



Physical Factors and Microbubble Formation Explain Differences in CH₄ Dynamics Between Shallow Lakes Under Alternative States

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Submerged macrophytes play a key role in maintaining clear vegetated states in shallow lakes, but their role on methane (CH₄) dynamics is less explored. They might enhance methanogenesis by providing organic matter but they can also supply oxygen to the sediments increasing methanotrophy. They may also affect gas exchange by diminishing wind turbulence in the water column. We previously measured seasonal CO₂ and CH₄ partial pressure ($p\text{CO}_2$ and $p\text{CH}_4$) and diffusive fluxes from two clear vegetated and two turbid algal shallow lakes of the Pampean Plain, Argentina, and we reported that clear lakes had higher mean annual $p\text{CH}_4$ despite states having similar mean annual CH₄ diffusive flux. In this study we explore the contribution of physical and biological factors regulating surface $p\text{CH}_4$. Mean annual CH₄ diffusive fluxes and CH₄ fraction of oxidation (F_{ox}) were similar between states, implying a comparable mean annual CH₄ input. $k\text{CH}_4$ was significantly higher than $k\text{CO}_2$, suggesting occurrence of CH₄ microbubbles, yet $k\text{CH}_4$ was higher in turbid lakes than in clear lakes, implying a higher microbubble formation in turbid lakes. Furthermore, in turbid lakes there were positive relationships between k and wind speed, and between k and $p\text{CH}_4$, yet in clear lakes these relations were absent. Results suggest that submerged vegetation suppresses wind induced turbulence in clear vegetated lakes, decoupling $k\text{CH}_4$ from wind and reducing microbubble formation, therefore augmenting $p\text{CH}_4$ in their surface waters. Overall, physical rather than biological factors appear to control the observed differences in $p\text{CH}_4$ between states.

Keywords: methane, submerged macrophytes, gas exchange, microbubbles, turbulence, methane oxidation

INTRODUCTION

Freshwater systems are a significant component of the global carbon cycle (Tranvik et al., 2018) and they emit substantial amounts of methane (CH₄) to the atmosphere (Bastviken et al., 2011). Within freshwater systems, shallow lakes are considered to be biogeochemical hot spots and are distributed worldwide (Downing 2010; Holgerson and Raymond 2016). In some regions, shallow lakes can present two contrasting states: a clear water state dominated by submerged macrophytes, with low turbidity and low phytoplankton biomass, and a turbid water state dominated by phytoplankton, with high turbidity and no submerged vegetation (Scheffer et al., 1993; Sánchez et al., 2015). Submerged vegetation plays a key role in maintaining clear vegetated states by preventing sediment

resuspension, by taking up nutrients from the water column, and by providing refuge for zooplankton, among others (Scheffer 2001; Hilt 2015). Their presence can also affect other processes, such as primary production, carbon burial rates and greenhouse gas (GHG) emissions (Hilt et al., 2017). In particular, the effect of submerged vegetation or phytoplankton on CH₄ dynamics is not well understood (Hilt et al., 2017). Submerged vegetation can enhance methanogenesis by providing macrophyte-derived carbon to the sediments (Emilsson et al., 2018; Grasset et al., 2019), but phytoplankton-derived carbon has also been reported to enhance methanogenesis in sediments (Schwarz et al., 2008; West et al., 2012). Similarly, alternative states could have a differential effect on methane oxidation (MOX). The activity of methane oxidizing bacteria (MOB) depends mainly on, O₂ concentration and light penetration, where lower O₂ concentrations in combination with a reduction of light favors methanotrophs (Thottathil et al., 2018). Both submerged vegetation and phytoplankton can generate high oxygen concentrations and they can also diminish light penetration in the water column (Torremorell et al., 2009; Andersen et al., 2017). At the same time, it has been shown that submerged vegetation diminishes wind induced turbulence in the water column (Herb and Stefan 2005; Andersen et al., 2017), which could have a physical effect on gas exchange with the atmosphere, and this effect is not present in turbid phytoplanktonic lakes. Thus, it is not straightforward to predict potential biological—methanogenesis and methanotrophy—and physical - gas exchange with the atmosphere and also vertical and horizontal transport - differences in CH₄ dynamics between clear vegetated and turbid algal shallow lakes.

In a previous study we reported that clear vegetated shallow lakes from the Pampean Plain of Argentina had higher mean annual surface water CH₄ partial pressure ($p\text{CH}_4$) in comparison with turbid algal lakes (Baliña et al. under revision). However, we also reported that clear and turbid lakes presented similar mean annual CH₄ diffusive fluxes. The average CH₄ concentration in the water is the net balance between the rates of input to the water column, oxidation within the water column, and outflux to the atmosphere (Vachon et al., 2019; Noyce and Megonigal, 2021). Given that the average fluxes to the atmosphere were similar between states (Baliña et al. under revision), the differences in average $p\text{CH}_4$ could be the result of a physical effect due to differences in gas exchange, potentially combined with a biological effect, due to differences in the net balance between input and oxidation in the water column between the two states. CH₄ can be emitted from surface waters by diffusive flux, a strictly fickian process which depends on the concentration gradient at the water-air interface and the gas exchange velocity (k) and, in some cases, CH₄ can also be emitted in the form of microbubbles (Bastviken et al., 2004; Beaulieu et al., 2012). If CH₄ microbubbles are present, they can generate an additional flux of CH₄ to the atmosphere which will lead to increased measured k that is difficult to distinguish from that of purely diffusive k , and to a decoupling between CH₄ and CO₂ exchange velocities (Beaulieu et al., 2012; Prairie and del Giorgio 2013; McGinnis et al., 2015). This is a CH₄ emission pathway that is thought to relate positively to both water column turbulence and surface water CH₄

concentration (Prairie and del Giorgio 2013; McGinnis et al., 2015; Tang et al., 2016), yet it is currently difficult to predict whether these two contrasting lake states may be associated with an increased incidence of microbubbles.

In this study we assess both biological and physical factors influencing ambient surface $p\text{CH}_4$ in these shallow lakes: as biological factors, we explored potential differences in overall CH₄ oxidation between clear vegetated and turbid algal lakes, and by combining the patterns of oxidation and diffusive flux we infer potential differences in CH₄ input between states. As physical factors, we explored potential differences in $k\text{CH}_4$ between clear vegetated and turbid algal shallow lakes and also possible differences in the relationship between $k\text{CH}_4$ and wind, and between $k\text{CH}_4$ and $p\text{CH}_4$. In addition, we compared the patterns of $k\text{CO}_2$ and $k\text{CH}_4$ to infer differences in CH₄ microbubble dynamics between the two states.

