# Nitrogen mineralization and nitrification in a mixed-conifer forest in southern California: controlling factors, fluxes, and nitrogen fertilization response at a high and low nitrogen deposition site

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**Abstract:** Net fluxes of nitrogen (N) mineralization and nitrification were measured in situ on a monthly basis for 3 years at a high (HN) and low (LN) N deposition site in the San Bernardino Mountains, California. Mean N mineralization fluxes in the forest floor and top 10 cm of mineral soil were 19.0 and 59.8 kg $N{\cdot}ha^{-1}{\cdot}year^{-1}$ at LN and HN, respectively. Mean net nitrification fluxes were 11.2 and 55.9 kg $N{\cdot}ha^{-1}{\cdot}year^{-1}$ at LN and HN, respectively. Relative nitrification (the percent N mineralized that was nitrified) was generally lower under *Pinus ponderosa* Dougl. ex P. & C. Laws. (or *Pinus jeffreyi* Grev. & Balf.) canopies than under *Quercus kelloggii* Newb. or open canopies. The rate of net N mineralization was the key factor for predicting the rate of net nitrification. Fertilization with 50 and 150 kg $N{\cdot}ha^{-1}$ at LN significantly increased the rates of net mineralization and net nitrification. At HN fertilization had no significant effect on net nitrification. We conclude that at low-deposition sites increased nitrification occurs in the short term in response to added N, but that sustained elevated net nitrification is driven by the accumulation of N-enriched litter and soil organic matter in conjunction with chronic throughfall N deposition inputs.

**Résumé :** Les flux nets de minéralisation de l'azote (N) et de nitrification ont été mesurés in situ sur une base mensuelle, pendant 3 ans, dans des stations avec un niveau élevé (NE) ou faible (NF) de dépôts de N dans les montagnes de San Bernardino, en Californie. Les flux moyens de minéralisation de N dans la couverture morte et dans les premiers 10 cm du sol minéral ont atteint respectivement 19,0 et 59,8 kg $N{\cdot}ha^{-1}{\cdot}an^{-1}$ pour NF et NE. Les flux moyens nets de nitrification ont atteint respectivement 11,2 et 55,9 kg $N{\cdot}ha^{-1}{\cdot}an^{-1}$ pour NF et NE. La nitrification relative (le pourcentage de N minéralisé qui a été nitrifié) était généralement plus faible sous les canopées de *Pinus ponderosa* Dougl. ex P. & C. Laws. (ou *Pinus jeffreyi* Grev. & Balf.) que sous canopées de *Quercus kelloggii* Newb. ou sous des canopées ouvertes. Le taux de minéralisation nette de N était le facteur clé pour prédire le taux de nitrification nette. La fertilisation avec 50 et 150 kg $N{\cdot}ha^{-1}$ a significativement accru les taux de minéralisation nette et de nitrification nette dans le cas de NF. Dans le cas de NE, la fertilisation n'a pas eu d'effet significatif sur la nitrification nette. Nous concluons que dans les sites où les dépôts sont faibles, l'accroissement de la nitrification apparaît à court terme en réponse à l'ajout de N mais qu'un niveau élevé et soutenu de nitrification nette est sous le contrôle d'une litière et d'une matière organique du sol enrichies en N en conjonction avec les apports chroniques associés aux dépôts de N dans la précipitation au sol.

[Traduit par la Rédaction]

## Introduction

The global nitrogen (N) cycle has been perturbed by human activities and anthropogenic emissions, and atmospheric deposition of inorganic N has risen about threefold above preindustrial levels (Smil 2001). Increased inputs of N from anthropogenic activities cause excessive N enrichment of aquatic and terrestrial systems in many parts of the world. Nitrogen deposition also stimulates N mineralization and nitrification, thus further contributing to mobilization of N and N-saturation conditions (Aber et al. 1989). Nitrification is the key process that mobilizes N from accumulated organic N in N-saturated ecosystems. The principal pathways by which N is lost from the system is as leachable nitrate ($NO_3^-$) and as nitrogenous trace gas emissions from soil. More information on the ecological effects of reactive N inputs can be found in Aber et al. (2003), Fenn et al. (2003*a*), and Galloway et al. (2003).

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**Table 1.** Description of the two mixed-conifer forest sites used in this study.

| Characteristic | Camp Paivika | Camp Osceola |
|---|---|---|
| Elevation (m) | 1580 | 2135 |
| Average annual precipitation (mm) | 987 | 608 |
| Average annual temperature (°C) | 12.9 | 10.6 |
| **Nitrogen deposition as throughfall (kg N·ha$^{-1}$·year$^{-1}$)** | | |
| Under tree canopy | 193.9 | 18 |
| Integrated stand total | 81.6 | 8.3 |
| **Ozone (ppb)** | | |
| Summertime 24-h hourly average | 67.5 | 60.9 |
| Summertime average peak values | 101.6 | 91.3 |
| **Annual precipitation (mm)** | | |
| 1997 | 742 | 401 |
| 1998 | 1772 | 699 |
| 1999 | 415 | 187 |
| Soil type | Coarse-loamy, mixed mesic Ultic Haploxerolls of the Shaver series | Coarse-loamy, mixed, frigid Xerumbrepts and Xerochrepts |
| Dominant overstory species | *Pinus ponderosa* Dougl. ex P. & C. Laws., *Quercus kelloggi* Newb., *Calocedrus decurrens* (Torr.) Florin., *Pinus lambertiana* Dougl. | *Pinus jeffreyi* Grev. & Balf., *Abies concolor* Gord. & Glend. |

Montane forests and watersheds exposed to air pollution in the San Gabriel and San Bernardino Mountains (SBM) in southern California are N saturated, as indicated by stream-water $NO_3^-$ export patterns, elevated nitric oxide emissions from soil, and other edaphic and vegetative indicators of N enrichment (Fenn et al. 1996, 1998). Nitrogen deposition in the western end of the SBM is unusually high as a result of emissions from fossil fuels in the greater Los Angeles area and from dairy farms in the Chino–Norco area 34 km to the southwest. Nitrogen deposition is also elevated in the SBM because of high levels of occult deposition during periodic fog episodes (Fenn et al. 2000; Fenn and Poth 2004). Nitrogen deposition in the SBM declines sharply with distance from the source areas, presumably because of the high deposition velocities of nitric acid vapor and ammonia, and varying N-deposition inputs in fog.

The ratio of mineral N that is nitrified has been referred to as "relative nitrification" (Robertson 1982) and has frequently been used as an indicator of the nitrification activity in soils (Aber et al. 2003; Gilliam et al. 2001; Lavoie and Bradley 2003; Williard et al. 1997). Relative nitrification is high in mineral soil from the SBM, with little ammonium ($NH_4^+$) present (Fenn et al. 1996; Fenn and Poth 2001). However, relative nitrification is lower in the litter layer than in the mineral soil (Fenn et al. 1996). Relative nitrification is high in soils throughout the SBM and in the southern Sierra Nevada, and values increase with N deposition (Fenn et al. 1996, 2003*b*), but this has not been tested in situ.

The primary objectives of this study were (*i*) to quantify rates of net N mineralization and nitrification in the humus layer and mineral soil under field conditions in fertilized and unfertilized plots at a high N deposition forest site that is severely N saturated and at a low N deposition site, (*ii*) to determine whether relative nitrification patterns in field assays are similar to the results of laboratory studies, (*iii*) to determine the main factors affecting N cycling rates in the mineral soil and in the forest floor, and (*iv*) to test the hypothesis that after 2 to 3 years of N fertilization with a slow-release urea formulation, net nitrification rates at the low-N site would approach those of the high-N site.

## Materials and methods

### Study sites

These N cycling measurements were carried out from March 1997 to January 2000 at a high and a low N deposition research site in the SBM. The SBM are located ca. 70 km east of Los Angeles, California. Camp Paivika (HN) is a high-pollution site on the western end of the air pollution gradient in the SBM, and Camp Osceola (LN) is a relatively low N deposition site 46 km to the east of HN (Fenn et al. 2000). Throughfall N inputs are 10-fold greater at HN than at LN (Table 1). Forests at the study sites are classified as mixed-conifer forest. Because of the prevalent Mediterranean climate, moisture stress is common, although plant growth often responds to N fertilization (Fenn and Poth 2001). Annual precipitation at HN and LN was 25% and 34% below normal in 1997, 80% and 15% above normal in 1998, and 42% and 69% below normal in 1999. The primary use of these forests is recreational. Logging has not occurred for many years, and forest fires have been suppressed since the early 1900s, leading to stand densification and allowing greater forest floor and N accumulation; N deposition is believed to contribute further to these stand effects (Fenn et al. 2003*b*). Data are not available on the effects of chronic N deposition on vegetation community changes, but bracken fern (*Pteridium aquilinum* var. *pubescens* Underw.), an N-loving species, dominates the understory at HN. The sparse understory at LN is composed of a few shrubs and assorted herbaceous species. The parent material of the soils at both sites is partially weathered or decomposed granite. Foliar ozone injury is negligible in pine at LN, but at HN this pollutant causes pre-

**Table 2.** Mean values for pH, forest floor mass, percent C, percent N, and C/N in mineral soil and forest floor at the two study sites (unfertilized plots).

| Site and canopy type | pH | pH *p* value* | Forest floor mass (kg·m$^{-2}$) | Forest floor mass *p* value* | % C | % N | %N *p* value* | C/N | C/N *p* value* |
|---|---|---|---|---|---|---|---|---|---|
| **Forest floor** | | | | | | | | | |
| LN | | | | | | | | | |
| Oak | 5.15 (0.15)a | 0.0001 | 9.13 (0.62)b | 0.0001 | 26.61 (2.16)a | 0.76 (0.06)a | 0.005 | 36.86 (3.71)a | 0.03 |
| Open | 4.09 (0.11)b | | 7.24 (0.80)c | 0.0001 | 22.01 (4.82)a | 0.62 (0.19)a | | 37.15 (3.71)a | 0.05 |
| Pine | 4.17 (0.10)b | | 9.34 (0.66)a | 0.0001 | 27.63 (2.85)a | 0.67 (0.06)a | 0.001 | 40.70 (3.11)a | 0.004 |
| HN | | | | | | | | | |
| Oak | 4.20 (0.06)a | | 13.48 (0.78)b | | 30.18 (2.06)a | 1.07 (0.08)a | | 28.57 (1.19)ab | |
| Open | 4.34 (0.18)a | | 17.13 (1.23)a | | 15.00 (1.70)b | 0.57 (0.07)b | | 26.25 (1.52)b | |
| Pine | 4.09 (0.06)a | | 16.16 (0.28)a | | 30.30 (2.27)a | 1.00 (0.07)a | | 29.91 (0.79)a | |
| **Mineral soil** | | | | | | | | | |
| LN | | | | | | | | | |
| Oak | 5.56 (0.13)a | 0.0001 | | | 3.33 (0.30)a | 0.13 (0.01)a | 0.03 | 25.75 (0.96)a | 0.0001 |
| Open | 4.97 (0.07)b | 0.05 | | | 2.63 (0.58)a | 0.10 (0.03)a | | 25.61 (1.88)a | 0.05 |
| Pine | 5.13 (0.08)b | 0.0001 | | | 2.92 (0.26)a | 0.11 (0.009)a | 0.05 | 25.53 (0.69)a | 0.0001 |
| HN | | | | | | | | | |
| Oak | 4.21 (0.09)ab | | | | 3.12 (0.18)a | 0.16 (0.008)a | | 19.81 (0.32)a | |
| Open | 4.55 (0.13)a | | | | 2.50 (0.25)a | 0.13 (0.01)a | | 19.94 (0.08)a | |
| Pine | 4.10 (0.09)b | | | | 3.02 (0.29)a | 0.15 (0.01)a | | 19.66 (0.27)a | |

**Note:** LN, low N deposition site; HN, high N deposition site. Across canopy cover types, means with different letters are significantly different ($p \leq 0.05$) within a given site and soil horizon (e.g., LN oak, open, and pine forest floor).

*The *p* values for each variable are for site to site comparisons for a given canopy cover type and soil horizon (e.g., LN oak forest floor versus HN oak forest floor). Only significant *p* values are given.

mature abscission of luxurious foliar growth in pine (as a result of N deposition; Grulke and Balduman 1999). The end result is a high rate of N-enriched litter production and accumulation (Arbaugh et al. 1999; Fenn et al. 2003*b*). Additional site information is presented in Tables 1 and 2.

### Experimental design

At both study sites, the experimental plots were established in a randomized complete-block design with three blocks. Each block included three plots: an unfertilized control and a low (50 kg N·ha$^{-1}$·year$^{-1}$) and a high (150 kg N·ha$^{-1}$·year$^{-1}$) N fertilization plot. Each plot included at least 20 ponderosa pine (*Pinus ponderosa* Dougl. ex P. & C. Laws.) or Jeffrey pine (*Pinus jeffreyi* Grev. & Balf.) trees, 20 California black oak (*Quercus kelloggii* Newb.) trees, and a large, open area with no canopy cover. Only trees without mistletoe or other pest damage were chosen. Selected trees were permanently tagged for long-term studies. At both HN and LN, one of the unfertilized plots was located within long-term ozone injury study plots established in the early 1970s (Miller and McBride 1999). Fertilizer was applied annually beginning in 1997 on an individual-tree basis to an area circumscribed by the drip line and a 4-m diameter zone beyond the drip zone. Fertilizer was applied in winter or early spring as a slow-release granular ureaformaldehyde formulation.

