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Chronic Nitrogen Deposition Enhances Nitrogen Mineralization Potential of Semiarid Shrubland Soils

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Semiarid chaparral and coastal sage shrublands of southern California have been exposed to high levels of atmospheric N for decades, which has the capacity to increase both N and C storage and cycling in these N-limited systems. Thus we hypothesize that soil C and N mineralization will be higher in areas that have been exposed to high atmospheric N deposition. This hypothesis was tested in a 50-wk laboratory incubation experiment where the inorganic N (NH_4 + NO_3) and CO_2 production of chaparral and coastal sage soils were repeatedly measured. Soil was incubated in the dark at a constant temperature of 25°C and a soil moisture of 0.25 kg H_2O kg^{-1} dry soil (65% water-filled pore space). Relative differences in N deposition exposure between the study sites were quantified by repeatedly rinsing and collecting the N accumulated on branch surfaces during 1 yr. Temporal trends in cumulative C and N mineralization were best described by single-pool first-order and zero-order models, respectively. Total N mineralization, but not C mineralization, increased linearly with relative N deposition, and NO_3 accounted for 95% of the total inorganic N accumulated during the 50-wk incubation. The soil δ^{15}N natural abundance increased with relative N deposition (r = 0.85, P < 0.05) and the soil C/N ratio declined with relative N deposition (r = −0.74, P < 0.05), suggesting that N deposition exposure enhanced N mineralization in part because of increases in the soil organic matter quality (i.e., lower C/N ratio). Furthermore, soil C storage declined as a function of relative N deposition exposure, indicating that high atmospheric N inputs are not likely to stimulate soil C storage in these semiarid ecosystems.

Abbreviations: δ^{15}N, ratio of ^{15}N/^{14}N of a sample relative to a standard; MRR, Motte Rimrock Reserve; SDEF, San Dimas Experimental Forest; SLW, specific leaf weight; SMER, Santa Margarita Ecological Reserve; SOFS, Sky Oaks Field Station.

Anthropogenic N deposition represents a significant input of N into southern Californian semiarid shrublands, including evergreen chaparral and drought-deciduous coastal sage (Westman, 1981; Bytnerowicz and Fenn, 1996; Padgett et al., 1999; Fenn et al., 2003b). Concentrations of atmospheric N in urban areas of Riverside and San Bernardino counties are 20 times higher than in remote areas, resulting in 25 to 50 kg N ha^{-1} to be deposited to urban shrublands annually (Bytnerowicz and Fenn, 1996; Meixner and Fenn, 2004). Most atmospheric N (85%) accumulates as dry deposition on vegetation and soil surfaces during the summer and fall when primary production is limited by drought and becomes available as a large and ephemeral pulse after the first rainfall event (Bytnerowicz and Fenn, 1996; Fenn et al., 2003a).

Nitrogen enrichment of soil and shrub tissue has been reported in semiarid forests and shrublands exposed to chronic, high N deposition (Fenn et al., 1996; Padgett et al., 1999; Korontzi et al., 2000; Vourlitis and Zorba, 2007; Vourlitis et al., 2007). Soil N enrichment has the potential to stimulate N mineralization through direct fertilization and by altering soil organic matter and litter quality (Marion and Black, 1988; Fenn et al., 1996, 2003a; Vitousek et al., 1997; Currie, 1999; Padgett et al., 1999; Korontzi et al., 2000; Li et al., 2006; Vourlitis and Zorba, 2007). Nitrification is rapid in western soils, however (Fenn et al., 1996; Vourlitis and Zorba, 2007), and because NO_3 is highly mobile in soil (Paul and Clark, 1989), shrublands and forests exposed to high N deposition can also be large sources of NO_3 to aquatic systems (Riggan et al., 1985; Fenn and Poth, 1999; Meixner and Fenn, 2004).

In N-limited systems, such as chaparral and coastal sage (Mooney and Rundel, 1979; Westman, 1981; Gray and Schlesinger, 1983), increases in atmospheric N input and retention can also cause an increase in C storage and cycling because tight coupling between C and N cycles causes changes in N storage to be matched by changes in C storage (Vitousek and Howarth, 1991; Rastetter et al., 1992; Asner et al., 1997). The soil and vegetation C/N ratios of semiarid forests and shrublands is often observed to decline, however, following exposure to N deposition (Fenn et al., 2003a; Korontzi et al., 2000; Vourlitis and Zorba, 2007; Vourlitis et al., 2007), suggesting that atmospheric N inputs have little effect on soil C storage in these systems. Rather, declines in soil C/N ratios imply higher rates of soil organic matter decomposition and CO_2 emission (Micks et al., 2004), which could potentially offset any gain in soil C in response to atmospheric N deposition.

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Table 1. Location and selected characteristics for the Santa Margarita Ecological Reserve (SMER), Motte Rimrock Reserve (MRR), Sky Oaks Field Station (SOFS), and San Dimas Experimental Forest (SDEF) study sites. Soil and relative N deposition data are mean (±SE, n = 4) for the upper 0- to 10-cm soil layer sampled in September 2002. Rainfall data were obtained from the Western Regional Climate Center (www.wrcc.dri.edu, verified 6 Feb. 2007) for locales near the study sites and represent >50-yr averages.