MATERIALS AND METHODS

Study Area and Design

This study was carried out in the Pampean Plain (Buenos Aires, Argentina), a region with an exceptionally flat landscape that has a mean annual precipitation of 935 mm and mean annual temperature of 15.3°C (Allende et al., 2009). This region is characterized by the presence of hundreds of thousands of shallow lakes (Geraldini et al., 2011) that are eutrophic to hypereutrophic, polymictic (Diovisalvi et al., 2015), and that can be mostly found under two alternative states: a clear vegetated state dominated by submerged macrophytes, and a turbid algal state dominated by phytoplankton (Allende et al., 2009). For this study, we used data collected from four shallow lakes of the Pampean Plain: two in a clear vegetated state dominated by submerged macrophytes—La Segunda (SG) and Kakel Huincul (KH)—and other two in a turbid algal state, dominated by phytoplankton and with no submerged macrophytes—El Burro (BU) and La Salada Monasterio (SA) - (Figure 1). Lakes were sampled seasonally between 2018 and 2019, in winter (11–25 June 2018), spring (16–23 October 2019), summer (3–7 February 2019) and autumn (22–30 April 2019). In each field campaign physical, chemical, and biogeochemical parameters were measured (see specific parameters and related details below).

Baliña et al. (under revision) presented the environmental background data, $p\text{CH}_4$ and $p\text{CO}_2$, and flux data obtained for these lakes during the above-mentioned campaigns. Here we focus on the patterns of $k\text{CH}_4$ and $k\text{CO}_2$ derived from those diffusive fluxes and surface water $p\text{CH}_4$ and $p\text{CO}_2$, as well as on the isotopic signature of the surface water CH₄, which was used to derive CH₄ oxidation extent. Below we provide a summary of the methods used to obtain the surface water gas concentrations and diffusive fluxes (further details can be found in Baliña et al. (under revision)) and also the methods used to obtain the gas exchange velocities, the isotopic signature of surface water CH₄ and fresh CH₄ bubbles, and the calculation of CH₄ fraction of oxidation. Background information of the studied lakes can be found in **Supplementary Table S1**.

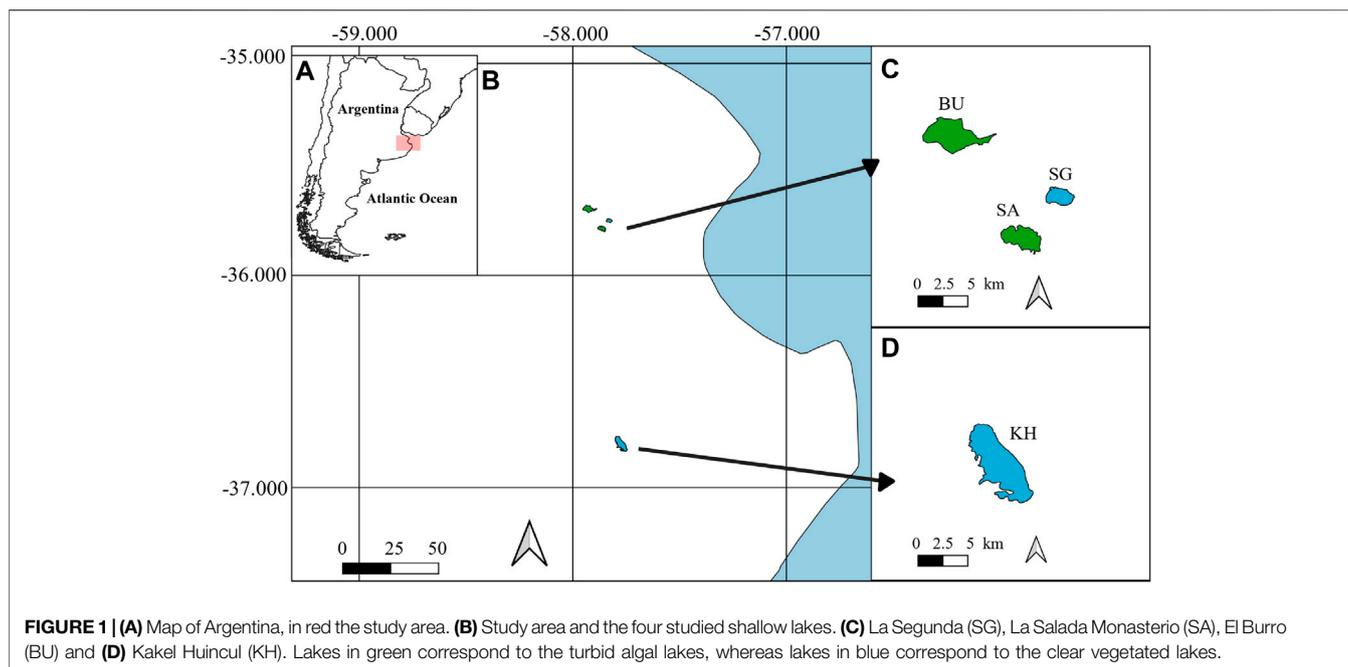


FIGURE 1 | (A) Map of Argentina, in red the study area. (B) Study area and the four studied shallow lakes. (C) La Segunda (SG), La Salada Monasterio (SA), El Burro (BU) and (D) Kakel Huincul (KH). Lakes in green correspond to the turbid algal lakes, whereas lakes in blue correspond to the clear vegetated lakes.

Environmental Parameters

In each shallow lake we measured surface water temperature and dissolved oxygen using a multi parameter HACH HQ30D portable sensor (HACH, United States). We also measured air temperature, atmospheric pressure, and wind speed using a Kestrel (4,000 Pocket Weather Tracker, Nielsen-Kellerman).

CH₄ and CO₂ Dissolved in the Water and Their Isotopic Signature

We took samples of surface waters to determine CH₄ and CO₂ partial pressure (*p*) in the water using the headspace technique, as described in Baliña et al. (under revision). Briefly, we filled two 60 ml syringes with 30 ml of water and 30 ml of atmospheric air, creating a 1:1 ratio of water: air. The syringes were then shaken for 2 min to ensure equilibration of the gas between the two phases. After equilibration, the 30 ml of air in the syringe were injected into a 30 ml glass pre-evacuated vial equipped with a crimped rubber stopper (Exetainer, Labco) for subsequent analysis in a cavity ringdown spectrometer (CRDS, Picarro G2201-i) (Maher et al., 2013) that determines *p*CH₄ and *p*CO₂ along with δ¹³C-CH₄ isotopic signature. To obtain the original *p* and isotopic signature of the CH₄ in the water, these data were subsequently corrected for the ambient air *p*CO₂ and *p*CH₄, the headspace ratio, *in situ* temperature of the water, water temperature after equilibration of the gas, the atmospheric pressure and the isotopic fractionation in the liquid:gas interface (Soued and Prairie 2020). *p*CH₄ and *p*CO₂ are reported as parts per million in volume (ppmv) and CH₄ isotopic data are reported in the standard delta notation (δ) expressed in per mil (‰) relative to the Vienna Pee Dee Belemnite standard (Whiticar 1999).

