Limnetica, 41(1): 43-60 (2022). DOI: 10.23818/limn.41.04
 ISSN: 0213-8409

Spatio-temporal variability of carbon dioxide and methane emissions from a Mediterranean reservoir

J.J. Montes-Pérez[1], B. Obrador[2], T. Conejo-Orosa[1], V. Rodríguez[1], R. Marcé[3], C. Escot[4], I. Reyes[4], J. Rodríguez[1] and E. Moreno-Ostos[1,*]

[1] University of Málaga. Department of Ecology and Geology. Marine Ecology and Limnology Research Group. Málaga, Spain.
[2] Department of Evolutionary Biology, Ecology and Environmental Sciences, Institut de Recerca de la Biodiversitat (IRBio), University of Barcelona, Spain.
[3] Catalan Institute for Water Research (ICRA). Girona, Spain.
[4] Empresa Metropolitana de Abastecimiento y Saneamiento de Aguas de Sevilla (EMASESA). Sevilla, Spain.

* Corresponding author: quique@uma.es

Received: 19/10/20 Accepted: 19/01/21

ABSTRACT

Spatio-temporal variability of carbon dioxide and methane emissions from a Mediterranean Reservoir

Freshwater reservoirs constitute a significant source of carbon dioxide (CO_2) and methane (CH_4) to the atmosphere, and a precise quantification of the magnitude of these greenhouse gas emission on an annual scale is required. This quantification must consider both temporal and spatial variability of reservoir carbon gas fluxes. In addition, it is relevant to reinforce research focusing on the emission of CO_2 and CH_4 in Mediterranean reservoirs. Here, we simultaneously measured CO_2 fluxes and CH_4 ebullitive and diffusive emissions in the riverine and lacustrine zones of a Mediterranean reservoir (El Gergal, Spain) throughout a complete year to quantify their magnitude, explore their spatial and temporal variability, and investigate the potential limnological and hydrological factors influencing gases emissions. Our results show that during the study year El Gergal riverine zone was a CO_2 sink, while the lacustrine zone was a CO_2 source. In addition, both areas were CH_4 sources to the atmosphere. CO_2 and CH_4 fluxes in El Gergal showed a marked temporal variability, with significant differences between mixing and thermally stratified periods. CO_2 emissions were significantly influenced by surface chlorophyll-*a* concentration and pH, suggesting the prevalent role of primary production as CO_2 flux driver. CH_4 emissions were influenced by hypolimnetic methane concentration and hydrological factors potentially affected by climate change, such as water renewal rate and water column depth.

Key words: emissions of greenhouse gases, carbon dioxide, methane, Mediterranean reservoirs

RESUMEN

Variabilidad espacio-temporal en las emisiones de dióxido de carbono y metano desde un embalse mediterráneo

Los embalses constituyen una fuente significativa de dióxido de carbono (CO_2) y metano (CH_4) a la atmósfera, y resulta necesario alcanzar una cuantificación precisa de la magnitud a escala anual de las emisiones de estos gases de efecto invernadero desde este tipo de ecosistemas. Dicha cuantificación debería considerar la variabilidad espacial y temporal en los flujos de gases de carbono desde los embalses. Además, es también necesario profundizar en la investigación sobre emisiones de CO_2 y CH_4 desde los embalses mediterráneos. En este trabajo se midieron simultáneamente el flujo de CO_2 y las emisiones difusivas y ebullitivas de CH_4 en las zonas fluvial y limnética de un embalse mediterráneo (El Gergal, España) a lo largo de un ciclo anual completo, con el objetivo de cuantificar sus magnitudes, explorar su variabilidad espacial y temporal, e investigar los principales factores limnólogicos e hidrológicos que regulan estos flujos gaseosos en el embalse. Nuestros resultados demuestran que durante el año de estudio la zona fluvial de El Gergal constituyó un sumidero de CO_2, mientras que la zona limnética fue una fuente de este gas a la atmósfera. Además, ambas zonas constituyeron fuentes de CH_4. Los flujos de CO_2 y CH_4 en el embalse se caracterizaron por una notable variabilidad temporal, con diferencias significativas entre los periodos de mezcla

y estratificación térmica. Los flujos de CO_2 se relacionaron significativamente con la concentración de clorofila a y el pH en superficie, lo que sugiere que la producción primaria juega un importante papel como proceso regulador de las emisiones de este gas en el embalse. Las emisiones de CH_4 estuvieron reguladas por la concentración de CH_4 en el hipolimnion, así como por factores de hidrológicos susceptibles de ser afectados por el cambio climático, tales como la tasa de renovación del agua y la profundidad.

Palabras clave: *emisiones de gases de efecto invernadero, dióxido de carbono, metano, embalses mediterráneos*

INTRODUCTION

Population growth and the consequent increase in global demand for water, energy and food has stimulated dam construction throughout the world. As a consequence, the number of large dams (those with a wall higher than 15 meters) in the world has dramatically increased over the last 60 years, and accordingly to current estimates there are around 58 10^3 of these large dams worldwide, with a storage capacity equivalent to one-sixth of the total annual river flow into the oceans (Mulligan et al., 2020). This number significantly increases when taking into consideration smaller dams, which constitutes around 16.7 million water bodies that increases the Earth´s natural inland waters surface in more than 7 % (Lehner et al., 2011). St. Louis et al. (2000) estimated that global surface area of reservoirs is approximately 1.5 10^6 Km^2, an area equivalent to the estimated global area of natural lakes. In addition, it is expected that reservoir surface area will be significantly increased in coming decades (Zarfl et al., 2015).

Although until recently inland waters were neglected as significant sources of greenhouse gas to the atmosphere, this picture has rapidly changed. Today it is well-known that continental waters contribute to the global carbon cycle in a disproportionate scale in relation with their small global surface, actively regulating continental carbon fluxes to the ocean and the atmosphere (Tranvik et al., 2009). Lakes and reservoirs emit carbon dioxide (CO_2) and methane (CH_4) to the atmosphere (Raymond et al., 2013; Bastviken et al., 2011) and accumulate large quantities of carbon in their sediments (Einsele et al., 2001; Heathcote et al., 2015; Mendonça et al., 2017), where it can be preserved for millennia (Catalán et al., 2016).

Focusing on reservoir ecosystems, a preliminary estimation by St. Louis et al. (2000) depicted that CO_2 and CH_4 emissions from reservoir surfaces could be around 4-7 % of all anthropogenic emission of these gases to the atmosphere. These authors also quantified the combined fluxes of CO_2 and CH_4 of global reservoirs as 0.3 Gt yr^{-1} of carbon. More recently, a review by Deemer et al. (2016) stressed that reservoir emissions contribute significantly to global budgets of anthropogenic CO_2 equivalent emissions, with a remarkable contribution of reservoir per unit area CH_4 fluxes, showing higher values than any other aquatic ecosystem.

The surface waters of many reservoirs are often supersaturated in CO_2, which results in net CO_2 emissions to the atmosphere and represents a significant contribution to global carbon budgets (Raymond et al., 2013). In this context, Deemer et al. (2016) estimated that globally reservoirs emit around 36.8 Tg CO_2 yr^{-1}. The CO_2 supersaturation in the surface waters of reservoirs can be the result of net heterotrophic ecosystem metabolism in those water masses where community respiration exceeds primary production (Cole et al., 2000; Duarte & Prairie, 2005). In addition, in reservoirs located within calcareous watersheds CO_2 supersaturation can also be attributed to catchment carbonate weathering (Marcé et al., 2015; León-Palmero et al., 2020a).

Reservoirs are also important CH_4 sources to the atmosphere, a relevant greenhouse gas with about 28 times more warming potential than CO_2 over a 100-year period (Myhre et al., 2013). It has been recently estimated that global reservoirs emit 13.4 Tg CH_4 yr^{-1} (Deemer et al., 2016). An

important part of the CH_4 production in reservoirs occurs within the anoxic sediments, and the gas can be exported to the water column and the atmosphere by ebullition and diffusion processes (Beaulieu et al., 2014). In the ebullition process gas bubbles directly fluxes from the sediment to the atmosphere, with low oxidation in the water column, while in the diffusive export a large amount of CH_4 (50-95 %) is oxidized in the water column by methanotrophic microorganisms and just a small fraction reaches the atmosphere (Bastviken et al., 2004; Gruca-Roskosz, 2020). As a consequence, bubbling is the dominant CH_4 flux in lakes and reservoirs (Deemer et al., 2016). Shallow areas of warm lakes and reservoirs constitute hot spots for CH_4 ebullition, and it has been shown that water level fluctuations can substantially enhance bubbling CH_4 emissions due to changes in hydrostatic pressure at low water levels (Harrison et al., 2017).

Recent studies have demonstrated that CO_2 and CH_4 fluxes in lakes and reservoirs depicts a marked spatial variability (Beaulieu et al., 2014; Natchimuthu et al., 2016, Paranaíba et al., 2018; Yang, 2019, McClure et al., 2020), and that greenhouse gas emissions assessments which do not account for this spatial heterogeneity could substantially (and systematically) bias annual estimations of carbon fluxes to the atmosphere. In spite of this, there are still few studies on inland waters greenhouse gas emissions taking into account spatial and temporal variability simultaneously, and including both diffusive and ebullitive fluxes (i.e. Beaulieu et al., 2014; Natchimuthu et al., 2016), while most studies focus mainly in the deep areas of lakes and reservoirs.