### Net N mineralization and nitrification measurements

Annual net N mineralization and net nitrification rates were determined monthly for the forest floor (L, F, and H horizons combined) and the upper 10 cm of mineral soil using the soil tube method of in situ incubation (Raison et al. 1987). Tubes were inserted through the forest floor and into the underlying mineral soil with a rubber mallet. Insertion of the soil tubes (i.d. = 3.3 cm) caused minor soil compaction. Only the organic horizon and the top 10 cm of the mineral soil core were used for these assays. However, because of soil compaction caused by insertion, we actually sampled the mineral soil to a depth slightly greater than 10 cm. After insertion, a PVC cap was placed on the tube to exclude precipitation and soil disturbance. Holes were drilled into the sides of the caps for aeration. Subsamples of the initial (day 0) and incubated forest floor and mineral soil samples (after ca. day 30) were extracted with 2 mol/L KCl and analyzed for $NH_4^+$ and $NO_3^-$ with a Technicon TRAACS 800 Autoanalyzer[4] (Tarrytown, N.Y.), and net monthly $NH_4^+$ and $NO_3^-$ production were calculated (day 30 – day 0). Annual rates of net N mineralization and net nitrification were calculated as the sum of the monthly means under each canopy type for each calendar year. The net rates for months with missing data were estimated as the average of the two nearest months. The moisture contents of soil and the forest floor were also determined in subsamples from each soil core collected throughout the study.

Soil cores were incubated under three different canopy cover types — mature ponderosa pine or Jeffrey pine, California black oak, and canopy-free open areas — to test the effect of canopy cover or plant species on N cycling. However, because of the mixed-species nature of these forest stands, the forest floor includes litter from a mix of tree species. For each 30-day incubation period, soil tubes were installed under randomly selected oak and pine trees or in the open area of each of the long-term plots. Random sampling locations

[4] Mention of trade names or products is for information only and does not imply endorsement by the USDA.

**Table 3.** Significant variables in the general additive regression model used to determine the type and significance of the relationships between the explanatory variables and net N mineralization and nitrification rates.

| Variable name | Description of variable |
|---|---|
| Canopy type | Oak, open, or pine |
| Sqrt moisture | Square root of average of day 0 and day 30 (mineral soil or forest floor) moisture content (%) |
| Soil temperature | Average of day 0 and day 30 soil temperature (°C) |
| Sqrt initial $NH_4$+ | Square root of day 0 $NH_4^+$ (mg $NH_4^+$-N·(kg forest floor or mineral soil)$^{-1}$) |
| Sqrt initial $NO_3^-$ | Square root of day 0 $NO_3^-$ (mg $NO_3^-$-N·(kg forest floor or mineral soil)$^{-1}$) |
| Net mineralization | Simultaneous measured rate of net mineralization (mg N·m$^{-2}$·d$^{-1}$) |
| Sqrt precipitation | Square root of total precipitation (mm) in the 30 days preceding day 0 of the soil core incubation |
| Percent C | Carbon content (%) of forest floor or mineral soil horizon |
| Percent N | Nitrogen content (%) of forest floor or mineral soil horizon |
| C/N ratio | (% C / % N) |
| Julian date | Day 0 sampling date relative to 1 January 1900 |
| Slope % | Topographic slope (%) |
| pH | Mineral soil or forest floor pH in 0.01 mol/L $CaCl_2$ |
| Wood cover | Amount of surface covered by woody debris (%) |

were relocated every 6 months to avoid excessive soil disturbance. Soil tubes were installed in each of three replicate plots per fertilization level each month. Thus, $n = 3$ for net N mineralization and nitrification measurements in the forest floor and mineral soil of each of the canopy cover types (open, pine, or oak) for each fertilization level. In spring 2003, forest floor and mineral soil (0–10 cm depth) samples were collected near the study trees and open areas for measurement of pH and total carbon (C) and N in the forest floor and mineral soil. Mineral soil and forest floor pH values were determined in 0.01 $CaCl_2$ (soil–solution mixtures of 1:2 in mineral soil and 1:4 in forest floor, *m*/*m*) and total C and N were determined by combustion analysis (Carlo Erba Instruments, Milan, Italy; Model NA 1500, series 2).

### Statistical analyses

Statistical comparisons were made using the nonparametric Kruskal–Wallis rank-sum test in S-PLUS 2000 (Venables and Ripley 2002) because data were not normally distributed and did not have similar variances. Differences between treatments with $p$ value of $\leq 0.10$ were considered to be statistically significant. Both median and mean rates of net mineralization and nitrification better define the distribution of the data at the two sites. Median values demonstrate the general distribution of the data over the 3-year period, while mean values reflect the importance of spikes in microbial activity during the growing season. Box and whiskers plots were used to demonstrate the distribution of the data over the 3-year period. Relative nitrification (Robertson 1982) was calculated as the percentage of the N mineralized that was nitrified. When average net values for net N mineralization or nitrification were negative, these values were excluded from calculations of relative nitrification.

A general additive regression model (Hastie and Tibshirani 1990) was used to study the type and significance of relationships between various explanatory variables and the response variable of interest. The following model was used for studying the effects of covariates on the rates of net mineralization and net nitrification:

$$(\text{N transformation}) = \mu + f(x_1) + f(x_2) + \ldots + \varepsilon$$

where the rate of N transformation was either net mineralization or net nitrification (mg N·m$^{-2}$·d$^{-1}$) at a given site and soil horizon and for given environmental conditions, $\mu$ is the overall mean rate of N transformation (mg N·m$^{-2}$·d$^{-1}$) for the given site and soil horizon over varying environmental conditions, $f$ is the nonparametric transformation of the explanatory variables ($x_1$, $x_2$, etc.), and $\varepsilon$ is an estimate of random error. Explanatory variables that were significant in the model are given in Table 3.

The general additive model technique, GAM in S-PLUS 2000 (Venables and Ripley 2002), uses a locally weighted smoothing routine (Cleveland and Devlin 1988) to estimate the nonparametric transformations simultaneously with the other terms in the model. The model lets the data suggest the shape of the relationship between the explanatory variables and the response of interest within the context of holding variables in the model constant. The following factors were included in the statistical model testing for the main factors affecting N mineralization and nitrification rates: inorganic N at time 0, net mineralization (in the case of net nitrification), soil moisture content, soil temperature, mineral soil or forest floor pH, topographic slope and position, Julian date, canopy type, total precipitation (30 days prior to time 0), C and N content, C/N ratio, woody debris cover, and amount of litter in the forest floor. The least significant variables were removed one by one from the model based on the strength of their individual significance ($p > 0.05$ in the linear summary.lm and the nonparametric summary S-PLUS functions), the effect of their removal on the overall model fit (multiple $r^2$ reduced by less than 0.02), and to alleviate correlations among the independent variables creating false levels of significance. Square-root transformations of some of the variables were used, as they improved the overall model fit better than did log transformations.

## Results

### Low-N versus high-N sites: unfertilized plots

Net nitrification rates in the forest floor and mineral soil were significantly higher at HN than at LN in all three canopy cover types. Nitrogen mineralization rates were also significantly greater at HN than at LN in every instance

**Table 4.** Three-year median, mean, and standard error of the mean values for net N mineralization and nitrification.

| Site and canopy type | N mineralization mg N·m$^{-2}$·d$^{-1}$ | *p* value* | mg N·kg$^{-1}$·d$^{-1}$ | *p* value* | Nitrification mg N·m$^{-2}$·d$^{-1}$ | *p* value* | mg N·kg$^{-1}$·d$^{-1}$ | *p* value* |
|---|---|---|---|---|---|---|---|---|
| **Forest floor** | | | | | | | | |
| LN | | | | | | | | |
| Oak | 0.76, 3.42 (1.51)a | | 0.08, 0.28 (0.12)a | 0.04 | 0.52, 1.97 (0.64)a | 0.0001 | 0.04, 0.16 (0.05)a | 0.0002 |
| Open | 0.97, 1.28 (0.35)a | 0.009 | 0.11, 0.17 (0.04)a | 0.002 | 0.20, 0.52 (0.13)ab | 0.0001 | 0.03, 0.08 (0.02)ab | 0.0001 |
| Pine | 1.49, 0.34 (1.33)a | 0.0007 | 0.10, 0.0004 (0.09)a | | 0.18, 0.39 0.27)b | 0.0003 | 0.02, 0.03 (0.02)b | 0.0006 |
| HN | | | | | | | | |
| Oak | 5.20, 9.21 (6.34)a | | 0.37, 0.62 (0.36)a | | 9.13, 11.75 (2.49)a | | 0.55, 0.68 (0.13)a | |
| Open | 11.48, 9.87 (4.53)a | | 0.60, 0.50 (0.23)a | | 8.94, 10.45 (2.43)a | | 0.41, 0.54 (0.12)ab | |
| Pine | 13.34, 16.99 (9.02)a | | 0.67, 0.84 (0.38)a | | 6.82, 4.03 (3.17)a | | 0.36, 0.30 (0.11)b | |
| **Mineral soil** | | | | | | | | |
| LN | | | | | | | | |
| Oak | 1.05, 2.40 (0.76)a | 0.017 | 0.01, 0.02 (0.01)a | 0.017 | 1.05, 1.88 (0.37)b | 0.0002 | 0.01, 0.02 (0.004)b | 0.0002 |
| Open | 3.16, 4.70 (1.13)a | 0.001 | 0.03, 0.04 (0.01)a | 0.001 | 2.11, 3.52 (0.57)a | 0.0001 | 0.02, 0.03 (0.01)a | 0.0001 |
| Pine | 2.11, 4.00 (0.87)a | 0.005 | 0.02, 0.04 (0.01)a | 0.005 | 1.05, 1.55 (0.29)b | 0.0001 | 0.01, 0.01 (0.003)b | 0.0001 |
| HN | | | | | | | | |
| Oak | 7.38, 5.22 (2.23)b | | 0.07, 0.05 (0.02)b | | 7.38, 6.30 (1.93)b | | 0.07, 0.06 (0.02)b | |
| Open | 11.07, 10.38 (2.92)a | | 0.11, 0.10 (0.03)a | | 10.02, 11.97 (2.00)a | | 0.10, 0.11 (0.02)a | |
| Pine | 8.96, 10.99 (2.40)a | | 0.09, 0.10 (0.02)a | | 8.43, 9.20 (1.98)ab | | 0.08, 0.09 (0.02)ab | |

**Note:** The first value is the median, the second value is the mean, and the standard error is in parentheses. LN, low N deposition site; HN, high N deposition site. Across canopy cover types, means with different letters are significantly different ($p \leq 0.10$) within a given site and soil horizon (e.g., LN oak, open, and pine forest floor).

*The *p* values for each variable are for site to site comparisons for a given canopy cover type and soil horizon (e.g., LN oak forest floor versus HN oak forest floor). Only significant *p* values are given.

except in forest floor under oak canopies (Table 4). Median values of net N mineralization (mg N·m$^{-2}$·d$^{-1}$) in forest floor were 7–12 times higher at HN than at LN, and values of net nitrification were 18- to 45-fold greater at HN than at LN under the three canopy cover types. Nitrogen fluxes in forest floor on an area basis were much greater at HN because of greater fluxes per litter mass and the high litter accumulation at HN. Median rates of net N mineralization and nitrification (mg N·m$^{-2}$·d$^{-1}$) in mineral soil were 4–8 times greater at HN than at LN (Table 4).

Net N mineralization rates in the forest floor from the three canopy cover types, on a per-mass basis (mg N·kg$^{-1}$·d$^{-1}$), were 5–7 times higher at HN than at LN, while net nitrification rates were 14–18 times higher at HN (Table 4). There was much greater variability in net N mineralization and net nitrification at HN, as expected because of the much higher activity levels in mineral soil and forest floor at HN (Table 4). Net mineralization and nitrification rates with negative values were found in some instances, indicating net immobilization of $NH_4^+$ and $NO_3^-$ during some of the 30-day field incubations. Greater negative values or higher net inorganic N immobilization rates were measured at HN compared with LN.

### Total fluxes and forest floor versus mineral soil: unfertilized plots

The mean annual rate of net N mineralization and the mean annual rate of nitrification in the soil column (the forest floor plus top 10 cm of mineral soil) for the three canopy cover types combined over the 3 years of the study were 19.0 and 11.2 kg N·ha$^{-1}$·year$^{-1}$ at LN compared with 59.8 and 55.9 kg N·ha$^{-1}$·year$^{-1}$ at HN, respectively. Net nitrification in the soil column ranged from 4.8 to 19.0 kg N·ha$^{-1}$·year$^{-1}$ at LN and from 26.0 to 82.8 kg N·ha$^{-1}$·year$^{-1}$ at HN among the three canopy types and the 3 years of the study (Table 5).

Under open and pine canopies at LN, the forest floor accounted for only 5%–16% of net N mineralization and 10%–15% of net nitrification. Under oak at LN, the forest floor accounted for 48% of net N mineralization and 39% of net nitrification (Table 5). Under oak and open canopies at HN the forest floor accounted for 55%–56% of net N mineralization and 38% of net nitrification. Under pine at HN, the forest floor accounted for 48% of net N mineralization and 26% of net nitrification.

### Relative nitrification index in unfertilized plots

Relative nitrification is a potential indicator of N saturation. In mineral soil and forest floor, relative nitrification was higher at HN than at LN, except for pine forest floor (Table 5). Relative nitrification in mineral soil under oak and open canopies was >100% at HN compared with ~75% at LN. Relative nitrification in forest floor under oak and open canopies was 92% and 78% at HN compared with 53% and 43% at LN, respectively. Relative nitrification in pine forest floor was only 21% and 40% at HN and LN compared with 80% and 36% in mineral soil under pine at HN and LN, respectively (Table 5).

