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Elizabeth León-Palmero¹ , Rafael Morales-Baquero¹ and Isabel Reche^{1,2} ¹ Instituto del Agua and Departamento de Ecología, Universidad de Granada, E-18071 Granada, Spain² Research Unit Modeling Nature (MNat), Universidad de Granada, E-18071 Granada, SpainE-mail: ireche@ugr.es**Keywords:** watershed lithology, reservoir radiative forcing, land-use, human pressureSupplementary material for this article is available [online](#)**Abstract**

Human population growth has increased the demand for water and clean energy, leading to the massive construction of reservoirs. Reservoirs can emit greenhouse gases (GHG) affecting the atmospheric radiative budget. The radiative forcing due to CO₂, CH₄, and N₂O emissions and the relative contribution of each GHG in terms of CO₂ equivalents to the total forcing is practically unknown. We determined simultaneously the CO₂, CH₄, and N₂O fluxes in reservoirs from diverse watersheds and under variable human pressure to cover the vast idiosyncrasy of temperate Mediterranean reservoirs. We obtained that GHG fluxes ranged more than three orders of magnitude. The reservoirs were sources of CO₂ and N₂O when the watershed lithology was mostly calcareous, and the crops and the urban areas dominated the landscape. By contrast, reservoirs were sinks of CO₂ and N₂O when the watershed lithology was predominantly siliceous, and the landscape had more than 40% of forestal coverage. All reservoirs were sources of CH₄, and emissions were determined mostly by reservoir mean depth and water temperature. The radiative forcing was substantially higher during the stratification than during the mixing. During the stratification the radiative forcings ranged from 125 mg CO₂ equivalents m⁻² d⁻¹ to 31 884 mg CO₂ equivalents m⁻² d⁻¹ and were dominated by the CH₄ emissions; whereas during the mixing the radiative forcings ranged from 29 mg CO₂ equivalents m⁻² d⁻¹ to 722 mg CO₂ equivalents m⁻² d⁻¹ and were dominated by CO₂ emissions. The N₂O contribution to the radiative forcing was minor except in one reservoir with a landscape dominated by crops and urban areas. Future construction of reservoirs should consider that siliceous bedrocks, forestal landscapes, and deep canyons could minimize their radiative forcings.

Introduction

Human population growth has increased the need for water and clean energy, promoting the construction of reservoirs for irrigation, consumption, and hydropower. The number of reservoirs has increased significantly over the past 60 years, reaching over 16.7 million dams globally (Lehner *et al* 2011). This trend is still ongoing, especially in countries with emerging economies, where over 3000 major hydropower dams are either planned or under construction (Zarfl *et al* 2015). Now it widely is accepted that inland waters, including reservoirs, despite their small global surface area, contribute much in proportion to the global

carbon cycle (Tranvik *et al* 2009, Raymond *et al* 2013). Reservoirs have a radiative forcing dependent on their greenhouse gas (GHG) emissions (Barros *et al* 2011, Deemer *et al* 2016). The CO₂ emissions from inland waters (ca. 2.1 Pg C yr⁻¹) are similar in magnitude to the estimate of the global uptake of CO₂ by the global ocean (2.4 Pg C yr⁻¹) (Le Quéré *et al* 2018). Lakes and reservoirs are usually CO₂ supersaturated (Cole *et al* 1994), releasing 0.32 Pg C yr⁻¹ (Raymond *et al* 2013). In carbonate-poor lakes, an excess of respiration over primary production produces supersaturation, whereas, in calcareous watersheds, supersaturation is due to the loadings of inorganic carbon during the weathering (López *et al* 2011, McDonald *et al* 2013,

Marcé *et al* 2015, Weyhenmeyer *et al* 2015). Inland waters are not only sources of CO₂, but they can be significant sources of CH₄ and N₂O (Tranvik *et al* 2009, Bastviken *et al* 2011, Soued *et al* 2015) with warming potential of 34 and 298 times higher than CO₂ in a 100 year timescale (IPCC 2013).

CH₄ emissions from reservoirs appear to be responsible for the majority of their radiative forcings (ca. 80% of the CO₂ equivalents) and are comparable to emissions from paddies or biomass burning (Deemer *et al* 2016, Samiotis *et al* 2018). Reservoirs, collectively considered, emit 13.3 Tg C yr⁻¹ of CH₄, although there is an astonishing lack of data, which severely limits our confidence in this global estimation (Deemer *et al* 2016). Methanogenesis is a microbial process more sensitive to temperature than other processes as, for instance, methanotrophy, respiration, and photosynthesis (Marotta *et al* 2014, Yvon-Durocher *et al* 2014, Rasilo *et al* 2015, Aben *et al* 2017, Sepulveda-Jauregui *et al* 2018). Therefore, the current rising temperatures can particularly intensify CH₄ emissions (Marotta *et al* 2014, Rasilo *et al* 2015, Aben *et al* 2017) due to changes both in CH₄ solubility and in the methanogenesis versus methanotrophy balance. On the other hand, the eutrophic reservoirs emit at least one order of magnitude more CH₄ than the oligotrophic ones. Indeed CH₄ emissions seem to be closely linked to primary productivity (Schmidt and Conrad 1993, Grossart *et al* 2011, Bogard *et al* 2014, Tang *et al* 2014, Deemer *et al* 2016). Phytoplankton-derived organic carbon appears to fuel higher rates of methane production than terrestrial-derived organic carbon (West *et al* 2012, 2016). Reservoir eutrophication is increasing worldwide as a result of the intensification of agriculture and the use of fertilizers (Canfield *et al* 2010, Heathcote and Downing 2012). Then, the expected increase in global temperatures along with reservoirs eutrophication might exacerbate CH₄ emissions.

The anthropogenic production of nitrogen fertilizer has doubled the inputs of this element to the Earth's surface, changing the nitrogen cycle. This change likely exceeds all the other human interventions in the cycles of nature (Gruber and Gallo-way 2008, Schlesinger 2009), but in comparison with the carbon cycle has received less attention (Battye *et al* 2017). Changes in land-use from forestal to agricultural or urban can boost the production of N₂O due to nitrogen loadings into the aquatic systems (Seitzinger *et al* 2000, Mulholland *et al* 2008, Beaulieu *et al* 2011). N₂O is produced aerobically by nitrification and anaerobically by denitrification depending on oxygen availability (Canfield *et al* 2010). In reservoirs, the few available data suggest that they are relevant in agricultural landscapes (Beaulieu *et al* 2015). Unfortunately, the importance of the reservoirs in global N₂O emissions is practically unknown. Deemer *et al* (2016) estimated, using a very scarce database, that the global N₂O emission from reservoirs is 0.03 Tg N yr⁻¹

accounting for 4% of the radiative forcing in a 100 year timescale.

