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Diffuse CO_2 and CH_4 emissions of two volcanic lakes on Pico Island (Azores)

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Abstract

This study investigates the diffuse flux of carbon dioxide (ΦCO_2) and methane (ΦCH_4) from Capitão and Caiado lakes, on Pico Island (Azores archipelago, Portugal), aiming to characterize the spatial and temporal variability of greenhouse gas (GHG) emissions in volcanic lake systems. Field measurements were conducted using dynamic and static accumulation chambers for ΦCO_2 and ΦCH_4 during multiple seasonal surveys.

The study highlights that ΦCO_2 and ΦCH_4 in these volcanic lakes are mainly driven by biogeochemical processes rather than direct volcanic degassing. Total ΦCO_2 at Capitão Lake ranged from 0.10 t d^{-1} (4 t km^{-2} d^{-1}) in spring to 0.08 t $^{-1}$ (3.64 t km^{-2} d^{-1}) in summer, likely due thermal stratification limiting CO_2 release in the latter period. In contrast, Caiado Lake exhibited higher ΦCO_2, increasing from 0.31 t $^{-1}$ (5.96 t km^{-2} d^{-1}) to 0.40 t $^{-1}$ (7.69 t km^{-2} d^{-1}), possibly influenced by methane oxidation. Methane emissions were significantly lower than CO_2 but showed notable seasonal variation. The ΦCH_4 at Capitão Lake increased tenfold from 0.096 kg $^{-1}$ (4 kg km^{-2} d^{-1}) in warmer conditions to 0.96 kg $^{-1}$ (40 kg km^{-2} d^{-1}) in winter, likely due to water column mixing allowing methane to easily escape from oxidation. At Caiado Lake, ΦCH_4 increased from 1.39 kg $^{-1}$ (23.96 kg km^{-2} d^{-1}) to 2.67 kg $^{-1}$ (46.03 kg km^{-2} d^{-1}) in the same period. Carbon dioxide largely dominates GHG emissions in the studied lakes, even computing CH_4 in terms of CO_2-eq, being the ΦCO_2 2 to 3 orders of magnitude higher than ΦCH_4.

Keywords:
Greenhouse gases, CO_2 flux, CH_4 flux, volcanic lakes, Pico Island, Azores

1. Introduction

Methane (CH_4) and carbon dioxide (CO_2) levels in the atmosphere have been increasing significantly in the last decades, therefore contributing to global warming, because of rising emissions of greenhouse gases (GHG) fueled by human activities (Houghton, 2015).

Lakes have been identified as important CO_2 and CH_4 sources to the air (DelSontro et al., 2018; Saunois et al., 2025). The global carbon dioxide emission rate has been estimated as in the range of 2.44×10^2 to 5.83×10^2 Tg yr^{-1} (Cole et al., 1994; Holgerson and Raymond, 2016; DelSontro et al., 2018), despite higher computations ranging from 1.28×10^3 to 1.4×10^3 Tg yr^{-1} (Tranvik et al., 2009; Raymond et al., 2013). Regarding methane, the global emission rate was estimated as in the range between 8 and 75 Tg yr^{-1} Smith and Lewis, 1992; Bastviken et al., 2004, 2011; Saunois et al., 2016, 2020; Johnson et al., 2022). Despite the lower CH_4 emission rate from surface water bodies relative to CO_2, the global warming potential of methane is far greater, estimated at 27 times the one of carbon dioxide over a century-long period (Forster et al., 2021).

GHG emissions from lakes mostly depend on their surface area and trophic state (Bhushan et al., 2024), and a seasonality effect has been identified in several studies (Lesley and Lewis, 1992; Eugster et al., 2020). For example, ΦCH_4 variation along spatial and temporal scales are influenced by various factors, such as salinity (Liu et al., 2024), lake level and depth (Li et al., 2021; Yuan et al., 2021), trophic state (Beaulieu et al., 2019) and temperature (Duc et al., 2010).

Lakes located within active volcanic areas are often affected by the interaction with magmatic systems (Varekamp et al., 2015 and references therein). Besides other endmember components, such as meteoric, hydrothermal and biogenic processes, magmatic volatiles are a main source of gases in volcanic lakes, which can even lead to hazardous processes (Christenson and Tassi, 2015). The overall CO_2 emission rate from volcanic lakes was estimated at about 32 ± 5.2 Tg yr^{-1}, 80% of which presenting a magmatic origin (Pérez et al., 2011). No global estimation for CH_4 emissions from volcanic lakes is available so far, nevertheless methane is a minor component in geothermal and volcanic emissions worldwide in comparison to CO_2 (Etiope et al., 2019). To proceed with direct measurement of ΦCO_2 several methods have been widely used (Mazot and Bernard, 2015 and references therein), being the floating accumulation chamber a simple and low-cost method, able to provide meaningful results in low to moderate wind conditions (lower than 8 to 10 m s^{-1}; Kremer et al., 2003). Regarding ΦCH_4 several methods are also available, among which the widely used static floating chambers, that might lack sufficient accuracy to address the highly temporal variation commonly associated to CH_4 emissions or ebullition pathways (Mu et al., 2022, 2022).

The present study was made at Pico, one of the volcanic islands belonging to the Azores archipelago, located in the North Atlantic Ocean between latitudes 37ºN and 40ºN and longitudes 25ºW and 31ºW, at approximately 1,500 km from mainland Portugal (Figure 1A). Pico Island covers an area of 447 km^2, being the second largest in the Azores (Figure 1B). At Pico Island 28 lakes and ponds have been inventoried, about 32% of the lakes in the Azores, summing up a total area of about 0.16 km^2 and approximately a storage of 2.32×10^5 m^3 (Porteiro, 2000). Excluding the small ponds spread at Pico, the six major lakes in the island (Capitão, Caiado, Peixinho, Rosada, Paúl and Seca) are located within scoria cones craters (33%), tectonic depressions (33%) and undifferentiated depressions (33%) (Cruz et al., 2006; Andrade et al., 2019c). The two studied lakes are the largest surface water bodies in the Island, being located at about 800 m a.s.l (Figure 1C).

Several studies have addressed the impact of volcanic activity on lake water chemistry in the Azores (Martini et al., 1994; Cruz et al., 2006; Antunes, 2009; Andrade et al., 2024). Recent research has established a comprehensive and representative dataset of diffusive ΦCO_2 values from 45 lakes (Andrade et al., 2021 and references therein), being the total emission rate estimated as approximately 1.71×10^5 t d^{-1}, from which 42% are of volcanic origin (~7.1×10^4 t d^{-1}; Andrade et al., 2021). However, diffusive ΦCH_4 from the lakes of the Azores remain poorly studied, with the only relevant study addressing dissolved CH_4 from selected lakes at São Miguel Island (Tassi et al., 2018).

The current study aims to characterize both diffuse ΦCO_2 and ΦCH_4 in two lakes on Pico Island, considering a spatial and temporal perspective, thus allowing to identify the key factors driving the fluxes of those GHG from the studied water bodies.

2. Study area

2.1 Geological setting

The studied lakes are located in the western sector of Planalto da Achada Fissural Volcanic (also known as São Roque – Piedade Volcanic System). Planalto da Achada Fissural Volcanic System is one of the two active volcanic systems of Pico Island. It consists of an elongated triangular-shaped volcanic ridge broadly WNW–ESE-oriented that occupies the central and eastern sectors of the island. Its geomorphology is characterised by a central upland area (above ~600 m altitude, reaching a maximum elevation of 1,076 m a.s.l.) that extends from the eastern flank of Pico central volcano to the eastern tip of the island, which is marked by several alignments of scoria and spatter cones, spatter ramparts, and eruptive fissures. The 30 km-long volcanic ridge is sided by steep slopes of up to 25°-30°, made by basaltic lava flows that extend to the north and south coastlines, occasionally forming coastal lava deltas and fossil cliffs (Cruz, 1997; Madeira, 1998; Nunes, 1999).

Capitão Lake corresponds to a small sag pond, with a length of 350 m and a maximum width of 150 m, which occupies an elongated tectonic depression along the Capitão Lake fault scarp trending WNW–ESE (Madeira, 1998; Madeira and Brum da Silveira, 2003). This tectonic depression lies in an area of undifferentiated pyroclastic deposits. However, the neighbouring scoria cones belong to the Inferior Unit of the São Roque – Piedade Volcanic Complex, with an estimated age of over 50 ka (Nunes, 1999). Radiocarbon dates of paleosols from a nearby trench revealed ages between ~5,300 and 1,000 years BP (Madeira, 1998; Madeira and Brum da Silveira, 2003). Although the age of Capitão Lake is unknown, the earliest lake sediments recovered are dated at 2,118 cal years BP (Saez et al., 2025).

Caiado Lake is in the central sector of Planalto da Achada Fissural Volcanic System, lying in the central part of the WNW–ESE-oriented Capitão Lake fault zone. It fills a small, broadly circular, undifferentiated depression with gentle slopes, approximately 450 m by 400 m across. Caiado Lake fills a depression in an area of undifferentiated pyroclastic deposits. However, most of the neighbouring scoria cones belong to the Inferior Unit of the São Roque – Piedade Volcanic Complex, with an estimated age of over 50 ka. A few younger cones are also found in the vicinity, belonging to the Inferior Subunit of the Intermediate Unit, with an estimated age between 50 and 10 ka (Nunes, 1999). Although the age of Caiado Lake is unknown, the earliest lake sediments recovered are dated at 1,418 cal years BP (Saez et al., 2025).

Secondary manifestations of volcanism at Pico Island comprises mostly steam emissions dominated by water vapor with minor concentrations of N_2, CO_2, O_2 and Ar (Viveiros et al., 2017). Few CO_2 soil diffuse degassing anomalies were identified in the island associated with tectonic structures, and the most relevant are coupled with thermal anomalies in the summit of the stratovolcano (Viveiros et al., 2017).

2.2 Hydrological setting

The Azores archipelago experiences a high average annual precipitation of 1930 mm yr^{-1}, which significantly exceeds the mean actual evapotranspiration of 581 mm yr^{-1}, resulting in substantial surface runoff, though of torrential nature, estimated at 3.22×10^8 m^3 yr^{-1} (DROTRH-INAG, 2001).

The average annual precipitation on Pico Island is strongly dependent on altitude, being estimated as in the range of 3,000 mm yr^{-1} to 3,500 mm yr^{-1} in the Capitão watershed and between 3,500 mm yr^{-1} to 4,000 mm yr^{-1} at the Caiado watershed (DROTRH, 2021). The same study estimated the average annual temperature in the coastal area of Pico Island as 18ºC, decreasing with altitude, following a gradient of about -0.9ºC for every 100 m-altitude increment, until the 400 – 600 m altitudinal range, above which the gradient decreases to -0.5ºC per 100 m-altitude step. However, at Pico Island, and despite the precipitation exceedance over actual evapotranspiration, surface runoff is entirely of torrential nature and the geological conditions favors infiltration, thus enhancing aquifer recharge (Cruz and Silva, 2001).

Capitão Lake occurs within a tectonic depression, presenting a surface area of 2.4×10^{-2} km^2 and a maximum depth of 4.9 m (Table S1 - supplementary material). The respective storage volume is estimated as 5.4×10^4 m^3 and taking into account a runoff inflow equal to 3×10^4 m^3 yr^{-1} (DROTRH, 2021) a residence time is computed (1.8 yr).

Caiado Lake, lying in an undifferentiated depression, has a surface area of 5.8×10^{-2} km^2 and a maximum depth of 6.9 m (Table S1 - supplementary material). The respective storage volume is estimated as 1.5×10^5 m^3, thus considering a runoff inflow equal to 4×10^4 m^3 yr^{-1} (DROTRH, 2021) a relatively higher residence time is computed (3.75 yr). The water level interannual variation is about ±2 m at Capitão Lake, and about ±2.5 m at Caiado Lake.

The watersheds of studied lakes have an area equal to 0.15 km^2 and 0.19 km^2 at Capitão and Caiado lakes, respectively (Table S1 - supplementary material). Land use at both catchments is dominated by forest and wetlands, being the total nitrogen and total phosphorous loads to the water bodies as high as 14.7 kg yr^{-1} and 3.67 kg yr^{-1}, respectively, at Caiado Lake (DROTRH, 2021). Nevertheless, nutrient loads are considered negligible nowadays.

Most lakes in the Azores archipelago are suffering an ongoing eutrophication process, and research about the trophic state on these water bodies has been extensively researched (Porteiro, 2000; Santos et al., 2005; Ribeiro et al., 2008; Martins et al., 2008, 2012; Gonçalves, 2008; Pacheco et al., 2005, 2010; Cruz et al., 2015; Malcata et al., 2022). Accordingly, both studied lakes have been designated as vulnerable zones following the EU Nitrates Directive (Directive 91/676/EEC) due to their trophic status.

Capitão Lake is nowadays in poor ecological status according to the EU Water Framework Directive criteria due to the ongoing eutrophication, while Caiado Lake, currently in mesotrophic conditions, has been classified as in good ecological status. This status is particularly relevant as eutrophication influences ΦCO_2 and ΦCH_4 from surface water bodies (Beaulieu et al., 2019).

3. Methodology

3.1 Water chemistry

The composition of the water of the studied lakes was characterized along vertical profiles made in different periods of the year, namely late spring (1st survey – May 2023), summer (2nd survey – August 2023), late autumn (3rd survey – November 2023) and winter (4th – February 2024). Samples were collected at 1-m depth interval in selected locations at each lake (P in both lakes; Figure 1.D and 1.E), using a 1 L-capacity SEBA sampling bottle, resulting in a total of 19 samples at each lake water body.

The pH, temperature, and electrical conductivity (EC), as well as titrations for the determination of the alkalinity and dissolved carbon dioxide content, following APHA-AWWA-WPCF (1985) guidelines, were determined in the field. The sampling and analytical procedures used were applied in previous investigations made in lakes from the Azores archipelago and are described in detail by Andrade et al. (2016).

For the determination of the δ^{13}C-DIC aliquots were collected following the International Atomic Energy Agency guidelines (IAEA, 2017) at the surface and bottom of each water body along the 1st survey). Analyses were made using a continuous-flow isotope-ratio mass spectrometry system (Thermo Electron), interfaced with a Flash HT plus elemental analyzer and a Delta V Advantage mass spectrometer (Stable Isotope Laboratory of Estación Biológica Doñana, CSIC). The maximum error range for δ^{13}C was ±0.15‰.

