

RESEARCH ARTICLE

10.1002/2014JG002791

Key Points:

- Model-data fusion of N cycle elicits climate response in Mediterranean soils
- Moisture drives soil N cycle in upland forests but not in riparian forest
- Positive effects of warming on soil N cycle may be offset by increased drought

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Citation:

Lupon, A., S. Gerber, F. Sabater, and S. Bernal (2015), Climate response of the soil nitrogen cycle in three forest types of a headwater Mediterranean catchment, *J. Geophys. Res. Biogeosci.*, 120, doi:10.1002/2014JG002791.

Received 2 SEP 2014

Accepted 15 MAR 2015

Accepted article online 26 MAR 2015

Climate response of the soil nitrogen cycle in three forest types of a headwater Mediterranean catchment

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Abstract Future changes in climate may affect soil nitrogen (N) transformations, and consequently, plant nutrition and N losses from terrestrial to stream ecosystems. We investigated the response of soil N cycling to changes in soil moisture, soil temperature, and precipitation across three Mediterranean forest types (evergreen oak, beech, and riparian) by fusing a simple process-based model (which included climate modifiers for key soil N processes) with measurements of soil organic N content, mineralization, nitrification, and concentration of ammonium and nitrate. The model describes sources (atmospheric deposition and net N mineralization) and sinks (plant uptake and hydrological losses) of inorganic N from and to the 0–10 cm soil pool as well as net nitrification. For the three forest types, the model successfully recreated the magnitude and temporal pattern of soil N processes and N concentrations (Nash-Sutcliffe coefficient = 0.49–0.96). Changes in soil water availability drove net N mineralization and net nitrification at the oak and beech forests, while temperature and precipitation were the strongest climatic factors for riparian soil N processes. In most cases, net N mineralization and net nitrification showed a different sensitivity to climatic drivers (temperature, soil moisture, and precipitation). Our model suggests that future climate change may have a minimal effect on the soil N cycle of these forests (<10% change in mean annual rates) because positive warming and negative drying effects on the soil N cycle may counterbalance each other.

1. Introduction

Global climate is anticipated to become significantly warmer over the next decades, accompanied with shifts in the water cycle, which in turn can compromise both terrestrial and aquatic nutrient cycles and budgets [Pendall *et al.*, 2008; Luo *et al.*, 2011]. Among other things, climate affects soil nitrogen (N) dynamics through changing soil N mineralization and nitrification rates, influencing plant nutrition and formation of soil organic matter. Furthermore, changes in the terrestrial N cycle could affect N losses from soils to streams and thus influence headwater stream N loads, in-stream N retention, and downstream water quality [Goodale and Aber, 2001; Rogora, 2007; Brookshire *et al.*, 2009].

Soil moisture, temperature, and precipitation pulses are important drivers of key steps of the soil N cycling [Miller *et al.*, 2007; Bell *et al.*, 2008], although each of these climatic variables may impact differently on the various soil processes. Warming can stimulate soil mineralization and increase soil nutrient availability [Rustad *et al.*, 2001; Emmett *et al.*, 2004], while decreased water availability can reduce mineralization and nutrient availability in the soil pool [Niboyet *et al.*, 2011; Manzoni *et al.*, 2012]. The magnitude of this climatic response is likely ecosystem specific. Cold climate ecosystems tend to be more sensitive to changes in temperature than warmer ecosystems [Rustad *et al.*, 2001; Dessureault-Rompré *et al.*, 2010], while arid ecosystems tend to be more sensitive to increases in soil moisture than mesic ecosystems [Borken and Matzner, 2009]. Less clear is the response of soil nutrient cycles to precipitation pulses; yet most of studies suggest that it increases with dryness and substrate availability [Collins *et al.*, 2008; Borken and Matzner, 2009].

Furthermore, changes in water availability and temperature can promote shifts in vegetation and drive tree species ranges toward higher elevations in headwater catchments [Peñuelas and Boada, 2003; Colwell *et al.*, 2008; Chen *et al.*, 2011]. The impact of species substitution on the soil N cycle and catchment N losses is difficult to assess empirically, and it is largely unknown. Soil organic matter, litter quality, and soil microbial population can vary widely among forest types [Lovett *et al.*, 2004; Booth *et al.*, 2005], and thus, changes in vegetation together with forest type specific responses to climate may both contribute to shifts in N

cycling patterns at the landscape level. Therefore, understanding the response of the soil N cycle to changes in climate in different forest types coexisting within catchments is central for evaluating present and future characteristics of N cycling in these ecosystems, but it still remains a major challenge of ecological research.

Most of studies analyzing the climate sensitivity of the soil N cycle are based on manipulation experiments [Rustad *et al.*, 2001; Borken and Matzner, 2009]. However, field observations that consider natural climate variability are complementary tools that add to our understanding of how ecosystems work, especially when combined with process-based models that allow to explicitly link the response of biogeochemical processes to climate variability [e.g., Ise and Moorcroft, 2006; Brookshire *et al.*, 2011]. Another appealing feature of process-based models is that they allow testing the sensitivity of ecosystem processes to specific environmental drivers in isolation and thus provide the opportunity to separate the simultaneous effect of different environmental drivers on biogeochemical processes [Luo *et al.*, 2011].

The aim of this study was to investigate the response of soil N cycling to changes in soil moisture, soil temperature, and precipitation across three forest types (evergreen oak, beech, and riparian) that coexist in Mediterranean catchments by using a simple process-based model. To do so, we analyzed a detailed empirical data set of soil N cycling rates from a headwater catchment in the Montseny Mountains Natural Park (NE, Spain) with a simple ad hoc model that represents the interrelated processes of N mineralization, nitrification, and removal of ammonium and nitrate from the soil pool. We hypothesized that the sensitivity of the soil N cycle to climate variables will differ among the three forest types because these forests differ in ecosystem properties (e.g., species composition and C and N stocks) and microclimatic conditions, which both of them are strong drivers of soil N processes. The evergreen oak and beech forests are Mediterranean and cold-temperate ecosystems, respectively, that grow in steep upland areas with poorly developed soils and fast water drainage toward the stream channel [Peñuelas and Boada, 2003]. In contrast, riparian forests are settled in flatter and lower areas with stable groundwater tables, higher moisture content, and organic N-rich soils [Bernal *et al.*, 2015]. Therefore, we expected that (i) N cycling rates in the oak and beech forests will show strong responses to soil moisture and precipitation compared to the riparian forest because the formers are water-limited ecosystems and (ii) N cycling in the beech forest will be more sensitive to soil temperature than in the oak and riparian forests because beech forests typically grow in colder environments.

Currently, little is known about the combined effect of future changes in temperature and soil water availability on soil N dynamics in seasonally dry forests [Bai *et al.*, 2013; Cameron *et al.*, 2013]. In scenarios of medium to severe climate change, Mediterranean regions will experience a year-round decrease in soil moisture and increase in temperature and decreased precipitation in summer [Intergovernmental Panel on Climate Change (IPCC), 2013]. We hypothesized that any positive effect of temperature on the soil N cycle will be reduced by the simultaneous negative effect of dryness, at least in the oak and beech forests, which commonly exhibit severe dry conditions in Mediterranean regions [Peñuelas and Boada, 2003]. Further, Mediterranean mountains are experiencing a progressive climate-induced beech-by-oak substitution at medium altitudes (800–1400 m) that may result in a complete replacement by the end of this century [Peñuelas and Boada, 2003]. Thus, we additionally considered the hypothesis that this shift in species composition will affect future soil N cycle in these catchments.

2. Materials and Methods

2.1. Study Site and Empirical Data Set

Font del Regàs is a headwater catchment (14.2 km²) located in the Montseny Natural Park, NE Spain (41°50'N, 2°30'E). The climate is subhumid Mediterranean, with an annual precipitation of 925 ± 151 mm (mean ± standard deviation) and a mean annual temperature of 12.1 ± 2.5°C (values for the period of 1940–2000; Catalan Meteorological Service: <http://www.meteo.cat/servmet/index.html>). Total inorganic N deposition is ~15 kg N ha⁻¹ yr⁻¹, with wet and dry deposition fractions being about equally important (45% versus 55%) [Àvila *et al.*, 2009; Àvila and Rodà, 2012].

The catchment is dominated by biotitic granite, and its altitude ranges from 300 to 1200 m above sea level [Institut Cartogràfic de Catalunya, 2010]. Evergreen oak (*Quercus ilex*) and beech (*Fagus sylvatica*) forests cover 54% (500–1000 m above sea level (asl)) and 38% (800–1400 m asl) of the catchment, respectively.

