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**Simulating climate change and land use effects on soil nitrous
oxide emissions in Mediterranean conditions using the Daycent
model**

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1 **Abstract**

2 In Mediterranean agroecosystems, limited information exists about possible impacts of
3 climate change on soil N₂O emissions under different land uses. This paper presents a
4 modelling study with a dual objective. Firstly, the biogeochemical model Daycent was
5 evaluated to predict soil N₂O emissions in different land uses in a typical Mediterranean
6 agroecosystem. Secondly, the study aimed to determine the impact of climate change on
7 soil N₂O emissions in different Mediterranean land uses over a 85-year period. Soil N₂O
8 emissions were measured in three land uses (cropland, abandoned land and afforested
9 land) during 18 months (December 2011 to June 2013) in a characteristic Mediterranean
10 site in Spain. For climate change simulations, Daycent was run with and without
11 atmospheric CO₂ enrichment using climate data from the CGCM2-A2 model. The
12 cumulative N₂O emissions predicted by the Daycent model agreed well with the
13 observed values. The lack of fit (LOFIT) and the relative error (E) statistics determined
14 that the model error was not greater than the error in the measurements and that the bias
15 in the simulation values was lower than the 95% confidence interval of the
16 measurements. For the different land uses and climate scenarios, annual cumulative
17 N₂O emissions ranged from 126 to 642 g N₂O-N ha⁻¹ yr⁻¹. Over the 85-year period
18 simulated, climate change decreased soil N₂O emissions in all three land uses. At the
19 same time, under climate change, water filled pore space (WFPS) values decreased
20 between 4% and 15% depending on the land use and climate change scenario
21 considered. This study demonstrated the ability of the Daycent model to simulate soil
22 N₂O emissions in different land uses. According to model predictions, in Mediterranean
23 conditions, climate change would lead to reduction in N₂O emissions in a range of land
24 uses.

25

1 Keywords: Daycent model, Soil greenhouse gas emissions; Land use; Mediterranean
2 agroecosystems

3

4 **1. Introduction**

5 In southern European drylands, agricultural landscapes are a mosaic of different land
6 uses, mainly croplands, abandoned fields and afforested areas. The presence of different
7 land uses responds to different causes such as limited plot access and workability,
8 agricultural policies and subsidies. The co-existence of croplands and other land uses
9 within the same area is recognized as an optimal strategy to enhance resources for
10 agriculture and resilience during environmental change (Rey Benayas and Bullock,
11 2012). In this context, the new Common Agricultural Policy (CAP) reform encourages
12 European farmers to maintain natural areas (the so-called “ecological focus areas”)
13 within their farms through the Greening payment scheme (European Commission,
14 2013). Under the new CAP, fallow land, afforested areas and field margins, are some of
15 the land uses that shall be maintained in at least 5% of the total arable land in order to
16 receive part of the total subsidy. Consequently, the reform could promote changes in the
17 distribution of land dedicated to different uses in European agroecosystems.

18 Agricultural soils are the main contributor to global atmospheric nitrous oxide (N₂O)
19 levels (Smith et al., 2007). Nitrous oxide is not only a powerful greenhouse gas but also
20 an important stratospheric ozone-depleting substance (Ravishankara et al., 2009). Over
21 the last 150 years, N₂O emissions from soils have increased from 11 to 18 Tg N yr⁻¹
22 (Kroeze et al., 1999). Land use change has a significant impact on soil N₂O emissions
23 (Mosier et al., 1997; Merino et al., 2004; Galbally et al., 2008). Variations in
24 environmental and soil factors after a change from cropland to either forest or grassland
25 can also have important impacts on soil N₂O emissions (Corre et al., 1996; Stehfest and

1 Bouwman, 2006). Thus, the adoption of certain on-farm decisions affecting the
2 distribution of land uses throughout agricultural landscapes can have a noteworthy
3 impact on the global atmospheric N₂O balance. At the same time, changes in climate
4 can also impact the processes and factors controlling soil N₂O production and emission
5 (Brevik, 2012). Thus, for instance, not only changes in soil water content and soil
6 temperature but also changes in soil mineral nitrogen (N) and carbon (C) availability
7 due to different climate conditions can have significant effects on N₂O emissions
8 (Weier et al., 1993; Brevik, 2012; Luo et al., 2013). In this sense, biogeochemical
9 models are interesting tools to evaluate the future impacts of climate on C and N
10 dynamics and, in turn, on N₂O emissions. The link of climate outputs from atmosphere-
11 ocean general circulation models (AOGCM) and biogeochemical models have been
12 successfully used to predict climate change impacts on soil N₂O emissions (Kesik et al.,
13 2006; Abdalla et al., 2010).

14 Mediterranean areas surround the homonymous sea and extend between latitudes 40 and
15 30° N over an area of some 4,300,000 km² (LeHouerou, 1992). In these areas, future
16 climate scenarios predict an increase in warming and a decrease in precipitation
17 (Gibelin and Dequé, 2003). These changes can have a significant impact on the
18 processes controlling soil N₂O emissions in these areas, characterized by low annual
19 precipitation and high evapotranspiration rates limiting net primary production. Up to
20 date, the information about soil N₂O emissions in semiarid areas is limited (Galbally et
21 al., 2008). At the same time, limited information exists about possible impacts of
22 warming and CO₂ enrichment on soil N₂O emissions in Mediterranean agroecosystems.
23 Accordingly, this paper presents a modelling study with a dual objective. Firstly, the
24 biogeochemical model Daycent was evaluated to predict soil N₂O emissions in different
25 land uses in a typical Mediterranean agroecosystem. Secondly, the study aimed to

1 determine the impact of climate change and atmospheric CO₂ enrichment on soil N₂O
2 emissions in different Mediterranean land uses. To accomplish both objectives soil N₂O
3 emissions measurements were carried out in three land uses (cropland, abandoned land
4 and afforested land) during 18 months in a typical Mediterranean site. Experimental
5 data was used to evaluate the Daycent model, which was next used to simulate soil N₂O
6 emissions under climate change conditions.

7

8 **2. Methods**

9 *2.1. Experimental data*

10 An experiment to evaluate the performance of the Daycent model in Mediterranean
11 conditions was set up in Senés de Alcubierre, NE Spain (41° 54' 12'' N; 0° 30' 15'' W;
12 395 masl). The climate is continental Mediterranean with a mean annual precipitation
13 and mean air temperature of 334 mm and 13.4 °C, respectively. The most frequent soil
14 type in the study area is *Typic Calcixerept* (Soil Survey Staff, 1994), whose main
15 characteristics are presented in Table 1. The study area was selected as a representative
16 Mediterranean dryland area with low annual precipitation (<350 mm) and high PET
17 (1207 mm), showing the typical north-central Spain rainfall distribution with most
18 precipitation occurring in spring and autumn (Austin et al., 1998) (Fig. 1). The
19 agricultural landscape of the selected area represents the typical dryland Mediterranean
20 agroecosystem with a mosaic of barley and wheat fields, almond and vineyard orchards,
21 abandoned fields and pine plantations.