3.2 CO_2 flux

The ΦCO_2 measurements followed the accumulation chamber method (Chiodini et al., 1998), through portable equipment adapted to assure floatability (Mazot and Bernard, 2015). This approach was successfully employed in research made worldwide (e.g. Mazot and Taran, 2009; Hernández et al., 2011), as well as in studies made over surface water bodies spread in the Azores archipelago (Andrade et al., 2021 and references therein). A detailed description of the field equipment being used along the present study, as well as of the measurement procedures, is available in previous papers (Andrade et al., 2016).

ΦCO_2 measurements were done at the water surface according to a grid kept uniform whenever possible, totalizing 72 and 61 determinations at Capitão Lake along the 1st (spring) and 2nd (summer) surveys, respectively, and 101 and 95 measurements at Caiado Lake. The accurate location of each grid node was recorded with a GPS, and the water depth measurements were performed using a Garmin ECHOTM 500c bathymetric probe.

Statistical data processing methods were accomplished through the Graphical Statistical Approach (GSA) (e.g. Chiodini et al., 1998) and the sequential Gaussian simulation (sGs) (Deutsch and Journel, 1998; Cardellini et al., 2003). The description and expected outcomes from both methods were already comprehensively presented in previous research (Chiodini et al., 1998; Cardellini et al., 2003; Viveiros et al., 2010, 2017; Mazot and Bernard 2015).

Similar approaches were used in numerous studies made to quantify ΦCO_2 from surface water bodies spread in volcanic regions worldwide (e.g. Padrón et al. 2008; Mazot and Taran, 2009; Hernández et al. 2011; Mazot et al. 2011; Arpa et al. 2013; Mazot and Bernard, 2015; Sun et al. 2017), including research made in the Azores archipelago (Andrade et al. 2021 and references therein).

3.3 Methane flux

3.3.1 ΦCH_4 measurements

Static accumulation chambers were used to collect gas samples along several transects at the surface of the studied lakes, thus allowing to proceed to diffuse ΦCH_4 measurements. This approach is an adaptation of the static gas chamber system originally developed to perform gaseous diffuse fluxes measurements from surface to air (e.g. Livingston and Hutchinson, 1995).

To proceed with sampling collection, several static floating chambers (SFC) units were made from the lower sections of HDPE buckets, which were carefully cut to create cylindrical-shaped containers with a diameter of 40 cm and a height of 14 cm. For buoyancy, an inner tube of a tire was inflated and used as the floating base (Figure S1 – supplementary material). The bucket container was placed securely inside the tube, ensuring no air could enter. When the system was placed in the water around 2 to 3 cm of the inner tube stayed submerged, sealing the container´s interior from the surrounding atmosphere. A small opening at the top of the container was fitted with a three-way valve, which was utilized to collect gas samples. The valve stayed closed until a syringe was attached for sample extraction. The samples were then injected into 12 mL glass vials with screw caps and pierceable rubber septa using a two-needle system. These vials were pre-filled with slightly acidified deionized water (pH ~4) to avoid CO_2 dissolution, which was displaced by the sample during injection.

Samples are taken considering the increase of CH_4 concentration over time inside a chamber of known geometry (Cole et al., 2010). For that purpose, samples were collected at each SFC at two different time intervals, three minutes after placing the chamber in the water and again after 30 minutes.

The ΦCH_4 was measured during both the 3rd and the 4th surveys, respectively along autumn and winter. Each transect comprised six SFC located at regular intervals along a straight line, and during the 3rd survey 2 transects were made in both lakes, while 5 transects were completed during the 4th survey, which location was selected to ensure representativeness. Alongside gas samples, lake water temperature, pH and dissolved oxygen were measured at each sampling location, as well as water depth and air temperature. Gas analyses were made by gas chromatography (Department of Earth Sciences, University of Florence, Italy) following the procedure already described by Ghioldi (2021).

Equation (1) was used to compute ΦCH_4 in each SFC from the methane content in the vials (Tassi et al., 2013):

$$\Phi CH_4 = \frac{dCH_4}{dt} \times \frac{V}{A} \tag{1}$$

Where:

dCH_4/dt, increment of the CH_4 concentration inside the SFC chamber over time

V, volume of the SFC chamber

A, basal area of the SFC chamber

3.3.2 Modeled ΦCH_4

The diffusive ΦCH_4 across the water-air interface was also estimated from the measured dissolved concentration. For that purpose, the thin boundary layer model (Liss and Slater, 1974) was used, being the rationale and the required mathematical equations summarized by Venturi et al. (2021). For that purpose, ΦCH_4 results from multiplying gas transfer velocity by the difference between the measured and calculated CH_4 concentrations. Briefly summarizing, gas transfer velocity was previously calculated using an expression that combines a gas transfer coefficient normalized at 600, considering local wind speed data, as outlined by Crusius and Wanninkhof (2003), and the Schmidt number, obtained according to the temperature by a fourth order polynomial (Wanninkhof, 2014).

The dissolved gas content (CO_2, N_2, Ar, CH_4, O_2) was determined over water samples collected at each SFC location by filling 30-mL glass vials plunged just beneath the lake surface, preventing gas bubbles inside. The vials were filled by ¾ of their volume to make a headspace where dissolved gases equilibrate. Dissolved gases analysis through gas chromatography took place at the Department of Earth Sciences, University of Florence (Italy), following a methodology described in detail by Venturi et al. (2021).

4. Results

4.1 Water chemistry

Descriptive statistics for the main physico-chemical parameters and major-ion content are presented in Table S2 (supplementary material). Lake water temperature exhibited substantial variability across the different surveys. Higher temperatures are observed during the 2nd survey (summer), with values at surface as high as 26.7ºC and 22.6ºC, at Capitão and Caiado lakes, respectively, and in the former thermal stratification is observed, with a gradient between the surface and the bottom of -4.2ºC (Figure 2.A). Along the 1st survey (spring), water temperature ranged from 15.7ºC to 18.5ºC and between 14.7ºC and 16.7ºC. The lowest temperatures were recorded along the 3rd (autumn) and 4th (winter) surveys, during which values are homogeneous along the water column, ranging from 11.9ºC and 13.1ºC and between 12ºC and 12.3ºC, respectively at Capitão and Caiado lakes.

The pH values ranged from 6.69 to 8.76 at Capitão Lake, and from 6.98 to 8.06 at Caiado Lake. Most of the surveys reach values as high as 8.11, except for pH measurements made at Capitão Lake at the surface of the water body during the 2nd survey (max. = 8.76; summer). No major shifts are observed along the water column, despite a gradient between the surface and the bottom on the 1st survey (spring) at Capitão Lake that reaches 1.42 pH units (Figure 2.B). The highest values at surface are observed during the 2nd survey (summer) at both lakes, made in August 2023, as well as during the 1st survey (spring) at Capitão Lake, corresponding to the more elevated water temperatures, suggesting the influence of CO_2 removal through the enhanced biological activity (Finlay et al., 2019; Engel et al., 2019; Liang et al., 2017). At Capitão Lake, the deepest of the studied water bodies, this pattern could also reflect the stratification of the water column, with pH decrease with depth. Nevertheless, dissolved CO_2 profiles do not relate clearly to the pH variation along the water column (Figure 2.D), suggesting that besides pH other drivers seem to control the CO_2 dissolved in water. Values are in the range of 1.2 to 4.7 mg L^{-1} at Capitão Lake, while at Caiado vary between 0.9 and 2.3 mg L^{-1}.

EC measurements are very low, suggesting that lake waters have a very slightly dissolved content. Values range between 22 µS cm^{-1} and 28 µS cm^{-1} at Capitão Lake, and between 24 µS cm^{-1} to 31 µS cm^{-1} at Caiado Lake, being almost constant along the water column during the several surveys made (Figure 2.C).

The relative major-ion content is primarily dominated by Na^+ and Cl^-. Sodium ranges from 16.54% to 31.45% of the major-ionic content, and chloride explains 27.05% to 42.07% at Capitão Lake. Values for Caiado Lake are similar, ranging from 18.85% to 29.68% and from 33.94% to 44.37%, in both surveys respectively. Bicarbonate only explains 10.24% to 18.96%

and 8.09% to 23.34% of the relative ionic content at Capitão and Caiado lakes, respectively. Therefore, lake waters are mainly of the Na-Cl type (Figure 3), showing that seawater spraying is a major driver of lake water chemistry, despite a very few samples that present a slight alkali earth enrichment. This process was already suggested by previous work (Cruz et al., 2006; Andrade et al., 2024).

Despite the high altitude of the studied lakes, both are exposed to prevailing northern winds, facilitating sea salt deposition, and groundwater discharging from springs located at a similar altitudinal range and geographical also exhibits marine influence (Cruz and Silva, 2000). This influence is well documented in the Azores (Cruz and Amaral, 2004), and a similar effect was also described in the Madeira Island (Almeida and Romariz, 1984; Fernandes et al., 2020), even at high altitude areas.

The dissolved gas content is shown in Table S3 (supplementary material). Along Figure 4 the dissolved gas content at the surface of the studied lakes is shown through a box plot. The dissolved gases composition is dominated by N_2, that accounts for 63.5% to 68.6%, and from 67.8% to 75.4%, at Capitão and Caiado lakes, respectively. The N_2/Ar ranges from 36.1 to 44.1, and from 36.7 to 43.1, in both lakes, thus in the range of the Air Saturated Water (ASW) that varies between 38 and 42. The relative abundance of CO_2 ranges from 5.1% to 9.8% at Capitão Lake, being higher at Caiado Lake, ranging from 7.5% to 14.3%. Instead, CH_4 relative abundance does not exceed 1% across both lakes.

The N_2/O_2 molal ratio ranges between 2.5 and 3.0 at Capitão Lake, thus above the value for ASW (~1.9; Ghioldi, 2021), thus suggesting some O_2 consumption. At Caiado Lake, this ratio is even higher, ranging from 3.63 and 6.55, supporting O_2 depletion. This O_2 consumption may derive from biological activity, namely methane oxidation caused by microorganisms, as further discussed.

Along the 4th survey (winter) a positive correlation is observed among dissolved CO_2 and CH_4 content at Caiado Lake, although weak ($r = 0.354$), suggesting a common process of release. A similar relationship was observed during the 1st survey (spring) made at Capitão Lake ($r = 0.848$), although during the 4th survey (winter) an inverse linear relationship was observed ($r = -0.163$) in this water body. For both surveys a linear relationship was also observed between dissolved CH_4 and Ar/O_2 and despite been very weak seems to suggest that larger methane content may be associated to lower dissolved O_2.

4.2 GHG diffusive flux

The ΦCO_2 measurements descriptive statistics are presented in Table 1, and the respective spatial distribution is depicted in Figure 5. Values are higher in Caiado Lake in both surveys, varying between 3.2 and 11.7 g m^{-2} d^{-1} and from 2.9 to 26.5 g m^{-2} d^{-1}, respectively for the 1st (spring) and the 2nd (summer) field surveys. At Capitão Lake, ΦCO_2 values ranged from 1.9 to 9.1 g m^{-2} d^{-1} and from 1.1 to 7.3 g m^{-2} d^{-1}, during the same surveys, respectively. Values observed are in the same order of magnitude relative to previous studies made in Pico Island (Andrade et al., 2019).

Two contrasting behaviors are observed, as from spring to summer ΦCO_2 decreases at Capitão Lake but increases at Caiado Lake. Moreover, cumulative probability plots reveal that for Capitão Lake there is a single lognormal population of ΦCO_2 values (population “A” on Figures S2.A and S2.B – supplementary material). Instead, for Caiado Lake two populations are depicted (Figures S2.C and S2.D – supplementary material), population “A” corresponding to very low ΦCO_2 values, in the range of 2.9 g m^{-2} d^{-1} to 6.7 g m^{-2} d^{-1} and population “B” to slightly elevated measurements, varying between 4.2 g m^{-2} d^{-1} to 26.5 g m^{-2} d^{-1}, observed in the section of the lake where the vegetation in denser. However, for both lakes, values are lower than the 35 g m^{-2} d^{-1} threshold proposed in previous studies made in Furnas Lake (Andrade et al., 2016), under which ΦCO_2 may be associated only to a biogenic source. The δ^{13}C-DIC analysis performed further support a CO_2 biogenic origin, with values ranging from -23,66‰ to -25,02‰ and from -22,04‰ to -23,02‰, at Capitão and Caiado lakes, respectively, which are well below the isotopic signature of atmospheric CO_2 (~ -8.3‰; Clark, 2015). As Pico is an active volcanic Island is also relevant that δ^{13}C values are also lighter relative to typical mantellic values, that are on the range between -3.5‰ to -6‰ (Cartigny et al., 2001) (Figure S3 – supplementary material).

Spatial analysis using variograms for ΦCO_2 data revealed a spherical or exponential structure, with nugget values ranging from 0.28 to 0.6 for Capitão Lake (Figure S4.A and S4.B – supplementary material) and from 0.01 to 0.35 at Caiado Lake (Figure S4.C and S4.D – supplementary material). The spatial influence of each measurement point extended from 60 to 75 m at Capitão Lake and from 70 to 110 m at Caiado Lake.

The distribution of observed and calculated ΦCH_4 data across the different transects for both surveys are shown by means of a boxplot, showing that theoretical estimates derived from the TBL model are in close agreement with field measurements made through the SFC (Tables S4 and S5 – supplementary material). This outcome agrees with findings from Ghioldi (2021) which compared field measurements with model predictions using three different approaches, showing that Crusius and Wanninkhof (2003) was the most accurate.

At Capitão Lake, the measured ΦCH_4 values during the two surveys ranged from 0.003 to 0.006 g m^{-2} d^{-1} for the 3rd survey (autumn) and from 0.025 to 0.210 g m^{-2} d^{-1} (winter; Table 2). The interquartile range (IQR) was smaller in the 3rd survey (0.001 g m^{-2} d^{-1} compared to the 4th survey (0.007 g m^{-2} d^{-1}, indicating a slightly greater variability in the latter.

For Caiado Lake, measured ΦCH_4 values ranged from 0.021 to 0.029 g m^{-2} d^{-1} in the 3rd survey (autumn) and from 0.031 to 0.066 g m^{-2} d^{-1} in the 4th survey (winter; Table 2). Like Capitão Lake, the IQR for Caiado was lower in autumn (0.003 g m^{-2} d^{-1}) compared to the winter survey (0.015 g m^{-2} d^{-1}, indicating a greater variability in the latter. This variability is also evident in the boxplot comparison of the two surveys (Figure 6), as well as in the ΦCH_4 distribution across the studied lakes (Figure 7), reflecting the spatial and temporal heterogeneity of dissolved methane in aquatic systems (Hoffman, 2013). Alterations in lake dynamics across temporal and spatial scales affect the spatial distribution and timing of methane production (Ward et al., 2020), and the balance between CH_4 oxidation and formation is influenced by several factors, such as temperature (Duc et al., 2010) and the hydrological characteristics of the water body itself, that controls oxygen availability along the water column (Bastviken et al., 2002).

