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Plant and Soil N Response of Southern Californian Semi-arid Shrublands After 1 Year of Experimental N Deposition

George L. Vourlitis,* Sarah Pasquini, and Gypsi Zorba

Department of Biological Sciences, California State University, San Marcos, California 92096, USA

Abstract

Large inputs of atmospheric N from dry deposition accumulate on vegetation and soil surfaces of southern Californian chaparral and coastal sage scrub (CSS) ecosystems during the late-summer and early-fall and become available as a pulse following winter rainfall; however, the fate of this dry season atmospheric N addition is unknown. To assess the potential for dry season atmospheric N inputs to be incorporated into soil and/or vegetation N pools, an in situ N addition experiment was initiated in a post-fire chaparral and a mature CSS stand where 10 × 10 m plots were exposed to either ambient N deposition (control) or ambient +50 kg N ha^{-1} (added N) added as NH_4NO_3 during a single application in October 2003. After 1 year of N addition, plots exposed to added N had significantly higher accumulation of extractable inorganic N (NH_4–N + NO_3–N) on ion exchange resins deployed in the 0–10 cm mineral soil layer and higher soil extractable N in the subsurface (30–40 cm) mineral soil than plots exposed to ambient N. Chaparral and CSS shrubs exposed to added N also exhibited a significant increase in tissue N concentration and a decline in the tissue C:N ratio, and added N significantly altered the shrub tissue $\delta^{15}N$ natural abundance. Leaching of inorganic N to 1 m below the soil surface was on average 2–3 times higher in the added N plots, but large within treatment variability cause these differences to be statistically insignificant. Although a large fraction of the added N could not be accounted for in the shrub and soil N pools investigated, these observations suggest that dry season N inputs can significantly and rapidly alter N availability and shrub tissue chemistry in Mediterranean-type chaparral and CSS shrublands of southern California.

Key words: *Adenostoma fasciculatum*; *Artemisia californica*; biogeochemistry; chaparral; coastal sage scrub; Mediterranean-type ecosystems; *Salvia mellifera*.

Introduction

Atmospheric N deposition from human activities has significantly increased since the beginning of the industrial revolution (Galloway and others 1994; Vitousek and others 1997; Fenn and others 1998, 2003a). Most of the anthropogenic N is from fertilizer use (80 Tg N/year; 1 Tg N = 10^{12} g N); however, an additional 20–25 Tg N/year is produced from fossil fuel burning and deposited as nitrogen oxides in terrestrial and marine systems (Galloway and others 1994; Vitousek and others 1997). Anthropogenic N deposition represents a

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*Corresponding author; e-mail: georgev@csusm.edu

significant input of N into many southern Californian semi-arid ecosystems (Bytnerowicz and Fenn 1996; Fenn and others 2003a). In heavily polluted areas, oxidized N compounds including NO, NO_2, HNO_3, peroxyacetyl nitrate (PAN) and particulate NO_3 are important components of dry atmospheric deposition, whereas in areas close to agricultural enterprises, such as in Riverside and San Bernardino counties, compounds such as NH_3 and particulate NH_4 may be larger sources of atmospheric N (Bytnerowicz and Fenn 1996). Wet deposition, which comprises only about 10–15% of annual N deposition in southern California, is primarily composed of NH_4 and NO_3 (Bytnerowicz and Fenn 1996). Concentrations of atmospheric N close to urban source areas are 20 times higher than in remote areas, resulting in 20–45 kg N ha^{-1} to be deposited to heavily polluted southern Californian shrublands annually (Riggan and others 1985; Bytnerowicz and others 1987; Bytnerowicz and Fenn 1996; Meixner and Fenn 2004); however, some more exposed locales can receive up to 145 kg N ha^{-1} annually (Fenn and Poth 2004).

High N deposition leads to significant increases in the production of nitrate (NO_3) in soil (Riggan and others 1985; Fenn and others 1996; Vourlitis and Zorba 2007). This is especially true for southern California chaparral and coastal sage scrub (CSS) soils, where soil NO_3 concentration is typically 10–20-times higher than ammonium (NH_4) concentration because of rapid nitrification (Vourlitis and Zorba 2007). Because NO_3 is highly mobile in soil (Paul and Clark 1989), NO_3 can be rapidly exported to groundwater and aquatic systems where it accumulates causing a cascade of ecological changes (Riggan and others 1985; Carpenter and others 1998). In southern California, groundwater and aquatic systems are critical sources for drinking water for urban, suburban, and rural populations, and stream water concentrations of NO_3 in highly polluted areas often exceed the maximum contaminant level of 10 mg/l set by the US Environmental Protection agency (US EPA 1995; Carpenter and others 1998; Fenn and Poth 1999). Given that most of atmospherically derived N (>90%) falls on terrestrial surfaces, and thus must be ''processed'' by terrestrial ecosystems before it is exported to groundwater and downstream aquatic ecosystems (Fenn and Poth 1999; Meixner and Fenn 2004; Li and others 2006), understanding the possible N deposition-induced alterations to terrestrial N storage and cycling is critically important to predicting terrestrial export of N to aquatic systems.

Chaparral and coastal sage scrub (CSS) are the dominant semi-arid ecosystems of southern California (Keeley 2000), and many chaparral and CSS shrublands are adjacent to urban areas and exposed to high levels of atmospheric N (Riggan and others 1985; Byterowicz and Fenn 1996; Padgett and others 1999; Fenn and others 2003b). Also known as ''soft-chaparral,'' CSS shrubs tolerate more xeric conditions than chaparral shrubs and are restricted to drier, low-elevation habitats on fine-textured soils that limit the infiltration of water (Westman 1981). During late-summer and early-fall, drought-deciduous CSS shrubs are dormant and the physiological activity of evergreen chaparral shrubs is at a seasonal minimum owing to the lack of rainfall and low soil water availability (Poole and Miller 1975; Gray and Schlesinger 1981; Oechel and others 1981). CSS has a lower rate of annual net primary production than chaparral; however, during the spring growing season CSS shrubs can accumulate 2–3 times more biomass than evergreen chaparral shrubs and CSS is more responsive than chaparral to added N (Gray and Schlesinger 1981, 1983). Chaparral shrubs are also thought to be more efficient in regenerating stored tissue N than CSS shrubs (Gray 1983) and have a deeper root system with less horizontal proliferation of roots at the soil surface (Hellmers and others 1955). Fire is an important agent of disturbance that has a return interval of every 48–66 years (Davis and Michaelsen 1995). Depending on intensity, fire causes ecosystem N storage to decline; however, ash deposited from the charred remains of shrubs and litter is rapidly mineralized following fire causing a transient increase in available inorganic N (DeBano and Conrad 1978; DeBano and others 1979; Dunn and others 1979; Rundel 1983; Riggan and others 1985, 1994; Stock and Lewis 1986; Grogan and others 2000).

The majority of dry atmospheric N deposition in southern California accumulates during the summer and early fall when inversion conditions trap pollutants in the lower atmosphere (Bytnerowicz and others 1987; Bytnerowicz and Fenn 1996; Padgett and others 1999; Fenn and others 2003a). Furthermore, because rainfall and fog are infrequent during the summer and early fall, dry N deposition that accumulates on shrub and soil surfaces becomes available as a pulse after the first rainfall or heavy fog event (Riggan and others 1985; Bytnerowicz and Fenn 1996; Fenn and others 1998, 2003b). The fate of this N pulse is largely unknown, and the potential for atmospheric N to be retained in Mediterranean-type shrublands is likely to be a function of the intensity and/or duration of the precipitation event, state of ecosystem development following fire, and the time scales of the vegetation and soil microbial response

to rainfall and N (Poole and Miller 1975; Gray and Schlesinger 1981; Riggan and others 1994; Bilbrough and Caldwell 1997; Richstein and others 2002; D'Odorico and others 2003).