Finally, although CO_2 and CH_4 fluxes have been extensively studied in tropical and temperate regions, there is still a lack of research on Mediterranean reservoirs (Morales-Pineda et al., 2015; Samiotis et al., 2018; León-Palmero et al., 2020a). Mediterranean reservoirs constitute a frequent aquatic ecosystem providing relevant ecosystem services in semi-arid zones, and are also especially sensitive and reactive to environmental changes. A recent paper (León-Palmero et al., 2020a) pointed out the necessity of more simultaneous measurements of greenhouse gas emissions from Mediterranean reservoirs to get more accurate estimates of their global relevance.

In the present study we simultaneously analyze the CO_2 and CH_4 (ebullitive and diffusive) fluxes in the riverine and lacustrine zones of a Mediterranean reservoir throughout a complete year to evaluate their magnitude and investigate potential limnological and hydrological drivers.

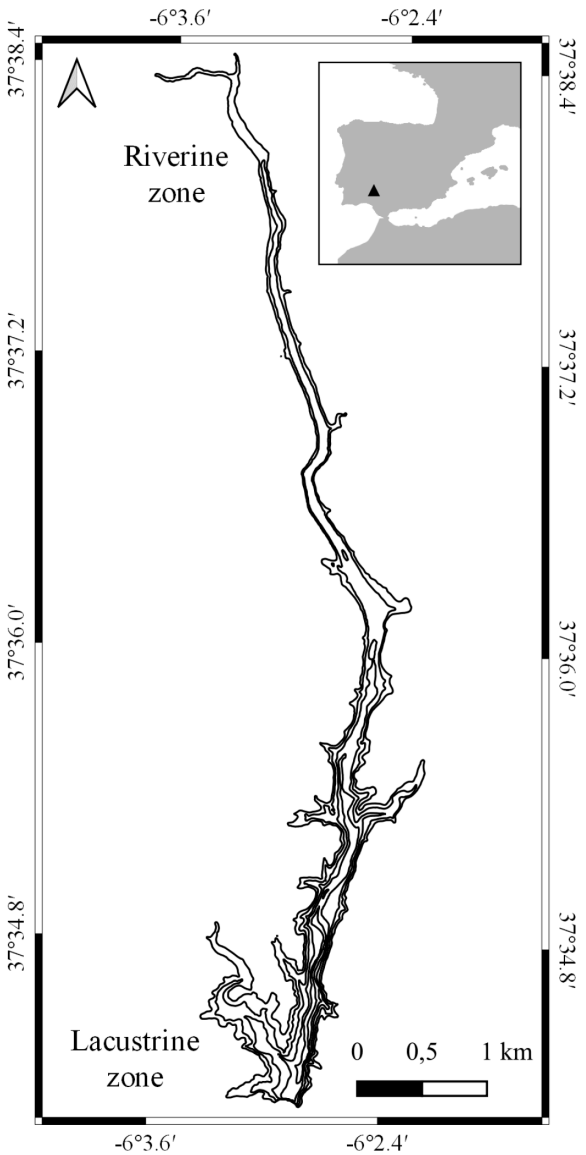

Figure 1. El Gergal reservoir bathymetric map, showing the riverine and lacustrine study sites location. *Mapa batimétrico del embalse El Gergal. Se detalla la localización de las zonas de estudio fluvial y limnética.*

MATERIALS AND METHODS

Study site

El Gergal (37º 34' 13'' N, 6º 02' 57'' W) is medium-size (maximum surface area: 250 ha; maximum depth: 37 m; mean depth: 15.7 m; maximum water storage capacity: 35 hm^3), canyon-type reservoir located in the Rivera de Huelva River (a tributary of Guadalquivir River) within a siliceous watershed (Fig. 1).

It was commissioned in 1979 as part of a network of four reservoirs which supplies water to the city of Seville and its metropolitan area (ca. 1.3 million inhabitants).

The thermal regime of El Gergal is warm monomictic (Cruz-Pizarro et al., 2005), and its trophic status is meso-eutrophic (Cruz-Pizarro et al., 2005; Gilling et al., 2017).

As a typical Mediterranean reservoir, both area and the water volume can vary severely as a result of hydrological changes (Cruz-Pizarro et al., 2005). Water renewal rate in the reservoir is consequently very variable and ranges from a maximum of 2 $month^{-1}$ to a minimum of 0.4 $month^{-1}$ during severe droughts (Toja et al., 1992; Moreno-Ostos et al., 2007).

Further information on the physical, biogeochemical and biological features of El Gergal reservoir can be found elsewhere (Cruz-Pizarro et al., 2005; Moreno-Ostos et al., 2007; Moreno-Ostos et al., 2008; Hoyer et al., 2009; Moreno-Ostos et al., 2009a; Moreno-Ostos et al., 2009b; Moreno-Ostos et al., 2012; Moreno-Ostos et al., 2016).

Survey

Surveys of the temporal and spatial distribution of CO_2 and CH_4 emissions in the reservoir were conducted at approximately monthly intervals between January 2019 and November 2019.

Every month CO_2 and CH_4 emissions and associated physico-chemical and biological variables were measured at two contrasting bathymetric sites within the reservoir: the shallow and narrow riverine zone (mean depth 4.5 ± 2.5 meters) and the deep and wide lacustrine zone (mean depth 30.7 ± 3.7 meters) (Fig. 1).

Carbon dioxide emissions

Direct measures of CO_2 surface fluxes (mg CO_2 m^{-2} d^{-1}) were performed in situ using the floating chamber method (Frankignoulle, 1988). At each sampling station (both riverine and lacustrine sites) we performed three randomly distributed replicate CO_2 flux measurements using an opaque enclosed floating chamber connected to an infrared gas analyser (IRGA EGM-5, PP-Systems, Amesbury, USA). The CO_2 concentration inside the chamber was monitored every 5 s, with an accuracy of 1 %. The floating chamber for air-water flux measurements had a surface area of 0.2 m^2 and a volume of 29.5 dm^3, and was covered with insulating and sun-reflective material to counter the effects of temperature raise in the chamber. The flux measurements lasted until at least 10 µatm of change in CO_2 were reached, with a maximum duration of 300 s. Fluxes were determined by linear regression between the CO_2 concentration in the chamber and time ($R^2 > 0.9$), correcting for temperature and atmospheric pressure (Lambert & Fréchette, 2005). Positive fluxes indicated CO_2 emissions from the reservoir to the atmosphere, while negative fluxes indicate reservoir CO_2 uptake.

Methane emissions

Ebullitive CH_4 emissions (mg CH_4 m^{-2} d^{-1}) were collected at the riverine and lacustrine sites using bubble traps. Following DelSontro et al. (2016) the bubble traps consisted in inverted plastic funnels (90 cm diameter, 0.64 m^2 surface area), with a 0.5 L graduate plastic bottle attached to the apex as gas collector. The collector was equipped with a rubber stopper at its base to extract gas with a syringe in the case the emission exceeded the volume of the collector bottle. The collectors were screwed into the funnel once submerged to fill them completely with water avoiding the presence of air. The funnels were weighted to ensure that they remain in a vertical position, and deployed from previously installed fixed buoys to avoid disturbances in the sediment. Once installed, the funnel gas collector was 0.5 m deep.

At each sampling site we deployed three equally-distanced bubble traps. Once installed, riverine

and lacustrine bubble traps remained around 24 hours collecting gas. After this time, gas collectors were detached and closed underwater with a cap fitted with a rubber stopper to extract the gas sample. After measurement of total collected gas volume, gas was sampled from the collector using a syringe and injected into 10 mL pre-evacuated glass vials (Agilent). In the laboratory gas samples were analyzed using an Agilent 7820A gas chromatograph to determine the concentration of CH_4 in the captured bubbles. Finally, CH_4 ebullitive flux was computed from CH_4 concentration in the gas collector, volume of total gas collected, deployment time, and funnel surface.

Diffusive CH_4 emissions (mg CH_4 m^{-2} d^{-1}) from water to air was calculated as the product of gas exchange coefficient for CH_4 and the difference between CH_4 concentrations in surface water and air equilibrated water:

$$CH_{4\,diffusive} = k \times \left[CH_{4_{water}} - CH_{4_{air}}\right]$$

Where $CH_{4\ diffusive}$ is methane diffusive flux, $CH_{4\ water}$ is the concentration of methane in surface water, $CH_{4\ air}$ is the theoretical methane concentration in equilibrium with the atmosphere at the ambient temperature and measured salinity (Wiesenburg & Guinasso, 1979), and k is the gas exchange coefficient for CH_4. This gas exchange was calculated as a function of wind speed and water temperature following Cole & Caraco (1998):

$$k = [2.07 + 0.215 \times U_{10}^{1.7}] \times \left(\frac{SC_{CH_4}}{600}\right)^{-n}$$

Where U_{10} is the wind speed at 10 m height above the reservoir level, SC is the Schmidt number for CH_4 at the measured water temperature (Wannikhof, 1992), and the exponent n is $1/2$ when wind speed is higher than 3.7 m/s and $2/3$ when wind speed is lower than 3.7 m/s.

Total CH_4 emissions were calculated by summing CH_4 diffusive and ebullitive fluxes.