5. Discussion

5.1 ΦCO_2 variation pattern and main drivers

The CO_2 emission rate estimated through the sGs method was equal to 0.10 t d^{-1} and 0.08 t d^{-1} for the 1st (spring) and 2nd (summer) surveys made in Capitão Lake, respectively, which normalized by the area corresponds to a ΦCO_2 of 4.00 t km^{-2} d^{-1} and 3.64 t km^{-2} d^{-1} (Table 3). Values for Caiado Lake were equal to 0.31 t d^{-1} (5.96 t km^{-2} d^{-1}) and 0.40 t d^{-1} (7.69 t km^{-2} d^{-1}) along the 1st and 2nd surveys, respectively.

Emission estimates based on the GSA method are consistent with the sGs data, with rates ranging from 0.10 t d^{-1} to 0.07 t d^{-1} and from 0.29 t d^{-1} to 0.45 t d^{-1} in the two studied lakes. These total ΦCO_2 values are lower to those by Andrade et al. (2021) which reported CO_2 output values from 45 lakes in the Azores archipelago ranging from 0.43 t km^{-2} d^{-1} to 503.33 t km^{-2} d^{-1} (mean = 18.05 ±71.7 t km^{-2} d^{-1}; median = 4.61 t km^{-2} d^{-1}). Although, this dataset is biased as included two lakes that are clearly influenced by deep-seated CO_2 input of volcanic origin, thus excluding this water bodies the range from Andrade et al. (2021) is much lower (mean = 5.70 ± 6.04 t km^{-2} d^{-1}; median = 4.51 t km^{-2} d^{-1}), and values from Capitão and Caiado are aligned with this typical values for lakes where the CO_2 is of biogenic origin. The biogenic dominance also explains how ΦCO_2 in the studied lakes is much lower than the normalized average value for neutral volcanic lakes worldwide (201.2 t km^{-2} d^{-1}; Pérez et al., 2011).

As pointed out, the ΦCO_2 at Caiado Lake are higher during summer compared to those measured during spring, which is likely linked to the increasing water temperature in the former survey (Figure 2.A). As water temperature is known to enhance photosynthetic activity, a reduction of the CO_2 concentration maybe expected, thereby leading to a decrease in ΦCO_2, explaining how shallow lakes may act as carbon dioxide sinks from the atmosphere (Balmer and Downing, 2011), which however is not occurring at Caiado Lake. In this water body the increase in ΦCO_2 from the 1st (spring) to the 2nd survey (summer) may also be explained by methane oxidation (MOX), an aerobic process through which methanotrophic bacteria converts methane into CO_2, but consuming O_2 (Langenegger et al., 2022), which is consistent with the observed dissolved oxygen depletion compared to ASW. Methane oxidation has been described as effective in mitigating CH_4 emissions from aquatic environments, although resulting in higher ΦCO_2 (Sawacuchi et al., 2016).

Regardless the higher water temperature during summer, ΦCO_2 is slightly lower at Capitão Lake during this season relative to the spring survey. However, as shown by the temperature variation along the water column, the lake is stratified in the summer, thus most of the carbon dioxide is kept in the hypolimnion, limiting its diffusion to the atmosphere. A similar effect has been observed in the deepest lakes in the Azores, the ones that present a monomictic character, as for example at Furnas Lake, where the overall CO_2 emission is equal to ~52 t d^{-1} in the summer but reach values as high as ~600 t d^{-1} during winter full-mixing conditions (Andrade et al., 2016). Besides gas imprisonment in the hypolimnion, MOX efficiency at the epilimnion is expected to be lower, as oxidation is limited by reduced hydrostatic pressure and shorter gas transport paths leading to high gas transfer velocities (DelSontro et al., 2011; Li et al., 2020).

Through 100 equiprobable sGs simulations ΦCO_2 mapping was achieved for each survey, highlighting spatial variability across the lakes. Mapping for both field campaigns at Capitão Lake shows the effect of stratification along the water column in the 2nd (summer) survey as ΦCO_2, previously depicting a heterogeneous pattern in the 1st survey (spring), are concentrated in the lower depth areas, mainly close to the southeast and southwest margins (Figure 8.A and 8.B). Instead, when depth is higher ΦCO_2 decreases as CO_2 is kept in the hypolimnion. At

Caiado Lake, from spring to the summer survey is possible to show a shift in the spatial pattern, as in the latte ΦCO_2 is especially higher in the southwestern most area of the lake, where the vegetation is much denser (Figure 8.C and 8.D). A similar relation was observed in other lakes of the Azores (Andrade et al., 2020), and elevated ΦCO_2, as well as ΦCH_4, are associated to vegetated habitats compared to unvegetated ones, especially at shallow lakes (Desrosiers et al., 2022).

5.2 ΦCH_4 variation pattern and main drivers

Variations on ΦCH_4 are controlled by several internal and external factors, and even interannual variations often exceed diel variability (Smith and Lewis, 1992; Eugster et al., 2020). Within the internal factors being described in several studies worldwide, lake depth and surface area, hydrological behaviour, water level fluctuations and trophic state are the most common, summing up to external factors, such as climate and watershed characteristics (Bastviken et al., 2004; Duc et al., 2010; Sanches et al., 2019; Li et al., 2020; Li et al., 2021; Yuan et al. 2021; Zhang et al., 2021; Zhong et al, 2023).

ΦCH_4 are higher in the 4th survey (winter) compared to the 3rd survey (autumn), despite similar water temperature in both surveys (Figure 2.A). Therefore, despite the control of temperature over methane production from lake sediment biota (Fuchs et al., 2016; Duc et al., 2010), this driver seems not explaining the much higher ΦCH_4 values from the autumn to the winter survey. During winter at Capitão lake, there is a positive linear relationship between the ΦCH_4 values and depth, although weak ($r = 0.304$), suggesting that in full-mixing conditions in this lake, as no stratification is observed in the water column, CH_4 is less able to avoid oxidation during ascent to the surface. Along the same survey at Capitão Lake there is a very weak linear relationship between dissolved CO_2 and CH_4 content, indicating that CH_4 oxidation may be limiting methane persistence in the water column. Instead, at the same water body, the dissolved CO_2 and CH_4 content are closely positively related during the autumn survey ($r = 0.848$).

At Caiado Lake, the ΦCH_4 values versus depth present an opposite trend relative to that show by Capitão Lake, as both variables present an inverse linear relationship ($r = 0.494$), and the dissolved CO_2 and CH_4 content are positively related during the autumn survey ($r = 0.354$). Despite the lower biological activity expected due to the lower temperature, as Caiado Lake is deeper than Capitão Lake, CH_4 should present low ability to escape to avoid oxidation. However, although not explored in the current research, the potential for CH_4 production by microbial production under aerobic conditions remains plausible. Moreover, in the studied lakes the water is oxygenated during autumn and winter when they are fully mixed due to their relatively low depths. This condition may support microbial CH_4 production in oxic waters, a process documented by Tassi et al. (2018) in lakes on São Miguel Island. This process involves microorganisms that metabolize methylated compounds, leading to the release of CH_4 even in oxygenated environments (Grossart et al., 2011; Schroll et al., 2023; Ordóñez et al., 2023).

Eutrophication of lake water bodies can also lead to relatively high ΦCH_4 values (Bealieu et al., 2019; Zhang et al., 2021, 2024), since CH_4 production is up to three times higher in eutrophic lakes relative to oligotrophic or mesotrophic systems (Casper, 1992; Ma et al., 2024; West et al., 2016; Yang et al., 2020; Zhang et al., 2021). This effect is particularly pronounced in shallow lakes, being characterized by a limited self-cleaning capacity (Havens et al., 2001; Li et al., 2020). Thus, the contrasting trophic state of the studied lakes may also influence the ΦCH_4 values, and the Chl-a content can be a measure of the biological activity in lake water (DelSontro et al., 2018). Unpublished quarterly monitoring data from February 2022 to December 2024, produced by the Azores water authorities (Directorate Regional for Climate Action and the Environment), show that Chl-a is much higher at Capitão Lake (mean = 41.04 ± 24.83 µg L^{-1}) relative to Caiado Lake (mean = 1.98 ± 049 µg L^{-1}). Therefore, the expected CH_4 enhanced production due to the trophic status is likely confined to Capitão Lake.

The total CH_4 emission from Capitão Lake, computed integrating the average flux by lake surface area, was 9.6×10^{-2} kg d^{-1} (4 kg km^{-2} d^{-1}) during the 3rd survey (autumn), being 10 times higher along the 4th survey (winter). Similar computation for Caiado Lake provides a total CH_4 output of 1.39 kg d^{-1} (23.96 kg km^{-2} d^{-1}) during the autumn survey, and 2.67 kg d^{-1} (46.03 kg km^{-2} d^{-1}) in winter. These estimates are falling below the mean ΦCH_4 computed by Rosentreter et al. (2021) for a dataset of lakes with areas between 0.01 and 0.1 km^2 (0.098 g m^{-2} d^{-1}), although are like the median value of ΦCH_4 from those water bodies (0.041 g m^{-2} d^{-1}).

Methane is a very effective greenhouse gas (GHG), being the global warming potential 27 times higher than CO_2 on a 100-year time span (Forster et al., 2021). Nevertheless, carbon dioxide largely dominates GHG emissions in the studied lakes, even computing CH_4 in terms of $CO_{2\text{-eq}}$, being the former 2 to 3 orders of magnitude higher than the latter,

5. Summary and conclusions

This study provides a detailed assessment of diffuse ΦCO_2 and ΦCH_4 from Capitão and Caiado lakes, on Pico Island, offering new insights into greenhouse gas (GHG) emissions in volcanic lake systems of the Azores. By analyzing both spatial and temporal variations, we identified the key factors influencing gas fluxes, including water temperature, lake stratification, biological activity, and trophic status. Main findings reveal distinct seasonal patterns and suggest that while biogenic processes dominate, eutrophication also plays a significant role in regulating GHG emissions.

The CO_2 emissions varied between lakes and seasons; at Capitão Lake, total CO_2 emission was estimated at 0.10 t d^{-1} (4 t km^{-2} d^{-1}) during the first survey and decreased slightly to 0.08 t d^{-1} (3.64 t km^{-2} d^{-1}) in the second survey. At Caiado Lake, emissions were significantly higher, increasing from 0.31 t d^{-1} (5.96 t km^{-2} d^{-1}), in the spring survey, to 0.40 t d^{-1} (7.69 t km^{-2} d^{-1}) during summer. The observed variations in ΦCO_2 between seasons were closely linked to water temperature and stratification. During summer, Caiado Lake exhibited higher ΦCO_2, potentially due to enhanced methane oxidation, which converts CH_4 into CO_2 while consuming oxygen, consistent with observed dissolved O_2 depletion. In contrast, Capitão Lake showed a decrease in ΦCO_2 during the warmer months, likely due to thermal stratification preventing CO_2 from escaping from deeper layers.

Methane emissions, while much lower than CO_2, showed considerable seasonal variation. At Capitão Lake, CH_4 emission rate was 0.096 kg d^{-1} (4 kg km^{-2} d^{-1}) in the third survey (autumn), but increased tenfold to 0.96 kg d^{-1} (4o kg km^{-2} d^{-1}) in the fourth survey (winter), coinciding with full water column mixing, allowing methane to easily reach the surface before being oxidized. At Caiado Lake, values were significantly higher, increasing from 1.39 kg d^{-1} (23.96 kg km^{-2} d^{-1}) in the autumn survey to 2.67 kg d^{-1} (46.03 kg km^{-2} d^{-1}) during winter. Data suggests that biological processes, particularly methane oxidation and primary productivity, play a crucial role in controlling CH_4 concentrations. Additionally, trophic status appears to be a key driver of ΦCH_4, with Capitão Lake, which is in a poorer ecological condition due to eutrophication, showing a greater potential for methane production compared to the mesotrophic Caiado Lake. This aligns with previous studies indicating that eutrophic lakes tend to have higher ΦCH_4 due to increased organic matter availability and microbial activity.

Although both lakes are in a volcanic setting, the measured ΦCO_2 and ΦCH_4 align with values expected for lakes dominated by biogenic sources rather than deep-seated volcanic degassing. CO_2 emissions from Capitão and Caiado lakes were well within the range observed for other surface water bodies in the Azores. However, the role of microbial CH_4 production under aerobic conditions remains an open question, as some recent studies suggest that methylated compounds may serve as precursors for methane formation even in oxygenated environments. From a broader perspective, this study provides valuable data for assessing the contribution of volcanic island lakes to regional carbon cycling. While CO_2 emissions are dominant, the potential climate impact of CH_4 should not be overlooked, given its global warming potential, which is 27 times greater than CO_2 over a 100-year time scale. Even though ΦCH_4 in the studied lakes are relatively low compared to highly eutrophic or anoxic systems, their variability over time highlights the need for continued monitoring, particularly in the context of climate change and potential shifts in lake trophic status.

Future research should focus on the microbial mechanisms controlling CH_4 production and oxidation in these lakes, as well as long-term changes in eutrophication and their effects on GHG fluxes, besides pursuing a denser measurement network, namely for the measurement of ΦCH_4. Regarding specifically the ΦCH_4 there is the need to make research about ebullition emissions, that were no studied in the present paper. Moreover, expanding similar studies across other lakes in the Azores would provide a more comprehensive understanding of how volcanic, hydrological, and biological factors interact to shape greenhouse gas dynamics in island environments.

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References

Almeida, C., Romariz, C., 1984. Hidroquímica da ilha da Madeira. Recursos Hídricos 5, 33-42 (in Portuguese)

Andrade, C., Viveiros, F., Cruz, J.V., Coutinho, R., Silva, C., 2016. Estimation of the CO_2 flux from Furnas volcanic lake (São Miguel, Azores). J. Volcanol. Geoth. Res. 315, 51–64.

Andrade, C., Cruz, J.V., Viveiros, F., Branco, R., Coutinho, R., 2019. CO_2 degassing from Pico Island (Azores, Portugal) volcanic lakes. Limnologica 76, 72–81.

Andrade, C., Cruz, J.V., Viveiros, F., Coutinho, R., 2020. Diffuse CO_2 emissions from Sete Cidades volcanic lake (São Miguel Island, Azores): influence of eutrophication processes. Environ. Pollut. 268, 115624.