### Effect of canopy cover type: unfertilized plots

There were no significant differences in net mineralization in the forest floor among the three canopy types at either site. However, net nitrification rates in forest floor under oak canopies were generally higher than rates under pine at LN and HN (Table 4). Relative nitrification was lower under

**Table 5.** Net N mineralization, net nitrification, and relative nitrification (%) by species and soil horizon (FF, forest floor; MS, mineral soil) and comparison with values from the literature.

| Site and canopy type | Soil horizon | N mineralization (kg N·ha$^{-1}$·year$^{-1}$) | Nitrification (kg N·ha$^{-1}$·year$^{-1}$) | Relative nitrification (%) | Reference* |
|---|---|---|---|---|---|
| LN | | | | | |
| Oak | FF | 12.4, 5.7, 8.3 | 4.5, 5.7, 3.9 | 52.9 | This study |
| Open | FF | 2.4, 4.2, 3.6 | 2.2, 1.1, 1.1 | 42.9 | |
| Pine | FF | –5.7, 6.9, 1.4 | –0.3, 2.3, 1.0 | 39.9 | |
| Mean relative nitrification (all cover types) | FF | | | 45.2 | |
| HN | | | | | |
| Oak | FF | 42.3, 35.8, –0.8 | 24.7, 47.2, 25.9 | 92.0 | This study |
| Open | FF | –12.3, 38.5, 43.3 | 14.3, 31.9, 31.8 | 77.8 | |
| Pine | FF | –48.3, 86.6, 62.9 | –0.7, 13.0, 19.0 | 21.4 | |
| Mean relative nitrification (all cover types) | FF | | | 63.7 | |
| LN | | | | | |
| Oak | MS | 11.2, 7.3 10.2 | 7.7, 8.2, 5.9 | 75.7 | This study |
| Open | MS | 15.8, 19.0, 19.2 | 16.8, 11.4, 11.8 | 74.2 | |
| Pine | MS | 18.3, 15.1, 15.4 | 6.3, 7.5, 3.8 | 35.9 | |
| Mean relative nitrification (all cover types) | MS | | | 61.9 | |
| HN | | | | | |
| Oak | MS | 30.4, 35.8, –1.7 | 36.8, 35.6, 5.7 | 109.6 | This study |
| Open | MS | 55.3, 28.6, 31.2 | 51.4, 32.7, 45.0 | 112.2 | |
| Pine | MS | 43.8, 55.5, 11.7 | 29.3, 52.1, 7.0 | 79.6 | |
| Mean relative nitrification (all cover types) | MS | | | 100.5 | |
| **Additional data from the SBM and Sierra Nevada mixed-conifer sites (8-week laboratory incubations)** | | | | | |
| HN (SBM) | FF | | | 40.0 | Average value from Fenn et al. 1996, 2003*b* |
| HN (SBM) | MS | | | 98.3 | Average value from Fenn et al. 1996, 2003*b* |
| Dogwood (SBM, high-pollution site) | FF | | | 94.5 | Fenn et al. 1996 |
| Dogwood (SBM, high-pollution site) | MS | | | 78.2 | Fenn et al. 1996 |
| LN (SBM) | FF | | | 47.1 | Average value from Fenn et al. 1996, 2003*b* |
| LN (SBM) | MS | | | 82.3 | Average value from Fenn et al. 1996, 2003*b* |
| Heart Bar (SBM, low-pollution site) | FF | | | 82.5 | Fenn et al. 1996 |
| Heart Bar (SBM, low-pollution site) | MS | | | 80.1 | Fenn et al. 1996 |
| Mountain Home (southern Sierra, moderate-pollution site) | FF | | | 87.7 | Fenn et al. 2003*b* |
| Mountain Home (southern Sierra, moderate-pollution site) | MS | | | 93.9 | Fenn et al. 2003*b* |
| **Sites from western North America** | | | | | |
| Northern California, Cascade Range, mixed-conifer forest | FF | 18.1 | 10.7 | 59.1 | Powers 1990 |
| Northern California, Cascade Range, mixed-conifer forest upper 15 cm | MS | 40.4 | 28.8 | 71.3 | Powers 1990 |
| Northern Arizona, ponderosa pine – bunchgrass | FF | 2.0 | 0.5 | 25.0 | Kaye and Hart 1998 |
| Northern Arizona, ponderosa pine – bunchgrass, upper 15 cm | MS | 7.5 | 3.6 | 48.0 | Kaye and Hart 1998 |
| New Mexico, ponderosa pine | FF | | | 0.4 | Gosz and White 1986 |
| New Mexico, ponderosa pine, upper 10 cm | MS | | | 36.2 | Gosz and White 1986 |
| Old-growth Douglas-fir and western hemlock, central Oregon, upper 15 cm | MS | 18.6 | 4.5 | 24.2 | Hart and Perry 1999 |
| British Columbia, old-growth coastal coniferous forest | FF | | | 5.9 | Prescott 1997 |
| British Columbia, old-growth coastal coniferous forest, upper 20 cm | MS | | | 40.6 | Prescott 1997 |
| **Sites from eastern North America** | | | | | |
| Harvard Forest, central Massachusetts, red pine forest (average of 4 years) | FF | 46.5 | 2.2 | 4.7 | Magill et al. 1997 |
| Harvard Forest, central Massachusetts, red pine forest (average of 4 years) | MS | 50.4 | 16.7 | 33.0 | Magill et al. 1997 |

**Table 5.** (*concluded*).

| Site and canopy type | Soil horizon | N mineralization (kg N·ha$^{-1}$·year$^{-1}$) | Nitrification (kg N·ha$^{-1}$·year$^{-1}$) | Relative nitrification (%) | Reference* |
|---|---|---|---|---|---|
| Harvard Forest, central Massachusetts, hardwood forest (average of 4 years) | FF | 48.8 | 0.0 | 0.0 | Magill et al. 1997 |
| Harvard Forest, central Massachusetts, hardwood forest (average of 4 years) | MS | 27.3 | 0.5 | 1.8 | Magill et al. 1997 |
| Northwestern Pennsylvania, hardwood forest, upper 15 cm, includes shallow forest floor | MS + FF | 121.0 | 85.8 | 70.9 | Bowden et al. 2000 |
| Fernow, West Virginia, N-saturated mature forest, upper 5 cm | MS | 123.8 | 114.3 | 92.3 | Gilliam et al. 2001 |
| Six mid-Appalachian watersheds with $NO_3^-$-N export of 1–5 kg·ha$^{-1}$·year$^{-1}$, primarily hardwood forests, upper 10 cm | MS | | | 83.8 | Williard et al. 1997 |
| Adirondack mountains, New York; 0–15 cm depth consisting mainly of forest floor, conifer forest | FF | 82.4 | 2.4 | 2.9 | Ohrui et al. 1999 |
| Adirondack mountains, New York; 0–15 cm depth including forest floor in upper 5 cm and mostly mineral soil at 5–15 cm, hardwood forest | MS + FF | 106.9 | 29.0 | 27.1 | Ohrui et al. 1999 |
| Mount Ascutney, Vermont, predominantly red spruce (data are average of 3 years) | FF | 15.1 | 0.03 | 0.20 | McNulty and Aber 1993 |
| **Summary results from literature surveys** | | | | | |
| Hardwood forests | | 87.4 | 39.4 | 40.3 | Gilliam et al. 2001 |
| Hardwood forests | | 87.0 | 64.0 | 73.6 | Bonilla and Rodà 1992 |
| Conifer forests | | 67.0 | 22.7 | 23.4 | Gilliam et al. 2001 |
| Conifer forests | | 43.0 | 14.0 | 32.6 | Bonilla and Rodà 1992 |

**Note:** LN, low N deposition site; HN, high N deposition site. Nitrogen mineralization and nitrification values given from this study are for 1997, 1998, and 1999, while the relative nitrification values were calculated from average values for the 3 years. Data for net mineralization and nitrification for those treatment combinations (site – canopy cover – soil horizon – year) in this study when annual net N mineralization was negative (5 of 36 instances) were not included in the data summarized in this table and when calculating relative nitrification.

*For Prescott (1997) no annual rate data for N mineralization or nitrification are available, and the field assay was a 63-day incubation. In Williard et al. (1997), the field incubation time was 5 weeks. For Gosz and White (1986) relative nitrification values were calculated from five 10-week incubations. Data from the literature surveys of Gilliam et al. (2001) and Bonilla and Rodà (1992) are presumably mainly mineral soil data, but may also include forest floor horizons in some cases.

pine than under oak and open canopies in mineral soil at both sites and in forest floor at HN (Table 5). At LN net N mineralization in soil did not differ significantly among the three cover types, but at HN the median N mineralization value for mineral soil was significantly lower under oak ($p$ = 0.09) than under pine or in open areas (Table 4). At LN net nitrification rates in mineral soil were low, but they were greater in open areas than in oak ($p$ = 0.05) and pine ($p$ = 0.02). At HN there were no significant differences in nitrification in mineral soil among the three canopy types (mg N·m$^{-2}$·d$^{-1}$) except that rates in open mineral soil were higher than those in oak mineral soil ($p$ = 0.09).

## General additive models

The general additive models display the nonlinear relationships between the explanatory variables — soil chemical and physical conditions and environmental parameters — and the rates of net mineralization and net nitrification. The models for net mineralization show that the most important terms are the initial $NH_4^+$ and $NO_3^-$ concentrations. Soil moisture and temperature combined explained only 1% to 6% of the variability of net mineralization at each site, while the initial $NH_4^+$ and $NO_3^-$ concentrations combined explained from 3% to 25% of the variability. The model for net mineralization in the forest floor shows a threshold initial $NH_4^+$ concentration of 14 mg $NH_4^+$-N·(kg forest floor)$^{-1}$ at LN (Fig. 1*c*) and of 47.3 mg $NH_4^+$-N·(kg forest floor)$^{-1}$ at HN (Fig. 2*b*) above which net mineralization significantly decreased (or net immobilization increased). Only at HN was there a threshold initial $NO_3^-$ concentration (27.0 mg $NO_3^-$-N·(kg forest floor)$^{-1}$; Fig. 2*c*) above which net mineralization in the forest floor significantly decreased. The threshold $NH_4^+$ concentration in the mineral soil above which net mineralization in the mineral soil significantly decreased was 1.7 mg $NH_4^+$-N·(kg soil)$^{-1}$ at LN (Fig. 1*g*) and 2.0 mg $NH_4^+$-N·(kg soil)$^{-1}$ at HN (Fig. 2*j*). Only HN has a threshold $NO_3^-$ concentration (7.0 mg $NO_3^-$-N·(kg soil)$^{-1}$) above which net mineralization in the mineral soil significantly decreased.

Net mineralization was the best predictor of net nitrification rates at both sites, explaining from 29% to 88% of the variability. Net mineralization was positively related to net nitrification (Figs. 3*a*, 3*g*, 4*b*, 4*e*) with a slope of the linear portion of the relationship of 0.25 and 0.42 in the forest floor at LN and HN and 0.39 and 0.89 in the mineral soil at LN and HN, respectively. The higher slopes in mineral soil relative to the forest floor and at HN relative to LN reflect the higher relative nitrification in soil and at HN. The saturation point above which further increases in the rate of net mineralization led to no change or a decrease in net nitrification was higher at HN than at LN. The addition of initial $NH_4^+$ concentrations to the model for net nitrification increased the multiple $r^2$ by 0.01–0.18. Initial $NH_4^+$ concentrations in the models show threshold values above which the rates of net nitrification increase. The threshold $NH_4^+$ concentrations

**Fig. 1.** General additive model output showing the nonlinear relationships of soil chemical, soil physical, and environmental parameters in predicting the rate of net N mineralization in forest floor (*a–d*; $r^2$ = 0.19) and mineral soil (*e–h*; $r^2$ = 0.15) at Camp Osceola (low N deposition site). The *y* axis in each of the plots represents the individual effect (mg $N \cdot m^{-2} \cdot d^{-1}$) of each dependent variable on predicting net mineralization. The broken lines in each plot represent the standard error, while the tick marks along the *x* axis represent individual sample values. In the case of nonnumeric independent variables (e.g., canopy cover type), the plots show the effect of a given discrete nonnumeric value of *x* (e.g., pine canopy) on the predicted rate of N transformation.