Surface CH_4 concentration was estimated by the headspace equilibration technique and gas chromatography according to Gómez-Gener et al. (2015). Briefly, at each measurement site we sampled surface water filling three 60 mL airtight syringes with 30 mL of surface water and 30 mL of atmospheric air, thus creating a headspace with atmospheric air of 1:1 ratio. The syringes were submerged in water of known temperature and vigorously shaken for 30 minutes to allow the gas and water phases to equilibrate, and equilibrium temperature was recorded. 20 mL of the headspace gas was injected into 10 mL pre-evacuated glass-tight vials (Agilent). In the laboratory gas vials were analyzed using gas chromatography as previously exposed for ebullitive fluxes.

Hydrological, physico-chemical and biological variables

Water renewal rate ($month^{-1}$) was calculated for each month according to Toja et al. (1992) as:

$$\frac{V_{inflow} + V_{stored}}{V_{reservoir}}$$

Where V_{inflow} is water inflow into the reservoir (hm^3/month); V_{stored} is volumen stored in the reservoir (hm^3), and $V_{reservoir}$ is maximum reservoir water storage (hm^3).

At each sampling station we used a YSI-EXO2 multiparameter probe to measure water temperature, dissolved oxygen concentration, salinity, pH and Chlorophyll-*a* (Chl-*a*) concentration at fixed depth intervals (0.5 m in the riverine, 1 m in the lacustrine) from surface to the bottom.

A vertical temperature gradient of at least 1 degree Celsius per meter depth was used as a threshold value to evaluate if the water column was thermally stratified (gradient $\geq$ 1 C m^{-1}) or mixed (gradient < 1 C m^{-1}).

In addition, at the lacustrine sampling station a Van Dorn horizontal bottle was used to collect three water samples at regular depth intervals from the thermocline (when thermally stratified) or light compensation depth (when mixed) to the sediment. These water samples were used to determine in the laboratory dissolved CO_2 and CH_4 concentration in the hypolimnion (when stratified) or aphotic zone (when mixed) at the lacustrine zone. CH_4 concentration in deep waters

was determined following the headspace method previously exposed. For deep CO_2 concentration, water samples collected with the Van Dorn bottle were directly circulated through a gas transfer membrane contactor (MiniModule, Liqui-Cel, USA) coupled, by a closed system, to a portable CO_2 gas analyzer (EGM-5 PP Systems). The water was circulated via gravity through the contactor at 300 mL/min, and the equilibrated gas was continuously recirculated into the infrared gas analyzer for instantaneous pCO_2 measurements (Gómez-Gener et al., 2015).

RESULTS

General limnological features

Reservoir water level was high during the whole study period. In winter and spring mean water level was 48.9 ± 0.4 meters above sea level (being 50 m a.s.l. the highest water level in El Gergal), whereas water level slightly decreased during summer and autumn, depicting mean values of 44.5 ± 1.3 m a.s.l. Water renewal rate was low (average 0.74 ± 0.18 month^{-1}, ranging between 0.98 month^{-1} in February and 0.5 month^{-1} in November). As a consequence, in the riverine site water column depth was 6.8 ± 0.2 m from January to May, and it decreased to only 2.6 ± 1.5 m from June to December. In the lacustrine site water column depth was very constant from January to May (33.4 ± 2.5 m), and it slightly decreased from June to December (27.4 ± 1.6 m).

Water column in the riverine site was generally isothermal, although some thermal vertical temperature gradients ≥ 1 C m^{-1} were measured during spring (March and May) and autumn (September, October and November). In the lacustrine site water column was vertically mixed from January to April, when it became thermally stratified until the end of the year. The thermocline was located at ~9 depth at the beginning of the stratification (April), and progressively sank during the thermal stratification period, reaching ~19 m depth in November, just before complete turnover in December (Fig. 2)

In the riverine site water column was typically well-oxygenated, with some bottom anoxia in spring and autumn. By contrast, in the lacustrine zone water column was only vertically oxygenated during the turbulent mixing period, while the

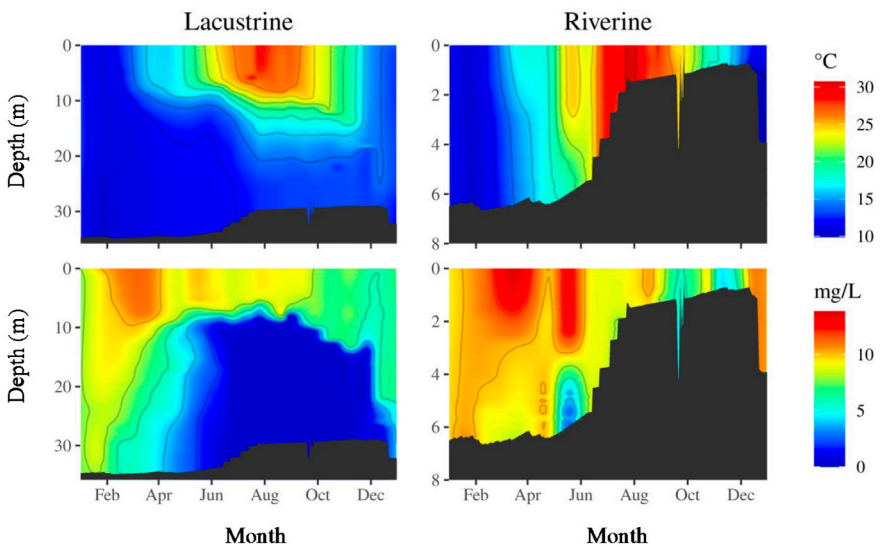

Figure 2. Spatio-temporal variability of water column thermal structure (top panel) and oxygen concentration (bottom panel) in the riverine zone (right) and lacustrine zone (left). *Variabilidad espacio-temporal de la estructura térmica de la columna de agua (parte superior del panel) y de la concentración de oxígeno disuelto (parte inferior del panel) en la zona fluvial (derecha) y limnética (izquierda).*

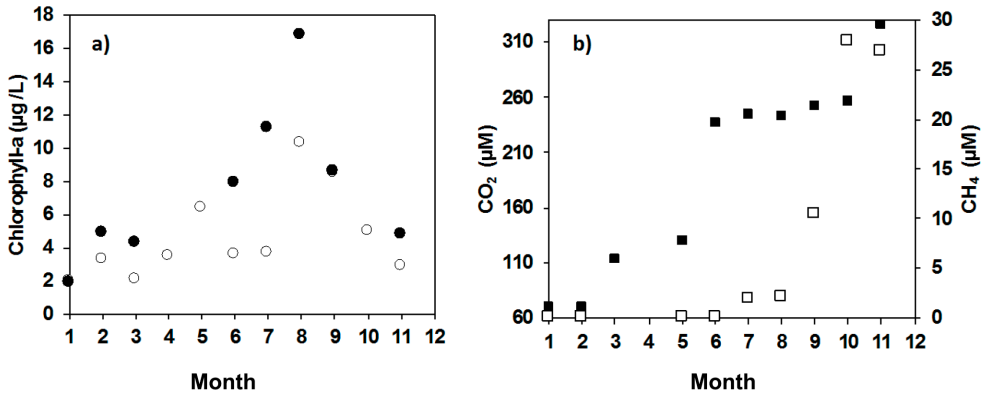

Figure 3. a) Temporal dynamics of Chl-*a* concentration (mean concentration in the first five meters of water column) in lacustrine (white dots) and riverine (black dots) sites. b) Temporal dynamics of dissolved CO_2 (black squares) and dissolved CH_4 (white squares) in the hypolimnion of the lacustrine zone. *a) Dinámica temporal de la concentración de Chl-*a *(valor medio de los primeros cinco metros de columna de agua) en las zonas limnética (puntos blancos) y fluvial (puntos negros). b) Dinámica temporal de la concentración de CO_2 (cuadros negros) y CH_4 (cuadros blancos) en el hipolimnion de la zona limnética.*

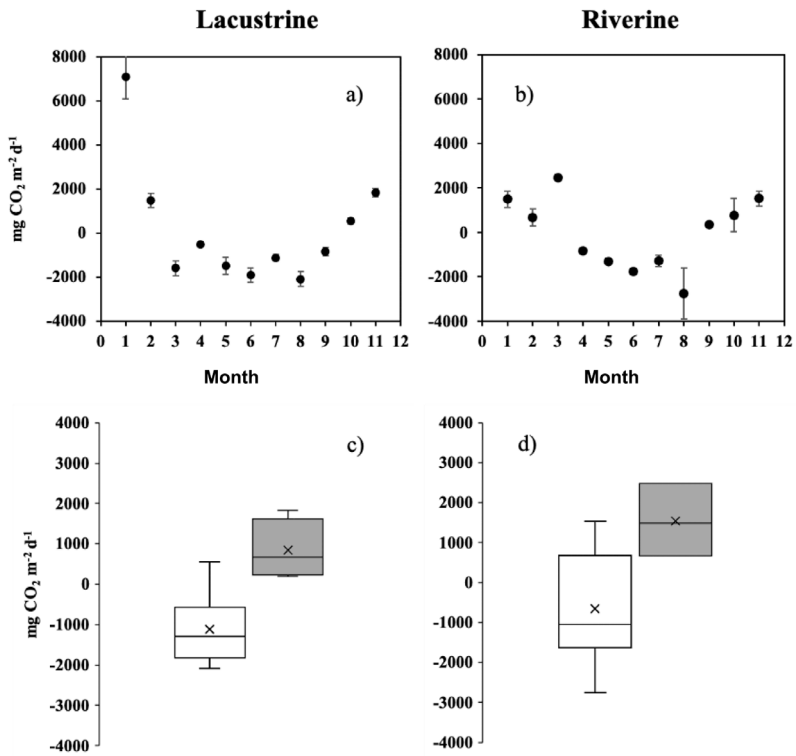

Figure 4. CO_2 flux measured in the lacustrine (a) and riverine (b) zones. Box and whiskers plots depict mean CO_2 fluxes during mixing (grey box) and stratification (white box) periods in the lacustrine (c) and riverine zones (d). Box represent first and third quartiles, whiskers are maximum and minimum values, horizontal line is median, and x is mean. *Flujo de CO_2 en las zonas limnética (a) y fluvial (b). Los gráficos de cajas y bigotes muestran el flujo medio de CO_2 durante los periodos de mezcla (cajas grises) y estratificación térmica (cajas blancas) en la zona limnética (c) y fluvial (d) del embalse. Las cajas representan el primer y tercer cuartil, los bigotes los valores máximos y mínimos, la línea horizontal es la mediana, y x sitúa la media.*

thermally stratified period was characterized by anoxic waters below the thermocline. Oxygen depletion started at the onset of stratification, and complete anoxia was reached around June and lasted until overturn in December (Fig. 2).

