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# Soil water content drives spatiotemporal patterns of $CO_2$ and $N_2O$ emissions from a Mediterranean riparian forest soil

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**Abstract.** Riparian zones play a fundamental role in regulating the amount of carbon (C) and nitrogen (N) that is exported from catchments. However, C and N removal via soil gaseous pathways can influence local budgets of greenhouse gas (GHG) emissions and contribute to climate change. Over a year, we quantified soil effluxes of carbon dioxide ($CO_2$) and nitrous oxide ($N_2O$) from a Mediterranean riparian forest in order to understand the role of these ecosystems on catchment GHG emissions. In addition, we evaluated the main soil microbial processes that produce GHG (mineralization, nitrification, and denitrification) and how changes in soil properties can modify the GHG production over time and space. Riparian soils emitted larger amounts of $CO_2$ (1.2–10 $g\,C\,m^{-2}\,d^{-1}$) than $N_2O$ (0.001–0.2 $mg\,N\,m^{-2}\,d^{-1}$) to the atmosphere attributed to high respiration and low denitrification rates. Both $CO_2$ and $N_2O$ emissions showed a marked (but antagonistic) spatial gradient as a result of variations in soil water content across the riparian zone. Deep groundwater tables fueled large soil $CO_2$ effluxes near the hillslope, while $N_2O$ emissions were higher in the wet zones adjacent to the stream channel. However, both $CO_2$ and $N_2O$ emissions peaked after spring rewetting events, when optimal conditions of soil water content, temperature, and N availability favor microbial respiration, nitrification, and denitrification. Overall, our results highlight the role of water availability on riparian soil biogeochemistry and GHG emissions and suggest that climate change alterations in hydrologic regimes can affect the microbial processes that produce GHG as well as the contribution of these systems to regional and global biogeochemical cycles.

## 1 Introduction

Riparian zones are hotspots of nitrogen (N) transformations across the landscape, providing a natural filter for nitrate ($NO_3^-$) transported from surrounding lands via runoff and subsurface flow paths (Hill, 1996; Vidon et al., 2010). Although interest in riparian zones has primarily been motivated by the benefits of these ecotones as effective N sinks, enhanced microbial activity in riparian landscapes can play a key role in atmospheric pollution. For instance, riparian zones can account by 70 % of global (natural processes and human activities) terrestrial emissions of nitrous oxide ($N_2O$) to the atmosphere, a powerful greenhouse gas (GHG) with 298 times the global warming potential of carbon dioxide ($CO_2$) (Audet et al., 2014; Groffman et al., 2000; Hefting et al., 2003). Moreover, riparian soils can significantly contribute to global $CO_2$ emissions because they can hold high rates of heterotrophic and autotrophic respiration (Chang et al., 2014). Soil respiration is the main natural carbon (C) efflux to the atmosphere, contributing to 20 % of the global emission of $CO_2$ (Kim and Verma, 1990; Raich et al., 2002; Rastogi et al., 2002). Finally, riparian zones can support large methane ($CH_4$) fluxes that account for the 15–40 % of global emissions (Audet et al., 2014; Segers, 1998). However, there are still many uncertainties regarding the magnitude and spatiotemporal variability of soil GHG emissions in riparian zones, reaching contradictory results concerning the potential role of riparian zones as sinks or sources of C and N (Bruland et al., 2006; Groffman et al., 1992; Harms et al., 2009; Walker et al., 2002).

Understanding the processes regulating GHG emissions from riparian soils is essential to quantify the role of riparian zones in the global C and N cycles. Multiple environmental variables, such as soil temperature, soil water content, and both C and N availability, have been identified as key factors influencing the rate and variability of soil microbial activities that produce GHG (Chang et al., 2014; Hefting et al., 2003; Mander et al., 2008; McGlynn and Seibert, 2003). Among them, riparian hydrology seems to play a fundamental role on GHG production because it controls the substrate subsides and, most importantly, the redox conditions of riparian soils (Jacinthe et al., 2015; Vidon, 2017). Under saturated conditions, anaerobic processes such as methanogenesis (i.e., the transformation of $CO_2$ to $CH_4$) and denitrification (i.e., the transformation of $NO_3^-$ to N gas ($N_2$) or $N_2O$) are the primary processes involved in the C and N cycles (Clément et al., 2002). Conversely, in dry soils, aerobic transformations involved in the oxidation of the organic matter (i.e., respiration, mineralization, nitrification, methane oxidation) dominate the riparian biogeochemistry (Harms and Grimm, 2008). From such observations, one would expect that there is a strong correlation between soil wetness and the relative importance of $CO_2$, $N_2O$, and $CH_4$ riparian soil emissions to the total GHG fluxes. However, there are still relatively few studies that analyze the direct influence of soil water content on several GHG effluxes simultaneously (but see Harms and Grimm, 2008; Jacinthe et al., 2015), and even less that combine such analyses with other environmental factors and soil processes. Thus, it is still unclear under which circumstances soil water content (rather than temperature or substrate availability) is the primary control factor of the riparian functionality.

Mediterranean systems are a unique natural laboratory to understand the close link between spatiotemporal variations in hydrology and riparian biogeochemistry because they are characterized by a marked spatial gradient of soil water content, that can range from $< 10\,\%$ in the hillslope edge to $> 80\,\%$ close to the stream (Chang et al., 2014; Lupon et al., 2016). Moreover, Mediterranean regions are subjected to seasonal alterations of precipitation and temperature regimes that might affect riparian hydrology as well as microbial activity in the riparian soils (Bernal et al., 2007; Bruland et al., 2006; Harms and Grimm, 2008; Harms et al., 2009). Increments in GHG emissions in riparian zones might occur following storms or flood events because sharp increments in soil water content enhance nitrification, denitrification, respiration, and methanogenesis rates (Casals et al., 2011; Jacinthe et al., 2015; Werner et al., 2014). However, recent studies have shown that high temperatures can sustain large respiration and N mineralization rates in riparian soils (Chang et al., 2014; Lupon et al. 2016), and, hence, the contribution of rewetting microbial pulses to annual $CO_2$ and $N_2O$ production in Mediterranean riparian soils is still under debate. Moreover, improved understanding of interactions among hydrology, microbial processes, and gas emissions within Mediterranean riparian zones is not only fundamental to understand the temporal pattern of riparian biogeochemistry but also necessary to estimate the contribution of these ecosystems to atmospheric GHG budgets at local and global scale.

