

## Decadal-scale dynamics of water, carbon and nitrogen in a California chaparral ecosystem: DAYCENT modeling results

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**Abstract.** The Mediterranean climate, with its characteristic of dry summers and wet winters, influences the hydrologic and microbial processes that control carbon (C) and nitrogen (N) biogeochemical processes in chaparral ecosystems. These biogeochemical processes in turn determine N cycling under chronic N deposition. In order to examine connections between climate and N dynamics, we quantified decadal-scale water, C and N states and fluxes at annual, monthly and daily time steps for a California chaparral ecosystem in the Sierra Nevada using the DAYCENT model. The daily output simulations of net mineralization, stream flow and stream nitrate ( $\text{NO}_3^-$ ) export were developed for DAYCENT in order to simulate the N dynamics most appropriate for the abrupt rewetting events characteristic of Mediterranean chaparral ecosystems. Overall, the magnitude of annual modeled net N mineralization, soil and plant biomass C and N, nitrate export and gaseous N emission agreed with those of observations. Gaseous N emission was a major N loss pathway in chaparral ecosystems, in which nitric oxide (NO) is the dominant species. The modeled C and N fluxes of net primary production (NPP), N uptake and N mineralization,  $\text{NO}_3^-$  export and gaseous N emission showed both high inter-annual and intra-annual variability. Our simulations also showed dramatic fire effects on NPP, N uptake, N mineralization and gaseous N emission for three years of postfire. The decrease in simulated soil organic C and N storages was not dramatic, but lasted a longer time. For the seasonal pattern, the predicted C and N fluxes were greatest during December to March, and lowest in the summer. The model predictions suggested that an increase in the N deposition rate would increase N losses through gaseous N emission and stream N export in the chaparral ecosystems of the Sierra Nevada due to changes in N saturation status. The model predictions could not capture stream  $\text{NO}_3^-$  export during most rewetting events suggesting that a dry-rewetting mechanism representing the increase in N mineralization following soil wetting needs to be incorporated into biogeochemical models of semi-arid ecosystems.

## Introduction

The effects of chronic nitrogen (N) deposition in areas of the western United States include increased greenhouse gas emissions (Fenn et al. 1996, 2003b), higher N concentrations in plant tissues (Fenn et al. 2003a), and increased nitrification rates and nitrate ( $\text{NO}_3^-$ ) levels in soil, streams, and lakes (Riggan et al. 1985; Williams et al. 1996; Fenn and Poth 1999; Sickman et al. 2002). N deposition has caused some environmental problems such as reduced drinking water quality and eutrophication of recipient water bodies,  $\text{NO}_3^-$ -induced changes in plant community composition, disruption, and contributions to regional haze and impaired visibility Fenn et al. (2003a, b). Among the ecosystems being impacted, there has been little attention paid to shrublands, such as the chaparral of California.

Chaparral is the dominant ecosystem in foothill areas of southern and central California. The long-term dynamics of water, carbon (C) and N in chaparral ecosystems under the effects of N deposition are not well known. Field studies of C and N biogeochemistry in chaparral ecosystems over the last three decades have included biomass and net primary production (NPP) (Mooney and Rundel 1979; Schlesinger and Gill 1980; Parsons and Stohlgren 1986), nutrient cycling (Christensen and Muller 1975; Rundel and Parsons 1980; Gary and Schlesinger 1983; Graham and Wood 1991; Ulery et al. 1995; Fenn et al. 1996), ecological effects of N deposition (Riggan et al. 1985, 1994; Fenn et al. 1996, 2003a), greenhouse gaseous N emissions (Anderson and Poth 1989; Fenn et al. 1996), and stream  $\text{NO}_3^-$  export (Davis 1989; Fenn et al. 2003c). Our understanding of ecological processes in chaparral ecosystems is derived from short-term studies of less than a few years at a limited set of intensively studied sites. To better understand C and N processes of chaparral ecosystems and their potential effects on environmental problems, this short-term, plot-derived understanding must be projected to much broader spatial and temporal scales. One approach for projecting to the broader space and time scale is the use of process-based biogeochemical models. The field observations then provide the necessary data for the parameterization, validation, and evaluation of C and N biogeochemical models.

Characteristics of semi-arid ecosystems, such as chaparral ecosystems include abrupt shifts from dry to wet conditions and from low to high runoff periods, and seasonal transitions from warm to cold temperatures. These characteristics induce changes in soil moisture, temperature, and redox conditions that mediate the community structure, biomass and activity of soil microbes (Schlesinger et al. 1982; Fierer et al. 2003). These abrupt climatic shifts cause changes in microbial and hydrological processes within short time periods. It is unknown whether or not biogeochemical models, like DAYCENT (Parton et al. 1998), correctly represent the seasonal transition in chaparral and other seasonally dry ecosystems. It has been argued that such models should do poorly under such conditions (Schimel 2001).

Fire is known to be a critical process in chaparral ecosystems (Riggan et al. 1988). Fire has been shown to impact stand structure, species diversity and biogeochemical export from chaparral ecosystems (Riggan et al. 1988, 1994; Keeley et al. 1999; Keeley and Fotheringham 1998; Thanos and Rundel 1995). It is important to represent and understand the impact of fire when simulating the biogeochemistry of chaparral ecosystems.

The goal of our research is to extend our understanding of N biogeochemistry of southern California chaparral ecosystems from short-term observations to the decadal-scale, and further understand the effects of long-term chronic N deposition and fire disturbance. Our research attempted to answer the following questions: Can the complex DAYCENT biogeochemical model correctly predict the decadal-scale N biogeochemistry of Mediterranean chaparral ecosystems? What processes cannot be successfully represented? What are the potential impacts of increasing N deposition trends on N losses from chaparral ecosystems? How does fire disturb the overall patterns of C and N dynamics at decadal scale?

### **Model description**

The DAYCENT biogeochemical model (Parton et al. 1998; Kelly et al. 2000; Del Grosso et al. 2001) is the daily time step version of the CENTURY model (Parton et al. 1994). A flow chart of the DAYCENT model can be found in the literature (Del Grosso et al. 2001). DAYCENT and CENTURY both simulate the biogeochemical processes of carbon, nitrogen, phosphorus, and sulfur cycling associated with soil organic matter (SOM) for grasslands, agricultural lands, forests and savannas. In addition to modeling decomposition, nutrient flows, soil water, and soil temperature on a finer time scale than CENTURY, DAYCENT also has increased vertical spatial resolution for soil layers. DAYCENT includes submodels for plant productivity, decomposition of dead plant material and SOM, soil water and temperature dynamics, and trace gas fluxes. Required inputs to the model include daily maximum/minimum temperature and precipitation, site specific soil properties, and current and historical land use. Disturbances and management practices such as fire, grazing, cultivation, harvest, irrigation, and organic matter or fertilizer additions can be simulated. Since most major processes in the daily version of DAYCENT, such as plant productivity, the decomposition of dead plant material, and SOM processes, remain unchanged with the monthly version CENTURY, DAYCENT can be used for decadal to millennial scale simulation.

One feature of DAYCENT is its improvement of the N cycling algorithms in CENTURY. For example, DAYCENT added the simulation of  $N_2O$ , NO, and  $N_2$  gas emissions from soils resulting from nitrification and denitrification as well as  $CH_4$  release from soils (Del Grosso et al. 2001, 2002). The second improvement compared with CENTURY is its soil water and temperature algorithms (Parton et al 1998). The new land surface submodel of DAYCENT

simulates daily dynamics of soil water and temperature from a multi-layered soil system. The soil water submodel was modified to simulate above field-capacity water-content, unsaturated water flow using Darcy's equation, runoff, snowpack processes, and the effect of soil freezing on saturated water flow.

The daily outputs in DAYCENT include soil moisture, temperature, and trace gas fluxes of  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{CH}_4$ , however, daily outputs of soil  $\text{CO}_2$  and stream N export are not included. In order to enhance our insights of biogeochemical and hydrological processes under the effect of seasonal transitions, we developed the daily outputs for stream flow,  $\text{NO}_3^-$  export, net N mineralization, and soil  $\text{CO}_2$  for the DAYCENT model. The development of the new daily outputs was based on the existing DAYCENT code.