Andrade, C., Viveiros, F., Cruz, J.V., Coutinho, R., 2021. Global carbon dioxide output of volcanic lakes in the Azores archipelago, Portugal. Journal of Geochemical Exploration, 229, 106835 (doi: 10.1016/j.gexplo.2021.106835).

Andrade, C., Cruz, J.V., Viveiros, F., Moreno, L., Ferreira, L., Coutinho, R., 2024. Hydrogeochemical evolution and characterization study in volcanic lakes of the Azores archipelago (Portugal). App. Geochem. 164, 105933 (doi: 10.1016/j.apgeochem.2024.105933).

Antunes, P., 2009. Estudo hidrogeoquímico e vulcanológico de lagos no arquipélago dos açores: aplicações para a mitigação de riscos naturais. PhD Thesis. Universidade dos Açores, Ponta Delgada, 485 p. (in Portuguese with English abstract).

APHA-AWWA-WPCF, 1985. Standard methods for the examination of water and methods for the examination of water and wastewater. American Public Health Association, Washington.

Arpa, M.C., Hernández, P.A., Padrón, E., Reniva, P., Padilla, G.D., Bariso, E., Melián, G. V., Barrancos, J., Nolasco, D., Calvo, D., Pérez, N., Solidum Jr., R.U., 2013. Geochemical evidence of magma intrusion inferred from diffuse CO_2 emissions and fumaroles plume chemistry: the 2010–2011 volcanic unrest at Taal Volcano, Philippines. Bull. Volcanol. 75, 747 (doi: 10.1007/s00445-013-0747-9).

Balmer, M., Downing, J., 2011. Carbon dioxide concentrations in eutrophic lakes: undersaturation implies atmospheric uptake. Inland Waters 1, 125–132.

Bastviken, D., Ejlertsson, J., Tranvik, L., 2002. Measurement of methane oxidation in lakes: a comparison of methods. Environ. Sci. Technol. 36, 3354-3361.

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 Biogeochem. Cycles, 18, GB4009 (doi: 10.1029/2004GB002238).

Bastviken, D., Tranvik, L.J., Downing, J.A., Crill, P.M., Enrich-Prast, A., 2011. Freshwater methane emissions offset the continental carbon sink. Science, 331, 50 (doi: 0.1126/science.1196808).

Beaulieu, J.J., DelSontro, T., Downing, J.A., 2019. Eutrophication will increase methane emissions from lakes and impoundments during the 21st century. Nature Communications 10, 1375 (doi: 10.1038/s41467-019-09100-5).

Bhushan, A., Goyal, V.C., Srivastav, A.L., 2024. Greenhouse gas emissions from inland water bodies and their rejuvenation: a review. J. Water and Climate Change 15, 5626 (doi: 10.2166/wcc.2024.561).

Cardellini, C., Chiodini, G., Frondini, F., 2003. Application of stochastic simulation to CO_2 flux from soil. Mapping and quantification of gas release. J. Geophys. Res., 108 (B9), 2425 (doi: 10.1029/2002JB002165).

Cartigny, P., Harris, J.W., Javoy, M., 2001. Diamond genesis, mantle fractionations and mantle nitrogen content: a study of δ^{13}C–N concentrations in diamonds. Earth Planet Sci. Lett. 185, 85-98.

Casper, P., 1992. Methane production in lakes of different trophic state. Arch. Hydrobiol. 37, 139-154.

Chiodini, G., Cioni, R., Guidi, M., Raco, B., Marini, L., 1998. Soil CO_2 flux measurements in volcanic and geothermal areas. App. Geochem. 13, 543-552.

Christenson, B., Tassi, F., 2015. Gases in volcanic lake environments. In: Rouwet, D., Christenson, B., Tassi, F., Vandemeulebrouck, J., (Eds.), Advances in Volcanology. Springer, Heidelberg, 125-153.

Clark, I., 2015. Groundwater Geochemistry and Isotopes. CRC Press, Taylor & Francis Group, Boca Raton, 456 p.

Cole, J.J., Caraco, N.F., Kling, G.W., Kratz, T.K., 1994. Carbon dioxide supersaturation in the surface waters of lakes, Science 265, 1568-1570.

Cole, J.J., Bade, D.L., Bastviken, D., Pace, M.L., Van de Bogert, M., 2010. Multiple approaches to estimating air-water gas exchange in small lakes. Limnol. Oceanogr.: Methods 8, 285-293.

Crusius, J., Wanninnkhof, R., 2003. Gas transfer velocities measured at low wind speed over a lake. Limnol. Oceanogr. 48, 1010-1017.

Cruz, J.V., 1997. Estudo hidrogeológico da ilha do Pico (Açores - Portugal). PhD thesis, University of the Azores, 433 p

Cruz, J., Silva, M., 2000. Groundwater salinization in Pico Island (Azores, Portugal): origin and mechanisms. Environ. Geol. 39, 1181-1189.

Cruz, J., Silva, M., 2001. Hydrogeologic framework of Pico Island, Azores, Portugal. Hydrogeol. J. 9, 177-189.

Cruz, J.V., Amaral, C.S., 2004. Major ion chemistry of groundwater from perched-water bodies of the Azores (Portugal) volcanic archipelago. App. Geochem. 19, 445-459.

Cruz, J.V., Antunes, P., França, Z., Nunes, J.C., Amaral, C., 2006. Volcanic lakes from the Azores archipelago (Portugal): geological setting and geochemical characterization. J. Volcanol. Geotherm. Res. 156, 135–157.

Cruz, J.V., Pacheco, D., Porteiro, J., Cymbron, R., Mendes, S., Malcata, A., Andrade, C., 2015. Sete Cidades and Furnas lake eutrophication (São Miguel, Azores): analysis of long-term monitoring data and remediation measures. Sci. Total Environ. 520, 168-186.

DelSontro, T., Kunz, M.J., Kempter, T., Wüest, A., Wehrli, B., Senn, D.B., 2011. Spatial heterogeneity of methane ebullition in a large tropical reservoir. Environ. Sci. Technol. 45, 9866-9873

DelSontro, T., Beaulieu, J.J., Downing, J.A., 2018. Greenhouse gas emissions from lakes and impoundments: upscaling in the face of global change. Limnol. Oceanogr. Lett. 3, 64–75.

Desrosiers, K., DelSontro, T., del Giorgio, P.A., 2022. Disproportionate contribution of vegetated habitats to the CH_4 and CO_2 budgets of a boreal lake. Ecosystems 25, 1522-1541.

Deutsch C.V., Journel A.G., 1998. GSLIB: Geostatistical software library and user guide, 2nd ed., Oxford University, 363 p.

DROTRH, 2021. Plano de Gestão da Região Hidrográfica dos Açores (RH9) 2022-2027 – Relatório Técnico – Versão para consulta pública. Relatório Técnico. Direção Regional do Ordenamento do Território e do Ordenamento do Território, Ponta Delgada (in Portuguese).

DROTRH-INAG, 2001. Plano Regional da Água. Relatório técnico. Direção Regional do Ordenamento do Território e do Ordenamento do Território, Ponta Delgada, 575 p. (in Portuguese).

Duc, N.T., Crill, P., Bastviken, D., 2010. Implications of temperature and sediment characteristics on methane formation and oxidation in lake sediments. Biogeochemistry 100, 185-196.

Engel, F., Drakare, S., Weyhenmeyer, G.A., 2019. Environmental conditions for phytoplankton influenced carbon dynamics in boreal lakes. Aquat. Sci. 81, 35 (doi: 10.1007/s00027-019-0631-6).

Eugster, W., DelSontro, T., Shaver, G.R., Kling, G.W., 2020. Interannual, summer, and diel variability of CH_4 and CO_2 effluxes from Toolik Lake, Alaska,during the ice-free periods 2010–2015. Environ. Sci.: Processes Impacts 22, 2181-2198.Ghioldi (2021)

Etiope, G., Ciotoli, G., Schwietzke, S., Schoell, M., 2019. Gridded maps of geological methane emissions and their isotopic signature. Earth Syst. Sci. Data 11, 1-22.

Ferreira, L., Cruz, J.V., Viveiros, F., Durães, N., Coutinho, R., Andrade, C. Santos, J.F., Acciaioli, M.H., 2023. Hydrogeochemistry and strontium isotopic signatures of mineral waters from Furnas and Fogo volcanoes (São Miguel, Azores). Water 15, 245 (doi.org/10.3390/w15020245).

Fernandes, A.L., Cruz, J.V., Figueira, C., Prada, S., 2020. Groundwater chemistry in Madeira Island (Portugal): main processes and contribution to the hydrogeological conceptual model. Environ. Earth Sci. 79, 413 (doi: 10.1007/s12665-020-09151-8.

Finlay, K., Vogt, R.J., Simpson, G.L., Leavitt, P.R., 2019. Seasonality of pCO_2 in a hard-water lake of the northern Great Plains: The legacy effects of climate and limnological conditions over 36 years. Limnol. Oceanogr. 64, 2019, S118–S129.

Forster, P., Storelvmo, T., Armour, K., Collins, W., Dufresne, J.-L., Frame, D., Lunt, D.J., Mauritsen, T., Palmer, M.D., Watanabe, M., Wild, M., Zhang, H., 2021. The Earth's energy budget, climate feedbacks, and climate sensitivity. In: Masson-Delmotte, V., Zhai, P., Pirani, A., Connors, S.L., Péan, C., Berger, S., Caud, N., Chen, Y., Goldfarb, L., Gomis M.I., Huang, M., Leitzell, K., Lonnoy, E., Matthews, J.B.R., Maycock, T.K., Waterfield, T., Yelekçi, O., Yu, R., Zhou, B., (eds.), Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, p. 923–1054 (doi:10.1017/9781009157896.009).

Fuchs, A., Lyautey, E., Montuelle, B., Casper, P., 2016. Effects of increasing temperatures on methane concentrations and methanogenesis during experimental incubation of sedimentsfrom oligotrophic and mesotrophic lakes. J. Geophys. Res. Biogeosci., 121 1394-1406.

Ghioldi, G.C., 2021. An appraisal on methane emissions from wetlands based on direct estimates and theroretical computations: the case of Lake Porta wetland, northern Tuscany (Italy). Tesi di Laurea Magistrale, Università degli Studi di Firenze, Florence, Italy, 92 p.

Gonçalves, V., 2008. Contribuição para o estudo da qualidade ecológica das lagoas dos açores — fitoplâncton e diatomáceas bentónicas. PhD Thesis. Universidade dos Açores, Ponta Delgada (in Portuguese with English abstract).

Grossart, H-.P., Frindte, K., Dziallas, C., Eckert, W., Tang, K.W., 2011. Microbial methane production in oxygenated water column of an oligotrophic lake. Proc. Natl. Acad. Sci. 108, 19657–19661.

Havens, K., Fukushima, T., Xie, P., Iwakuma, T., James, R., Takamura, N., Hanazato, T.,Yamamoto, T., 2001. Nutrient dynamics and the eutrophication of shallow lakesKasumigaura (Japan), Donghu (PR China), and Okeechobee (USA). Environ. Pollut. 111, 263–272.

Hernández, P.A., Mori, T., Padrón, E., Sumino, H., Pérez, N., 2011. Carbon dioxide emission from Katanuma volcanic lake, Japan. Earth Planets Space 63, 1151–1156.

Hofmann, H., 2013. Spatiotemporal distribution patterns of dissolved methane in lakes: how accurate are the current estimations of the diffusive flux path? Geophys. Res. Lett. 40, 2779–2784.

Holgerson, M., Raymond, P., 2016. Large contribution to inland water CO_2 and CH_4 emissions from very small ponds. Nature Geosci. 9, 222-226.

Houghton, J., 2015. Global warming. The Complete briefing. Cambridge University Press, Cambridge, 396 p.

IAEA, 2017. Sampling Procedures for Isotope Hydrology. Water Resources Programe, p. 8.

Johnson, M. S., Matthews, E., Du, J., Genovese, V., Bastviken, D., 2022. Methane emission from global lakes: new spatiotemporal data and observation-driven modeling of methane dynamics indicates lower emissions. J. Geophys. Res. Biogeosci. 127, e2022JG006793 (doi: 10.1029/2022JG006793).

Langenegger, T., Vachon, D., Donis, D., McGinnis, D.F., 2022. Methane oxidation dynamics in a stratified lake: Insights revealed from a mass balance and carbon stable isotopes. Limnol. Oceanogr. 67, 2157–2173.

Li, L., Fuchs, A., Ortega, S.R., Xue, B., Casper, P., 2021. Spatial methane pattern in a deep freshwater lake: Relation to water depth and topography. Sci. Total Environ. 764, 142829 (doi: 10.1016/j.scitotenv.2020.142829).

Li, M., Peng, C., Zhu, Q., Zhou, X., Yang, G., Song, X., Zhang, K., 2020. The significant contribution of lake depth in regulating global lake diffusive methane emissions. Water Res. 172, 115465 (doi: 10.1016/J.watres.2020.115465).

Liang, Y.T., Zhang, Y.Y., Wang, N.N., Luo, T.W., Zhang, Y., Rivkin, R.B., 2017. Estimating primary production of picophytoplankton using the carbon-based ocean productivity model: a preliminary study. Front. Microbiol. 8, 1926 (doi: 10.3389/fmicb.2017.01926).

Liss, P.S., Slater, P.G., 1974. Flux of gases across the Air-Sea Interface. Nature 247, 182-184.

Liu, H., Xiao, S., Liu, W., Wang, H., Liu, Z., Li, X., Zhang, P., Liu, J., 2024. Salinity decreases methane concentrations in Chinese lakes. Sci. Total Environ. 937, 173412 (doi: 10.1016/j.scitotenv.2024.173412).

Livingston, G.P., Hutchinson, G.L., 1995. Enclosure-based measurement of trace gas exchange: applications and sources of error, in: Matson, P., Harriss, R. (eds.), Biogenic trace gases: measuring emissions from soil and water, Blackwell Science, 14-51.

Ma, B.J., Wang, Y., Jiang, P., Li, S.Y., 2024. The influence of seasonal variability of eutrophication indicators on carbon dioxide and methane diffusive emissions in the largest shallow urban lake in China. Water 16, 136 (doi: 10.3390/w16010136).

Madeira, J., 1998. Estudos de neotectónica nas ilhas do Faial, Pico e S. Jorge: uma contribuição para o conhecimento geodinâmico da junção tripla dos Açores. PhD thesis, Universidade of Lisbon, 481 p.