Fluxes of CO₂, CH₄, and N₂O have been reported mostly for tropical and boreal reservoirs, lacking the data of these fluxes in the Mediterranean biome, where the reservoirs are the preponderant aquatic ecosystems (Naselli-Flores 2003, Barros *et al* 2011, Lehner *et al* 2011, Morales-Pineda *et al* 2014, Deemer *et al* 2016). In this region, reservoirs provide drinking and irrigation water (Naselli-Flores 2003, Morales-Pineda *et al* 2014); consequently, they are close to agriculture and urban areas having high human pressure. Therefore, we need more simultaneous measurements of CO₂, CH₄, and N₂O emissions in Mediterranean reservoirs submitted to contrasting anthropogenic pressure to get more accurate estimates of the global reservoir radiative forcing.

Here, we simultaneously measured the fluxes of CO₂, CH₄, and N₂O in a group of Mediterranean reservoirs. We covered the vast idiosyncrasy of temperate reservoirs to obtain their radiative forcings in terms of CO₂ equivalents. We hypothesized that reservoirs located in anthropogenic landscapes would have higher radiative forcings than forestal reservoirs. Besides, we postulated that CH₄ emissions would be the main responsible for the positive radiative forcings.

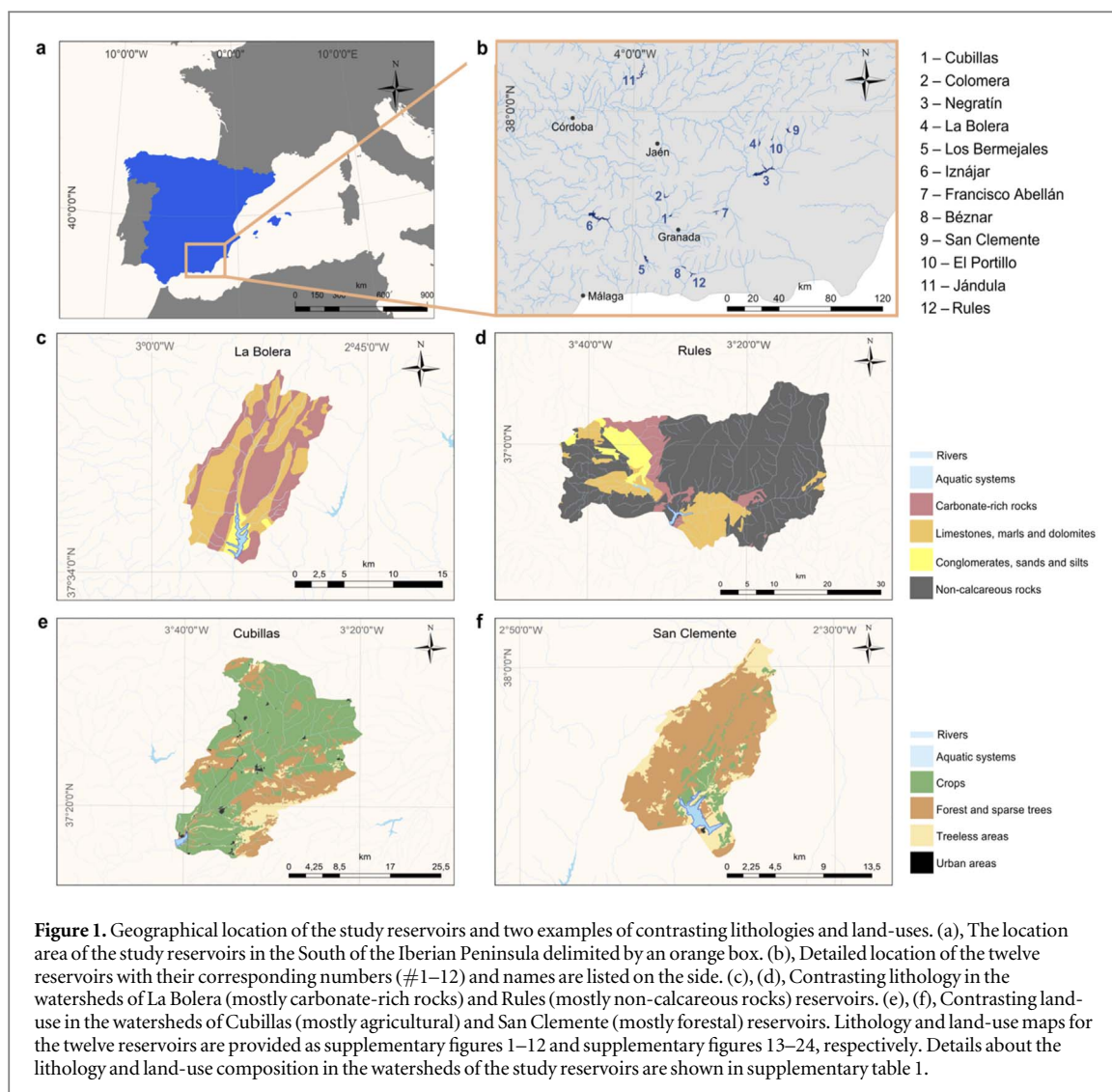
Methods

Study reservoirs

We sampled 12 reservoirs between July 2016 and August 2017 in the South of Spain (figures 1(a), (b)). The reservoirs are located in watersheds with diverse lithology (figures 1(c), (d); supplementary figures 1–12 is available online at stacks.iop.org/ERL/15/044012/mmedia), different land-use (figures 1(e), (f); supplementary figures 13–24), morphometries, and ages (supplementary table 1). We quantified the CO₂, CH₄, and N₂O fluxes using a PICARRO Cavity Ring-Down Spectroscopy (CRDS) gas analyzer connected to a floating chamber during the stratification (summer) and mixing (fall-winter) periods at one representative location. The reservoirs were built between 1932 and 2003, and they also differ in chemical and trophic characteristics with a range of chlorophyll-a from 0.6 to 18.6 µg l⁻¹ and a range of dissolved organic carbon (DOC) from 0.79 to 4.95 mg l⁻¹. More basic details on the study reservoirs in León-Palmero *et al* (2019) and supplementary tables 1 and 4. We collected data on reservoir area, capacity, age, watershed lithology, and land use from open databases (more details in supplementary methods).