22 For model evaluation purposes, three adjacent fields were chosen with different land
23 uses: cropland (CR), afforested land (FR) and abandoned land (AB). The CR field, with
24 2.3 ha, consisted of a barley (*Hordeum vulgare L.*) monoculture system under no-tillage
25 for the last six years. Previously, the barley field had been tilled with a chisel plough

1 every September during the last 30 years. Over this period, applications of mineral
2 fertilizers were performed regularly at planting (September) and tillering (February)
3 stages of the crop providing 30 to 40 kg N ha⁻¹ per crop. During the two growing
4 seasons in which soil N₂O measurement were performed (i.e., 2011-2012 and 2012-
5 2013) the field was only fertilized during the first growing season at planting
6 (September 2011) with 40 kg N ha⁻¹ in the form of ammonium sulphate (21% N). The
7 FR plantation, with a total surface of 0.9 ha and a tree density of 625 trees ha⁻¹, was
8 established 50 years ago as part of an Aleppo pine (*Pinus halepensis L.*) afforestation
9 plan in the area. In the pine plantation, which remained unmanaged since its
10 establishment, the only exploitation has been the harvest of the pinecones once per year.
11 Pine needles have accumulated on the forest floor to form a 7-8 cm thick layer. The AB
12 field, with a total surface of 0.7 ha, was cultivated until 2003. From that year, no
13 operations were performed and spontaneous vegetation growths with the predominance
14 of the following grass species: Poaceae (*Bromus sp L.*; *Hordeum murinum L.*);
15 Brassicaceae (*Lepidium draba L.*; *Sinapsis arvensis L.*); Fabaceae (*Medicago orbicularis*
16 *L.*; *Vicia sativa L.*); Asteraceae (*Silybum marianum L.*, *Anacyclus clavatus L.*);
17 Papaveraceae (*Papaver rhoeas L.*); Malvaceae (*Malva silvestris L.*); and Tamaricaceae
18 (*Tamarix gallica L.*).

19 In November 2011, a representative area of 400 m² was delimited in each land use and
20 six (FR and CR) and five (AB) subsampling points were randomly selected. In each of
21 these points, one polyvinyl chloride ring (31.5 cm internal diameter) was inserted into
22 the soil to a depth of 5 cm. The rings were left in the soil for the entire study except in
23 the CR land use in which they were removed during planting and reinserted in the same
24 place afterwards. Vented chambers of the same material and 20-cm height were fitted
25 into the rings when the measurements were performed. The chambers were covered

1 with a reflective insulation layer to avoid internal increases of temperature during their
2 deployment. Soil N₂O emissions were measured every two to three weeks throughout
3 the entire study period (December 2011-June 2013). Gas samples of 17 mL were
4 obtained with polypropylene syringes at 0, 30 and 60 minutes after closing the chamber.
5 Measurements were carried out at the same time on each sampling date to avoid diurnal
6 variation. Each sample was immediately injected into 12 mL Exetainer® borosilicate
7 vials (model 038W, Labco, High Wycombe, UK). Gas samples were analysed with an
8 Agilent 7890A gas chromatography system equipped with an electron-capture (ECD)
9 detector. Emission rates were calculated taking into account the linear increase in gas
10 concentration in the chamber over time and correcting for air temperature. At every
11 sampling date, and near each gas sampling chamber (less than 1 m apart), soil
12 temperature at 5 cm depth was measured with a soil temperature probe and a soil
13 sample from the 0-5 cm soil depth was collected for soil water content determination by
14 oven drying the soil samples at 105 °C until constant weight and soil nitrate (NO₃⁻) by
15 extraction with KCl. The water filled pore space (WFPS) was calculated as the quotient
16 between soil volumetric water content (VWC) and total porosity. Soil porosity was
17 estimated as a function of soil bulk density assuming a soil particle density of 2.65 Mg
18 m⁻³ (e.g. Plaza-Bonilla et al. 2014). Soil bulk density was determined by with the
19 cylinder method (Grossman and Reinsch, 2002).

20

21 *2.2. Daycent model description and evaluation*

22 The Daycent model (Parton et al., 1998; Del Grosso et al., 2011) is the daily version of
23 the biogeochemical model Century (Parton et al., 1987) created to simulate C, N,
24 sulphur (S) and phosphorous (P) dynamics at a monthly step in different ecosystems.
25 Daycent includes several submodels that simulate plant production, soil organic carbon

1 (SOC) decomposition, methane (CH₄) oxidation, nitrification, denitrification and soil
2 temperature and water content from a multi-layered soil system (Parton et al., 1998).
3 Primary model inputs are: daily maximum and minimum air temperature, daily
4 precipitation, management data (e.g. fertilization, tillage, harvest), and soil texture by
5 horizon (Del Grosso et al., 2011).

6 The N gas submodel simulates N₂O, NO_x from nitrification and denitrification, and N₂
7 from denitrification. In the model, different soil parameters control N fluxes from
8 nitrification (i.e., water content, NH₄⁺, temperature and texture) and from denitrification
9 (i.e., NO₃⁻, water content and labile C) (Parton et al., 2001). Furthermore, in Daycent
10 denitrification increases exponentially between 50-60% and 70-80% WFPS and
11 heterotrophic respiration is used as a proxy for labile C availability (del Grosso et al.,
12 2011). A more detailed description of the Daycent model can be found in Del Grosso et
13 al. (2011) and Parton et al. (2001).

14 The SOC submodel is composed of different pools with different turnover rates. Four of
15 these C pools represent surface and soil litter (metabolic and structural) and the other
16 three pools (i.e., active, low and passive) represent SOC. The initialization of C pools of
17 the model was done similarly to previous studies performed with the Century model
18 under similar conditions (Álvaro-Fuentes et al., 2009; 2012). Briefly, the model was run
19 for 5000 years under a grazed grass system to initialize the most recalcitrant pool. For
20 the last 200 years previous to the establishment of the experiment, past agricultural
21 management in the area was obtained from the literature and directly from farmers
22 (Álvaro-Fuentes et al., 2011). Historically, management in the study area consisted of
23 cereal-fallow rotation, with use of intensive tillage and removal of most of the straw
24 produced. For the last 30 years, tillage intensity was reduced (i.e., substitution of
25 mouldboard ploughs by cultivators) and mineral fertilizers were applied. Table 2

1 presents the observed and simulated total SOC values at the beginning of the
 2 experiment once the initialization process was completed (December 2011).
 3 Measured soil parameters at the beginning of the experiment (Table 1), climate data
 4 obtained from a weather station located 2-km apart (Fig. 2) and specific land use and
 5 management data for the three experimental fields were used to run the model. Crop and
 6 tree growth was parameterized differently for each land use. Barley crop and pine tree
 7 were modelled with similar crop.100 and tree.100 parameterization files used in
 8 previous studies under similar conditions (Álvaro-Fuentes et al., 2009; 2012). However,
 9 the grass growth in the AB field was modelled considering a default Daycent grass
 10 parameterization (i.e., GI4) consisting of a mix of grasses (25% warm and 75% cool).
 11 Model evaluation was performed comparing simulated values with the daily observed
 12 data obtained in the land use experiment. Two statistical tests were chosen to evaluate
 13 the performance of the model in simulating N₂O emissions. The first one was the lack
 14 of fit (LOFIT), which has been proposed as a suitable test to determine degree of
 15 coincidence when replicated values are available (Smith et al., 1997).
 16 The LOFIT was calculated, together with its associated *F* value in order to compare the
 17 variances of the model predictions with the error in the measurements, as follows:

$$\text{LOFIT} = \sum_{i=1}^n m_i (O_i - P_i)^2$$

$$F = \frac{\sum_{i=1}^n (m_i - 1) \times \text{LOFIT}}{n \sum_{i=1}^n \sum_{j=1}^{m_i} \left((O_{ij} - P_i) - (O_i - P_i) \right)^2}$$

20

1 where m_i is the number of replicates in each land use, O_i is the mean of the observed
2 values in the i th sampling date, P_i is the simulated value in the i th sampling date, and n
3 is the number of sampling dates.

4 The relative error (E) was also calculated to evaluate the bias in the difference between
5 simulated and measured N₂O values:

6

$$E = \frac{100 \sum_{i=1}^n (O_i - P_i)}{n \bar{O}}$$

7

8 where \bar{O} is the average of all the observed values.

9 The E statistics was evaluated against the E value assuming a deviation of the 95%
10 confidence interval of the measurements (Smith and Smith, 2007).

11

$$E_{95\%} = \frac{100 \sum_{i=1}^n (SE_i - t_{m,95})}{n \bar{O}}$$

12

13 where SE_i is the standard error of the observed values in the i th sampling date and $t_{m,95}$
14 is the Student's value for $n - 2$ and 95% probability (P value of 95%).

15 Calculations were made using the MODEVAL program (Smith et al., 1996). Likewise,
16 regression analyses between observed and simulated soil surface temperature (5 cm
17 depth) and VWC (0-5 cm depth) were also performed.