## Study site and data sources

### *Site description*

The Chamise Creek watershed ( $36^\circ30'42''$  N,  $118^\circ42'23''$  W) is located along the southwestern slope of the Sierra Nevada within Sequoia and Kings Canyon National Parks, California (Figure 1). The watershed is about 4.3 ha, with an elevation range of 680-800 m. The soil type is an Ultic Haploxeralf. This soil is deep and well-drained with a well-developed argillic horizon and is formed from gabbro-dioritic residuum (Huntington and Akeson 1987). This soil is usually moist during the late fall through spring, and dry during the summer. Vegetative cover consists of dense stands of chaparral shrubs with an understory of sparse annual grasses. The chamise community is dominated by *Adenostema fasciculatum* with subdominants of *Cercocarpus betuloides*, *Ceanothus cuneatus* and *Eriodictyon californicum*. The watershed has not been

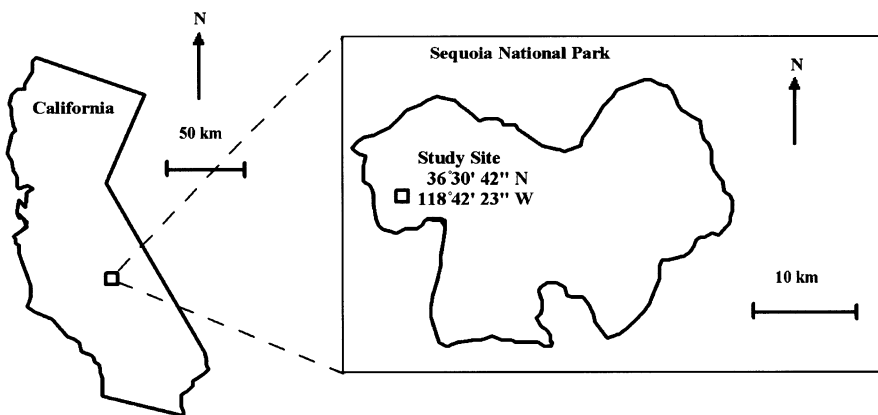
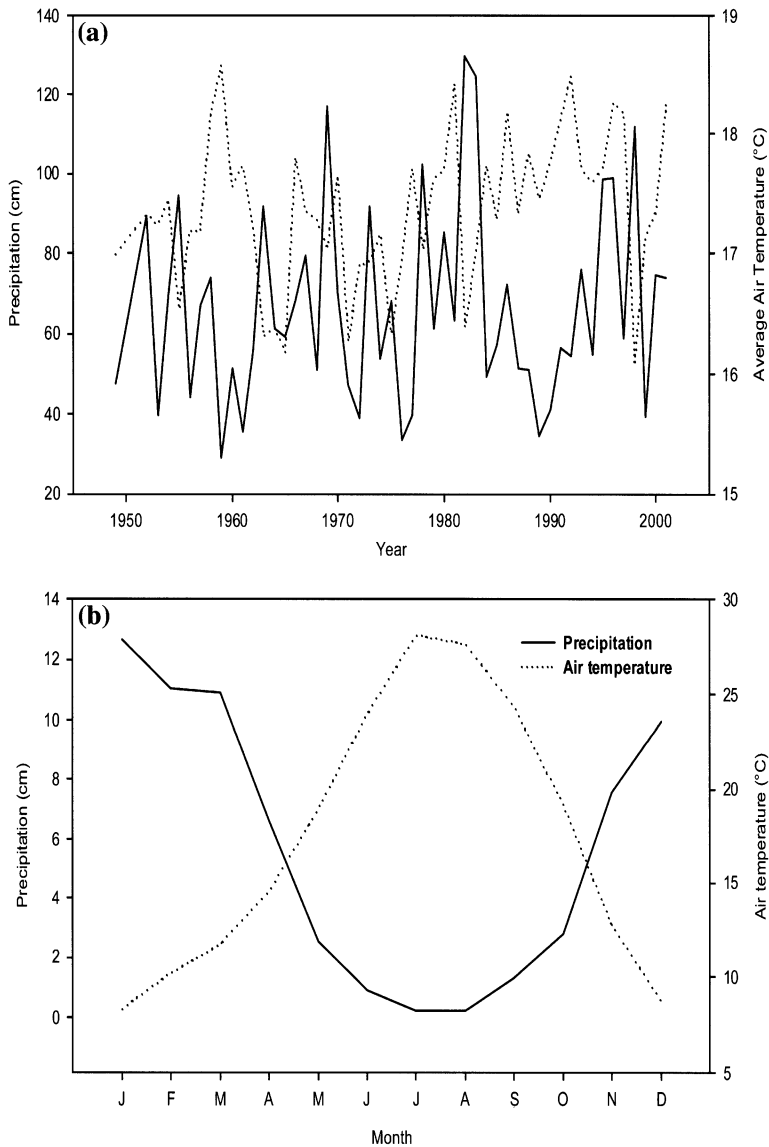


Figure 1. Map showing the location of Sequoia and Kings Canyon National Parks and the Chamise watershed.

burned for 43 years. The site has granitic bedrock, and the stream flows only during moderately heavy storm events, a hydrologic condition similar to other chaparral and semi-arid landscapes of the southwestern U.S.

The climate of the study site has a typical Mediterranean pattern. Figure 2 shows the annual and monthly average precipitation and air temperature



*Figure 2.* Annual and monthly average precipitation and air temperature: 1949-2001. The meteorological station is located at the headquarter of Sequoia and Kings Canyon National Parks, 4 km west of the Chamise watershed.

during 1949 to 2001 at the Ash Mountain research station of Sequoia and Kings Canyon National Parks, 4 km west of the Chamise site. The annual precipitation exhibits a high variation among years. For instance, the average annual precipitation during wet years (1952, 1955, 1963, 1973, 1978, 1982, 1983, 1995, 1996 and 1998) is about 2.8-fold of that during dry years (1953, 1959, 1961, 1972, 1976, 1977, 1989, 1990 and 1999). Precipitation falls predominantly as rain during the winter, with very little from May through October. Mean monthly temperatures increase from January until July and decline thereafter.

### *Measurement of N deposition*

We measured bulk N deposition in throughfall using ion exchange resin (IER) columns developed by Fenn and Poth (2004). The precipitation columns consisted of a rain collector funnel connected to a 1.27 cm × 35.6 cm polyvinyl chloride (PVC) tube. Throughfall columns consisted of PVC tubes mounted horizontally and cut to create an open-topped trough sealed with nylon mesh. The columns were filled with 60 ml of a mixed-bed H<sup>+</sup>/OH<sup>-</sup> polystyrene ion-exchange resin (Amberlite MB150, Rohm and Hass, Philadelphia, PA) and were capped at both ends with polyester floss and perforated PVC fittings to allow for drainage. A double-walled plastic tube was placed around all IER columns to protect them from direct solar radiation.

We installed a total of 12 IER columns (precipitation  $n = 5$ ; throughfall  $n = 7$ ) in the Chamise Creek watershed in July, 2002, and collected the columns the following spring, in March, 2003. Columns collected from the field were processed as outlined in Fenn and Poth (2004). Resin extracts were analyzed for NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> using a Lachat autoanalyzer (Lachat Instruments, Milwaukee, WI). Blanks ( $n = 3$ ) were used to calculate background concentrations of inorganic N.

### *Parameterization*

Environmental data required in DAYCENT include daily climate data, soil physical properties and external nutrient input. The longterm daily climate data (1949–2001) used in our simulations were daily maximum temperature, daily minimum temperature and daily precipitation. The site, biomass and soil parameters that DAYCENT requires are listed in Tables 1 and 2. In the Chamise watershed, external N input includes atmospheric deposition and symbiotic and non-symbiotic N fixation. From our measurement, we estimated that the annual N deposition was 0.77 g m<sup>-2</sup> yr<sup>-1</sup>, and the wet and dry N depositions were 0.28 and 0.49 g m<sup>-2</sup> yr<sup>-1</sup>, respectively. The symbiotic and non-symbiotic N fixations were set at 0.2 and 0.1, respectively (Kummerow et al. 1978; Gary and Schlesinger 1981). The soil saturated

hydraulic conductivity  $K_s$  was estimated by the pedotransfer function software, Rosetta, developed by Schaap et al. (2001). Initial soil biochemistry and plant biomass chemistry parameters (Appendix A) are not required to be

*Table 1.* Site and biomass parameters at the Chamise watershed, Sequoia and Kings Canyon National Parks.

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Site latitude/longitude: 36°30'42" N, 118°42'23" W Elevation: 710 m

Mean daily minimum temperature, maximum temperature and mean monthly precipitation

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Min. temperature (°C)	2.2	3.9	5.3	7.3	11.2	15.7	19.0	18.7	15.4	10.7	5.2	2.2
Max. temperature (°C)	14.5	16.5	18.1	21.3	26.5	32.2	36.2	35.9	32.6	26.8	18.8	14.9
Precipitation (cm)	12.67	11.05	10.90	6.63	2.51	0.89	0.23	0.24	1.31	2.78	7.56	9.95

Annual N deposition ( $\text{g N m}^{-2} \text{ yr}^{-1}$ ) (Data from this study)  
 Total N deposition: 0.77, Wet deposition: 0.28, Dry deposition: 0.49

N fixation ( $\text{g N m}^{-2} \text{ yr}^{-1}$ )  
 Symbiotic N: 0.2 (Gray and Schlesinger 1981), Non-symbiotic N: 0.1 (Kummerow et al. 1978)

Initial values of soil organic matter pools and plant biomass<sup>a</sup>  
 Litter C storage:  $595 \text{ g C m}^{-2}$  (Gray and Schlesinger 1981), Mineral soil C storage:  $3509 \text{ g C m}^{-2}$  (Huntington and Akeson 1987)  
 Litter C/N: 50.54 (Miller et al. 2005, Mineral soil C/N: 18.55 (Miller et al. 2005)  
 Above ground live biomass:  $1933 \text{ g m}^{-2}$  (Rundel and Parsons 1979)

Fire events  
 Average fire return time interval: 45 years  
 Streamflow and stream  $\text{NO}_3^-$  export calibration parameters<sup>b</sup>  
 BASEF: 0.3 (0.0–1.0), STORMF: 0.5 (0.0–1.0)

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<sup>a</sup>Initial values of soil organic matter pools and plant biomass were not required to be accurate in DAYCENT simulations, but suitable initial values would reduce the time taken for the model to reach equilibrium.

<sup>b</sup>BASEF: The fraction of deep storage soil water which is lost via base flow; STORMF: The fraction of flow which goes into storm flow. The numbers are final values and ranges (in parentheses) for the calibration of streamflow and stream  $\text{NO}_3^-$  export.

*Table 2.* Soil parameters at the Chamise watershed, Sequoia and Kings Canyon National Parks<sup>a</sup>.