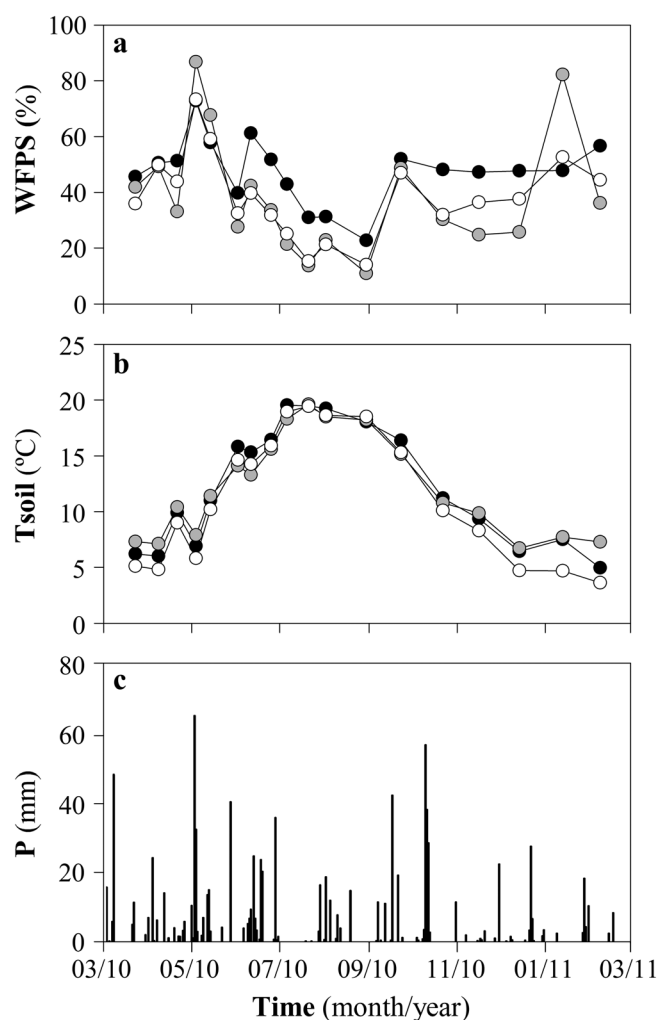


Figure 1. Temporal pattern of (a) soil water-filled pore space (WFPS), (b) soil temperature (T_{soil}), and (c) precipitation (P) during the study period. For both WFPS and T_{soil} , mean values for each incubation period are shown for the riparian (black), oak (grey), and beech (white) forest.

size 1 dm^2) of soil organic nitrogen (SON), ammonium (NH_4^+), and nitrate (NO_3^-) concentrations. Moreover, it incorporated mean rates of net N mineralization (NNM) and net nitrification (NN) measured with in situ soil incubations by using the polyethylene bag technique [Eno, 1960]. At each sampling date, soil was buried into the soil for 12–15 days and then removed from the soil. The polyethylene bags prevented leaching but allowed temperature and gas exchange, and thus, measured NNM and NN were the net result between either gross N mineralization or gross nitrification and microbial N immobilization and denitrification. In addition, the data set included mean rates of potential NO_3^- losses from the soil pool (PNL, in $\mu\text{g N g soil}^{-1} \text{ d}^{-1}$) measured with ion exchange resins, which were buried into the soil close to each polyethylene bag during each incubation period (which started at each sampling date). The NO_3^- content in resin bags was used as a proxy of NO_3^- leaching, infiltration, and uptake expressed as N content per bag weight [Lovett et al., 2004; Berger et al., 2009]. Following Berger et al. [2009], we expressed resin bags data as N content per soil weight by taking into account the bag volume and the soil bulk density. Although this is a rough transformation, it is useful for our purposes because it allows comparing PNL to other soil N processing rates.

The data set further included environmental variables such as mean values of soil moisture (expressed as water-filled pore space (WFPS)) and soil temperature (T_{soil}) for each sampling date and forest type

Hillslope soils (pH~6) are sandy and have a 3 cm deep organic layer followed by 10 cm deep A horizon. Soil bulk density is 1.40 and 1.35 g cm^{-3} at the oak and beech forests, respectively. The riparian zone covers the remaining 6% of the catchment area, and it consists mainly of alder (*Alnus glutinosa*), black locust (*Robinea pseudoacacia*), ash (*Fraxinus excelsior*), sycamore (*Platanus hybrida*), and poplar (*Populus nigra*). Riparian soils (pH~7) are sandy loam and have a 5 cm deep organic layer followed by a 30 cm deep A horizon. Soil bulk density in the riparian forest is 1.09 g cm^{-3} . During base flow conditions, the riparian groundwater table is located 50 ± 10 cm below the soil surface, and thus, it is disconnected from organic soil layers most of the time.

In order to explore the climatic sensitivity of soil microbial N processes, we took advantage of a preexisting empirical data set of soil N processes and concentrations at the upper soil layer (0–10 cm depth) collected every 2–4 weeks during the period of 2010–2011 (18 sampling dates) at three sites (~1 ha each), one for each dominant forest type (evergreen oak, beech, and riparian). For each forest type, the data set included mean values (from 12 averaged plots, sample

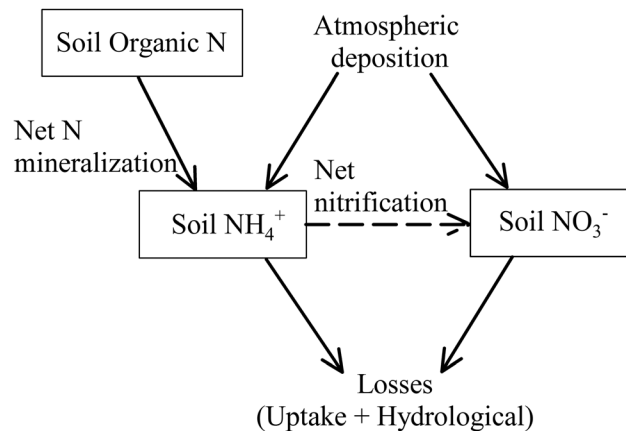


Figure 2. The model presented here concerns soil inorganic nitrogen (N) at the upper soil layer (0–10 cm) and the fluxes into and out of this pool (solid arrows). Inputs of soil inorganic N pool are atmospheric deposition and net N mineralization from soil organic matter. The proportion of ammonium (NH_4^+) and nitrate (NO_3^-) in the soil depends on net nitrification (dashed line). Outputs from the soil inorganic N pool are plant and microbial uptake (uptake) and infiltration and leaching (hydrological losses).

2.2. Model Development and Climatic Modifiers

We developed an ad hoc ecosystem model similar to Brookshire *et al.* [2011] to evaluate soil N dynamics at the upper soil layer (0–10 cm) over time (Figure 2). This model describes sources and sinks of soil inorganic N and therefore incorporates key mechanisms to link the different measured variables. In our model, inorganic N enters to the system from atmospheric deposition (D_{NH_4} and D_{NO_3} , in $\mu\text{g N g soil}^{-1} \text{d}^{-1}$) and net N mineralization (NNM, in $\mu\text{g N g soil}^{-1} \text{d}^{-1}$), which depends on the amount of soil organic N (SON, in $\mu\text{g N g soil}^{-1}$). In turn, inorganic N losses are plant and microbial uptake (U_{NH_4} and U_{NO_3} , in $\mu\text{g N g soil}^{-1} \text{d}^{-1}$) and hydrological leaching (H_{NH_4} and H_{NO_3} , in $\mu\text{g N g soil}^{-1} \text{d}^{-1}$). Simulated concentrations of both ammonium (NH_4^+) and nitrate (NO_3^-) (in $\mu\text{g N g soil}^{-1}$) change over time as a result of changes in input and output fluxes of inorganic N to and from the soil pool, and as a consequence of net nitrification (NN, in $\mu\text{g N g soil}^{-1} \text{d}^{-1}$), which transforms NH_4^+ to NO_3^- . For each forest type, changes of soil N concentration over time were described as

$$\frac{d\text{NH}_4}{dt} = \text{SON} \times k_{\text{NNM}} + D_{\text{NH}_4} - \text{NH}_4 \times k_{\text{NN}} - \text{NH}_4 \times k_{\text{UNH}_4} - \text{NH}_4 \times k_{\text{HNNH}_4} \quad (1)$$

$$\frac{d\text{NO}_3}{dt} = \text{NH}_4 \times k_{\text{NN}} + D_{\text{NO}_3} - \text{NO}_3 \times k_{\text{UNO}_3} - \text{NO}_3 \times k_{\text{HNO}_3} \quad (2)$$

where k_{NNM} is the first-order rate for net N mineralization, k_{NN} is the rate for net nitrification, and k_U and k_H are the first-order rates of NH_4^+ and NO_3^- biological uptake and hydrological losses, respectively (all rates in d^{-1}). Following Brookshire *et al.* [2011], the model assumed that plants are N limited, and thus, plant uptake was scaled to available N. In our case, this assumption can be justified by the strong N limitation usually reported in these Mediterranean forests [Ávila and Rodà, 2012]. Note that our model considers biological uptake and hydrological losses separately; however, disentangling these two processes is difficult as we do not have independent empirical data to constrain each of them. Thus, we considered that the assumption of N limitation is adequate if there is a fast turnover of mineral N and strong sink strength (high values of $k_U + k_H$) for the inorganic N pool, NH_4^+ , and NO_3^- . Finally, the possible nitrogen fixed by symbionts in riparian tree roots is often directly incorporated into biota, and thus, it is implicit in the model in the form of SON mineralization. As such, higher levels of SON and N mineralization in the riparian forest (see below) may be at least partly attributable to N_2 fixation.