Chaparral and CSS shrub physiology is substantially limited by drought during the summer and early fall when the majority of N is deposited, causing a potential temporal asynchrony between N availability and biotic demand (Fenn and others 2003b; Meixner and Fenn 2004). Thus, we hypothesize that N deposited during the fall will result in a significant but transient increase in available N; however, the aboveground N storage of chaparral and CSS shrubs will not be significantly affected by dry season N inputs because drought-induced limitations in physiological activity will constrain the utilization of these available N pulses.

To determine whether N deposited during the dry summer and early-fall increases soil N availability and/or alters shrub tissue chemistry in chaparral and CSS ecosystems, N fertilizer (NH_4NO_3) was added to a CSS and chaparral stand in fall 2003. Unfortunately the chaparral stand experienced a fire prior to N addition, and given the differences in recent fire history, quantitative comparisons between the chaparral and CSS response to N addition are problematic and not the focus of this report. Rather, we focus on whether dry season N addition causes changes in soil and shrub tissue chemistry in these different Mediterranean-type ecosystems after only 1 year of exposure. The results reported here represent the first year of an in situ N addition experiment that will be conducted over a minimum of 5 years.

Materials and Methods

Site Description and Experimental Design

N-addition experiments were conducted at the Santa Margarita Ecological Reserve (SMER: 33°29′N:117°09′W) and the Sky Oaks Field Station (SOFS: 33°21′N:116°34′W), which are research reserves managed by San Diego State University. These sites were chosen because they are secure and long-term field manipulative experiments are both encouraged and logistically feasible. In addition, these reserves have a rich history of ecological research that extends over several decades, and this long-term data base will be useful for interpreting the results obtained over the course of this field experiment.

The SMER field site is located in SW Riverside County, California, USA at an elevation of 338 m and is composed of CSS vegetation on a 9–11°S-SW facing slope. Soil is a sandy clay loam of the Las Posas Series derived of igneous and weathered Gabbro parent material (Knecht 1971) with a bulk density of 1.22 g cm^{-3}. SMER receives an average of 36 cm of rainfall annually. The site is approximately 35 years old and is dominated almost entirely by mature, drought deciduous shrubs *Artemisia californica* Less. and *Salvia mellifera* Greene (nomenclature according to Munz 1974) that support considerable standing dead wood. Shrub cover is 0.5–2.5 m^2 m^{-2} and density is 2–6 shrubs m^{-2} at the end of the summer drought and spring rainy seasons, respectively. Herbaceous species in the understorey are limited to *Gnaphalium californicum*, and the cover and density of this species comprise approximately 1 and 25%, respectively of the total plant cover and density during the spring rainy season.

SOFS is located in NE San Diego County, California, USA at an elevation of 1,418 m on a 4–10° SE-SW facing slope. The stand was approximately 50 years old when it burned in July 2003. Unfortunately this unplanned perturbation limits the potential for direct comparison to the mature CSS stand; however, given the extensive pre-fertilization (and fire) measurements and the unprecedented opportunity to assess the long-term effects of N deposition on a regenerating chaparral stand, fertilization proceeded as scheduled in fall 2003. Before fire the site was a virtual monoculture of the evergreen shrub *Adenostoma fasciculatum* H. & A. After fire the stand was again dominated by *A. fasciculatum* but *Ceanothus* sp. became a sub-dominant toward the end of the first year of N addition. Prior to the fire shrub cover was 0.83 m^2 m^{-2} and density was 1.3 shrubs m^{-2}, whereas 5 months post-fire shrub cover was 0.02 m^2 m^{-2} and density was 0.4 shrubs m^{-2}. *A. fasciculatum* resprouts were present as soon as 2 months post-fire, and herbaceous ''fire-followers'' and *Ceanothus* sp. that largely depend on fire-induced germination (Keeley 2000) began to appear shortly after the spring 2004 rainy season. The site receives an average of 53 cm of precipitation annually (mostly rain with occasional snow), and the soil is an Ultic Haploxeroll derived of micaceous schist (Moreno and Oechel 1992) with a sandy loam texture and a bulk density of 1.34 g cm^{-3}.

Published estimates of atmospheric N pollution exposure are not available for the research sites; however, data for regions similar to SMER and SOFS are available from the US EPA (http://www.epa.gov/). For SOFS, data averaged for Escondido and Alpine, CA located approximately

55 km from SOFS indicates a mean (±1 SD) annual atmospheric NO_2 exposure of 31.4 ± 2.5 μg m^{-3}. For SMER, data from Camp Pendelton Marine Base (33 km to the SW) and Escondido, CA (56 km to the SSE) indicate a potential annual NO_2 exposure of 30.8 ± 1.8 μg m^{-3}. Estimates of $NH_4 + NO_3$ inputs of atmospheric N deposition derived from throughfall traps (Vourlitis and others unpublished) and a high-resolution (4 km) model (Tonnesen unpublished) suggest that both sites receive approximately 2–4 kg N ha^{-1} annually.

The experimental layout at each site consisted of a randomized design where four-10 × 10 m plots were randomly selected to receive 50 kg N ha^{-1} as granular NH_4NO_3 (added N) in October 2003 and an additional four-10 × 10 m plots served as unmanipulated controls. The $\delta^{15}N$ natural abundance of the NH_4NO_3 fertilizer was −0.8‰. Given the estimated background levels of atmospheric N deposition (2–4 kg N ha^{-1} annually), plots exposed to added N received 52–54 kg N ha^{-1} $year^{-1}$, whereas control plots received a maximum of 4 kg N ha^{-1} $year^{-1}$. The added N treatment is generally higher than the average estimates of N deposition for urban chaparral shrublands (25–35 kg N ha^{-1} $year^{-1}$; Riggan and others 1985; Bytnerowicz and Fenn 1996; Fenn and others 2003b); however, the spatial pattern of N deposition in southern California is highly variable and poorly understood, and sites at slightly higher elevations can receive between 40 and 145 kg N ha^{-1} $year^{-1}$ (Meixner and Fenn 2004; Fenn and Poth 2004). In light of the large spatial variation in estimated N deposition, we decided to expose the chaparral and CSS shrublands to N deposition levels that were intermediate for low and high elevation southern Californian urban shrublands and forests.

Granular NH_4NO_3 was added during a single application using a handheld spreader. Given that some of the dry anthropogenic N deposition to southern California shrublands is from gaseous N (Bytnerowicz and Fenn 1996) the use of granular NH_4NO_3 does not account for possible foliar N uptake. However, drought deciduous CSS shrubs are virtually leafless and the conductance of evergreen shrubs is at a seasonal minimum during the dry summer and fall months (Poole and Miller 1975; Gray and Schlesinger 1981) when the majority of atmospheric dry deposition occurs (Bytnerowicz and Fenn 1996; Padgett and others 1999; Fenn and others 2003a), so foliar N uptake is presumably low when inputs of dry N deposition are at a seasonal maximum. Application of granular N fertilizer also does not simulate potential atmospheric N inputs from wet deposition; however, because wet deposition accounts for only 10–15% of the total atmospheric N deposited to southern California shrublands (Bytnerowicz and Fenn 1996; Padgett and others 1999; Fenn and others 2003a) and rainfall and/or fog events are infrequent during the late summer and early fall, the inability to adequately simulate wet deposition presumably does not limit the ability to determine the effects of dry season N inputs on the short term soil–plant N dynamics.

Field Sampling

Soil and shrub tissue samples were collected quarterly at each site between January 2003 and September 2004 to coincide with the seasonal variation in rainfall (spring = March–April, summer = June–July, fall = September–October, and winter = January), and samples were obtained from 2–4 randomly chosen points in each plot.

Soil samples were obtained from the surface (0–10 cm) and subsurface (30–40 cm) mineral layers using a 4.7 cm diameter × 10 cm deep (173.5 cm^3) bucket auger or a 1.8 cm diameter × 10 cm deep (25.5 cm^3) T-bar. As opposed to soil surface samples, which were collected quarterly, subsurface soil samples were obtained in the spring and fall. Samples were transferred from the core samplers to polyethylene (Whirl-Pak) sample bags and immediately returned to the lab and stored at 4°C until laboratory analysis (described below).