Diffusive Flux

Diffusive fluxes of CH₄ and CO₂ at the water-air interface were measured using a floating chamber (volume = 18.8 L, area = 0.1 m²) equipped with a valve that allows to sample the chamber headspace, and also with an internal thermometer to track headspace temperature. We took samples from the chamber headspace at intervals of 5 min for 15 min, obtaining four time points. At each time point, we took two samples of air that were injected into 30 ml glass pre-evacuated vials equipped with crimped rubber stoppers (Exetainer, Labco), for subsequent analysis in a cavity ringdown spectrometer (CRDS, Picarro G2201-i). At each sampling time we also registered temperature. The diffusive flux of each gas (*Flux gas*) was determined in mmol m⁻² d⁻¹ following Eq. 1:

$$Flux\ gas = \left(\frac{s \cdot V}{mV \cdot A} \right) \cdot t \quad (1)$$

Where *s* is the accumulation rate of gas in the chamber (ppmv min⁻¹), *V* is the volume of the chamber (L), *mV* is the molar volume of the gas (L mmol⁻¹) - which is corrected for the temperature in the chamber -, *A* is the chamber surface area (m²), and *t* is a factor that converts minutes to days (1 day = 1,440 min) (DelSontro et al., 2016).

Isotopic Signature of Fresh Methane Bubbles

We captured fresh CH₄ bubbles to estimate the isotopic signature of fresh CH₄ that we subsequently used as a source endmember in the oxidation mass balance. We used an inverted funnel (area = 0.3 m²) tied to a floating device that was deployed in the water. A glass bottle was filled with water from the lake and screwed to the

neck of the funnel. After this, sediments were stirred using an oar, causing the liberation of fresh CH₄ bubbles from the sediment through the water column and into the bottle (**Supplementary Figure S1**). We took two 30 ml air samples from the headspace that was generated in bottle and injected this air into 30 ml glass pre-evacuated vials equipped with crimped rubber stoppers (Exetainer, Labco), for subsequent analysis in a cavity ringdown spectrometer (CRDS, Picarro G2201-i). We determined δ¹³C-CH₄ signature, as described for the gas dissolved in the water.

Estimation of the Extent of Water Column CH₄ Oxidation (F_{ox})

To explore possible differences in CH₄ oxidation between clear vegetated and turbid algal shallow lakes, we performed isotopic mass balances using two different models: a steady state open model (**Eq. 2**; Happell et al., 1994) and a non-steady state closed model (**Eq. 3**; Liptay et al., 1998). These models estimate a fraction of oxidation (F_{ox}) based on different assumptions. The first model assumes a steady state system whereas the second considers that the water body may be in a dynamic, not at steady state condition (Thottathil et al., 2018).

$$F_{ox} = \frac{(\delta^{13}C_{WT} - \delta^{13}C_{source})}{(\alpha - 1) * 1000} \quad (2)$$

$$\ln(1 - F_{ox}) = \frac{(\ln(\delta^{13}C_{source} + 1000) - \ln(\delta^{13}C_{WT} + 1000))}{(\alpha - 1)} \quad (3)$$

δ¹³C_{source} is the isotopic signature of the source of methane, in this case the isotopic signature of the fresh CH₄ bubbles; δ¹³C_{WT} is the isotopic signature of the CH₄ within the water column; and α is the isotopic fractionation factor related to microbial CH₄ oxidation. We used a value of α = 1.021 following Coleman et al. (1981) and Thottathil et al. (2018). Additionally, we also calculated F_{ox} using values of α = 1.005 and α = 1.031 (Alperin et al., 1988; Whiticar 1999; Clayer et al., 2018) to better qualify the uncertainty around the selected α value, which is an intermediate value within the mentioned range.

Exchange Velocities Derived From Flux Measurements

The gas exchange velocity (*k*) is a rate equivalent to the depth of the water column that is equilibrated with the atmosphere per unit time (Prairie and del Giorgio 2013). This parameter was obtained using the measurements of diffusive flux and of gas dissolved in the surface waters, following **Eq. 4**:

$$k = \frac{Flux\ gas}{Kh * \Delta pGas} \quad (4)$$

Where *Flux gas* is the diffusive flux for CH₄ or CO₂ determined using **Eq. 1** (mmol m⁻² d⁻¹), *Kh* is the Henry's constant correspondent to each gas corrected for atmospheric pressure and water temperature, and Δ*pGas* is the difference between the

partial pressure of the respective gas in the water (P_w) and the partial pressure of the gas in equilibrium with the atmosphere (P_{eq}), i.e., Δ*pGas* (ppmv) = P_w - P_{eq}.

In order to allow comparison between gas exchange velocities, individual *k*_{CH₄} and *k*_{CO₂} were standardized to a Schmidt number of 600, following **Eq. 5**:

$$k_{600} = \frac{k_{CO_2\ or\ CH_4}}{(Sc_{CO_2\ or\ CH_4}/600)^{-n}} \quad (5)$$

Where *Sc* is the Schmidt number of a given gas at a given temperature (Wanninkhof 1992), and *n* is a value that depends on wind speed. We used a value of *n* = 2/3 for ambient wind speeds <3.7 m s⁻¹ and of *n* = 1/2 for ambient wind speeds >3.7 m s⁻¹ (Guérin et al., 2007).