Quantification of CO₂, CH₄ and N₂O fluxes

We measured CO₂, CH₄, and N₂O fluxes using a high-resolution laser-based CRDS (PICARRO G2508) coupled to a floating chamber. For each reservoir in



each sampling period, we took 3–5 measurements for 40 min. We calculated the daily (from 10 am to 4 pm) average and the standard error from these measurements. We obtained the flux calculation using the equation (1) (Zhao *et al* 2015):

$$Flux_{water-air} = \frac{b \cdot V \cdot P_0}{A \cdot R \cdot T_0}, \quad (1)$$

where $Flux_{water-air}$ ($\mu\text{mol m}^{-2} \text{s}^{-1}$) is the flux from the water surface to the atmosphere; the b (ppmv s^{-1}) value is the slope of the linear regression between the time and the concentration of each gas inside the chamber; the V (m^3) is the floating chamber volume; the A (m^2) is the floating chamber area; the P_0 (Pa) is the barometric pressure; the R is the gas constant ($8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}$); and T_0 (K) is the ambient temperature. We checked that the slope was significantly different from zero for each measurement using a two-tailed t-Student test. We also calculated the coefficient of determination (R^2) for each measurement, accepting those whose $R^2 > 0.85$ (Moseman-Valtierra *et al* 2016). We measured ambient temperature, barometric pressure (HANNA HI 9828), and

wind speed (MASTECH MS6252A) at the beginning of each flux measurement.

Determination coefficients (R^2) for CO_2 fluxes were always >0.85 . For CH_4 fluxes, most cases R^2 were >0.85 , but it decreased until 0.65 when ebullition events were relevant. In these cases, we computed the b value using the end-point concentrations and the time interval between them (equation (2)) (Zhao *et al* 2015):

$$b = \frac{[ppm \text{ CH}_4]_f - [ppm \text{ CH}_4]_i}{t_f - t_i}, \quad (2)$$

where $[ppm \text{ CH}_4]_f$ and $[ppm \text{ CH}_4]_i$ are the CH_4 concentration in the floating chamber at the end and the beginning of the time considered; t_f and t_i are the time at the end and the beginning of the measurement.

For N_2O flux measurements, most of R^2 values were low (even when the regression was significantly different from zero). For those cases, we first checked the analyzer precision (<25 ppb). If the changes were larger than the analyzer precision, we assumed these fluxes were different from zero. We also compared the N_2O fluxes with the percentage of saturation of dissolved N_2O in the water column. Details for the

measurements of dissolved N_2O are in supplementary methods. N_2O undersaturated waters and negative slopes mean N_2O influxes (i.e. N_2O sinks). By contrast, N_2O supersaturated waters and positive slopes mean N_2O outfluxes (i.e. N_2O sources).

To obtain the reservoir radiative forcings we summed the corresponding forcing due to CO_2 emissions, the warming potential (GWP) of CH_4 in terms of CO_2 equivalents, and the warming potential of N_2O in terms of CO_2 equivalents. We used 34 to convert CH_4 in CO_2 equivalent and 298 to convert N_2O in CO_2 equivalent in a 100 year time horizon, including the climate-carbon feedbacks (IPCC 2013).

C, N and P analysis in the water column

We sampled the epilimnion of each reservoir for C, N and, P analysis. We measured total nutrient concentrations using unfiltered water, while we filtered through $0.7 \mu\text{m}$ pore-size Whatman GF/F glass-fiber filters samples for dissolved nutrients. We acidified with phosphoric acid (final $\text{pH} < 2$) the samples for DOC, total dissolved nitrogen (TDN), and total nitrogen (TN). We measured DOC, dissolved inorganic carbon (DIC), TN, and TDN by high-temperature catalytic oxidation using a Shimadzu total organic carbon (TOC) analyzer (Model TOC-V CSH) coupled to nitrogen analyzer (TNM-1) (Álvarez-Salgado and Miller 1998). The instrument was calibrated using a four-point standard curve of dried potassium hydrogen phthalate for DOC, dried sodium bicarbonate and sodium carbonate for DIC, and dried potassium nitrate for TN and TDN. We analyzed two replicates and three to five injections per replicate for each sample. Samples for DOC analysis were purged with phosphoric acid for 20 min to eliminate DIC.

We measured the NO_3^- concentration using the ultraviolet spectrophotometric method, using a Perkin Elmer UV-Lambda 40 spectrophotometer at wavelengths of 220 nm and correcting for DOC absorbance at 275 nm (Baird *et al* 2012). We measured NH_4^+ and NO_2^- concentrations by inductively coupled plasma optical emission spectrometry. Total phosphorus concentration was measured by triplicate using the molybdenum blue method (Murphy and Riley 1962) after digestion with a mixture of potassium persulphate and boric acid at 120°C for 30 min (Baird *et al* 2012).

We also measured dissolved CH_4 and N_2O by headspace equilibration in a 50 ml air-tight glass syringe by duplicate in the water column (Sierra *et al* 2017a, 2017b). We analyzed simultaneously the concentration of dissolved CH_4 and N_2O using gas chromatography (more details in supplementary methods).

Biological analyses and reservoir metabolism

We determined chlorophyll-*a* concentration by collecting the particulate material of 500 to 2000 ml of

water by filtering through $0.7 \mu\text{m}$ pore-size Whatman GF/F glass-fiber filters, then extracting the filters with 95% methanol in the dark at 4°C for 24 h (Baird *et al* 2012). We measured pigment absorption using a Perkin Elmer UV-Lambda 40 spectrophotometer at wavelengths of 665 and 750 nm for scattering correction.

We recorded dissolved oxygen concentration and temperature using a miniDOT (PME) submersible water logger during the stratification period. We got measurements every 10 min for 24–48 h. We established the start and ended time for photosynthesis as 30 min before sunrise and 30 min after dawn (Schlesinger and Bernhardt 2013). We calculated the respiration rate during the night (the period between 60 min after dawn and 60 min before sunrise) (Staeher *et al* 2010), and we assumed that the respiration rate over-night was similar to the respiration rate over the day. The equations used to calculate lake metabolism were taken from Staeher *et al* (2010).