Characteristic	SMER	MRR	SOFS	SDEF
Latitude and longitude	33°29′, 117°09′	33°48′, 117°15′	33°21′, 116°34′	34°10′,117°44′
Vegetation	Coastal sage	Coastal sage	Chaparral	Chaparral
Elevation, m	338	485	1418	451
Stand age, yr†	35	24	50	42
Annual rainfall, cm	33	28	57	44
Relative N deposition, mg N m^{-2}	22.6 ± 2.2	83.6 ± 13.7	10.6 ± 2.8	32.2 ± 5.8
Soil texture class	Sandy clay loam	Sandy clay loam	Sandy loam	Sandy loam
Soil taxonomy‡	Lithic Haploxeroll	Typic Xerorthern	Ultic Haploxeroll	Typic Xerorthent
Soil N, g N m^{-2}	101.3 ± 13.6	118.9 ± 11.5	98.1 ± 6.9	137.2 ± 22.3
Soil C, kg C m^{-2}	1.4 ± 0.2	1.4 ± 0.2	2.3 ± 0.1	1.7 ± 0.3
Soil C/N	14.1± 0.3	11.9 ± 0.2	23.6 ± 1.0	12.6 ± 0.3
Soil $\delta^{15}N$, ‰	1.6 ± 0.2	3.5 ± 0.1	1.4 ± 0.4	2.0 ± 0.3
Soil $\delta^{13}C$, ‰	−26.3 ± 0.1	−25.9 ± 0.1	−25.0 ± 0.3	−26.6 ± 0.2
pH	6.6 ± 0.1	6.3 ± 0.2	6.3 ± 0.1	5.9 ± 0.1

†SOFS and SDEF burned after soil samples were obtained in July 2003 and September 2002, respectively.

‡Soil taxonomy for SOFS from Moreno and Oechel (1992), for SDEF from Riggan et al. (1985), and for SMER and MRR from Knecht (1971).

Given the significant inputs of atmospheric N (Bytnerowicz and Fenn, 1996; Meixner and Fenn, 2004) and the potential for these inputs to alter C and N storage and cycling (Fenn et al., 1996, 2003a; Padgett et al., 1999; Vourlitis and Zorba, 2007; Vourlitis et al., 2007), we hypothesized that N and C mineralization of semi-arid shrubland soils will increase as a function of N deposition. This hypothesis was tested in a 50-wk laboratory incubation experiment where the C and N mineralization was quantified from chaparral and coastal sage soils exposed to varying N deposition levels.

MATERIALS AND METHODS

Soil samples were obtained in September 2002 from chaparral and coastal sage sites located in southern California along a N pollution gradient described by Padgett et al. (1999) and Fenn et al. (2003b). The chaparral sites consisted of the Sky Oaks Field Station (SOFS) and the San Dimas Experimental Forest (SDEF) while the coastal sage sites consisted of the Santa Margarita Ecological Reserve (SMER) and Motte Rimrock Reserve (MRR). Each study site had four 10- by 10-m plots, and selected characteristics of these sites are displayed in Table 1. Chaparral sites were 50 (SOFS) and 42 (SDEF) yr old at the time the soil samples were obtained, but both have since burned.

Sample Collection and Laboratory Analysis

Soil samples at each site (four subsamples per plot) were obtained from the surface (0–10 cm) in September 2002 using a 4.7-cm-diameter by 10-cm-deep (173.5-cm^3) bucket auger. Chaparral sites had not yet experienced fire so all the sites consisted of mature vegetation that varied in age between 24 and 50 yr (Table 1). Soil samples were sieved to remove mineral and organic material >2 mm before chemical analysis. Soil samples were dry at the time of sample collection (soil water content <0.04 kg H_2O kg^{-1} dry soil), and were stored in polyethylene bags at room temperature until laboratory analyses and incubation experiments were performed.

Soil pH was measured 1 to 4 d after collection in 1:2 (w/v) soil slurries, where 15 g of fresh soil was added to 30 mL of deionized water and pH was measured after 30 min using a standard pH meter (Model MP 220, Mettler-Toledo, Columbus, OH). Approximately 6.5 to 7.0 mg of oven-dried litter material and 45 to 50 mg of air-dried soil were analyzed for $\delta^{13}C$ and $\delta^{15}N$ natural abundance and total C and N at the Kansas State University Stable Isotope Mass Spectrometry Laboratory using a mass spectrometer (ThermoFinnigan Delta Plus, Thermo Electron Corp., Bremen, Germany) coupled to an elemental analysis system (CE 1110, Carlo-Erba, Milan, Italy).

Potential Mineralization Laboratory Incubation Experiments

Potential N mineralization laboratory incubations were conducted using sequential leaching techniques (Stanford and Smith, 1972; Nadelhoffer, 1990). Triplicate samples of air-dried soil (50 g) were placed into microlysimeters (Falcon Filter Unit 7102, Becton Dickinson, Lincoln Park, NJ) and incubated in the dark at a constant temperature of 25°C during a 50-wk period. Soils were leached weekly (first 4 mo), bimonthly (Months 4–6), and approximately every 3 mo thereafter by adding 100 mL of N-free nutrient solution (Stanford and Smith, 1972; Nadelhoffer, 1990). Soil saturated with N-free nutrient solution was left to stand for 30 min, and leachate was removed using a 0.06-MPa vacuum pump and stored at 4°C until analysis for extractable NH_4 and NO_3 using an autoanalyzer (Lachat Quikchem 3000, Lachat Instruments, Milwaukee, WI). Mean (±1 SD) soil moisture was maintained at 0.25 ± 0.05 kg H_2O kg^{-1} dry soil by weighing the soil + lysimeter units weekly and adding distilled H_2O as needed. This soil moisture corresponded to a 65% water-filled pore space, which is considered optimal for microbial activity (Robertson et al., 1999).

Soil respiration (hereafter referred to as *C mineralization*) was determined by measuring the change in CO_2 concentration in the lysimeter head space during a 2- to 4-h period (Nadelhoffer, 1990). Carbon dioxide evolution was measured weekly (first 4 mo), bimonthly (Months 4–6), and approximately every 3 mo thereafter. Lysimeters were purged of CO_2 by flowing 1.5 L min^{-1} of N_2 for 3 to 5 min and were immediately sealed and incubated at 25°C for 2 to 4 h; gas samples were obtained using a 10-mL syringe immediately after purging and after the incubation period. The CO_2 concentration of the lysimeter head space was measured using an infrared gas analyzer (LI-6200, LI-COR Inc., Lincoln, NE) equipped to integrate the CO_2 concentration of the injected air sample (LI-COR, 1998).