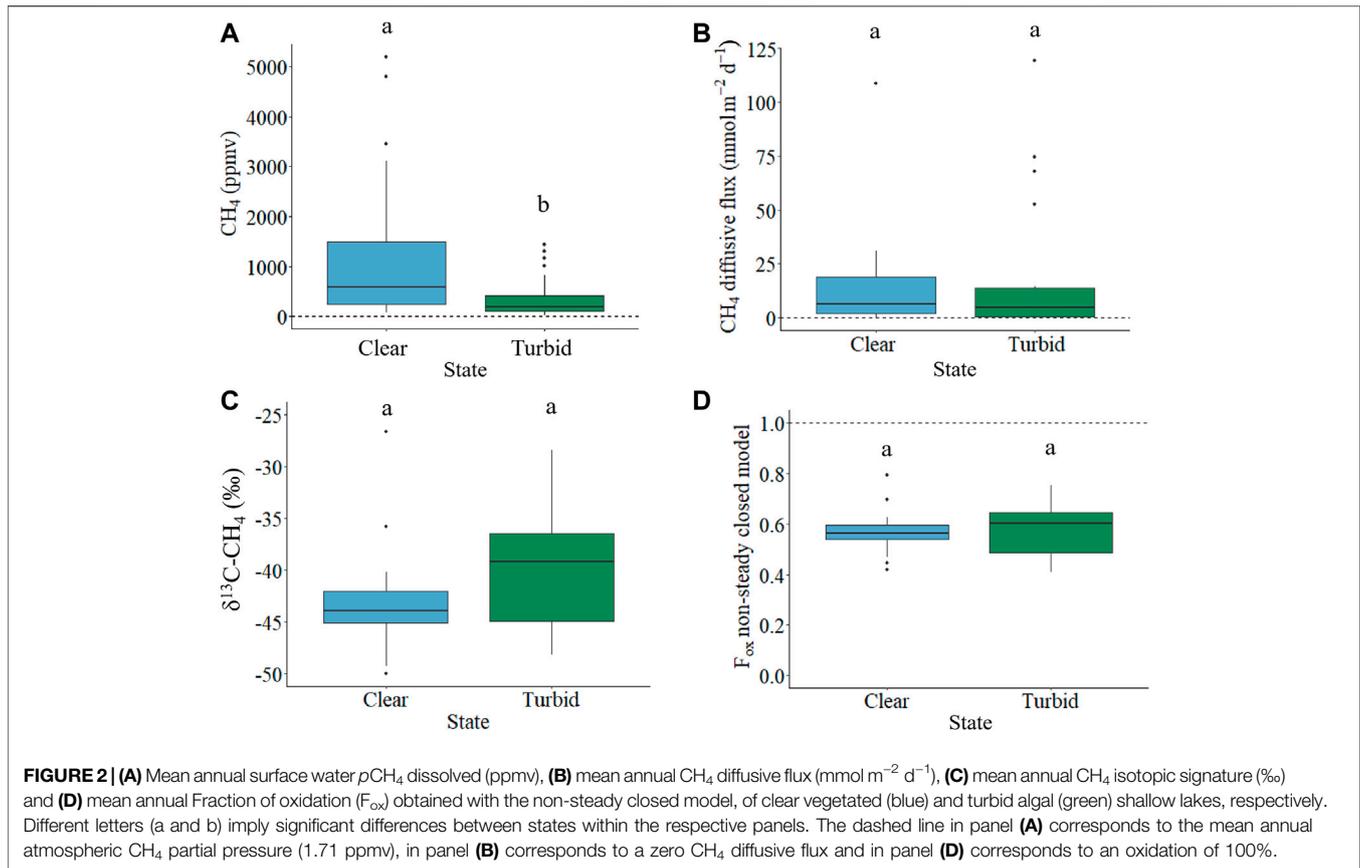
Statistical Analyses

To explore differences in mean annual CH₄ F_{ox} between states, we used a mixed generalized linear model with one fixed factor (state) and two random factors (season and lake). Since F_{ox} is a fraction we used the Beta distribution, which has a fixed domain between 0 and 1. We tested differences between *k*₆₀₀ CO₂ and *k*₆₀₀ CH₄ using a mixed general linear model with one fixed factor (gas, CO₂ or CH₄) and two random factors (season and lake). To test differences between states in *k*₆₀₀ derived from CH₄ and *k*₆₀₀ derived from CO₂, we used a mixed general linear model with one fixed factor (state) and two random factors (season and lake). To explore relations between *k*₆₀₀ CH₄ vs. wind, *k*₆₀₀ CH₄ vs. *p*CH₄, and *k*₆₀₀ CO₂ vs. wind, we performed simple linear regressions for each state, including in all cases two random factors (season and lake).

We tested the assumptions for each model: for the F_{ox} model we analyzed the distribution of standardized residuals vs. predicted values to explore homogeneity of variances. For the rest of the models, residuals were tested to fit the assumptions of normality and homogeneity of variances. The F_{ox} model was carried out using the package “glmmTMB” (Brooks et al., 2017). The rest of the models were done using package “lmerTest 3.1-2” (Kuznetsova et al., 2017). Normality was checked with package “Stats 3.6.2” (Royston 1982) and homogeneity of variances was checked by exploring the relation between standardized residuals vs. predicted values and also with package “Car 3.0-8” (Fox and Sanford., 2018). If homogeneity of variances was not fulfilled, we modeled heteroscedasticity by means of three different functions: varIdent, varPower and varExp (Zuur et al., 2009) using package nlme 3.1-142 (Jose et al., 2019). All tests were performed at the 95% significance level using R version 3.6.2 in the RStudio environment version 1.2.5019 (R Core Team 2019). Figures were plotted with the package “ggplot2 3.3.2” (Hadley, 2016).

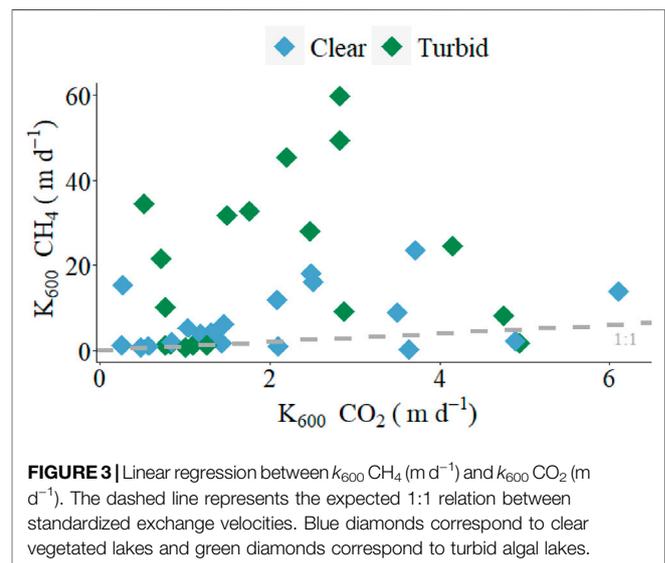
RESULTS

Clear vegetated lakes had three-fold higher mean annual *p*CH₄ than turbid algal lakes (1,181.7 ± 1,375.8 ppmv and 358.9 ± 390.4 ppmv, respectively) (*p* = 0.002, *df* = 1, *F* = 10.6; **Figure 2A**; data from Baliña et al. (under revision)).