In this study, soil properties, soil N processes, and $CO_2$ and $N_2O$ soil emissions were measured over a year across a Mediterranean riparian forest that exhibited a strong gradient in soil water content (Fig. 1a). We did not measure $CH_4$ emissions because previous studies reported extremely low values in dry systems ($-0.06$–$0.42\,\mathrm{mg\,C\,m^{-2}\,d^{-1}}$; Batson et al., 2015; Gómez-Gener et al., 2015). Specifically, we aimed (i) to evaluate the spatiotemporal patterns of $CO_2$ and $N_2O$ emissions in Mediterranean riparian soils, (ii) to analyze under which conditions soil water content rules microbial processes and GHG over other physicochemical variables, and (iii) to provide some reliable estimates of GHG emissions from Mediterranean riparian soils. We hypothesized that the magnitude and the relative contribution of $N_2O$ and $CO_2$ to total GHG emission strongly depend on soil water content conditions rather than other variables during all year long (see conceptual approach in Fig. 1b). In the near-stream zone, we expected that saturated anoxic soils would enhance denitrification but constrain both respiration and nitrification. Thus, we predicted higher $N_2O$ than $CO_2$ emissions in this zone. In the intermediate zone, we expected that wet (but not saturated) soils would enhance aerobic processes such as respiration, N mineralization or nitrification, and thus we predicted high $CO_2$ emissions compared to $N_2O$. Finally, we expect that dry soils would deplete (or even inhibit) the soil microbial activity near the hillslope edge, and therefore we predicted low GHG emissions in this zone. Because Mediterranean regions are subjected to strong intra-annual variations in soil water content, we expected that this general behavior would be maximized in summer, when only near-stream soils would keep wet. Conversely, we expected that all microbial processes would be enhanced shortly after rainfall events, and thus simultaneous pulses of $CO_2$ and $N_2O$ emissions would occur in spring and fall.

## 2 Materials and methods

### 2.1 Study site

The research was conducted in a riparian forest of Font del Regàs, a forested headwater catchment ($14.2\,\mathrm{km^2}$, 500–1500 m a.s.l. (above sea level), located in the Montseny Natural Park, NE Spain (41°50′ N, 2°30′ E) (Fig. 1a). The climate

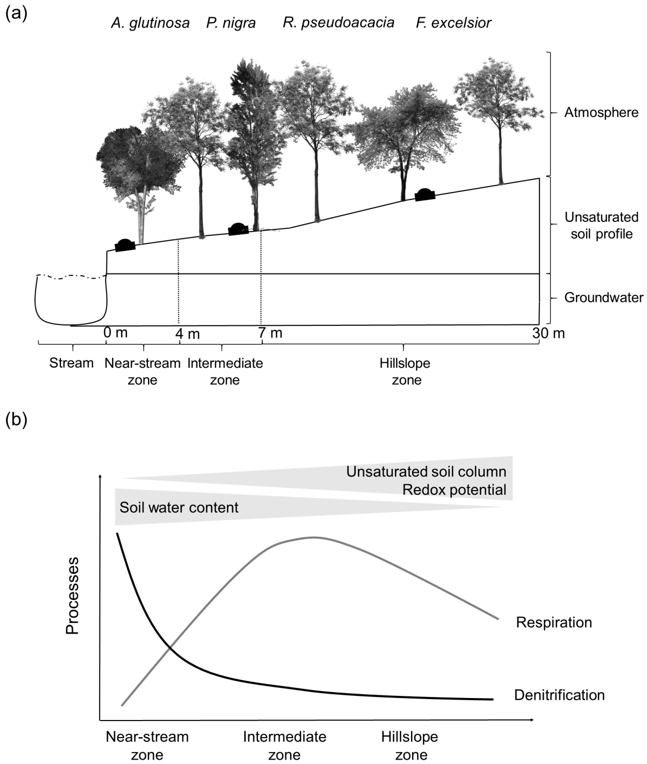


**Figure 1. (a)** Plot layout for the studied Mediterranean riparian forest showing the three riparian zones and the location of the chambers ($n = 5$ for each riparian zone). **(b)** Conceptual approach of the influence of riparian hydrology on soil microbial processes across a Mediterranean riparian zone. Soil water content decreases from the near-stream to the hillslope zone due to changes in groundwater table, increasing unsaturated soil column and oxic conditions. Anaerobic processes (denitrification) occur under anoxic conditions while aerobic processes (respiration) are optimized under a moderate range of soil water content.

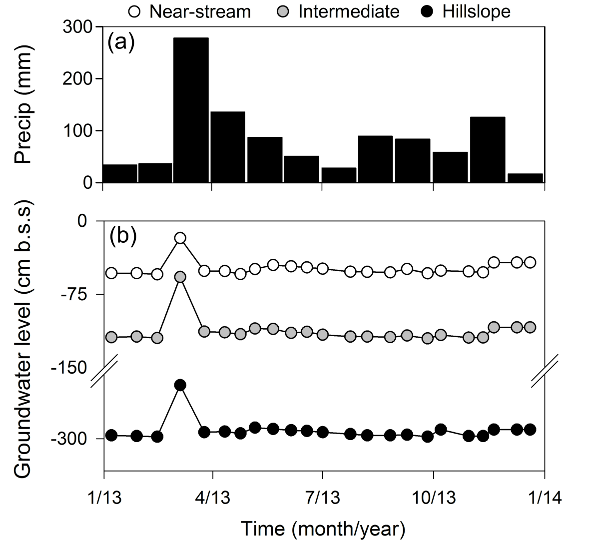


**Figure 2.** Temporal pattern of **(a)** mean monthly precipitation and **(b)** biweekly groundwater level at the studied riparian site during the year 2013. Circles are mean values of groundwater level at the near-stream (white), intermediate (grey), and hillslope (black) zones. Precipitation data were obtained from a meteorological station located at ca. 300 m from the studied riparian site. At each riparian zone, groundwater level was measured in three PVC piezometers (32 mm diameter, 1–3 m long) with a water level sensor (Eijkelkamp 11.03.30).

is sub-humid Mediterranean, with mean temperature ranging from 5 °C in February to 25 °C in August. In 2013, annual precipitation (1020 mm) was higher than long-term average (925 ± 151 mm), with most of rain falling in spring (500 mm) (Fig. 2a). Total inorganic N deposition oscillates between 15 and 30 $kg\,N\,ha^{-1}\,yr^{-1}$ (period 1983–2007; Àvila and Rodà, 2012).