Soil depth (cm)	Sand (%)	Silt (%)	Clay (%)	BD ( $\text{g cm}^{-3}$ )	WP ( $\text{cm}^3 \text{ cm}^{-3}$ )	FC ( $\text{cm}^3 \text{ cm}^{-3}$ )	$K_s^b$ ( $\text{cm s}^{-1}$ )	pH
0–1	48.0	35.2	16.8	1.1	0.34	0.17	0.00359 (0.00351–0.00367)	6.0
1–4	48.0	35.2	16.8	1.1	0.34	0.17	0.00359 (0.00351–0.00367)	6.0
4–15	48.0	35.2	16.8	1.1	0.34	0.17	0.00359 (0.00351–0.00367)	6.0
15–54	33.8	29.4	36.8	1.3	0.48	0.28	0.00126 (0.00116–0.00136)	6.2
54–90	35.6	28.2	36.2	1.3	0.50	0.30	0.00129 (0.00119–0.00139)	6.3
90–125	45.2	30.7	24.1	1.3	0.39	0.24	0.00293 (0.00273–0.00313)	6.4
125–150+	50.2	27.4	22.4	1.3	0.34	0.24	0.00307 (0.00293–0.00321)	6.5

<sup>a</sup>All soil parameters are from Huntington and Akeson (1987) except for  $K_s$ . WP is soil moisture at wilting point. FC is soil moisture at field capacity.  $K_s$  is saturated hydraulic conductivity.

<sup>b</sup> $K_s$  was estimated by a pedotransfer functions software Rosetta version 1.2 (Schaap et al. 2001). The numbers are final values and ranges for calibration (in parentheses).



accurate, but suitable values greatly reduce the time taken for the model to reach equilibrium.

Daily stream flow and  $\text{NO}_3^-$  export data (1985–1999) at Chamise Creek were obtained from the literature (Fenn et al. 2003c).

Fire return intervals and fire severity were estimated by an expert on chaparral fire ecology (J. Keeley, personal communication, 2003). For the fire return intervals, we used actual recorded data in the model simulation period of 1901–2001. Two fire events since 1901 at the study site were recorded during July 5 to July 17 of 1921 and June 26 to August 26 of 1960. Prior to the 20th century, the actual fire data were not available for the study site. Keeley (personal communication, 2003) estimated that the fire return interval for foothill chaparral located at Chamise watershed was 30 to 60 years. We assumed a fire event every 45 years in the model simulation period of 0–1900. The fire severity parameters are listed in Table 3. We assumed that the burned biomass fractions during each fire event were 95, 95, 99, 99 and 95% for live shoots, standing dead plant material, surface litter, dead fine branches, and dead stems, respectively. C and N return fractions for each fire event were 2% and 5% from the burned above ground material respectively. Root/shoot ratio was set as 0.2 to account for the additive effect of burning. The DAYCENT model does not consider the fire effects on SOM pools, soil temperature and decomposition, and hydrologic processes.

Table 3. DAYCENT fire parameters at the Chamise watershed, Sequoia and Kings Canyon National Parks<sup>a</sup>.

Parameter	Value	Description
FLFREM	0.95	fraction of live shoots removed by a fire event
FDREM(1)	0.95	fraction of standing dead plant material removed by a fire event
FDREM(2)	0.99	fraction of surface litter removed by a fire event
FDREM(3)	0.99	fraction of dead fine branches removed by a fire event
FDREM(4)	0.95	fraction of dead large wood removed by a fire event
FRET(1,1)	0.02	fraction of C in the burned aboveground material returned to the system following a fire event
FRET(1,2)	0.05	fraction of N in the burned aboveground material returned to the system following a fire event
FRET(2,1)	0.003	fraction of C in the burned dead fine branch material returned to the system following a fire event
FRET(2,2)	0.20	fraction of N in the burned dead fine branch material returned to the system following a fire event
FRET(3,1)	0.003	fraction of C in the burned dead large wood material returned to the system following a fire event
FRET(3,2)	0.05	fraction of N in the burned dead large wood material returned to the system following a fire event
FRTSH	0.20	additive effect of burning on root/shoot ratio
FNUE(1)	10.00	effect of fire on increase in maximum C/N ratio of shoots
FNUE(2)	20.00	effect of fire on increase in maximum C/N ratio of roots

<sup>a</sup>Initial parameter values are not required to be accurate, but suitable values greatly reduce the time taken for the model to reach.



To assess sensitivity to changes in atmospheric deposition of nitrogen, four levels of atmospheric deposition (wet plus dry) were simulated for our study. The lowest level ( $0.1 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) represents the rate with background value (Galloway et al. 1995). The highest level ( $10 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) represents the highest levels observed in southern California (Meixner and Fenn 2004). The simulations were also conducted with current rate ( $0.77 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) and twice the current rate of atmospheric deposition ( $1.54 \text{ g N m}^{-2} \text{ yr}^{-1}$ ).

### Simulation procedure and model calibration

Long runs of DAYCENT (2001 years) were executed to ensure equilibrium of the modeled ecosystem. We analyzed the last 31 years of output (1971–2001) since most observations fell in this time period. We used the last 101 years of output (1901–2001) for analysis of fire disturbance. When we ran the 2001 year simulation, we used the entire available weather data set of 1949–2001 and started reading the weather file at the beginning of the simulation. This record was then repeated. The model period of 2001 years is generally sufficient for SOM pools to reach steady state. We checked our simulations for equilibrium conditions by comparing the change of summary amount of active, slow and passive SOM pools (parameter: SOMSC in output file). This comparison was made between the same months of the following years during non-fire time period. The change of SOMSC values after 1901 was less than 5% so we believed that the system had reached equilibrium.

The data set of daily stream flow and  $\text{NO}_3^-$  export was split into two periods for model calibration (1985–1995) and validation (1996–1999). All parameter values were fixed with these estimates described in above section “Study site and data sources” except for three parameters used for calibration of stream flow and  $\text{NO}_3^-$  export. These parameters used for calibration were BASEF, STORMF and  $K_s$  (Tables 1 and 2), which represented fractions of base flow and storm flow and soil saturated hydraulic conductivity. The value range of BASEF or STORMF was 0–1.  $K_s$  value range was determined by the value and uncertainty estimates from a pedotransfer function software (Schaap et al. 2001). We manually adjusted the above three parameter values until the model outputs of daily stream flow and  $\text{NO}_3^-$  export best fitted the observations during the calibration period 1985–1995. The observed daily flow and  $\text{NO}_3^-$  export during 1996–1999 were used for model validation (Figure 4). The  $R^2$  values between our model simulations and observations for daily flow and  $\text{NO}_3^-$  export was 0.131 and 0.011 during calibration period, and 0.030 and 0.130 during validation period, respectively.

These other environmental variables represent a cross check on our calibrated model. The observed values from literature, such as biomass, net primary productivity, soil C and N storage and seasonal net N mineralization, were used to evaluate model performance.

We simulated C and N storages and fluxes under various N deposition scenarios. The annual and average monthly values of decomposition factor (DF) or the ratio of precipitation to potential evapotranspiration (P/PET) were used in the analysis of results. The DF represents the combined effect of soil temperature and water on SOM decomposition, which is a function of soil temperature and water filled pore space (WFPS). Annual stream flow and  $\text{NO}_3^-$  export were summarized by water year. Each water year indicates the time period from October 1st to the following September 30th.

Fire effects on C and N dynamics during 1901–2001 were analyzed through comparison of carbon and nitrogen storages and fluxes between fire and non-fire model simulations.

### Statistical analyses

Variations of C and N fluxes between years or months were indicated as the coefficient of variation (CV%), which is calculated as

$$\text{CV}\% = \frac{\sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}}{\bar{x}} \times 100\% \quad (1)$$

where  $x_i$  is the observed or simulated value,  $\bar{x}$  is the mean value, and  $n$  is the number of samples.

The Nash–Sutcliffe coefficient (Nash and Sutcliffe 1970) was used to evaluate model predictions for stream flow and stream  $\text{NO}_3^-$  export:

$$E = 1 - \frac{\sum_{i=1}^n (Q_{mi} - Q_{pi})^2}{\sum_{i=1}^n (Q_{mi} - \bar{Q}_m)^2} \quad (2)$$

where  $Q_{mi}$  is the measured value,  $Q_{pi}$  is predicted value, and  $\bar{Q}_m$  is the average measured value.  $E$  indicates how well the plot of measured versus predicted values fits the 1:1 line.  $E$  varies from negative infinity to 1. The value of 1 indicates a perfect fit; a value of zero would indicate that the model is merely as good as the mean of observations in predicting fluxes while a negative value indicates the model is inferior to the mean in predicting environmental conditions.

### Results

#### *C and N pools and average annual fluxes*

All observed data in Table 4 were collected from previous studies at the Chamise watershed (Rundel and Parsons 1979, 1980; Huntington and

Table 4. Simulated and observed carbon and nitrogen pools in the chaparral ecosystem of Chamise watershed ( $\text{g m}^{-2}$ ).

Plant <sup>a</sup>	C		N		Soil (10 cm)	C or N	
	Observed <sup>a</sup>	Simulated <sup>b</sup>	Observed <sup>c</sup>	Simulated <sup>b</sup>		Observed	Simulated <sup>b</sup>
Leaves	99	58	1.87	2.41	Total soil organic C <sup>d</sup>	3405	3029
Stems <sup>e</sup>	771	664	6.44	6.14	Total soil N <sup>f</sup>	258	202
Roots	N/A	415	5.77	4.86	Soil mineral N <sup>f</sup>	3.74	2.47

<sup>a</sup>Observed plant biomass data were from Rundel and Parsons (1979), multiplied by 0.45 to convert biomass to g carbon.