Madeira, J., Brum da Silveira, A., 2003. Active tectonics and first paleoseismological results in Faial, Pico and S. Jorge Islands (Azores, Portugal). Annals of Geophysics, 46, 733–761

Malcata, A., Pacheco, D., Cymbron, R., 2022. Monitorização da qualidade da água das lagoas de São Miguel, Pico, Flores e Corvo. Comparação de resultados entre 2017 e 2020. SRAAC, Ponta Delgada, 336 p. (in Portuguese).

Martini, M., Giannini, L., Prati, F., Tassi, F., Capaccioni, B., Iozzelli, P., 1994. Chemical characters of crater lakes in the Azores and Italy: the anomaly of Lake Albano. Geochem. J. 28, 173–184

Martins, G., Ribeiro, D., Pacheco, D., Cruz, J.V., Cunha, R., Gonçalves, V., Nogueira, R., Brito, A.G., 2008. Prospective scenarios for water quality and ecological status in Lake Sete Cidades (Portugal): the integration of mathematical modeling in decision processes. Appl. Geochem. 23, 2171–2181.

Martins, G., Henriques, I., Ribeiro, D.C., Correia, A., Bodelier, P.L.E., Cruz, J.V., Brito, A.G., Nogueira, R., 2012. Bacterial diversity and geochemical profiles in sediments from eutrophic Azorean lakes. Geomicrobiol. J. 29, 704-715.

Mazot, A., Bernard, A., 2015. CO_2 Degassing from Volcanic. In: Rouwet, D., Christenson, B., Tassi, F., Vandemeulebrouck, J. (Eds.), Volcanic Lakes, Advances in Volcanology. Springer, Heidelberg, 341-354.

Mazot, A., Taran, Y., 2009. CO_2 flux from the volcanic Lake of El Chichon (Mexico). Geofis. Int. 48, 73–83.

Mazot, A., Rouwet, D., Taran, Y., Inguaggiato, Y., Varley, N., 2011. CO_2 and He degassing at El Chichon volcano, Chiapas, Mexico: Gas flux, origin and relationship with local and regional tectonics. Bull. Volcanol. 73, 423–441.

Mu, J., Qi, J., Yu, H., Hu, C., Mu, Y., Qu, J. 2022. Dynamic chamber as a more reliable technique for measuring methane emissions from aquatic ecosystems. Sci. Total Environ. 851, 158147 (doi: 10.1016/j.scitotenv.2022.158147).

Nunes, J.C., 1999. Actividade vulcânica na ilha do Pico do Plistocénico Superior ao Holocénico: mecanismo eruptivo e hazard vulcânico. PhD thesis, University of the Azores, 357 p

Ordóñez, C., DelSontro, T., Langenegger, T., Donis, D., Suarez, E.L., McGinnis, D.F., 2023. Evaluation of the methane paradox in four adjacent pre-alpine lakes across a trophic gradient. Nature Communications 14, 2165 (doi: 10.1038/s41467-023-37861-7).

Pacheco, D., Cruz, J.V., Malcata, A., Mendes, S., 2005. Monitorização da qualidade da água das lagoas de São Miguel. SRAM, Ponta Delgada, 178 p. (in Portuguese).

Pacheco, D., Malcata, A., Mendes, S., Cruz, J.V., Gaspar, J.L., 2010. Monitorização da qualidade da água das lagoas de São Miguel. Comparação de resultados entre 2004 e 2008. SRAM, Ponta Delgada, 211 p. (in Portuguese).

Padrón, E., Hernández, P.A., Toulkeridis, T., Pérez, N.M., Marrero, R., Melián, G., Virgili, G., Notsu, K., 2008. Diffuse CO_2 emission rate from Pululahua and the lake filled Cuicocha calderas, Ecuador. J. Volcanol. Geotherm. Res. 176, 163-169.

Parkhurst, D.L., Appelo, C.A.J., 1999. User's guide to phreeqc (version 2) - a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resources Investigations Report, 99–4259, USGS, Denver.

Pérez, N.M., Hernández, P.A., Padilla, G., Nolasco, D., Barrancos, J., Melián, G., Padrón, E., Dionis, S., Calvo, D., Rodríguez, F., Notsu, K., Mori, T., Kusakabe, M., Arpa, M.C., Reniva, P., Ibarra, M., 2011. Global CO_2 emission from volcanic lakes. Geology 39. 235-238.

Porteiro, J., 2000. Lagoas dos Açores: elementos de suporte ao planeamento integrado. PhD Thesis. Universidade dos Açores, Ponta Delgada (in Portuguese).

Raymond, P.A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Durr, H., Meybeck, M., Ciais, P., Guth, P., 2013. Global carbon dioxide emissions from inland waters. Global carbon dioxide emissions from inland waters. Nature 503, 355-359.

Ribeiro, D.C., Martins, G., Nogueira, R., Cruz, J.V., Brito, A.G., 2008. Phosphorus fractionation in volcanic lake sediments (Azores — Portugal). Chemosphere 70, 1256-1263.

Rosentreter, J.A., Borges, A.V., Deemer, B.R., Holgerson, M.A., Liu, S., Song, C., Melack, J., Raymond, P.A., Duarte, C.M., Allen, G.H., Olefeldt, D., Poulter, B., Battin, T.I., Eyre, B.D., 2021. Half of global methane emissions come from highly variable aquatic ecosystem sources. Nat. Geosci. 14, 225-230.

Sáez, A., Hernández, A., Pimentel, A., Andrade, M., Bao, R., Raposeiro, P.M., Gonçalves, V., Benavente, M., Pla-Rabes, S., Ramalho, R., Giralt, S., 2025. Westerlies migrations and volcanic records over the past 4000 years from the Azores lacustrine sequences. Exploring correlations and impacts on Western Europe. Global and Planetary Change, 246, 104698 (doi.org/10.1016/j.gloplacha.2025.104698).

Sanches, L.F., Guenet, B., Marinho, C.C., Barros, N., Esteves, F.A., 2019. Global regulation of methane emissions from natural lakes. Sci. Rep. 9, 255 (doi: 10.1038/s41598-018-36519-5).

Santos, M., Pacheco, D., Santana, A.F., Muelle, H., 2005. Cyanobacteria blooms in Sete Cidades lake (São Miguel Island - Azores). Algol. Stud. 117, 393-406.

Saunois, M., Bousquet, P., Poulter, B., Peregon, A., Ciais, P., Canadell, J. G., Dlugokencky, E. J., Etiope, G., Bastviken, D., Houweling, S., Janssens-Maenhout, G., Tubiello, F. N., Castaldi, S., Jackson, R. B., Alexe, M., Arora, V. K., Beerling, D. J., Bergamaschi, P., Blake, D. R., Brailsford, G., Brovkin, V., Bruhwiler, L., Crevoisier, C., Crill, P., Covey, K., Curry, C., Frankenberg, C., Gedney, N., Höglund-Isaksson, L., Ishizawa, M., Ito, A., Joos, F., Kim, H.-S., Kleinen, T., Krummel, P., Lamarque, J.-F., Langenfelds, R., Locatelli, R., Machida, T., Maksyutov, S., McDonald, K. C., Marshall, J., Melton, J. R., Morino, I., Naik, V., O'Doherty, S., Parmentier, F.-J. W., Patra, P. K., Peng, C., Peng, S., Peters, G. P., Pison, I., Prigent, C., Prinn, R., Ramonet, M., Riley, W.J., Saito, M., Santini, M., Schroeder, R., Simpson, I. J., Spahni, R., Steele, P., Takizawa, A., Thornton, B. F., Tian, H., Tohjima, Y., Viovy, N., Voulgarakis, A., van Weele, M., van der Werf, G. R., Weiss, R., Wiedinmyer, C., Wilton, D. J., Wiltshire, A., Worthy, D., Wunch, D., Xu, X., Yoshida, Y., Zhang, B., Zhang, Z., Zhu, Q., 2016. The global methane budget 2000-2012, Earth Syst. Sci. Data, 8, 697–751 (doi: 10.5194/essd-8-697-2016).

Saunois, M., Stavert, A.R., Poulter, B., Bousquet, P., Canadell, J.G., Jackson, R.B., Raymond, P.A., Dlugokencky, E.J., Houweling, S., Patra, P.K., Ciais, P., Arora, V.K., Bastviken, D., Bergamaschi, P., Blake, D.R., Brailsford, G., 15, Bruhwiler, L., Carlson, K.M., Carrol, M., Castaldi, S., Chandra, N., Crevoisier, C., Crill, P.M., Covey, K., Curry, C.L., Etiope, G., Frankenberg, C., Gedney, N., Hegglin, M.I., Höglund-Isaksson, L., Hugelius, G., Ishizawa, M., Ito, A., Janssens-Maenhout, G., Jensen, K.M., Joos, F., Kleinen, T., Krummel, P.B., Langenfelds, R.L., Laruelle, G.G., Liu, L., Machida, T., Maksyuto, S., McDonald34, K.C., McNorton, J., Miller, P.A., Melton, J.R., Morino, I., Müller, J., Murguia-Flores, f., Naik, V., Niwa; Y., Noce, S., O'Doherty, S., Parker, R.J., Peng, C., Peng, S., Peters, G.P., Prigent, C., Prinn, R., Ramonet, M., Regnier, M., Riley, W.J., Rosentreter, J.A., Segers, A., Simpson, I.J., Shi, H., Smith, S.J., Steele, L.P., Thornton, B.F., Tian, H., Tohjima, Y., Tubiello, F.N., Tsuruta, A., Viovy, N., Voulgarakis, A., Weber, T.S., van Weele, M., van der Werf, G.R., Weiss, R.F., Worthy, D., Wunch, D., Yin, Y., Yoshida, Y., Zhang, W., Zhang, Z., Zhao, Y., Zheng, B., Zhu, Q., Zhu, Q., Zhuang, Q., 2020. The global methane budget 2000–2017. Earth Syst. Sci. Data 12, 1561-1623.

Saunois, M., Martinez, A., Poulter, B., Zhang, Z., Raymond, P.A., Regnier, P., Canadell, J.G., Jackson, R.B., Patra, P.K., Bousquet, P., Ciais, P., Dlugokencky, E.J., Lan, X., Allen, G.H., Bastviken, D., Beerling, D.J., Belikov, D.A., Blake, D.R., Castaldi, S., Crippa, M., Deemer, B.R., Dennison, F., Etiope, G., Gedney, N., Höglund-Isaksson, L., Holgerson, M.A., Hopcroft, P.O., Hugelius, G., Ito, A., Jain, A.K., Janardanan, R., Johnson, M.S., Kleinen, T., Krummel, P.B., Lauerwald, R., Li, T., Liu, X., McDonald, K.C., Melton, J.R., Mühle, J., Müller, J., Murguia-Flores, F., Niwa, Y., Noce, S., Pan, S., Parker, R.J., Peng, C., Ramonet, M., Riley, W.J., Rocher-Ros, G., Rosentreter, J.A., Sasakawa, M., Segers, A., Smith, S.J., Stanley, E.H., Thanwerdas, J., Tian, H., Tsuruta, A., Tubiello, F.N., Weber, T.S., van der Werf, G.R., Worthy. D.E.J., Xi, Y., Yoshida, Y., Zhang, W., Zheng, B., Zhu, Q., Zhu, Q., Zhuang, Q., 2025. Global Methane Budget 2000–2020. Earth Syst. Sci. Data, 17, 1873–1958.

Sawakuchi, H. O., Bastviken, D., Sawakuchi, A. O., Ward, N. D., Borges, C. D., Tsai, S. M., Richey, J.E., Ballester, M.V.R., Krusche, A.V., 2016. Oxidative mitigation of aquatic methane emissions in large Amazonian rivers. Glob. Chang. Biol. 22, 1075-1085.

Schroll, M., Liu, L., Einzmann, T., Keppler, F., Grossart, H.-G., 2023. Methane accumulation and its potential precursor compounds in the oxic surface water layer of two contrasting stratified lakes. Sci. Total Environ. 903, 166205 (doi: 10.1016/j.scitotenv.2023.166205).

Smith, L.K., Lewis, W.M., 1992. Seasonality of methane emissions from five lakes and associated wetlands of the colorado rockies. Global Biogeochem. Cycles 6, 323-338.

Sun, Y., Guo, Z., Liu, J., Du, J., 2017. CO_2 diffuse emission from maar lake: an example in Changbai volcanic field, NE China. J. Volcanol. Geotherm. Res. 349, 146–162.

Tassi, F., Nisi, B., Cardellini, C., Capecchiacci, F., Donnini, M., Vaselli, O., Avino, R., Chiodini, G., 2013. Diffuse soil emission of hydrothermal gases (CO_2, CH_4, and C_6H_6) at Solfatara crater (Campi Flegrei, southern Italy). App. Geochem. 35, 142-153.

Tassi, F., Cabassi, J., Andrade, C., Callieri, C., Silva, C., Viveiros, F., Corno, G., Vaselli, O., Selmo, E., Gallorini, A., Ricci, A., Giannini, L., Cruz, J.V., 2018. Mechanisms regulating CO_2 and CH_4 dynamics in the Azorean volcanic lakes (São Miguel Island, Portugal). J. Limnology 77(3), 483-504.

Tranvik, L.J., Downing, J.A., Cotner, J.B., Loiselle, S.A., Striegl, R.G., Ballatore, T.J., Dilon, P., Finlay, K., Fortino, K., Knoll, L.B., Kortelainen, P.L., Kutser, T., Larsen, S., Laurion, I., Leech, D.M., McCallister, S.L., McKnight, D.M., Melack, J.M., Overholt, E., Porter, J.A., Prairie, Y., Renwick, W.H., Roland, F., Sherman, B.S., Schindler, D.W., Sobek, S., Tremblay, A., Vanni, M.J., Verschoor, A.M., Von Wachenfeldt, E., Weyhenmeyer, G.A., 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnol. Oceanogr. 54, 2298-2314.

Varekamp, J.C., 2015. The Chemical Composition and Evolution of Volcanic Lakes. In: Rouwet, D., Christenson, B., Tassi, F., Vandemeulebrouck, J., (Eds.), Advances in Volcanology. Springer, Heidelberg, 93-123.

Venturi, S., Tassi, F., Cabassi, J., Randazzo, A., Lazzaroni, M., Capecchiacci, Vietina, B., Vaselli, O., 2021. Applied Sciences 11, 12156 (doi: 10.3390/app112412156).

Viveiros, F., Cardellini, C., Ferreira, T., Caliro, S., Chiodini, G., Silva, C., 2010. Soil CO_2 emissions at Furnas Volcano, São Miguel Island, Azores archipelago: Volcano monitoring perspectives, geomorphologic studies, and land use planning application. J. Geophys. Res., 115, B12208, 1-17.