Relative Nitrogen Deposition

Published estimates of atmospheric N pollution and deposition exposure are not available for the research sites, and estimates derived from high-resolution (4-km) models (Tonnesen, unpublished data,

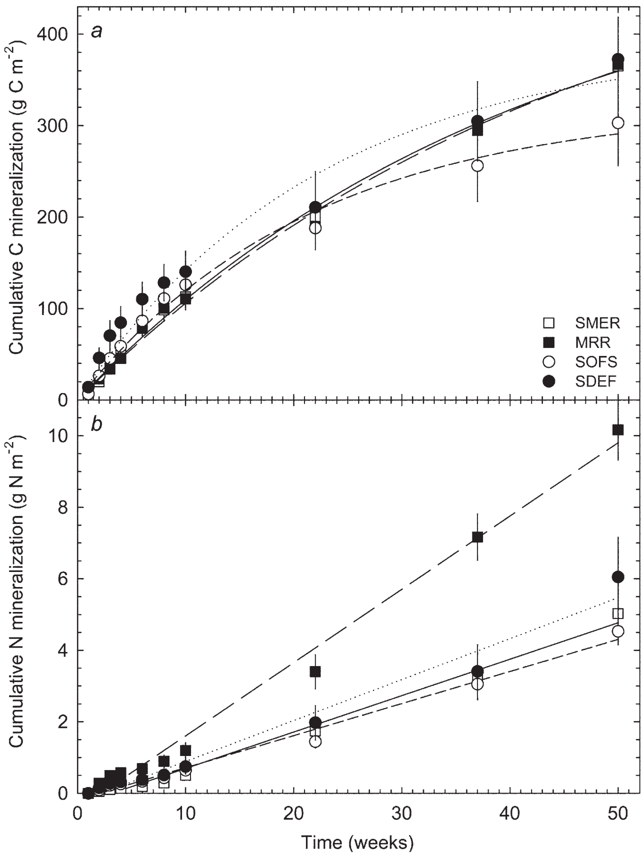

Fig. 1. The mean (±1 SE, *n* = 4 plots per site) cumulative (a) C and (b) N mineralization for the Sky Oaks Field Station (SOFS, open circles and short-dashed line), San Dimas Experimental Forest (SDEF, closed circles and dotted line), Motte Rimrock Reserve (MRR, closed squares and long-dashed line), and the Santa Margarita Ecological Reserve (SMER, open squares and solid line). Lines were fit to data using (a) nonlinear and (b) linear regression.

2004) or sparse measurement networks may be too coarse to provide point estimates required for the study sites (Bytnerowicz and Fenn, 1996; Padgett et al., 1999; Fenn et al., 2003b; Fenn and Poth, 2004; Meixner and Fenn, 2004). Thus, an estimate of relative N deposition was derived for each study site using branch rinsing techniques (Bytnerowicz and Fenn, 1996) where inorganic N ($NH_4 + NO_3$) that accumulated on vegetation surfaces was collected every 3 mo for 1 yr. Between 8 and 16 apical branches of the dominant shrubs at each site (one branch per shrub) were rinsed with 30 mL of distilled H_2O, and the inorganic N collected from the branch rinsing was analyzed using an autoanalyzer (Lachat Quikchem 3000, Lachat Instruments, Milwaukee, WI). Apical shoots approximately 5 cm in length were selected for sampling, and after rinsing the shoot was collected and oven dried at 70°C for 1 wk to obtain the shoot dry weight.

Concentration data (mg N L^{-1}) were converted to a mass per unit ground area estimate (mg N m^{-2}) by (1) converting the concentration data to a mass of N per unit dry leaf mass (mgN/g dry weight), (2) multiplying the mass of N per unit dry leaf mass by the specific leaf weight (SLW; g m^{-2}) to derive the mass of N per unit leaf area (mg N m^{-2}), and (3) multiplying the mass of N per unit leaf area by the leaf area index (LAI; m^2 leaf area m^{-2} ground area). SLW was determined by measuring the leaf area of a fresh apical shoot using a portable leaf area meter (CI-202, CID, Inc., Camas, WA, USA), oven drying the shoot at 70°C for 1 wk to obtain the dry weight, and dividing the leaf area by the leaf dry weight. LAI was measured using a portable PAR-ceptometer (AccuPAR PAR-80, Decagon, Inc., Pullman, WA, USA) which calculates LAI based on the extinction of photosynthetically-active radiation (PAR) by the shrub canopy. Inorganic N collected from each branch rinsing event was summed over a 1 yr period to obtain an annual estimate of the relative N deposition for each study site.

Estimates of relative N deposition are clearly not appropriate for estimating the absolute value of N deposition for the study sites because (i) a significant amount of accumulated N could have been lost from the vegetation surface from rainfall between each sampling event, (ii) ground-area-based estimates of relative N deposition derived from apical shoots assume that shrub biomass composition is uniform and similar to the apical shoot, and (iii) branch rinsing techniques fail to account for N deposited as wet deposition, which accounts for 10 to 15% of the total annual N deposition in these shrublands (Bytnerowicz and Fenn, 1996), and the N that may be directly taken up by leaves (Padgett and Bytnerowicz, 2001). Thus, the estimates of N deposition reported here are best viewed as an index of relative N exposure for the study sites.