We selected a riparian site ($\sim 600\,m^2$, $\sim 30$ m wide) that flanked a third-order stream close to the catchment outlet (536 m a.s.l., 5.3 km from headwaters). The riparian site was divided into three zones characterized by different species compositions (Fig. 1a). The near-stream zone was located adjacent to the stream (0–4 m from the stream edge) and was composed of *Alnus glutinosa* (45 % of basal area) and *Populus nigra* (33 % of basal area). The intermediate zone (4–7 m from the stream edge) was composed by *P. nigra* and *Robinia pseudoacacia* (29 and 71 % of basal area, respectively). Finally, the hillslope zone (7–30 m from the stream edge) bordered upland forests and was composed by *R. pseudoacacia* (93 % of basal area) and *Fraxinus excelsior* (7 % of basal area). The three riparian zones had sandy-loam soils (bulk density = 0.9–1.1 $g\,cm^{-3}$), with a 5 cm deep organic layer followed by a 30 cm deep A horizon. The top soil layer (0–10 cm depth) was mainly composed by sands ($\sim 90$ %) and silts ($\sim 7$ %) at the near-stream zone, whereas gravels ($\sim 16$ %) and sands ($\sim 80$ %) were the dominant particle sizes at the intermediate and hillslope zones. During the study period, groundwater level averaged $-54 \pm 14$ cm b.s.s. (below the soil surface) at the near-stream zone, and decreased to $-125 \pm 4$ and $-358 \pm 26$ cm b.s.s. at the intermediate and hillslope zones, respectively (Figs. 1a and 2b).

## 2.2 Field sampling

We delimited five plots (1 × 1 m) within each riparian zone (near-stream, intermediate, and hillslope) (Fig. 1a). During the year 2013, soil physicochemical properties, soil N processes, and gas emissions were measured in each plot every 2–3 months in order to cover a wide range of soil water content and temperature conditions. On each sampling month, one soil sample (0–10 cm depth, including O and A horizons) was collected randomly from each plot to analyze soil physicochemical properties. Soil samples were taken with a 5 cm diameter core sampler and placed gently into plastic bags after carefully removing the litter layer. Close to each soil sample, we performed in situ soil incubations to measure soil net N mineralization and net nitrification rates (Eno, 1960). For this purpose, a second soil core (0–10 cm depth) was taken, placed in a polyethylene bag, and buried at the same depth. Soil incubations were buried for 4 days and then removed from the soil.

Gas emissions and denitrification rates were measured simultaneously and during four consecutive days (i.e., during the entire soil incubation period) in order to facilitate the direct comparison between microbial rates and gas fluxes. Soil $CO_2$ effluxes were measured with a SRC-1 soil chamber attached to an EGM-4 portable infrared gas analyzer (IRGA) (PP Systems, Amesbury, MA). The EGM-4 has a measurement range of 0–2000 ppm ($\mu mol\,mol^{-1}$), with an accuracy of 1 % and a linearity of 1 % throughout the range. Every field day, $CO_2$ measurements started at 12:00 and were conducted consecutively at the 15 plots starting for the near stream zone. At each plot, the SCR-1 soil chamber was placed over the top soil for a 120 s incubation. Before each measurement, we carefully removed the litter layer to ensure no leaks. Furthermore, we aerated the SCR-1 between samples to ensure the accuracy of the instrument as well as to avoid contamination between samples. For each plot, $CO_2$ emissions rates were calculated from the best-fit linear regression of the $CO_2$ accumulated in the headspace with incubation time (Fig. S1 in the Supplement). $CO_2$ fluxes on an areal basis ($F_{CO_2}$, in $\mu mol\,m^{-2}\,h^{-1}$) were calculated following Healy et al. (1996):

$$F_g = \frac{dg}{dt} \times \frac{VP_0}{SRT_0}, \tag{1}$$

where $dg/dt$ is the rate of change in gas concentration (in $\mu mol\,mol^{-1}\,h^{-1}$) in the chamber, $V$ is chamber volume (in $m^3$), $P_0$ is initial pressure (in Pa), $S$ is the soil surface area (in $m^2$), $R$ is the gas constant ($8.314\,Pa\,m^3\,K^{-1}\,mol^{-1}$), and $T_0$ is the initial chamber temperature (in K). For budgeting, moles of $CO_2$ and $N_2O$ were converted to grams of C and N, respectively.

In situ denitrification rates and $N_2O$ emissions were measured using closed cylinder (0.37 L) and open cylinder (0.314 $m^2$) chambers, respectively. For denitrification analyses, an intact soil core (0–10 cm depth) was introduced in the chamber, closed with a rubber serum stopper, amended with acetone-free acetylene to inhibit the transformation of $N_2O$ to $N_2$ (10 % $v/v$ atmosphere), and placed at the same depth. For $N_2O$ analysis, chambers were placed directly on the soil and no special treatment was carried out. Gas samples for both denitrification and $N_2O$ chambers were taken at the same time (0, 1, 2, and 4 h of incubation) with a 20 mL syringe and stored in evacuated tubes. All soil and gas samples were kept at < 4 °C until laboratory analysis (< 24 h after collection).

Soil physical properties were measured within each plot simultaneously to gas emissions. Volumetric soil water content (%) (five replicates per plot) and soil temperature (°C) (one replicate per plot) were measured at 10 cm depth by using a time-domain reflectometer sensor (HH2 moisture meter, Delta-T Devices) and a temperature sensor (CRISON 25), respectively. Soil pH and reduction potential (Eh, mV) (1 replicate per plot) were measured at 0–10 cm depth by water extraction (1 : 2.5 $v/v$) using a Thermo Scientific ORION sensor (STAR 9107BNMD). Although Eh measures performed by water extraction may not be as accurate as other field techniques, these values have been previously used as a good proxy of the soil redox potential (Yu and Rinklebe, 2013).

### 2.3 Laboratory analyses

Pre-incubation soil samples were oven dried at 60 °C, sieved, and the fraction < 2 mm was used for measuring soil chemical properties. The relative soil organic matter content (%) was measured by loss on ignition (450 °C, 4 h). Total soil C and N contents were determined on a gas chromatograph coupled to a thermal conductivity detector after combustion at 1000 °C at the Scientific Technical Service of the University of Barcelona.

To estimate microbial N processes, we extracted 5 g of pre- and post-incubation field-moist soil samples with 50 mL of 2 M KCl (1 g : 10 mL, ww : v; 1 h shacking at 110 rpm and 20 °C). The supernatant was filtered (Whatman GF/F 0.7 µm pore diameter) and analyzed for ammonium ($NH_4^+$) and nitrate ($NO_3^-$). $NH_4^+$ was analyzed by the salicylate–nitroprusside method (Baethgen and Alley, 1989) using a spectrophotometer (PharmaSpec UV-1700, Shimadzu). $NO_3^-$ was analyzed by the cadmium reduction method (Keeney and Nelson, 1982) using a Technicon autoanalyzer (Technicon, 1987). For each pair of samples, net N mineralization and net nitrification were calculated as the differences between pre- and post-incubations values of inorganic N ($NH_4^+$ and $NO_3^-$) and $NO_3^-$, respectively (Eno, 1960). Pre-incubation $NH_4^+$ and $NO_3^-$ concentrations were further used to calculate the availability of dissolved inorganic nitrogen in riparian soils.