Mixed anion–cation resin bags (n = 4 per plot) were installed in the surface (0–10 cm) mineral soil following soil sampling. Resin bags consisted of 15 g anion (USF-A244B) and 15 g cation (USF-C211) exchange resin (US Filter, Rockford, IL, USA) that were mixed within 6.25 × 15.0 cm nylon bags (160 mesh). Resin bags were deployed for the first time during the summer 2003 field sampling campaign and were exchanged on a seasonal (3 month) basis. Immediately after field sampling resin bags were returned to the lab and stored at 4°C until analysis.

Approximately 10–15 cm long samples of live apical shoots (leaf + stem) of *A. fasciculatum* (chaparral) and *A. californica* and *S. mellifera* (CSS) shrubs were randomly collected seasonally (n = 2–4 sub-samples per plot). Apical stems were selected because these stems represent current-years growth (Gill and Mahall 1986). Shrub tissue subsamples collected at each random point were pooled by plot, dried at 70°C for 1 week, and ground to pass through a 40 mesh sieve using a mechanical mill (Thomas-Wiley Mini Mill, Thomas Scientific, Swedesboro, NJ, USA).

The potential for N loss from leaching was measured using passive lysimeters (Gee and others 2002) installed 1 m below the soil surface (n = 3 per treatment at each site), which is generally below the surface rooting zone (Jobbagy and Jackson 2000). The lysimeters (Drain Gauge, Decagon, Inc., Pullman, WA, USA) consisted of two parts, a 50 cm long divergence control tube that funneled water into the drain gauge and a 100 cm long × 20.3 cm diameter gauge equipped with a fiberglass wick to hold captured water and a gauge to measure the flow of water through the lysimeters. Gauges were installed in December 2003, and flow rates were monitored by a solid-state datalogger (CR 10X, Campbell Scientific, Inc., Ogden, UT, USA). Water samples retained by the passive lysimeters were retrieved every 3 months using a 50 ml syringe.

Laboratory Analysis

Bulk density was determined from samples collected from the bucket auger because these samples experienced minimal compaction and the volume of the sampler was fixed. The fresh sample was weighed to determine the fresh weight of soil per unit volume and the bulk density was converted to a dry weight basis using the gravimetric soil moisture data (described below). Sub-samples of fresh soil were then removed for gravimetric soil moisture and soil extractable NH_4 and NO_3 analyses (described below) and the remaining soil was air dried and passed through a 2 mm sieve to remove large rocks and other debris.

Gravimetric soil water content was determined from 10 g of fresh soil that was placed into preweighed porcelain crucibles. Soil was then dried at 105°C for 2–4 days and reweighed to determine the soil dry weight. Percent gravimetric soil water was calculated as $[(w_f\text{-}w_d)/w_d]\times100$ where w_f was the fresh weight of the soil sample and w_d was the dry weight of the soil sample after drying at 105°C (Robertson and others 1999).

Extractable NO_3-N and NH_4-N from soil samples and resin bags was determined as soon as possible (usually 1–4 days) after sample collection. Short-term (up to 1 week) storage at 4°C does not preclude the accumulation of NH_4 and NO_3 (Binkley and Hart 1989), and unfortunately the potential for inorganic N accumulation during cold storage is unknown for our soils. However, although the absolute value of soil extractable NH_4 and NO_3 may be affected by cold storage, soils collected from added-N and control plots were stored and processed using the same protocol and relative differences between added-N and control soils were presumably unaffected by cold storage. For soil extractable NH_4 and NO_4, 10 g of fresh soil was added to 40 ml of 2 M KCl and continuously agitated on an orbital shaker for 1 h (Mulvaney 1996). The supernatant was filtered using a 0.2 µm filter and the NH_4–N (Hofer 2001) and NO_3–N (Knepel 2001) concentration of the extract was measured colorimetrically using an auto-analyzer (Quikchem 3000, Lachat Instruments, Milwaukee, WI, USA). Soil extractable N concentration determined from fresh soil was converted to a dry soil weight basis using the gravimetric soil moisture data and expressed as the mass of N per unit ground area basis by multiplying the soil extractable N concentration by the soil bulk density. Accumulated NH_4–N and NO_3–N from resin bags were extracted in a similar manner except that the resin bags were extracted in 100 ml of 2 M KCl. Resin extractable N that accumulated in the resin bags was expressed as a mass of N per bag.

Total N and P of soil and shrub tissue were determined using a micro-Kjeldahl method where 0.4 g of soil or 0.2 g of shrub tissue was digested for 3 h at 390°C in 3.5 ml concentrated H_2SO_4 and a catalyst containing 1.5 g K_2SO_4 and 0.015 g Se. Digests were measured colorimetrically for N (Sardina 2001) and P (Sardina 2000) using an auto-analyzer (Quikchem 3000, Lachat Instruments, Milwaukee, WI, USA). Approximately 50 mg of dried soil and 7 mg of dried plant tissue was analyzed for C and N and the $\delta^{15}N$ natural abundance at the Kansas State University, Stable Isotope Mass Spectrometry Laboratory. Isotopic and elemental analysis was conducted using a mass spectrometer (ThermoFinnigan Delta Plus, Thermo Electron, Bremen, Germany) coupled to a CHN analyzer (CE 1110, Carlo-Erba, Milan, Italy), respectively.

The concentration of leached inorganic N retrieved from the passive lysimeters was analyzed colorimetrically for NH_4–N (Diamond 2001) and NO_3–N (White 2001) using an auto-analyzer (Quikchem 3000, Lachat Instruments, Milwaukee, WI, USA). Leaching rates were calculated as the average concentration of NH_4–N or NO_3–N (mg N l^{-1}) multiplied by the total flow rate (l cm^{-2}) measured between December 2003 and October 2004.

Statistical Analysis

Differences in response variables as a function of N addition and time were assessed using repeated measures analysis of variance (ANOVA). Separate ANOVAs were conducted for periods before (winter-fall 2003) and after (winter-fall 2004)

N-addition to determine whether response variables differed significantly between control and added N plots before and after N addition. A two-way ANOVA with depth and N addition as fixed effects was performed on the annual average of response variables that did not show a statistically significant temporal trend (that is, total soil N, P, C, and $\delta^{15}N$ natural abundance). Data were analyzed using NCSS 2004 statistical software (Hintze 2004). Data were tested for normality and heteroscedasticity prior to analyses, and response variables violating these assumptions were LN-transformed (Zar 1984).

The temporal kinetics of cumulative N capture on anion–cation exchange resins was estimated using an exponential equation of the form $N_t = N_0[1-\exp(-kt)]$, where N_t is the cumulative N extracted from sequential harvest of anion–cation resin bags, N_0 is the maximum potentially accumulated N, and k is the rate constant (Stanford and Smith 1972). This model was chosen over other models (that is, linear or other non-linear models) because the temporal trend in resin accumulated N was non-linear over time and this model is commonly used to describe mineralization kinetics (Stanford and Smith 1972) even though resin accumulated N may not be synonymous with mineralization (Binkley and Hart 1989). Coefficients were estimated using non-linear least-squares regression, and the equality of added N and control cumulative curves was assessed using ANOVA (Hintze 2004).

Mean differences in the total amount of inorganic N leached below the surface (1 m) rooting zone were assessed using a two-tailed t-test (degrees of freedom = 4) on LN-transformed data to satisfy the assumption of normality.

Results

Seasonal Trends in Soil Moisture

Surface (0–10 cm) mineral soil moisture in chaparral during the winter and spring rainy season was 10–11% in 2003 and 5–9% in 2004 (Figure 1a), whereas subsurface (30–40 cm) mineral soil moisture was approximately 8% for both 2003 and 2004 (Figure 1c). During the summer and fall dry season, surface soil moisture was 1–3% in 2003 and 2004 and subsurface soil moisture was 2–4% (Figure 1a, c). In CSS, surface soil moisture in 2003 was 8–10 % during the winter and spring and 2–4 % during the summer and fall, whereas in 2004, surface soil moisture was 4–6 % during the winter and spring and 1–2 % during the summer and fall (Figure 1b). Similarly, subsurface soil moisture was on average 13 and 7% during the spring of 2003 and 2004, respectively, and 6% during the fall of 2003 and 2004 (Figure 1d).