We assumed that SON was invariant over time, because soil organic matter changes relatively slowly compared to soil N fluxes and inorganic N concentrations [Lawrence *et al.*, 2000]. Our empirical data set supports this assumption because the variation of soil organic matter content and soil C:N ratios ($\text{CV} < 15\%$) was consistently lower than the variation of soil microbial processes ($\text{CV} \sim 50\text{--}200\%$) for the three forests

(Figures 1a and 1b). *WFPS* was calculated from soil volumetric moisture content measured at 10 cm depth (four replicates per plot) with a time domain reflectometry sensor (HH2 Delta-T Devices Moisture Meter). *T_{soil}* was recorded at 10 cm depth (two replicates per plot) by using a temperature sensor (CRISON 25). In addition, we recorded daily precipitation (*P*), which showed the expected seasonal pattern for this region with higher values in spring than in summer and winter (Figure 1c). More details can be found in A. Lupon *et al.*, Contribution of pulses of soil nitrogen mineralization and nitrification to soil nitrogen availability in three Mediterranean forests, *European Journal of Soil Science*, in review (2015).

(Lupon et al., in review, 2015). Based on available data of soil N content at Font del Regàs soils, SON in the model was fixed to 120, 54, and 60 $\mu\text{g N g soil}^{-1}$ for the riparian, oak, and beech forests, respectively.

D_{NH_4} and D_{NO_3} were calculated as the sum of wet and dry deposition values for each day by assuming constant dry and wet deposition over time. We used published values of annual N deposition at the Montseny Mountains as a reference (dry deposition values are 4.12 and 4.04 $\text{kg N ha}^{-1} \text{yr}^{-1}$ and wet deposition value is 3.36 $\text{kg N ha}^{-1} \text{yr}^{-1}$ for NH_4^+ and NO_3^- , respectively) [Ávila et al., 2009; Ávila and Rodà, 2012]. Deposition rates were divided by soil depth (in cm) and bulk density (in g cm^{-3}) to obtain deposition values per soil weight ($\mu\text{g N g soil}^{-1} \text{d}^{-1}$).

Finally, we approximated soil concentrations of NH_4^+ and NO_3^- to be in equilibrium with respect to environmental drivers and inputs from mineralization and deposition. This assumption is based on the observation that turnover times of mineral forms of N in soils are fast (approximately 1 day) and thus equilibrate rapidly compared to changes in the driving variables [Stark and Hart, 1997; Gerber and Brookshire, 2014]. For each forest type, we estimated inorganic N concentrations in the soil as (equations (1) and (2) equal 0)

$$\text{NH}_4 = (\text{SON} \times k_{\text{NNM}} + D_{\text{NH}_4}) / (k_{\text{UNH}_4} + k_{\text{HNNH}_4} + k_{\text{NN}}) \quad (3)$$

$$\text{NO}_3 = (\text{NH}_4 \times k_{\text{NN}} + D_{\text{NO}_3}) / (k_{\text{UNO}_3} + k_{\text{HNO}_3}) \quad (4)$$

Most of existing models have formulated climate dependency of soil N processes [Raich et al., 1991; Rastetter et al., 1997; Brookshire et al., 2011]. Here the first-order rates k_{NNM} , k_{NN} , k_U , and k_H for each forest type were multiplied by factors that parameterize soil moisture (r_θ and r'_θ), soil temperature (r_T), and precipitation (r_p) [Raich et al., 1991; Brookshire et al., 2011], such that

$$k_n = k_{0,n} \times r_{\theta,n} \times r_{T,n} \times r_{p,n} \quad (5)$$

where k_n is the first-order rate for the process n ($n = \text{NNM}, \text{NN}, \text{uptake}, \text{or leaching}$); $k_{0,n}$ is a constant base rate; and $r_{\theta,n}$, $r_{T,n}$, and $r_{p,n}$ are the moisture, temperature, and rainfall modifier for each process.

The moisture modifier (r_θ) was used as a proxy of the effect of soil water availability on k_{NNM} and k_{NN} , and thus, it relies on the combined effect of precipitation, evapotranspiration, and groundwater level. Following Brookshire et al. [2011], r_θ was parameterized as a Gaussian function for both NNM and NN mimicking moisture limitation at low soil moisture levels and possible oxygen limitation at high levels of soil wetness. Yet rather than inferring soil moisture from stream discharge time series as in Brookshire et al. [2011], we calculated r_θ from empirically measured values of WFPS with

$$r_\theta = 1/\sigma\sqrt{2\pi} \times \exp^{-(\text{WFPS}-\mu)^2/2\sigma^2} \quad (6)$$

where WFPS is the water-filled pore space in percent measured at the beginning of each incubation period, μ is a parameter indicating the optimal WFPS value for each soil N process, and σ is a parameter that indicates the sensitivity to changes in WFPS of each process. Values of μ close to 0 imply an overall negative effect of soil moisture on soil N processes, whereas values close to 100 indicate that soil N processes may be limited by low soil wetness for the measured moisture range. In turn, values of σ close to 0 indicate a narrow range of moisture conditions under which a given soil N process occurs, whereas large values (up to 100) indicate little sensitivity to soil moisture. r_θ is assumed to be 1 for k_U .

The rate of hydrological N losses, k_H , was modified by using a potential function to simulate an increase in leaching and infiltration during high soil moisture conditions:

$$r'_\theta = \text{WFPS}^x \quad (7)$$

where x is the exponent representing soil moisture sensitivity. The r'_θ replaces r_θ in equation (5). Values of x close to 0 indicate that hydrological N losses do not depend on soil moisture, whereas larger values (>0.5) indicate that leaching and infiltration increase substantially during wet periods.

We used a Q_{10} function to estimate the temperature dependence (r_T) for k_{NNM} , k_{NN} , and k_U :

$$r_T = Q_{10}^{(T_{\text{soil}} - \overline{T_{\text{soil}}})/10} \quad (8)$$

where T_{soil} is the average of the soil temperature measured empirically at the beginning and at the end of each incubation period, $\overline{T_{\text{soil}}}$ is the mean annual soil temperature, and Q_{10} is the factor by which soil N

processes are multiplied when temperature increases by 10°C. Typically, Q_{10} values are close to 2, and thus, deviation of Q_{10} values indicates either oversensitivity or undersensitivity of soil N processes to temperature [Emmett et al., 2004]. The r_T is assumed to be 1 for k_H .

We further explored the influence of hydrological conditions on k_{NNM} and k_{NN} , by considering a precipitation modifier (r_P), that was used to consider the typical pulse behavior reported for microbial activity during rewetting in Mediterranean systems [Borken and Matzner, 2009]. The r_P was parameterized as a linear function for both NNM and NN, because empirical soil N processes increased linearly with precipitation in our data set:

$$r_P = a \times P + b \quad (9)$$

where P is the precipitation accumulated during 24 h before each incubation period, a is the slope representing precipitation sensitivity, and b is the modifier value if no precipitation occurs. Large values of a indicate that soil N processing rates sharply increase after precipitation, whereas a values close to 0 indicate that precipitation affects soil N processes only marginally. In turn, b can be interpreted as the baseline rate in absence of any precipitation pulse in the system. The r_P is assumed to be 1 for k_H and k_U .

2.3. Model Analysis

The model was fitted to empirical observations obtained at the study site using maximum-likelihood estimation [Edwards, 1992]. According to the present SON and climate data (year 2010), we optimized the parameter set for obtaining the best possible fit between simulated and observed values for NNM, NN, and between simulated NO_3^- sinks (uptake + hydrological losses) and empirical PNL on the timeframe of the 18 incubation periods (12 months).