Statistical tests

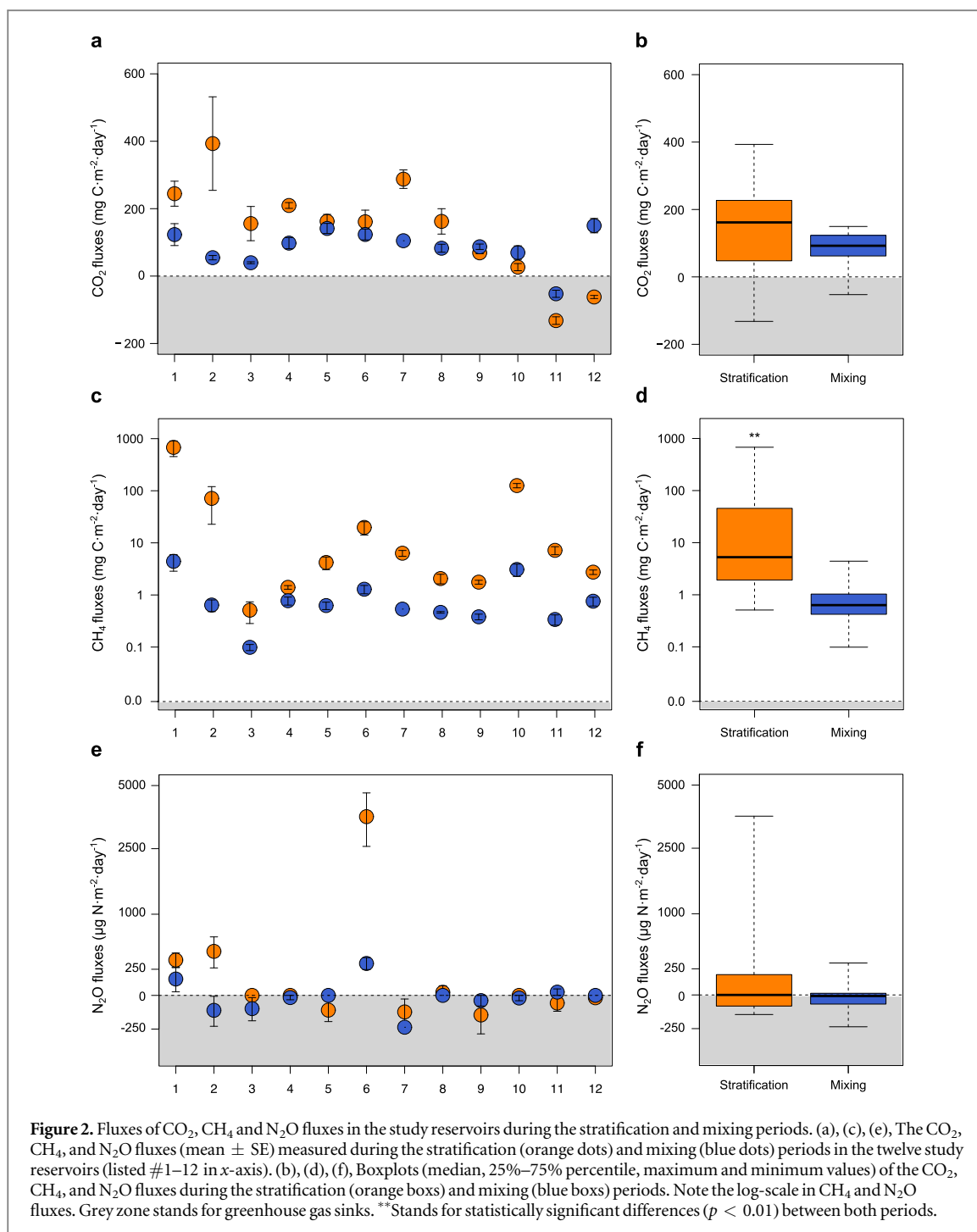
We performed all the statistical analysis in R (R Core Team 2014) using the packages car (Fox and Weisberg 2011), nortest (Gross and Ligges 2015), and mgcv (Wood 2011). More details on T-test and generalized additive models (GAMs) (Wood 2006) in supplementary methods.

Results and discussion

CO_2 , CH_4 and N_2O fluxes

We found that some reservoirs were sinks (fluxes < 0) and other sources (fluxes > 0) for CO_2 and N_2O fluxes, but all reservoirs were CH_4 sources (figure 2, supplementary table 2). The daily average of CO_2 fluxes ranged from -131.97 to $393.11 \text{ mg C m}^{-2} \text{ d}^{-1}$ during the stratification period (figure 2(a), orange dots) and from -52.51 to $149.62 \text{ mg C m}^{-2} \text{ d}^{-1}$ during the mixing period (figure 2(a), blue dots). We measured the lower value in the Jándula reservoir (#11) consistently in both periods. We did not find significant differences between the stratification and mixing periods (figure 2(b); supplementary table 3). The median of these fluxes in both periods was $114.00 \text{ mg C m}^{-2} \text{ d}^{-1}$, similar to previous data for northern temperate reservoirs (Barros *et al* 2011) and smaller than the fluxes measured in other Mediterranean reservoirs (Morales-Pineda *et al* 2014, Samiotis *et al* 2018), and the global average estimated by Deemer *et al* (2016).

The daily average of CH_4 fluxes varied more than three orders of magnitude from 0.51 to $678.84 \text{ mg C m}^{-2} \text{ d}^{-1}$ during the stratification period (figure 2(c), orange dots) and from 0.10 to $4.41 \text{ mg C m}^{-2} \text{ d}^{-1}$ during the mixing period (figure 2(c), blue dots). The maximum values were reached in Cubillas (#1), a shallow reservoir with evident ebullition fluxes. The



median value during the stratification period was $5.27 \text{ mg C m}^{-2} \text{ d}^{-1}$, whereas during the mixing period was $0.63 \text{ mg C m}^{-2} \text{ d}^{-1}$. Emissions were significantly higher during the summer stratification than during the winter mixing (figure 2(d); supplementary table 3) as it has been found in previous works (Beaulieu *et al* 2014, Musenze *et al* 2014) and emphasized the need to perform seasonal studies to obtain accurate annual rates of CH₄ emissions. This wide range in CH₄ emissions covers from typical values found in tropical reservoirs to values found in northern temperate reservoirs (Barros *et al* 2011), although lower than in other Mediterranean reservoirs (Samiotis *et al* 2018).