Chlorophyll-*a* concentration in the lacustrine and riverine zones showed a similar seasonal trend (Fig. 3a). It was low during the mixed period and increased throughout the thermally stratified period, reaching maximum values in August (10.28 µg/L and 16.84 µg/L in lacustrine and riverine zones, respectively). At late stratification Chl-*a* depicted similar values than during mixing.

Carbon dioxide concentration in the deep waters of the lacustrine site progressively increased from 68 µM in the winter mixing period to maximum values of 326 µM at the end of thermal stratification. Methane in the lacustrine deep waters was very low in the presence of oxygen (< 1 µM), while it increased exponentially as hypolimnion became anoxic, reaching ~28 µM in the late-stratification (Fig. 3b).

Carbon dioxide fluxes

Carbon dioxide fluxes in the lacustrine zone revealed a marked temporal pattern, with positive values (CO_2 emission) in winter and autumn (four months), and negative values (CO_2 uptake) recorded during seven months in spring and summer (Fig. 4a). The highest CO_2 flux (7103.7 ± 1015.6 mg CO_2 m^{-2} d^{-1}) was recorded in January, and the lowest (-2096.6 ± 343.3 mg CO_2 m^{-2} d^{-1}) corresponded to August. Mean annual CO_2 flux in the lacustrine zone was 128.7 ± 2666.1 mg CO_2 m^{-2} d^{-1}, which denoted that in an annual scale this zone was a net CO_2 source to the atmosphere.

CO_2 fluxes in the riverine zone depicted a similar temporal pattern (Fig. 4b), although the period with positive CO_2 flux was longer (six months), and the time period with negative CO_2 flux was shorter (four months). In spite of this, mean annual CO_2 flux in the riverine zone was –59.99 ± 1629.5 mg CO_2 m^{-2} d^{-1}, with values ranging between a minimum flux of –2756.07 ± 1143 mg m^{-2} d^{-1} in August and a maximum flux of 2477.46 ± 134.2 mg CO_2 m^{-2} d^{-1} in March. In an annual scale, the riverine zone constituted a net CO_2 sink to the atmosphere.

During thermally stratified months both the lacustrine and riverine zones were CO_2 sinks, while when turbulent mixing conditions prevailed, both zones were CO_2 sources (Fig. 4c and 4d).

Methane emissions

El Gergal reservoir was also a source of methane

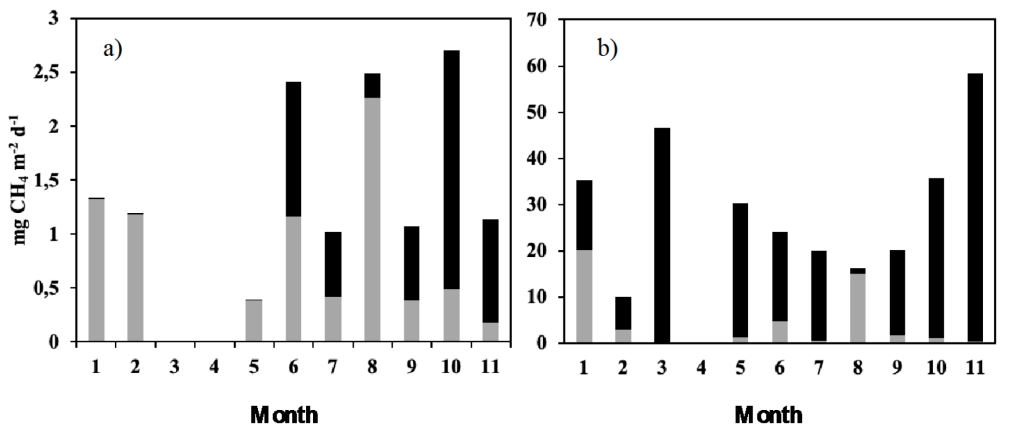

Figure 5. CH_4 emissions in the lacustrine (a) and riverine (b) zones. Grey portion of bars represents diffusive emission, black portion represents ebullitive emission. *Emisiones de CH_4 en las zonas limnética (a) y fluvial (b). La porción gris de las barras representa la emisión difusiva, y la porción negra la emisión ebullitiva.*

to the atmosphere throughout the studied year.

Mean total methane emissions in the lacustrine zone was 1.5 ± 0.8 mg CH_4 m^{-2} d^{-1}, with a minimum value of 0.38 ± 0.27 mg CH_4 m^{-2} d^{-1} in May and a maximum of 2.71 ± 1.4 mg CH_4 m^{-2} d^{-1} in October. Monthly CH_4 emissions in this deep zone depicted increasing values during the thermal stratification period (Fig. 5a). Diffusive emission was detected throughout the year, and showed a 60 % mean contribution to annual total methane flux in the lacustrine zone.

By contrast, no clear temporal trend in methane emissions was found in the shallow riverine zone (Fig. 5b). Total methane emissions in this zone showed an annual average total CH_4 emission of 30.17 ± 14.8 mg CH_4 m^{-2} d^{-1}. Maximum values were recorded in spring (46.56 ± 40.50 mg CH_4 m^{-2} d^{-1} in March) and autumn (58.43 ± 67.40 mg CH_4 m^{-2} d^{-1}), and minimum in winter (9.89 ± 8.95 mg CH_4 m^{-2} d^{-1} in February). Interesting-

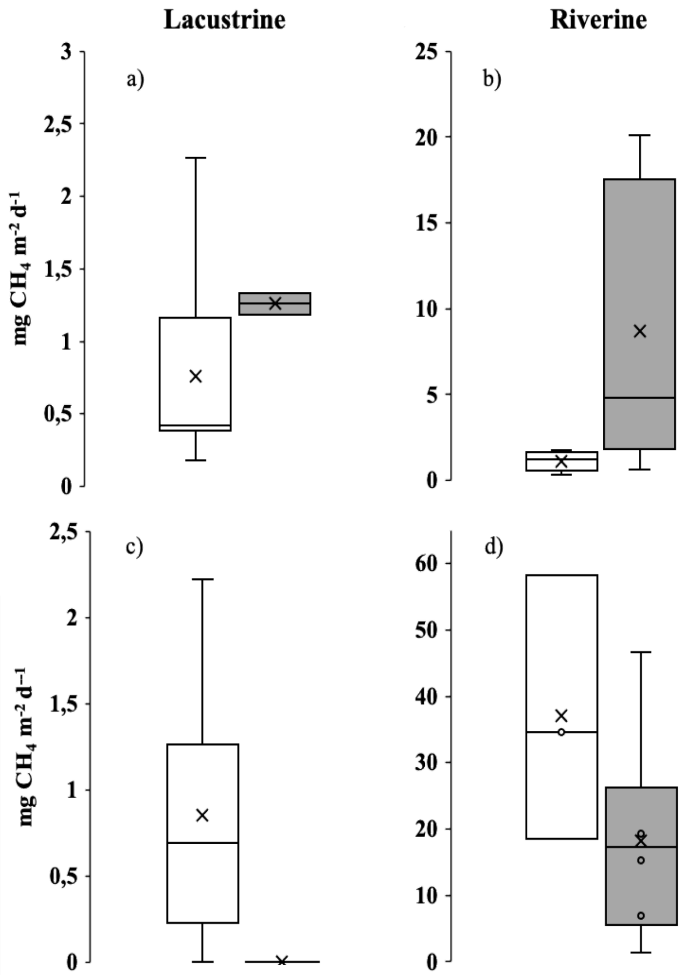

Figure 6. CH_4 emissions in the lacustrine and riverine zones during mixing (grey boxes) and stratification (white boxes) periods. a) and b) depicts lacustrine and riverine diffusive emissions, c) and d) depicts lacustrine and riverine ebullitive emissions. Box represent first and third quartiles, whiskers are maximum and minimum values, horizontal line is median, and x is mean. *Emisiones de CH_4 en las zonas limnética y fluvial durante los periodos de mezcla (cajas grises) y estratificación térmica (cajas blancas). a) y b) muestran las emisiones difusivas en las zonas limnética y fluvial, c) y d) muestrean las emisiones ebullitivas en las mismas zonas. Las cajas representan el primer y tercer cuartil, los bigotes los valores máximos y mínimos, la línea horizontal es la mediana, y x sitúa la media.*