The likelihood (L) for the processes (j) in each incubation period (i) was calculated as follows:

$$L_{(j,i)} = \frac{d_{j,i}^{a_j-1}}{b^{a_j} \Gamma(a_j)} \exp\left(-\frac{d_{j,i}}{b_j}\right) \quad (10)$$

where a_j and b_j are the parameters for the gamma function (Γ), which allow for nonnormal error distribution [Ise and Moorcroft, 2006]. The $d_{j,i}$ is the absolute difference between the simulated and the observed values of each process (i.e., NNM, NN, and PNL) for each incubation period ($n = 18$) ($|j_i^{\text{modeled}} - j_i^{\text{observed}}|$). The best model fit is achieved when the sum of the log-transformed likelihoods ($l = \sum(\log(L_{j,i}))$) is maximized. To estimate model and gamma distribution parameters for optimization, we used GNU Octave functions *bfgsmin* and *gamfit*, respectively. Since optimization procedure with GNU Octave depends on the first guess of the parameters, we performed a Monte Carlo simulation with 500 random draws, where the first guess was randomly chosen within a large a priori range for the whole suite of parameters (k_n : from 10^{-6} to 100 d^{-1} ; σ , μ : from 10^{-6} to 100%; x : from 0 to 1; Q_{10} : from 10^{-6} to 5; and a, b : from 0 to 1).

To investigate the sensitivity of NNM and NN to climate factors at each forest type, base models that included all climatic modifiers were compared with reduced versions, which discount the effect of moisture, temperature, or precipitation by setting the relevant modifiers to 1. To quantitatively compare these nested model versions, we used Akaike information criterion (AIC) [Akaike, 1974], where $\text{AIC} = 2p - 2l$, with p being the number of parameters and l is the sum of the log-transformed likelihoods (see above). Following Burnham and Anderson [2002], we considered that the nested model with minimum AIC was the best one, that is the simplest model minimizing the loss of information. In order to compare the nested models against each other, we rescaled the AIC value ($\Delta_m = \text{AIC}_m - \text{AIC}_{\text{best}}$, where the subscripts m and best denote a particular and the best model, respectively) and calculated the relative likelihood ($L_r = L_m / L_{\text{best}}$, with L_m and L_{best} being the product of the likelihoods across variables and incubation periods; equation (10)) to assess which climatic modifier contributed the most to the best fit of the temporal pattern of either NNM or NN for each forest type [Burnham and Anderson, 2002]. Large values of Δ_m and small values of L_r indicate that the nested model lost significant information relative to the best model, and thus, it can be interpreted that the discounted climatic variable was a major driver of the temporal dynamics of the soil N cycle.

In order to understand the predictive power of our model, we explored the uncertainty of the parameters by assuming that the more curved the likelihood function is, the more certainty we have that we have estimated

the right parameter [Burnham and Anderson, 2002]. The standard error (S) of each parameter (p_i) was calculated as follows:

$$s(p_i) = \sqrt{\left[\frac{\partial^2 L}{\partial p_i^2} \right]^{-1}} \quad (11)$$

where L again is the product of the likelihoods across incubation periods and variables. Since the analytical form of the likelihood function (L) is not known, we estimated the second derivative by perturbing each parameter by an arbitrary $\pm 10\%$ to obtain slopes around the maximum likelihood.

Further, we evaluated the goodness of fit between empirical and simulated values of NNM and NN and between empirical PNL and simulated NO_3^- losses (uptake + hydrological) with the Nash-Sutcliffe model efficiency coefficient (E):

$$E = 1 - \frac{\sum_{i=1}^n (O_i - M_i)^2}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad (12)$$

where O_i is the empirical value of a particular process at the incubation period i , M_i is the simulated value, and \bar{O} is the mean empirical value over the entire period of length n . The E coefficient is an important determinant of the predictive power of biogeochemical models [Moriarty *et al.*, 2007]. An $E = 1$ corresponds to a perfect match of simulated to observed data, whereas an $E = 0$ indicates that the simple mean of the data has the same predictive power as the model. Finally, we validated the performance of our model by comparing an independent empirical data set of soil inorganic N concentrations with simulated values. We used mean seasonal concentrations for both NH_4^+ and NO_3^- because soil N concentrations were empirically measured at the beginning of each incubation period, while our model simulated mean soil N concentration between sampling dates (average of 15 days of incubation).

2.4. Climate Change Scenarios

In order to understand how climate change may affect soil N dynamics in Mediterranean forests, we calculated future soil N dynamics given the predicted changes in climate for the period of 2081–2100. We assumed that climatic conditions during the study period (2010–2011) were representative for the period of 1986–2005 because they fall within the annual precipitation and temperature long-term average. We based our simulations on the Representative Concentration Pathway 4.5 (RCP4.5) projections for Mediterranean zones [IPCC, 2013], which reported a mean annual decrease in soil moisture of 0.8 mm at 10 cm depth, and an increase in air temperature of 1.25°C and 2.5°C from December to May and from June to November, respectively. We considered that soil moisture will decrease equally in the three forest types because we cannot reliably estimate future effects of groundwater level on soil moisture at the riparian site. In turn, we constructed future T_{soil} based on the air temperature Intergovernmental Panel on Climate Change (IPCC) projections and then, we inferred T_{soil} values from the linear regression between observed mean daily air and soil temperature during the study period ($R^2 > 0.90$, $n = 18$). According to RCP4.5 projections, future precipitation may not significantly differ from today for winter time (October–March) and may decrease 5% during summer (April–September). Finally, we considered that atmospheric N deposition would not change in the future as both empirical and modeling studies indicate no significant trend for this region [Ávila and Rodà, 2012; Lamarque *et al.*, 2013].

Our model is not able of addressing the larger plant-soil cycle, and we therefore do not have the means to predict future levels of soil organic matter and mineralization *per se*. We therefore developed two scenarios which bracket potential alterations of the plant-soil cycle. In our first scenario (i.e., transition), we assumed that due to climate change, the terrestrial N cycle would be in transition toward a future equilibrium, and thus, the SON stock would be similar to the present stock. This transition scenario can be justified by the small temporal variation of soil organic matter stocks over time [Lawrence *et al.*, 2000]. In our second scenario (i.e., equilibrium), we assumed that the terrestrial N cycle would be in equilibrium with the new climate regime, and thus, mean annual NNM rate would revert to present mean rates, provided that overall productivity does not change. Clearly, these assumptions are afflicted with uncertainty, but the two scenarios (transition and equilibrium) help bracket the effects from rapid and long-term adjustments of the N cycle to climate change.

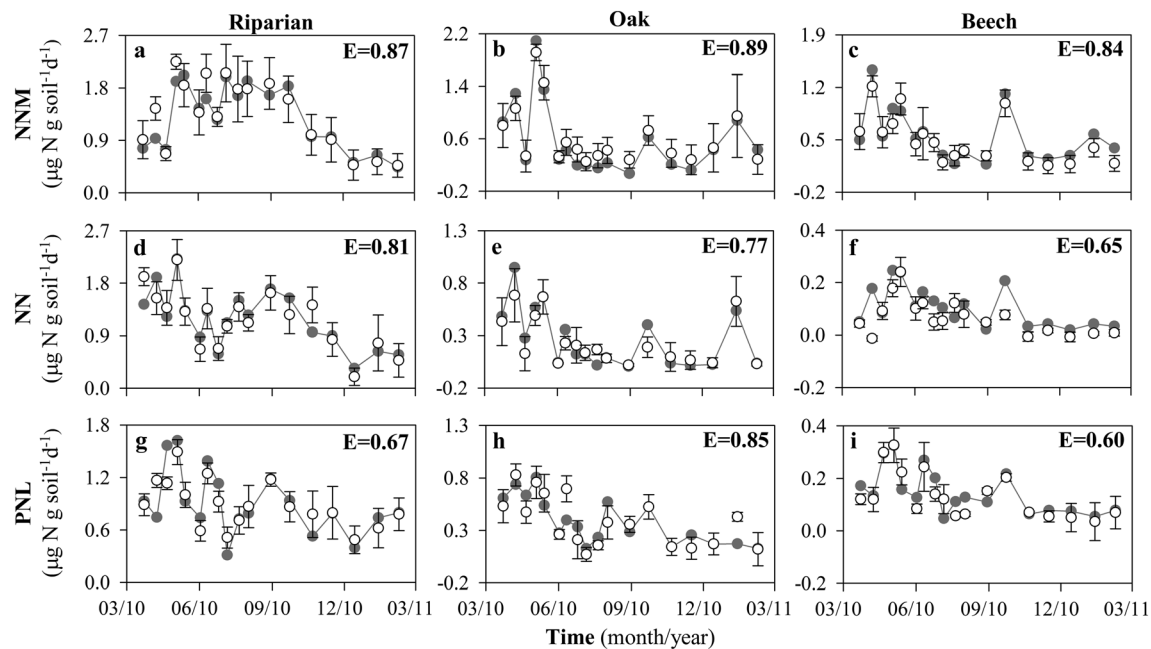


Figure 3. (a–c) Net N mineralization (NNM), (d–f) net nitrification (NN), and (g–i) potential nitrate losses (PNL) at the (left) riparian, (middle) oak, and (right) beech forests. Circles are mean values of measured soil N processing rates, and error bars standard deviations. Gray circles are simulated values. The Nash-Sutcliffe model efficiency coefficient (E) is shown in each panel.