18

19 *2.3. Simulation under climate change conditions*

20 The Daycent model was used to simulate the impact of climate change on soil N₂O
21 emissions under different land uses in Mediterranean conditions. The parameterization
22 obtained for each land use was used to run the model for the 2015-2100 period, under

1 three different future scenarios: (i) a baseline scenario with current mean weather
2 conditions (baseline); (ii) a climate change scenario with weather data from the climate
3 model CGCM2 forced by the A2 IPCC emission scenario previously used in Álvaro-
4 Fuentes et al. (2012) (CC); and (iii) a climate change plus atmospheric CO₂ increase
5 scenario (CC+CO₂). This last scenario was built with the weather outputs from the same
6 CGCM2-A2 climate model and considering an atmospheric CO₂ concentration of 856
7 ppmv by the year 2100 (Nakicenovic et al., 2000). We assumed a linear CO₂ con-
8 centration increase over time. For the study area, the CGCM2-A2 model predicted a
9 reduction in annual precipitation (from 345 mm yr⁻¹ to 310 mm yr⁻¹ in the baseline and
10 climate change scenarios, respectively) and an increase in maximum and minimum air
11 temperature (from 21.0 and 7.0 °C to 21.5 and 9.6 °C, in the baseline and climate
12 change scenarios, respectively). Also, the climate model predicted a change in the
13 monthly distribution of precipitation in which the autumn and spring rainfall peaks
14 characteristics of some Mediterranean-climate areas would disappear and a steady
15 monthly precipitation distribution would occur (Fig. 3). The climate change data were
16 produced by the Meteorological State Agency (Spanish Ministry for Environment and
17 Rural and Marine Affairs) using a regionalization technique explained in Brunet et al.
18 (2008) to better adjust the climate change scenario to the conditions of the study area.
19 For the 2015-2100 period, the same three land uses were simulated under the three
20 climate scenarios. The FR and AB land uses were modelled with the same
21 parameterization and events as for the files used during the 2011-2013 model evaluation
22 period. In the CR land use, however, the agricultural management simulated consisted
23 of a barley no-tillage, medium-fertilized barley system, with annual mineral fertilizer
24 rates of 60 kg N ha⁻¹ split between sowing (50%) and top dressing (50%). This could be

1 considered a typical cropping system in southern European dryland agroecosystems in
2 which NT adoption is successfully spreading (Soane et al., 2012).

3

4 **3. Results**

5 *3.1. Weather conditions*

6 Monthly air temperature and precipitation over the study period is presented in Fig. 2.
7 From December 2011 to June 2012 (first growing season) the precipitation registered
8 was 172 mm. However, in the second growing season sampled (from December 2012 to
9 June 2013) the precipitation raised to 270 mm (Fig. 2). Comparing these two values
10 with the average seasonal precipitation for the site (204 mm; Fig. 1), the 2011-2012 and
11 2012-2013 growing seasons could be considered drier and wetter than the average,
12 respectively. Air temperatures during the experimental period followed the same pattern
13 as the average values with hot summers and cold winters typical of the Mediterranean
14 region (Figs. 1 and 2).

15

16 *3.2. Daycent model performance*

17 Soil N₂O emissions were measured in three land uses from December 2011 till June
18 2013. Figure 4 shows the comparison between observed and simulated daily N₂O
19 emissions for the three land uses. In the CR land use, the Daycent model tended to
20 underestimate N₂O emissions in four out of ten sampling dates during the 2011-2012
21 growing season (December 2011 – June 2012). However, in the three sampling dates of
22 April and May 2013 the model overestimated N₂O emissions (Fig. 4). In late August,
23 the model predicted a sharp increase in the emissions, which lasted one day (achieving
24 37 g N₂O-N ha⁻¹ day⁻¹). During the summer fallow season (July – October 2012), net
25 N₂O uptake was observed in four out of five sampling dates, while for the same dates,

1 the Daycent model estimated a net N₂O emission (Fig. 4). In the AB land use, during
2 November and December of 2012, the model was able to predict the observed increase
3 in N₂O emissions, but for a shorter period of increased N₂O emissions than the observed
4 values (Fig. 4). From December 2012, the Daycent model predicted quite well the
5 steady and near zero observed N₂O emissions. In the FR land use, the model tended to
6 underestimate N₂O emissions during three out of the five sampling dates performed
7 during the first four months (December 2011 – March 2012), when observed values
8 showed the greatest deviation, but came close to the observed values throughout the
9 remaining study period. The model predicted two sharp increases in June and
10 September 2012. Similar to the observed in the CR field, these increases lasted for one
11 day (Fig. 4).

12 The LOFIT and E tests were used to statistically analyse the performance of the model.
13 In the three land uses, the *F* values associated to the LOFIT statistic were lower than the
14 *F* critical 5% (Table 3). Consequently, the model error is not greater than the error in
15 the measurements. In the three land uses, the calculated E statistic was lower than the
16 95% confidence interval of E (E_{95}) denoting that the bias in the simulation values was
17 lower than the 95% confidence interval of the measurements (Table 3).

18 Observed and simulated cumulative N₂O emissions throughout the entire study are
19 shown in Fig. 5. The cumulative N₂O emissions predicted by the Daycent model agreed
20 well with the observed values. Simulated cumulative N₂O emissions were 868, 569 and
21 501 g N₂O-N ha⁻¹ while observed values were 787, 618 and 442 g N₂O-N ha⁻¹ for CR,
22 AB and FR, respectively (Fig. 5). Consequently, in the three land uses, the difference
23 between the observed and the simulated cumulative N₂O value ranged between 8% and
24 13%.

1 In general, the linear regressions between observed and simulated soil temperature and
2 VWC values showed good agreement in the three land uses (Table 4). The only
3 exception was the VWC for the AB and FR land uses where the slope somewhat
4 differed from 1 (Table 4). However, the model was not able to simulate well the soil
5 nitrate levels in the first 5 cm soil depth (Table 4).

6

7 *3.3. Simulated N₂O emissions under climate change*

8 Over the 85-year period simulated, climate change decreased soil N₂O emissions in all
9 three land uses. For the different land uses and climate scenarios, annual cumulative
10 N₂O emissions ranged from 126 to 642 g N₂O-N ha⁻¹ yr⁻¹ (Table 5). The reduction was
11 different depending on the land use considered. In the CR land use, N₂O reductions in
12 the CC+CO₂ and CC scenarios were about 11% and 17%, respectively, compared with
13 the baseline scenario (Table 5). In the AB land use, the reduction in the N₂O emitted
14 was about 4% and 20% for the CC and CC+CO₂ scenarios, respectively, and, finally, in
15 the FR land use about 3% and 10%, respectively (Table 5).

16 For the 2015-2100 period, the Daycent model predicted higher cumulative N₂O
17 emissions in the climate change scenarios (CC and CC+CO₂) than in the baseline
18 scenario until the 2050-2060 decade (Fig. 6). However, after 2060, cumulative
19 emissions in the baseline scenario tended to be slightly higher than in the other two CC
20 scenarios until 2100.

21 All three land uses showed higher soil temperature to 20 cm depth (between 0.9 and 1.8
22 °C) under climate change conditions. However, WFPS decreased in all three scenarios
23 under climate change. The decrease in WFPS varied between 4% and 15% depending
24 on the land use and climate change scenario considered (Table 5). In the case of the CR
25 land use, the yearly evolution of the WFPS through the 2015-2100 period showed a

1 sharply decrease after 2040 in both climate change scenarios while the values in the
2 baseline scenario kept steady (Fig. 7).