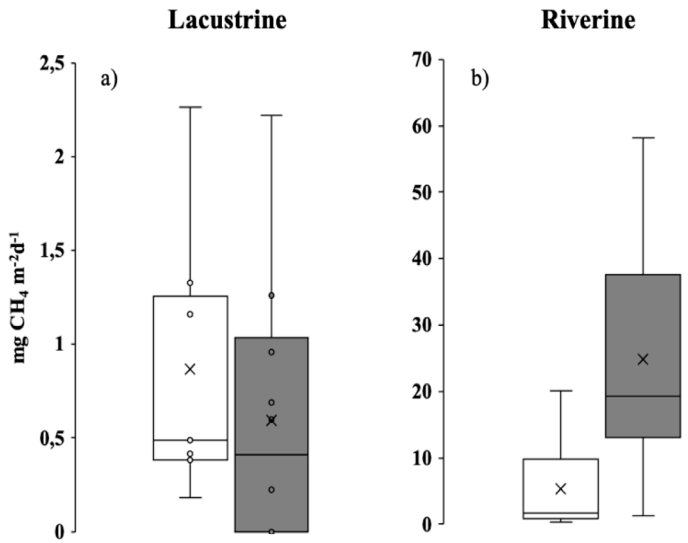

Figure 7. CH_4 diffusive (white boxes) and ebullitive (grey boxes) emissions measured in the lacustrine (a) and riverine (b) zones. Box represent first and third quartiles, whiskers are maximum and minimum values, horizontal line is median, and x is mean. *Flujo difusivo (cajas blancas) y ebullitivo (cajas grises) en las zonas limnética (a) y fluvial (b) del embalse. Las cajas representan el primer y tercer cuartil, los bigotes los valores máximos y mínimos, la línea horizontal es la mediana, y x sitúa la media.*

ly, in this shallow zone bubbling was the prevailing CH_4 emission pathway throughout the whole year, with a mean contribution to total CH_4 emission of 78.13 %.

Both in the lacustrine and riverine sites CH_4 diffusive emissions were higher during mixing than during thermally stratified months (Fig. 6a and 6b). By contrast, CH_4 ebullitive emissions depicted an opposite temporal pattern, with significantly higher fluxes during the thermal stratification period (Fig. 6c and 6d).

Marked differences were found between the magnitude of CH_4 emissions in the riverine and lacustrine zones. In the upstream riverine zone ebullitive flux was significantly higher than diffusive flux. Mean annual CH_4 ebullitive emission was 24.85 ± 17.53 mg CH_4 m^{-2} d^{-1}, with values ranging from 1.28 ± 2.05 mg CH_4 m^{-2} d^{-1} and 58.13 ± 87.40 mg CH_4 m^{-2} d^{-1}. Mean annual CH_4 diffusive emission was 5.30 ± 7.16 mg CH_4 m^{-2} d^{-1}, with minimum values of 0.30 ± 0.07 mg CH_4 m^{-2} d^{-1} and maximum of 20.11 ± 1.71 mg CH_4 m^{-2} d^{-1}. By contrast, in the lacustrine zone the diffusive flux was undistinguishable from the ebullitive flux. Mean annual CH_4 ebullitive emission was 0.59 ± 0.72 mg CH_4 m^{-2} d^{-1}, with a range from 0 mg CH_4 m^{-2} d^{-1} and 2.22 ± 2.17 mg CH_4 m^{-2} d^{-1}. Mean annual CH_4 diffusive emission was 0.86 ± 0.67 mg CH_4 m^{-2} d^{-1}, values ranging between 0.17 mg CH_4 m^{-2} d^{-1} and 2.26 mg CH_4 m^{-2} d^{-1} (Fig. 7).

Factors influencing CO_2 and CH_4 emissions

We did not find any significant relation between CO_2 fluxes and the considered hydrological variables (thermal stability, water renewal rate, and water column depth) in El Gergal reservoir. However, we found a negative and significant correlation between CO_2 flux and Chl-*a* ($r = -0.55$; $p < 0.05$), pH also being negatively correlated to CO_2 fluxes ($r = 0.57$; $p < 0.01$) (Fig. 8a and 8b).

On the other hand, CH_4 emissions were influenced both by hydrological and hypolimnetic biogeochemistry factors. No significant relation was found between CH_4 fluxes and Chl-*a* in El Gergal reservoir. Regarding hydrological drivers, in the lacustrine zone log CH_4 emissions were negatively correlated to reservoir water renewal rate ($r = -0.86$; $p < 0.005$), while no significant correlation was

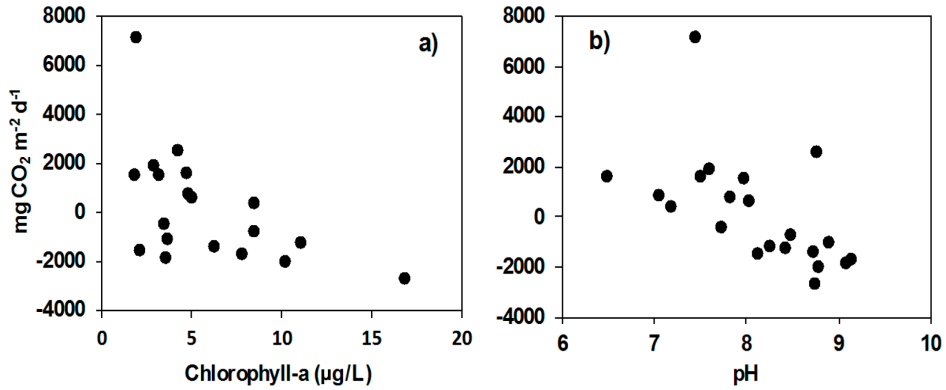

Figure 8. a) Relationship between CO_2 flux and mean Chl-*a* in the first five meters of water column, and b) CO_2 flux and surface pH. *a) Relación entre el flujo de CO_2 y la concentración media de Chl-*a *en los primeros cinco metros de la columna de agua, y b) relación entre el flujo de CO_2 y el pH en superficie.*

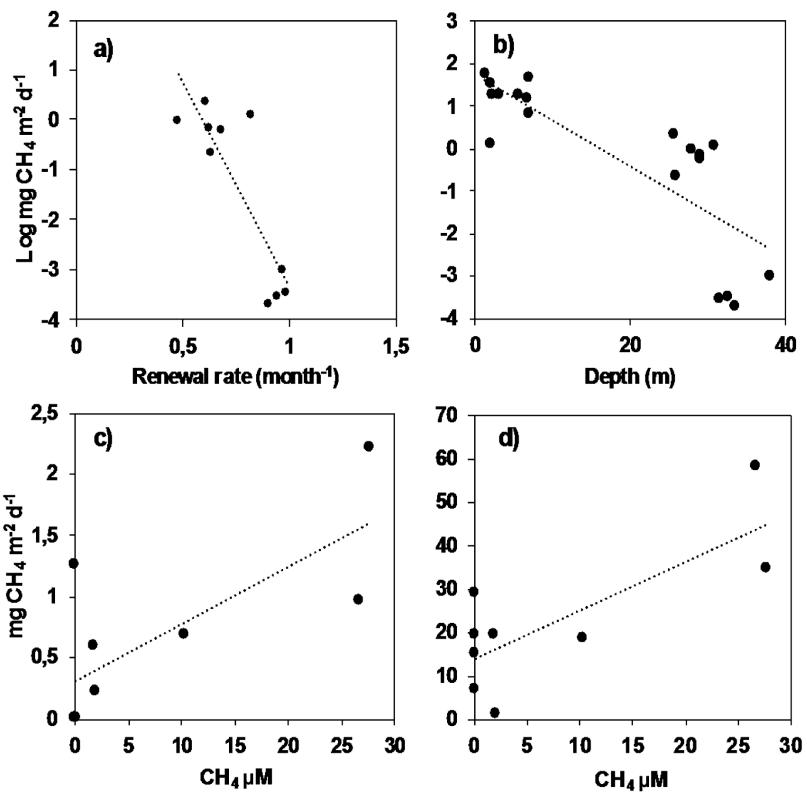

Figure 9. Relationship between a) water renewal rate and log CH_4 ebullitive flux in the lacustrine zone; b) water column depth and log CH_4 ebullitive flux in riverine and lacustrine zones; c) hypolimnetic CH_4 concentration and CH_4 ebullitive emissions in the lacustrine zone; d) hypolimnetic CH_4 concentration and CH_4 ebullitive emissions in the riverine zone. *Relación entre a) tasa de renovación del agua y log flujo ebullitivo de CH_4 en la zona limnética; b) profundidad de la columna de agua y log flujo ebullitivo de CH_4 en las zonas fluvial y limnética; c) concentración hipolimnética de CH_4 y emisión ebullitiva de CH_4 en la zona limnética; d) concentración hipolimnética de CH_4 y emisión ebullitiva de CH_4 en la zona fluvial.*

found between CH_4 emissions and water renewal rate in the riverine zone. In addition, log CH_4 ebullitive emissions were negatively related to water column depth both in lacustrine and riverine zones ($r = -0.80$; $p < 0.001$) (Fig. 9a and 9b, respectively).

In respect of hypolimnetic biogeochemical drivers, ebullitive CH_4 emissions in the lacustrine and riverine zones were positively correlated to hypolimnetic CH_4 concentration ($r = 0.74$; $p < 0.05$ and $r = 0.77$; $p < 0.05$, respectively) (Fig. 9c and 9d).