To estimate denitrification and natural $N_2O$ emissions, we analyzed the $N_2O$ of all gas samples using a gas chromatograph (Agilent Technologies, 7820A GC) that was calibrated using certified standards (4.66 ppm $N_2O$; Air Liquide). Both denitrification and $N_2O$ emissions rates were calculated similarly to $CO_2$ fluxes (Fig. S1). In addition, we measured the denitrification enzyme activity (DEA) for three soil cores of each riparian zone to determine the factors limiting denitrification. For each soil core, four sub-samples (20 g of fresh soil) were placed into 125 mL glass jars containing different treatments. The first jar ($DEA_{MQ}$) contained Milli-Q water (20 mL) to test anaerobiosis limitation. The second jar ($DEA_C$) was amended with glucose solution (4 g glucose $kg\,soil^{-1}$) to test C limitation. The third jar ($DEA_{NO_3}$) was amended with nitrate solution (72.22 mg $KNO_3$ $kg\,soil^{-1}$) to test N limitation. Finally, the fourth jar ($DEA_{C+NO_3}$) was amended with both nitrate and glucose solutions (4 g glucose kg soil$^{-1}$ and 72.22 mg $KNO_3$ kg soil$^{-1}$) to test simultaneously C and N limitation. All jars were capped with rubber serum stoppers, made anaerobic by flushing $N_2$, and amended with acetone-free acetylene (10 % $v/v$) (Smith and Tiedje, 1979). Gas samples were collected after 4 and 8 h of incubation and analyzed following the same procedure of field DNT samples. DEA rates were calculated similarly to denitrification rates.

### 2.4 Statistical analysis

Statistical analyses were carried out using the package *lmer* and *pls* of R 2.15.1 statistical software (R Development Core Team, 2012). We performed linear mixed-model analysis of variance (ANOVA) to test differences in soil properties, microbial N processes, and gas emissions across riparian zones and seasons. We used riparian zone and season as fixed effects and plot (nested within riparian zones) as a random effect. When multiple samples were taken within a plot (soil physical properties, denitrification, and gas emissions), the ANOVA was performed on plot means, with $n = 75$ (5 plots × 3 zones × 5 dates). For each model, post hoc Tukey contrasts were used to test which zones or seasons differed from each other. In all cases, residuals were tested for normality using a Shapiro–Wilk test and homogeneity of variance was examined visually by plotting the predicted and residual values. In those cases that the normality assumption was unmet, data were log transformed. In all analyses, differences were considered significant when $p < 0.05$.

We used partial least squares regression (PLS) to explore how soil properties, C and N availability, groundwater level, and soil N processes predict variation in $CO_2$ and $N_2O$ emissions. PLS identifies the relationship between independent ($X$) and dependent ($Y$) data matrices through a linear, multivariate model and produces latent variables (PLS components) representing the combination of $X$ variables that best describe the distribution of observations in "$Y$ space" (Eriksson et al., 2006). We determined the goodness of fit ($R^2Y$) and the predictive ability ($Q^2Y$) of the model by comparing modeled and actual $Y$ observations through a cross-validation process. Each model was refined by iteratively removing variables that had non-significant coefficients in order to minimize the model overfitting (i.e., low $Q^2Y$ values) as well as the multicollinearity of the explanatory variables (i.e., variance inflation factor (VIF) < 5). Furthermore, we identified the importance of each $X$ variable by using variable importance on the projection (VIP) scores, calculated as the sum of square of the PLS weights across all components. VIP values > 1 indicate variables that are most important to the overall model (Eriksson et al., 2006). In all PLS models, data were ranked and centered prior to analysis.

## 3 Results

### 3.1 Spatial pattern of soil properties, microbial rates, and gas emissions

During the study period, all riparian zones had similar mean soil temperature (11–12 °C), pH (6–7), and redox potential (170–185 mV) (Table 1). However, soil water content exhibited strong differences across riparian zones (Table 2), with the near-stream zone holding wetter soils than the intermediate and the hillslope zones (Table 1). There were significant differences in most of soil chemical properties (Tables 1 and 2). Both organic matter and soil C and N content were 2-fold lower in the near-stream zone than in the intermediate and hillslope zones, though all zones exhibited similar C : N ratios (C : N = 14). Moreover, inorganic N concentrations ($NH_4^+$ and $NO_3^-$) were from 2- to 5-fold lower for the near-stream zone than for the other two zones.

On annual basis, net N mineralization averaged 0.14 ± 0.40, 0.39 ± 1.23, and 0.22 ± 1.03 mg N kg$^{-1}$ d$^{-1}$ at the near-stream, intermediate, and hillslope zones, respectively. Mean annual net nitrification rates were close to net N mineralization, averaging 0.17 ± 0.38, 0.25 ± 0.69, and 0.28 ± 0.73 mg N kg$^{-1}$ d$^{-1}$ at the near-stream, intermediate, and hillslope zones, respectively. There were no significant differences in mean annual net N mineralization and net nitrification rates among riparian zones (in both cases: mixed-model ANOVA test, $F > F_{0.05}$, $p > 0.05$). Mean annual denitrification was higher at the near-stream zone (2.69 ± 5.30 µg N Kg$^{-1}$ d$^{-1}$) than at the intermediate (0.72 ± 1.85 µg N Kg$^{-1}$ d$^{-1}$) and hillslope (0.76 ± 1.59 µg N Kg$^{-1}$ d$^{-1}$) zones (mixed-model ANOVA test, $F = 4.33$, $p = 0.038$). However, potential denitrification rates were lower in the near-stream zone (0.3–0.6 mg N kg$^{-1}$ d$^{-1}$) compared to intermediate (1.0–2.4 mg N kg$^{-1}$ d$^{-1}$) and hillslope (1.3–3.8 mg N kg$^{-1}$ d$^{-1}$) zones (Table 3).

Natural $CO_2$ and $N_2O$ emissions differed among riparian zones, yet they showed opposite spatial patterns. Near-stream zone exhibited lower $CO_2$ emissions (318 ± 195 mg C m$^{-2}$ h$^{-1}$) compared to the intermediate (472 ± 298 mg C m$^{-2}$ h$^{-1}$) and hillslope (458 ± 308 mg C m$^{-2}$ h$^{-1}$) zones (mixed-model ANOVA test, $F = 7.08$, $p = 0.009$). Conversely, near-stream zone showed higher $N_2O$ emissions (0.035 ± 0.022 mg N m$^{-2}$ h$^{-1}$) than the other two zones (intermediate = 0.032 ± 0.025 mg N m$^{-2}$ h$^{-1}$; hillslope = 0.022 ± 0.012 mg N m$^{-2}$ h$^{-1}$) (mixed-model ANOVA test, $F = 7.31$, $p = 0.008$).