To understand how climate-induced changes in vegetation may affect future soil N budgets and soil N export, we compared the contribution of soil N dynamics of each forest to the overall catchment response according to the areal extent of each forest type for both the present and expected future scenario. Based on *Peñuelas and Boada* [2003], we considered complete beech-by-oak substitution by the end of this century and that future riparian forest area remains the same.

Future scenarios were based on the same 18 incubation periods as the present-day simulations but with adjusted soil organic N concentrations and climate drivers. In order to compare present and future soil N dynamics among forests, we estimated mean daily rates of both soil N processing rates and soil inorganic N concentrations. The average rates of the simulated soil N dynamics allowed us to explore the central tendency of soil N cycling. We multiplied daily soil N processing rates and mean soil inorganic N concentrations by soil bulk density (in g cm^{-3}) and soil depth (in cm) to obtain areal estimates. We then aggregated the areal values into annual averages and multiplied simulated mean annual soil N processing rates and NO_3^- concentrations of each forest type (and taking into account the changing extent of forest types in the beech-by-oak substitution scenario).

3. Results

3.1. Data-Model Fusion and Model Evaluation

The empirical data set showed substantial differences in mean daily rates of soil N processing and PNL among forests. At the oak and beech forests, mean daily rates of NNM (0.625 and $0.495 \mu\text{g N g soil}^{-1} \text{d}^{-1}$), NN (0.240 and $0.067 \mu\text{g N g soil}^{-1} \text{d}^{-1}$), and PNL (0.383 and $0.135 \mu\text{g N g soil}^{-1} \text{d}^{-1}$) were low compared to rates measured at the riparian forest (1.352 , 1.178 , and $0.892 \mu\text{g N g soil}^{-1} \text{d}^{-1}$ for NNM, NN, and PNL, respectively). Moreover, the oak and beech forests showed minimum soil N processing rates in summer, contrasting with the high rates measured at the riparian forest (Figure 3). Consideration of climatic modifiers was essential to model-data agreement (Table 1), which allowed the model to capture both the magnitude and the seasonal pattern exhibited by NNM, NN, and PNL for the three forest types as indicated by the high Nash-Sutcliffe (E) coefficients (Figure 3).

Table 1. Akaike Index Criterion (AIC), Distance Between AIC_m and AIC_{best} (Δ_m), and Model Likelihood (L_m) for the Best Model (Best), the Null Model (No Climate Sensitivity, Null), the Base Model Including the Three Climatic Modifiers (Base), and the Reduced Versions of the Base Model With No Sensitivity to Moisture ($r_\theta = 1$), Temperature ($r_T = 1$), or Precipitation ($r_P = 1$) for Net N Mineralization (NNM) and Net Nitrification (NN)^a

Model	Riparian			Oak			Beech		
	AIC	Δ_m	L_m	AIC	Δ_m	L_m	AIC	Δ_m	L_m
Best	20.25	0.000	1.000	41.908	0.000	1.000	-17.896	0.000	1.000
Null	41.989	21.742	$<10^{-3}$	49.304	7.396	0.025	-0.844	17.052	$<10^{-3}$
Base model	28.670	8.423	0.015	41.908	0.000	1.000	-17.896	0.000	1.000
Base - r_θ NNM	24.904	4.657	0.097	60.319	18.411	$<10^{-3}$	4.125	22.021	$<10^{-3}$
Base - r_T NNM	52.653	32.406	$<10^{-3}$	50.860	8.952	0.011	-4.847	13.049	0.001
Base - r_P NNM	43.342	23.095	$<10^{-3}$	57.114	15.206	$<10^{-3}$	-5.306	12.590	0.002
Base - r_θ NN	25.343	5.096	0.078	50.842	8.934	0.011	-11.666	6.230	0.044
Base - r_T NN	36.721	16.474	$<10^{-3}$	47.952	6.044	0.049	-7.472	10.424	0.005
Base - r_P NN	49.048	28.801	$<10^{-3}$	45.450	3.542	0.170	-7.410	10.486	0.005

^aData are shown separately for each forest type.

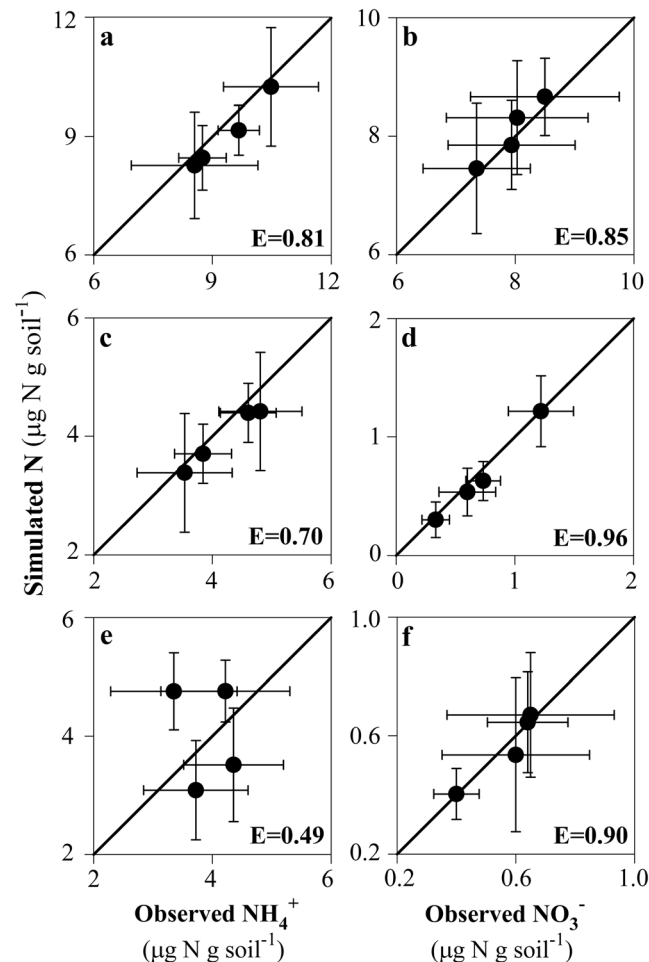


Figure 4. Relationship between observed and simulated soil nitrogen concentrations in the (a and b) riparian, (c and d) oak, and (e and f) beech forests. (left) Ammonium (NH_4^+) and (right) nitrate (NO_3^-) concentrations, respectively, are shown. Circles are mean seasonal concentrations, and error bars show the standard deviation. The 1:1 relation and the Nash-Sutcliffe model efficiency coefficient (E) are shown in each panel.

The good fit obtained through the data-model fusion was corroborated by the model validation process: simulated and independently measured soil inorganic N concentrations across seasons and forests yielded a high E , except for NH_4^+ at the beech site (Figure 4). In all forests, simulated mean daily concentrations differed from empirical data $<10\%$ and $<5\%$ for NH_4^+ and NO_3^- , respectively.

We calculated mean first-order rates (\bar{k}_n) by averaging each k_n over the 18 incubation periods (Tables 2 and 3). The model-data analysis yielded distinct mean first-order rates for NNM (\bar{k}_{NNM}) and NN (\bar{k}_{NN}), being tenfold lower for the former than for the latter. Mean \bar{k}_{NNM} and \bar{k}_{NN} were 40–60% lower at the beech than at the oak and riparian forests (Table 2). Mean NO_3^- removal rates from the mineral pool ($\bar{k}_U + \bar{k}_H$) showed small differences among forests and were threefold to fivefold higher than those for NH_4^+ (Table 3). In turn, mean $\bar{k}_U + \bar{k}_H$ for NH_4^+ were 15% higher for the beech than for the riparian and oak forests, indicating that NH_4^+ was more efficiently removed from the soil pool at the former than at the latter (Table 3).