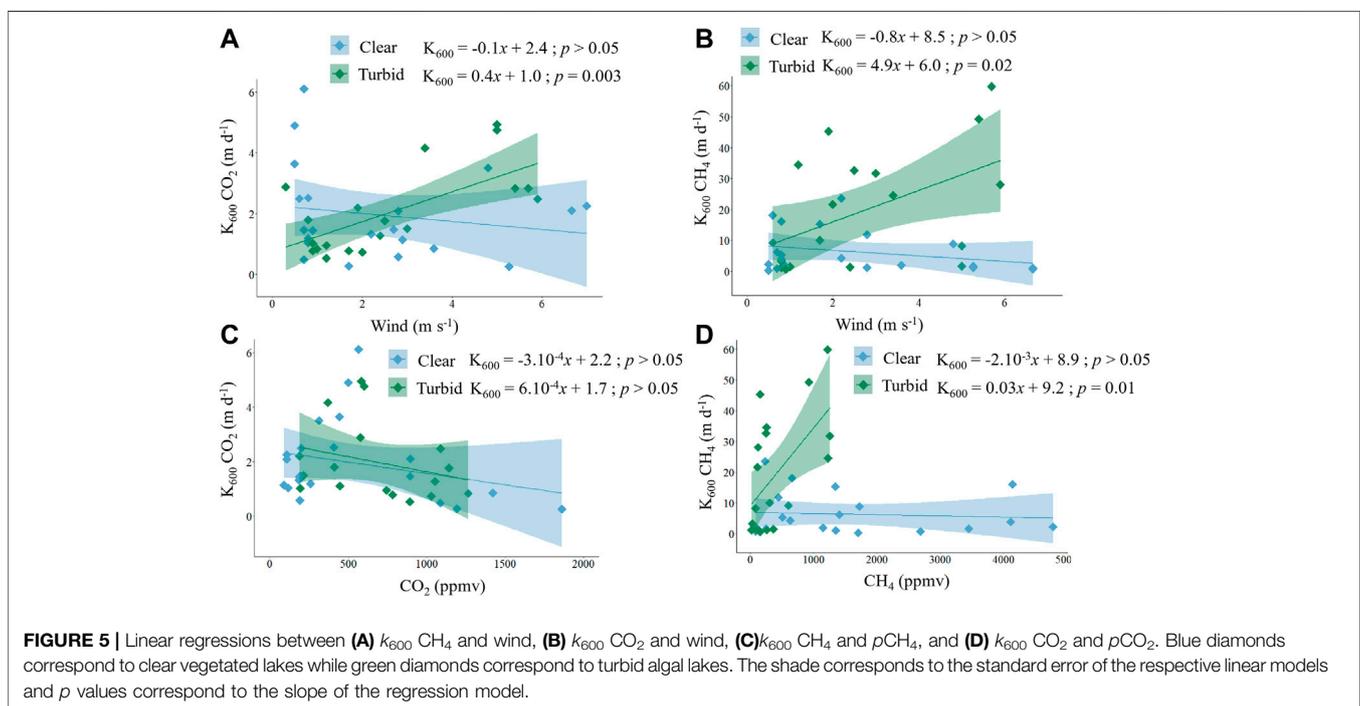
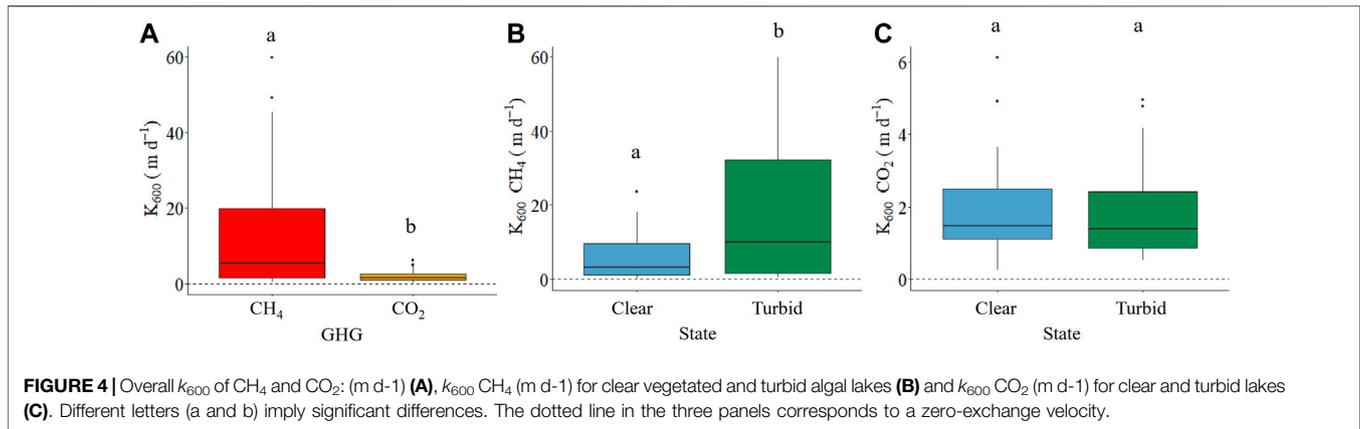


Nonetheless, clear vegetated and turbid algal lakes had similar mean annual CH_4 diffusive fluxes (14.4 ± 24.2 and $19.9 \pm 33.5 \text{ mmol m}^{-2} \text{d}^{-1}$, respectively) (Figure 2B; data from Baliña et al. (under revision)). Mean annual $\delta^{13}\text{C}-\text{CH}_4$ was similar between clear vegetated and turbid algal shallow lakes and in both states and the isotopic signatures corresponded to enriched values related to fresh sediment CH_4 (Figure 2C and Supplementary Table S2). Our estimates of mean annual CH_4 fraction of oxidation (F_{ox}), obtained using the non-steady state closed model and assuming an average fractionation (α) of 1.021, were also very similar between clear vegetated and turbid algal lakes (average 0.57 ± 0.09 and 0.58 ± 0.11 , respectively; Figure 2C). The steady state open model was not appropriate for these systems, since in a significant number of cases it yielded F_{ox} values higher than one (Supplementary Figure S2), as has been observed in other studies (Bastviken et al., 2002; Barbosa et al., 2018; Thottathil et al., 2018). Using $\alpha = 1.005$ we obtained nonsensical F_{ox} values for both closed and open models, whereas using $\alpha = 1.031$ we obtained logical F_{ox} values for both closed and open models that were in the range of the results obtained with α of 1.021 (Supplementary Figure S3).