### 3.2 Temporal pattern of soil properties, microbial rates, and gas emissions

During the study period, there was a marked seasonality in most of soil physical properties, except for pH and Eh, which did not show any temporal pattern (Table 2). Soil water content exhibited a marked seasonality, though it differed among

**Table 1.** Mean annual values (±SD) of soil water content (volumetric), soil temperature, soil pH, soil redox capacity (Eh), soil organic matter, soil molar C : N ratio, soil carbon (C) and nitrogen (N) content, and soil ammonium ($NH_4^+$) and nitrate ($NO_3^-$) concentrations for the three riparian zones. For each variable, different letters indicate statistical significant differences between riparian zones (post hoc Tukey HSD test, $p < 0.05$).

| | Near-stream | Intermediate | Hillslope |
|---|---|---|---|
| Soil water content (%) | $29.58 \pm 7.55^A$ | $19.36 \pm 6.00^B$ | $19.81 \pm 6.24^B$ |
| Temperature (°C) | $11.37 \pm 5.39^A$ | $11.82 \pm 5.90^A$ | $12.01 \pm 6.34^A$ |
| Eh | $170 \pm 111^A$ | $184 \pm 103^A$ | $184 \pm 95^A$ |
| pH | $6.66 \pm 0.42^A$ | $6.31 \pm 0.50^A$ | $6.68 \pm 0.53^A$ |
| Organic matter (%) | $4.41 \pm 0.71^A$ | $7.98 \pm 2.88^B$ | $9.53 \pm 1.99^C$ |
| C : N ratio | $14.25 \pm 3.64^A$ | $14.09 \pm 1.78^A$ | $13.63 \pm 1.18^A$ |
| C (mg kg$^{-1}$) | $2004 \pm 1038^A$ | $4007 \pm 1785^B$ | $4923 \pm 1428^B$ |
| N (mg kg$^{-1}$) | $160 \pm 44^A$ | $330 \pm 135^B$ | $418 \pm 107^C$ |
| $NH_4^+$ (mg N kg$^{-1}$) | $1.88 \pm 1.21^A$ | $5.58 \pm 3.48^B$ | $3.90 \pm 2.07^B$ |
| $NO_3^-$ (mg N kg$^{-1}$) | $0.75 \pm 0.58^A$ | $4.66 \pm 4.25^B$ | $5.30 \pm 4.20^B$ |

**Table 2.** Results from the mixed-model analysis of variance (ANOVA) showing the effects of riparian zones and seasons on soil water content, soil temperature, soil pH, soil redox capacity (Eh), soil organic matter, soil molar C : N ratio, soil carbon (C) and nitrogen (N) content, and soil ammonium ($NH_4^+$) and nitrate ($NO_3^-$) concentrations. Plot was treated as a random effect in the model, whereas riparian zones, seasons, and their interactions were considered fixed effects. Values are $F$ values and the $p$ values are shown in brackets. $P$ values < 0.05 are shown in bold.

| | Riparian zone | Seasons | Zone × season |
|---|---|---|---|
| Soil water content | **18.6 [< 0.001]** | **100 [< 0.001]** | **13.6 [< 0.001]** |
| Temperature | 0.33 [0.721 ] | **2117 [< 0.001]** | 0.42 [0.906] |
| pH | 1.97 [0.182] | 2.43 [0.060] | 2.73 [0.052] |
| Eh | 1.34 [0.247] | 3.53 [0.062] | 1.88 [0.084] |
| Organic matter | **27.8 [< 0.001]** | 2.77 [0.053] | 1.62 [0.144] |
| C : N ratio | 0.99 [0.400] | **10.9 [< 0.001]** | 1.72 [1.118] |
| C | **27.1 [< 0.001]** | 1.86 [0.132] | 0.77 [0.630] |
| N | **39.7 [< 0.001]** | 1.22 [0.311] | 0.63 [0.746] |
| $NH_4^+$ | **12.4 [0.001]** | 2.71 [0.051] | 1.52 [0.176] |
| $NO_3^-$ | **22.4 [< 0.001]** | **5.63 [< 0.001]** | **4.09 [< 0.001]** |

Zone: near-stream, intermediate, hillslope.
Season: Feb, Apr, Jun, Aug, and Nov.

riparian zones (Table 2, "zone × season"). In the intermediate and hillslope zones, soil water content was maxima in November and minima in August, while the near-stream soils were wetter during both spring (April–June) and fall (November) (Fig. 3a). Conversely, soil temperature showed similar seasonality but opposite values in all riparian zones (Table 2), with a maxima in summer (August) and minima in winter (February) (Fig. 3b). Soil chemical properties (soil organic matter and both soil C and N content) did not show any seasonal trend, but all riparian zones exhibited lower C : N ratios in February compared to the other seasons (Fig. 3c). There was no seasonality in soil $NH_4^+$ concentrations at any riparian zone (Table 2). However, soil $NO_3^-$ concentrations showed a marked temporal pattern, yet it differed among riparian zones (Table 2, "zone × season"). The highest soil $NO_3^-$ concentrations occurred in February at both the near-stream and hillslope zones, but in June–August at the intermediate zone (Fig. 3d).

Soil N processes showed similar seasonal patterns in all riparian zones (in all cases: $F_{date} < F_{0.05}$, $F_{interaction} > F_{0.05}$). Both net N mineralization and net nitrification rates were higher in April than February, June, and November (Fig. 4a and b), while denitrification rates were higher in April and June compared to the rest of the year (Fig. 4c). In April, both net N mineralization and net nitrification rates differed across riparian zone, with higher rates in the intermediate zone than in the near-stream one. Net N mineralization rates also differed in August, when the intermediate zone exhibited 2-fold higher rates than the other two zones. Finally, denitrification was higher at the near-stream than at the other two zones in both June and August.

Natural gas emissions showed a clear seasonal pattern (in both cases: mixed-model ANOVA test, $F_{date} < F_{0.05}$, $p <$

**Table 3.** Mean values (± SD) of potential denitrification rates (in $mg\,N\,kg^{-1}\,d^{-1}$) after anoxia ($DEA_{MQ}$), carbon addition ($DEA_C$), nitrogen addition ($DEA_{NO_3}$), and carbon and nitrogen addition ($DEA_{C+NO_3}$) treatments for the three riparian zones during the study period. For each zone, different letters indicate statistical significant differences between treatments (post hoc Tukey HSD test, $n = 15$, $p < 0.01$).

| | Potential denitrification rates ($mg\,N\,kg^{-1}\,d^{-1}$) | | | |
|---|---|---|---|---|
| | $DEA_{MQ}$ | $DEA_C$ | $DEA_{NO_3}$ | $DEA_{C+NO_3}$ |
| Near-stream | $0.31 \pm 0.41^{A}$ | $0.26 \pm 0.27^{A}$ | $0.42 \pm 0.42^{A}$ | $0.63 \pm 0.85^{A}$ |
| Intermediate | $1.01 \pm 1.12^{A}$ | $1.88 \pm 1.59^{A}$ | $2.28 \pm 3.57^{A}$ | $2.40 \pm 2.45^{A}$ |
| Hillslope | $1.34 \pm 1.33^{A}$ | $2.35 \pm 1.97^{AB}$ | $1.73 \pm 1.43^{AB}$ | $3.82 \pm 2.78^{B}$ |