3.2. Climate Sensitivity of Soil N Processes

The AIC model evaluation indicated that climatic modifiers contributed

Table 2. Best Fit Model Parameters of Soil Moisture Sensitivity (μ , σ), Temperature Sensitivity (Q_{10}), Precipitation Sensitivity (a , b), and Mean First-Order Rates (\bar{k}) for Net N Mineralization (NNM) and Net Nitrification (NN) for Each Forest Type^a

	Riparian		Oak		Beech	
	NNM	NN	NNM	NN	NNM	NN
Moisture						
μ (%)	-	-	100 \pm 7	72 \pm 5	66 \pm 4	100 \pm 5
σ (%)	-	-	62 \pm 13	21 \pm 11	25 \pm 5	37 \pm 8
Temperature						
Q_{10}	2.9 \pm 0.3	1.7 \pm 0.1	1.6 \pm 0.4	2.3 \pm 0.3	1.7 \pm 0.3	2.9 \pm 0.3
Precipitation						
a	0.05 \pm 0.01	0.10 \pm 0.01	0.01 \pm 0.01	0.07 \pm 0.02	0.01 \pm 0.01	0.05 \pm 0.01
b	0.92 \pm 0.58	0.94 \pm 0.1	0.45 \pm 0.32	0.81 \pm 1.00	0.56 \pm 0.34	0.80 \pm 0.1
Constants						
\bar{k} (d ⁻¹)	0.011 \pm 0.007	0.114 \pm 0.058	0.012 \pm 0.009	0.121 \pm 0.024	0.008 \pm 0.006	0.077 \pm 0.021

^aData are average \pm standard deviation.

significantly to improve the model fitness (Table 1). For the oak and beech forests, the best fit models required all three climatic modifiers (r_θ , r_T , and r_P). However, inclusion of soil moisture did not improve riparian NNM and NN to pass the AIC test. We tested the effect of individual climate modifiers by omitting one at a time from the all-inclusive base model (Table 1). The optimization of climatic modifiers generally yielded a bigger effect on likelihood estimation (i.e., higher values of Δ_m and lower values of L_m) for NNM than for NN, likely because model errors in NNM propagated into NN. For the riparian forest model, r_T had the strongest effect on NNM, while r_P was the most important environmental driver for NN. For the oak forest, the fitness of the model notably decreased when we excluded r_θ for both NNM and NN, whereas the effect of r_P on NN rates was small. For the beech forest model, r_θ was the dominant driver for NNM, whereas r_T and r_P were critical to improve NN.

In Figure 5, we illustrate the sensitivity of each rate to individual climate variables. The model analysis revealed that the response of soil N processes to changes in *WFPS* differed between NNM and NN as well as among forest types (Table 2). The lack of response of riparian soil N processes to soil moisture contrasted with the pattern exhibited by both NNM and NN at the oak and beech forests, which were sensitive to a narrow range of moisture conditions ($\sigma < 40$) in most cases (Table 2). The model-data fusion yielded a sustained increase in oak NNM and beech NN for the whole range of *WFPS* values. In contrast, oak NN and beech NNM showed a strong reduction at *WFPS* $< 20\%$ and at *WFPS* $> 66\%$ and $> 75\%$, respectively. Yet there were only few data points at *WFPS* $< 20\%$ and $> 60\%$ (Table 2 and Figure 5a). Soil moisture had a positive effect on hydrological losses, being higher for NO_3^- ($x > 0.5$) than for NH_4^+ ($x < 0.05$) (Table 3).

The results indicate distinct temperature sensitivity among processes and forest types, being the highest for riparian NNM and for beech NN, which showed a $Q_{10} = 2.9$ (Table 2). For the oak and beech forests, NN ($Q_{10} > 2$)

Table 3. Best Fit Model Parameters of Soil Moisture Sensitivity (x), Temperature Sensitivity (Q_{10}), and Mean First-Order Rates of N Losses From the Soil Pool ($\bar{k}_U + \bar{k}_H$) for Both Ammonium (NH_4^+) and Nitrate (NO_3^-) for Each Forest^a

	Riparian		Oak		Beech	
	NH_4^+	NO_3^-	NH_4^+	NO_3^-	NH_4^+	NO_3^-
Moisture						
x	0.01 \pm 0.02	0.71 \pm 0.4	0.05 \pm 0.07	0.80 \pm 0.5	0.05 \pm 0.04	0.62 \pm 0.5
Temperature						
Q_{10}	1.9 \pm 0.4	2.5 \pm 0.5	1.8 \pm 0.4	1.5 \pm 0.4	1.5 \pm 0.4	1.8 \pm 0.3
Constants						
$\bar{k}_U + \bar{k}_H$ (d ⁻¹)	0.049 \pm 0.013	0.223 \pm 0.065	0.054 \pm 0.022	0.248 \pm 0.104	0.059 \pm 0.029	0.209 \pm 0.072

^aN losses are the sum of mean rates of biological uptake and hydrological losses. Data are average \pm standard deviation.

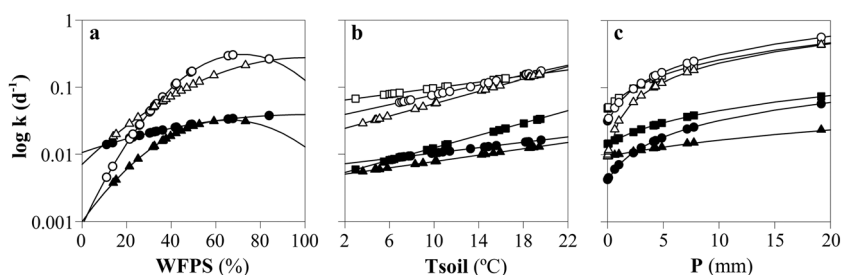


Figure 5. Sensitivity of first-order rates (k_n) for net mineralization (black) and net nitrification (white) to (a) soil moisture (WFPS), (b) soil temperature (T_{soil}), and (c) precipitation (P) at the riparian (squares), oak (circles), and beech (triangles) forests. Symbols are data for each incubation period, and lines represent the considered function (Gaussian, Q_{10} , and linear for moisture, temperature, and precipitation, respectively). Note that first-order rates are log transformed. The response of k_n to changes in a particular climatic variable was examined by setting the value of the other two climatic variables to its mean. For example, in Figure 5a, T_{soil} and P equaled the average of the 18 sampling dates.

was more sensitive to changes in temperature than NNM ($Q_{10} < 2$), whereas Q_{10} values for NN and NNM showed the opposite pattern at the riparian forest (Table 2 and slope in Figure 5b). The model fit also suggested a stronger effect of temperature on NO_3^- uptake by biota at the riparian forest ($Q_{10} = 2.5$) compared to the oak and beech forests ($Q_{10} \sim 1.8$) (Table 3).

Pulses of precipitation had a larger influence on microbial activity at the three forest types but especially for NN at the riparian and oak forests (slope $a > 0.07$) (Table 2 and Figure 5c). Both oak and beech NNM appeared to be little responsive to rewetting events (slope $a = 0.01$) (Table 2). Responses of NNM and NN to rewetting were relatively high at the riparian forest compare to upland forests (Figure 5c).

3.3. Soil N Dynamics Under Climate Change Scenarios

The application of our model projections of soil N dynamics for the period of 2081–2100 revealed a distinct change for NNM and NN because each soil N process showed a different moisture and temperature sensitivity at each forest type. In the transition scenario, where we held SON constant (see Method section), changes in mean daily NNM rates were small but differed among forest types (+8%, −12%, and −8% for the riparian, oak, and beech forests, respectively) (Table 4). Changes in mean daily NN rates were similar or even smaller than for NNM (+6%, −8%, and −8% for the riparian, oak, and beech forests, respectively). While all forest types experienced the positive effect of warming, the negative effect of drying on soil transformation rates offsets the positive effect of temperature in the two upland forest types. In the equilibrium scenario, where mean NNM rates revert to the present value, the response of NN to climate change became diminishingly small for all forest types (+2%, −4%, and −1% for the

Table 4. Simulated Mean Annual Rates of Net N Mineralization (NNM), Net Nitrification (NN), and Soil Nitrate Concentration (NO_3) for the Present Climate, the Transition Phase (Increased Mean NNM), and the Future Equilibrium (Mean NNM Reverts to Present Value) Scenarios^a

	Riparian	Oak	Beech
NNM ($\mu\text{g N g soil}^{-1} \text{ d}^{-1}$)			
Present	1.311 ± 0.460	0.596 ± 0.531	0.502 ± 0.374
Transition	1.421 ± 0.552	0.526 ± 0.633	0.462 ± 0.459
Equilibrium	1.311 ± 0.460	0.596 ± 0.531	0.502 ± 0.374
NN ($\mu\text{g N g soil}^{-1} \text{ d}^{-1}$)			
Present	1.188 ± 0.458	0.264 ± 0.496	0.074 ± 0.242
Transition	1.268 ± 0.476	0.244 ± 0.530	0.068 ± 0.295
Equilibrium	1.208 ± 0.503	0.254 ± 0.586	0.073 ± 0.310
NO_3 ($\mu\text{g N g soil}^{-1}$)			
Present	8.10 ± 3.19	0.90 ± 1.66	0.60 ± 1.05
Transition	8.50 ± 3.54	0.80 ± 1.55	0.57 ± 1.10
Equilibrium	8.21 ± 3.85	0.81 ± 1.40	0.58 ± 1.04

^aData are shown as average ± standard deviation for each forest type.