DISCUSSION

The magnitude of CO_2 and CH_4 fluxes varied substantially over space (riverine and lacustrine zones) and time. Both CO_2 and CH_4 emissions in the reservoir revealed a marked an opposite seasonal pattern. The highest CO_2 and minimum CH_4 emissions were recorded during the winter turbulent mixing conditions, while at the thermally stratified period CO_2 fluxes became negative (CO_2 uptake) and CH_4 fluxes increased, especially at the late-stratification months preceding overturn. Similar seasonal patterns in reservoir CO_2 and CH_4 emissions have been recently reported (Beaulieu et al., 2014; Musenze et al., 2014; Samiotis et al., 2018; León-Palmero et al., 2020a).

In El Gergal both CO_2 and CH_4 emissions showed marked differences between riverine and lacustrine zones, highlighting the importance of including riverine areas to achieve accurate reservoir CO_2 and CH_4 emission assessments (Beaulieu et al., 2014; Yang, 2019), especially in heterogeneous ecosystems such as reservoirs.

Mean CO_2 flux in the riverine zone was negative, and consequently this shallow area constituted a CO_2 sink at an annual scale. By contrast, mean CO_2 flux in the lacustrine was positive, water mass being a source of CO_2 to the atmosphere at an annual scale. Magnitude of lacustrine CO_2 fluxes measured in El Gergal was very similar to the CO_2 fluxes reported by Morales-Pineda et al. (2015) and León-Palmero et al. (2020a) for southern Spain Mediterranean reservoirs, and also coherent with emission values provided by Barros et al. (2011) for temperate reservoirs.

On the other hand, total CH_4 emission rates in El Gergal were also within the ranges provided by León-Palmero et al. (2020a) for Mediterranean reservoirs, and by St. Louis et al. (2000) and Barros et al. (2011) for temperate reservoirs. Ebullitive and diffusive fluxes were respectively 40 and 6 times greater in the riverine zone than those measured in the lacustrine. Shallow riverine areas have been previously identified as CH_4 emission hot spots in lakes and reservoirs (Bastviken et al., 2002; Beaulieu et al., 2014; Paraníba et al. 2018; Yang, 2019), where CH_4 production is enhanced by deposition of fluvial organic matter, and a large fraction of sedimentary CH_4 is directly evading to the atmosphere through bubbling. The ebullitive CH_4 emissions measured in the shallow riverine zone of El Gergal were comparable to ebullitive fluxes found in temperate shallow ponds (Dove et al., 1999; DelSontro et al., 2016), a kind of ecosystem typically supporting higher CH_4 emission rates than temperate deep lakes and reservoirs. The contribution of ebullition to total CH_4 emissions was ~ 40 % in the lacustrine zone, and ~ 80 % in the riverine, both values within the range of 38 % - 96 % reported by Bastviken et al. (2011) and higher than those reported in northern ponds and shallow lakes (Dove et al., 1999; Weyhenmeyer et al., 1999; DelSontro et al., 2016). Productive reservoirs as El Gergal tend to accumulate organic carbon in sediments, and consequently there is a great potential for CH_4 ebullition from these ecosystems, leading to higher total CH_4 emissions as bubbles directly to the atmosphere with limited dissolution and oxidation losses (McGinnis et al., 2006; DelSontro et al., 2010; DelSontro et al., 2016).

In addition, measured CH_4 ebullitive fluxes in El Gergal showed high standard deviation values, revealing the strong fine-scale spatio-temporal heterogeneity that characterizes benthic CH_4 bubbling in inland waters, which makes it challenging to quantify ebullition emissions (DelSontro et al., 2015; Scandella et al., 2016, Lindgren et al., 2019).

Our results show that variability in CO_2 fluxes in El Gergal reservoir can be explained by the seasonal changes in CO_2 depletion in surface waters as a consequence of primary productivity, as previously reported by Saidi & Koschorreck

(2017) for 39 German reservoirs. Indeed, Chl-*a* concentration and pH were both negatively related to CO_2 fluxes in El Gergal. During summer and early autumn phytoplankton biomass in the reservoir increases significantly, and primary production promotes CO_2 uptake and reduces CO_2 concentration in surface waters, enhancing the absorption of this gas from the atmosphere. In addition, primary production also increases pH, which favors the formation of carbonates. This reduces CO_2 concentration in surface waters, which again would fuel CO_2 absorption (Soumis et al., 2004; Xiao et al., 2013; Schrier-Uijil et al., 2011; Paranaíba et al., 2018; Gruca-Rokosz, 2020). Similar correlations between pH and CO_2 fluxes have been reported for reservoirs (Soumis et al., 2004; Halbedel & Koschorreck, 2013; Quiñones-Rivera et al., 2015; Saidi & Koschorreck, 2017) and lakes (Lazzarino et al., 2009; Trolle et al., 2012). In this context, Saidi & Koschorreck (2017) have suggested the use of pH as a proxy of CO_2 fluxes in low alkalinity reservoirs.

In productive reservoirs such as El Gergal most of the inorganic carbon fixed by primary production is later decomposed in the anoxic hypolimnion and returned back to the atmosphere, a relatively large fraction of it in the form of CH_4 (St. Louis et al., 2000). In addition to supply organic carbon and contribute to decrease hypolimnetic oxygen content, phytoplankton biomass also affects the quality of the organic matter reaching the anoxic hypolimnion, and it has been demonstrated that phytoplankton-derived labile organic matter fuel higher rates of methane production than carbon of terrestrial origin (West et al., 2012; Deemer et al., 2016; León-Palmero et al., 2020b).

Regarding factors influencing methane emissions in El Gergal, we found that there is a strong dependency of CH_4 emissions on net CH_4 production and its storage capacity in the water column, as León-Palmero et al. (2020a) have recently demonstrated. We have also found a negative relation between water column depth and CH_4 ebullitive emissions, as previously reported by León-Palmero et al. (2020a) for Mediterranean reservoirs with similar hydrological characteristics to El Gergal. Water column depth is known as a relevant hydrological driver for CH_4 emissions, with a positive relationship between hydrostatic pressure and the CH_4 storage capacity, and negative relationship with CH_4 emissions (León-Palmero et al., 2020a). Depth also plays a relevant role on the spatial variability of CH_4 fluxes from lakes and reservoirs, especially in relation to bubbling emissions (Casper et al., 2000; Bastviken et al., 2004; Wik et al., 2013, West et al., 2015; DelSontro et al., 2016; Natchimuthu et al., 2016; Deemer et al., 2016). Shallow areas, such as the riverine zone in El Gergal, depicts low CH_4 storage capacity and high ebullition rates, while the higher hydrostatic pressure and deeper water column in the lacustrine zone prevents CH_4 bubbling to the atmosphere. In agreement, fluctuating water level has a relevant influence on CH_4 ebullitive flux (Keller & Stallard, 1994; Harrison et al., 2017). Finally, our results also suggest that variability in water renewal rate constitute a relevant hydrological factor affecting CH_4 emissions in El Gergal. The higher the renewal rate, the lower the proportion of deep anoxic zones in El Gergal reservoir (Toja et al., 1992), where methanogenesis typically occurs.

Changes in hydrological patterns are one of the major impacts of global change. Precipitation and temperature trends are significantly changing water availability in many regions (Fekete et al., 2002). In the Mediterranean region this trend has been projected to continue with potentially up to 50 % decreases in river discharge (Schewe et al., 2014). These changes will impact hydrology in the whole river network (Catalán et al., 2016), including lakes and reservoirs, which will modify the regime of incoming materials, flooded surface, water renewal rate, and water column depth. Draughts and reservoir withdrawn will increase the proportion of shallow areas in Mediterranean reservoirs and decrease water renewal rate, consequently enhancing CH_4 emissions (especially bubbling). In addition, projected increases in phytoplankton biomass (Trolle et al., 2014) could intensify CO_2 uptake during the thermally stratified period, but simultaneously fuel hypolimnetic respiration processes and the occurrence of relevant CO_2 and CH_4 emissions at the overturn. As a consequence, hydrological changes expected in the Mediterranean region could intensify the role of reservoirs as emitters of greenhouse gases.

ACKNOWLEDGMENTS

This study was funded by project C-Hydro-Change (CGL2017-86788-C3-1P) of the Spanish Ministry of Economy and Competiveness. JJM-P was supported by a FPI grant from the same Ministry. EMASESA staff provide essential technical support during field surveys. We also acknowledge Leonardo Pozzo-Pirotta and José Luis Diez for sampling support.