Statistical Analysis

Cumulative potential C mineralization (C_0), the total cumulative N mineralization (N_{min}), and the C and N mineralization rate constants (k_C and k_N) for the 50-wk incubation were estimated using regression. Comparisons of response variables within a given vegetation type (chaparral or coastal sage) were not possible because only one high- and low-deposition stand was sampled in each vegetation type, and such comparisons would have amounted to simple pseudoreplication (Hurlbert, 1984). Rather, linear regression and correlation were used to assess the relationship between relative N deposition and the bulk soil C and N properties and C and N mineralization kinetics for both vegetation types combined. Data were tested for normality and heteroscedasticity before analyses, and response variables violating these assumptions were lognormally transformed (Zar, 1984).

RESULTS AND DISCUSSION

Cumulative Carbon and Nitrogen Mineralization Kinetics

Cumulative C mineralization was best described by a single-pool, first-order model, $C_t = C_0[1 - \exp(-k_C t)]$, where C_0 = cumulative potential C mineralization, k_C = the C mineralization rate constant, and t = time with a mean (±1 SD) coefficient of determination (r^2) of 0.987 ± 0.015 (Fig. 1a, Table 2). While single-pool models have been used extensively to describe cumulative C mineralization dynamics for a variety of soils (Stanford and Smith, 1972; Zak et al., 1994; Updegraff et al., 1995), multiple pool models may be more appropriate given the heterogeneous nature of soil organic matter (Parton et al., 1987; Paul et al., 2006; Piñeiro et al., 2006). The r^2 was higher and the standard error of the regression was lower, however, with the single-pool model and the coefficients for the "slower" C pools calculated from the multiple-pool model were highly variable and not significantly different from zero.

Mean (±SE, n = 4) C_0 varied between 365 ± 104 g C m^{-2} for the chaparral stand at the SOFS and 649 ± 189 g C m^{-2} for the coastal sage stand at the SMER, and C_0 tended to be higher for coastal sage shrublands than chaparral (Table 2). These values are higher than those reported by Zak et al. (1994) for other semiarid and arid woodlands and shrublands; however, these differences are probably due to the 18 wk longer incubation period used in this study. Chaparral soils exhibited lower values of C_0 and the C_0 fraction of the total soil organic C (C_0/C) than coastal sage scrub

(Table 2), presumably because the soil organic matter derived from evergreen chaparral shrubs is richer in lignin than the soil organic matter derived from drought-deciduous coastal sage shrubs (Schlesinger and Hasey 1981).

The rate constant of cumulative C mineralization (k_C) ranged between 0.052 wk^{-1} for the chaparral stand at SOFS and 0.022 wk^{-1} for the coastal sage stand at the MRR, and in contrast to the trend in C_0 observed between the vegetation types, the average k_C was twofold higher for chaparral soil than for coastal sage soil (Table 2). Differences in k_C between chaparral and coastal sage may be due to differences in soil microbial activity or community composition, or to differences in the content of labile C from dead microbial cells that is rapidly mineralized following soil rewetting (Zak et al., 1994; Miller et al., 2005). Regardless, k_C values reported here are lower than those reported by Zak et al. (1994) for comparable vegetation types; however, this difference is presumably due to the 10°C lower incubation temperature used here.

Table 2. Regression statistics for cumulative potential C and N mineralization as a function of time during the 50-wk incubation period for soils from the Santa Margarita Ecological Reserve (SMER), Motte Rimrock Reserve (MRR), Sky Oaks Field Station (SOFS), and San Dimas Experimental Forest (SDEF) study sites. Cumulative potential C mineralization with time (C_t) was estimated using a first-order exponential equation; $C_t = C_0[1 - \exp(-k_C t)]$, where C_0 = cumulative potential C mineralization, k_C= the C mineralization rate constant, and t = time. Cumulative potential N mineralization with time (N_t) was estimated using a zero-order (linear) equation where N_{min} = cumulative N mineralization during the incubation period and k_N = the slope of the regression of N_t vs. t. Also shown is the average coefficient of determination (R^2) for the regression equations, the ratio of mineralized C to total soil C (C_0/C), and the ratio of mineralized N to total soil N (N_{min}/N). Data are means ± SE (n = 4).

Parameter	SMER	MRR	SOFS	SDEF
C mineralization				
C_0, g C m^{-2}	649 ± 189	559 ± 98	365 ± 104	412 ± 36
k_C, wk^{-1}	0.024 ± 0.006	0.022 ± 0.005	0.052 ± 0.014	0.042 ± 0.008
R^2	0.99 ± 0.001	0.99 ± 0.002	0.99 ± 0.004	0.97 ± 0.012
C_0/C	0.47 ± 0.17	0.45 ± 0.12	0.16 ± 0.03	0.25 ± 0.03
N mineralization				
N_{min}, g N m^{-2}	5.0 ± 0.8	10.2 ± 0.8	4.5 ± 0.4	6.1 ± 1.1
k_N, g N m^{-2} wk^{-1}	0.10 ± 0.02	0.21 ± 0.02	0.09 ± 0.01	0.12 ± 0.02
R^2	0.99 ± 0.001	0.98 ± 0.005	0.98 ± 0.004	0.97 ± 0.018
N_{min}/N	0.049 ± 0.008	0.089 ± 0.011	0.050 ± 0.007	0.044 ± 0.003

Cumulative N mineralization was best described by a zero-order model (Fig. 1b, Table 2), and while most investigators have used first-order models to describe potential cumulative N mineralization (i.e., Stanford and Smith, 1972; Juma et al., 1984; Wang et al., 2004), the increase in performance of a zero-order model (i.e., higher r^2 and lower standard error) may arise because of low or variable first-order rate constants, which can produce a linear response if N is mineralized from stable organic matter (Zak et al., 1994; Springob and Kirchmann, 2003).