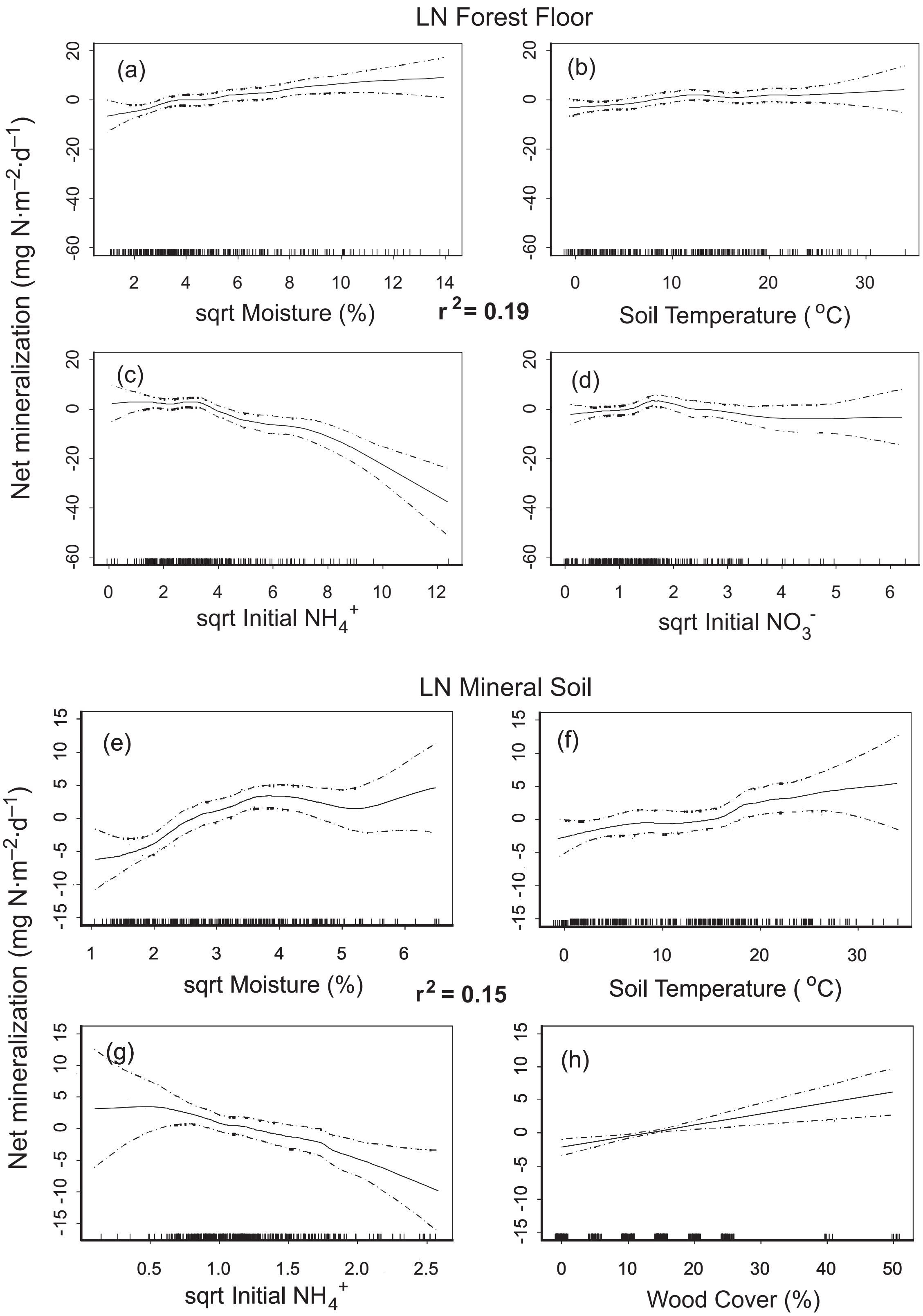


**Fig. 2.** General additive model output showing the nonlinear relationships of soil chemical, soil physical, and environmental parameters in predicting the rate of net N mineralization in forest floor (*a–f*; $r^2$ = 0.31) and mineral soil (*g–l*; $r^2$ = 0.35) at Camp Paivika (high N deposition site). See caption of Fig. 1 for a detailed description of the figure.

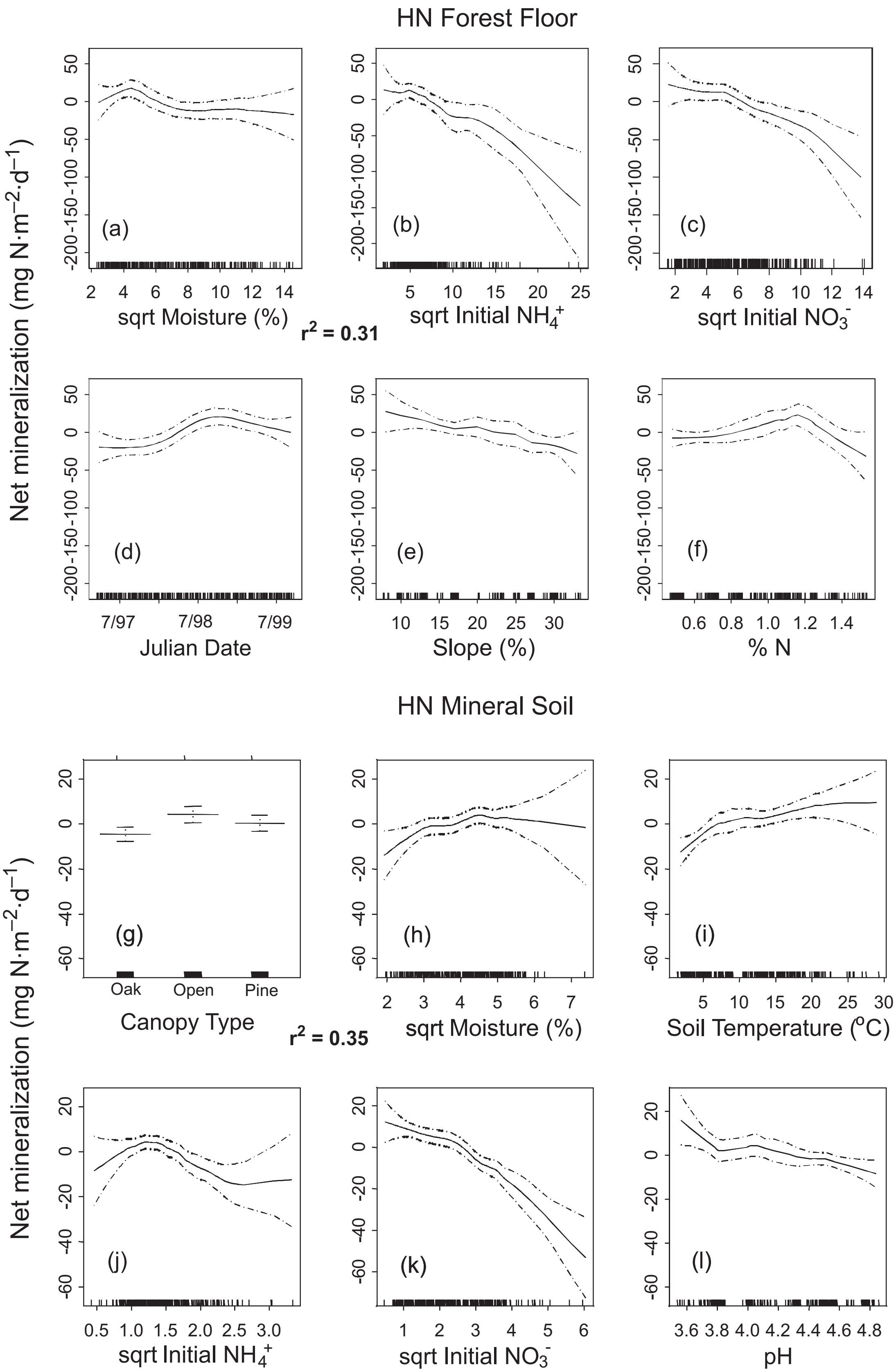


**Fig. 3.** General additive model output showing the nonlinear relationships of soil chemical, soil physical, and environmental parameters in predicting the rate of net nitrification in forest floor (*a–e*; $r^2$ = 0.40) and mineral soil (*f–j*; $r^2$ = 0.53) at Camp Osceola (low N deposition site). See caption of Fig. 1 for a detailed description of the figure.

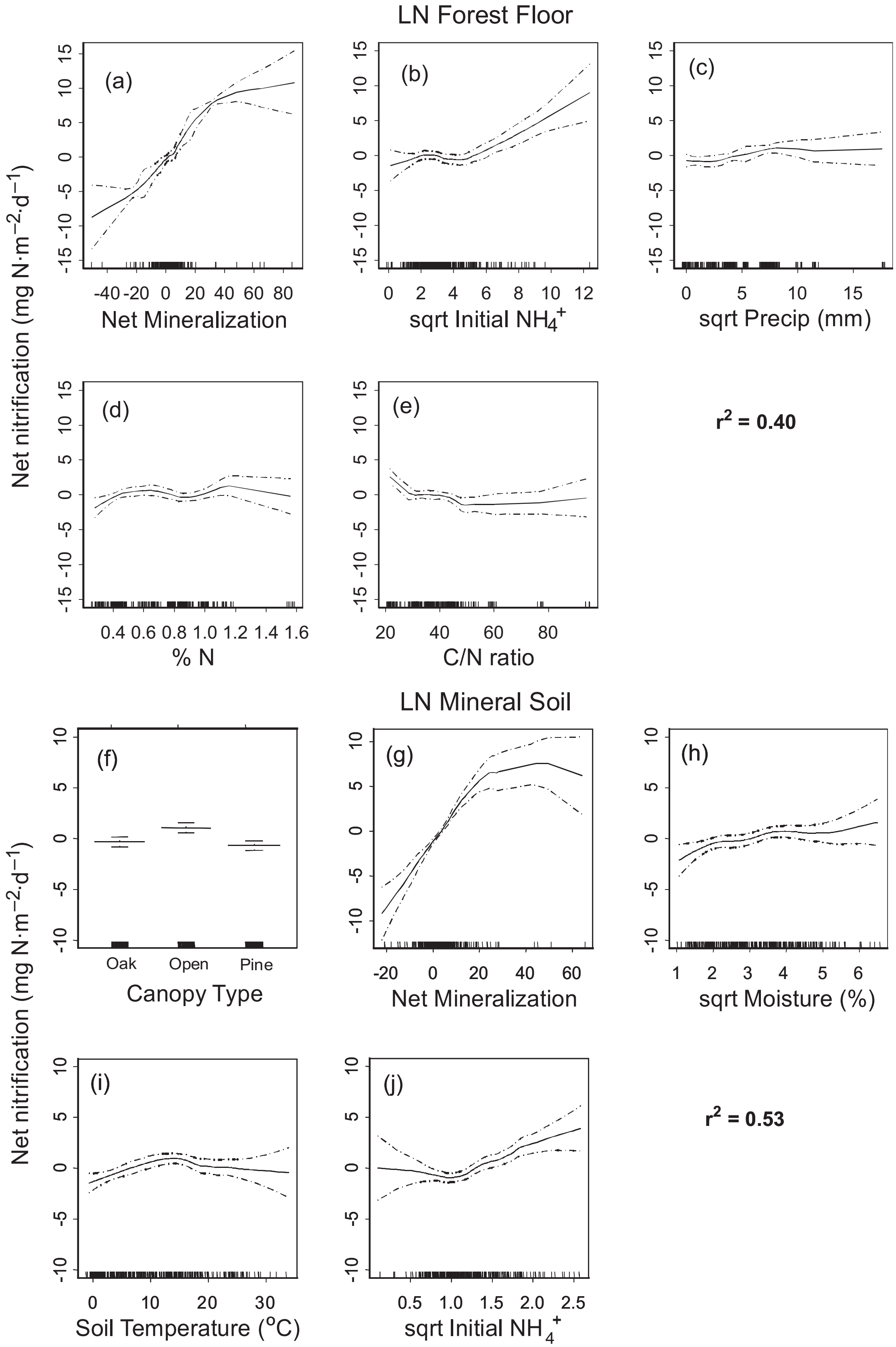
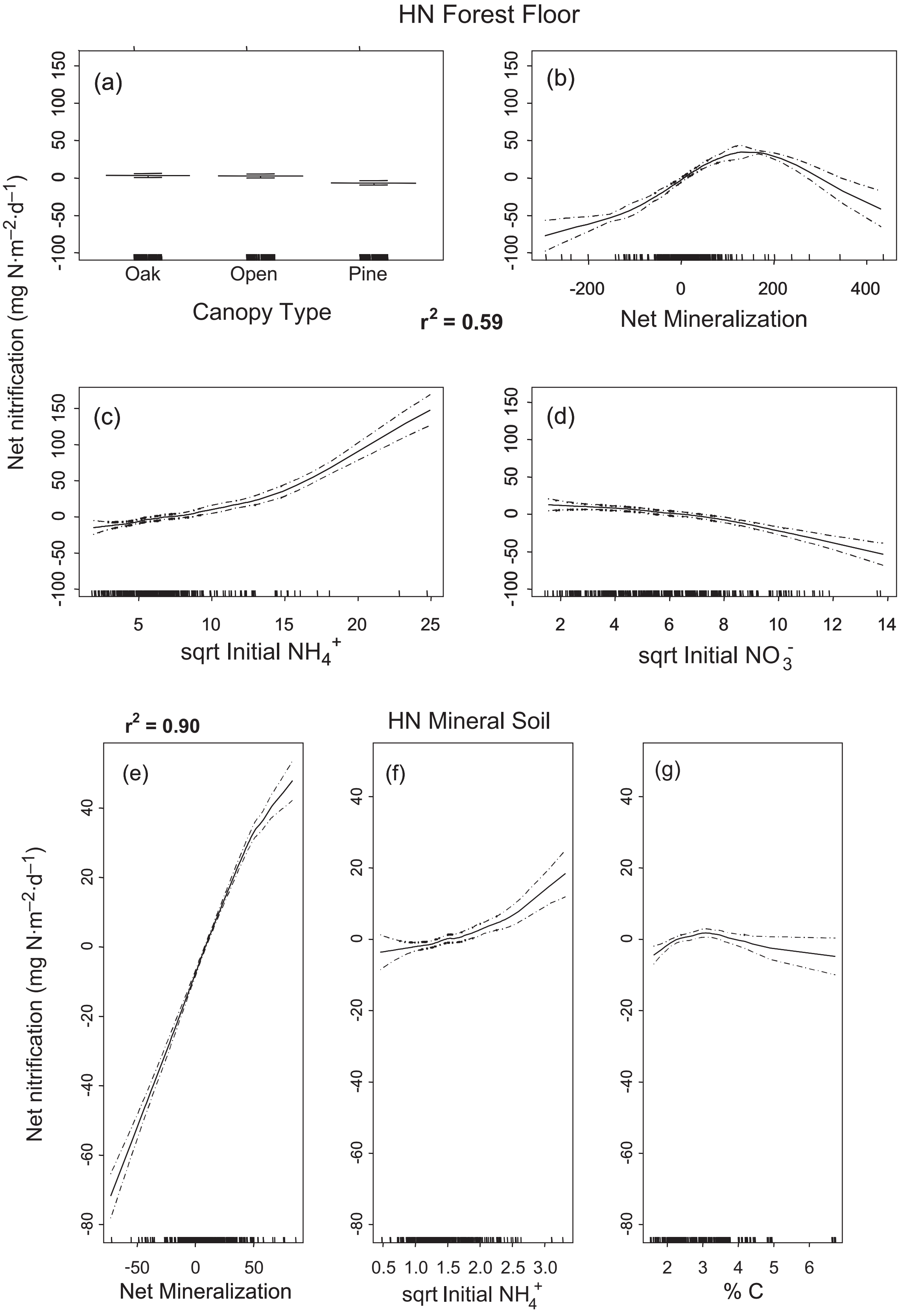


**Fig. 4.** General additive model output showing the nonlinear relationships of soil chemical, soil physical, and environmental parameters in predicting the rate of net nitrification in forest floor (*a–d*; $r^2$ = 0.59) and mineral soil (*e–g*; $r^2$ = 0.90) at Camp Paivika (high N deposition site). See caption of Fig. 1 for a detailed description of the figure.



were 26.7 and 36.8 mg $NH_4^+$-N·(kg litter)$^{-1}$ in the forest floor at LN and HN and 1.6 and 2.7 mg $NH_4^+$-N·(kg soil)$^{-1}$ in the mineral soil at LN and HN, respectively. The addition of initial $NO_3^-$ concentrations to the model for net nitrification in HN forest floor increased the multiple $r^2$ by 0.10. The model for net nitrification of the forest floor at HN shows a threshold $NO_3^-$ concentration (36.0 mg $NO_3^-$-N·(kg soil)$^{-1}$) above which net nitrification decreased (or the net immobilization of $NO_3^-$ increased).