Viveiros, F., Marcos, M., Faria, C., Gaspar, J.L., Ferreira, T., Silva, C.., 2017. Soil CO_2 degassing path along volcano-tectonic structures in the Pico-Faial-São Jorge islands (Azores archipelago, Portugal). Front. Earth Sci 5, 50 (doi: 10.3389/feart.2017.00050).

Wanninnkhof, R., 2014. Relationship between wind speed and gas exchange over the ocean revisited. Limnol. Oceanogr. Methods 12, 351-362.

Ward, N., Bianchi, T.S., Martin, J.B., Quintero, C.J., Sawakuchi, H.O., Cohen, M.J., 2020. Pathways for methane emissions and oxidation that influence the net carbon balance of a subtropical cypress swamp. Front. Earth Sci. 8, 573357 (doi: 10.3389/feart.2020.573357.

West, W.E., Creamer, K.P., Jones, S.E., 2016. Productivity and depth regulate lake contributions to atmospheric methane. Limnol. Oceanogr. 61, s51–s61.

Yuan, X., Liu, Q., Cui, B., Xu, X., Liang, L., Sun, T., Yan, S., Wanga, X., Li, C., Li, S., Li, M., 2021. Effect of water-level fluctuations on methane and carbon dioxide dynamics in a shallow lake of Northern China: Implications for wetland restoration. J. Hydrol. 597, 126169 (doi: 10.1016/j.jhydrol.2021.126169).

Yang, Y., Chen, J., Tong, T., Xie, S., Liu, Y., 2020. Influences of eutrophication on methanogenesis pathways and methanogenic microbial community structures in freshwater lakes. Environ. Pollut. 260, 114106 (doi: 10.1016/j.envpol.2020.114106).

Zhang, L., Liao, Q., Gao, R., Luo, R., Liua, C., Zhonga, J., Wanga, Z., 2021. Spatial variations in diffusive methane fluxes and the role of eutrophication in a subtropical shallow lake. Sci. Total Environ. 759, 143495 (doi: 10.1016/j.scitotenv.2020.143495).

Zhang, J., Cao, L., Liu, Z., Wan, L., Cao, X., Zhou, Y., Songa, C., 2024. Relationship between eutrophication and greenhouse gases emission in shallow freshwater lakes. Sci. Total Environ. 925, 171610 (doi: 10.1016/j.scitotenv.2024.171610).

Zhong, J., Yang, F., Zhang, M., Sun, C., Wang, S., Chen, Q., Wanga, H.,Zhang, L., 2023. Water depth and productivity regulate methane (CH_4) emissions from temperate cascade reservoirs in northern China. J. Hydrol. 626, 130170 (doi: 10.1016/j.jhydrol.2023.130170).

Figures captions

Figure 1 – Location of the studied lakes in Pico Iland (Azores archipelago). A, location of the Azores archipelago, about 1,500 km West from Portugal mainland; B, location of Pico Island (red) in the so-called central group of the Azores archipelago; C, Pico island (447 km^2), being the study areas outlined by red squares (main geological units: 1 – Montanha Volcanic System; 2 - Planalto da Achada Fissural Volcanic System; 3 – Topo - Lajes Volcanic System); D and E, Capitão and Caiado lakes, respectively.

Figure 2 – Changes in the main physico-chemical parameters along the vertical profiles made in the studied lakes.

Figure 3 – Durov-type diagram depicting the major-ion relative composition of lake water samples from the studied lakes.

Figure 4 – Boxplot of dissolved gas compositions at the lake surface for the various field campaigns (A, 3rd survey – Capitão Lake; B, 4th survey – Capitão Lake; C, 3rd survey – Caiado Lake; D, 4th survey – Caiado Lake).

Figure 5 – ΦCO_2 measurements from the surveys conducted at thew studied lakes (A, 3rd survey – Capitão Lake; B, 4th survey – Capitão Lake; C, 3rd survey – Caiado Lake; D, 4th survey – Caiado Lake).

Figure 6 – Boxplot of ΦCH_4 measurements from the different surveys at the studied lakes (A, 3rd survey – Capitão Lake; B, 3rd survey – Caiado Lake; C, 4th survey – Capitão Lake; D, 4th survey, Caiado Lake).

Figure 7 – ΦCH_4 measurements from the various sampling campaigns at the studied lakes (A, 3rd survey – Capitão Lake; B, 4th survey – Capitão Lake; C, 3rd survey – Caiado Lake; D, 4th survey – Caiado Lake).

Figure 8 – ΦCO_2 mapping for the studied lakes (A, 1st survey – Capitão Lake; B, 2nd survey – Capitão Lake; C, 1st survey – Caiado Lake; D, 2nd survey, Caiado Lake).

Tables captions

Table 1 – Descriptive statistics of ΦCO_2 in the Capitão and Caiado lakes presented according to the measurement survey (n, number of measurements).

Table 2 – Descriptive statistics of ΦCH_4 measurements in the Capitão and Caiado lakes presented according to the sampling survey.

Table 3 – Descriptive statistics of CO_2 emissions in the Capitão and Caiado lakes presented according to the sampling survey.

Electronic supplementary material

Figures captions – supplementary material

Figure S1 – (A) View of one of the static floating chambers (SFC) used to collect gas samples placed at the surface of Santiago Lake. At the top of the container a small opening was fitted with a three-way valve, which was utilized to collect gas when opened through an attached syringe; (B) and (C) transects made along Santiago Lake Each, each made by six SFC located at regular intervals along a straight line.

Figure S2 – Cumulative probability plots of ΦCO_2 measurements across the different campaigns in the lakes (A, 1st survey – Capitão Lake; B, 2nd survey – Capitão Lake; C, 1st survey – Caiado Lake; D, 2nd survey, Caiado Lake).

Figure S3 – δ^{13}C-DIC (‰) versus dissolved inorganic carbon (DIC) relationship on a binary plot, supplemented by data from mineral waters on São Miguel Island (Ferreira et al., 2023), river water also from São Miguel Island (Cruz et al., 2025) and other lake water bodies in the Azores (Andrade et al., 2024). DIC concentrations calculated using PHREEQC (Parkhurst and Appelo, 1999).

Figure S4 – Modelled variograms for ΦCO_2 data from the various surveys conducted at the studied lakes (A, 1st survey – Capitão Lake; B, 2nd survey – Capitão Lake; C, 1st survey – Caiado Lake; D, 2nd survey, Caiado Lake).

Tables captions – supplementary material

Table S1 – Main geomorphological and geological characteristics of the Capitão and Caiado lakes (data from Andrade et al., 2019a, except for the geological setting, from Cruz et al., 2006).

Table S2 – Descriptive statistics for the main physico-chemical parameters and major-ion content along the four sampling surveys made in Capitão and Caiado lakes (n, total number of water samples by lake).

Table S3 – Dissolved gas content for the several transects made in both surveys at Capitão and Caiado lakes.

Table S4 – Calculated and measured ΦCH_4 for the several transects made in both surveys at Capitão Lake.

Table S5 – Calculated and measured ΦCH_4 for the several transects made in both surveys at Caiado Lake.

Table 1 – Descriptive statistics of CO_2 flux in the Capitão and Caiado lakes presented according to the measurement survey (n, number of measurements).

Lake	Survey	n	Min. ($g.m^{-2}.d^{-1}$)	Max. ($g.m^{-2}.d^{-1}$)	Mean ± SD ($g.m^{-2}.d^{-1}$)	Median ($g.m^{-2}.d^{-1}$)
Capitão	1	72	1.9	9.1	4.0 ± 1.6	3.8
	2	61	1.1	7.3	3.1 ± 1.4	2.7
Caiado	1	101	3.2	11.7	5.5 ± 1.7	5.2
	2	95	2.9	26.5	8.4 ± 5.0	6.8

Table 2 – Descriptive statistics of methane flux in the Capitão and Caiado lakes presented according to the measurement survey (n, number of measurements)

Lake	**Survey**	**n**	**Type**	**Min. (g.m^{-2}·d^{-1})**	**Max. (g.m^{-2}·d^{-1})**	**Mean ± SD (g.m^{-2}·d^{-1})**	**Median (g.m^{-2}·d^{-1})**
Capitão	3	12	Meas	0.003	0.006	0.004 ± 0.001	0.003
			Calc	0.003	0.005	0.004 ± 0.001	0.004
	4	30	Meas	0.025	0.210	0.040 ± 0.033	0.033
			Calc	0.025	0.230	0.041 ± 0.036	0.035
Caiado	3	12	Meas	0.021	0.029	0.024 ± 0.003	0.024
			Calc	0.021	0.034	0.028 ± 0.004	0.030
	4	30	Meas	0.031	0.066	0.046 ± 0.009	0.045
			Calc	0.026	0.062	0.045 ± 0.009	0.045

Table 3 – Descriptive statistics for CO_2 emissions in both lakes according the sampling survey.

Lake	Survey	Working Area (km^2)	CO_2 Flux ($t.d^{-1}$) (sGs)	CO_2 Flux ($t.d^{-1}$) (GSA)	CO_2 Flux ($t.km^{-2}.d^{-1}$)
Capitão	1	2.5×10^{-2}	0.10	0.10	4.00
	2	2.2×10^{-2}	0.08	0.07	3.64
Caiado	1	5.2×10^{-2}	0.31	0.29	5.96
	2	5.2×10^{-2}	0.40	0.45	7.69

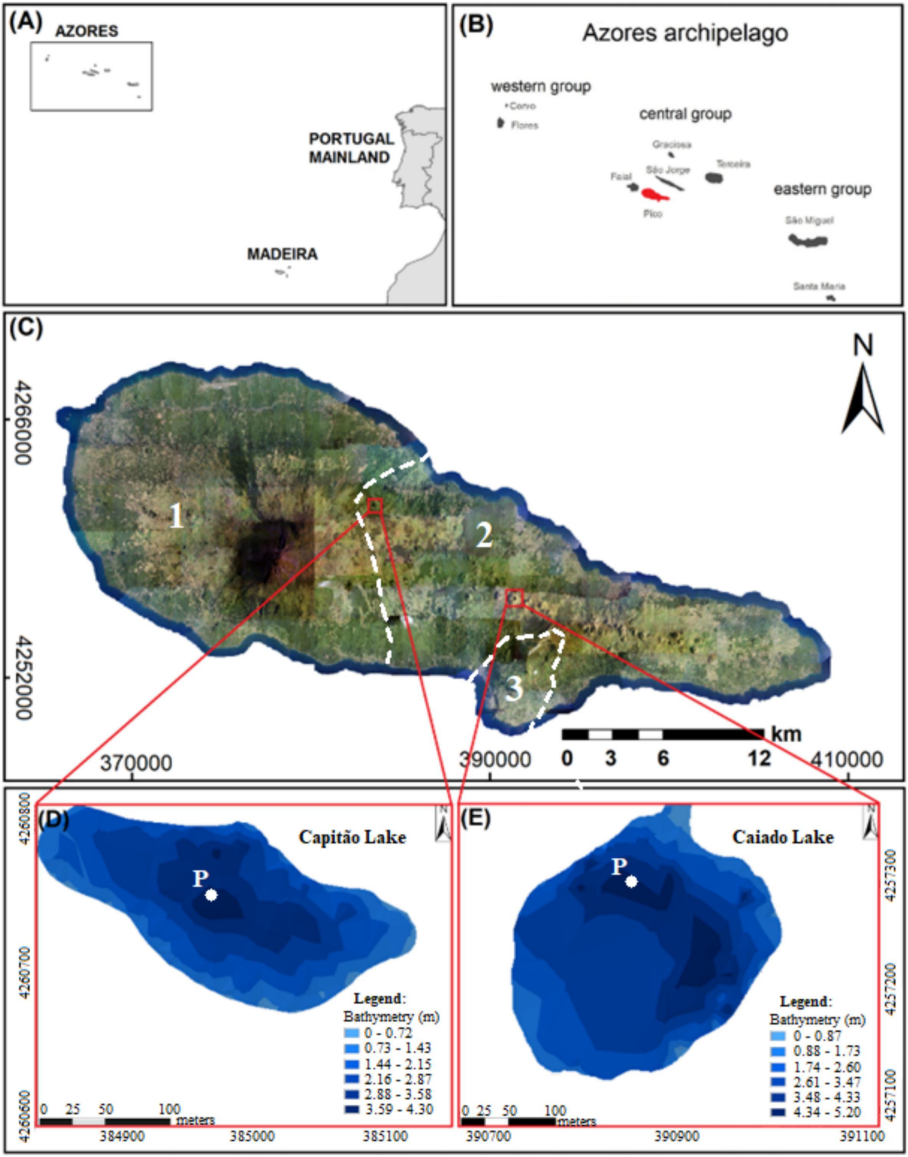
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Mean ΦCO_2 values are higher on Caiado Lake (5.5 to 8.4 g m^{-2} d^{-1}) comparing to Capitão Lake (3.1 to 4.0 g m^{-2} d^{-1})
- Mean ΦCH_4 values ranged from 0.004 to 0.040 g m^{-2} d^{-1} at Caiado Lake and from 0.024 to 0.046 g m^{-2} d^{-1} at Capitão Lake
- ΦCO_2 and ΦCH_4 are driven by biological processes, not volcanic input
- Stratification affects CO_2 emission values (lower in summer in Capitão Lake)
- Despite the much higher global warming potential comparing to CO_2, in terms of $CO_{2\text{-}eq}$ the ΦCH_4 is 2 to 3 orders of magnitude lower than ΦCO_2


(A)
AZORES
PORTUGAL MAINLAND
MADEIRA
(B)
Azores archipelago
western group
Corvo
Flores
central group
Graciosa
São Jorge
Terceira
Faial
Pico
eastern group
São Miguel
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Capitão Lake
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4260800
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4260600
Legend:
Bathymetry (m)
0 - 0.72
0.73 - 1.43
1.44 - 2.15
2.16 - 2.87
2.88 - 3.58
3.59 - 4.30
0
25
50
100
meters
384900
385000
385100
(E)
Caiado Lake
P
4257300
4257200
4257100
Legend:
Bathymetry (m)
0 - 0.87
0.88 - 1.73
1.74 - 2.60
2.61 - 3.47
3.48 - 4.33
4.34 - 5.20
0
25
50
100
meters
390700
390900
391100