The average (±SE, n = 4) total amount of N mineralized during the 50-wk incubation (N_{min}) ranged between 4.5 ± 0.4 g N m^{-2} for the chaparral stand at SOFS to 10.2 ± 0.8 g N m^{-2} for the coastal sage stand at MRR, and N_{min} tended to be higher for the sites that experienced higher relative N deposition (MRR and the SDEF) (Tables 1 and 2). These values are comparable to those reported for a variety of Mediterranean-type shrublands (Marion and Black, 1988; Monokrousos et al., 2004), desert shrublands of the arid Southwest (Zak et al., 1994), and Great Basin sagebrush (*Artemisia tridentata* Nutt.) scrub (Chen and Stark, 2000). Most of the accumulated N (~95%) was in the form of NO_3, and there was no statistically significant difference in the amount of NO_3–N produced between the study sites, indicating a high nitrification potential for the semiarid shrublands studied here (Fenn et al., 1996; Vourlitis and Zorba, 2007). Similar trends were observed with k_N (Table 2), which is expected given that N_{min} and k_N were estimated from a zero-order model and were highly correlated (r = 0.99).

Relationships between Relative Nitrogen Deposition and Carbon and Nitrogen Mineralization

There was no significant trend between C_0 (Fig. 2a) or k_C (Fig. 2b) and relative N deposition, implying that microbial respiration was not limited by available N (Micks et al., 2004). Nitrogen addition has been found to stimulate the decomposition of labile soil C while stabilizing more recalcitrant C fractions (Neff et al., 2002), and given the inability to differentiate between various C fractions using the single-pool model, it is unclear whether differences in C pool decomposition for the

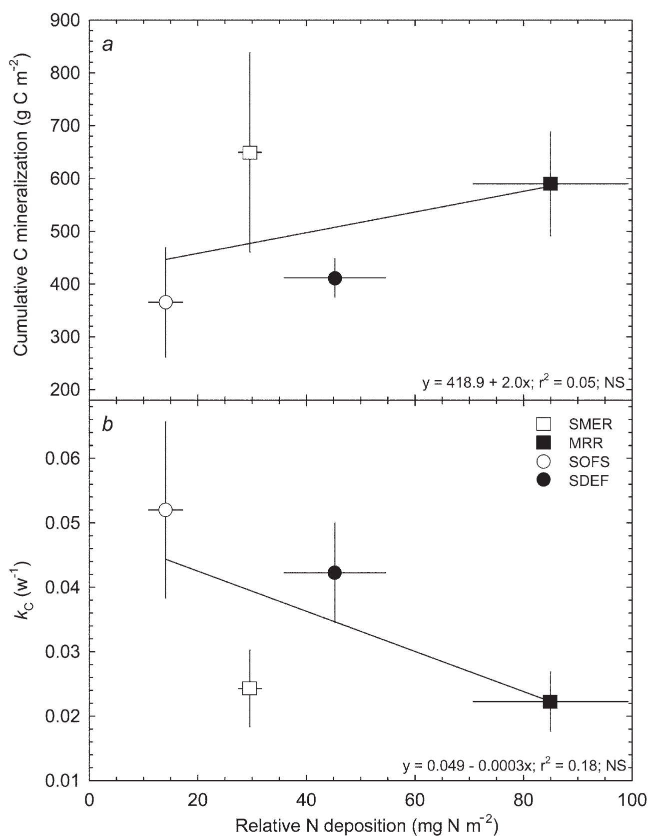

Fig. 2. The (a) mean (±1 SE, n = 4 plots per site) cumulative C mineralization potential and (b) the C mineralization rate constant (k_C) for the Sky Oaks Field Station (SOFS, open circles), San Dimas Experimental Forest (SDEF, closed circles), Motte Rimrock Reserve (MRR, closed squares), and the Santa Margarita Ecological Reserve (SMER, open squares). Lines were fit to data using linear regression; also shown is the equation, coefficient of determination (r^2), and probability of type-I error (P) for the regression. NS = P > 0.05.

Table 3. Linear correlation coefficient between relative N deposition (independent variable) and several bulk soil properties and C and N potential mineralization kinetics (dependent variables).

Dependent variable	*r*	*P*†
$\delta^{15}N$ natural abundance	0.85	<0.001
Total N	0.33	NS
$\delta^{13}C$ natural abundance	−0.29	NS
Total C	−0.52	<0.05
C/N ratio	−0.74	<0.01
pH	−0.21	NS
Cumulative potential C mineralization (C_0)	0.22	NS
Potential C mineralization rate constant	−0.42	NS
Cumulative N mineralization (N_{min})	0.82	<0.001
Potential N mineralization rate constant	0.82	<0.001
C_0/total C ratio	0.34	NS
N_{min}/total N ratio	0.67	<0.01

† *P* = probability of type-I error calculated with 14 degrees of freedom; NS = not significant.

soils studied here were significantly correlated with relative N deposition. The fraction of potential C mineralization to total organic carbon (C_0/C) was between 16 and 47% and, in general, C_0 comprised a larger fraction of the total organic C for coastal sage shrublands than chaparral (Table 2) and was not significantly related to relative N deposition (Table 3).