General additive models of soil temperature and moisture content combined explained only 3% to 16% (highest in mineral soil at LN) of the variability in net nitrification. The models (not shown here) show threshold soil temperatures (4–8 °C) and soil moisture contents (9%–15% ovendry mass) above and below which net nitrification at each site increased or decreased, respectively, with optimal rates reached at soil temperatures of 10 to 12 °C. However, positive values of net nitrification were also found under snowpack.

### Forest floor and mineral soil pH and litter mass: unfertilized plots

The median forest floor pH values ranged from 4.09 to 5.15 under the three canopy cover types at LN and from 4.09 to 4.34 at HN (Table 2). Only the pH of forest floor under oak was significantly higher at LN than at HN. At LN the pH of oak forest floor (5.15) was significantly greater than that of pine (4.17) and open (4.09) forest floor (Table 2). The pH of mineral soil was significantly higher at LN than at HN for all three cover types (Table 2). Median mineral soil pH values ranged from 4.97 to 5.56 under the three canopy cover types at LN and from 4.10 to 4.55 at HN. At LN the pH of oak mineral soil was greater than that of open and pine mineral soils. At HN, the pH of the open mineral soil was greater than that of pine mineral soil but not significantly different from that of the mineral soil under oak.

The average forest floor mass was significantly greater at HN than at LN for all three canopy cover types (Table 2). Median values ranged from 4.6 to 9.4 kg·m$^{-2}$ at LN and from 11.3 to 12.2 kg·m$^{-2}$ at HN. At LN forest floor mass was greater under pine than in open and oak sites, and forest floor mass was greater under oak than in open areas. At HN forest floor mass under pine and the forest floor mass in the open area were both significantly greater than that under oak.

### Carbon and N content of forest floor and mineral soil: unfertilized plots

There were no significant differences in the percent C of forest floor or mineral soil between the two sites (Table 2). The median percent C of the forest floor at HN was significantly greater under oak and pine than in the open. No significant differences existed in the percent C among the canopy types in mineral soil at HN, nor among canopy types in forest floor and mineral soil at LN. The median percent N of forest floor and the median percent N of mineral soil under oak and pine canopy at HN were significantly greater than those at LN, but there were no significant differences between both sites under open canopy (Table 2). At HN the median percent N in the forest floor was greater under oak and pine than under open canopy. The median C/N ratios of forest floor and mineral soil at LN were significantly greater than those at HN for all of the canopy types. At HN the median C/N ratio was significantly greater under pine than under open canopy (Table 2).

### Effects of fertilization on net N mineralization in forest floor

Because of significant differences in the mass of the forest floor among plots, the rates of net mineralization and nitrification are given on a mass (mg N·kg$^{-1}$·d$^{-1}$) and on an area basis (mg N·m$^{-2}$·d$^{-1}$) for the forest floor (Fig. 5*a*; Tables 6 and 7). The median (mean) rates of net mineralization in the forest floor at LN (all species combined) on an area basis were 1.10 (1.67), 1.80 (5.47), and 2.74 (9.01) mg N·m$^{-2}$·d$^{-1}$ in the control, low, and high fertilization treatments, respectively. Fertilization significantly increased the rates of net mineralization in forest floor at LN for both the low and high fertilization treatments relative to the control on both a mass and an area basis. The rates of net mineralization in the high fertilization treatment at LN were also significantly greater than those in the low fertilization treatment but only on a mass basis (Tables 6 and 7).

The median (mean) rates of net mineralization in the forest floor at HN (all species combined) were 11.32 (12.03), 9.45 (10.26), and 10.95 (23.58) mg N·m$^{-2}$·d$^{-1}$ in the control, low, and high fertilization treatments, respectively. The mean (but not the median) net mineralization rate of oak forest floor was significantly greater in the high fertilization treatment than in the control at HN on both a mass ($p$ = 0.035) and an area basis ($p$ = 0.07). This increase was not observed in forest floor in the open or under pine (Tables 6 and 7). No other significant differences were found in the rates of net mineralization of the forest floor at HN among the fertilization treatments. Nor were there significant differences in net mineralization among canopy types at HN.

The rates of net mineralization for all treatments at HN were significantly higher than those in the control and low fertilization treatments at LN on both a mass ($p \leq 0.07$) and an area basis ($p \leq 0.005$). Only with the addition of 150 kg N·ha$^{-1}$·year$^{-1}$ in the high fertilization treatment did the rates of net mineralization at LN approach those of the control at HN. Analyzed separately by canopy type, net mineralization in the high fertilization treatment at LN significantly exceeded that in the control plots at HN only in open litter and only on a mass basis ($p$ = 0.07). Because of N immobilization and the high variability in mineralization rates at HN, the rates of net mineralization were not significantly different between the two sites in some cases.

### Effects of fertilization on net nitrification in the forest floor

The median (mean) rates of net nitrification in the forest floor at LN (all species combined) were 0.30 (0.96), 0.42 (1.67), and 0.63 (4.91) mg N·m$^{-2}$·d$^{-1}$ in the control, low, and high fertilization treatments, respectively (Fig. 5*b*; Tables 6 and 7). The rates of net nitrification in the high fertilization treatment were significantly greater than those in the control at LN on both a mass and an area basis and significantly greater than those in the low fertilization treatment only on a mass basis. In the low fertilization treatment rates were greater than in the control only on a mass basis.

**Fig. 5.** Box plots of median rates of net mineralization and net nitrification on an area basis (mg N·m$^{-2}$·d$^{-1}$) for forest floor (*a*–*b*) and mineral soil (*c*–*d*) for each of the fertilizer treatments (kg N·ha$^{-1}$·year$^{-1}$) at a high (HN) and a low (LN) N deposition site for the sampling period March 1997 – January 2000. Data for the three canopy types are combined. In the box plots the shaded area represents the approximate 95% confidence interval of the median, the box represents the interquartile range (spread of 50% of the data), and the span of the whiskers represent either 1.5 times the interquartile range or the extremes of the data, whichever is less. Horizontal lines outside of the box and whiskers represent individual outliers whose values are greater or less than the 1.5 interquartile range.

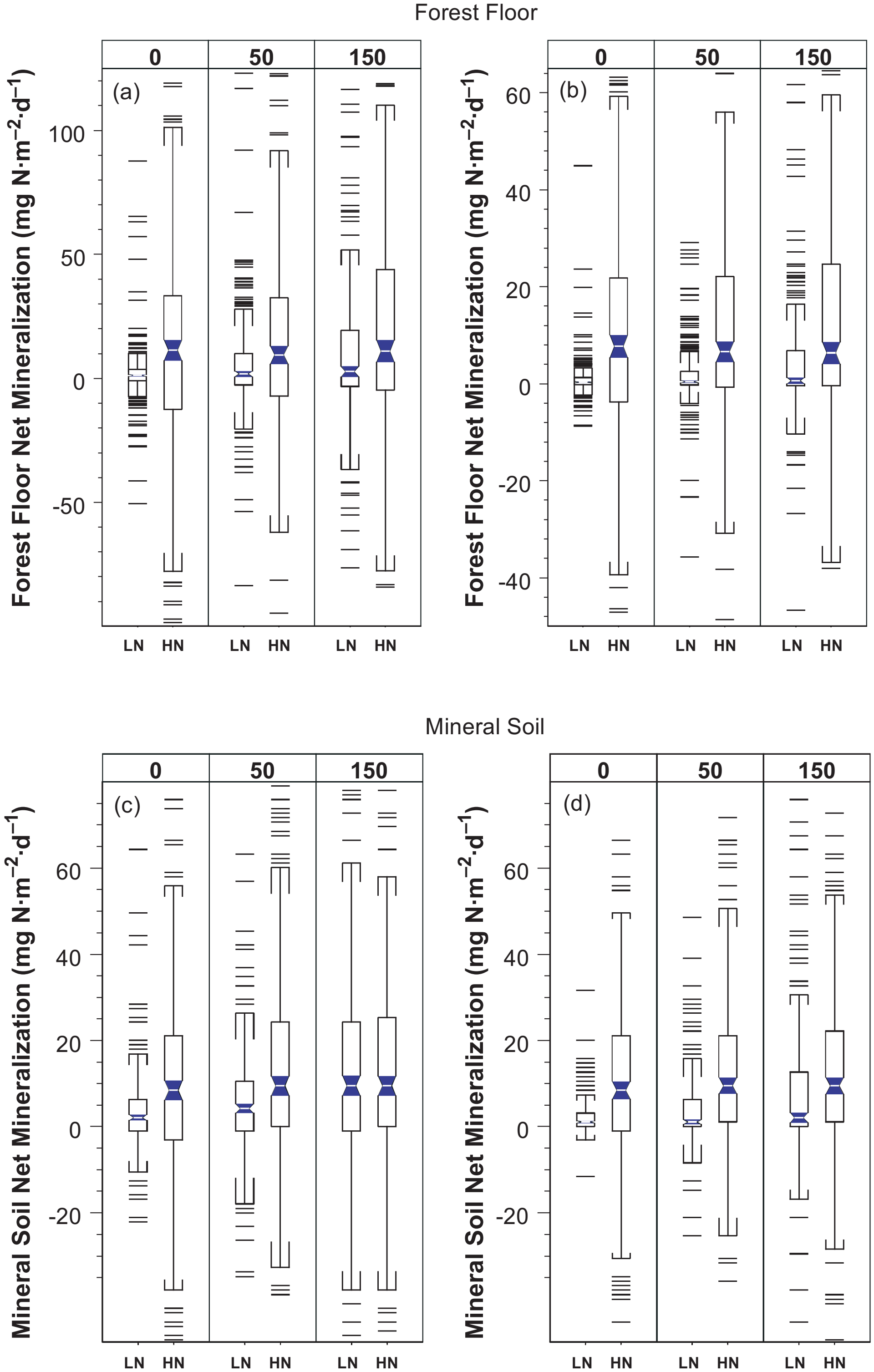


**Table 6.** Mean rates of net N mineralization and net nitrification at a low N deposition site (LN) and high N deposition site (HN) on an area basis.

| | | Net mineralization (mg N·m$^{-2}$·d$^{-1}$) | | | | Net nitrification (mg N·m$^{-2}$·d$^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Fertilization rate (kg N·ha$^{-1}$·year$^{-1}$) | LN | *p* value* | HN | *p* value* | LN | *p* value* | HN | *p* value* |
| Oak forest floor | 0 | 1.60 (0.70)a | 0.06 | 4.30 (2.93)a | 0.02 | 0.92 (0.29)a | 0.07 | 5.49 (1.15) | |
| | 50 | 1.47 (0.90) | | 8.20 (2.73) | | 1.40 (0.43)b | | 6.50 (1.36) | |
| | 150 | 3.49 (1.14)b | | 14.36 (3.36)b | | 1.40 (0.38) | | 9.38 (1.66) | |
| Open forest floor | 0 | 0.60 (0.16)a | 0.002 | 4.61 (2.09) | | 0.24 (0.06)a | 0.02 | 4.88 (1.12) | |
| | 50 | 1.55 (0.60)a | 0.02 | 3.76 (2.59) | | 0.29 (0.08)a | 0.03 | 5.41 (1.30) | |
| | 150 | 4.23 (1.12)b | | 8.63 (2.19) | | 1.80 (0.38)b | | 6.08 (1.19) | |
| Pine forest floor | 0 | 0.16 (0.62)a | 0.05 | 7.94 (4.17) | | 0.18 (0.13) | | 1.88 (1.47) | |
| | 50 | 4.63 (1.79)b | | 2.34 (2.85) | | 0.65 (0.23) | | 3.86 (1.25) | |
| | 150 | 4.88 (2.69) | | 10.10 (3.16) | | 3.61 (1.04) | | 7.43 (1.71) | |
| Oak mineral soil | 0 | 1.56 (0.48)a | 0.0001 | 3.40 (1.43)a | 0.05 | 1.22 (0.24)a | 0.01 | 4.11 (1.24) | |
| | 50 | 3.33 (0.94)a | 0.006 | 5.56 (1.61) | | 2.42 (0.49) | | 5.98 (1.42) | |
| | 150 | 8.76 (1.51)b | | 10.50 (2.34)b | | 5.03 (0.99)b | | 9.52 (2.01) | |
| Open mineral soil | 0 | 3.07 (0.71)a | 0.009 | 6.77 (1.88) | | 2.30 (0.36)a | 0.0001 | 7.81 (1.29) | |
| | 50 | 5.07 (1.80)a | 0.03 | 7.18 (2.42) | | 3.27 (0.60)a | 0.007 | 8.15 (1.63) | |
| | 150 | 11.20 (3.47)b | | 10.70 (2.03) | | 8.03 (1.22)b | | 9.90 (1.70) | |
| Pine mineral soil | 0 | 2.61 (0.57)a | 0.05 | 7.17 (1.52)a | 0.05 | 1.01 (0.19) | | 6.00 (1.26)a | 0.05 |
| | 50 | 3.57 (2.95) | | 14.71 (2.89)b | | 0.15 (2.01) | | 10.16 (1.55)b | |
| | 150 | 6.86 (2.42)b | | 8.88 (2.25)a | 0.02 | 2.45 (0.80) | | 7.44 (1.55)a | 0.05 |

**Note:** Standard errors of the mean are given in parentheses; *n* = 98–100. Values with the same lowercase letter are not significantly different based on least significant difference comparisons for the three fertilization treatments within each site, canopy type, and soil horizon combination.