The daily average of N₂O fluxes ranged from -154.03 to $3600.88 \text{ } \mu\text{gN m}^{-2} \text{ d}^{-1}$ during the stratification period (figure 2(e), orange dots) and from -238.08 to $313.44 \text{ } \mu\text{gN m}^{-2} \text{ d}^{-1}$ during the mixing period (figure 2(e), blue dots). In both periods, we obtained the maximum values in the Iznájar reservoir (#6). We did not find significant differences between stratification and mixing periods (figure 2(f); supplementary table 3). The median value was $0.00 \text{ } \mu\text{gN m}^{-2} \text{ d}^{-1}$ acting globally as neutral systems. In the particular case of the Iznájar reservoir (#6), however, it acted as a relevant source of N₂O with values similar to those found in tropical reservoirs (Guérin *et al* 2006). N₂O

flux variability in these Mediterranean reservoirs was more comprehensive than the variability found in boreal lakes and reservoirs (Soued *et al* 2015).

CO₂ flux drivers

To determine the main drivers (predictors) of GHG fluxes in the study reservoirs, we used GAMs (see supplementary methods, supplementary tables 4 and 5). The inputs of dissolved inorganic and organic carbon and net ecosystem metabolism (i.e. the budget between photosynthesis and respiration) are considered the main drivers of CO₂ fluxes in lakes and reservoir (Tranvik *et al* 2009, McDonald *et al* 2013, Marcé *et al* 2015, Weyhenmeyer *et al* 2015). In fact, the non-calcareous area in the watershed and the reservoir respiration were the main drivers of CO₂ fluxes during the stratification period with a fit deviance of 93.4% ($\text{Log}_{10}(\text{CO}_2 + 150) = -6.6 \cdot 10^{-4} \text{ non-calcareous area} + 1.70 \log_{10}(\text{Respiration rate})^{0.35}$) and an explained variance of 91% (figure 3(a); supplementary table 5). The non-calcareous area in the watershed was a linear function inversely related to CO₂ fluxes (figure 3(b)), and most of the deviance was 90.7%, whereas respiration only explained the 9.4%. Unlike this linear function, reservoir respiration showed a power function with the CO₂ flux (figure 3(c)). The smaller the calcareous watershed, the lower the export of DIC is. Indeed, we found a significant and negative relationship between non-calcareous area and the DIC concentration in the reservoirs irrespectively of the sampling period (linear regression results $n = 24$, $R^2 = 0.50$, $p < 0.001$) (figure 3(d)). This result agrees with previous studies showing that a significant fraction of CO₂ emissions in boreal lakes is related to inorganic carbon loading from watershed (Weyhenmeyer *et al* 2015). In other Mediterranean reservoirs, carbonate weathering was also related to CO₂ supersaturation and, consequently, to CO₂ evasion (López *et al* 2011, Marcé *et al* 2015). We obtained a significant and positive function between reservoir respiration and the concentration of chlorophyll-a during the stratification period (linear regression results $n = 12$, $R^2 = 0.43$, $p < 0.05$) (figure 3(e)), but not with the concentration of DOC (linear regression results $n = 12$, $p = 0.64$). Overall, we show, for the first time, a remarkable and direct link between watershed lithology and the CO₂ fluxes from reservoirs.

CH₄ flux drivers

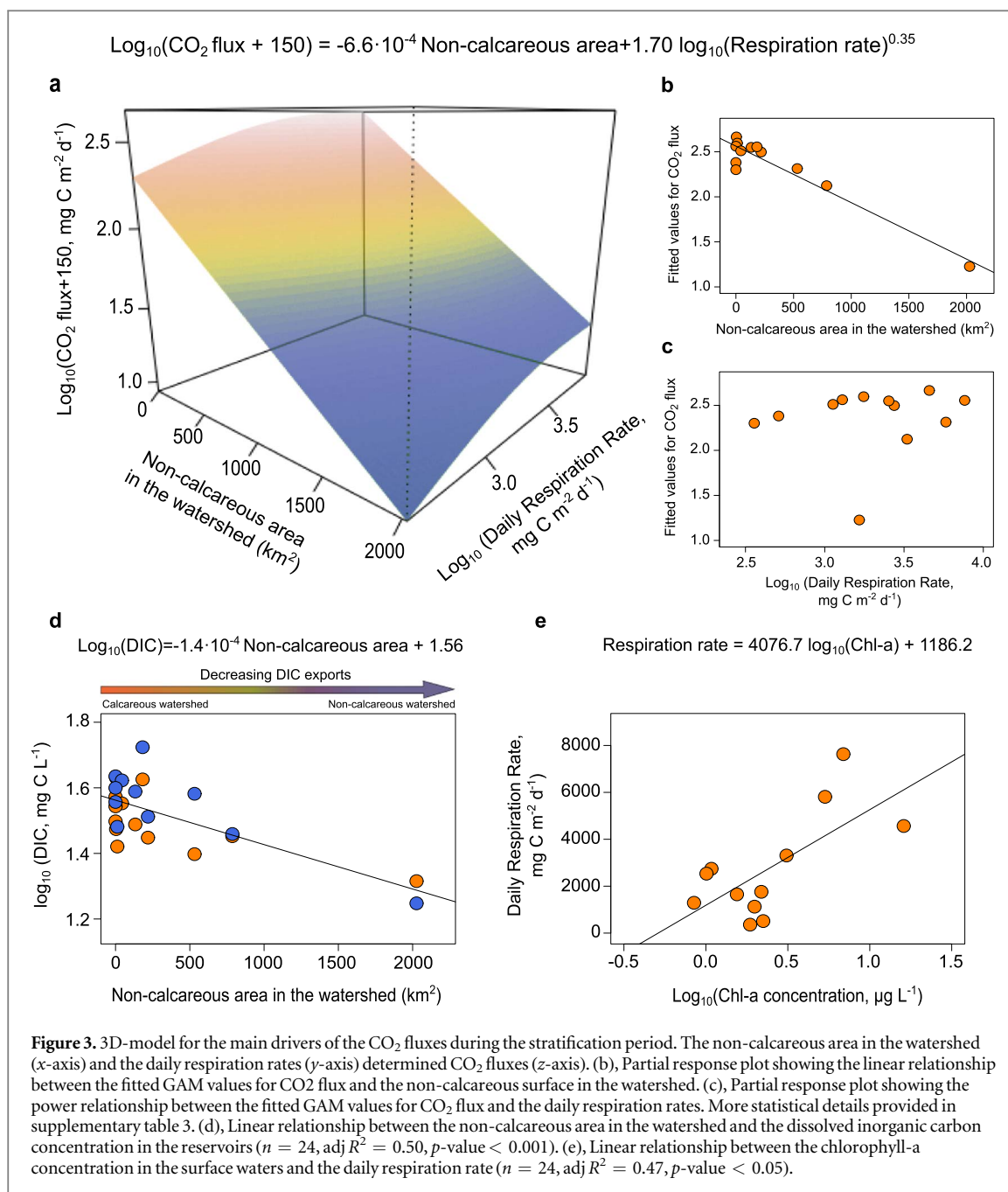
CH₄ emissions from a reservoir depend on its net production (i.e. the budget between methanogenesis and methanotrophy) and its storage capacity into the water column. Dissolved CH₄ storage is related to water mean depth (i.e. the higher the hydrostatic pressure, the higher storage capacity is) and temperature (i.e. the lower temperature, the higher solubility is) (Keller and Stallard 1994, West *et al* 2016).