Figure 1

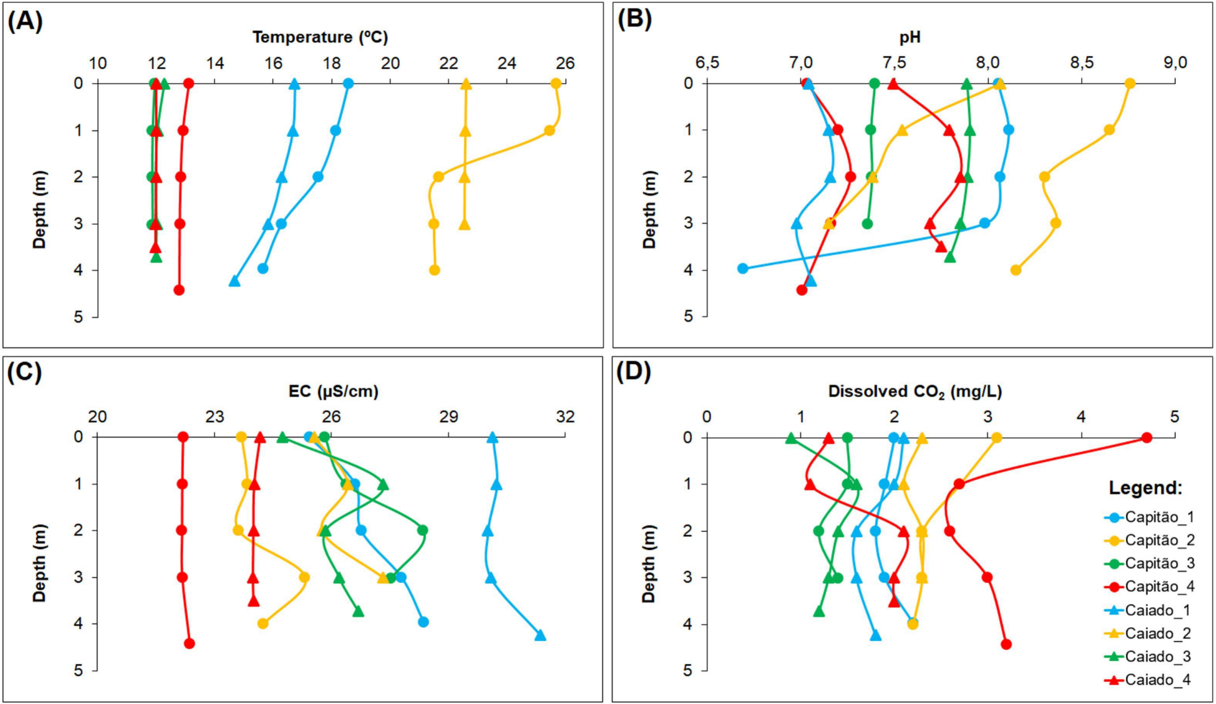
(A)
Temperature (ºC)
10
12
14
16
18
20
22
24
26
Depth (m)
0
1
2
3
4
5
(B)
pH
6,5
7,0
7,5
8,0
8,5
9,0
Depth (m)
0
1
2
3
4
5
(C)
EC (µS/cm)
20
23
26
29
32
Depth (m)
0
1
2
3
4
5
(D)
Dissolved CO_2 (mg/L)
0
1
2
3
4
5
Depth (m)
0
1
2
3
4
5
Legend:
Capitão_1
Capitão_2
Capitão_3
Capitão_4
Caiado_1
Caiado_2
Caiado_3
Caiado_4

Figure 2

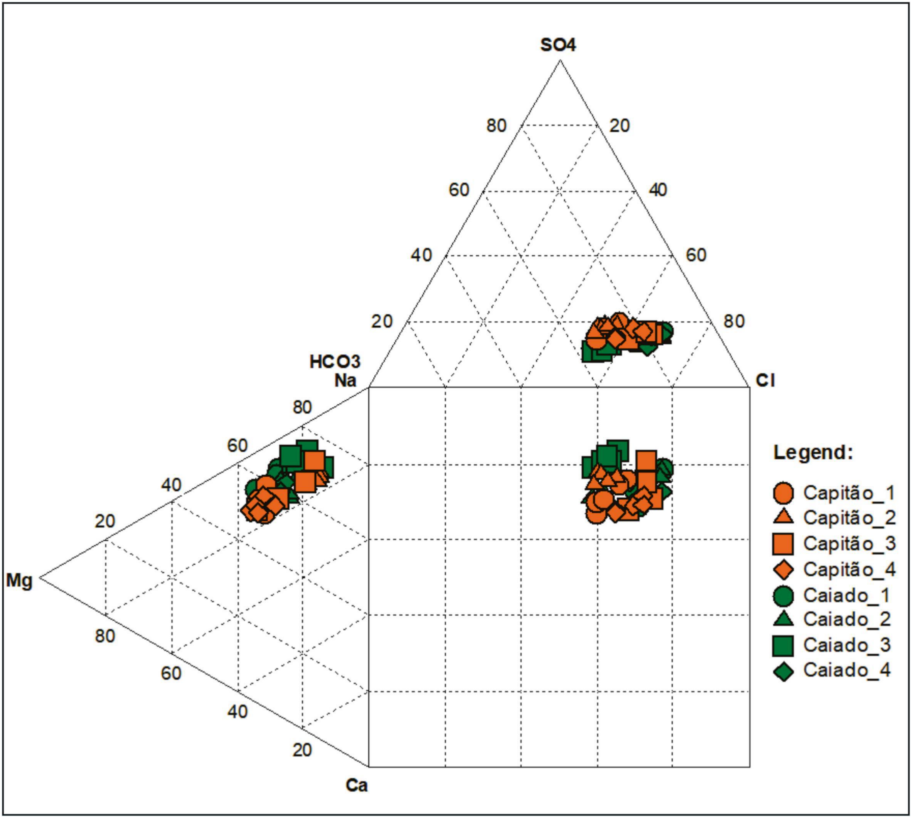
SO4
80
20
60
40
40
60
20
80
HCO3
Na
Cl
80
60
40
20
Mg
80
60
40
20
Ca
Legend:
Capitão_1
Capitão_2
Capitão_3
Capitão_4
Caiado_1
Caiado_2
Caiado_3
Caiado_4

Figure 3

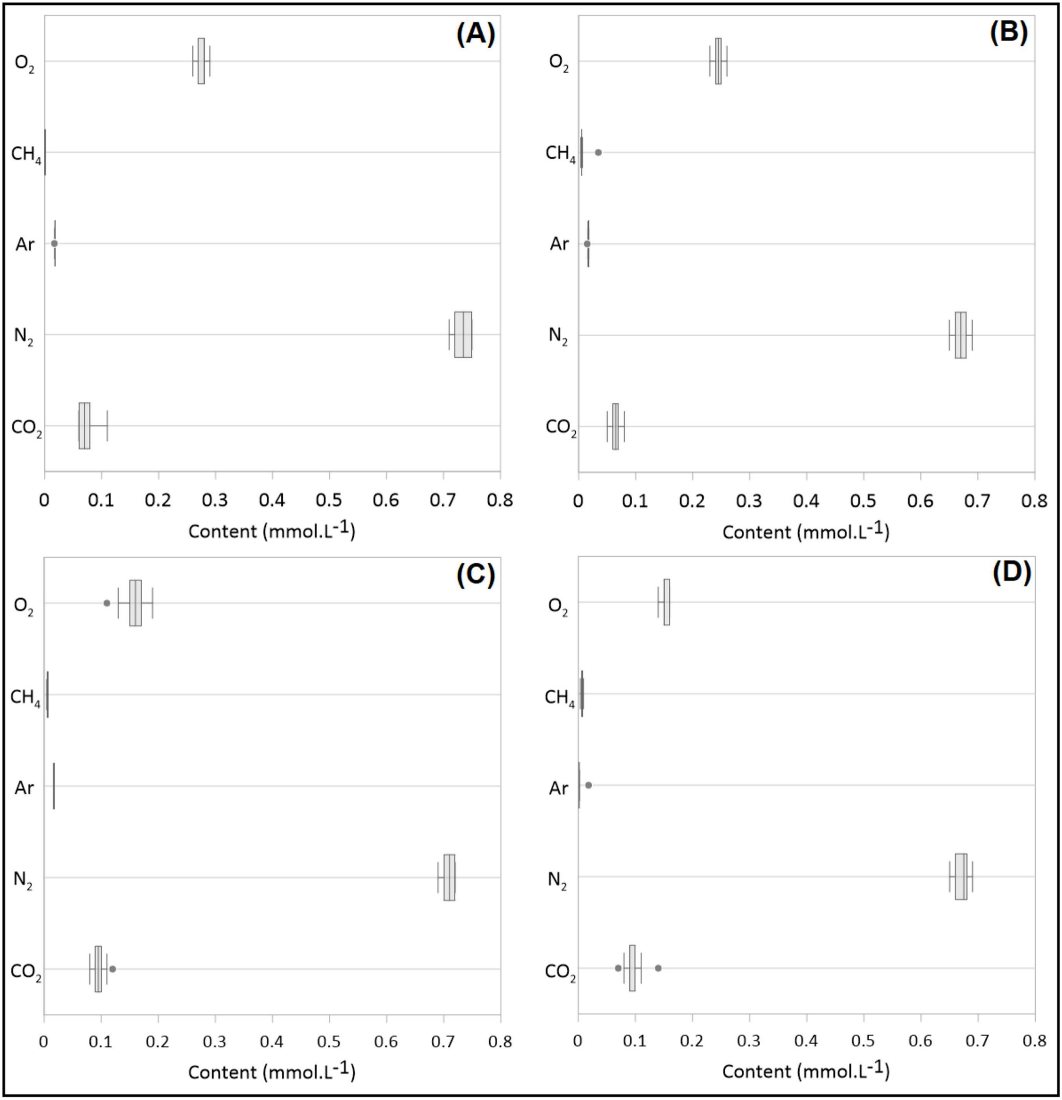

Figure 4

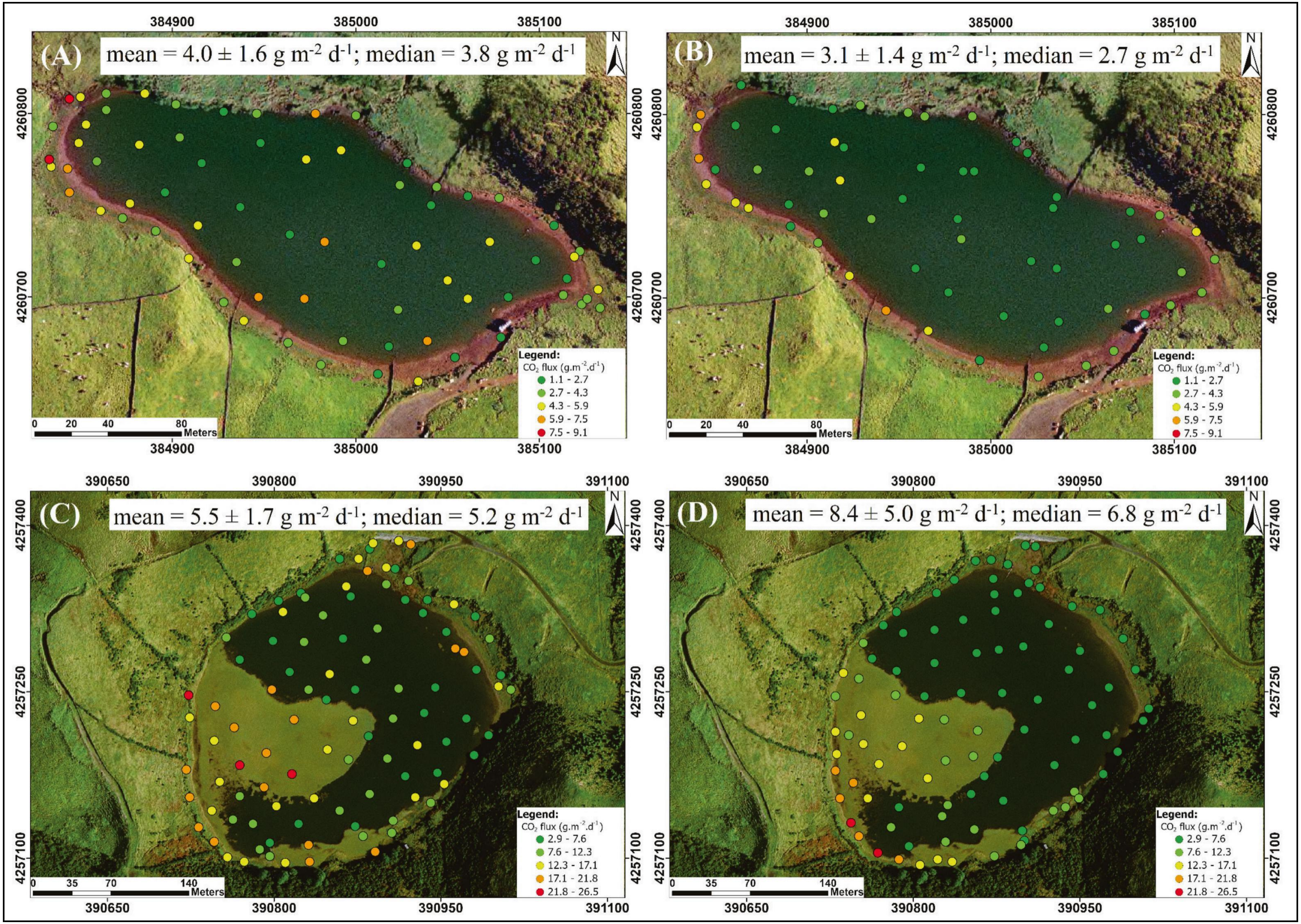
(A)
mean = 4.0 ± 1.6 g m^{-2} d^{-1}; median = 3.8 g m^{-2} d^{-1}
(B)
mean = 3.1 ± 1.4 g m^{-2} d^{-1}; median = 2.7 g m^{-2} d^{-1}
(C)
mean = 5.5 ± 1.7 g m^{-2} d^{-1}; median = 5.2 g m^{-2} d^{-1}
(D)
mean = 8.4 ± 5.0 g m^{-2} d^{-1}; median = 6.8 g m^{-2} d^{-1}
N
384900
385000
385100
4260800
4260700
390650
390800
390950
391100
4257400
4257250
4257100
Legend:
CO$_2$ flux (g.m^{-2}.d^{-1})
● 1.1 - 2.7
● 2.7 - 4.3
● 4.3 - 5.9
● 5.9 - 7.5
● 7.5 - 9.1
● 2.9 - 7.6
● 7.6 - 12.3
● 12.3 - 17.1
● 17.1 - 21.8
● 21.8 - 26.5
0 20 40 80 Meters
0 35 70 140 Meters