*The *p* values indicate the level of significance for the individual comparisons that were significantly different within each site, canopy type, and soil horizon combination. Only significant *p* values are given.

**Table 7.** Mean rates of net N mineralization and net nitrification at a low N deposition site (LN) and high N deposition site (HN) on a mass basis.

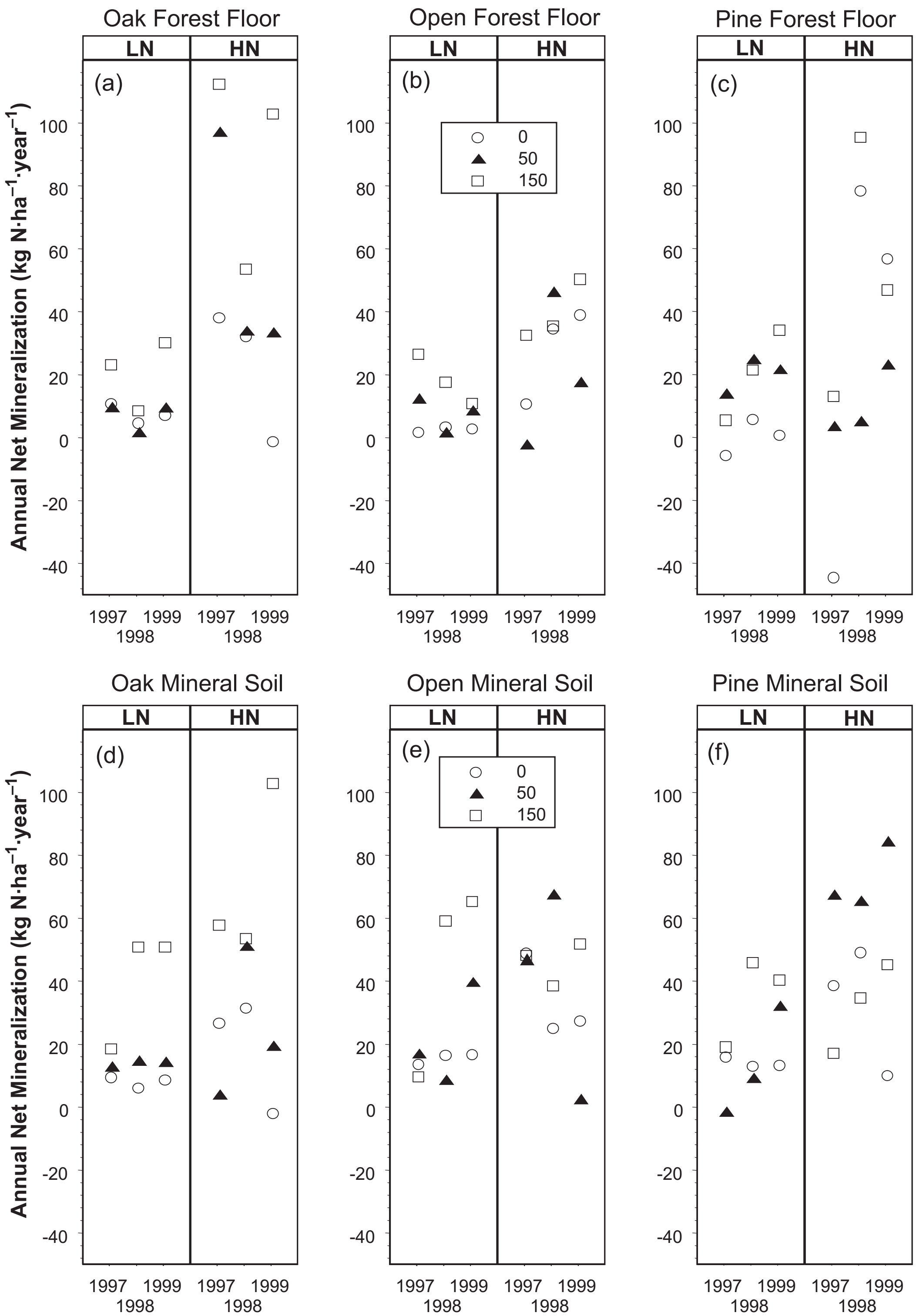
| | | Net mineralization (mg N·kg$^{-1}$·d$^{-1}$) | | | | Net nitrification (mg N·kg$^{-1}$·d$^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|
| Canopy type and soil horizon | Fertilization rate (kg N·ha$^{-1}$·year$^{-1}$) | LN | *p* value* | HN | *p* value* | LN | *p* value* | HN | *p* value* |
| Oak forest floor | 0 | 0.28 (0.12)a | 0.06 | 0.62 (0.36)a | 0.02 | 0.16 (0.05) | | 0.68 (0.13) | |
| | 50 | 0.22 (0.13) | | 0.90 (0.31) | | 0.23 (0.06) | | 0.81 (0.13) | |
| | 150 | 0.74 (0.23)b | | 1.91 (0.42)b | | 0.30 (0.08) | | 1.25 (0.22) | |
| Open forest floor | 0 | 0.17 (0.04)a | 0.0001 | 0.60 (0.22) | | 0.08 (0.02)a | 0.0008 | 0.54 (0.12) | |
| | 50 | 0.41 (0.12)a | 0.008 | 0.51 (0.34) | | 0.12 (0.02)a | 0.01 | 0.72 (0.17) | |
| | 150 | 1.10 (0.27)b | | 1.08 (0.27) | | 0.41 (0.07)b | | 0.72 (0.13) | |
| Pine forest floor | 0 | 0.00 (0.09)a | 0.06 | 0.84 (0.37) | | 0.03 (0.02) | | 0.30 (0.11) | |
| | 50 | 0.67 (0.25)b | | 0.34 (0.31) | | 0.09 (0.03) | | 0.47 (0.13) | |
| | 150 | 0.46 (0.27) | | 0.94 (0.30) | | 0.47 (0.12) | | 0.67 (0.17) | |
| Oak mineral soil | 0 | 0.02 (0.01)a | 0.0001 | 0.05 (0.02)a | 0.05 | 0.02 (0.00)a | 0.01 | 0.06 (0.02) | |
| | 50 | 0.05 (0.01)a | 0.006 | 0.08 (0.02) | | 0.04 (0.01) | | 0.09 (0.02) | |
| | 150 | 0.13 (0.02)b | | 0.15 (0.03)b | | 0.07 (0.01)b | | 0.14 (0.03) | |
| Open mineral soil | 0 | 0.04 (0.01)a | 0.009 | 0.10 (0.03) | | 0.03 (0.01)a | 0.0001 | 0.11 (0.02) | |
| | 50 | 0.07 (0.03)a | 0.03 | 0.10 (0.04) | | 0.05 (0.01)a | 0.007 | 0.12 (0.02) | |
| | 150 | 0.16 (0.05)b | | 0.16 (0.03) | | 0.12 (0.02)b | | 0.14 (0.02) | |
| Pine mineral soil | 0 | 0.04 (0.01)a | 0.05 | 0.10 (0.02)a | 0.05 | 0.01 (0.00) | | 0.09 (0.02)a | 0.05 |
| | 50 | 0.05 (0.04) | | 0.21 (0.04)b | | 0.00 (0.03) | | 0.15 (0.02)b | |
| | 150 | 0.10 (0.04)b | | 0.13 (0.03)a | 0.02 | 0.04 (0.01) | | 0.11 (0.02)a | 0.05 |

**Note:** Standard errors of the mean are given in parentheses; *n* = 98–100. Values with the same lowercase letter are not significantly different based on least significant difference comparisons for the three fertilization treatments within each site, canopy type, and soil horizon combination.

*The *p* values indicate the level of significance for the individual comparisons that were significantly different within each site, canopy type, and soil horizon combination. Only significant *p* values are given.

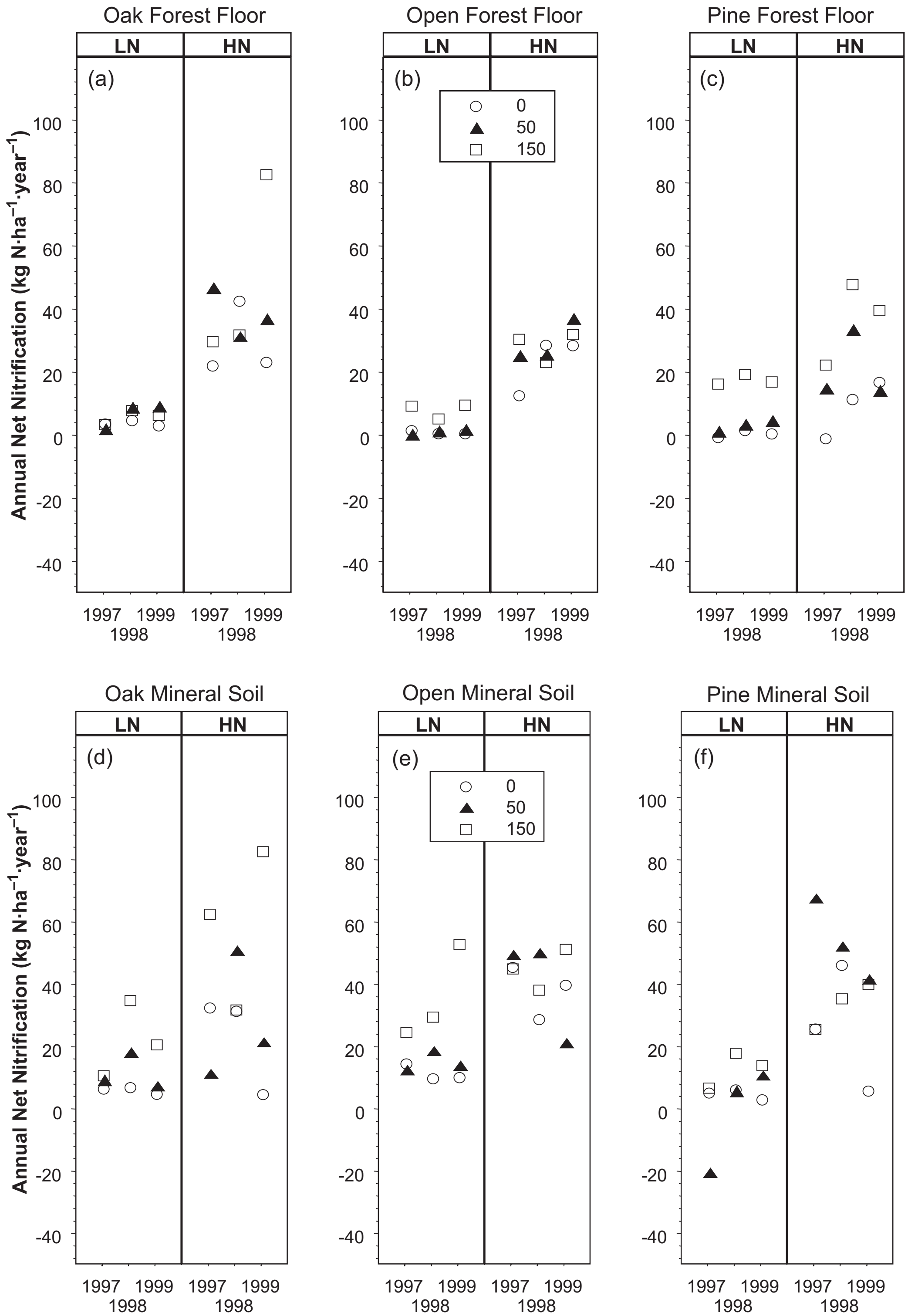
The median (mean) rates of net nitrification in the forest floor at HN (all species combined) were 7.71 (8.73), 6.59 (11.25), and 6.34 (16.31) mg N·m$^{-2}$·d$^{-1}$ in the control, low, and high fertilization treatments, respectively. There were no significant differences in the rates of net nitrification of the forest floor at HN among the fertilization treatments on a mass or an area basis. Net nitrification (on a mass basis only) was significantly greater under oak than under pine in

**Fig. 6.** Annual rates of net mineralization for forest floor (*a*–*c*) and mineral soil (*d*–*f*) for the calendar years 1997–1999. LN, low N deposition site; HN, high N deposition site.




all treatments, and it was greater under oak than in the open only in the high fertilization treatment. The rates of net nitrification at HN were consistently much greater than those at LN on both a mass ($p \leq 0.01$) and an area basis ($p \leq 0.0001$), even with the addition of 150 kg N·ha$^{-1}$·year$^{-1}$ in the high fertilization treatment at LN. However, when analyzed separately by canopy type, net nitrification under pine in the high fertilization treatment at LN approached that of the control and low fertilization treatments at HN on both a mass and an area basis (Tables 6 and 7). Under open canopy, net nitrification in the high fertilization treatment at LN approached that of the control at HN but only on a mass basis. In oak lit-

**Fig. 7.** Annual rates of net nitrification for forest floor (*a*–*c*) and mineral soil (*d*–*f*) for the calendar years 1997–1999. LN, low N deposition site; HN, high N deposition site.




ter, however, net nitrification was significantly greater at HN than at LN for all treatment comparisons on both a mass and an area basis ($p \leq 0.02$).