There was a large range in measured k_{600} values based on either CO_2 or CH_4 across lakes (from 0.3 to 59.8 m d^{-1}), and although both agreed well for approximately 32% of observations, there was a high proportion of points that



deviated significantly from the expected 1:1 relationship, and most of these points corresponded to turbid shallow lakes (Figure 3). The overall mean annual $k_{600} \text{CH}_4$ ($12.7 \pm 15.1 \text{ m d}^{-1}$) was significantly (6.4 times) higher than mean annual $k_{600} \text{CO}_2$ ($1.98 \pm 1.43 \text{ m d}^{-1}$), ($p < 0.0001$, $df = 1$, $F =$



19.7; **Figure 4A**). There were also differences between states in the patterns of gas exchange: mean annual k_{600} CH_4 was 3 times higher in turbid lakes ($19.3 \pm 18.9 \text{ m d}^{-1}$) than in clear lakes ($6.7 \pm 7.0 \text{ m d}^{-1}$) ($p = 0.0092$, $df = 1$, $F = 7.5$, **Figure 4B**), whereas mean annual k_{600} CO_2 was similar between clear and turbid lakes ($2.0 \pm 1.5 \text{ m d}^{-1}$ and $2.0 \pm 1.4 \text{ m d}^{-1}$, respectively, **Figure 4C**).

We explored the relationships between K_{600} and wind speed and also between K_{600} and CH_4 and CO_2 partial pressure in the water, separately for clear vegetated and turbid algal lakes. Mean annual wind speed was similar between clear vegetated and turbid algal lakes (**Supplementary Figure S4**). There was a significant positive relationship between k_{600} CO_2 and wind speed (**Figure 5A**) and also between k_{600} CH_4 and wind speed

(**Figure 5B**), but in both cases these relationships were present only for turbid algal lakes and were not significant for clear vegetated lakes. These two relationships with wind in turbid lakes, however, are strikingly different: the slope of the k_{600} CH_4 vs. wind relationship (4.9 ± 1.9) is one order of magnitude higher than that of k_{600} CO_2 (0.4 ± 0.1), and the intercepts are significantly different as well (6 ± 7.7 vs. 1 ± 0.5 , respectively). Regarding dissolved GHG, $p\text{CO}_2$ was weakly and negatively related to k_{600} CO_2 in both clear vegetated and turbid algal shallow lakes, and the relationship was similar for both states (**Figure 5C**). Likewise, there was a weak (but not significant) negative relationship between ambient $p\text{CH}_4$ and k_{600} CH_4 in clear vegetated lakes yet, interestingly, there was a strong significant positive relationship between $p\text{CH}_4$ and k_{600} CH_4 in turbid algal lakes (**Figure 5D**).

DISCUSSION

Surface water $\delta^{13}\text{C}\text{-CH}_4$ corresponded to enriched methane in both clear vegetated and turbid algal shallow lakes (between -50% and -25%), followed by also similar percentages of CH_4 oxidation (mean of 57%) and, therefore, implying a high methanotrophic activity in both states. A comparable range of $\delta^{13}\text{C}\text{-CH}_4$ was reported for a subtropical shallow wetland from Australia (-53 and -39% , Jeffrey et al., 2019) and a shallow Boreal lakes (-60 and -35% , Desrosiers et al., 2021). A wider range of F_{ox} , also obtained using a non-steady state model, was reported for different habitat types within a shallow boreal lake (Desrosiers et al., 2021), with values ranging from 34% to 56% in *Brasenia* and *Typha* dominated habitats and down to 31% in open water areas. A wide range has also been reported for subtropical (15%–36%, Jeffrey et al., 2019), tropical (34%–100%; Barbosa et al., 2018), boreal (57%–75%; Bastviken et al., 2002) and temperate lakes (2%–97%; Thottathil et al., 2018) of varying size. This broad range of F_{ox} both within and across aquatic systems, highlights the complexity in the regulation of CH_4 oxidation. In this regard, the convergence in annual average F_{ox} between clear vegetated and turbid algal lakes despite their contrasting environmental conditions is remarkable.

Although there was significant seasonal variability in $p\text{CH}_4$ in both clear vegetated and turbid algal lakes (Baliña et al. (under revision)), this variation was centered around very different mean annual $p\text{CH}_4$ values for each state. Assuming that these annual means reflect an average steady state partial pressure of each lake state and are not varying greatly, then the amount of CH_4 exchanged at the water-air interface on an annual basis reflects the total CH_4 input to the water column (which includes CH_4 production in the sediments and water column, as well as lateral input) minus the CH_4 oxidized. Considering that annually the fraction of oxidation and the rates of diffusive flux were similar between states, we can infer that on an annual basis CH_4 input would be rather comparable between clear vegetated and turbid algal shallow lakes. CH_4 production in the sediments depends mainly on temperature, oxygen concentration and on the amount and type of organic matter (Megoñigal et al., 2003; Duc et al., 2010). Both macrophyte and phytoplankton derived organic matter are known to favor methanogenesis (Emilsson et al., 2018; Yan et al., 2019), but the extent to which the dominance of these different sources of organic matter may condition carbon cycling and methanogenesis at the ecosystem level is not well understood, with few studies having assessed this impact (Brothers et al., 2013). Although in this study we do not explicitly address CH_4 production, these results imply a comparable mean annual CH_4 input between clear vegetated and turbid algal states, which could be plausible since the characteristics of both states seem to favor sediment methanogenesis. Independent of sediment production, several authors have demonstrated that there is also a significant potential for CH_4 production in the water column (Grossart et al., 2011; Bogard et al., 2014; Günthel et al., 2019). Whereas there are studies that have explored possible isotopic signatures for this CH_4 (Günthel et al., 2020; Hartmann et al., 2020), there is to date no clear information of what the isotopic signature of this

fresh pelagic CH_4 could be. Therefore, we could not include this source of CH_4 in the isotopic mass balance. Nonetheless, we consider that for the purpose of the present study it is sufficient to include a sedimentary methane source to derive a first order estimate of oxidation extent.

In our study, $k_{600}\text{CH}_4$ was 6.4 times higher than $k_{600}\text{CO}_2$. Previous studies have reported $k_{600}\text{CH}_4$ to be on average 1.8-fold higher than $k_{600}\text{CO}_2$ in two boreal lakes (Rantakari et al., 2015), 2.3-fold higher in a Canadian hydroelectric reservoir and boreal lakes (Prairie and del Giorgio 2013), 2.5-fold times higher in oligotrophic Lake Stechlin (McGinnis et al., 2015), and 2.5-fold higher in a tropical reservoir from Brazil (Paranaíba et al., 2018). In all cases, the differences between CH_4 and CO_2 exchange velocities were explained by the presence of CH_4 microbubbles, which result in a $k_{600}\text{CH}_4$ that is higher than that from diffusive exchange alone (Beaulieu et al., 2012; Prairie and del Giorgio 2013) and, therefore, generates a decoupling between $k_{600}\text{CH}_4$ and $k_{600}\text{CO}_2$ (Prairie and del Giorgio 2013; McGinnis et al., 2015). Moreover, we observed that turbid lakes had higher $k_{600}\text{CH}_4$ than clear lakes, which would suggest a differential CH_4 microbubble formation between states. CH_4 microbubbles are thought to be produced as a combination of CH_4 supersaturation and turbulence (Vagle et al., 2010; Prairie and del Giorgio 2013; McGinnis et al., 2015). Although clear vegetated lakes had a higher mean annual $p\text{CH}_4$ than turbid algal lakes, overall $p\text{CH}_4$ was high in both states, and even higher in comparison with other studies that reported CH_4 microbubble formation (Prairie and del Giorgio 2013; McGinnis et al., 2015; Tang et al., 2016). Therefore, both clear vegetated and turbid algal lakes could potentially harbor the production of CH_4 microbubbles in terms of the amount of CH_4 present in the water column. On the other hand, water column turbulence is substantially different between states, as evidenced by the different relationship that exists between $k_{600}\text{CO}_2$ and wind speed and as has been reported in previous studies (Herb and Stefan 2005; Andersen et al., 2017): in clear vegetated lakes submerged vegetation tends to suppress wind induced turbulence in the water column, whereas in turbid algal lakes the absence of submerged vegetation allows a higher wind induced turbulence. This might explain the observed apparent higher CH_4 microbubble formation in turbid algal lakes, leading to higher $k_{600}\text{CH}_4$ in comparison with clear vegetated lakes, in spite of average lower $p\text{CH}_4$.