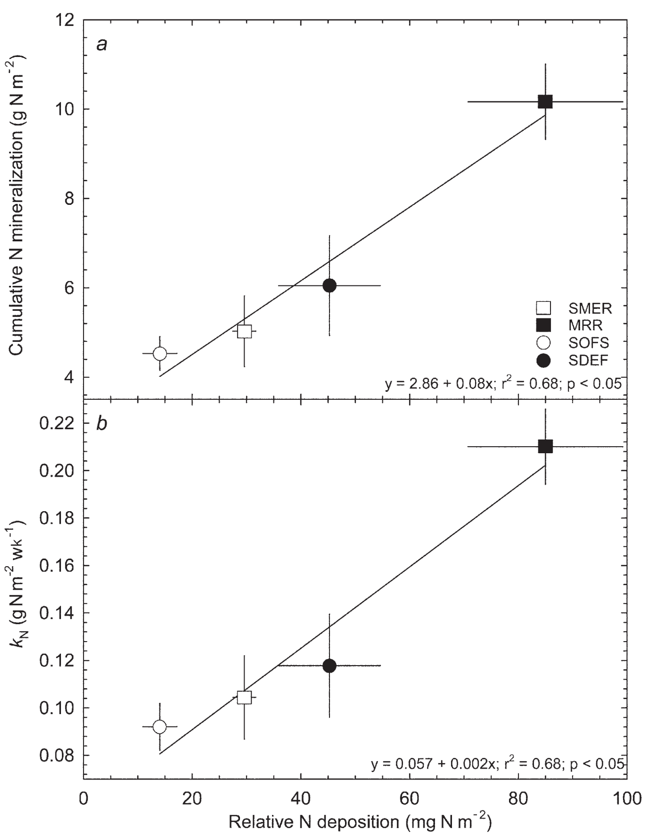

Fig. 3. The (a) mean (±1 SE, *n* = 4 plots per site) cumulative N mineralization and (b) the N mineralization rate constant for the Sky Oaks Field Station (SOFS, open circles), San Dimas Experimental Forest (SDEF, closed circles), Motte Rimrock Reserve (MRR, closed squares), and the Santa Margarita Ecological Reserve (SMER, open squares). Lines were fit to data using linear regression; also shown is the equation, coefficient of determination (r^2), and probability of type-I error (*P*) for the regression. NS = *P* > 0.05.

In contrast, N mineralization, expressed as either N_{min} (Fig. 3a) or k_N (Fig. 3b), increased linearly with relative N deposition, which is consistent with results from deciduous broadleaf and evergreen coniferous forests (Fenn et al., 1996; Currie, 1999; Baron et al., 2000) and grasslands exposed to N enrichment (Wedin and Tilman, 1990; Turner et al., 1997). Furthermore, the mineralized N fraction of total soil N (N_{min}/N) varied between 4.4% for SDEF and 8.9% for MRR (Table 2) and was significantly positively correlated with relative N deposition ($r = 0.67$, $P < 0.01$; Table 3). Assuming that relative N deposition is proportional to the long-term N deposition exposure, these data suggest that N deposition significantly enhanced the potential for N mineralization.

Relationships between Relative Nitrogen Deposition and Bulk Soil Carbon and Nitrogen

Several other bulk soil properties, such as the $\delta^{15}N$ natural abundance, total soil C, and the soil C/N ratio were significantly correlated with relative N deposition (Table 3). The soil $\delta^{15}N$ natural abundance was positively correlated with relative N deposition ($r = 0.85$, $P < 0.001$; Table 3), and soil exposed to chronic atmospheric N deposition reportedly has a higher $\delta^{15}N$ natural abundance because dry deposition tends to be enriched in ^{15}N (Heaton, 1986) or N deposition enhances processes such as mineralization, leaching, and denitrification that discriminate against ^{15}N (Johannisson and Högberg, 1994; Emmett et al., 1998; Korontzi et al., 2000).

The soil C/N ratio declined as a function of relative N deposition ($r = -0.74$, $P < 0.01$), and the decline in soil C/N was due to a decline in total soil C ($r = -0.52$, $P < 0.05$) and not an increase in total N ($r = 0.33$, $P > 0.05$; Table 3). A decline in the soil C/N ratio with an increase in N deposition has been widely observed, but N deposition usually leads to soil N enrichment, not soil C loss (Aber et al., 1998; Gundersen et al., 1998; Baron et al., 2000). Assuming that C_0 is not significantly affected by N deposition (Fig. 2), C input to soil organic matter must also decline with N deposition for a decline in total soil C to be realized. Research in deciduous and evergreen coniferous forest indicates that chronic N deposition can inhibit root production and have little overall effect on aboveground primary production and litterfall (Aber et al., 1998; Grulke and Balduman, 1999; Bauer et al., 2004; Magill et al., 2004), suggesting that long-term N deposition exposure can result in a decline in soil C inputs. Litter produced under high N deposition is also N enriched, with a low C/N ratio (Fenn et al., 1996; Korontzi et al., 2000; Magill et al., 2004), which enhances litter decomposition (Gundersen et al., 1998) and further reduces soil C storage. Thus, while potential C mineralization was not significantly related to relative N deposition in this laboratory incubation (Fig. 2), long-term exposure to high N deposition may cause a decline in soil C input, and thus soil C storage. Unfortunately, this hypothesis cannot be assessed with the data provided.

In conclusion, the N mineralization potential of semiarid shrubland soil increased linearly with relative N deposition exposure, and the increase in N mineralization was apparently due in part to a concomitant increase in soil organic matter quality (i.e., decline in soil C/N ratio) with relative N deposition. Nitrogen mineralization increased as a function of N deposition; however, C mineralization was not significantly affected by N deposition, suggesting that C mineralization was not N limited. While the laboratory incubations may not provide realistic estimates of in situ C or N mineralization, the long incubation period (50 wk) and simultaneous determination of C_0 and N_{min} provides a powerful tool for assessing the potential effects of atmospheric N deposition on soil C and N cycling in southern Californian semiarid shrublands.

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REFERENCES

Aber, J., W. McDowell, K. Nadelhoffer, A. Magill, G. Berntson, M. Kamakea, S. McNulty, W. Currie, L. Rustad, and I. Fernandez. 1998. Nitrogen saturation in temperate forest ecosystems. Bioscience 48:921–934.

Asner, G.P., T.R. Seastedt, and A.R. Townsend. 1997. The decoupling of terrestrial carbon and nitrogen cycles. Bioscience 47:226–234.

Baron, J.S., H.M. Rueth, A.M. Wolfe, K.R. Nydick, E.J. Allstott, J.T. Minear, and B. Moraska. 2000. Ecosystem responses to nitrogen deposition in the Colorado Front Range. Ecosystems 3:352–368.