REFERENCES

Barros, N., J. Cole, J. Tranvik, L. Prairie, Y. T., Bastviken, D., Huszar, V. L. M., …Roland, F. (2011). Carbon emission from hydroelectric reservoirs linked to reservoir age and latitude. *Nature Geoscience*, 4, 593-596. DOI: 10.1038/ngeo1211

Bastviken, D., Cole, J., Pace, M. L., & Tranvik, L. (2004). Methane emissions from lakes: Dependence on lake characteristics, two regional assessments, and a global estimate. 2004. *Global Biogeochemical Cycles*, 18, 1-12. DOI: 10.1029/2004GB002238

Bastviken, D., Cole, J. J., Pace, M. L., & Van De Bogert, M. C. (2008). Fates of methane from different lake habitats: Connecting whole-lake budgets and CH_4 emissions. *Journal of Geophysical Research: Biogeosciences*, 113, G02024. DOI: 10.1029/2007JG000608

Bastviken, D., Tranvik, J., Downing, J. A., Crill, P. M., & Enrich-Prast, A. (2011). Freshwater methane emissions offset the continental carbon sink. *Science*, 331, 50. DOI: 10.1126/science.1196808

Beaulieu, J. J., Smolenski, R. L., Nietch, C. T., Townsend-Small, A., & Elovitz M. S. (2014). High methane emission from a midlatitude reservoir draining an agricultural watershed. *Environmental Science and Technology*, 48, 11100-11108. DOI: 10.1021/es501871g

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

Casper, P., Maberly, S. C., Hall, G. H., & Finlay, B. J. (2000). Fluxes of methane and carbon dioxide from a small productive lake to the atmosphere. *Biogeochemistry*, 49, 1.19. DOI: 10.1023/A:1006269900174

Catalán, N., Marcé, R., Kothawala, D. N., & Tranvik, L. J. (2016). Organic carbon decomposition rates controlled by water retention time across inland waters. *Nature Geoscience*, 9, 501–504. DOI: 10.1038/ngeo2720

Cole, J. J., Pace, M. L., Carpenter, S. R., & Kitchell, J. F. (2000). Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations. *Limnology and Oceanography*, 45, 1718–1730. DOI: 10.4319/lo.2000.45.8.1718

Cole, J. J., & Caraco, N. F. (1998). Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF_6. *Limnology and Oceanography*, 43, 647-656. DOI: 10.4319/lo.1998.43.4.0647

Cruz-Pizarro, L., Basanta, A., Escot, C., Moreno-Ostos, E., & George, D. G. (2005). Temporal and spatial variations in the quality of water in El Gergal reservoir, Seville, Spain. *Freshwater Forum*, 23, 62–77.

Deemer, B. R., Harrison, J. A., Li, S., Beaulieu, J. J., DelSontro, T., Barros, N., Bezerra-Neto, J. F., ...Vonk, J. A. (2016). Greenhouse gas emissions from reservoir water surfaces: A new global synthesis. *Bioscience*, 66, 949-964. DOI: 10.1093/biosci/biw117

DelSontro, T., McGinnis, D. F., Sobek, S., Ostrovsky, I., & Wehrli, B. (2010). Extreme methane emissions from a Swiss hydropower reservoir: contribution from bubbling sediments. *Environmental Science and Technology*, 44, 2419-2425. DOI: 10.1021/es9031369

DelSontro, T., McGinnis, D. F., Wehrli, B., & Ostrovsky, I. (2015). Size does matter: Importance of large bubbles and small-scale hot spots for methane transport. *Environmental Science and Technology*, 49, 1268-1276. DOI: 10.1021/es5054286

DelSontro, T., Boutet, L., St-Pierre, A., Del Giorgio, P. A., & Prairie, Y. (2016). Methane ebullition and diffusion from northern ponds and lakes regulated by the interaction between temperature and system productivity. *Limnology and Oceanography*, 61, S62-S77. DOI: 10.1002/lno.10335

Dove, A., Roulet, N., Crill, P., Chanton, J., &

Bourbonniere, R. (1999). Methane dynamics of a northern boreal beaver pond. *Ecoscience*, 6, 577-586.

Duarte, C. M., & Prairie, Y. T. (2005). Prevalence of heterotrophy and atmospheric CO_2 emissions from aquatic ecosystems. *Ecosystems*, 8, 862–870. DOI: 10.1007/s10021-005-0177-4

Einsele, G., Yan, J., & Hinderer, M. (2001). Atmospheric carbon burial in modern lake basins and its significance for the global carbon budget. *Global and Planetary Change*, 30(3), 167-195. DOI: 10.1016/S0921-8181(01)00105-9

Fekete, B. M., Vörösmarty, C. J., & Grabs, W. (2002). High-resolution fields of global runoff combining observed river discharge and simulated water balances. *Global Biogeochemical Cycles*, 16 (3), 15-1 -15-10. DOI: 10.1029/1999GB001254

Frankignoulle, M. (1988). Field measurements of air-sea CO_2 exchange. *Limnology and Oceanography*, 33, 313–322.

Gómez-Gener, L., Obrador, B., Von Schiller, D., Marcé, R., Casas-Ruiz, J. P., Proia, L., …Koschorreck, M. (2015). Hot spots for carbon emissions from Mediterranan fluvial networks during summer drought. *Biogeochemistry*, 125, 409-426. DOI: 10.1007/s10533-015-0139-7

Gruca-Rokosz, R. (2020). Quantitative fluxes of the greenhouse gases CH_4 and CO_2 from the surfaces of selected Polish reservoirs. *Atmosphere*, 11, 286. DOI: 10.3390/atmos11030286

Halbedel, S., & Koschorreck, M. (2013). Regulation of CO_2 emissions from temperate streams and reservoirs. *Biogeosciences*, 10, 7539-7551. DOI: 10.5194/bg-10-7539-2013

Harrison, J. A., Deemer, B. R., Birchfield, M. K., & O'Malley, M. T. (2017). Reservoir water-level drawdowns accelerate and amplify methane emission. *Environmental Science and Technology*, 51, 1267–1277. DOI: 10.1021/acs.est.6b03185

Heathcote, A. J., Anderson, N. J., Prairie, Y. T., Engstrom, D. R., & Del Giorgio, P. (2015). Large increases in carbon burial in northern lakes during the Anthropocene. *Nature Communications*, 6, 10016. DOI: 10.1038/ncomms10016

Hoyer, A. B., Moreno-Ostos, E., Vidal, J., Blanco, J.M., Palomino-Torres, R. L., Basanta, A.,… Rueda, F. J. (2009). The influence of external perturbations on the functional composition of phytoplankton in a Mediterranean reservoir. *Hydrobiologia*, 627, 1–17. DOI: 10.1007/s10750-009-9934-2

Imberger, J., & Patterson, J. C. (1990). Physical limnology. *Advances in Applied Mechanics*, 27, 353-370.

Keller, M., & Stallard, R. F. (1994). Methane emission by bubbling from Gatun Lake, Panama. *Journal of Geophysical Research*, 99, 8307-8319.

Lambert, M., & Fréchette, J. L. (2005). Analytical techniques for measuring fluxes of CO_2 and CH_4 from hydroelectric reservoirs and natural water bodies. In: A. Tremblay, L. Varfalvy, C. L. Roehm, M. Garneau (eds). *Greenhouse Gas Emissions-Fluxes and Processes*. *Hydroelectric Reservoirs and Natural Environments*. (pp. 37–60). Springer. Berlin.

Lazzarino, J. K., Bachmann, R. W., Hoyer, M. V., & Canfield, D. E. (2009). Carbon dioxide supersaturation in Florida lakes. *Hydrobiologia*, 627, 169-180. DOI: 10.1007/s10750-009-9723-y

Lehner, B., Liermann C. R, Revenga, C., Vörösmarty, C., Fekete, B., Crouzet, P.,… Wisser, D. (2011). High-resolution mapping of the world´s reservoirs and dams for sustainable river-flow management. *Frontiers in Ecology and the Environment*, 9, 494-502. DOI: 10.1890/100125

León-Palmero, E., Morales-Baquero, R., & Reche, I. (2020a). Greenhouse gas fluxes from reservoirs determined by watershed lithology, morphometry, and anthropogenic pressure. *Environmental Research Letters*, 15, 044012. DOI: 10.1088/1748-9326/ab7467

León-Palmero, E., Contreras-Ruiz, A., Sierra, A., Morales-Baquero, R., & Reche, I. (2020b). Dissolved CH_4 coupled to photosynthetic picoeukaryotes in oxic waters and to cumulative chlorophyll *a* in anoxic waters of reservoirs. *Biogeosciences*, 17 (12), 3223-3245. DOI: 10.5194/bg-17-3223-2020

Lindgrenm P., Grosse, G., Meyer, F. J., & Anthony, K. W. (2019). An object-based classification method to detect methane ebullition bubbles in early Winter lake ice. *Remote Sensing*, 11, 822. DOI: 10.3390/rs11070822

Marcé, R., Obrador, B., Morguí, J.A., Riera, J. L.,

López, P., & Armengol, J. (2015). Carbonate weathering as a driver of CO_2 supersaturation in lakes. *Nature Geoscience*, 8,107–111. DOI: 10.1038/ngeo2341

McClure, R. P., Lofton, M. E., Chen, S., Krueger, K. M., Little, J. C., & Carey, C. C. (2020). The magnitude and drivers of methane ebullition and diffusion vary on a longitudinal gradient in a small freshwater reservoir. *Journal of Geophysical Research: Biogeosciences*, 125. DOI: 10.1029/2019JG005205

McGinnis, D. F., Greinert, J., Artemov, Y., Beaubien, S. E., & Wüest, A. (2006). Fate of rising methane bubbles in stratifies waters: How much methane reaches the atmosphere? *Journal of Geophysical Research*, 111, C09007. DOI: 10.1029/2005JC003183

Mendonça, R., Müller, R.A., Clow, D., Verpoorter, C., Raymond, P., Tranvik, L. J., & Sobek, S. (2017). Organic carbon burial in global lakes and reservoirs. *Nature Communications*, 8 (1), 1694. DOI: 10.1038/s41467-017-01789-6

Morales-Pineda, M., Úbeda, B., Cózar, A., Obrador, B., & Gálvez, J. (2015). Organic carbon sedimentation dominates over CO_2 emission in two net heterotrophic Mediterranean reservoirs during stratification. *Aquatic Sciences*, 78, 279-290. DOI: 10.1007/s00027-015-0423-6

Moreno-Ostos, E., Elliott, J. A, Cruz-Pizarro, L., Escot, C., Basanta, A., & George, D. G. (2007). Using a numerical model (PROTECH) to examine the impact of water transfers on phytoplankton dynamics in a Mediterranean reservoir. *Limnetica*, 26, 1–11.