<sup>b</sup>Simulated values are mean for last 31 years of a 2001 year simulation.

<sup>c</sup>Observed plant nitrogen data was from Rundel and Parsons (1980). The field nitrogen and biomass data were measured at the same year and same location.

<sup>d</sup>Observed total soil organic carbon data was from Huntington and Akeson (1987).

<sup>e</sup>Simulated carbon or nitrogen contents of stems were summarized from large wood and fine branch.

<sup>f</sup>Observed soil mineral N data was from Rundel and Parsons (1980).

Akeson 1987). Overall, simulated total C and N pools in plants and soil were close to most observed values (Table 4). The above ground biomass C was  $722 \text{ g C m}^{-2} \text{ yr}^{-1}$  for simulation and  $870 \text{ g C m}^{-2} \text{ yr}^{-1}$  for observation. The modeled C allocation proportion to leaves was lower than the observed value. The simulated C in leaf biomass was 41% lower than the observed value while the simulated C in stem biomass was 14% lower than the observed value. The total plant N was  $13.4 \text{ g N m}^{-2} \text{ yr}^{-1}$  for simulation and  $14.1 \text{ g N m}^{-2} \text{ yr}^{-1}$  for observation. The modeled N allocation in leaf was 29% higher than observed value while the simulated N in stem and root was 5% and 16% lower than their observed values, respectively. The simulated values for total soil organic C and N and soil mineral pools were lower than the observed values.

On an average annual basis, DAYCENT simulations matched the magnitude of the observations for net primary production (NPP), plant N uptake, net N mineralization and stream  $\text{NO}_3^-$  export, but the accuracy of simulations varied (Table 5). For example, the simulated NPP ( $234 \text{ g C m}^{-2} \text{ yr}^{-1}$ ) was 21% higher than the value ( $194 \text{ g C m}^{-2} \text{ yr}^{-1}$ ) observed from the Echo Valley near San Diego of California, which is representative of the Chamise study site (Mooney and Rundel 1979). The model under predicted stream  $\text{NO}_3^-$  export ( $0.024 \text{ g N m}^{-2} \text{ yr}^{-1}$ ), but the order of magnitude of the observation was captured. The simulated value of N uptake is  $6.9 \text{ g N m}^{-2} \text{ yr}^{-1}$ , which is close to simulated net N mineralization ( $6.3 \text{ g N m}^{-2} \text{ yr}^{-1}$ ). The model simulated higher values of gaseous N flux ( $0.4 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) than that of stream  $\text{NO}_3^-$  export ( $0.015 \text{ g N m}^{-2} \text{ yr}^{-1}$ ). The simulation also captured the seasonal pattern of net N mineralization, but observed values had higher seasonal variation (P. Matson, personal communication, 1985).

Table 5. Simulated and observed carbon and nitrogen fluxes in the chaparral ecosystem of Chamise watershed.

Annual C or N fluxes (g C or N m <sup>-2</sup> yr <sup>-1</sup> )			Net N mineralization (top 10 cm, g m <sup>-2</sup> month <sup>-1</sup> ), 1985		
	Observed	Simulated <sup>a</sup>	Observed <sup>b</sup>	Simulated	
Net primary production					
Above ground C <sup>c</sup>	163	189	Early spring	0.21	0.35
Below ground C <sup>c</sup>	58	45	Late spring	0.87	0.56
Plant uptake N	N/A	6.9	Summer	0.02	0.14
NO <sub>3</sub> <sup>-</sup> export <sup>d</sup>	0.024	0.015			
NO + N <sub>2</sub> O emissions	N/A	0.4			
Net N mineralization	N/A	6.3			

<sup>a</sup>Simulated NO<sub>3</sub><sup>-</sup> export is mean of the values during 1985–1998, and all other simulated values of annual C or N are means for last 31 years of a 2001 years simulation.

<sup>b</sup>Observed net N mineralization format Chamise watershed from P. Matson (personal communication, 1985).

<sup>c</sup>Observed annual above and below ground net primary production and plant uptake nitrogen data were from another similar site – the Echo Valley near San Diego, California, estimated by Mooney and Rundel (1979), multiplied by 0.45 to convert biomass to g carbon.

<sup>d</sup>Observed annual NO<sub>3</sub><sup>-</sup> export is mean of the values during 1985–1998.

### *C and N pools and annual fluxes at different deposition levels*

Our modeled C and N pools and fluxes showed different sensitivities to changes in N deposition rate (Table 6). Under a 2 × N deposition rate, predicted rates of N loss through NO<sub>3</sub><sup>-</sup> export increased approximately 4-fold; predicted rates of gaseous N emission doubled. If the deposition rate

Table 6. Simulated C and N fluxes for the Chamise watershed under various N deposition scenarios<sup>a,b</sup>.

N deposition rate (g N m <sup>-2</sup> yr <sup>-1</sup> )	0.1	0.77	1.54	10
Live biomass C (g C m <sup>-2</sup> )	611	1137	1336	2206
Live biomass N (g N m <sup>-2</sup> )	7.45	13.41	15.74	24.81
Total soil organic C (g C m <sup>-2</sup> )	1814	3029	3490	5392
Total soil N (g N m <sup>-2</sup> )	128	202	227	325
NPP (g C m <sup>-2</sup> yr <sup>-1</sup> )	185	234	29	295
N uptake (g N m <sup>-2</sup> yr <sup>-1</sup> )	4.3	6.9	8.2	12.5
Net N mineralization (g N m <sup>-2</sup> yr <sup>-1</sup> )	4.1	6.3	6.6	7.7
NO <sub>3</sub> <sup>-</sup> export (g N m <sup>-2</sup> yr <sup>-1</sup> )	0.0003	0.0110	0.0412	0.6804
DON export (g N m <sup>-2</sup> yr <sup>-1</sup> )	0.0095	0.0181	0.0219	0.0231
N <sub>2</sub> O emission (g N m <sup>-2</sup> yr <sup>-1</sup> )	0.002	0.0096	0.0233	0.1048
NO emission (g N m <sup>-2</sup> yr <sup>-1</sup> )	0.078	0.417	0.887	4.325

<sup>a</sup>N deposition of 0.77 g N m<sup>-2</sup> yr<sup>-1</sup> represents current N deposition rate. 1.54 g N m<sup>-2</sup> yr<sup>-1</sup> represents the double of the current level. 0.1 g N m<sup>-2</sup> yr<sup>-1</sup> represents the rate with background value. 10 g N m<sup>-2</sup> yr<sup>-1</sup> represents the highest deposition level observed in southern California mountains.

<sup>b</sup>Simulated values are means for last 31 years of a 2001 year simulation.

increased from the current level ( $0.77 \text{ g N m}^{-2} \text{ yr}^{-1}$ ) to  $10 \text{ g N m}^{-2} \text{ yr}^{-1}$  (13-fold), predicted rates of N losses through  $\text{NO}_3^-$  export and gaseous N emissions ( $\text{N}_2\text{O}$  plus  $\text{NO}$ ) were 62 and 10 times higher, but predicted N loss through gaseous emissions would be 7-fold higher than predicted  $\text{NO}_3^-$  losses through predicted stream flow. NPP, N uptake and net N mineralization, however, increased by smaller proportions than the N losses under higher deposition scenarios (Table 6). Predicted plant and soil C and N storage increased when deposition rate increased although there was little influence on dissolved organic N (DON) export. If the deposition rate was reduced from current level to  $0.1 \text{ g N m}^{-2} \text{ yr}^{-1}$  (13% of current N deposition), predicted N losses through  $\text{NO}_3^-$  export, DON export and gaseous N emissions reduced by 97%, 47% and 81%, respectively.

### Annual water, C and N dynamics

Model simulations of C and N fluxes, stream flow and  $\text{NO}_3^-$  export exhibited significant fluctuations at a decadal-scale (Figures 3 and 4). In most simulation years, the changing patterns of net primary production and N uptake followed that of P/PET. The changing patterns of gross and net N mineralization followed that of the decomposition factor, which reflected variations in soil temperature and moisture. Variations in  $\text{N}_2\text{O}$  or  $\text{NO}$  flux only partly followed

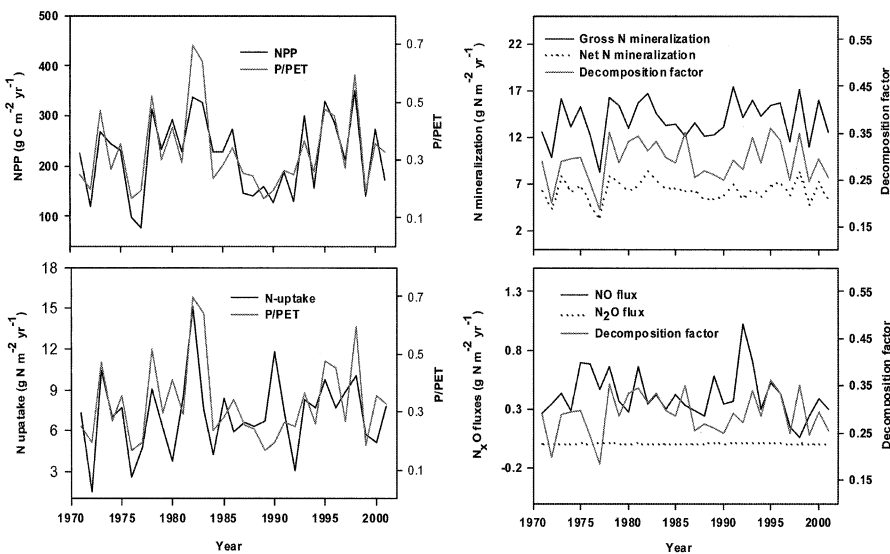


Figure 3. Simulated annual C&N fluxes at Chamise: 1971-2001. P/PET represents the ratio of precipitation to potential evapotranspiration. Decomposition factor represents the combined effect of soil temperature and water on decomposition of soil organic matter. The modeled annual C and N fluxes generally follow the pattern of P/PET or the decomposition factor.