Bauer, G.A., F.A. Bazzaz, R. Minocha, S. Long, A. Magill, J. Aber, and G.M. Berntson. 2004. Effects of chronic N additions on tissue chemistry, photosynthetic capacity, and carbon sequestration potential of a red pine (*Pinus resinosa* Ait.) stand in the NE United States. For. Ecol. Manage. 196:173–186.

Bytnerowicz, A., and M.E. Fenn. 1996. Nitrogen deposition in California forests: A review. Environ. Pollut. 92:127–146.

Chen, J., and J.M. Stark. 2000. Plant species effects and carbon and nitrogen cycling in a sagebrush–crested wheatgrass soil. Soil Biol. Biochem. 32:47–57.

Currie, W.S. 1999. The responsive C and N biogeochemistry of the temperate forest floor. Trends Ecol. Evol. 14:316–320.

Emmett, B.A., O.J. Kjønaas, P. Gundersen, C. Koopmans, A. Tietema, and D. Sleep. 1998. Natural abundance of ^{15}N in forests across a nitrogen deposition gradient. For. Ecol. Manage. 101:9–18.

Fenn, M.E., J.S. Baron, E.B. Allen, H.N. Rueth, K.P. Nydick, L. Geiser, W.D. Bowman, J.O. Sickman, T. Meixner, D.W. Johnson, and P. Neitlich. 2003a. Ecological effects of nitrogen deposition in the western United States. Bioscience 53:404–420.

Fenn, M.E., R. Haeuber, G.S. Tonnesen, J.S. Baron, S. Grossman-Clarke, D. Hope, D.A. Jaffe, S. Copeland, L. Geiser, H.N. Rueth, and J.O. Sickman. 2003b. Nitrogen emissions, deposition, and monitoring in the western United States. Bioscience 53:391–403.

Fenn, M.E., and M.A. Poth. 1999. Temporal and spatial trends in streamwater nitrate concentrations in the San Bernardino Mountains, southern California. J. Environ. Qual. 28:822–836.

Fenn, M.E., and M.A. Poth. 2004. Monitoring nitrogen deposition in throughfall using ion exchange resin columns: A field test in the San Bernardino Mountains. J. Environ. Qual. 33:2007–2014.

Fenn, M.E., M.A. Poth, and D.W. Johnson. 1996. Evidence for nitrogen saturation in the San Bernardino Mountains in southern California. For. Ecol. Manage. 82:211–230.

Gray, J.T., and W.H. Schlesinger. 1983. Nutrient use by evergreen and deciduous shrubs in Southern California. II. Experimental investigations of the relationship between growth, nitrogen uptake, and nitrogen availability. J. Ecol. 71:43–56.

Grulke, N.E., and L. Balduman. 1999. Deciduous conifers: High N deposition and O_3 exposure effects on growth and biomass allocation in Ponderosa pine. Water Soil Air Pollut. 116:235–248.

Gundersen, P., B.A. Emmett, O.J. Kjønaas, C.J. Coopmans, and A. Tietema. 1998. Impact of nitrogen deposition on nitrogen cycling in forests: A synthesis of NITREX data. For. Ecol. Manage. 101:37–55.

Heaton, T.H.E. 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: A review. Chem. Geol. 59:87–102.

Hurlbert, S.H. 1984. Pseudoreplication and the design of ecological field experiments. Ecology 54:187–211.

Johannisson, C., and P. Högberg. 1994. ^{15}N abundance of soils and plants along an experimentally induced forest nitrogen supply gradient. Oecologia 97:322–325.

Juma, N.G., E.A. Paul, and B. Mary. 1984. Kinetic analysis of net nitrogen mineralization in soil. Soil Sci. Soc. Am. J. 48:753–757.

Knecht, A.A. 1971. Soil survey for western Riverside area, California. Soil Conserv. Serv., Washington, DC.

Korontzi, S., S.A. Macko, I.C. Anderson, and M.A. Poth. 2000. A stable isotopic study to determine carbon and nitrogen cycling in a disturbed southern Californian forest ecosystem. Global Biogeochem. Cycles 14:177–188.

Li, X., T. Meixner, J.O. Sickman, A.E. Miller, J.P. Schimel, and J.M. Melack. 2006. Decadal-scale dynamics of water, carbon and nitrogen in a California chaparral ecosystem: DAYCENT modeling results. Biogeochemistry 77:217–245.

LI-COR. 1998. Measuring small volumes of CO_2 with the LI–COR LI-6200 system. LI–COR Application Note 121. LI–COR Inc., Lincoln, NE.

Magill, A.H., J.D. Aber, W.S. Currie, K.J. Nadelhoffer, M.E. Martin, W.H. McDowell, J.M. Melillo, and P. Steudler. 2004. Ecosystem response to 15 years of chronic nitrogen additions at the Harvard Forest LTER, Massachusetts, USA. For. Ecol. Manage. 196:7–28.

Marion, G.M., and C.H. Black. 1988. Potentially available nitrogen and phosphorus along a chaparral fire cycle chronosequence. Soil Sci. Soc. Am. J. 52:1155–1162.

Meixner, T., and M.E. Fenn. 2004. Biogeochemical budgets in a Mediterranean catchment with high rates of atmospheric N deposition: Importance of scale and temporal asynchrony. Biogeochemistry 70:331–356.

Micks, P., J.D. Aber, R.D. Boone, and E.A. Davidson. 2004. Short-term soil respiration and nitrogen immobilization response to nitrogen applications in control and nitrogen-enriched temperate forests. For. Ecol. Manage. 196:57–70.

Miller, A.E., J.P. Schimel, T. Meixner, J.O. Sickman, and J.M. Melack. 2005. Episodic rewetting enhances carbon and nitrogen release from chaparral soils. Soil Biol. Biochem. 37:2195–2204.

