic limnological features. *Hydrobiologia*. doi:10.1007/s10750-014-1946-x.
- Dukatz, F. (2008). Capítulo IX: Nuestros ojos en el cielo: Los satélites de aplicación científica. In F. Grosman (Ed.), *Espejos en la llanura. Nuestras lagunas de la región pampeana* (pp. 119–127). Buenos Aires: Universidad Nacional del Centro de la Provincia de Buenos Aires.
- Fonseca, A. L. S., Minello, M., Marinho, C. C., & Esteves, F. A. (2004). Methane concentration in water column and in pore water of a coastal lagoon (Cabiúnas lagoon, Macaé, RJ, Brazil). *Brazilian Archives of Biology and Technology*. doi:10.1590/S1516-89132004000200018.
- Forster, P., Ramaswamy, V., Artaxo, P., Bernsten, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., M., S., & Van Dorland, R. (2007). Changes in atmospheric constituents and in radiative forcing. In S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, & H. L. Miller (Eds.), *Climate change 2007: the physical science basis. Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change* (pp. 129–234). Cambridge: Cambridge University Press.
- Furlanetto, L. M., Marinho, C. C., Palma-Silva, C., Albertoni, E. F., Figueiredo-Barros, M. P., & de Assis Esteves, F. (2012). Methane levels in shallow subtropical lake sediments: dependence on the trophic status of the lake and allochthonous input. *Limnologia - Ecology and Management of Inland Waters*. doi:10.1016/j.limno.2011.09.009.
- Gondwe, M. J., & Masamba, W. R. (2014). Spatial and temporal dynamics of diffusive methane emissions in the Okavango Delta, northern Botswana, Africa. *Wetlands ecology and management*. doi:10.1007/s11273-013-9323-5.
- Guerra, L., Piovano, E. L., Córdoba, F. E., Sylvestre, F., & Damatto, S. (2015). The hydrological and environmental evolution of shallow Lake Melincué, central Argentinean Pampas, during the last millennium. *Journal of Hydrology*. doi:10.1016/j.jhydrol.2015.01.002.
- Hem, J. D. (1985). *Study and interpretation of the chemical characteristics of natural water*. Washington: Department of the Interior, US Geological Survey.
- Huarte, A., Cifuentes, V., Gratton, R., & Clausse, A. (2010). Correlation of methane emissions with cattle population in Argentine Pampas. *Atmospheric Environment*. doi:10.1016/j.atmosenv.2010.03.012.
- Iriondo, M. (2004). Large wetlands of South America: a model for Quaternary humid environments. *Quaternary International*. doi:10.1016/S1040-6182(03)00037-5.
- Kankaala, P., Ojala, A., & Käki, T. (2004). Temporal and spatial variation in methane emissions from a flooded transgression shore of a boreal lake. *Biogeochemistry*. doi:10.1023/B:BIOG.0000031030.77498.1f.
- Le Mer, J., & Roger, P. (2001). Production, oxidation, emission and consumption of methane by soils: a review. *European Journal of Soil Biology*. doi:10.1016/S1164-5563(01)01067-6.
- Li, T., Zhang, W., Zhang, Q., Lu, Y., Wang, G., Niu, Z., et al. (2015). Impacts of climate and reclamation on temporal variations in CH<sub>4</sub> emissions from different wetlands in China: from 1950 to 2010. *Biogeosciences*. doi:10.5194/bg-12-7055-2015.
- Lopes, F., Viollier, E., Thiam, A., Michard, G., Abril, G., Groleau, A., Prévot, F., Carrias, J.-F., Albéric, P., & Jézéquel, D. (2011). Biogeochemical modelling of anaerobic vs. aerobic methane oxidation in a meromictic crater lake (Lake Pavin, France). *Applied Geochemistry*. doi:10.1016/j.apgeochem.2011.06.021.
- Marani, L., & Alvalá, P. C. (2007). Methane emissions from lakes and floodplains in Pantanal, Brazil. *Atmospheric Environment*. doi:10.1016/j.atmosenv.2006.10.046.