Moreno-Ostos, E., Cruz-Pizarro, L., Basanta, A., & George, D. G. (2008). The spatial distribution of different phytoplankton functional groups in a Mediterranean reservoir. *Aquatic Ecology*, 42, 115–128. DOI: 10.1007/s10452-007-9087-1

Moreno-Ostos, E., Cruz-Pizarro, L, Basanta, A., & George, D. G. (2009a). Spatial heterogeneity of cyanobacteria and diatoms in a thermally stratified canyon-shaped reservoir. *International Review of Hydrobiology*, 94(3), 245–257. DOI: 10.1002/iroh.200811123

Moreno-Ostos, E., Cruz-Pizarro, L., Basanta, A., & George, D. G. (2009b). The influence of wind-induced mixing on the vertical distribution of buoyant and sinking phytoplankton species. *Aquatic Ecology*, 43, 271–284. DOI: 10.1007/s10452-008-9167-x

Moreno-Ostos, E., Blanco, J. M., Palomino-Torres, R. L., Lucena, J., Rodríguez, V., George, D. G., …Rodríguez. (2012). The Gulf Stream position influences the functional composition of phytoplankton in El Gergal reservoir (Spain). *Limnetica*, 31, 251–260.

Moreno-Ostos, E., Palomino-Torres, R. L., Escot, C., & Blanco, J. M. (2016). Planktonic metabolism in a Mediterranean reservoir during a near-surface cyanobacterial bloom. *Limnetica*, 35(1), 117-130.

Mulligan, M., Van Soesbergen, A., & Sáenz, L. (2020). GOODD, a global dataset of more than 38000 georeferenced dams. *Nature Scientific Data*, 7, 31. DOI: 10.1038/s41597-020-0362-5

Musenze, R. S., Grinham, A., Werner, U., Gale, D., Sturm, K., Udy, J., & Yuan, Z. (2014). Assessing the spatial and temporal variability of diffusive methane and nitrous oxide emissions from subtropical freshwaters reservoirs. *Environmental Science and Technology*, 38, 14499-14507. DOI: 10.1021/es505324h

Myhre, G., Shindell, D., Bréon, F. M., Collins, W., Fuglestvedt, J., Huang, J.… Zhang, H. (2013). Anthropogenic and natural radiative forcing. In: Stocker, T. F., D. Qin, G. K. Plattner, M. Tignor, S. K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P. M. Midgley (eds.) *Climate Change 2013: The physical science basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel of Climate Change*. (pp. 659-740). Cambridge University Press, Cambridge (UK) and New York (USA). DOI: 10.1017/CBO9781107415324.018.

Natchimuthu, S., Sundgren, I., Galfalk, M., Klemedtsson, L., Crill, P., Danielsson, A., & Bastviken, D. (2016). Spatio-temporal variability of lake CH_4 fluxes and its influence on annual whole lake emission estimate. *Limnology and Oceanography*,61,S13-S26.DOI:10.1002/lno.10222

Paranaíba, J. R., Barros, N., Mendonça, R., Linkhorst, A., Isidorova, A., Roland, F.,…Sobek, S. (2018). Spatially resolved measurements of

CO_2 and CH_4 concentration and gas-exchange velocity influence carbon-emissions estimates of reservoirs. *Environmental Science and Technology*, 52, 607-615. DOI: 10.1021/acs.est.7b05138

Quiñones-Rivera, Z. J., Finlay, K., Vogt, R. J., Leavitt, P. R., & Wissel, B. (2015). Hydrologic, metabolic and chemical regulation of water-column metabolism and atmospheric CO_2 exchange in a large continental reservoir during spring and summer. *Journal of Great Lakes Research*, 41, 144-154. DOI: 10.1016/j.jglr.2015.05.005

Raymond, P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., & Guth, P. (2013). Global carbon dioxide emissions from inland waters. *Nature*, 503, 355–359. DOI: 10.1038/nature12760

Saidi, H., & Koschorreck, M. (2017). CO_2 emissions from German drinking water reservoirs. Science of the Total Environment, 581-582, 10-18. DOI: 10.1016/j.scitotenv.2017.01.004

Scandella, B. P., Pillsburg, L., Weber, T., Ruppel, C., Hemond, H. F. & Juanes, R. (2016). Ephemerality of discrete vents in lake sediments. *Geophysical Research Letters*, 43, 4374-4381. DOI: 10.1002/2016GL068668

Samiotis, G., Pekridis, G., Kaklidis, N., Trikoilidou, E., Taousanidis, N., & Amanatidou, E. (2018). Greenhouse gas emissions from two hydroelectric reservoirs in Mediterranean region. *Environmental Monitoring and Assessment*, 190, 363. DOI: 10.1007/s10661-018-6721-4

Schewe, J., Heinke, J., Gerten, D., Haddeland, I., Arnell, N. W., Clark, D. B.,…Kabat, P. (2014). Multimodel assessment of water scarcity under climate change. *Proceedings of the Naional Academy of Sciences*, 11(9), 3245-3250. DOI: 10.1073/pnas.1222460110

Schirer-Uijil, A. P., Veraat, A. J., Leffelaar, P. A., Berendse, F., & Veenendaal, E. M. (2011). Release of CO_2 and CH_4 from lakes and drainage ditches in temperate wetlands. *Biogeochemistry*, 102, 265-279. DOI: 10.1007/s10533-010-9440-7

Soumis, N., Duchemin, E., Canuel, R., & Lucotte, M. (2004). Greenhouse gas emissions from reservoirs of the western United States. *Global Biogeochemical Cycles*, 18, GB3022. DOI: 10.1029/2003GB002197

St. Louis, V. L., Kelly, C. A., Duchemin, É, Rudd, J. W. M., & Rosenberg, D. M. (2000). Reservoir surfaces as sources of greenhouse gases to the atmosphere: a global estimate. *Bioscience*, 50(9), 766-775. DOI: 10.1641/00063568(2000)050[0766:RSASOG]2.0.CO;2

Toja, J., Basanta, A., & Fernández Alés, R. (1992). Factors controlling algal biomass in the complex of water supply reservoirs of Seville (Spain). *Limnetica*, 8, 267-277.

Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatoer, T. J.,…Weyhenmeyer, G. A. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and Oceanography*, 54, 2298-2314. DOI: 10.4319/lo.2009.54.6_part_2.2298

Trolle, D., Staehr, P. A., Davidson, T. A., Bjerring, R., Lauridsen, T. L., Sondergaard, M., & Jeppesen, E. (2012). Seasonal dynamics of CO_2 flux across the surface of shallow temperate lakes. *Ecosystems*, 15, 336-347. DOI: 10.1007/s10021-011-9513-z

Trolle, D., Elliott, J. A., Mooij, W. M., Janse, J. H., Bolding, K., Hamilton, D. P., & Jeppesen, E. (2014). Advancing projections of phytoplankton responses to climate change through ensemble modelling. *Environmental Modelling and Software*, 61, 371-379. DOI: 10.1016/j.envsoft.2014.01.032

Wanninkhof, R. 1992. Relationship between wind-speed and gas-exchange over the Ocean. *Journal of Geophysical Research: Oceans*, 97, 7373-7382. DOI: 10.1029/92JC00188

West, W. E., Coloso, J. J., & Jones, S. E. (2012). Effects of algal and terrestrial carbon on methane production rates and methanogen community structure in a temperate lake sediment. *Freshwater Biology*, 57, 949-955. DOI: 10.1111/j.1365-2427.2012.02755.x

West, W. E., Creamer, K. P., & Jones, S. E. (2015). Productivity and depth regulate lake contributions to atmospheric methane: Lake productivity fuels methane emissions. *Limnology and Oceanography*, 54, 2298-2314. DOI: 10.1002/lno.10247

Weyhenmeyer, C. E. 1999. Methane emissions from beaver ponds: Rates, patterns, and

transport mechanisms. *Global Biogeochemical Cycles*, 13, 1079-1090. DOI: 10.1029/1999GB900047

Wiesenburg D. A., & Guinasso, N. L. 1979. Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water. *Journal of Chemical and Engineering Data*, 24, 356-360. DOI: 10.1021/je60083a006

Wik, M., Crill, P. M., Varner, R. K., & Bastviken, D. (2013). Multiyear measurements of ebullitive methane flux from three subartic lakes. *Journal of Geophysical Research: Biogeosciences*, 118, 1-15. DOI: 10.1002/jgrg.20103

Xiao, S., Liu, D., Wang, Y., Yang, Z., & Chen, W. (2013). Temporal variation of methane flux from Xiangxi Bay of the Three Gorges Reservoir. *Scientific Reports*, 3, 2500. DOI: 10.1038/srep02500

Yang, L. 2019. Contrasting methane emissions from upstream and downstream rivers and their associated subtropical reservoir in eastern China. *Scientific Reports*, 9, 8072. DOI: 10.1038/s41598-019-44470-2

Zarfl, C., Lumsdon, A. E., Berlekamp, J., Tydecks, L., & Tockner, K. (2015). A global boom in hydropower dam construction. *Aquatic Sciences*, 77, 161-170. DOI: 10.1007/s00027-014-0377-0