Shallow systems are prone to have warmer waters, higher sediment exposure enhancing significantly CH₄ ebullition rates, and, consequently, less capacity to store CH₄ (Keller and Stallard 1994, Marotta *et al* 2014, Aben *et al* 2017). In the study reservoirs, we obtained that water temperature and reservoir mean depth were the main drivers of the CH₄ emissions with a fit deviance of 65.0% and an explained variance of 59% ($\text{Log}_{10}(\text{CH}_4 \text{ flux} + 1) = 6.6 \cdot 10^{-2} \text{ Temperature} - 0.82 + 2.5 \cdot 10^{-4} e^{(8.44/\log_{10}(\text{mean depth}))}$) (figure 4(a); supplementary table 3). CH₄ emission rate was a linear and positive function of water temperature (figure 4(b)) and accounted for 38.1% of the fit deviance. CH₄ emission rate resulted in a negative exponential function of the reservoir mean depth (figure 4(c)) with fit deviance of 27.6%. At mean depths shallower than 16 meters, the CH₄ emissions increased exponentially (i.e. 1.2 in figure 4(c)). CH₄ emissions depended on concentration of CH₄ in the surface waters following a power function (figure 4(d)) ($n = 24$, $R^2 = 0.87$, $p < 0.001$). Previous studies have shown that CH₄ concentration in the water column is related to chlorophyll-a concentration (Schmidt and Conrad 1993, Grossart *et al* 2011, Bogard *et al* 2014, Tang *et al* 2014). We also found a positive and linear relationship between the concentration of chlorophyll-a and the concentration of CH₄ in the surface waters ($n = 24$, $R^2 = 0.19$, $p < 0.05$) (figure 4(e)), but not directly with the emissions. Recent studies point out the eutrophication as the primary driver of CH₄ emissions (Deemer *et al* 2016, Beaulieu *et al* 2019).

N₂O flux drivers

Nitrogen loading derived from human activities affects N₂O emissions from inland waters (Seitzinger *et al* 2000, Mulholland *et al* 2008, Baulch *et al* 2011, Beaulieu *et al* 2011). It is widely acknowledged that the N₂O production increases in streams and reservoirs located in agricultural and urban landscapes as a consequence of nitrate loading (Mulholland *et al* 2008, Baulch *et al* 2011, Beaulieu *et al* 2011, 2015). In the study reservoirs, consistently, the GAMs result showed that the TN concentration was the main driver of N₂O fluxes along with the wind speed ($\text{Log}_{10}(\text{N}_2\text{O flux} + 240) = 0.72 e^{0.21 \text{ TN}} + 1.30 \text{ Wind speed}^{0.21}$) with a fit deviance of 82.7% and an explained variance of 79.8% (figure 5(a); supplementary table 5). N₂O fluxes were an exponential function of TN concentration and explained most of the deviance 52.2% (figure 5(b)). Wind speed showed a positive power function with the fluxes and only explained 13.9% (figure 5(c)).

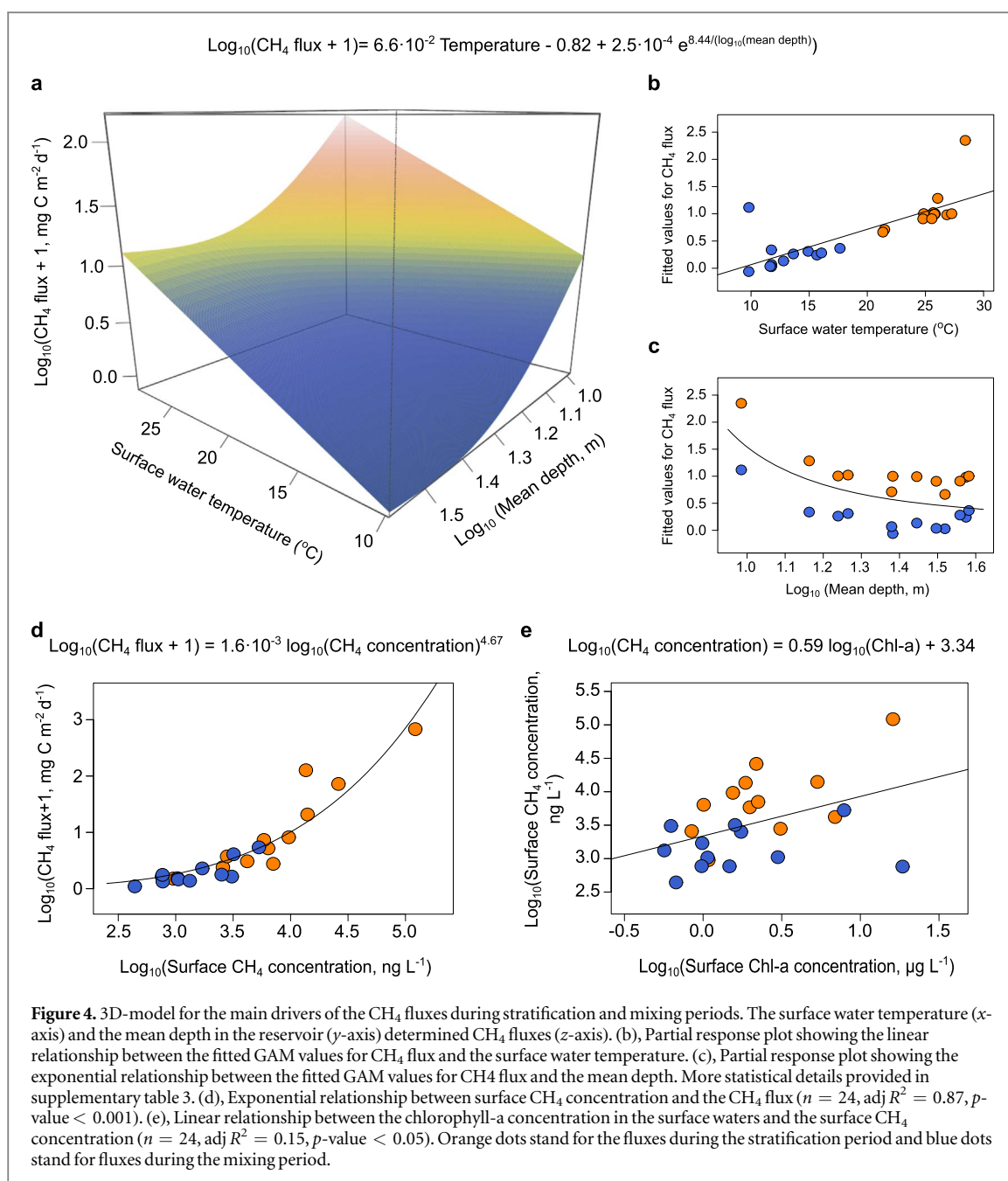
We determined the anthropogenic pressure in the reservoir watershed as the ratio of the area with crops plus the urban area divided by the forest area (i.e. the anthropogenic land-use ratio). We found a significant and positive relationship between this land-use ratio