3

4

5 **4. Discussion**

6 *4.1. Evaluation of the Daycent model*

7 The two statistics used demonstrated the ability of the Daycent model to simulate soil
8 N₂O emissions in different land uses of the Mediterranean region. The Daycent model
9 has been used to model soil N₂O emissions in different agroecosystems worldwide (e.g.,
10 Del Grosso et al., 2008; Fitton et al., 2014) but little work has been done previously in
11 Mediterranean conditions. Recently, Lee et al. (2015) simulated the effects of
12 switchgrass management on soil greenhouse gas emissions using the Daycent model in
13 the Mediterranean climate conditions of California. In our representative conditions of
14 the Mediterranean basin and for the three land uses, both the LOFIT and the E statistics
15 indicated good performance of the model despite some exceptions occurred.

16 The N₂O emissions measured in our study were relatively low compared with the values
17 observed in other agroecosystems located in more humid areas (Rees et al., 2013). In a
18 meta-analysis published in this same issue, Cayuela et al. (201X) have analysed N₂O
19 emissions from Mediterranean cropping systems. The observed values measured in the
20 CR land use were even lower than the mean cumulative N₂O emission of 0.7 kg N₂O-N
21 ha⁻¹ estimated in the meta-analysis for rainfed systems (Cayuela et al., 201X). Although
22 there are several factors that regulate the processes involved in the production of this
23 gas, soil water content has been identified as a key factor (Linn and Doran, 1984;
24 Butterbach-Bahl et al., 2013). The low N₂O fluxes observed are consistent with the low
25 WFPS values measured, and less than critical values often cited for invoking

1 denitrification (Barton et al., 1999, Sanz-Cobena et al., in press). Although nitrification
2 and denitrification are two major processes contributing to N₂O formation in soils
3 (Venterea et al., 2012), the limited soil water content observed in our study suggests that
4 N₂O emissions would be mostly originated from nitrification as indicated by Plaza-
5 Bonilla et al. (2014) working in similar conditions. Other processes could be also
6 contributing to N₂O emissions. Processes such as nitrifier denitrification could have a
7 significant effect in the production of soil N₂O under limited soil water availability
8 (Kool et al., 2011; van Groenigen et al., 2015). However, the Daycent model simulates
9 N₂O emissions derived only from nitrification and denitrification. Consequently, the
10 model does not simulate soil N₂O emissions derived from other processes (e.g., nitrifier
11 denitrification), which could result in the underestimation of N₂O emissions under low
12 soil water conditions. This last could contribute to explain the behaviour of the model in
13 certain sampling dates during the first growing season in which a slight tendency to
14 underestimate N₂O emissions was observed. Furthermore, in the three land uses,
15 negative N₂O fluxes were measured, especially during the fallow period (i.e., July-
16 October 2012) in the CR field. Despite the processes involved are not entirely
17 understood, N₂O sink records have been obtained under drought conditions in croplands
18 (Mejjide et al., 2009; Plaza-Bonilla et al., 2014) and forests (Goldberg and Gebauer,
19 2009). In our study, although the 85% of negative values were not statistically different
20 from zero, these negative emissions could contribute to reduce the adjustment between
21 observed and simulated values since the Daycent model does not simulate N₂O uptake.

22

23 *4.2. Climate change simulations*

24 In Mediterranean agroecosystems, limited information exists about the impacts of
25 climate change on N₂O emissions. Soil N₂O emissions from manipulative experiments

1 have not been previously reported for the Mediterranean basin (Dijkstra et al. 2012). At
2 the same time, to our knowledge, simulation models have not been previously used to
3 predict the impact of climate change on soil N₂O emissions in Mediterranean
4 agroecosystems.

5 The Daycent model predicted a reduction in soil N₂O emissions under climate change
6 conditions in all three land uses.. It is expected that the increase in soil temperature that
7 the model predicted under climate change conditions in our Mediterranean conditions
8 (1.5 °C to 20 cm soil depth) could stimulate microbial activity and thus nitrification and
9 denitrification processes (Smith, 1997). However, in our modelling experiment, the
10 increase in soil temperature did not result in an increase in soil N₂O emissions. As
11 commented previously, recent research suggest that in dryland conditions soil N₂O is
12 produced mainly throughout nitrification (Galbally et al., 2008; Plaza-Bonilla et al.,
13 2014) and the low soil moisture content typical of arid and semiarid areas is a main
14 limiting factor for soil N₂O emissions (Martins et al., 2015). The Daycent model
15 simulates an exponential increase in N₂O production by nitrification with temperature
16 but this increase is limited by soil moisture stress (Parton et al., 2001; Del Grosso et al.,
17 2011). Considering the three climate scenarios, the mean WFPS values predicted by the
18 Daycent model were about 42%, 25% and 22% for the CR, AB and FR land uses,
19 respectively. Particularly, for the AB and FR land uses, mean WFPS values are in the
20 lowest limit at which N₂O from nitrification is produced (Linn and Doran, 1984;
21 Davidson, 1991). For these two land uses, the Daycent model predicted about 20%
22 reduction in the N₂O produced by nitrification under climate change conditions (data
23 not shown). The mean WFPS did not vary substantially between the baseline and the
24 climate change scenarios since the CGCM2-A2 climate model only predicted about
25 10% reduction in annual precipitation under climate change conditions. However, more

1 important than the total reduction in precipitation would be the change in the typical
2 annual precipitation distribution pattern that the climate change model predicts. The
3 predicted increase in precipitation in summer under climate change could not greatly
4 contribute to enhance WFPS since higher summer temperatures would increase soil
5 water loss by evaporation.

6 The temporal evolution of the N₂O emissions during 2015-2100 was opposite to the
7 evolution of the WFPS. This difference in the two trends revealed that as the future
8 simulated period progressed, the more critical dry conditions in the climate change
9 scenarios constrained WFPS and thus N₂O emissions. It is important, however, to
10 remark that during the evaluation of the model, it was detected a slight underestimation
11 of N₂O fluxes in certain dates when WFPS was low. Consequently, the accuracy of the
12 predictions obtained in the climate change scenarios could be conditioned by the
13 performance of the model found under drought conditions.

14 Atmospheric CO₂ enrichment showed a different effect on N₂O emissions depending on
15 the land use analysed. CO₂ enrichment tends to stimulate crop growth and production,
16 particularly in C3 plants such as the barley crop simulated in the present study (Lobell
17 and Gourdjji, 2012). The Daycent model predicted about 40% greater mean barley
18 biomass production in the CC+CO₂ scenario compared with the CC scenario (data not
19 shown). Furthermore, over the 85 years simulated and for CR, the CC+CO₂ scenario
20 stored greater SOC when compared with the CC scenario (0.25 vs. 0.17 Mg C ha⁻¹ yr⁻¹
21 in CC+CO₂ and CC, respectively) but did not result in a marked effect on WFPS. After
22 certain rainfall events, the greater organic C levels in the CC+CO₂ scenario could
23 favour higher denitrification rates compared with the CC scenario as predicted by the
24 Daycent model (Dijkstra et al., 2013). However, in the FR and AB land uses the
25 opposite trend was observed, with lower N₂O emitted in the scenario with atmospheric

1 CO₂ enrichment. In these two land uses, the lack of N fertilization together with the
2 increase in N demand for plant growth due to CO₂ enrichment could limit soil N
3 availability for nitrification (Dijkstra et al., 2012).

4 The results observed in this work about the impacts of climate change on soil N₂O
5 emissions should be taken with caution due to the large sources of uncertainty
6 associated with this type of modelling studies, particularly that derived from input data
7 and model formulation (Hastings et al., 2010; Ogle et al., 2010). Regarding the input
8 data, the climate scenarios themselves can be a possible source of uncertainty (Álvaro-
9 Fuentes and Paustian, 2011). Biases in the precipitation and temperature predictions in
10 climate models can severely impact the N₂O emissions rates obtained due to the
11 significant control of climate over N₂O production and emission. Another limitation of
12 this study is the fixed agricultural management modelled in the CR land use over the 85
13 years. Regarding to this, it is expected that management practices will change over the
14 next decades introducing new plant material and technology (e.g., crop varieties,
15 machinery, fertilization) that may be designed in the future, especially if climate change
16 predictions are achieved (Álvaro-Fuentes et al., 2012). The functioning of the Daycent
17 model also presents some limitations that may contribute to the uncertainty of our
18 results. For example, as commented in the previous section, the Daycent model is not
19 able to simulate N₂O consumption values. Dijkstra et al. (2013) in a manipulative
20 semiarid grassland experiment found that soil moved from a net sink to a net source of
21 N₂O when climate change conditions were imposed. Consequently, in our experimental
22 conditions, climate change conditions could also modify the soil's ability to be a net or
23 sink of N₂O.