Figure 5

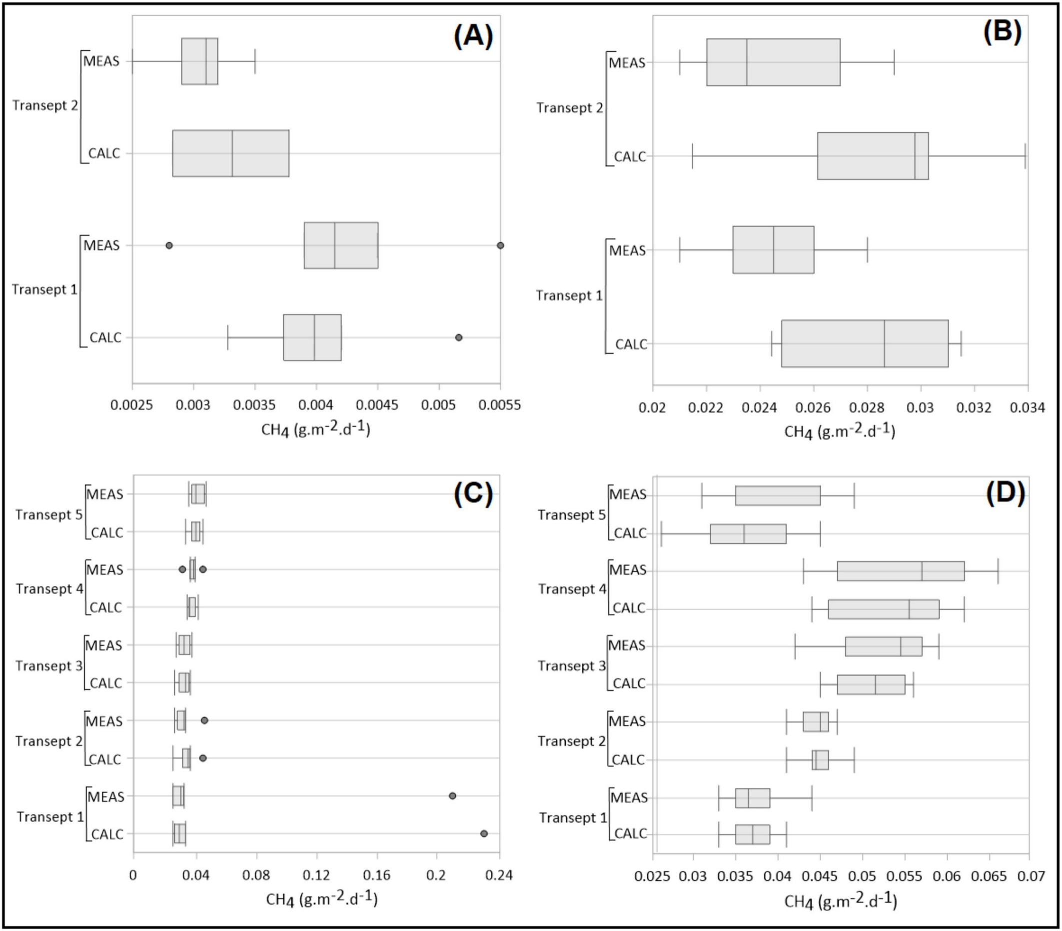
(A)
Transept 2
MEAS
CALC
Transept 1
MEAS
CALC
0.0025
0.003
0.0035
0.004
0.0045
0.005
0.0055
CH4 (g.m-2.d-1)
(B)
Transept 2
MEAS
CALC
Transept 1
MEAS
CALC
0.02
0.022
0.024
0.026
0.028
0.03
0.032
0.034
CH4 (g.m-2.d-1)
(C)
Transept 5
MEAS
CALC
Transept 4
MEAS
CALC
Transept 3
MEAS
CALC
Transept 2
MEAS
CALC
Transept 1
MEAS
CALC
0
0.04
0.08
0.12
0.16
0.2
0.24
CH4 (g.m-2.d-1)
(D)
Transept 5
MEAS
CALC
Transept 4
MEAS
CALC
Transept 3
MEAS
CALC
Transept 2
MEAS
CALC
Transept 1
MEAS
CALC
0.025
0.03
0.035
0.04
0.045
0.05
0.055
0.06
0.065
0.07
CH4 (g.m-2.d-1)

Figure 6

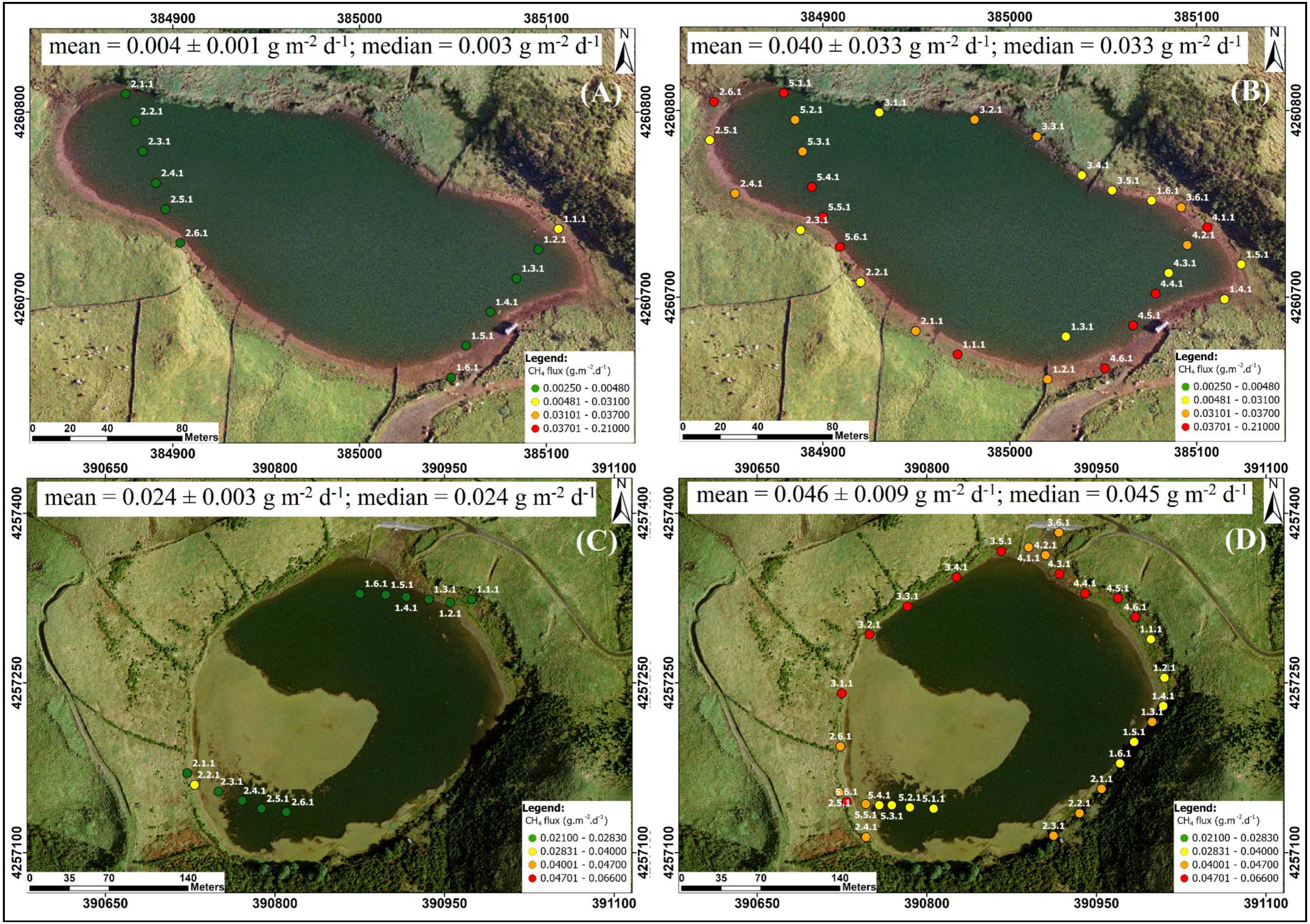
mean = 0.004 ± 0.001 g m-2 d-1; median = 0.003 g m-2 d-1
(A)
384900
385000
385100
4260800
4260700
2.1.1
2.2.1
2.3.1
2.4.1
2.5.1
2.6.1
1.1.1
1.2.1
1.3.1
1.4.1
1.5.1
1.6.1
Legend:
CH4 flux (g.m-2.d-1)
0.00250 - 0.00480
0.00481 - 0.03100
0.03101 - 0.03700
0.03701 - 0.21000
0 20 40 80 Meters
N
mean = 0.040 ± 0.033 g m-2 d-1; median = 0.033 g m-2 d-1
(B)
2.6.1
5.1.1
5.2.1
3.1.1
3.2.1
2.5.1
5.3.1
3.3.1
3.4.1
2.4.1
5.4.1
3.5.1
1.6.1
3.6.1
5.5.1
2.3.1
4.1.1
5.6.1
4.2.1
1.5.1
4.3.1
2.2.1
4.4.1
1.4.1
4.5.1
2.1.1
1.3.1
1.1.1
4.6.1
1.2.1
mean = 0.024 ± 0.003 g m-2 d-1; median = 0.024 g m-2 d-1
(C)
390650
390800
390950
391100
4257400
4257250
4257100
1.6.1
1.5.1
1.4.1
1.3.1
1.2.1
1.1.1
2.1.1
2.2.1
2.3.1
2.4.1
2.5.1
2.6.1
Legend:
CH4 flux (g.m-2.d-1)
0.02100 - 0.02830
0.02831 - 0.04000
0.04001 - 0.04700
0.04701 - 0.06600
0 35 70 140 Meters
mean = 0.046 ± 0.009 g m-2 d-1; median = 0.045 g m-2 d-1
(D)
3.6.1
3.5.1
4.2.1
4.1.1
4.3.1
3.4.1
4.4.1
4.5.1
3.3.1
4.6.1
3.2.1
1.1.1
1.2.1
3.1.1
1.4.1
1.3.1
2.6.1
1.5.1
1.6.1
2.1.1
5.6.1
2.5.1
5.4.1
5.5.1
5.3.1
5.2.1
5.1.1
2.2.1
2.4.1
2.3.1

Figure 7

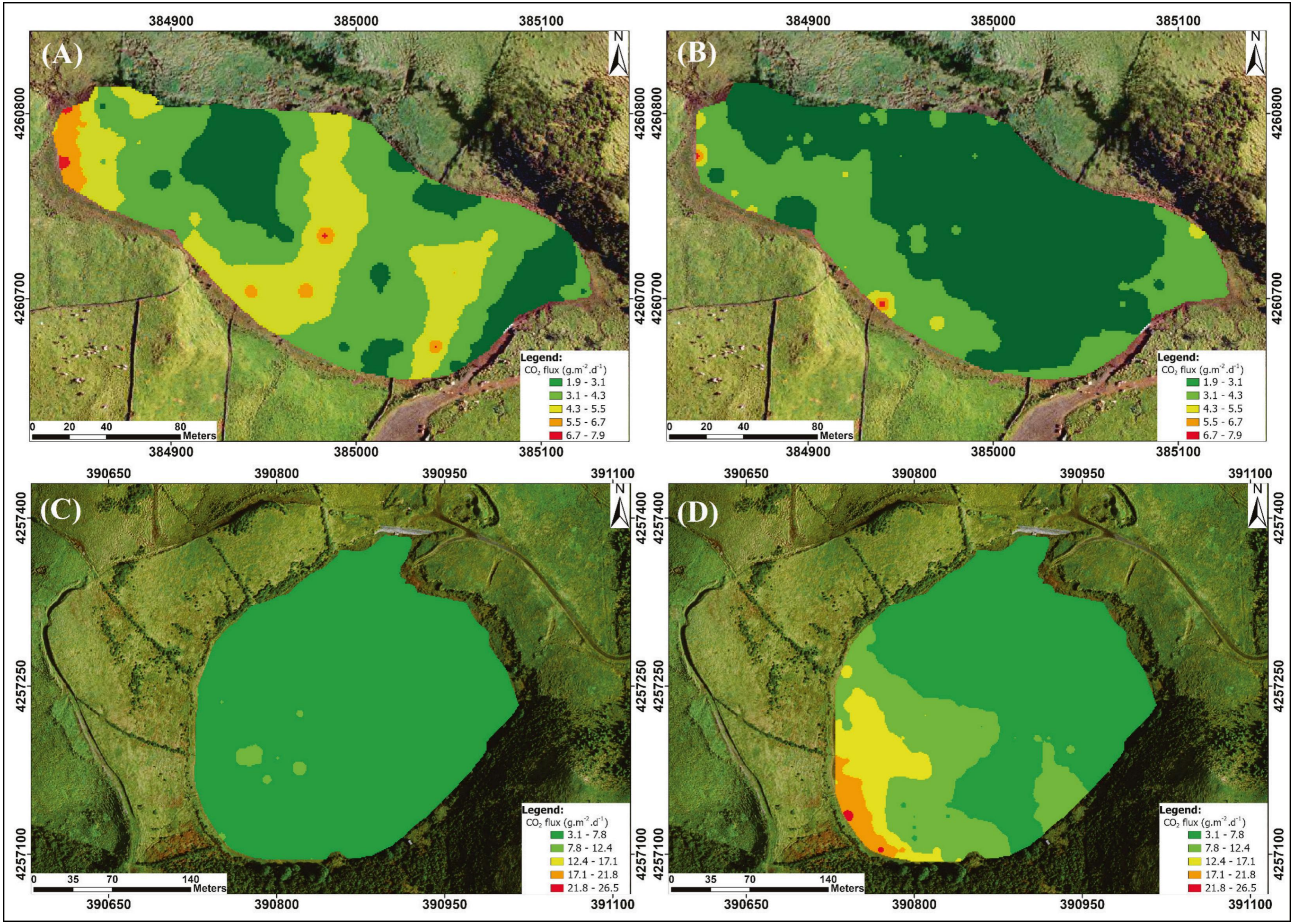
(A)
(B)
(C)
(D)
N
384900
385000
385100
4260800
4260700
390650
390800
390950
391100
4257400
4257250
4257100
Legend:
CO₂ flux (g.m⁻².d⁻¹)
🟩 1.9 - 3.1
🟩 3.1 - 4.3
🟨 4.3 - 5.5
🟧 5.5 - 6.7
🟥 6.7 - 7.9
🟩 3.1 - 7.8
🟩 7.8 - 12.4
🟨 12.4 - 17.1
🟧 17.1 - 21.8
🟥 21.8 - 26.5
0 20 40 80 Meters
0 35 70 140 Meters

Figure 8