and the concentration of TN in the reservoir waters ($n = 24$, $R^2 = 0.60$, $p < 0.001$) (figure 5(d); supplementary table 6). Both crops and urban areas increased the nitrogen concentration in their different compounds (TN, TDN, NO_3^- and NO_2^-) (supplementary table 6). The urban area, in square kilometer or in its percentage relative in the watershed, showed a higher slope than the slope in the crop areas (figure 5(e)). Therefore, the impact of urban development on nitrogen inputs is even higher than the influence of crop areas.

N₂O fluxes were a nonlinear function of the anthropogenic land-use ratio (figure 5(f)). For anthropogenic land-use ratios higher than 1 (i.e. crops and urban areas predominance over the forest area), the N₂O fluxes increased exponentially

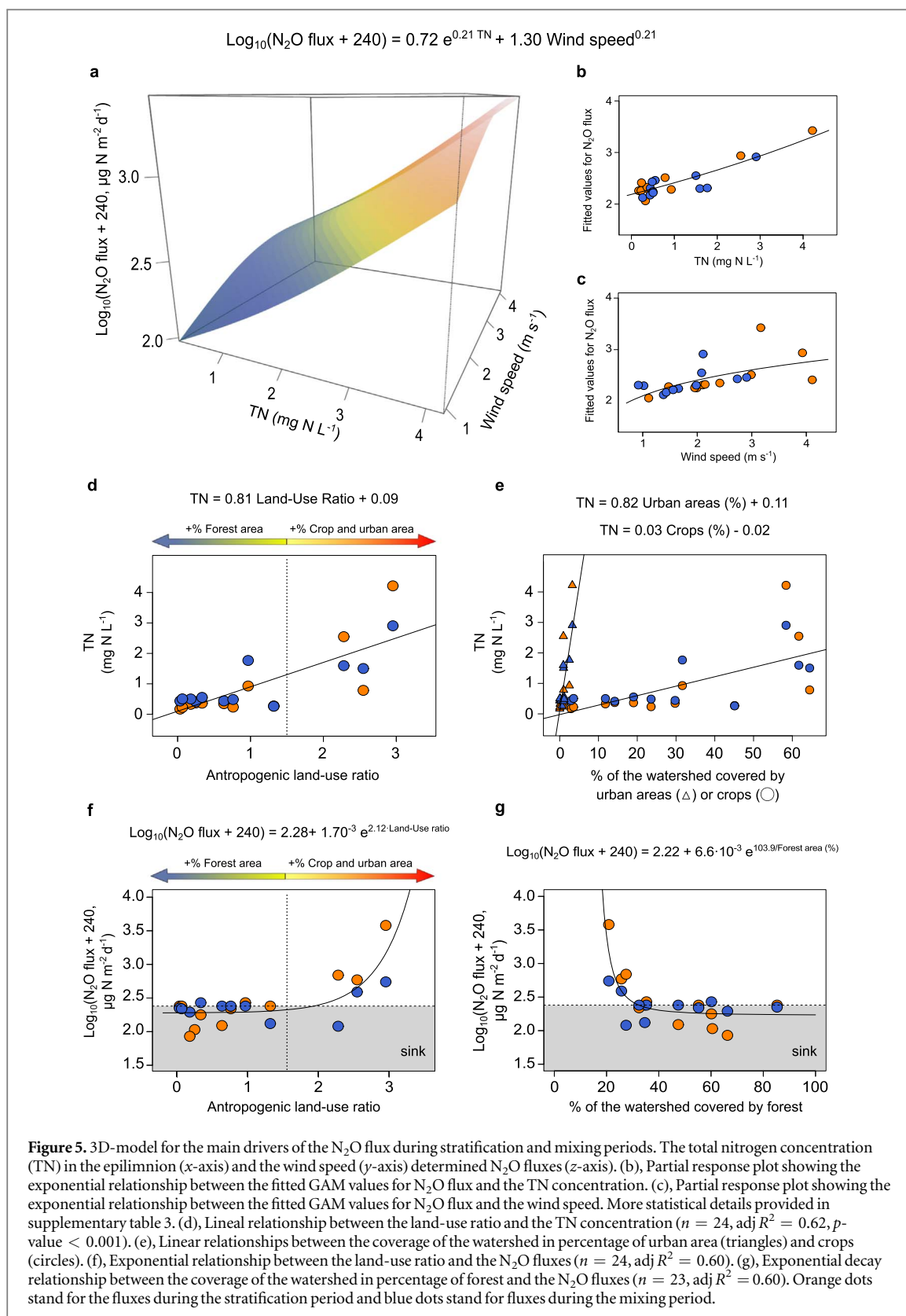
(figure 5(f)). In contrast, we observed that for watersheds with forestal coverage more extensive than ~40% of watershed, the N₂O emissions decreased drastically, even becoming an N₂O sink (figure 5(g)). Other authors also found that boreal forest reservoirs acted as N₂O sinks (Hendzel *et al* 2005). Therefore, the relevance of the nitrogen inputs from watershed on N₂O fluxes is mostly dependent on the anthropogenic land-use. Our results suggest an exponential influence of the agricultural and, mainly, urban areas in the watershed on the N₂O emissions. However, most of the previous studies have been mainly focused on the agricultural effects (Baulch *et al* 2011, Musenze *et al* 2014, Beaulieu *et al* 2015), relegating the urban influence on the background.