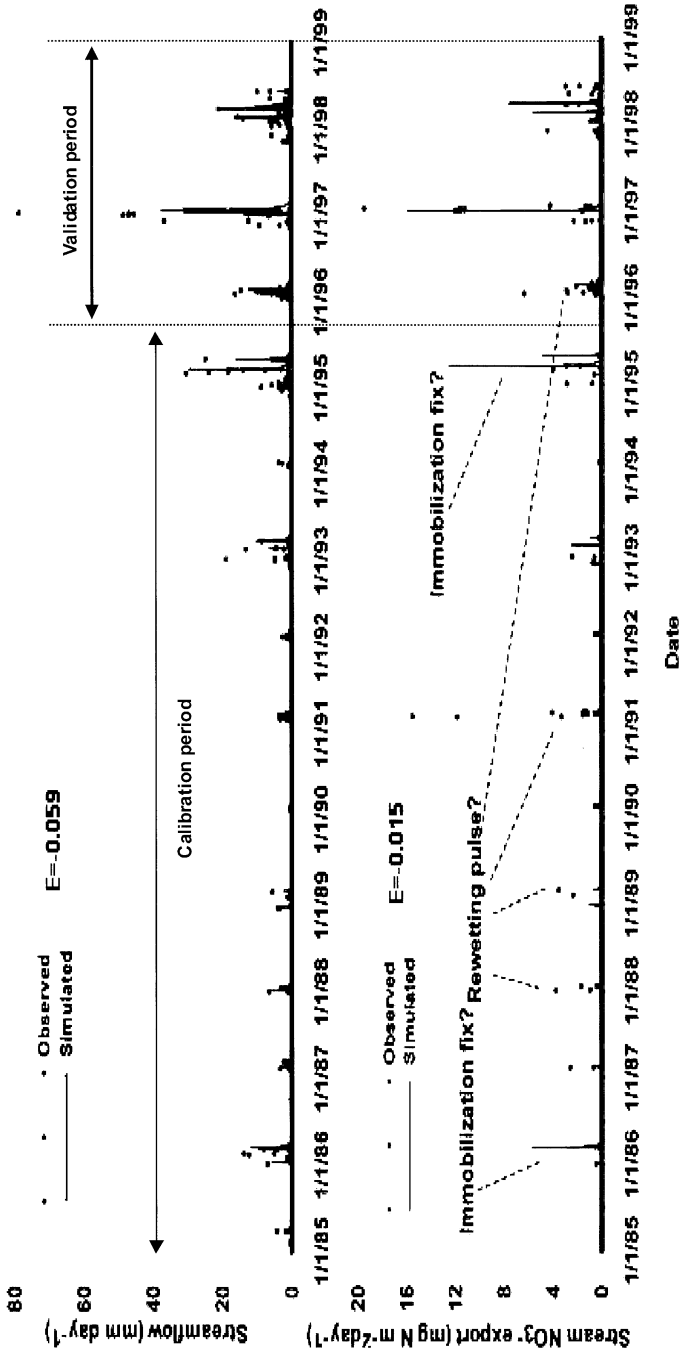


Figure 4. Simulated and observed daily stream flow and stream  $\text{NO}_3^-$  export at Chamise watershed: 1985-1999. The observed peaks of  $\text{NO}_3^-$  export in water years of 1988, 1989, 1991 and 1996 are assumed to be caused by rewetting pulses of mineralization that are not captured by DAYCENT. The peaks of  $\text{NO}_3^-$  export in water years of 1986 and 1995 are assumed to be caused by the underestimation of microbial N immobilization. The observed data during water years of 1985-1995 were used for calibration, and the data of 1996-1999 were used for validation. The correlation coefficient  $R^2$  of stream flow is 0.131 and 0.0030 for calibration and validation, respectively; the  $R^2$  value of  $\text{NO}_3^-$  export is 0.011 and 0.130 for calibration and validation, respectively.

the changes of soil temperature and moisture. The simulated average annual net N mineralization was  $6.3 \text{ g N m}^{-2} \text{ yr}^{-1}$ , which accounted for 45% of the simulated gross N mineralization ( $13.9 \text{ g N m}^{-2} \text{ yr}^{-1}$ ). NO was the dominant gaseous N flux in the model simulation. Simulated  $\text{N}_2\text{O}$  was as low as  $0.0096 \text{ g N m}^{-2} \text{ yr}^{-1}$  compared with  $0.42 \text{ g N m}^{-2} \text{ yr}^{-1}$  of NO flux. During 1971–2001, the modeled NPP, N uptake, net N mineralization and gaseous N (NO plus  $\text{N}_2\text{O}$ ) emission, stream flow and  $\text{NO}_3^-$  export showed substantial variations among years (Table 7). For example, stream flow and  $\text{NO}_3^-$  export had a CV of 169% and 144%, respectively.

The simulation for annual stream flow was consistent with the observations except for the high peak in the 1997 water year (Figure 4). However, the model failed in the simulation of annual stream  $\text{NO}_3^-$  export although the simulation was consistent with the magnitude of observations at the average annual level for the simulation period as a whole. The observed peaks in the water years of 1987, 1988, 1989, 1991 and 1996 were not captured by the simulation while the model produced peaks in 1986 and 1995 that did not occur in the observed record.

#### *Seasonal water, C and N dynamics*

The simulated average monthly values of C and N fluxes and stream flow for the Chamise watershed showed strong seasonal patterns (Figures 5 and 6). Modeled NPP, gross and net N mineralization, and NO and  $\text{N}_2\text{O}$  fluxes followed the changes of soil moisture and temperature through the seasons, and had higher values in the winter and spring months, and low values in the summer months. Modeled plant N uptake, however, did not follow the same pattern, but had higher values in late winter and spring months, lower values in summer and autumn months, and peaked in February. The modeled N uptake declined in March and April, but N mineralization still remained high during this time period, and gaseous N fluxes and stream  $\text{NO}_3^-$  export could not account for the difference (Figure 5). We assumed this difference was made up for by mineral N accumulation in the soil, however, further measurements are needed to demonstrate whether or not the model correctly simulated N uptake.

The simulations were compared with observations for average monthly stream flow and  $\text{NO}_3^-$  export at Chamise watershed during water years 1985–1999 (Figure 6). Stream flow and stream  $\text{NO}_3^-$  export mostly occurred in winter and spring months (December through next April) (Figure 6). The model captured this characteristic, but underestimated both stream flow and stream  $\text{NO}_3^-$  export in January, and overestimated them in April. The observed values were high in January for both stream flow and  $\text{NO}_3^-$  export. They were  $45.1 \text{ mm month}^{-1}$  for stream flow and  $14.1 \text{ mg N m}^{-2} \text{ month}^{-1}$  for  $\text{NO}_3^-$  export, which accounted for 51% and 59% of their annual values, respectively. Their simulated values in January were only  $18.6 \text{ mm month}^{-1}$  and  $3.0 \text{ mg N m}^{-2} \text{ month}^{-1}$ , which accounted for 25% and 20% of their annual values, respectively.



Table 7. Statistical values indicating the average values and variations of annual and monthly C and N fluxes in Chamise watershed<sup>a</sup>.

	Annual			Monthly		
	Mean	CV(%)	Low-high range	Mean	CV(%)	Low-high range
Simulated NPP (g C m <sup>-2</sup> )	234	34.95	78–352	19.5	85.55	0.97–49.89
Simulated N uptake (g N m <sup>-2</sup> )	6.9	38.31	15–14.5	0.58	119.40	0.017–1.95
Simulated Net N mineralization (g N m <sup>-2</sup> )	6.3	18.57	3.2–8.4	0.53	58.56	0.09–0.98
Observed streamflow (mm)	87.37	178.53	0.91–592.56	7.28	178.32	0–45.12
Simulated streamflow (mm)	74.47	169.33	0.0034–318.43	6.21	133.51	0.002–18.61
Observed NO <sub>3</sub> <sup>-</sup> export (g N m <sup>-2</sup> )	0.024	187.19	0.000014–0.14	0.0020	207.36	0–0.011
Simulated NO <sub>3</sub> <sup>-</sup> export (g N m <sup>-2</sup> )	0.015	144.30	0–0.046	0.0013	152.34	0–0.005
N <sub>2</sub> O emission (g N m <sup>-2</sup> )	0.0096	37.53	0.0045–0.021	0.0083	28.33	0.00046–0.0011
NO emission (g N m <sup>-2</sup> )	0.417	470.4	0.08–1.04	0.035	40.10	0.018–0.059

<sup>a</sup>Simulated or observed mineral N export is summarized from the data during 1985–1998. All other data are summarized from the simulated values in last 31 years of a 2001 years simulation.