Monokrousos, N., E.M. Papatheodorou, J.D. Diamantopoulos, and G.P. Stamou. 2004. Temporal and spatial variability of soil chemical and biological variables in a Mediterranean shrubland. For. Ecol. Manage. 202:83–91.

Mooney, H.A., and P.W. Rundel. 1979. Nutrient relations of the evergreen shrub, *Adenostoma fasciculatum*, in the California chaparral. Bot. Gaz. 140:109–113.

Moreno, J.M., and W.C. Oechel. 1992. Factors controlling postfire seedling establishment in southern California chaparral. Oecologia 90:50–60.

Nadelhoffer, K.J. 1990. Microlysimeter for measuring nitrogen mineralization and microbial respiration in aerobic soil incubations. Soil Sci. Soc. Am. J. 54:411–415.

Neff, J.C., A.R. Townsend, G. Gleixnerk, S.J. Lehman, J. Turnbull, and W.D. Bowman. 2002. Variable effects of nitrogen additions on the stability and turnover of soil carbon. Nature 419:915–917.

Padgett, P.E., E.B. Allen, A. Bytnerowicz, and R.A. Minnich. 1999. Changes in soil inorganic nitrogen as related to atmospheric nitrogenous pollutants in southern California. Atmos. Environ. 33:769–781.

Padgett, P.E., and A. Bytnerowicz. 2001. Deposition and adsorption of the air pollutant HNO_3 vapor to soil surfaces. Atmos. Environ. 35:2405–2415.

Parton, W.J., D.S. Schimel, C.V. Cole, and D.S. Ojima. 1987. Analysis of factors controlling soil organic matter levels in Great Plains grasslands. Soil Sci. Soc. Am. J. 51:1173–1179.

Paul, E.A., and F.E. Clark. 1989. Soil microbiology and biochemistry. Academic Press, San Diego.

Paul, E.A., S.J. Morris, R.T. Conant, and A.F. Plante. 2006. Does the acid hydrolysis–incubation method measure meaningful soil organic carbon pools? Soil Sci. Soc. Am. J. 70:1023–1035.

Piñeiro, G., M. Osterheld, W. Batista, and J.M. Paruelo. 2006. Opposite changes of whole-soil vs. pools C:N ratios: A case of Simpson's paradox with implications on nitrogen cycling. Global Change Biol. 12:804–809.

Rastetter, E.B., R.B. McKane, G.R. Shaver, and J.M. Melillo. 1992. Changes in C storage by terrestrial ecosystems: How C–N interactions restrict responses to CO_2 and temperature. Water Air Soil Pollut. 64:327–344.

Riggan, P.F., R.N. Lockwood, and E.N. Lopez. 1985. Deposition and processing of airborne nitrogen pollutants in Mediterranean-type ecosystems of southern California. Environ. Sci. Technol. 19:781–789.

Robertson, G.P., D.C. Coleman, C.S. Bledsoe, and P. Sollins. 1999. Standard soil methods for long-term ecological research. Oxford Univ. Press, New York.

Schlesinger, W.H., and M.M. Hasey. 1981. Decomposition from chaparral shrub foliage: Losses of organic and inorganic constituents from deciduous and evergreen leaves. Ecology 62:762–774.

Springob, G., and H. Kirchmann. 2003. Bulk soil C to N ratio as a simple measure of net N mineralization from stabilized soil organic matter in sandy arable soils. Soil Biol. Biochem. 35:629–632.

Stanford, G., and S.J. Smith. 1972. Nitrogen mineralization potentials of soils. Soil Sci. Soc. Am. Proc. 36:465–472.

Turner, C.L., J.M. Blair, R.J. Schartz, and J.C. Neel. 1997. Soil N and plant responses to fire, topography, and supplemental N in tallgrass prairie. Ecology 78:1832–1843.

Updegraff, K., J. Pastor, S.D. Bridgham, and C.J. Johnson. 1995. Environmental and substrate controls over carbon and nitrogen mineralization in northern wetlands. Ecol. Appl. 5:151–163.

Vitousek, P.M., J.D. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, C.W. Schindler, W.H. Schlesinger, and D.G. Tilman. 1997. Human alteration of the global nitrogen cycle: Sources and consequences. Ecol. Appl. 7:737–750.

Vitousek, P.M., and R.W. Howarth. 1991. Nitrogen limitation on land and in the seas: How can it occur? Biogeochemistry 13:87–115.

Vourlitis, G.L., S. Pasquini, and G. Zorba. 2007. Plant and soil N response of southern Californian semi-arid shrublands after one year of experimental N deposition. Ecosystems (in press).

Vourlitis, G.L. and G. Zorba. 2007. Nitrogen and carbon mineralization of semi-arid shrubland soil exposed to long-term atmospheric nitrogen deposition. Biol. Fertil. Soils, doi:10.1007/s00374-006-0137-y.

Wang, W.J., C.J. Smith, and D. Chen. 2004. Predicting nitrogen mineralization dynamics with a modified double exponential model. Soil Sci. Soc. Am. J. 68:1256–1265.

Wedin, D., and D. Tilman. 1990. Species effects on nitrogen cycling: A test with perennial grasses. Oecologia 84:433–441.

Westman, W.E. 1981. Factors influencing the distribution of species of Californian coastal sage scrub. Ecology 62:439–455.

Zak, D.R., D. Tilman, R.R. Parmenter, C.W. Rice, F.M. Fisher, J. Vose, D. Michunas, and C.W. Martin. 1994. Plant production and soil microorganisms in late-successional ecosystems: A continental-scale study. Ecology 75:2333–2347.

Zar, J.H. 1984. Biostatistical analysis. 2nd ed. Prentice Hall, Englewood Cliffs, NJ.

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