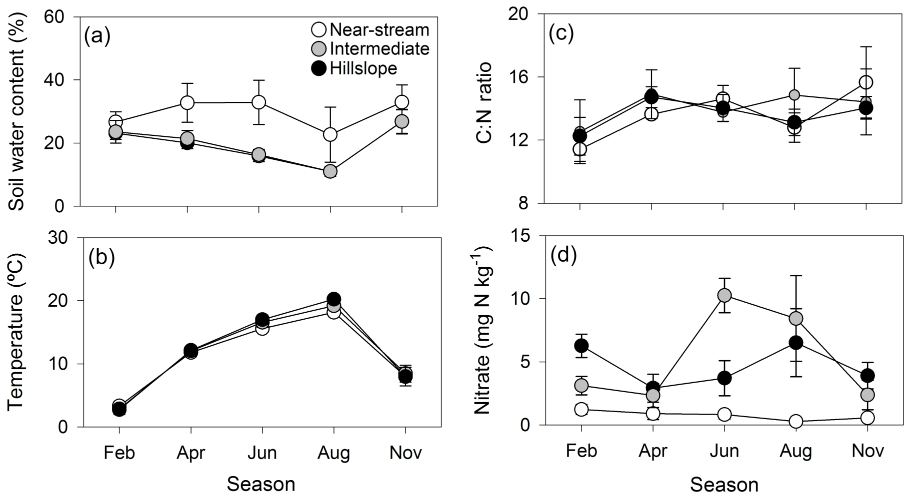


**Figure 3.** Temporal pattern of **(a)** soil water content, **(b)** soil temperature, **(c)** soil C : N molar ratio, and **(d)** soil nitrate concentration at 10 cm depth. Data are shown for the near-stream (white), intermediate (grey), and hillslope (black) zones during the study period. Circles are mean values and error bars are standard deviations.

0.001), yet it differed between $CO_2$ and $N_2O$ emissions. In all zones, $CO_2$ emissions were maxima in June and minima in February (Fig. 5a), while highest $N_2O$ emission rates occurred in April and lowest in both February and August (Fig. 5b). In spring (April and June), $CO_2$ emissions were higher at the intermediate and hillslope zones compared to the near-stream one (Fig. 5a). Moreover, the near-stream zone showed higher $N_2O$ emissions than the hillslope zone in February, April, and June (Fig. 5b).

### 3.3 Relationship between soil properties, microbial processes, and gas emissions

PLS models extracted two components that explained the 71 % and the 40 % of the variance in $CO_2$ and $N_2O$ emissions, respectively (Table 4). The model predictability was high for $CO_2$ ($Q^2Y = 0.66$), but weak for $N_2O$ ($Q^2Y = 0.34$). Moreover, PLS models identified few variables as key predictors of GHG emissions (VIF < 2, VIP > 0.8), yet these variables differed between $CO_2$ and $N_2O$ emissions (Table 4). Soil temperature (PLS coefficient [coef] = +0.60), and soil water content (coef = −0.24) explained most of the variation in $CO_2$ emissions (Table 4, Fig. S2a). Conversely, variations in $N_2O$ emissions were primarily related to changes in denitrification rates (coef = +0.45), soil water content (coef = +0.21) and, to a lesser extent, groundwater level (coef = −0.16) (Table 4, Fig. S2b).

## 4 Discussion

This study emphasized the role of soil water content as a main driver of riparian biogeochemistry and GHG emissions. By analyzing soil microbial processes and GHG emissions over a year in a Mediterranean riparian forest, we clearly demonstrate that soil water content has a major role in driving soil microbial processes, the spatiotemporal patters of $CO_2$ and $N_2O$ emissions and the overall role of Mediterranean riparian soils in the global C and N cycles.

### 4.1 Microbial processes regulating GHG emissions

Mean daily emissions of $CO_2$ found in the present study (1.2–10 $g\,C\,m^{-2}\,d^{-1}$) were generally high, especially during spring and summer months. These soil $CO_2$ emissions were higher than those reported for temperate riparian regions (0.2–4.8 $g\,C\,m^{-2}\,d^{-1}$; Batson et al., 2015; Bond-Lamberty

**Table 4.** Summary of the partial least squares (PLS) models produced for $CO_2$ and $N_2O$ emissions at the riparian site ($n = 75$). Values are the coefficients from PLS models which describe the relationship (direction and relative strength) between explanatory variables and gas emissions. The variance inflation factor (VIF) of each explanatory variable, indicative of collinearity, is shown in brackets. Bold values indicate the most influencing variables (variable importance in the projection (VIP) > 1.0).

| | *X* variable | Abbreviation | $CO_2$ | $N_2O$ |
|---|---|---|---|---|
| Soil properties | Soil water content | SWC | **−0.235 [1.72]** | **0.205 [1.32]** |
| | Groundwater level | GWL | – | −0.157 [1.24] |
| | Temperature | Tsoil | **0.599 [1.45]** | – |
| | pH | pH | – | – |
| | Redox potential | Eh | – | – |
| | Bulk density | BD | – | – |
| | Coarse texture | % Sand | – | – |
| | Organic matter | SOM | – | – |
| | Total carbon | C | – | – |
| | Total nitrogen | N | – | – |
| | Molar C : N ratio | C : N ratio | – | – |
| | Ammonium | $NH_4^+$ | 0.167 [1.61] | – |
| | Nitrate | $NO_3^-$ | 0.066 [1.80] | −0.060 [1.47] |
| Soil N processes | Net N mineralization | NNM | – | – |
| | Net nitrification | NN | – | – |
| | Denitrification | DNT | – | **0.449 [1.09]** |
| $R^2Y$ | | | **0.71** | **0.40** |
| $Q^2Y$ | | | **0.66** | **0.34** |

All abbreviations are used in Fig. S2 for PLS loading plots.

and Thomson, 2010; Mander et al., 2008), although similar values have been reported in some dry forested wetlands of Europe and North America (Harms and Grimm, 2008; Oertel et al., 2016). These substantially high $CO_2$ emissions observed in Font del Regàs may be attributed to high microbial respiration rates associated with relatively moist and organic-matter-enriched soils (Mitsch and Gosselink, 2007; Pacific et al., 2008; Stern, 2006). In agreement, previous studies have reported that microbial heterotrophic respiration can be an important contributor (> 60 %) to $CO_2$ soil effluxes in water-limited riparian zones (Harms and Grimm, 2012; McLain and Martens, 2006). However, the absence of a relationship between soil N processes and $CO_2$ emissions suggests that soil C and N cycles are decoupled in Mediterranean riparian forests, and thus soil N mineralization may be not a good descriptor of bulk organic matter mineralization. Moreover, plant root respiration and methane oxidation can increase the $CO_2$ emissions in riparian soils with deep groundwater tables such as in Font del Regàs (Chang et al., 2014).