Soil Chemistry

Greater than 94% of the seasonal variation in inorganic N (NH_4–N + NO_3–N) accumulation on ion exchange resins deployed in the surface (0–10 cm) mineral soil of chaparral and CSS was described by the exponential model. In chaparral, approximately 78% of the total inorganic N accumulation for 2004 occurred during the first 6 months of observation (winter and spring), whereas in CSS nearly 98% of the total inorganic N accumulation occurred during the first 6 months (Figure 2). This period corresponds to the winter and spring rainy season when surface soil moisture content was at a seasonal maximum (Figure 1a, b). Inorganic N accumulation during the last 6 months of observation (summer and fall) was substantially lower for chaparral and CSS (Figure 2), and the decline in resin N accumulation was coincident with a decline in surface soil moisture (Figure 1a, b). Experimental N addition significantly increased the accumulation of inorganic N on ion exchange resins (Figure 2). In chaparral, the mean ± 1 SE (n = 4) resin-accumulated N was 44.4 ± 3.1 and 22.8 ± 5.1 mg N bag^{-1} $year^{-1}$ in added N and control plots, respectively ($F_{2,36}$ = 30.2; $p < 0.001$; Figure 2a). In CSS, added N plots accumulated 12.8 ± 2.5 mg N bag^{-1} $year^{-1}$ whereas control plots accumulated 7.7 ± 2.3 mg N bag^{-1} $year^{-1}$ ($F_{2,36}$ = 5.5; $p < 0.05$; Figure 2b). Most of the resin accumulated N in chaparral and CSS (50–80%) was in the form of NO_3–N.

The soil extractable inorganic N (NO_3 + NH_4) content of the surface mineral soil (0–10 cm) was not significantly affected by N addition (Figure 3a, b); however, the extractable N content of the subsurface (30–40 cm) mineral soil increased significantly in response to N addition for chaparral ($F_{1,6}$ = 7.12; $p < 0.05$; Figure 3c) and CSS ($F_{1,6}$ = 5.60; p = 0.05; Figure 3d). Soil extractable N also varied significantly over time in chaparral surface and subsurface soil (Figure 3a, c), but in CSS temporal trends in soil extractable N were less consistent (Figure 3b, d). In general, soil extractable N in chaparral surface soil increased immediately following fire (fall 2003) and reached a maximum value in January 2004, whereas soil extractable N in the subsurface mineral soil was consistently higher in the fall of each year. Prior to the chaparral fire, surface and subsurface soil

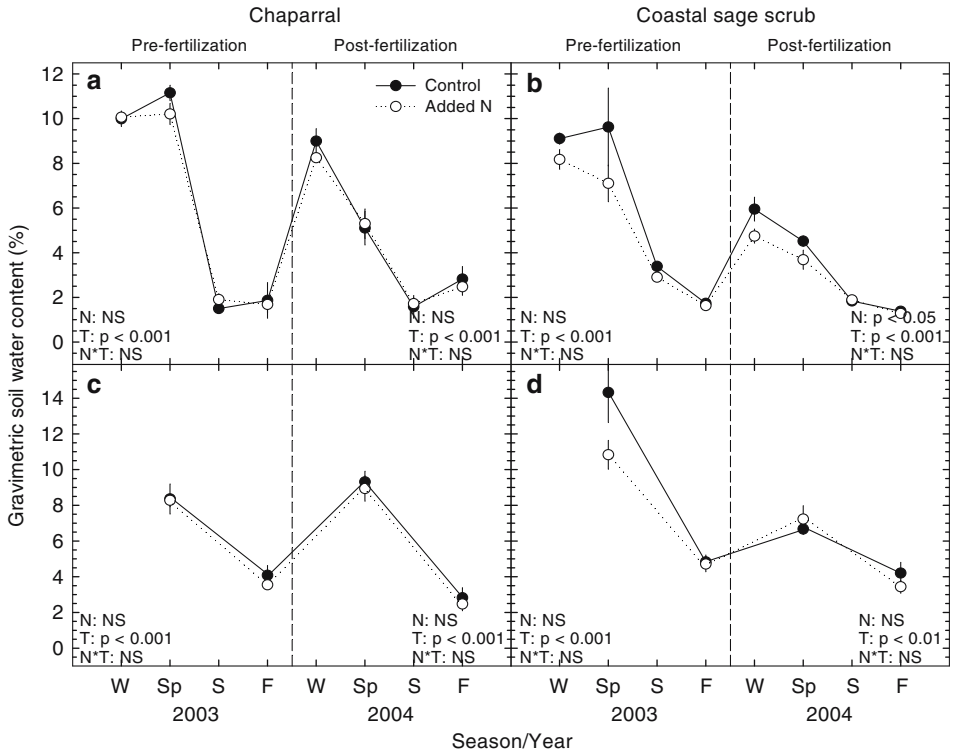

Figure 1. Mean (±1 SE, $n = 4$) gravimetric soil moisture for surface (0–10 cm; **a** and **b**) and subsurface (30–40 cm; **c** and **d**) mineral soil in chaparral (*left panels*) and coastal sage scrub (*right panels*) ecosystems exposed to 50 kg N ha^{-1} NH_4NO_3 (added N: *open symbols, dotted line*) or ambient N (control: *closed symbols, solid line*) before and after fertilization. Also shown are the results (*p*-values) from a repeated measures ANOVA for N (degrees of freedom (*df*) = 1,6), time (*df* = 3,18), and the N × time interaction (*df* = 3,18). NS = $p > 0.05$. W = winter (January), Sp = spring (March–April), S = summer (June–July), F = (September–October).

extractable N was similar in chaparral and CSS (0.5 and 0.2 g N m^{-2}, respectively), but after fire, chaparral control plots had 2–4 times higher soil extractable N pools than CSS control plots (Figure 3). As observed with the resin accumulated inorganic N most (50–80%) of the soil extractable N was in the form of NO_3–N.

Added N failed to significantly alter total N, C, and P pools in both chaparral and CSS; however, several variables were significantly affected by soil depth (Table 1). In chaparral, total N, P, and C content, and N:P ratio declined significantly as a function of depth whereas the soil C:N ratio increased significantly as a function of depth (Table 1). In CSS, only total soil C content declined significantly as a function of depth (Table 1). Chaparral soil $\delta^{15}N$ natural abundance increased significantly as a function of N addition and depth, whereas in CSS, soil $\delta^{15}N$ natural abundance increased significantly as a function of depth only (Table 1).

Rates of NH_4–N, NO_3–N, and total inorganic N leaching in chaparral were 2–3 times higher in added N plots than in control plots; however, high within-treatment variability caused these differences to be statistically insignificant (Table 2). In contrast, no leachate was retrieved from CSS plots during any of the sampling events because the lysimeters were always empty. In addition, no flow was ever recorded from the CSS lysimeters, indicating that rain water was lost as runoff and/or used effectively by CSS shrubs.

Tissue Chemistry

Prior to N addition the tissue N and P concentration of the chaparral shrub *A. fasciculatum* in added N and control plots was nearly identical and a significant increase in both tissue N (Figure 4a) and P (Figure 4c) occurred after the July 2003 fire. After N addition the tissue N and P concentration was significantly higher in *A. fasciculatum* shrubs exposed to added N and the relative difference between control and added N shrubs was particularly large during the winter and spring 2004 sample periods. In CSS, the average tissue N and P concentration of *A. californica* and *S. mellifera* shrubs prior to N addition was similar in control and added N plots and both declined significantly between the spring and fall 2003 sample dates (Figure 4b, d). After N addition the average tissue N concentration was significantly higher in shrubs exposed to added N ($F_{1,6} = 16.25$; $p < 0.01$), and tissue N concentration tended to be higher in the winter and spring whereas tissue P concentration tended to be higher during the spring and fall.