24

25

1 **5. Conclusions**

2 We evaluated the Daycent model to simulate soil N₂O emissions under three different
3 land uses (i.e., cropland, afforested land and abandoned land) in semiarid Mediterranean
4 conditions. Despite the differences found between observed and simulated daily N₂O
5 emissions values, the two statistics used (i.e., LOFIT and E) to evaluate model's
6 performance demonstrated the ability of the Daycent model to simulate annual soil N₂O
7 emissions from these land uses.

8 The Daycent model was also used to predict soil N₂O emissions from the same land
9 uses under climate change conditions. For all three land uses, the model predicted a
10 slight negative response of N₂O emissions to climate change. Significantly low soil
11 moisture contents, typical in semiarid Mediterranean areas, could weaken the possible
12 positive effect of warming on soil N₂O emissions. Since soils are the main contributors
13 to global atmospheric N₂O levels, and taking into account the uncertainty associated
14 with simulation studies, the results of the present work may contribute understanding
15 the future role of Mediterranean soils as net sinks or sources of greenhouse gases under
16 a changing climate as a function of land use.

17

18

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Figure captions

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3 Fig. 1. Average precipitation, potential evapotranspiration (PET) and air temperature in
4 the study area.

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6 Fig. 2. Precipitation (bars) and air temperature (continuous line) recorded at a weather
7 station in the vicinity of the field site during the study period (December 2011-June
8 2013).

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10 Fig. 3. Monthly precipitation distribution in the study area under two climate scenarios:
11 baseline and climate change. Values represent mean precipitation for the 85-year period
12 simulated.

13

14 Fig. 4. Simulated and observed daily soil N₂O emissions from December 2011 to June
15 2013 under three different land uses (CR, cropland; AB, abandoned land; and FR,
16 afforested land). Y-axis scale is different among graphs. Error bars represent standard
17 errors of the observed values (n=6 for CR and FR and n=5 for AB).

18

19 Fig. 5. Simulated and observed cumulative soil N₂O emitted under three different land
20 uses (CR, cropland; AB, abandoned land; and FR, afforested land) from December 2011
21 to June 2013. Error bars represent standard deviation of the observed values.

22

23 Fig. 6. Simulated cumulative N₂O emissions during the 2015-2100 period in three
24 different land uses (CR, cropped; AB, abandoned; and FR, afforested) and for three

1 climate scenarios (baseline; CC, climate change; and, CC+CO₂, climate change and
2 atmospheric CO₂ enrichment).

3

4 Fig. 7. Simulated mean yearly water filled pore space (WFPS) during the 2015-2100
5 period for cropland use under three climate scenarios (baseline; CC, climate change;
6 and, CC+CO₂, climate change and atmospheric CO₂ enrichment).

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TABLES

Table 1. Soil characteristics at the beginning of the study for different land uses.

Land use	Soil depth (cm)	pH (H ₂ O, 1:2.5)	EC _{1,5} (dSm ⁻¹)	Organic C (g kg ⁻¹)	Sand (g kg ⁻¹)	Silt (g kg ⁻¹)	Clay (g kg ⁻¹)
Cropland	0-5	8.0	2.1	10.8	37	666	297
	5-10	8.1	1.9	7.7	35	666	299
	10-25	8.0	2.0	7.2	45	655	300
Abandoned land	0-5	7.8	1.2	16.8	131	631	238
	5-10	8.1	0.5	8.8	100	652	248
	10-25	8.0	0.7	7.4	86	677	237
Afforested land	0-5	8.1	2.4	34.6	327	460	213
	5-10	7.9	2.3	12.0	291	482	227
	10-25	8.0	2.3	6.3	298	464	238

Table 2. Observed and simulated soil organic carbon content (SOC) in the 0-20 cm soil depth at the beginning of the experiment for different land uses.

Land use	Observed SOC content (Mg C ha ⁻¹)	Simulated SOC content (Mg C ha ⁻¹)
Cropland	31.95 (1.97) ^a	34.78
Abandoned land	33.27 (2.72)	35.31
Afforested land	45.95 (6.17)	45.25

^a In parenthesis the standard error of the mean

Table 3. Lack of fit (LOFIT) and relative error (E) statistics describing the performance of the Daycent model in simulating soil N₂O emissions for different land uses (CR, cropland; AB, abandoned land; FR, afforested land).

Statistics	Land use		
	Cropland	Abandoned land	Afforested land
LOFIT	1111	315	704
F	0.09	0.03	0.07
F critical ^a	1.44	1.44	1.44
E (%)	15	3	21
E_{95} (%) ^b	281	532	382

^a F value at 5% probability

^b 95% confidence interval of relative error

Table 4. Linear regressions between observed and simulated soil temperature (ST, 5 cm depth), soil volumetric water content (VWC, 0-5 cm depth) and soil nitrate content (SN, 0-5 cm depth) for different land uses.

Soil variable	Land use	Intercept	Slope	r ²
ST	Cropland	0.405	0.948	0.890***
	Abandoned land	0.428	0.997	0.852***
	Afforested land	0.433	0.997	0.832***
VWC	Cropland	0.062	0.897	0.762***
	Abandoned land	0.032	1.494	0.758***
	Afforested land	0.076	1.647	0.754***
SN	Cropland	1.586	1.146	0.051
	Abandoned land	2.980	-0.297	0.032
	Afforested land	2.546	-0.769	0.016

*** Significant at the 0.001 level

Table 5. Simulated mean annual cumulative soil N₂O emissions, water-filled pore space (WFPS, 0-20 cm soil depth) and soil temperature at 20 cm depth for different land uses and climate scenarios (baseline; CC, climate change; CC+CO₂, climate change plus atmospheric CO₂ increase).

Land use	Climate scenario	Cumulative N ₂ O (g N ₂ O-N ha ⁻¹ yr ⁻¹)	WFPS (%)	Soil temperature (°C)
Cropland	Baseline	642	46	13.8
	CC	533	39	15.2
	CC+CO ₂	572	40	14.7
Abandoned land	Baseline	158	27	13.8
	CC	151	24	15.6
	CC+CO ₂	126	25	15.3
Aforested land	Baseline	303	23	13.0
	CC	295	21	14.5
	CC+CO ₂	272	22	14.5