Conversely, $N_2O$ emissions of our riparian site (0.001–0.2 $mg\,N\,m^{-2}\,d^{-1}$) were relatively low during the whole year. Similar $N_2O$ emissions were reported in other water-limited riparian forests that are rarely flooded (−0.9–0.39 $mg\,m^{-2}\,d^{-1}$; Bernal et al., 2003; Harms and Grimm, 2012; Vidon et al., 2016), yet these values were, on average, much lower than those found in temperate riparian regions (0–54 $mg\,N\,m^{-2}\,d^{-1}$; Burgin and Groffman, 2012; Hefting et al., 2003; Mander et al., 2008). In Font del Regàs, most $N_2O$ was produced by denitrification, as we found an intimate link between this microbial process and $N_2O$ emissions. Additionally, other processes such as nitrification or nitrate ammonification can contribute to $N_2O$ emissions (Baggs, 2008; Hefting et al., 2003). However, it seems unlikely that nitrification could account for the observed $N_2O$ emissions because no relationship was found between net nitrification rates and $N_2O$ emissions. Likewise relatively oxic conditions (Eh > 100) and low C : N ratios (C : N < 20) in Font del Regàs suggest low nitrate ammonification in riparian soils (Schmidt et al., 2011). Currently, the influence of soil denitrification on $N_2O$ emissions in riparian zones is still under debate (Giles et al., 2012). Nonetheless, our results suggest that performing simultaneous measurements of different soil N can contribute to disentangling the mechanisms underlying net $N_2O$ emissions in riparian areas.

### 4.2 Effects of soil water content on soil $CO_2$ effluxes

As expected, we found higher soil $CO_2$ effluxes at the intermediate and hillslope zones than at the near-stream zone. This spatial pattern was negative and strongly related to soil water content (Table 4), suggesting that, as soils become less moist and more aerated, oxidizing aerobic respiration increases, ultimately stimulating $CO_2$ production in the top soil layer (Müller et al., 2015). In agreement, other aerobic processes, such as N mineralization, were also higher in the

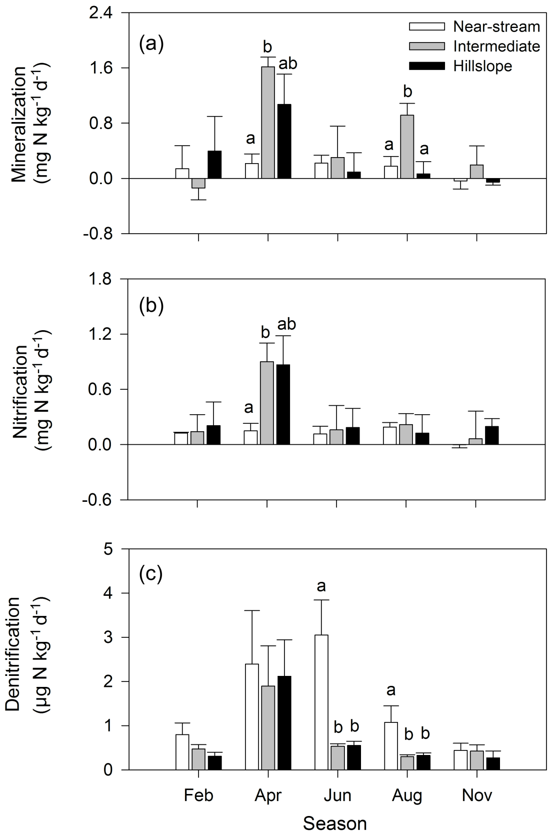


**Figure 4.** Temporal pattern of **(a)** soil net N mineralization, **(b)** net nitrification, and **(c)** denitrification rates at the near-stream (white), intermediate (grey), and hillslope (black) zones during the study period. Bars are mean values for each section and error bars are standard errors. For each season, different letters indicate significant differences among sections (mixed-model ANOVA, $p < 0.05$).

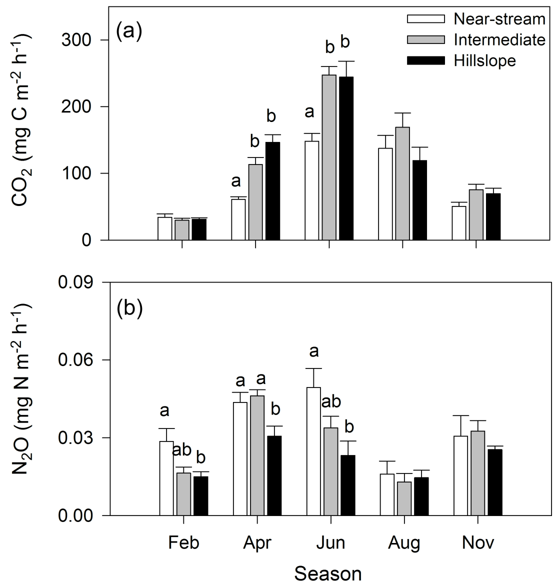


**Figure 5.** Temporal pattern of soil **(a)** $CO_2$ and **(b)** $N_2O$ emissions at the near-stream (white), intermediate (grey), and hillslope (black) zones during the study period. Bars are mean values for each section and error bars are standard errors. For each season, different letters indicate significant differences among sections (mixed-model ANOVA, $p < 0.05$).

intermediate and hillslope zones. Moreover, deep groundwater tables in the hillslope zone can increase the volume of aerated soil, which can increase the area-specific soil $CO_2$ emissions near the hillslope edge (Chang et al., 2014). Increasing $CO_2$ emissions from wet to dry zones has been reported in other wetlands and riparian forests (Batson et al., 2015; Morse et al., 2012; Welti et al., 2012), showing a close linkage between riparian hydrology and spatial variations in microbial respiration rates.

Nonetheless, the intra-annual variations of soil $CO_2$ emissions were strongly dependent on soil temperature (Table 4). Probably, cold temperatures ($< 4$ °C) limited soil respiration during winter, while warmer conditions ($> 15$ °C) stimulated this process in June and August (Emmett et al., 2004; Suseela et al., 2012; Teiter and Mander, 2005). However, lower $CO_2$ emissions than expected for temperature dynamics were reported in summer at the intermediate and hillslope zones, likely because extreme soil dryness (soil water content $< 20$ %) limited respiration rates during such period (Chang et al., 2014; Goulden et al., 2004; Wickland et al., 2010). Although the mechanisms by which soil dryness may affect microbial C demand are still poorly understood, suppressed microbial respiration in summer can be attributed to a disconnection between microbes and resources (Belnap et al., 2005; Davidson et al., 2006), decreases in photosynthetic and exo-enzymatic activities (Stark and Firestone, 1995; Williams et al., 2000), or a relocation of the invested energy on growth (Allison et al., 2010). Altogether, these results suggest that soil water content may be as important as soil temperature to understand soil $CO_2$ effluxes, and therefore future warmer conditions may not fuel higher $CO_2$ emissions, at least in those regions experiencing severe water limitation.