**Temporal trends of fertilization effects in the forest floor**

Plots of annual rates of net mineralization in the forest floor (Figs. 6*a*–6*c*) show a steady increase over the 3-year period in the high fertilization treatment under pine at LN from 6.06 to 34.59 kg N·ha$^{-1}$·year$^{-1}$. Open forest floor at LN, however, shows a decrease in net mineralization in the high fertilization treatment through the 3-year period from 27.00 to 11.32 kg N·ha$^{-1}$·year$^{-1}$. At HN an increase in net mineralization through the 3-year period can be seen in the high fertilization treatment in open forest floor (from 33.06

to 50.89 kg N·ha$^{-1}$·year$^{-1}$) and in the low fertilization treatment in pine forest floor (from 4.02 to 23.58 kg N·ha$^{-1}$·year$^{-1}$).

Net nitrification rates in open and pine forest floor at LN (Figs. 7*a*–7*c*) show an immediate increase in response to the high fertilization treatment relative to the control, and then they level off through the 3-year period (5.69 to 10.01 and 16.71 to 19.76 kg N·ha$^{-1}$·year$^{-1}$ in open and pine forest floor high fertilization treatments, respectively). No increase is observed in oak forest floor at LN (3.89 to 8.35 kg N·ha$^{-1}$·year$^{-1}$ in the high fertilization treatments). At HN the only significant fertilization effect on net nitrification in the forest floor is a spike in the high fertilization treatment in oak forest floor (83.13 kg N·ha$^{-1}$·year$^{-1}$) in the final year of the study. There was also a trend of higher net nitrification in pine forest floor at the high fertilization level at HN, but differences were not significant (Tables 1 and 2; Figs. 7*a*–7*c*). Other trends in net mineralization and net nitrification were obscured at both sites by the large differences in annual precipitation among the 3 years of the study.

### Effects of fertilization on net N mineralization in mineral soil

As was the case for the forest floor, fertilization caused a significant increase in the rate of net mineralization of the mineral soil at LN in each of the treatments and canopy types (Fig. 5*c*; Table 6). The median (mean) rates of net mineralization in the mineral soil at LN were 2.11 (3.70), 4.22 (6.11), and 9.49 (13.61) mg N·m$^{-2}$·d$^{-1}$ in the control, low, and high fertilization treatments, respectively. Contrary to LN, there were no significant differences in the rates of net mineralization in the mineral soil among the fertilization treatments at HN (Fig. 5*c*). The median (mean) rates of net mineralization in the mineral soil at HN were 8.43 (8.84), 9.49 (14.13), and 9.49 (15.37) mg N·m$^{-2}$·d$^{-1}$ in the control, low, and high fertilization treatments, respectively. However, when analyzed separately by canopy type, net mineralization increased in the high fertilization treatment relative to the control under oak and in the low fertilization treatment relative to both the control and the high fertilization treatment under pine (Table 6). A comparison of the two sites shows that net mineralization in all three treatments at HN was significantly greater than net mineralization in the control and low fertilization treatments at LN ($p \leq 0.003$) but not greater than net mineralization in the high fertilization treatment. However, when analyzed separately by canopy type, net mineralization in the low fertilization treatment at LN approached that at HN in the control under oak, in the low fertilization treatment under open canopy, and in the high fertilization treatment under pine.

### Effects of fertilization on net nitrification in mineral soil

Fertilization at LN also increased the rates of net nitrification in the mineral soil, but the values still remained low relative to HN (Fig. 5). The median (mean) rates of net nitrification at LN were 1.05 (2.30), 1.05 (2.98), and 2.11 (7.80) mg N·m$^{-2}$·d$^{-1}$ in the control, low, and high fertilization treatments, respectively. When analyzed separately by canopy type (Table 6), net nitrification under oak increased in the high fertilization treatment relative to the control, and net nitrification under open canopy increased in the high fertilization treatment relative to the control and low fertilization treatment. Net nitrification was consistently higher under open canopy than under oak and pine.

At HN there were no significant differences in the rates of net nitrification in the mineral soil among the fertilization treatments (Fig. 5*d*). The median (mean) rates of net nitrification at HN were 8.43 (9.17), 9.49 (12.38), and 9.49 (13.72) mg N·m$^{-2}$·d$^{-1}$ in the control, low, and high fertilization treatments, respectively. Nitrification rates at HN were much higher than those at LN for all treatment comparisons ($p \leq 0.009$; Fig. 5*d*). However, when analyzed separately by canopy type (Table 6), net nitrification in the high fertilization treatment at LN approached that of the control at HN under oak and approached that of all treatments at HN under open canopy. Net nitrification in pine mineral soil, however, was always significantly lower at LN than at HN.

### Temporal trends of fertilization effects in mineral soil

Plots of the annual rates of net mineralization in mineral soil (Figs. 6*d*–6*f*) show an increase in mineralization of about 16–50 kg N·ha$^{-1}$·year$^{-1}$ in the wetter second year of the high fertilization treatment in each of the three canopy types at LN. At HN net mineralization of the mineral soil increased by 44–49 kg N·ha$^{-1}$·year$^{-1}$ in the drier third year (compared with year 1 and 2) in the high fertilization treatment under oak. Under pine at HN, net mineralization of the mineral soil in the high fertilization treatment steadily increased from 17.59 to 45.80 kg N·ha$^{-1}$·year$^{-1}$ over the 3-year period but still remained lower than that in the low fertilization treatment (65.92–84.80 kg N·ha$^{-1}$·year$^{-1}$; Fig. 6*f*).

Annual rates of net nitrification (Figs. 7*d*–7*f*) in the high fertilization treatment in mineral soil at LN peaked in the wetter second year under oak (35.35 kg N·ha$^{-1}$·year$^{-1}$) and under pine (18.40 kg N·ha$^{-1}$·year$^{-1}$) and in the drier third year under open canopy (53.26 kg N·ha$^{-1}$·year$^{-1}$). Net nitrification in the high fertilization treatment at LN approached that in the control and low fertilization treatments at HN under oak by the second year and approached that in all treatments at HN under open canopy by the third year. Net nitrification, however, remained lower in the high fertilization treatment in pine mineral soil at LN (7.18–18.40 kg N·ha$^{-1}$·year$^{-1}$) than in all treatments at HN (26.03–67.90 kg N·ha$^{-1}$·year$^{-1}$) except for the control at HN during the 1999 drought year (6.25 kg N·ha$^{-1}$·year$^{-1}$). At HN net nitrification ranged from 5.11 to 83.13, 21.48 to 51.79, and 6.25 to 67.90 kg N·ha$^{-1}$·year$^{-1}$ in oak, open, and pine mineral soil, respectively, among the three fertilization treatments over the 3-year period (Figs. 7*d*–7*f*).

## Discussion

### Nitrogen cycling in forest floor and mineral soil at a high- and a low-deposition site

Increased nitrification is a key characteristic of N-saturated forests (Aber et al. 1989; Fenn et al. 1998). In this study, rates of net N mineralization, net nitrification, and relative nitrification were consistently higher at HN than at LN, with the exception of net mineralization of the forest floor under oak. The concentration of N in forest floor and mineral soil was significantly greater at HN than at LN for oak and pine canopy types, while the C/N ratios of forest floor and mineral soil were significantly lower at HN than at LN for all three canopy types. These findings concur with streamwater $NO_3^-$ export profiles and with a number of other hydrologic, edaphic, and botanic indicators of N enrichment (Fenn and Poth 1999, 2001; Fenn et al. 1996), demonstrating that the forest at HN is in the later stages of N saturation, while LN strongly conserves N.

Averaged over the three canopy types and 3 years of the study, net nitrification fluxes in forest floor and mineral soil were 2.4 and 8.8 kg $N \cdot ha^{-1} \cdot year^{-1}$ at LN and 23.0 and 32.9 kg $N \cdot ha^{-1} \cdot year^{-1}$ at HN, respectively. At LN approximately 21% of the net nitrification occurred in the forest floor (considering the forest floor and top 10 cm of mineral soil), compared with 41% at HN. Two primary factors are responsible for the greater proportion of nitrification taking place in the forest floor at HN compared with LN. Net nitrification rates per kilogram forest floor were 5–7 times greater at HN among the three canopy cover types, and forest floor accumulation was also 1.3–2.7 times greater at HN. Forest floor accumulation at HN is accelerated by the interactive effects of ozone and N deposition (Arbaugh et al. 1999; Fenn et al. 2003*b*; Grulke and Balduman 1999) and a decrease in the later stages of decomposition of N-rich litter (Berg 2000).

## Nitrate dominance of the inorganic N cycle

The $NO_3^-$ dominance of the inorganic N cycle and the much higher relative nitrification at HN demonstrate the elevated N status of the forest at HN. These findings also support the use of relative nitrification as an index of N saturation. It may be that chronic atmospheric N inputs at HN lead to sustained high levels of nitrification, possibly by maintaining a viable population of nitrifying organisms (Johnson 1992). Gross nitrification rates in pine forest floor and mineral soil at HN appear to be one to two orders of magnitude greater than those at LN (M.E. Fenn, unpublished data), supporting the conclusion that active nitrification is the key process controlling N loss at HN. Venterea et al. (2004) concluded that enhanced gross nitrification is the key process leading to N-saturation symptoms, and Tietema (1998) measured high gross nitrification rates in two N-saturated sites but not in the two N-limited forests. Nitrification is the presumed source for most of the $NO_3^-$ leached from N-saturated watersheds in southern California and is also believed to be the source of elevated nitric oxide emissions from soil (Fenn et al. 1996; Fenn and Poth 2001). However, recent stable isotope studies from the San Bernardino and San Gabriel Mountains show that a significant proportion (as high as 20%–40% during peak runoff in catchments, including HN) of the $NO_3^-$ exported in streamwater is direct throughput of atmospheric $NO_3^-$ that has not been biologically assimilated (Michalski et al. 2004). Such movement of $NO_3^-$ through the forest ecosystem without biological assimilation may partly explain why tree growth can still be N limited at HN (Fenn and Poth 2001), notwithstanding the high N deposition inputs and outputs.

## Relative nitrification and nitrification rate comparisons with other studies

Relative nitrification was significantly higher in the mineral soil than in the forest floor at both sites, as commonly reported in the literature (Table 5; Lavoie and Bradley 2003), possibly because of inhibitory organic compounds in the organic horizon (White 1994) and greater competition for $NH_4^+$ substrate in the forest floor. In two literature surveys (Bonilla and Rodà 1992; Gilliam et al. 2001), average net nitrification rates were 39 and 64 kg $N \cdot ha^{-1} \cdot year^{-1}$ in hardwood forests and 23 and 14 kg $N \cdot ha^{-1} \cdot year^{-1}$ in coniferous forests, respectively. Nitrification rates in mineral soil at HN are higher than these rates reported for coniferous forests and near the low end reported for hardwood forests (Table 5). Nitrification rates in mineral soil at LN are below the average for both types of forests. Nitrogen cycling rates in soil at HN and, particularly, at LN were generally lower than rates in mesic forests in the eastern United States with actively nitrifying soils or at N-saturated sites (Table 5; Bowden et al. 2000; Gilliam et al. 2001). However, some coniferous forest types in the eastern United States have reportedly low nitrification rates in the absence of disturbance (Table 5; McNulty and Aber 1993; Ohrui et al. 1999). In summary, relative nitrification at HN is higher than that of other western sites and is similar to that of N-saturated sites in eastern North America, although total net nitrification rates are higher in the more mesic eastern N-saturated forests (Table 5).

## Factors controlling nitrification rates

Although soil moisture and temperature were greater at HN than at LN, these did not seem to be major factors causing higher N cycling rates at HN. Mineral soil and forest floor moisture and temperature combined only explained 1%–6% of the variation in net N mineralization and 3%–16% (highest in mineral soil at LN) of the variation in nitrification at each site despite fourfold differences in the amount of precipitation among the 3 years of the study. Furthermore, at similar moisture contents and temperatures, N cycling rates were still generally greater at HN than at LN. Even in an unusually wet year (1998), nitrification rates at LN were still significantly lower than those observed at HN during years of similar or lower precipitation.

The results from the general additive models demonstrate the dominance of initial $NH_4^+$ concentrations (and initial $NO_3^-$ at HN) as controlling factors in the rates of net mineralization. Net nitrification was overwhelmingly controlled by net mineralization and the initial $NH_4^+$ concentrations (and initial $NO_3^-$ in HN litter). However, the models performed better in predicting net immobilization (negative values of net mineralization). Competition between heterotrophs and nitrifiers for $NH_4^+$ substrate determines the degree of net immobilization or net nitrification. High concentrations of $NH_4^+$ and $NO_3^-$ resulted in net immobilization. The threshold $NH_4^+$ concentrations resulting in net immobilization are 3.3 and 1.6 times higher in forest floor and mineral soil, respectively, at HN than at LN, indicating the more N-deficient condition of the microbial community at LN with less $NH_4^+$ available to be nitrified. Also the models for net nitrification show much steeper slopes in its relationship with net mineralization at HN than at LN, further indicating the higher relative nitrification at HN.