Tissue $\delta^{15}N$ natural abundance varied significantly as a function of N addition and time and there were significant interactions between N addition and time for both chaparral and CSS after

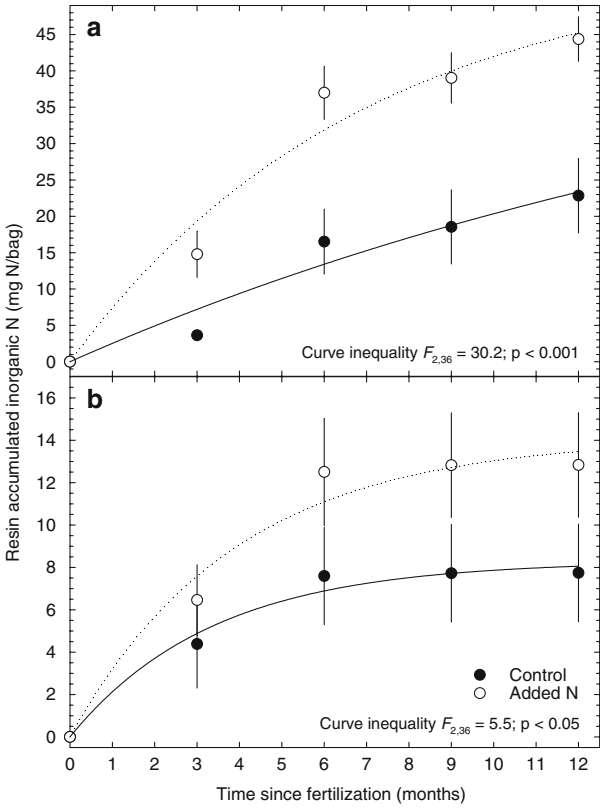

Figure 2. Mean (±1 SE, $n = 4$) cumulative inorganic N (NH_4–N + NO_3–N) accumulation on mixed anion–cation resins buried in the surface soil (0–10 cm) in chaparral (**a**) and coastal sage scrub ecosystems (**b**) exposed to 50 kg N ha^{-1} NH_4NO_3 (added N: *open symbols*) or ambient N (control: *closed symbols*) after fertilization. Also shown is the cumulative N estimated as $N_0[1-\exp(-kt)]$, where N_0 is the potentially accumulated N and k is the rate constant (per month) for plots exposed to added N (*dashed lines*) and ambient N (*solid lines*). The equality of added N and control curves was assessed using analysis of variance (ANOVA).

N addition (Figure 5). Prior to N addition the $\delta^{15}N$ natural abundance for chaparral and CSS shrub tissue increased significantly between the summer and fall 2003 sample campaigns and differences between control and added N plots were negligible. After the addition of NH_4NO_3 fertilizer, which had a $\delta^{15}N$ natural abundance of −0.8‰ (Figure 5), the tissue $\delta^{15}N$ of *A. fasciculatum* exposed to added N was consistently lower than shrubs exposed to ambient N ($F_{1,6} = 11.36$; $p < 0.05$), and these relative differences became larger over time causing a significant N × time interaction ($F_{3,18} = 3.34$; $p < 0.05$; Figure 5a). In CSS, the average $\delta^{15}N$ natural abundance of *A. californica* and *S. mellifera* shrub tissue was significantly higher in added N plots ($F_{1,6} = 49.44$; $p < 0.001$), and as with chaparral, these relative differences became larger over time causing a significant N × time interaction ($F_{3,18} = 3.53$; $p < 0.05$; Figure 5b).

The increase in tissue N for chaparral and CSS shrubs exposed to added N caused a decrease in the tissue C:N ratio (Figure 6). Prior to N addition the tissue C:N ratio of *A. fasciculatum* declined over time and differences between shrubs in control and added N plots were negligible (Figure 6a). After N addition, the *A. fasciculatum* tissue C:N ratio was on average 5–10 units lower in added N plots between winter and summer ($F_{1,6} = 8.62$; $p < 0.05$) and the tissue C:N ratio increased significantly over time ($F_{3,18} = 49.44$; $p < 0.001$; Figure 6a). In CSS, the average tissue C:N ratio of *A. californica* and *S. mellifera* shrubs prior to N addition was highest in the spring and fall and differences between added N and control plots were small (Figure 6b). After N addition, the average tissue C:N ratio was consistently 5–10 units lower for CSS shrubs exposed to added N ($F_{1,6} = 11.20$; $p < 0.05$) and the tissue C:N ratio for both control and added N shrubs was highest in the summer and fall ($F_{3,18} = 14.04$; $p < 0.001$; Figure 6b).

Discussion

Possible Fate of Added N

Dry N deposition accumulates on vegetation and soil surfaces of chaparral and coastal sage scrub (CSS) ecosystems during the summer and early fall (Bytnerowicz and others 1987; Bytnerowicz and Fenn 1996; Padgett and others 1999; Fenn and others 2003a) and becomes available as a pulse after the onset of winter rainfall (Riggan and others 1985; Fenn and others 2003b). Given the potential for a temporal asynchrony between N availability and biotic demand (Fenn and others 2003b; Meixner and Fenn 2004), we hypothesized that N deposited during the fall would result in a significant but transient increase in available N; however, the aboveground N storage of chaparral and CSS shrubs would not be significantly affected by dry season N inputs because drought-induced limitations in physiological activity constrain the utilization of these available N pulses.

Our results indicate that dry season N addition significantly increased the accumulation of inorganic N (NH_4 + NO_3) on ion exchange resins deployed in the surface (0–10 cm) mineral soil of chaparral and CSS (Figure 2). In contrast, the surface soil extractable inorganic N pool was not affected by added N whereas the subsurface (30–40 cm) soil extractable N was significantly

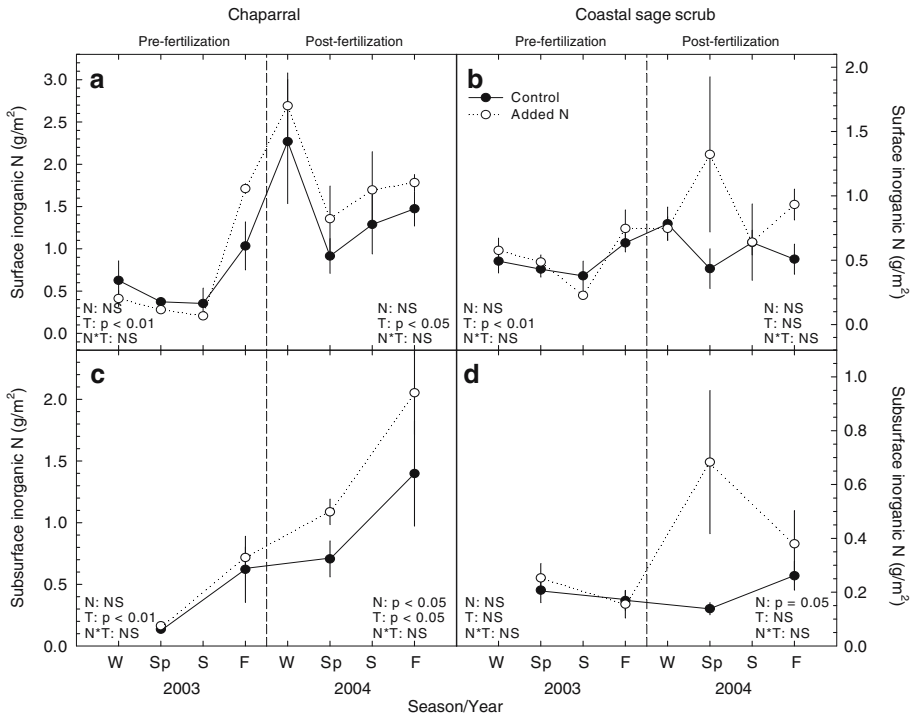

Figure 3. Mean (±1 SE, $n = 4$) soil extractable inorganic N (NH_4–N + NO_3–N) for surface (0–10 cm; **a** and **b**) and subsurface (30–40 cm; **c** and **d**) mineral soil in chaparral (*left panels*) and coastal sage scrub (*right panels*) ecosystems exposed to 50 kg N ha^{-1} NH_4NO_3 (added N: *open symbols, dotted line*) or ambient N (control: *closed symbols, solid line*) before and after fertilization. Also shown are the results (*p*-values) from a repeated measures ANOVA for N (degrees of freedom (*df*) = 1,6), time (*df* = 3,18), and the N × time interaction (*df* = 3,18). NS = $p > 0.05$. W = winter (January), Sp = spring (March–April), S = summer (June–July), F = (September–October).