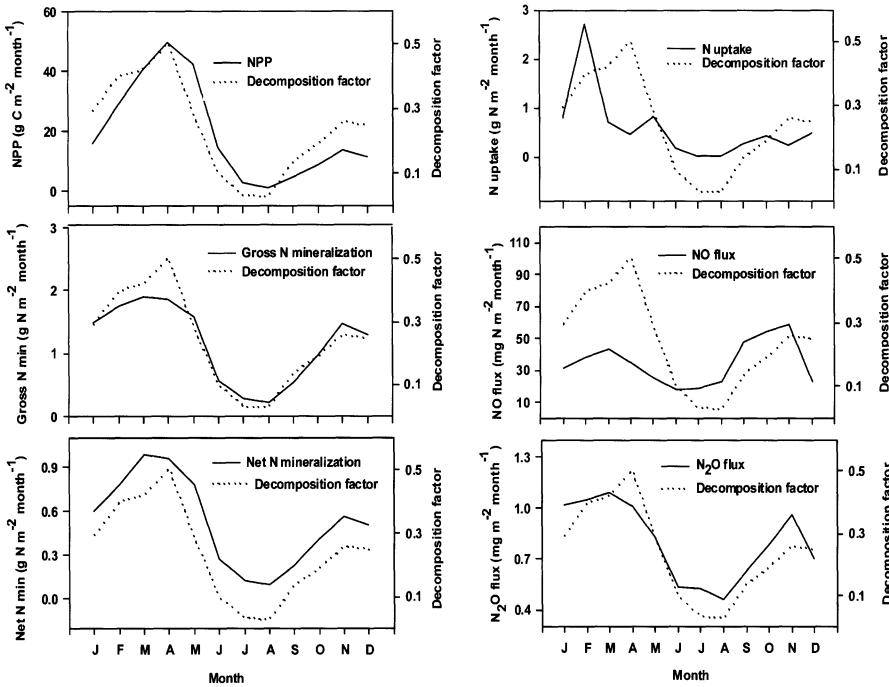


Figure 5. Simulated average monthly C&N fluxes at Chamise watershed: 1971–2001. Decomposition factor represents the combined effect of soil temperature and water on decomposition of soil organic matter. The modeled seasonal C and N fluxes generally follow the pattern of the decomposition factor.

#### *Daily stream flow and stream $\text{NO}_3^-$ export*

Figure 4 shows predicted and observed long term daily stream flow and stream  $\text{NO}_3^-$  export. Overall, the DAYCENT simulations did not fit the observations well. The Nash-Sutcliffe coefficient was  $-0.059$  for daily stream flow and  $-0.015$  for daily stream  $\text{NO}_3^-$  export. DAYCENT was able to simulate most stream flow peaks despite the underestimation in some water years. During water years 1993–1998, fewer flow days occurred in simulations than in the observations. In the water year periods of 1987–1991 and 1996–1997, some peaks of stream  $\text{NO}_3^-$  export were underestimated or missed in the simulation. The model overestimated  $\text{NO}_3^-$  loss through stream flow in the 1986 and 1995 water years.

#### *C and N pools and annual fluxes with and without fire disturbance*

Our DAYCENT model simulations exhibited important impacts of fire on C and N fluxes as well as C and N pools, but the effects varied in both severity

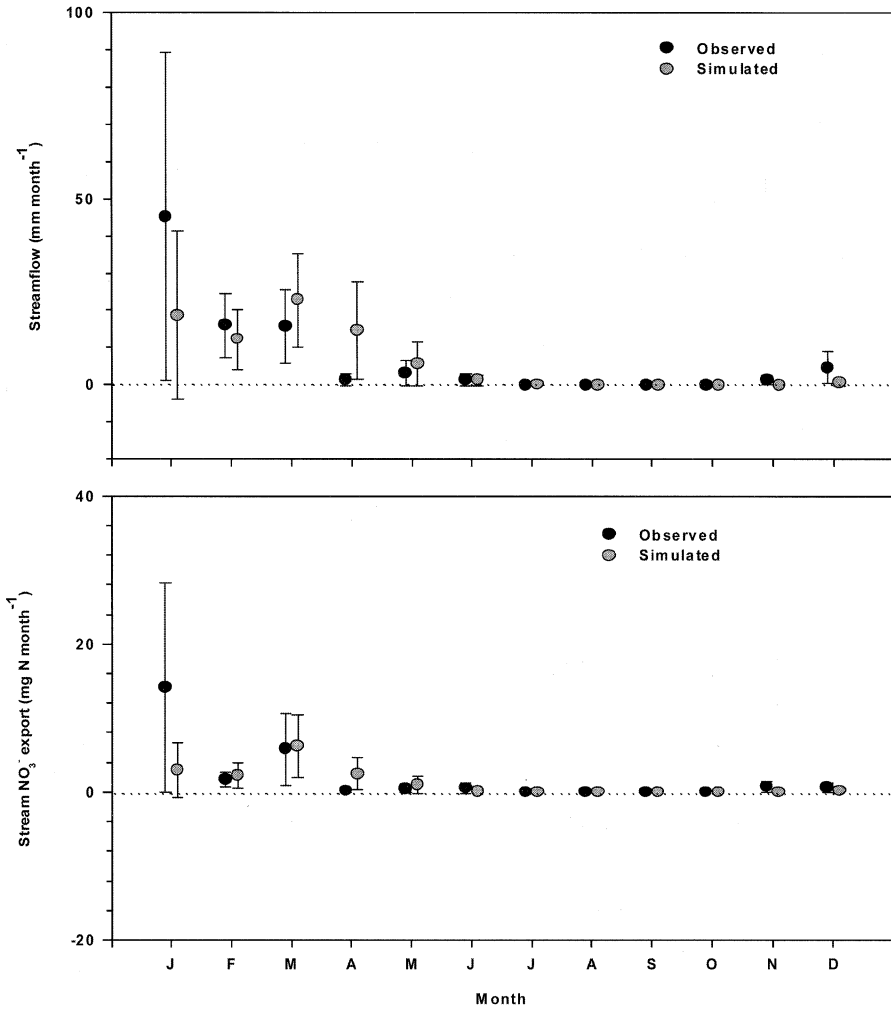


Figure 6. Simulated and observed average monthly stream flow and stream NO<sub>3</sub><sup>-</sup> export at Chamise watershed: 1985–1999. Error bars represent standard errors of the mean for each monthly stream flow or stream NO<sub>3</sub><sup>-</sup> export. Error bars on this graph are one third of their actual error values. DAYCENT captured the seasonal trends of monthly stream flow and stream NO<sub>3</sub><sup>-</sup> export, but failed in allocation among different months during January to April.

and duration (Figure 7). For example, when a 1921 fire event was included in the simulations, predicted NPP for the years 1921, 1922 and 1923 decreased by 94, 66 and 37% relative to predictions obtained when fire was not included. Three years after a fire event, NPP recovered to the same level as simulations without a fire event. Similarly, when a 1921 fire event was included in the simulations, predicted plant N uptake for the years 1921, 1922 and 1923 decreased by 92, 68 and 26% relative to predictions obtained when fire was not

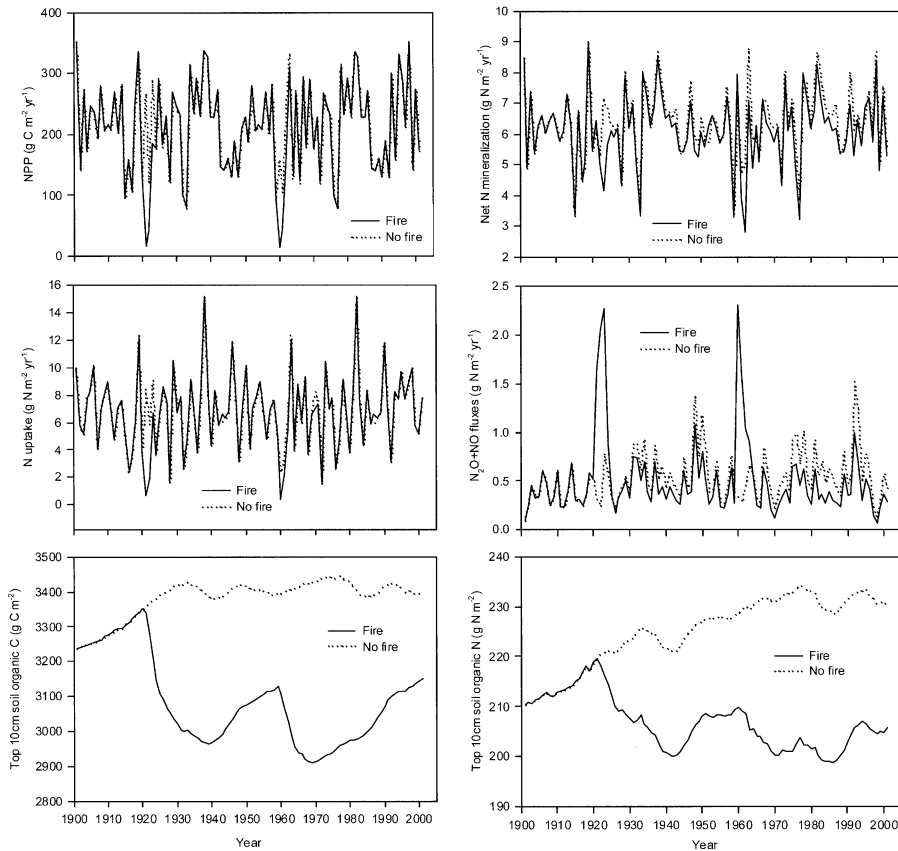


Figure 7. Comparison of fire and non-fire simulations: annual NPP, N uptake, net N mineralization, and  $\text{N}_2\text{O}$  and NO fluxes at Chamise watershed during 1901–2001. Fire events were set for simulations with fire events in 1921 and 1960 based on actual records.

included. Three years after the fire event, plant N uptake recovered to the same level as in simulations without a fire event. When a 1921 fire event was included in the simulations, predicted net N mineralization for years 1921, 1922, 1923 and 1924 sharply decreased by 6, 55, 42 and 17% relative to predictions obtained when fire was not included. This effect continued to decrease annual net N mineralization about 3–6% until the next simulated fire event. When a 1921 fire event was included in the simulations,  $\text{N}_2\text{O}$  and NO emissions dramatically increased by 437, 771, 189 and 55% in 1921, 1922, 1923 and 1924 after a fire event, but decreased by about 10–30% after 1924. A similar pattern was found for the effect of a second fire event that occurred in 1960. In contrast to the relatively short-term nature of fire effects on C and N fluxes, fire effects on C and N storage in soils perished for decades (Figure 7). Predicted soil C and N storage recovered only partially by 1960 when they were further reduced by the next fire event.