Mineral soil pH (all canopy cover types) and oak forest floor pH values were lower at HN than at LN. Although historical soil pH data from the San Bernardino Mountains are limited, mineral soils have acidified at HN (from ca. pH 5.6 in 1976 to 4.1 under pine currently; Table 2; Fenn and Poth 1996), presumably from high levels of atmospheric deposition and acidity produced from high rates of nitrification in the past 50+ years. The low mineral soil pH values at HN (median values ranging from 4.0 to 4.6 in the three canopy types) do not preclude the high relative nitrification we have measured in these field incubations and in laboratory assays. High nitrification rates have been reported in N-saturated acidic soils (Martikainen and Deboer 1993; Ohrui et al. 1999). Results of recent experiments using acetylene as an inhibiter of autotrophic nitrification in laboratory soil slurry assays suggest that heterotrophic nitrification is quantitatively important for $NO_3^-$ production in mineral soil at HN (Jordan et al. 2005). Previous studies in mixed-conifer forests in California have similarly reported that heterotrophic nitrification is an important process for $NO_3^-$ production (Pedersen et al. 1999).

### Effects of canopy cover type

The principal findings on the effects of canopy cover in our study were (*i*) low relative nitrification rates in mineral soil under pine, (*ii*) a lower proportion of inorganic N in the $NO_3^-$ form in forest floor under pine at both sites (data not shown), and (*iii*) very low relative nitrification in forest floor under pine at HN (21.4%). Net nitrification rates in forest floor were significantly lower under pine than under oak at both sites, but only on a mass basis (mg $N \cdot kg^{-1} \cdot d^{-1}$) at HN because of greater litter accumulation under pine than under oak at HN. Another finding on the effect of canopy cover in mineral soil at both HN and LN was greater net N mineralization and nitrification in open areas than under pine or oak canopies. No significant differences were found between the oak and pine canopy cover types in the rates of net mineralization in forest floor and mineral soil or net nitrification in mineral soil. Greater species differences are likely obscured by mixed-litter effects.

Plant species or forest type can have dramatic effects on nitrification in some cases, with little or no nitrification occurring under some species (Blew and Parkinson 1993; Lovett and Rueth 1999). Many studies have reported lower relative nitrification in conifer forests compared with hardwood forests (Table 5; Bonilla and Rodà 1992; Gilliam et al. 2001). Our field studies support the possibility that compounds from pine trees or pine litter may be inhibitory to nitrification or that N immobilization is higher under pine. Elevated gross nitrification rates (compared with those at LN) in mineral soil and forest floor collected under pine canopies at HN indicate that gross nitrification at HN is not strongly inhibited, suggesting that $NO_3^-$ immobilization may be higher under pine canopies (M.E. Fenn, unpublished data). Monoterpenes emitted from pine forests have been shown to inhibit nitrification by direct inhibition (White 1994) and indirectly by providing a carbon-rich substrate for N immobilization (Paavolainen et al. 1998).

The greater N cycling rates in open areas may be due to microclimatic effects (Knoepp and Swank 2002), greater input of compounds in throughfall under tree canopies that are inhibitory to nitrifiers or that supply carbon for microbial N immobilization (Bradley et al. 2000; Knops et al. 2002), or higher levels of $NH_4^+$ for nitrification in open areas because of lower competition with plants for $NH_4^+$ substrate (Priha et al. 1999). Throughfall or litter percolates could include secondary compounds with antimicrobial activity (White 1994), or the much greater N deposition under the canopy could have an inhibitory effect on litter decomposers (Berg 2000; Persson et al. 2000). Mladenoff (1987) reported that net nitrification rates in gaps in eastern hemlock (*Tsuga canadensis* (L.) Carrière) stands were more than double the rate under the canopy. Increased N mineralization and N availability in canopy gaps is common (Prescott 2002).

### Nitrogen input thresholds for stimulating net nitrification

With the addition of 150 kg $N \cdot ha^{-1} \cdot year^{-1}$ as slow-release ureaformaldehyde, net nitrification rates at the low N deposition site LN (ambient deposition of 4–13 kg $N \cdot ha^{-1} \cdot year^{-1}$) approached those at the high deposition site HN (ambient deposition of 40–80 kg $N \cdot ha^{-1} \cdot year^{-1}$) in just 2 to 3 years in open and pine forest floor and open and oak mineral soil, but not in oak forest floor or pine mineral soil. The application of 150 kg $N \cdot ha^{-1} \cdot year^{-1}$ in the high fertilization treatment is not unrealistic, since deposition as high as 100–200 kg $N \cdot ha^{-1} \cdot year^{-1}$ is commonly measured in throughfall underneath mature ponderosa pine trees at HN (Fenn and Poth 2004; M.E. Fenn, unpublished data). Most likely, more time is required for net nitrification rates in the low fertilization treatment (50 kg $N \cdot ha^{-1} \cdot year^{-1}$) at LN to approach the levels observed at HN, a site that has received elevated N deposition for over 50 years.

Our results contradict other studies using ureaformaldehyde fertilizer that report no enhanced nitrification or risk for $NO_3^-$ leaching (e.g., Martikainen 1984; Aarnio and Martikainen 1995; Aarnio et al. 1996). The cause of the differences in nitrification responses to ureaformaldehyde between our study and those cited above is likely a result of considerable differences in soil, vegetation, and climatic conditions between the study sites. The cited studies are mainly from podzolized boreal sandy soils that are inherently highly acidic and have low nitrification activity. In contrast, our study sites are in a Mediterranean climate with more moderate temperatures, high soil base saturation, and high nitrification activity, and the soils in our study sites were only highly acidic at HN, as a result of long-term atmospheric deposition.

### Limited response to N fertilization at HN

At HN, fertilization generally had no significant effect on $NH_4^+$ levels and led to decreased $NO_3^-$ levels in forest floor and mineral soil. The fairly constant levels of $NH_4^+$ in forest floor and mineral soil even with fertilization at HN are not surprising if we assume that a large percentage of the available $NH_4^+$ is nitrified, as suggested by the high relative nitrification values at HN. High rates of microbial immobilization of N may also explain the lack of an increase in inorganic N with fertilization at HN. The lack of an increase in $NH_4^+$ levels with fertilization at HN (and decrease in $NO_3^-$ levels) may also be due to N uptake by trees and understory vegetation (Olsson and Falkengren-Grerup 2003; Rodenkirchen 1995), which is dominated by bracken fern at HN. Bracken fern is not found at LN, but at HN bracken has been shown to accumulate high levels of $NO_3^-$ in foliage, particularly in the spring (Fenn et al. 1996). The fertilization treatments in this study caused significant increases in bolewood growth of pine and oak trees compared with the unfertilized control trees at HN but not at LN (Fenn and Poth 2001), demonstrating that the slow-release ureaformaldehyde fertilizer was being mineralized.

The decrease in nitrate levels in mineral soil and forest floor with fertilization at HN could also be explained by the increase in percent total C in the fertilized soils (M.E. Fenn and M.A. Poth, unpublished data). If labile C was also higher in fertilized soils, this would stimulate the activity of heterotrophs that could out compete nitrifiers for $NH_4^+$ substrate, resulting in lowered net nitrification (Riha et al. 1986). This hypothesis could explain why net nitrification and net mineralization rates in the mineral soil under pine at HN were higher in the low fertilization treatment than in the high fertilization treatment. A number of studies have also reported limited or no increase in net nitrification with added N treatments (Bengtsson and Bergwall 2000; Magill et al. 1997). In many cases, most of the added N retained in soil is fixed via biotic and abiotic mechanisms (Johnson et al. 2000), resulting in small amounts of added N being nitrified and denitrified (Bengtsson and Bergwall 2000; Hart et al. 1993; Nadelhoffer et al. 1995).

### Mechanisms of nitrification enhancement by N enrichment

Increased nitrification at LN in the fertilization treatments is presumably the result of increases in $NH_4^+$ substrate from the ureaformaldehyde fertilizer. It seems unlikely that in only 1 to 3 years the N content of litter and soil organic matter would increase sufficiently to cause the increased N mineralization seen in all the fertilizer treatments and the increased nitrification observed in some of the fertilization treatments at LN. Longer-term studies are needed to see when and if added N would lead to increased organic matter N content and sustained increases in nitrification at LN. At HN, the evidence strongly suggests that 50 years of elevated N deposition has resulted in increased nitrification rates. However, it is not clear to what degree this stimulation is due to direct effects on nitrification of the atmospheric N currently deposited in throughfall compared with long-term indirect stimulation via the production of N-rich foliage, litter, and soil organic matter. Throughfall N may also indirectly contribute to elevated nitrification rates by supplying available N in the soil solution for plant uptake, thus reducing the competition for N between plants and heterotrophic microorganisms and nitrifiers.

Presumably, the production of N-enriched litter and soil organic matter is an important mechanism of enhancing nitrification. Evidence for this conclusion includes the results of the net nitrification field assays in this study, previous laboratory assays of net N mineralization and nitrification (Fenn et al. 1996, 2003*b*), and gross N mineralization and nitrification assays (M.E. Fenn, unpublished data). In all of these studies N mineralization and nitrification rates were measured in the absence of plant uptake and N deposition, indicating that the inherent properties of the soils determined N cycling rates. In every case, nitrification rates were much greater in unfertilized soils and litter from HN than in unfertilized soils and litter from LN. Probably the strongest evidence that the major role of N deposition in increased nitrification is mediated through enriched organic matter production is the widely documented inverse relationship between forest floor and mineral soil C/N ratio and nitrification rates and $NO_3^-$ leaching (see Aber et al. (2003) and references therein). Rueth et al. (2003) conducted N fertilization studies in high-elevation old-growth Englemann spruce (*Picea engelmannii* Parry ex Engelm.) in the Colorado Front Range and also concluded that the size of the soil organic N pool and soil C/N ratios were key factors in controlling N cycling rates and the responsiveness of soil N pools and fluxes to fertilization. Tietema et al. (1998) concluded that in the long run N deposition changes the N status of an ecosystem by changing characteristics such as the C/N ratio of the forest floor. Thus, a major question remains as to how long elevated $NO_3^-$ production in soil would persist at HN without the continual inputs of high levels of N in throughfall.

In a survey of 33 forested sites in Europe, Dise et al. (1998) reported that for any given C/N ratio, nitrate leaching was higher at high N deposition sites than at intermediate N deposition sites, suggesting that N enrichment of soil organic matter and current N deposition levels are both important factors affecting nitrification and $NO_3^-$ losses. In the European NITREX studies it was found that in forests that do not exhibit N saturation symptoms, the response to increased N was small and delayed, whereas in the N saturated sites, decreases in throughfall N deposition led to large and rapid decreases in $NO_3^-$ leaching losses (Bredemeier et al. 1998; Gundersen et al. 1998), suggesting that chronic N deposition in throughfall is also an important source of $NO_3^-$ and a driver of $NO_3^-$ production in mineral soil and the forest floor.

At HN the largest source of $NH_4^+$ for nitrifiers was N mineralized from the large N-rich pool of organic matter, as evidenced by the fact that N mineralization was far and away the primary factor correlated with high nitrification rates at HN. Based on the data in Table 2 we calculate that the N pool in the forest floor and top 10 cm of mineral soil contains 3620 and 1950 kg $N \cdot ha^{-1}$ at HN and the LN, respectively. The total amount of organic N at HN is probably much higher in many areas where forest floor accumulation is excessive. We conclude that without continual fertilization treatments, nitrification rates in the fertilization treatments at LN would rapidly decrease to the level of the unfertilized control. Alternatively, for N-saturated sites such as HN, it would be useful from a resource management standpoint to know by how much N deposition must be reduced, and for how long, before excess $NO_3^-$ production and $NO_3^-$ leaching (over and above "normal" $NO_3^-$ losses) will return to levels observed in watersheds with low N deposition and a relatively closed N cycle (except following disturbance events, such as fire). Also of interest is whether reduced N capital in N-saturated watersheds, brought about by low-to-moderate intensity forest fires, will lead to lower $NO_3^-$ losses, particularly as vegetative regrowth and N demand gains momentum.

## Summary

Nitrogen cycling rates in the forest floor and top 10 cm of the mineral soil were compared for 3 years at a low (LN) and high (HN) N deposition site. Mean net nitrification fluxes were 11.2 kg N·ha$^{-1}$·year$^{-1}$ at LN and 55.9 kg N·ha$^{-1}$·year$^{-1}$ at HN. Relative nitrification patterns in field assays confirmed earlier laboratory studies showing virtually complete net nitrification of the N mineralized in the mineral soil of N-saturated stands (except under pine canopies), and lower relative nitrification in the forest floor. The rate of net N mineralization was the primary factor affecting net nitrification rates, explaining 29% to 88% of the variability. Net nitrate production in the forest floor was lower under ponderosa pine or Jeffrey pine canopies than under oak canopies at both study sites, and relative nitrification in mineral soil and forest floor was lower under pine canopies in most cases. Median mineral soil and forest floor pH at HN ranged from 4.0 to 4.6, indicating that nitrifying organisms are adapted to the highly acidic conditions at HN. After 2 to 3 years of fertilization (150 kg N·ha$^{-1}$·year$^{-1}$), net nitrification rates at a low N deposition site approached those at a high deposition site in open and pine forest floor and in open and oak mineral soil, but not in oak forest floor or pine mineral soil. The results in this study suggest that after only 2 to 3 years of elevated N amendments, forests in southern California begin to develop the cardinal sign of N saturation: stimulation of nitrification. This process can lead to elevated $NO_3^-$ in streamwater and groundwater, and to increased nitrogenous trace gas emissions. However, it is concluded that longer periods of N inputs are required to reach a fully N-saturated condition of elevated $NO_3^-$ production and N losses sustained by a large pool of N-rich organic matter. Continuing rapid population growth and urban sprawl in southern California is expected to increase the geographic extent over which elevated N effects are occurring. Enhanced N mobilization, meditated by the process of nitrification, is a key indicator of such effects.

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