- Matthews, C. J., St. Louis, V. L., & Hesslein, R. H. (2003). Comparison of three techniques used to measure diffusive gas exchange from sheltered aquatic surfaces. *Environmental Science & Technology*. doi:10.1021/es0205838.
- Ojala, A., Bellido, J. L., Tulonen, T., Kankaala, P., & Huotari, J. (2011). Carbon gas fluxes from a brown-water and a clear-water lake in the boreal zone during a summer with extreme rain events. *Limnology and Oceanography*. doi:10.4319/lo.2011.56.1.0061.
- Ortiz-Llorente, M. J., & Alvarez-Cobelas, M. (2012). Comparison of biogenic methane emissions from unmanaged estuaries, lakes, oceans, rivers and wetlands. *Atmospheric Environment*. doi:10.1016/j.atmosenv.2012.05.031.
- Quirós, R., & Drago, E. (1999). *The environmental state of Argentinean lakes: an overview*. Lakes & Reservoirs: Research and Management. doi:10.1046/j.1440-1770.1999.00076.x.
- Ringeval, B., Noblet-Ducoudré, N., Ciais, P., Bousquet, P., Prigent, C., Papa, F., & Rossow, W. B. (2010). An attempt to quantify the impact of changes in wetland extent on methane emissions on the seasonal and interannual time scales. *Global Biogeochemical Cycles*. doi:10.1029/2008GB003354.
- Sánchez, M. L., Lagomarsino, L., Allende, L., & Izaguirre, I. (2015). Changes in the phytoplankton structure in a Pampean shallow lake in the transition from a clear to a turbid regime. *Hydrobiologia*. doi:10.1007/s10750-014-2010-6.
- Schrier-Uijl, A. P., Veraart, A. J., Leffelaar, P. A., Berendse, F., & Veenendaal, E. M. (2011). Release of CO<sub>2</sub> and CH<sub>4</sub> from lakes and drainage ditches in temperate wetlands. *Biogeochemistry*. doi:10.1007/s10533-010-9440-7.
- Torremorell, A., Bustigorry, J., Escaray, R., & Zagarese, H. E. (2007). Seasonal dynamics of a large, shallow lake, laguna Chascomús: the role of light limitation and other physical variables. *Limnologia - Ecology and Management of Inland Waters*. doi: 10.1016/j.limno.2006.09.002Centro de investigaciones en Física e Ingeniería.
- U.S. EPA Region 1 (2002). Technical guidance for the natural attenuation indicators: methane, ethane, and ethene. In *Revisión 1*. New England: EPA New England.
- Vincent, W. F. (2010). Effects of climate change on lakes. In G. E. Likens (Ed.), *Lake ecosystem ecology: a global perspective* (pp. 65–71). New York: Academic Press.
- Wan, Z., Zhang, Y., Zhang, Q., & Li, Z. L. (2002). Validation of the land-surface temperature products retrieved from Terra moderate resolution imaging spectroradiometer data. *Remote Sensing of Environment*. doi:10.1016/S0034-4257(02)00093-7.

- Wiesenburg, D. A., & Guinasso Jr., N. L. (1979). Equilibrium solubilities of methane, carbon monoxide, hydrogen in water and seawater. *Journal of Chemical and Engineering Data*. doi:10.1021/je60083a006.
- Wu, H., Hayes, M. J., Wilhite, D. A., & Svoboda, M. D. (2005). The effect of the length of record on the standardized precipitation index calculation. *International Journal of Climatology*. doi:10.1002/joc.1142.
- Yang, S. S. (1998). Methane production in river and lake sediments in Taiwan. *Environmental Geochemistry and Health*. doi:10.1023/A:1006536820697.
- Zhou, Y., Zhang, Y., Shi, K., Liu, X., & Niu, C. (2015). Dynamics of chromophoric dissolved organic matter influenced by hydrological conditions in a large, shallow, and eutrophic lake in China. *Environmental Science and Pollution Research*. doi:10.1007/s11356-015-4556-x.