Table 1. Mean (±1 SE; $n = 4$ plots) Properties of Surface (0–10 cm) and Subsurface (30–40 cm) Mineral Soil for a Post-fire Chaparral and Mature Coastal Sage Scrub (CSS) Stand after 1 Year of Exposure to Experimental (50 kg N ha^{-1}; Added-N) and Ambient (Control) N Deposition

		Surface (0–10 cm)		Sub-surface (30–40 cm)		N-addition	Depth	N×Depth
Stand	Variable	Control	Added N	Control	Added N	$F_{1,12}$	$F_{1,12}$	$F_{1,12}$
Chaparral	Total N (g m^{-2})	77 ± 7	68 ± 6	48 ± 4	46 ± 2	0.90	24.69***	0.40
	Total P (g m^{-2})	33 ± 2	33 ± 1	26 ± 1	26 ± 1	0.01	23.35***	0.01
	Total C (kg m^{-2})	1.7 ± 0.3	1.3 ± 0.1	1.1 ± 0.1	1.0 ± 0.1	3.40	9.86**	1.57
	N:P	2.4 ± 0.2	2.1 ± 0.2	1.8 ± 0.1	1.8 ± 0.1	1.24	8.88*	0.59
	C:N	25.8 ± 1.8	24.3 ± 1.2	30.7 ± 1.5	26.2 ± 1.4	4.19	5.25*	0.99
	$\delta^{15}N$ (‰)	1.3 ± 0.2	2.4 ± 0.3	2.7 ± 0.5	3.2 ± 0.3	5.60*	10.34**	0.50
CSS	Total N (g m^{-2})	77 ± 4	65 ± 10	74 ± 6	61 ± 8	2.83	0.20	0.01
	Total P (g m^{-2})†	24 ± 4	25 ± 4	23 ± 4	24 ± 6	0.01	0.19	0.02
	Total C (kg m^{-2})	1.3 ± 0.2	1.1 ± 0.2	0.6 ± 0.1	0.6 ± 0.1	0.49	24.70***	0.29
	N:P	3.5 ± 0.5	2.7 ± 0.4	3.5 ± 0.6	2.6 ± 0.4	3.45	0.02	0.01
	C:N	15.4 ± 0.6	15.5 ± 0.4	14.4 ± 0.4	15.5 ± 0.2	1.70	1.33	1.44
	$\delta^{15}N$ (‰)	1.0 ± 0.2	1.2 ± 0.5	2.8 ± 0.2	2.6 ± 0.3	0.03	24.42***	0.26

*Data are annual averages calculated from the spring and fall 2004. Also shown are the results from a two-way ANOVA with N addition (N) and depth as fixed effects. *$p < 0.05$; **$p < 0.01$; ***$p < 0.001$. †Data were LN-transformed.*

enhanced by N addition (Figure 3). The lack of correspondence between the resin and soil extractable N data for the surface mineral soil is presumably a function of the integration time associated with each measurement technique. For example, soil extractable N provides an instantaneous estimate of N availability whereas ion exchange resins integrate N availability over a longer period of time providing a potentially better index of N availability (Bundy and Meisinger 1994; Binkley and Hart 1989). Because N accumulation on ion exchange resins is affected by a variety of processes, including N input, mineralization–immobilization reactions, soil transport, plant

Table 2. Mean (±1 SE; n = 3) Inorganic N Leaching from Passive Lysimeters installed 1 m below the Soil Surface for Plots Receiving Added N and Plots Exposed to Ambient N (control) at the Sky Oaks Field Station

Variable	Treatment (mg N m^{-2})		t_4	p
	Control	Added N		
NO_3–N	123.2 ± 27.5	221.8 ± 91.1	−1.11	0.349
NH_4–N	4.8 ± 1.8	17.5 ± 6.3	−1.96	0.114
TIN-N	127.9 ± 28.4	239.3 ± 69.6	−1.21	0.313

Data were collected between December 2003 and October 2004. Total inorganic N (TIN) = NH_4–N + NO_3–N. Also shown is the t-value from a 2–tailed t-test with 4 degrees-of-freedom and the probability of type-I error (p-value). Data for coastal sage scrub are not shown because there was no retrievable leachate in the CSS lysimeters.

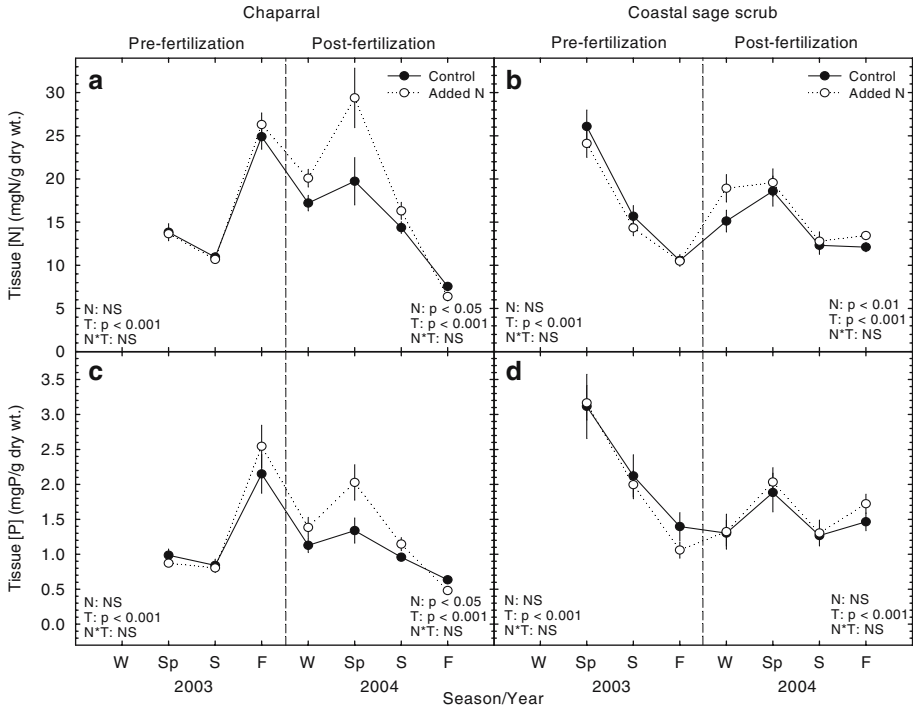

Figure 4. Mean (±1 SE, n = 4) tissue N (**a** and **b**) and P (**c** and **d**) concentration for the chaparral shrub *A. fasciculatum* (*left panels*) and the coastal sage shrubs *A. californica* and *S. mellifera* (*right panels*) exposed to 50 kg N ha^{-1} NH_4NO_3 (added N: *open symbols, dotted line*) or ambient N (control: *closed symbols, solid line*) before and after fertilization. Also shown are the results (p-values) from a repeated measures ANOVA for N (degrees of freedom (df) = 1,6), time (df = 2,12 before fertilization and 3,18 after fertilization), and the N × time interaction (df = 2,12 before fertilization and 3,18 after fertilization). NS = $p > 0.05$. W = winter (January), Sp = spring (March–April), S = summer (June–July), F = (September-October).

uptake, and gaseous efflux and/or leaching (Binkley and Hart 1989), the mechanism for the increase in N availability in response to added N is unknown.