Reservoir radiative forcings in CO₂ equivalents

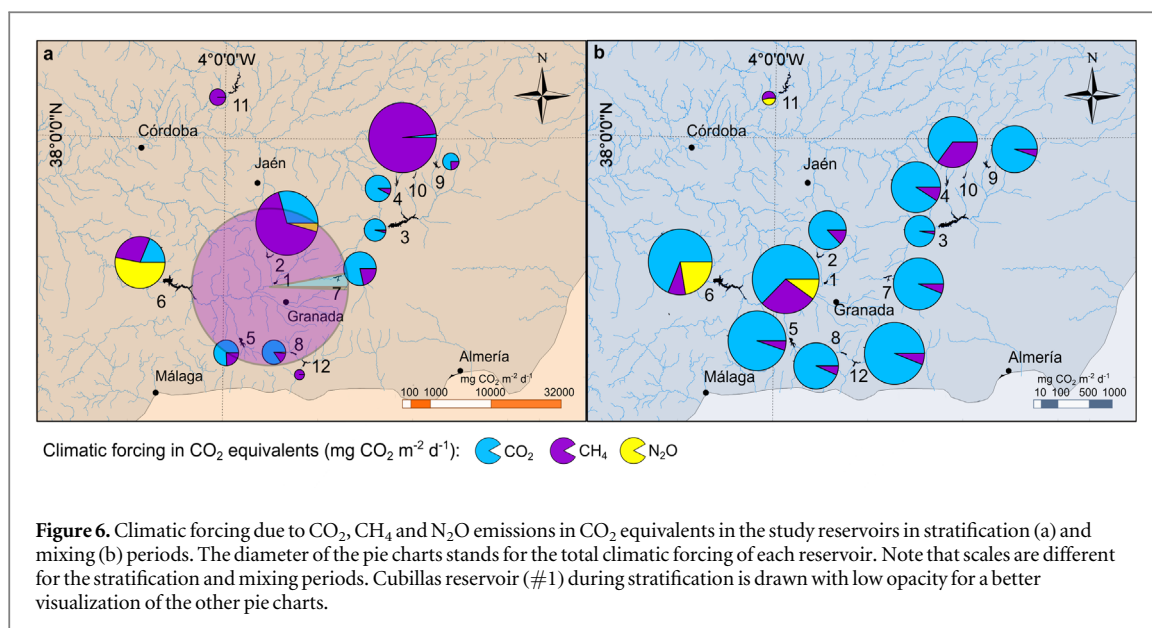
We obtained a variability range in the GHG fluxes larger than the latitudinal variability reported in previous works (Barros *et al* 2011). The radiative forcings due to the GHG emissions from the reservoirs differed substantially between the stratification (summer) and the mixing (fall-winter) (figure 6). Radiative forcings were substantially higher during the stratification than during the mixing. This difference could be related to the significantly higher emissions of CH₄ during the stratification than mixing (figure 2). Methanogenesis is a microbial process particularly sensitive to temperature (Marotta *et al* 2014, Yvon-Durocher *et al* 2014, Rasilo *et al* 2015, Aben *et al* 2017, Sepulveda-Jauregui *et al* 2018) that increase during summer. In addition, water mean depth decrease during this season and

these factors also affect to the CH₄ emissions (figure 4). Radiative forcings ranged from 124.53 mg CO₂ equivalents m⁻² d⁻¹ in Rules reservoir (#12) to 31,884.03 mg CO₂ equivalents m⁻² d⁻¹ in Cubillas reservoir (#1) (supplementary table 2). These last values were even higher than those found for tropical plantations (Laine *et al* 2016). In stratification, CH₄ emissions contributed significantly to the total radiative forcing (in terms of CO₂ equivalent), ranging from 3.9% to 98.32% (figure 6(a) purple sector). In contrast, the CO₂ emissions contributed to the total radiative forcing mostly during the mixing (fall and winter), accounting for up to 97% (figure 6(b) blue sector). During the mixing, the radiative forcing ranged from 28.68 mg CO₂ equivalents m⁻² d⁻¹ in Jándula reservoir (#11) to 721.65 mg CO₂ equivalents m⁻² d⁻¹ in Cubillas



reservoir (#1) (supplementary table 2). The contribution of N_2O emissions to the radiative forcing in the study reservoirs was secondary (supplementary table 2) with the exception of the Iznájar reservoir (#6) in both periods (figure 6) and the Cubillas and Jándula reservoirs (#1 and 11) during the mixing (figure 6(b)). In the Iznájar reservoir, the N_2O

emissions accounted for up to 53.1% of the radiative forcing during the stratification, whereas during the mixing period was 22.32% (supplementary table 2). CO_2 and N_2O emissions were driven by external factors as lithology and land-use without significant differences between mixing and stratification. In contrast, CH_4 emissions were driven by internal



factors as water temperature and mean depth with higher emissions during stratification, which affected the total radiative forcings of the reservoirs.

Future climatic scenarios for the Mediterranean biome suggest substantial warming, a decrease in total precipitation, and extreme heat-waves and heavy precipitations (Giorgi and Lionello 2008) that likely will enhance the CH₄ emissions due to a reduction in reservoir depth (i.e. lower precipitation and higher evaporation) and an increase in the water temperatures. Climatic change may also affect nutrient loading by runoff to the reservoirs. Hydrological models for Mediterranean watersheds suggest that nutrient concentrations in reservoirs may increase despite a runoff reduction (Molina-Navarro *et al* 2014). The potential increase in the N and P concentrations will boost water eutrophication and the resulting emissions of N₂O (Mulholland *et al* 2008, Baulch *et al* 2011, Beaulieu *et al* 2015) and CH₄ (Deemer *et al* 2016, Beaulieu *et al* 2019). Temperature increases and eutrophication may also have synergic effects on CH₄ emissions (Davidson *et al* 2018, Sepulveda-Jauregui *et al* 2018). Policies to reduce the fertilizers used in agricultural areas and, in particular, to promote the tertiary wastewater treatment in urban areas may decrease N and P loading to prevent water resources degradation and reduce GHG emissions and their subsequent radiative forcings from the already constructed reservoirs. For the construction of the projected reservoirs, the selection of optimal locations should consider that siliceous bedrock, in forestal locations, and deep canyons can minimize or even offset the GHG emissions and, consequently, reduce their radiative forcings.

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Data availability statement

The data that support the findings of this study are included within the article in supplementary material.

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