### 4.3 Effects of soil water content on soil $N_2O$ effluxes

As occurred for $CO_2$ emissions, $N_2O$ fluxes showed a clear spatial pattern associated with changes in soil water content across the riparian zone. In the near-stream zone, relatively wet conditions (SWC = 30–40 %) likely promoted denitrification rates, while dry soils (SWC = 10–25 %) could limit both nitrification and denitrification in the intermediate and hillslope zones (Linn and Doran, 1984; Pinay et al., 2007). Such spatial pattern differed from those found in non-water-limited riparian forests, where higher $N_2O$ emissions occurred in the hillslope edge as a result of high resource supply (DeSimone et al., 2010; Dhondt et al., 2004; Hedin et al., 1998). These results suggest that riparian hydrology is the primary mechanisms controlling denitrification but, once water is unlimited, substrate availability controls the magnitude of denitrification rates. This former idea is supported by our potential denitrification results, which showed that, after adding water, denitrification rates at the intermediate and hillslope zones were 3–4 times the rate at the near-stream zone. Moreover, $N_2 : N_2O$ ratios estimated from acetylene method suggest that there was a spatial pattern in denitrification efficiency as well. During the study period, $N_2 : N_2O$ ratios were always higher at the near-stream ($21.50 \pm 40.32$) than at the intermediate and hillslope zones ($5.90 \pm 16.02$ and $4.23 \pm 8.31$, respectively), yet all values were much lower than those reported for temperate riparian forests (184–844; Mander et al., 2014). All together, these results support the idea that saturated soils favored the complete denitrification process to $N_2$ and can potentially emit less $N_2O$ compared to less saturated soils (Giles et al., 2012).

Intra-annual variation in $N_2O$ emission was also related to riparian hydrology because high rates of $N_2O$ effluxes occurred in April, when large precipitation events (400 mm) raised the groundwater level and increased soil water content at the whole riparian plot. Such pulses of $N_2O$ emissions short-after rewetting events can reflect the microbial use of the $NO_3^-$ that has been accumulated during dry antecedent periods (Chang et al., 2014; Hefting et al., 2004; Pinay et al., 2007). In agreement, the PLS model showed a negative relation between soil water content and $NO_3^-$ concentrations. Moreover, our results further suggest that rewetting events promote a fast N cycle because all microbial N processes were maxima in April. Nevertheless, we also expected a fast N cycle as well as large $N_2O$ emissions following rains in November because, similarly to spring, environmental conditions (i.e., high soil water content and increments in soil $NO_3^-$ concentrations during the antecedent dry summer) should enhance microbial activity. Likely, low rates of N transformations during fall may be attributed to an increase in microbial N demand following large C inputs from litterfall (Guckland et al., 2010). Moreover, leaf litter from *R. pseudoacacia*, the main tree species in our study site, holds a high lignin content (Castro-Díez et al., 2009; Yavitt et al., 1997), which might enrich the riparian soil with phenolic compounds and ultimately limit the use of N by microbes (Bardon et al., 2014). These results suggest that the response of N cycling to changes in water availability is more complex and less predictable than C cycling, likely because N processes depend on the interplay of additional ecosystem factors not included in this study.

### 4.4 Riparian soils as hotspots of GHG effluxes

There are several studies that attempt to upscale riparian GHG emissions at catchment scale, yet there are still fundamental uncertainties regarding the magnitude and sources of GHG emissions (Hagedorn, 2010; Pinay et al., 2015; Vidon and Hill, 2006). When accounting for all GHG ($CO_2 + N_2O$), our study suggest that our riparian soils can emit between 438 and 3650 $g\,C\,m^{-2}\,yr^{-1}$. Assuming that GHG emissions ($CO_2 + N_2O$) from upland evergreen oak and beech soils (54 and 38 % of the catchment, respectively) are similar to other Mediterranean regions (oak: 19–1240 $g\,C\,m^{-2}\,yr^{-1}$; Asensio et al., 2007; Barba et al., 2016; Inclán et al., 2014; beech: 214–1182 $g\,C\,m^{-2}\,yr^{-1}$; Guidolotti et al., 2013; Kesik et al., 2005), then riparian soils (6 % of the catchment area) can contribute between 16 and 22 % to the total catchment soil GHG emissions. Although these estimates are rough (i.e., we assumed that riparian soils emit the same rate of GHG that our study site), our results clearly pinpoint that riparian soils can be potential hotspots of GHG emissions within Mediterranean catchments. These findings contrast with the common knowledge that water-limited soils are powerless GHG sources to the atmosphere (Bernal et al., 2007; Vidon et al., 2016) and stress the importance of simultaneously consider several GHG emissions (i.e., $CO_2$, $N_2O$, $CH_4$) to get a whole picture of the role of riparian soils in climate change.

## 5 Conclusions

Mediterranean riparian zones are dynamic systems that undergo spatial and temporal shifts in biogeochemical processes due to changes in both soil water content and substrate availability. In a first attempt to simultaneously quantify $CO_2$ and $N_2O$ emissions from Mediterranean riparian soils, we show that most of GHG emissions occur in the form of $CO_2$, even in the wet soils located near the stream. In addition, our results clearly illustrate a strong linkage between riparian hydrology and the microbial processes that produce GHG. Deep groundwater tables fueled large respiration rates in the relatively dry soils near the hillslope, while denitrification mostly occurred in the wet zones located near the stream channel. As occurred at spatial scale, riparian soil water content was a primarily control of the temporal patterns of $CO_2$ and $N_2O$ emissions. Soil dryness diminished respiration rates during summer, while a fast soil N cycling promoted high $N_2O$ emissions after a rewetting event in spring. Overall, our study shows that future variations in catchment hydrology due to climate change can potentially affect the riparian functionality in Mediterranean zones, as well as their contribution to regional and global C and N cycles.

*Data availability.* The data sets used in this paper can be obtained from the authors upon request.

**The Supplement related to this article is available online at https://doi.org/10.5194/bg-14-4195-2017-supplement.**

*Author contributions.* SP, SS, and FS designed the experiments. SP and AL carried them out. SP performed all laboratory analysis. AL and SP analyzed the data set and prepared the manuscript, with contributions from SS and FS.

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

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