Most models of diffusive gas exchange in lakes have positively linked k_{600} to wind speed (Sebacher et al., 1983; Raymond and Cole 2001; Guérin et al., 2007) and, if CH_4 microbubbles are present, $k_{600}\text{CH}_4$ is also expected to have a positive correlation with $p\text{CH}_4$ (Prairie and del Giorgio 2013). Our results suggest a fundamentally different response of CH_4 and CO_2 to wind forcing in turbid algal lakes, evidenced by the slope of the regressions, which also point towards CH_4 microbubble formation. In clear vegetated lakes, in contrast, neither $k_{600}\text{CH}_4$ nor $k_{600}\text{CO}_2$ were significantly related to wind, yet $k_{600}\text{CH}_4$ was nevertheless consistently higher than $k_{600}\text{CO}_2$, also implying CH_4 microbubble formation but with a different behavior towards wind turbulence. The positive and expected relationship between $k_{600}\text{CH}_4$ and $p\text{CH}_4$ was found only for turbid algal lakes and is consistent with a pattern of wind induced

microbubble formation that is enhanced by increasing supersaturation of CH_4 . This was not the outcome for clear vegetated lakes, implying that this wind vs. $p\text{CH}_4$ interaction is largely suppressed in vegetated habitats. On the other hand, ambient $p\text{CO}_2$ was weakly and negatively related to $k_{600} \text{CO}_2$ in both states in a very similar manner, which is coherent with the expected role of gas exchange as a modulator of ambient gas concentrations in surface waters, as has been previously reported for lakes (Lapierre et al., 2013) and rivers (Rocher-Ros et al., 2019). Therefore, in turbid algal lakes the combination of wind and $p\text{CH}_4$ determine $k_{600} \text{CH}_4$, yet in clear vegetated lakes, gas exchange is largely decoupled from wind, and under this circumstance a reciprocal relationship is established between $p\text{CH}_4$ and gas exchange: the wind-independent and relatively constant k in clear vegetated lakes leads to high $p\text{CH}_4$ because it acts as a lid, yet $p\text{CH}_4$ also appears to influence $k_{600} \text{CH}_4$, because the high $p\text{CH}_4$ leads to higher $k_{600} \text{CH}_4$ relative to CO_2 through microbubble formation. Submerged vegetation therefore influences gas dynamics two-fold in these clear vegetated lakes: directly by modulating the effect of wind on water column turbulence and therefore on gas exchange velocity, as is the case on CO_2 exchange, but also indirectly, by altering the dynamics of microbubble formation and therefore of CH_4 exchange.

Previous studies have also reported a strong impact of aquatic vegetation on gas exchange in shallow lakes. Kosten et al. (2016) reported a lower CH_4 exchange velocity in the presence of free-floating vegetation in comparison with open water sites, where the higher $p\text{CH}_4$ detected below the floating vegetation was partly explained by the lower k . Likewise, Barbosa et al. (2020) reported that vegetated and open water habitats from a tropical floodplain lake had similar CH_4 diffusive fluxes but that vegetated habitats

had higher $p\text{CH}_4$, which was linked to a higher k in open water sites. Martinsen et al. (2020) also reported a lower CO_2 exchange velocity in a small shallow lake when submerged macrophytes were more abundant and related this observation with a negative effect of vegetation on the mixing of the water column. In our case, $k_{600} \text{CO}_2$ did not differ in average magnitude between lake states, but as pointed out above, the relationship between $k_{600} \text{CO}_2$ and wind differed markedly between states. An almost complete decoupling between exchange velocity and wind has been reported in previous studies carried out in small lakes (Heiskanen et al., 2014; Tedford et al., 2014; Tan et al., 2021), where wind-based models (Cole and Caraco 1998; Crusius and Wanninkhof 2003; MacIntyre et al., 2010) did not adequately explain the observed patterns in gas exchange, and where other factors, such as convection, had a stronger influence on gas exchange velocities. In our study, wind speed was a good predictor for $k_{600} \text{CO}_2$ and $k_{600} \text{CH}_4$ but only in turbid algal lakes. In clear vegetated lakes, submerged vegetation seems to decouple this relationship, therefore the use of wind speed would not be a good predictor for exchange velocities in these systems.

Overall, our results imply a roughly comparable mean annual CH_4 input to the water column between lakes in turbid algal and clear vegetated states, the latter inferred from similar mean annual CH_4 diffusive fluxes and mean annual CH_4 fraction of oxidation. We also observed that mean annual $p\text{CH}_4$ in clear lakes was 3 times higher than in turbid lakes, while mean annual $k_{600} \text{CH}_4$ in turbid lakes was 3 times higher than in clear lakes. Furthermore, the higher $k_{600} \text{CH}_4$ in turbid lakes was associated with a positive relationship with wind and $p\text{CH}_4$, and these relationships were absent in clear vegetated shallow lakes. Therefore, the higher $p\text{CH}_4$ in clear vegetated lakes could be explained by their lower average $k_{600} \text{CH}_4$ and also by the absence