Figure 1
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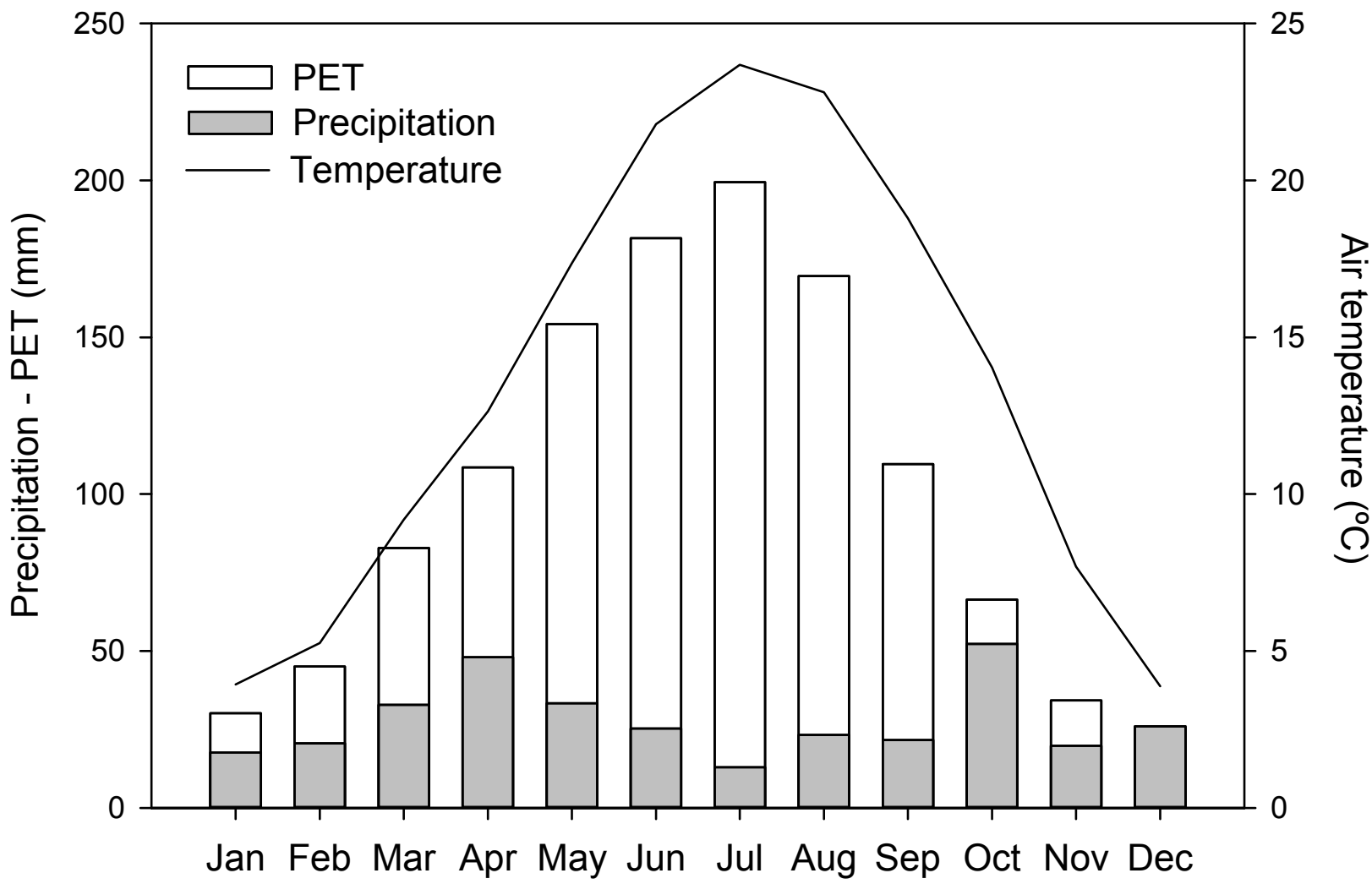


Figure 2
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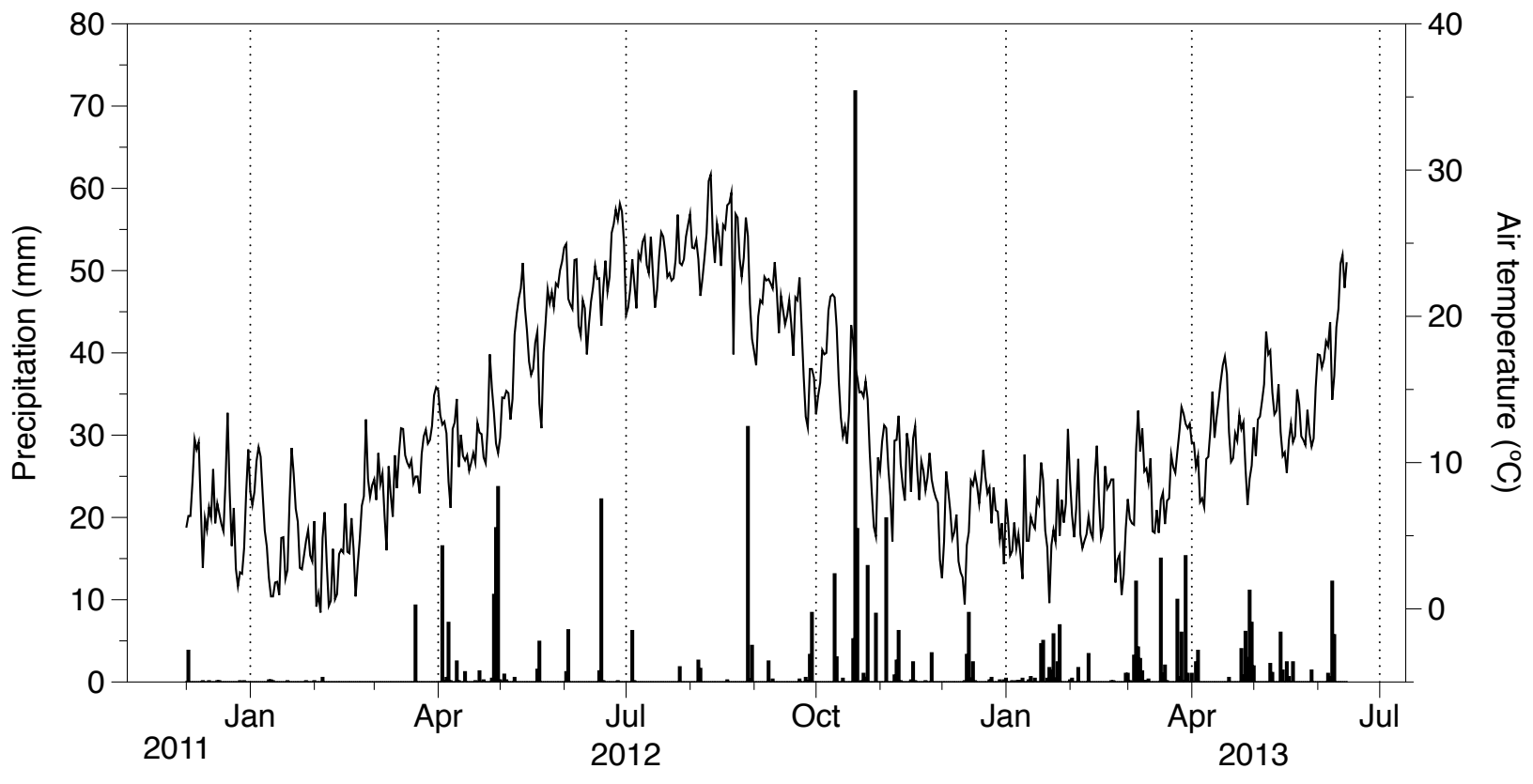