## Discussion

### *Net primary production*

The aboveground biomass C of a mature chaparral ecosystem (16 years old or older after fire) in southern California varies between 383 and 2852 g C m<sup>-2</sup>, while the aboveground NPP ranges from 115 to 382 g C m<sup>-2</sup> yr<sup>-1</sup> (Mooney et al. 1977; Mooney and Rundel 1979; Rundel and Parsons 1979; Schlesinger and Gill 1980; Schlesinger et al. 1982; Gray 1983; Parsons and Stohlgren 1986). The Chamise watershed has above ground biomass C of 870 g C m<sup>-2</sup>, which is at the low end of this range. The DAYCENT simulation for total above ground biomass was reasonable at 722 g C m<sup>-2</sup>. There were no NPP data at our site, but the simulated value was close to observed values from a similar chaparral site in the Echo Valley near San Diego, California (Mooney and Rundel 1979) (Table 5). The modeled NPP had high variability among years, ranging from 78 g C m<sup>-2</sup> to 352 g C m<sup>-2</sup> and varied with the annual precipitation to potential evapotranspiration ratio. The simulated monthly NPP followed the change of soil temperature and moisture factors (Figure 5). The simulation agreed with the observed growth trend: more growth occurred during winter and spring seasons, and reached its peak in March or April (Mooney and Rundel 1979).

### *N mineralization, NO<sub>3</sub><sup>-</sup> export, N<sub>2</sub>O and NO fluxes*

Mineralization associated with the decomposition of SOM is a crucial process in any nutrient biogeochemical model (Krug and Winstanley 2002; Li et al. 2004). Our simulation of net N mineralization at the Chamise watershed was consistent with the observations (Table 5), and with reported net N mineralization, 3.6–8.3 g N m<sup>-2</sup> yr<sup>-1</sup>, in the San Bernardino Mountains of southern California (Fenn et al. 1996), with increasing N deposition levels. Our modeled net N mineralization in the chaparral zone of the Sierra Nevada was 6.3 g N m<sup>-2</sup> yr<sup>-1</sup>. This demonstrated DAYCENT was successful in the simulation of N mineralization in the chaparral ecosystem at the annual scale, however, seasonal variations in the simulated net N mineralization were lower than the observations (Table 4). Additionally, the buried bag method used to measure N mineralization rates tends to underestimate the influence from abrupt transitions between dry and wet seasons (P. Matson, personal communication, 1985). Actual net N mineralization rates were expected to be more variable than the observed values and to be higher during seasonal transition periods. Thus, lower seasonal variation in the simulations versus the observations suggested that DAYCENT failed to capture critical influences on the chaparral N cycle such as the abrupt transitions between dry and wet periods.

In an undisturbed terrestrial ecosystem, N is lost through stream export and soil gaseous N emission. In areas of the western United States with a Mediterranean climate, long dry summers, high base cation saturation, low soil C:N ratios, and the aerobic condition of the coarse-textured soils favor high nitrification and gaseous losses of N. For example, trace gas emissions from chaparral and forested areas of the San Gabriel and San Bernardino Mountains in the Los Angeles air basin, produced during nitrification, balance a large proportion of atmospherically deposited N (Fenn et al. 1996). The DAYCENT estimation presented here was consistent with the observations in the San Gabriel and San Bernardino Mountains. At Chamise Creek, the model predicted that gaseous N emissions between 1971 and 2001 reached  $0.4 \text{ g N m}^{-2} \text{ yr}^{-1}$ , which was 56% of the atmospheric N deposition for this study site and thus represented major loss of N from the chaparral ecosystem. Of the gaseous N emission, modeled NO emission was 42 times higher than  $\text{N}_2\text{O}$ . The modeled stream  $\text{NO}_3^-$  export was  $0.015 \text{ g N m}^{-2} \text{ yr}^{-1}$ , which was only 2% of atmospheric N deposition. The observed annual  $\text{NO}_3^-$  export accounted for 3% of annual N deposition. In a typical hardwood forest ecosystem of the northeastern United States with similar atmospheric N deposition level, but lacking abrupt seasonal transitions, observations and DAYCENT simulation showed a much different pattern: stream  $\text{NO}_3^-$  export was much higher than gaseous N emissions (Li et al. 2004). Additionally our results showed that modeled gaseous N emissions were highly variable among years and across seasons. We believed that this variability was caused by inter- and intra-annual variations in Mediterranean climate and the timing of seasonal transitions which impacted soil physico-chemical conditions and control rates of soil microbial processes.

#### *$\text{NO}_3^-$ export at annual, monthly and daily scales*

$\text{NO}_3^-$  export results from an interplay between hydrologic and biogeochemical processes (Holloway and Dahlgren 2001). In DAYCENT,  $\text{NO}_3^-$  export is calculated as a function of stream flow (baseflow plus stormflow) and  $\text{NH}_4^+$  content released from net mineralization in soil. Therefore, for the simulation of stream  $\text{NO}_3^-$  export in a biogeochemical model, the correct calculation of stream flow and net N mineralization are crucial.

In chaparral ecosystems, stream flow export is highly variable. In our study site, runoff occurred during brief periods of intense rainfall in the winter and early spring months (Figure 4). The DAYCENT simulations were generally consistent with observations of stream flow at the annual time scale except for the unusual water year of 1997, in which the annual stream flow was 5.8-fold higher than the average. The monthly simulations of stream flow were underestimated in the months with higher runoff (January and February) and were shifted to the following months (March, April and May) (Figure 6). In wet years (1993, 1995–1998), the beginning of stream flow in each wet season

was not captured or was postponed several days. The poor model performance in these wet years, months or days with storm events suggested that more water was percolating into the soil in the model simulation, but that in reality surface runoff occurred much more readily. Thus, the stream flow simulation in DAYCENT needs to be improved when it is applied to chaparral ecosystems with a Mediterranean climate. Almost all runoff events in the simulations occurred during the seasonal transition periods, from dry season to wet season. The timing and magnitude of runoff events must be accurately simulated in a biogeochemical model to correctly simulate daily to annual time-scale  $\text{NO}_3^-$  export.

At our study site, nitrification was the major source of soil  $\text{NO}_3^-$  due to lower amount of wet deposition and the good aeration status of soil. In DAYCENT, nitrification was calculated as a function of soil ammonium ( $\text{NH}_4^+$ ), water content, temperature, pH, and soil texture (Del Grosso et al. 2002). Mineralization was the major source of soil  $\text{NH}_4^+$  at our study site since the wet deposition was low. Soil temperature and moisture and soil microbial activity were the most important controlling factors in mineralization. Therefore, the control of seasonal transitions on the variations of mineralization and nitrification can be used to explain  $\text{NO}_3^-$  flushes. The simulated annual  $\text{NO}_3^-$  export in dry years, 1988, 1989, 1991 and 1996 was lower than the observed values and not proportional to stream flow if compared with wetter years (Figure 4). We believed that these errors were caused by the lack of seasonal transition controls on soil biogeochemical processes in DAYCENT. The seasonal transition consists of a series of dry-rewetting events. Generally, C and N mineralization rates sharply increase for a few days following the rewetting of a dry soil (Birch 1958; Franzluebbers et al. 2000; Fierer and Schimel 2002, 2003). When a dry soil is rewetted, soil microbial activity is stimulated, and the mineralization rate is often elevated by as much as 500% compared with a soil kept continuously moist (Fierer and Schimel 2003). In chaparral ecosystems, where soils are dry in the summer, the rewetting mineralization pulse may constitute a significant proportion of the total amount of mineralization for the season. This mechanism may be more important in dry years with longer periods between rain events. By comparing observations with simulations, we found that in water years 1987–1989, 1991 and 1996, the average simulated stream flow was 38% lower than the observed value, but the average simulated  $\text{NO}_3^-$  export was 81% lower than the observed value (Figure 4). Greater underestimation of  $\text{NO}_3^-$  export suggests that  $\text{NH}_4^+$  released from mineralization and  $\text{NO}_3^-$  released from nitrification during seasonal transition periods could be underestimated due to lack of rewetting pulses in the model. In water years 1986 and 1995,  $\text{NO}_3^-$  exports were overestimated by the model, which might be caused by the underestimation of microbial N immobilization, but this problem would require further investigation.



*Influence of Increasing N deposition on C and N pools and fluxes*

Under twice ambient N deposition, the DAYCENT model predicted that  $\text{NO}_3^-$  export and gaseous N emissions would increase by 3-fold and by 1-fold, respectively while predicted NPP, N plant uptake and net N mineralization increased slightly (Table 6). These simulations suggested that the chaparral ecosystem of the Chamise watershed was near Stage 1 of N saturation as defined by Fenn et al. (1998) under doubled N loading. Under doubled N deposition rate, modeled stream  $\text{NO}_3^-$  export bore a more sensitive response in a chaparral ecosystem as compared to a high-elevation alpine (Meixner and Bales 2003).