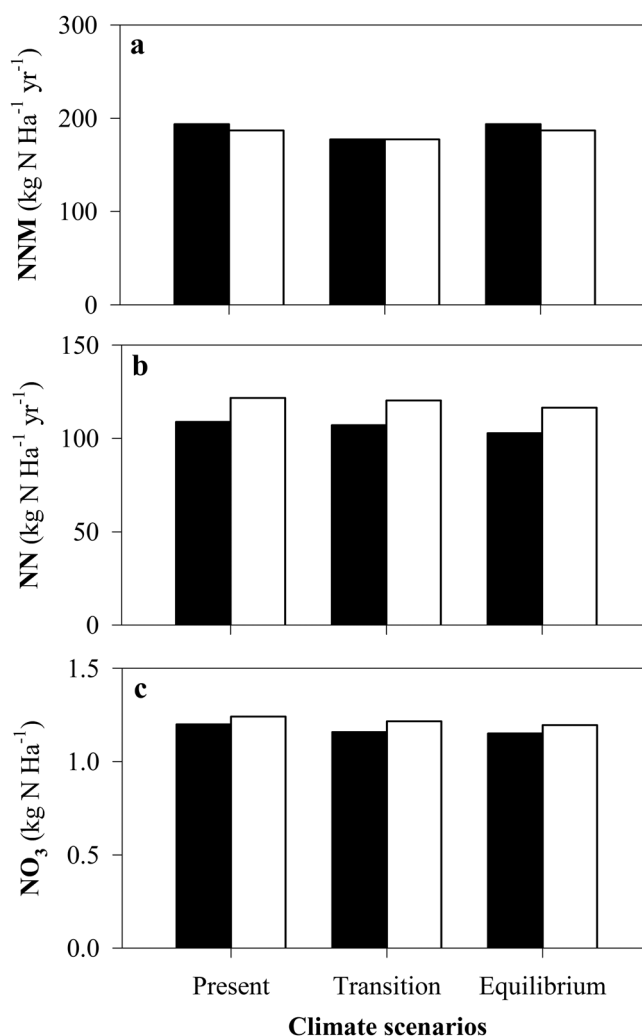


Figure 6. Simulated mean annual (a) net nitrogen mineralization (NNM), (b) net nitrification (NN), and (c) soil nitrate concentration (NO_3^-) in Font del Regàs catchment for the present climate, the transition phase (increased mean NNM), and the future equilibrium (mean NNM reverts to present value). Two vegetation cover scenarios were considered: present tree species composition (black) and a complete beech-by-oak substitution (white).

mineralization, nitrification, and removal of bioavailable N (NO_3^- and NH_4^+). To this end, we fused empirical data with a simple mechanistic model of the soil N cycle to evaluate and quantify the sensitivities of Mediterranean forest ecosystems to different environmental drivers simultaneously. Our framework recreated the temporal variation in soil NO_3^- and NH_4^+ concentrations over the course of a year in three forest types. The consideration of climatic modifiers into the model improved the goodness of fit between simulated and empirical data for NNM, NN, and PNL during most of the year, which support the idea that environmental variables are crucial to understand the seasonal behavior of soil N cycling [Miller *et al.*, 2007; Bell *et al.*, 2008]. Further, the good fit between simulated and empirical data indicates that our model was able to capture the net result of the main processes determining net rates of mineralization and nitrification. However, mismatches were observed, especially for soil NH_4^+ concentrations and NN rates at the beech forest, which possibly reflect aspects of NH_4^+ uptake not captured in our model such as transient microbial immobilization, biological NN inhibition, or sorption-desorption processes [Matschona and Matzner, 1995; Trap *et al.*, 2011]. We did not consider denitrification fluxes nor were we able to constrain this process with the available empirical data. Denitrification (and the absence of this process in

riparian, oak, and beech forests, respectively). In accordance with change in NNM and NN, simulated soil NO_3^- concentration slightly increased by +5% (transition) and +1% (equilibrium) in the riparian forest, while it declined by −11% and −4% at the oak and beech forests, respectively (Table 4).

At the catchment scale, our model projections indicated that the expected changes in climate could induce relatively small decreases in mean annual rates of NNM (−8%) and NN (−5%) and minimal changes in the soil NO_3^- pool (−4%) (black bars in Figure 6). This reduction is mainly caused by the negative effect of dryness in the upland forests. According to our model results, the beech-by-oak substitution expected by the end of this century could lead to small decreases in mean annual NNM (−4%) but could increase mean annual NN by +13%. As a result, modeled soil NO_3^- concentration increased slightly (+5%; white bars in Figure 6). The changes in NN and soil NO_3^- concentrations caused by this species substitution were similar for both the transition and the equilibrium scenarios.

4. Discussion

4.1. Data-Model Fusion

This study aimed to understand the impact of climate drivers on crucial steps in the N cycle, which are

the model) could skew the empirical estimate of NN rates as incubation bags allow for gas exchange. However, rates of denitrification in these Mediterranean forests are low (by 10 times or even more) compared to nitrification rates [Bernal *et al.*, 2007; Poblador, personal communication], and thus, the effect of denitrification on NN signal is likely small.

Our analysis further supports the idea that processes involved in soil N cycling have a rapid response to climate because the model-data fusion yielded short residence time (~ 3 – 4 days) for both NH_4^+ and NO_3^- . This result justifies the equilibrium assumption made for soil N concentrations [Stark and Hart, 1997; Gerber and Brookshire, 2014]. However, our results did not fully justify the assumption of chronic N limitation, at least in the riparian forest, because this forest showed weak sink strength (low $\bar{k}_U + \bar{k}_H$) for soil NH_4^+ and NO_3^- pools compared to upland soils. Such high N availability at the riparian forest could be partially explained by symbiotic N_2 fixation, a process that was not explicitly included in our model conceptualization, but that could supply extra NH_4^+ to riparian trees, increase soil organic nitrogen, and ultimately enhance both riparian NNM and NN [Booth *et al.*, 2005; Rennenberg *et al.*, 2009]. Nevertheless, the good matches obtained indicate that the consideration of a first-order N removal rate was not incompatible with the data.

4.2. Response of Soil N Dynamics to Climate Variation

As expected, we found that moisture dependence of N processing rates was key to improving the data-model fit at the oak and beech forests. These findings agree with previous empirical studies performed across semiarid biomes and provide further evidence that the seasonality of soil N dynamics can strongly rely on the temporal pattern of soil moisture [Niboyet *et al.*, 2011; Manzoni *et al.*, 2012]. Our results showed increases in soil N processes with increasing water availability, as well as strong decreases during severe dry conditions (i.e., $\text{WFPS} < 20\%$), suggesting that extended drought periods may lead to reduced inorganic N turnover in Mediterranean biomes [Larsen *et al.*, 2011]. Similar to previous studies, we found that sensitivity to dryness and wetness differed between NNM and NN [Manzoni *et al.*, 2012; Björnsne *et al.*, 2014], and further, that high moisture content ($> 60\%$) could reduce soil mineralization in some forest types [Linn and Doran, 1984].

In contrast to upland forests, soil moisture did not improve the model fit for the riparian forest, which suggests that water availability was not a limiting factor which was expected for riparian zones [Sleutel *et al.*, 2008]. The absence of soil moisture sensitivity was likely due to perennial moist conditions, as riparian soils kept relatively moist even in summer ($\text{WFPS} > 30\%$), when precipitation was low and evapotranspiration rates were the highest. At our study site, riparian groundwater usually flowed well below the soil surface, and thus, hydraulic lift by fine roots was likely responsible for keeping topsoil layers wet in summer [Tabacchi *et al.*, 2000]. As a consequence, riparian systems may be less vulnerable to drought than upland forests. Overall, this contrasting sensitivity to soil moisture highlights that distinct hydrologic dynamics in upland versus riparian sites ultimately lead to marked differences in soil N processing.