Figure 3
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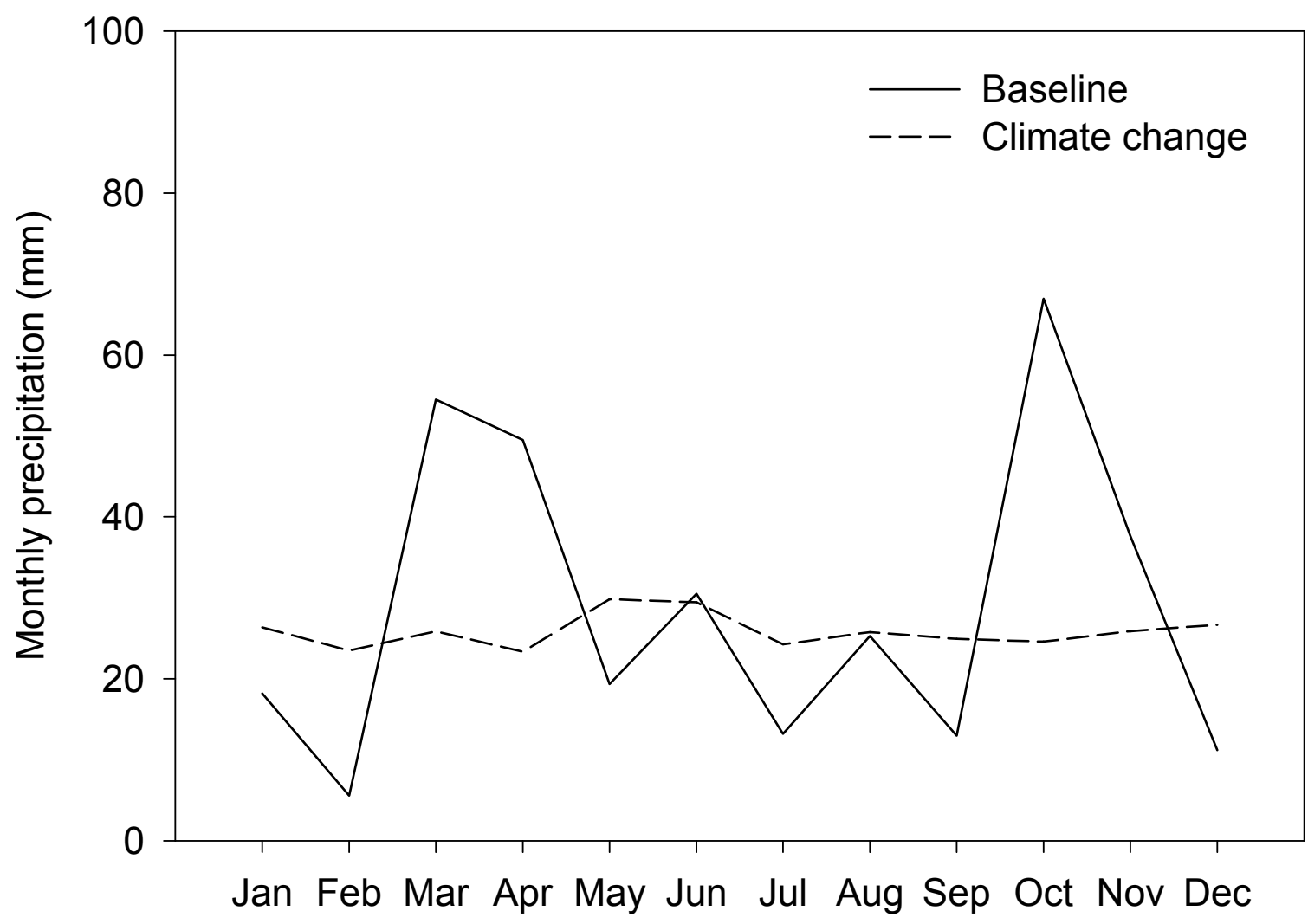


Figure 4

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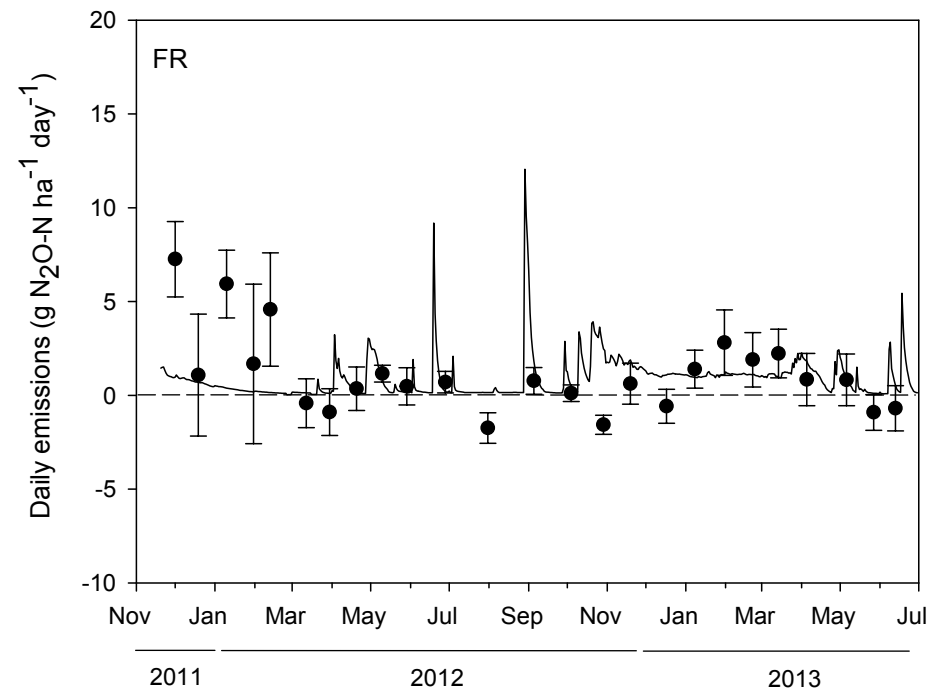
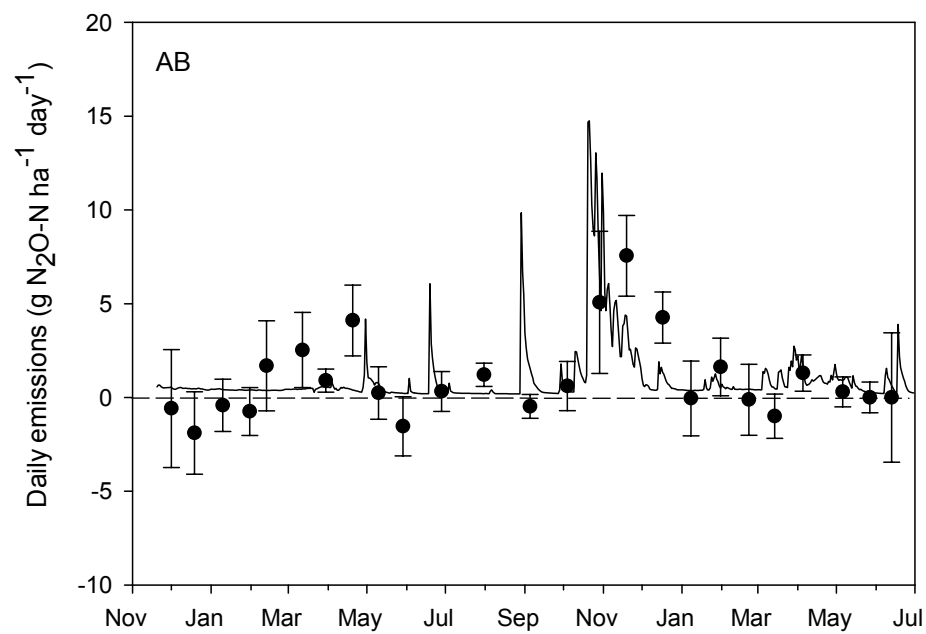
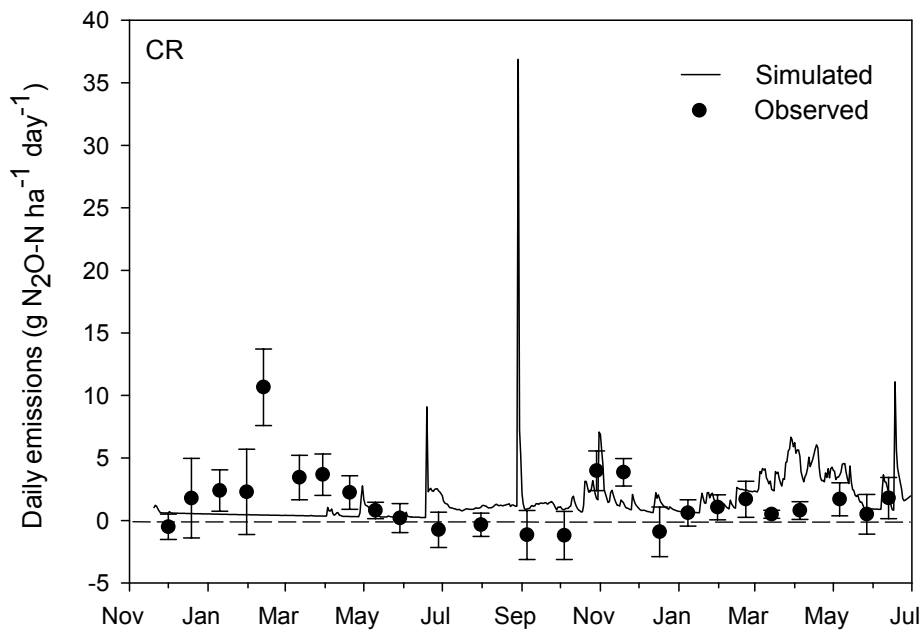