When the deposition rate was increased from the current ambient level of  $0.77 \text{ g N m}^{-2} \text{ yr}^{-1}$  to  $10 \text{ g N m}^{-2} \text{ yr}^{-1}$  (a value similar to mountainous areas of southern California), N inputs exceeded plant N uptake capacity and the predicted rate of N losses through stream flow and gaseous N emissions increased markedly. Increases in the size of predicted N pools in plants and soil (Table 6) indicated that the system had some capacity for sequestering higher levels of N deposition. In southern and central California, most chaparral ecosystems are adjacent to agricultural and urban centers, where ongoing urban expansion is likely to result in greater N deposition in some areas (Fenn et al. 2003b). Our modeling results imply that the exposure of the chaparral ecosystems to elevated N deposition will have higher greenhouse gaseous N emissions than at present, greater flux of smog-forming NO and impaired water quality through greater  $\text{NO}_3^-$  export.

*The overall patterns of C and N pools and fluxes under fire disturbance*

Fire disturbs C and N storages and fluxes through its wide range of impacts on ecosystem processes in chaparral such as: dynamics of biological populations, carbon and nutrient cycling, and hydrologic processes. In DAYCENT, several fire effects are considered, such as the removal of aboveground live and dead materials, and nutrient removal and return, and the effect on root to shoot ratio (Table 3). At decadal scales, the agreement between NPP or plant N uptake with ratio of precipitation to potential evapotranspiration implies that climate generally controls the patterns of NPP or plant N uptake (Figure 4). Fire disturbance may vary greatly from site to site, but most California chaparral shrubs reach their reproductive maturity 3 to 5 years of postfire (Barro and Conard 1991). Our model simulations indicated that the decadal patterns of NPP and N uptake could be dramatically impacted during the 3 years immediately postfire at the Chamise watershed, but this impact became minimal after that (Figure 7). The change in N mineralization agreed with that of the DAYCENT decomposition factor, which was influenced by soil moisture and temperature. Our model simulations indicated that one severe fire event could dramatically influence

soil net N mineralization and N loss through  $\text{NO}_2$  and NO emissions during the first 3 to 4 years after the fire, but the influence on soil organic C and N storages lasted for decades. If we assume our fire effect simulation patterns are true, then the unknown information of fire timing, severity and frequency prior to Euro-American settlement time should not have a big effect on C and N dynamics of recent decades. Due to the lack of actual observed data on long-term C and N dynamics with fire effects, we were unable to verify our simulation results. Several effects of fire disturbance in DAYCENT should be considered in future model modification, including the consideration of fire's impacts on soil temperature and decomposition, N volatilization, soil erosion, and hydrologic processes.

## Conclusions

The DAYCENT model simulations of water, C and N dynamics in a California chaparral ecosystem had variable success for different hydrologic and biogeochemical processes. The average annual C and N pool sizes were successfully simulated although the simulations of C and N allocation among plant tissues were not satisfied. The model captured the characteristic of high gaseous N emissions and low stream  $\text{NO}_3^-$  export in Mediterranean chaparral ecosystems. The consistency of modeled C and N dynamics with field observations generally supported the conclusion that N dynamics were successfully simulated at the decadal-scale using DAYCENT. During 1971–2001, the variation between lowest and highest simulation results of annual NPP, net N mineralization, plant N uptake and gaseous N emissions reached 4.5, 10.0, 2.6 and 13.9 fold, respectively. The DAYCENT soil water submodel successfully simulated annual stream flow except for the unusual water year of 1997. At the monthly time step, both simulation and observation showed an extremely high proportion of N stream flow loss through  $\text{NO}_3^-$  export in a few winter and early spring months. The high seasonal variation of net N mineralization was underestimated by the model simulation during dry years although its seasonal pattern was simulated well. In winter and early spring months with high values of stream flow, peak storm flows were shifted to the following months or incorrectly estimated by the model. At the daily time step, both modeled and observed  $\text{NO}_3^-$  export occurred in a relatively narrow time period in winter and early spring. Errors in stream flow (timing and magnitude) and N mineralization contributed to the underestimation of  $\text{NO}_3^-$  export in some water years. Our study suggests that the representation of N mineralization, catchment runoff and  $\text{NO}_3^-$  export need to be improved within the DAYCENT model for use in chaparral or similar semi-arid ecosystems with pronounced seasonal transitions (e.g., frequent drying-rewetting events). In future research, the effect of dry-rewetting events on stream flow, mineralization and gaseous N emissions should be considered at the event scale, and the mechanism for these short time rewetting pulses should be

incorporated into long-term C and N biogeochemistry models. Our model simulations indicated that predicted N losses through  $\text{NO}_3^-$  export and gaseous N emissions from the chaparral ecosystems of the Sierra Nevada increased under higher N deposition scenarios. Our model simulations on fire disturbance showed dramatic decreased in NPP and plant N uptake during the 3 years immediately postfire, and then recovered to the level of non-fire simulations. Fire disturbance also exhibited dramatic decrease in net N mineralization, and decrease in  $\text{N}_2\text{O}$  and NO emissions, but these effects declined to lower levels and last for the following decades. The fire effects on soil organic C and N storages likely last several decades. Our study suggests that the DAYCENT model needs to be modified for the simulation of fire disturbance in California chaparral ecosystems. The fire effects on soil temperature, SOM decomposition, N volatilization and hydrologic processes need to be considered in future's model modification.

### Acknowledgements

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### Appendix

*Appendix A.* Soil biochemistry, plant biomass chemistry parameters at the Chamise watershed, Sequoia and Kings Canyon National Parks<sup>a</sup>.

Parameter	Value	Description
Parameters of describing atmospheric and soil (non-symbiotic) N fixation		
EPNFA(1)	0.4928 I	Intercept for equation describing atmospheric N deposition, as a function of annual precipitation
EPNFA(2)	0.0041	Slope for equation describing atmospheric N deposition, as a function of annual precipitation
EPNFS(1)	30.0	Intercept for equation describing non-symbiotic N fixation, as a function of annual evapotranspiration
EPNFS(2)	0.0029	Slope for equation describing non-symbiotic N fixation, as a function of annual evapotranspiration
Initial parameter values of C content ( $\text{g C m}^{-2}$ ) in different soil organic matter pools		
SOM1CI(1,1)	71	Initial value for unlabeled C in surface organic matter with fast turnover
SOM1CI(2,1)	123	Initial value for unlabeled C in soil organic matter with fast turnover
SOM2CI(1)	2519	Initial value for unlabeled C in soil organic matter with intermediate turnover

*Appendix A. (Continued).*

Parameter	Value	Description
SOM3CI(1)	1135	Initial value for unlabeled C in soil organic matter with slow turnover
CLITTR(1,1)	256	Initial value for surface unlabeled plant C residue
CLITTR(2,1)	1089	Initial value for surface unlabeled plant C residue
Initial parameter values of C/N in different soil organic matter pools		
RCES1(1,1)	25.3	Initial C/N ratio in surface organic matter with fast turnover
RCES1(2,1)	13.0	Initial C/N ratio in soil organic matter with fast turnover
RCES2(1)	31.3	Initial C/N ratio in soil organic matter with intermediate turnover
RCES3(1)	16.2	Initial C/N ratio in soil organic matter with slow turnover
Initial parameter values of C content ( $\text{g C m}^{-2}$ ) in different plant tissues		
RLVCIS(1)	197	Initial value for unlabeled C in leaves
FRTCIS(1)	896	Initial value for unlabeled C in fine roots
FBRCIS(1)	947	Initial value for unlabeled C in fine branches
RLWCIS(1)	407	Initial value for unlabeled C in large wood
CRTCIS(1)	112	Initial value for unlabeled C in coarse roots
Initial parameter values of N content ( $\text{g N m}^{-2}$ ) in different plant tissues		
RLEAVE(1)	1.38	Initial value for N in leaves
FROOTE(1)	18.81	Initial value for N in fine roots
BRCHE(1)	22.73	Initial value for N in fine branches
RLWODE(1)	9.74	Initial value for N in large wood
CROOTE(1)	2.35	Initial value for N in coarse roots
Parameters of plant tissue C/N		
CERFOR(1,1,1)	20	Minimum C/N ratio for leaves
CERFOR(2,1,1)	59	Maximum C/N ratio for leaves
CERFOR(3,1,1)	59	Initial C/N ratio for leaves
CERFOR(1,2,1)	40	Minimum C/N ratio for fine roots
CERFOR(2,2,1)	50	Maximum C/N ratio for fine roots
CERFOR(3,2,1)	50	Initial C/N ratio for fine roots
CERFOR(1,3,1)	62	Minimum C/N ratio for fine branches
CERFOR(2,3,1)	85	Maximum C/N ratio for fine branches
CERFOR(3,3,1)	70	Initial C/N ratio for fine branches
CERFOR(1,4,1)	150	Minimum C/N ratio for large wood
CERFOR(2,4,1)	240	Maximum C/N ratio for large wood
CERFOR(3,4,1)	240	Initial C/N ratio for large wood
CERFOR(1,5,1)	150	Minimum C/N ratio for coarse roots
CERFOR(2,5,1)	240	Maximum C/N ratio for coarse roots
CERFOR(3,5,1)	240	Initial C/N ratio for coarse roots

<sup>a</sup>Initial parameter values are not required to be accurate, but suitable values greatly reduce the time taken for the model to reach equilibrium.

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