Temperature dependence applied for soil NNM and NN was crucial to improve the model's fitness at the three forest types, supporting the well-established idea that warming enhances microbial activity [Emmett *et al.*, 2004; Butler *et al.*, 2012]. The obtained Q_{10} values were within the range of other observations carried out in Mediterranean and temperate systems [Emmett *et al.*, 2004; Dessureault-Rompré *et al.*, 2010; Novem-Auyeung *et al.*, 2013]. Yet our results did not support the hypothesis that microbes adapted to cold climates would be more sensitive to changes in soil temperature because the highest temperature sensitive ($Q_{10} \sim 3$) was exhibited by both riparian NNM and beech NN. This finding suggests that other site-specific features can influence the temperature sensitivity of soil N cycling. For instance, NNM at the oak and beech forests was less responsive to increases in temperature than riparian NNM, which could be explained by the higher moisture stress experienced by upland forests [Suseela *et al.*, 2012; Novem-Auyeung *et al.*, 2013]. Additionally, SON availability was twofold higher at the riparian than at the upland soils, which could further contribute to enhance riparian soil mineralization during warm periods compared to upland soils that could be substrate limited [von Lützow and Kögel-Knabner, 2009; Schütt *et al.*, 2014].

Our results further suggest that the response to changes in temperature can substantially differ between NNM and NN. We found that NN was more responsive to increases in temperature than NNM at the oak and beech forests, in line with previous empirical studies showing that warming enhances NN in forest soils by reducing both NH_4^+ and NO_3^- immobilization [Emmett *et al.*, 2004; Rennenberg *et al.*, 2009; Butler

et al., 2012]. However, this pattern was not observed in the riparian forest, which showed lower Q_{10} values for NN compared to NNM. Overall, our model supports the idea that the various processes involved in soil N cycling can respond differently to warming [Emmett *et al.*, 2004; Bai *et al.*, 2013]. Further, our results point out that interaction between temperature and other site-specific features such as water and substrate availability is essential to understand future responses of ecosystem biogeochemical cycles to warming.

Finally, our results showed that including precipitation pulses into the model improved the goodness of fit at the three forest types. These results support the idea that rewetting episodes are essential to understand soil N cycling likely because they stimulate soil microbial activity through mobilizing soil N, the release of intracellular osmolites, and the enhancement of metabolic rates [Schimel *et al.*, 2007; Borken and Matzner, 2009]. In contrast to our expectation, the highest response to rewetting ($a > 0.5$) was shown by soil N processing rates in the riparian forest, which were expected to be less sensitive to increases in water availability than those in the upland soils. This seemingly counterintuitive result may be partly a modeling artifact and stems from the fact that part of a small but not model-relevant moisture effect has spilled over to a precipitation response in the riparian zone, as moisture and precipitation are somewhat correlated. As observed for soil moisture and temperature, our results point to a differential sensitivity of NNM and NN to rewetting events, being NN more responsive than NNM (as indicated by the steeper a slopes). The higher sensitivity of NN to increases in soil water availability has been previously observed and suggests that soil NO_3^- availability may be vulnerable to changes in the amount and timing of precipitation [Groffman *et al.*, 2009; Larsen *et al.*, 2011]. Our findings showed that rewetting episodes can be crucial to predict temporal patterns of soil N cycling, and therefore, the incorporation of water pulse dynamics within terrestrial models could help to our understanding of temporal patterns of nutrient biogeochemistry in Mediterranean systems.

4.3. Effect of Climate Change on Soil N Cycling

We developed climate change scenarios for our sites using broad IPCC model evaluations that suggest year-round decrease in soil moisture (−0.8 mm), year-round temperature increase (+2°C), and decreased precipitation in summer (−5%) when applying the RCP4.5 scenario. While the temperature increase would be similar to or lower than in other systems, Mediterranean forest systems are expected to experience a reduction in precipitation during summer months, which renders these regions more vulnerable to drought compared to other forested regions worldwide [IPCC, 2013]. Our model approximation allowed us to evaluate the effect of the expected climate change on the overall soil N cycle as the combination of simultaneous changes in the climatic drivers (soil moisture, temperature, and precipitation) and the sensitivity of the different soil N processes to these drivers.

Our model calculations were based on seasonal data obtained over 1 year. The model was designed to specifically address the short-term responses of the considered soil N processes to climate variability in presence of soil organic N. Therefore, we cannot predict future levels of soil organic matter, long-term mineralization rates, nor future changes in the climatic sensitivity of soil N cycling. However, given the derived sensitivity to climate drivers, the modeling framework allows us to explore how the interactive effect of moisture and temperature could affect soil N cycle in the future. The consideration of two future states of the long-term N cycle (a transition phase with fixed SON versus a steady state equilibrium with fixed mean mineralization fluxes) helps bracketing potential alterations of the long-term plant-soil cycle. Both states showed similar results under future climate scenarios, giving some consistency to the model predictions.

According to our model and our assumptions therein, the climate change projected for later in this century may have a relatively small effect on mean daily rates of soil N cycling. Our results indicate that mean NNM and NN at the riparian forest could increase by up to +8% from today's rates as a consequence of warmer temperatures, as observed for temperate systems [Rustad *et al.*, 2001; Bai *et al.*, 2013]. Contrarily, mean daily NNM and NN in upland forests may slightly decline in the future because the negative effect of decreases in water availability will likely outweigh the positive temperature effect. Our model simulations agree with the hypothesis that future warming and drying may have an antagonistic effect on soil N cycling and ultimately lead to minimal changes in mean NNM, NN, and soil NO_3^- concentrations in these Mediterranean upland forests. Similar antagonistic effects between temperature and soil moisture have

been recently reported in manipulative warming experiments in grassland systems [Liu *et al.*, 2009; Verburg *et al.*, 2009]. Our study adds a novel piece of knowledge to the growing evidence that terrestrial ecosystems can show a complex response to climate change and that the interaction between different climatic drivers can eventually lead to less pronounced responses than previously expected [Rustad *et al.*, 2001; Bai *et al.*, 2013].

When projected to the catchment scale, our results suggest that expected future changes in soil N cycling would not be enough to alter soil N concentration in this Mediterranean system. Moreover, we found that future climate-induced shifts in vegetation would have a relatively small effect on both soil N fluxes and pools because oak and beech forests may respond similar to climate. Our results differ from previous studies in temperate systems that have related long-term increases in hydrological N export to warming-induced increases in mineralization [Rogora, 2007; Brookshire *et al.*, 2011]. In those mesic regions, extrapolation of past climatic trends did not reveal future changes in soil moisture, and therefore, moisture did not affect function cycling rates. Yet our findings revealed that soil water availability can play a pivotal role in driving soil N cycling. Although our results have to be considered with caution, our study and method provide insights into how interaction among direct and indirect climatic drivers affects soil N processing in Mediterranean catchments and stresses that future response of soil N cycle to climate change cannot be generalized among biomes or forest types.

5. Conclusions

Our study adds to the growing evidence demonstrating the effects of changes in climate on soil N cycling in forests ecosystems [Rustad *et al.*, 2001; Larsen *et al.*, 2011]. To explore climate sensitivity of key soil N processes, we use a relatively short-term data set (18 sampling dates over 1 year) but take advantage of suite of detailed soil N cycle measurements (soil organic and inorganic N concentrations, net N mineralization, net nitrification, and potential N losses from the soil pool). We showed that the inclusion of climatic modifiers improves the model, supporting the idea that they are important drivers of the dynamics of the N cycle in Mediterranean systems. Soil moisture, temperature, and precipitation generally have a positive effect on soil N cycling rates, although sensitivity to climatic factors differed among processes and forests. Soil moisture was the major driver of soil N cycle at oak and beech forests, but temperature and precipitation shifted soil N dynamics at the riparian forest. In most cases, net nitrification was more sensitive to changes in climate than net N mineralization; yet the response of soil N processes to climate change was often masked by antagonistic effects of moisture availability and temperature. As a consequence of this interaction between warming and drying, we found that future climate may have a small influence on mean daily soil N processing rates, which would ultimately lead to minimal variation in mean annual soil NO_3^- concentration in these Mediterranean catchments. Together, our analyses provide mechanistic insights into the sensitivity of the soil N cycle to climate variation and add to our understanding of how future changes in climate may shape soil N cycling in Mediterranean regions.

Acknowledgments

We thank S. Poblador for the field and laboratory assistance. Financial support was provided by the Spanish Government through the projects MONTES-Consolider (CSD2008-00040-MONTES) and MEDFORESTREAM (CGL2011-30590). A.L. was funded by the Spanish Ministry of Education, Culture and Sport (MECD) with a FPU grant (AP-2009-3711). S.B. was supported by the Spanish Ministry of Economy and Competitiveness (MINECO) with a Juan de la Cierva contract (JCI-2010-594 06397). S.B. received additional funds from the Spanish Research Council (CSIC) with the contract JAEDOC027. The Vichy Catalan Company, the Regàs family, and the Catalan Water Agency (ACA) graciously gave us permission for at the Font del Regàs catchment. The data for this paper are available by contacting the corresponding author.

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