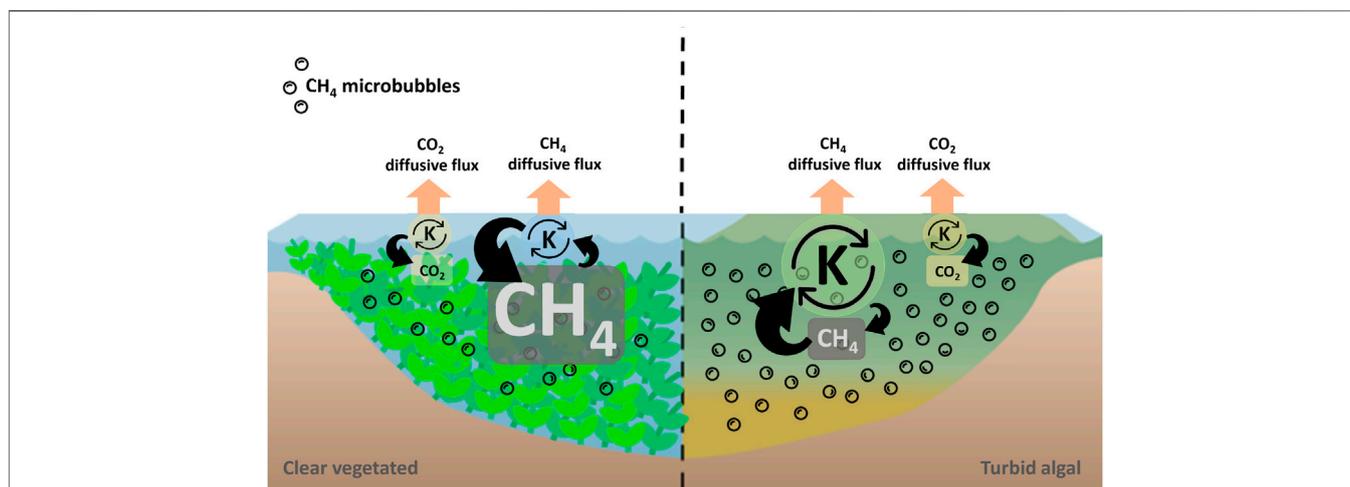


FIGURE 6 | Conceptual scheme of a plausible explanation for the observed results: states had similar mean annual CO_2 diffusive flux, $p\text{CO}_2$ and $k_{600} \text{CO}_2$. States also had similar mean annual CH_4 diffusive flux, but clear vegetated lakes had higher mean annual $p\text{CH}_4$ than turbid algal lakes. This difference in mean annual $p\text{CH}_4$ between states was explained by a lower mean annual $k_{600} \text{CH}_4$ in clear vegetated lakes, where submerged vegetation reduced wind induced turbulence in the water column, therefore diminishing CH_4 microbubbles formation. Overall, $p\text{CO}_2$ is controlled by $k_{600} \text{CO}_2$ in both states, as expected, but regulation of CH_4 is more complex: in clear lakes $p\text{CH}_4$ is mainly controlled by gas exchange ($k_{600} \text{CH}_4$) but there is also a minor control of $p\text{CH}_4$ over $k_{600} \text{CH}_4$, reflected in a consistently elevated $k_{600} \text{CH}_4$ relative to $k_{600} \text{CO}_2$ but that is independent of $p\text{CH}_4$ and wind. In turbid lakes, apparent $k_{600} \text{CH}_4$ is mainly controlled by wind and secondarily by $p\text{CH}_4$ through wind-driven CH_4 microbubble formation, whereas average $p\text{CH}_4$ is itself secondarily influenced by $k_{600} \text{CH}_4$.

of a relation between $k_{600} \text{CH}_4$ and wind, which further suggests a lower CH_4 microbubble formation. These patterns seem to be driven by a physical effect produced by the submerged vegetation over the mixing of the water column: a reduction of water column turbulence apparently leads to both a lower exchange velocity and also to a reduction of CH_4 microbubble formation, consequently leading to higher surface water $p\text{CH}_4$ in clear vegetated lakes (Figure 6). Furthermore, whereas $p\text{CO}_2$ is at least in part controlled by $k_{600} \text{CO}_2$, as expected, $p\text{CH}_4$ seems to be differentially controlled depending on the lake state: on one hand, in clear lakes $p\text{CH}_4$ is primarily controlled by gas exchange, yet $k_{600} \text{CH}_4$ is to some degree also influenced by $p\text{CH}_4$, since there is some degree of microbubble formation and $k_{600} \text{CH}_4$ is still systematically higher than $k_{600} \text{CO}_2$. In turbid algal lakes, on the other hand, $p\text{CH}_4$ appears to influence the apparent $k_{600} \text{CH}_4$ through wind-driven CH_4 microbubble formation, but there is also a control of $k_{600} \text{CH}_4$ over $p\text{CH}_4$ (Figure 6). Therefore, physical rather than biological processes - i.e. methanogenesis and methanotrophy - seem to be controlling the differences observed in surface water mean annual $p\text{CH}_4$ between clear vegetated and turbid algal shallow lakes from the Pampean plain.

The observation that $k_{600} \text{CH}_4$ is systematically higher than $k_{600} \text{CO}_2$ is consistent with the formation and subsequent emission of CH_4 microbubbles, and similar observations have been reported for rivers (Beaulieu et al., 2012; Campeau et al., 2014), lakes (McGinnis et al., 2015; Rantakari et al., 2015; Jansen et al., 2020), and reservoirs (Prairie and del Giorgio 2013; Paranaíba et al., 2018), with enhancement values ranging from 1.8 to 2.5. Although this appears to be a widespread phenomenon, the data are still sparse because there are surprisingly few studies that have measured CH_4 air-water exchange in parallel to that of another gas that can be used as a reference. As a result, the CH_4 microbubble dynamics in inland waters remains poorly constrained (Jansen et al., 2020), and this adds a large degree of uncertainty to current models and budgets of freshwater CH_4 emissions that already include ebullitive, diffusive and plant mediated fluxes. Here we have shown that there is indeed an interaction between wind velocity and surface water CH_4 concentration in determining the relative enhancement of $k_{600} \text{CH}_4$ but that this combined effect is only present in turbid shallow lakes. In vegetated clear lakes, the presence of submerged macrophytes seems to greatly dampen wind-induced water column turbulence, and under this scenario, $k_{600} \text{CH}_4$ responds to neither wind speed nor to $p\text{CH}_4$. Had we sampled lakes in only one state, we may have perhaps concluded that $p\text{CH}_4$ regulates k , or that k regulates $p\text{CH}_4$, and yet both are occurring but under different habitat and

climatic combinations. It is clear that the regulation of water-air CH_4 exchange is complex, and an improved understanding of this process will require parallel CH_4 and CO_2 - or another reference gas - measurements carried out in a wide range of habitat and climatic conditions.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

SB contributed substantially to the data acquisition, laboratory, and statistical analyses, as well as to the writing of the manuscript. MLS contributed substantially to the data acquisition and to the drafting of the manuscript. PdG contributed substantially to the study's conception, to the analyses of the results, and the drafting of the manuscript.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenvs.2022.892339/full#supplementary-material>

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