Assuming that the ion exchange resins provide an effective index of N availability (Binkley and Hart 1989), these data suggest that only a fraction of the N added was recovered from chaparral and CSS surface mineral soil. For example, accounting for the surface area of the resin bags, an estimated 2.2 and 0.5 g m^{-2} more inorganic N accumulated in resin bags deployed in added N plots of chaparral and CSS, which amounts to only 44 and 11%, respectively, of the N added as NH_4NO_3 (5 g N m^{-2}). These data suggest that most of the added N was lost and/or sequestered in other ecosystem N pools.

The mean (±1 SE) annual flux of inorganic N from leaching in the regenerating chaparral stand was 128 ± 28 and 239 ± 70 mg N m^{-2} in control and added N plots, respectively ($p > 0.05$; Table 2), suggesting that leaching losses in chaparral stands

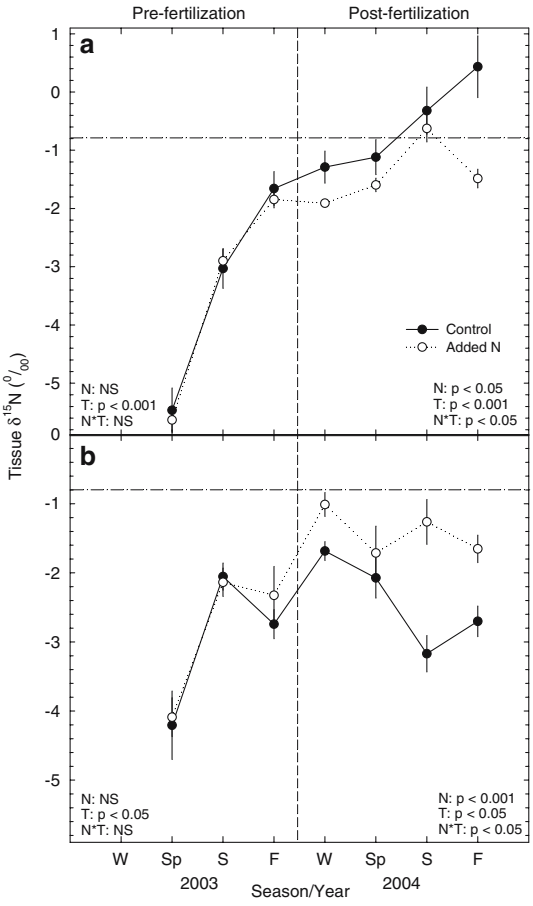

Figure 5. Mean (±1 SE, $n = 4$) tissue $\delta^{15}N$ natural abundance for the chaparral shrub *A. fasciculatum* (**a**) and the coastal sage shrubs *A. californica* and *S. mellifera* (**b**) exposed to 50 kg N ha^{-1} NH_4NO_3 (added N: *open symbols, dotted line*) or ambient N (control: *closed symbols, solid line*) before and after fertilization. The *horizontal dashed line* in each panel corresponds to the $\delta^{15}N$ natural abundance of the NH_4NO_3 fertilizer (−0.8‰). Also shown are the results (*p*-values) from a repeated measures ANOVA for N (degrees of freedom (*df*) = 1,6), time (*df* = 2,12 before fertilization and 3,18 after fertilization), and the N × time interaction (*df* = 2,12 before fertilization and 3,18 after fertilization). NS = $p > 0.05$. W = winter (January), Sp = spring (March–April), S = summer (June–July), *F* = (September–October).

were not significantly affected by added N. However, the low sample size ($n = 3$) resulted in low statistical power, and although leaching may not have been statistically different between added N and control chaparral plots, the significantly higher resin accumulated N and subsurface soil extractable N observed in added N plots suggest that bulk soil N transport may have been higher in added N plots. Assuming that chaparral shrubs are deep rooted (Hellmers and others 1955) and added N shrubs responded with increased root production (Kummerow and others 1982), it is possible that large subsurface N transport from bulk flow was assimilated by deep roots before being captured by the lysimeters. In the mature CSS stand; however, no leachate was recovered from the passive lysimeters in 2004 (Table 2). These data suggest that more rainfall was exported by runoff and/or the CSS shrubs were efficient in using the available soil water and N. CSS shrubs have shallower root systems than chaparral shrubs and a more extensive lateral spread of surface roots (Hellmers and others 1955), and CSS shrubs rapidly assimilate available N during the spring growing season (Gray and Schlesinger 1983; Gray 1983). Thus, it is possible that surface soil moisture and N were effectively assimilated by CSS shrubs, limiting the fraction of water and N exported to 1 m. However, CSS is also associated with fine-textured soils that limit the infiltration of water (Westman 1981), suggesting that a larger fraction of water and N was exported by surface runoff in CSS. The relatively smaller difference in resin extractable N between CSS plots exposed to added and ambient N (Figure 2) is consistent with this interpretation.

The increase in aboveground tissue N concentration for chaparral and CSS shrubs exposed to added N (Figure 4) suggests that added N stimulated plant N uptake and increased aboveground N storage. Furthermore, the observed decline in the chaparral and CSS tissue C:N ratio with added N (Figure 6) suggests that short-term increases in tissue C storage per unit added N were minimal (Rastetter and others 1992). However, aboveground tissue N concentration is often a poor indicator of aboveground N pool size because it is sensitive to N uptake, allocation, and aboveground biomass production (Chapin 1980). Although aboveground shrub biomass data are currently being processed, preliminary estimates indicate that the significant differences in aboveground tissue N concentration observed following N addition (Figure 4) probably did not translate to significant differences in aboveground N storage, supporting our hypothesis that the aboveground N storage of chaparral and CSS shrubs would not be significantly affected by dry season N inputs.

There are several other possible avenues of N sequestration and/or loss; however, the importance of these pools and fluxes has not yet been quantified, and thus, remains speculative. First, the relatively high C content and C:N ratio of chaparral and CSS soil (Table 1) and the rapid disappearance of added N in the surface soil (Figure 3) suggest that immobilization of added N was a distinct possibility

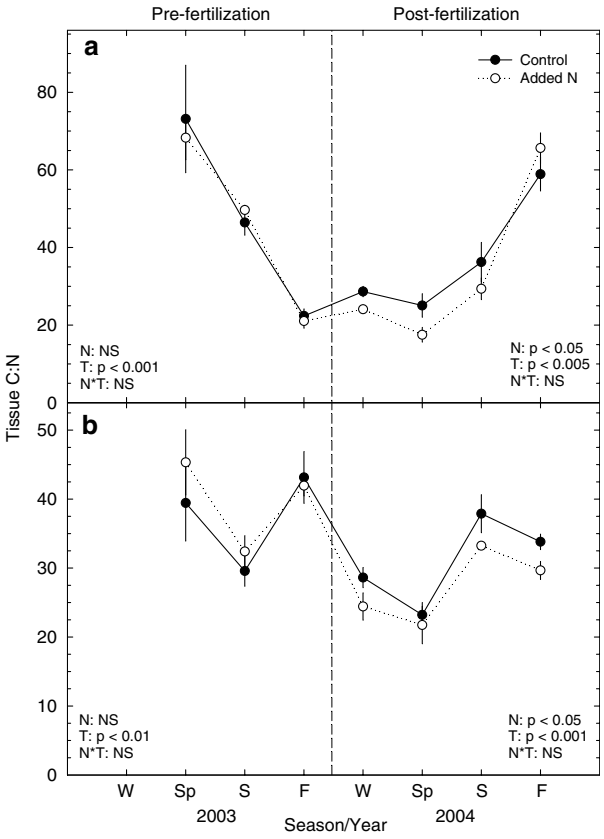

Figure 6. Mean (±1 SE, $n = 4$) tissue C:N ratio for the chaparral shrub *A. fasciculatum* (**a**) and the coastal sage shrubs *A. californica* and *S. mellifera* (**b**) exposed to 50 kg N ha^{-1} NH_4NO_3 (added N: *open symbols, dotted line*) or ambient N (control: *closed symbols, solid line*) before and after fertilization. Also shown are the results (*p*-values) from a repeated measures ANOVA for N (degrees of freedom (*df*) = 1,6), time (*df* = 2,12 before fertilization and 3,18 after fertilization), and the N × time interaction (*df* = 2,12 before fertilization and 3,18 after fertilization). NS = $p > 0.05$. W = winter (January), Sp = spring (March–April), S = summer (June–July), F = (September–October).