Figure 5
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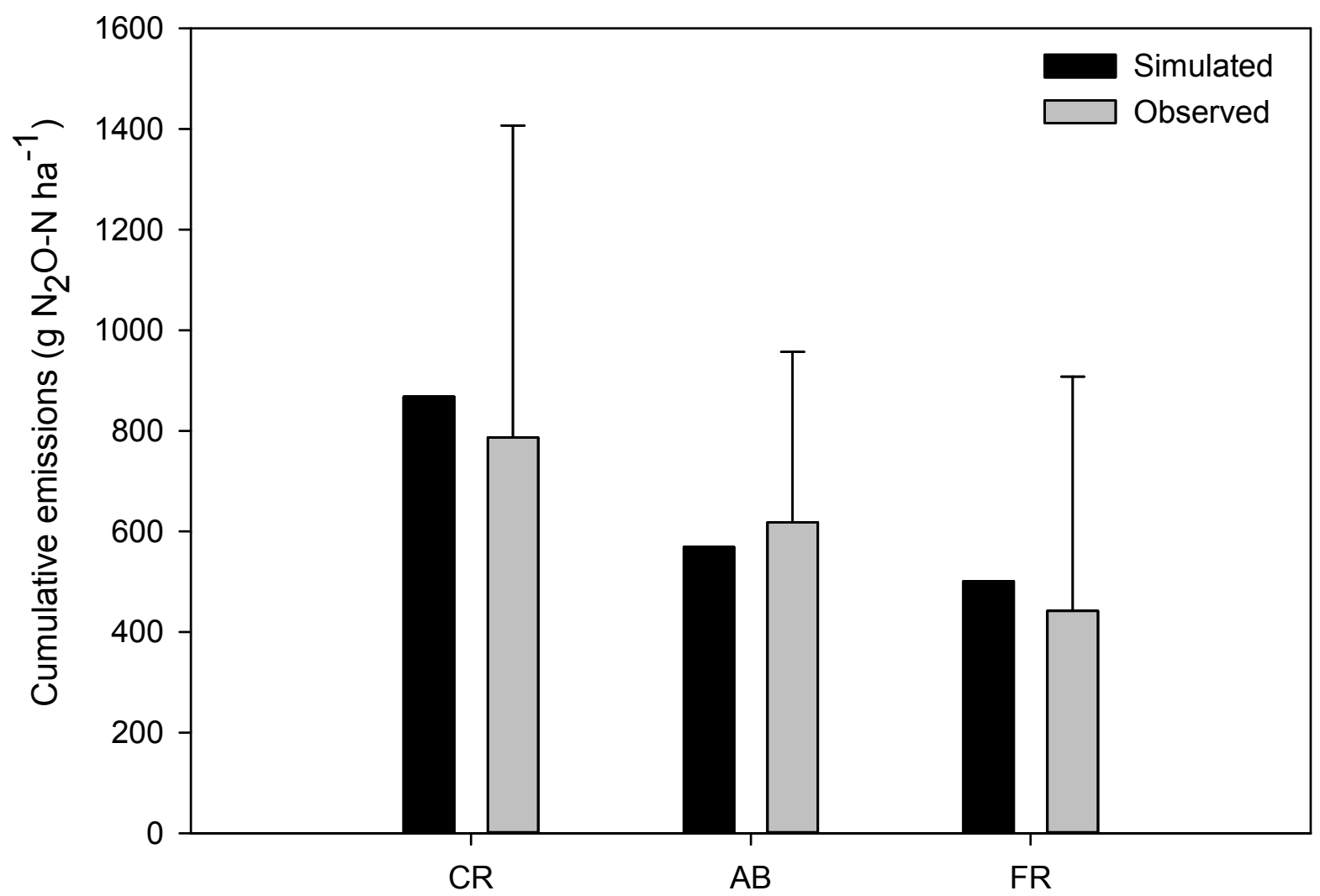


Figure 6

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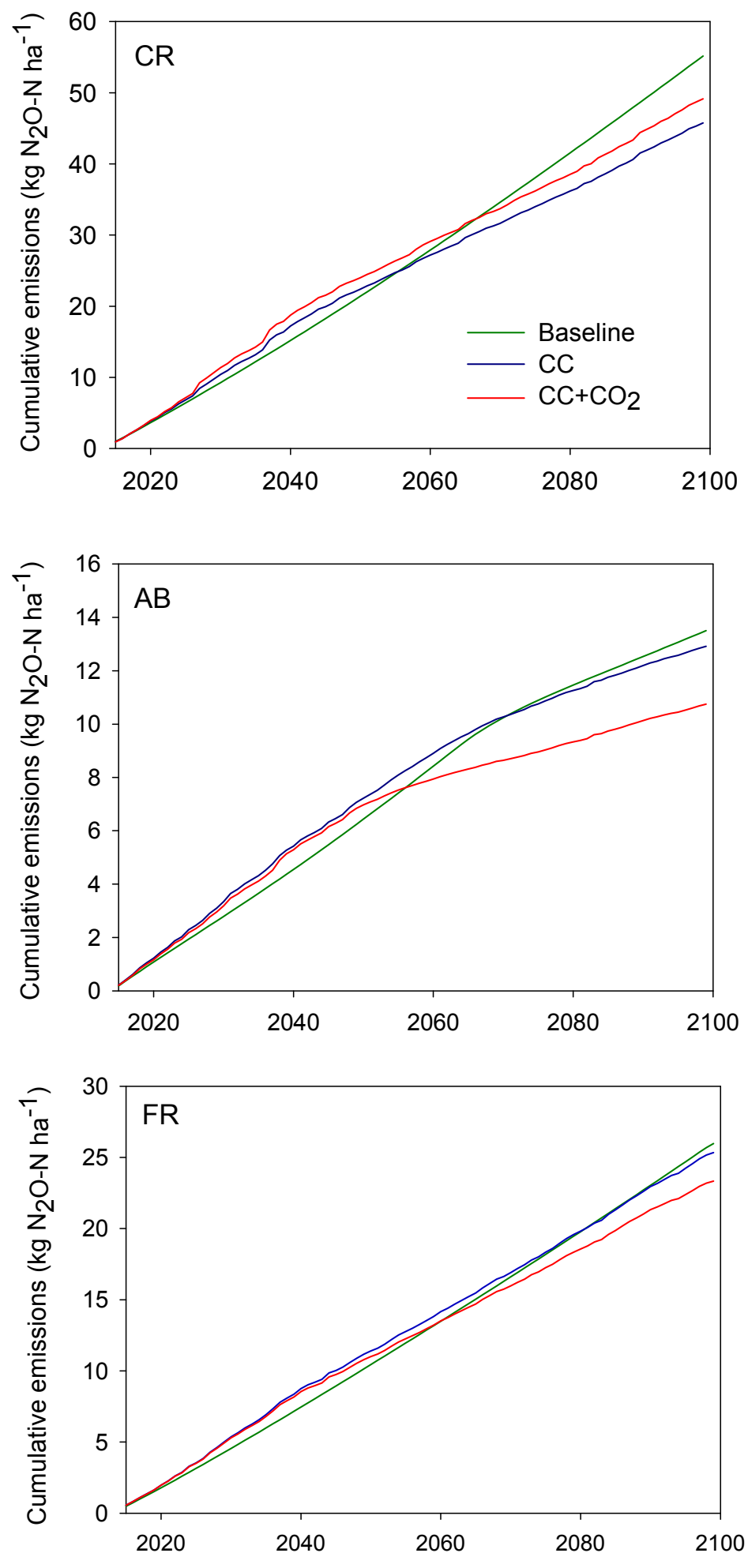


Figure 7
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