(Jeffries and Maron 1997; Aber and others 1998; Currie 1999; Micks and others 2004; Sigüenza and others 2005). Secondly, nitrogen loss from gaseous emission of NO and N_2O has been found to be several times higher in southern Californian coniferous forests exposed to long-term (decades) atmospheric N deposition and is significantly stimulated by soil moisture (Fenn and others 1996), suggesting that N losses during the winter and spring rainy season, when N accumulation on ion exchange resins was highest (Figure 2), may be substantial. Thirdly, root N uptake and turnover represent a significant avenue of N storage and cycling. Chaparral and CSS shrubs have an estimated root:shoot ratio of approximately 0.5 and store up to 30% of N below ground (Mooney and Rundel 1979; Gray and Schlesinger 1983), and annual fine root production greatly exceeds aboveground production (Kummerow and others 1981) indicating that belowground C and N fluxes are large and dynamic. Furthermore, root production of Mediterranean-type shrubs is significantly stimulated by added N (Kummerow and others 1982), and the chaparral and coastal sage shrubs observed here presumably respond in a similar manner. Herbaceous plants may also sequester large amounts of added N, especially in the recovering chaparral stand where the cover of herbaceous plants increased rapidly following fire. In CSS, however, the cover of annual plants is at least 1–2 orders of magnitude below the cover of *A. californica* and *S. mellifera*, and N addition experiments indicate that CSS shrubs are more nitrophilous than herbaceous annuals (Padgett and Allen 1999). Thus, the importance of annual herbs in sequestering added N at the CSS manipulation site is presumably minimal. Finally, as mentioned above, given the relatively steep slope of the study sites, runoff is a potentially important avenue of N loss.

Temporal Trends

Inorganic N accumulation in ion exchange resins was highest during the winter and spring rainy season (Figure 2) when soil moisture was at a seasonal maximum (Figure 1a, b). This result is not surprising given that N accumulation in ion exchange resins is sensitive to temporal variations in mineralization and soil N transport, both of which increase with concomitant increases in soil moisture (Binkley and Hart 1989). However, substantial differences in soil extractable N and resin accumulated N were observed between the chaparral and CSS stands (Figures 2, 3), and although differences in inorganic N pools and fluxes could be caused by many site-specific variables, the largest differences were observed following the July 2003 fire in the chaparral stand. For example, soil extractable N content was on average 0.5 and 0.2 g m^{-2} in the surface and subsurface mineral soil, respectively, at both sites prior to fire, whereas after fire, chaparral surface and subsurface soil extractable N pools were 1.0 and 0.8 g m^{-2}, respectively, higher in the recently burned chaparral stand (Figure 3). Resin accumulated N was 3–4 times higher in the recently burned chaparral stand (Figure 2), especially during the first 6 months of observation when soil moisture was at a seasonal maximum (Figure 1a, b), suggesting that

N mobility and/or mineralization may have been stimulated by fire. Transient increases in soil extractable N pools (DeBano and Conrad 1978; DeBano and others 1979; Dunn and others 1979; Rundel 1983; Stock and Lewis 1986; Grogan and others 2000), N mineralization (Marion and Black 1988), and soil N transport are frequently observed in post-fire chaparral, and differences in resin accumulated N (Figure 2), lysimeter water yield, and N leaching between the CSS and chaparral stands (Table 2) are consistent with differences in pore water (Chorover and others 1994) and stream flow discharges (Riggan and others 1994) observed between mature and recently burned and coniferous forest and chaparral stands.

The tissue N and P concentration of *A. fasciculatum* also increased substantially following fire (Figure 4a, c) whereas the tissue C:N ratio declined (Figure 6a), a result that is also consistent with those from other regenerating Mediterranean-type ecosystems (Rundel and Parsons 1980; Black 1987; Gillon and others 1999). The initial post-fire increase in tissue N and P is thought to be due to the fire-induced increase in available N (Figure 3) and P (Kutiel and Naveh 1987; Marion and Black 1988) and luxury consumption of N and P in regenerating shrubs (Rundel and Parsons 1980; Gillon and others 1999). However, tissue N and P concentration returned to pre-fire levels by the summer and fall of 2004 (12–15 months post-fire) suggesting that internal N and P were rapidly diluted as shrub biomass production ensued.

The seasonal pattern in tissue N and P concentration observed for CSS shrubs (Figure 4b, d) is consistent with that reported for *A. californica* and *S. mellifera* (Gray 1983). Rapid N and P uptake during the winter–spring growing season lead to an increase in tissue N and P concentration; however, internal N and P reserves become diluted during the late spring and summer when biomass production reaches a seasonal peak (Mooney and Rundel 1979; Gray and Schlesinger 1981; Gray 1983). Tissue N and P concentration during the summer and fall continued to decline presumably because low soil moisture during the summer and fall (Figure 1) limited N and P mineralization and/or transport.

Soil $\delta^{15}N$ natural abundance increases with depth because inputs of ^{15}N-depleted litterfall cause surface soil to be depleted in ^{15}N (Nadelhoffer and Fry 1988; Högberg 1997), and the spatial patterns of soil $\delta^{15}N$ natural abundance in chaparral and CSS were consistent with this pattern (Table 1). However, soils exposed to chronic atmospheric N deposition reportedly have a higher $\delta^{15}N$ natural abundance because N deposition enhances processes such as nitrification, leaching, and denitrification that discriminate against ^{15}N (Heaton 1986; Högberg 1991; Emmett and others 1998; Korontzi and others 2000). For chaparral (but not CSS) soil, the enrichment of soil exposed to added N (Table 1) was consistent with this pattern, and presumably, the ^{15}N enrichment of chaparral soil with added N may have stemmed from larger leaching (Table 2) and/or gaseous N losses (Fenn and others 1996).

Plant $\delta^{15}N$ natural abundance is a function of the $\delta^{15}N$ of the source N, although net fractionation of N during uptake may cause tissue $\delta^{15}N$ to be either higher or lower than the soil $\delta^{15}N$ value (Nadelhoffer and Fry 1988; Handley and Raven 1992). Chaparral shrubs are thought to have a deeper rooting depth than CSS shrubs and CSS shrubs tend to have a wider dispersion of surface roots than chaparral shrubs (Hellmers and others 1955). These data imply that chaparral shrubs should acquire more N from deeper soil layers that are relatively more enriched in ^{15}N. However, during the winter and spring of 2003, when plant N uptake is at a seasonal maximum (Gray 1983), tissue $\delta^{15}N$ natural abundance of chaparral and CSS shrubs was strongly depleted (−5.5‰ for *A. fasciculatum* and −4.2‰ for *A. californica* and *S. mellifera*; Figure 5), suggesting that chaparral and CSS shrubs were obtaining N from an ^{15}N-depleted surface soil N source. Between spring and summer 2003 substantial ^{15}N enrichment was observed for chaparral and CSS shrubs, which is presumably due to translocation of plant nitrogen during growth causing enrichment in tissue ^{15}N (Evans 2001). After summer 2003, tissue ^{15}N natural abundance showed little temporal variation for the drought-deciduous CSS shrubs, presumably because of rapid leaf abscission (Gray and Schlesinger 1981). CSS shrubs tend to regenerate a lower percentage of internal reserves than chaparral shrubs (Gray 1983), which may explain why continued ^{15}N enrichment of CSS shrub tissue was not observed during the fall. Similar seasonal patterns for CSS control shrubs were observed in 2004; however, the depletion of tissue ^{15}N was not as pronounced during the spring and summer growing season (Figure 5). The reason for the interannual difference in ^{15}N depletion is unknown but may have been due to interannual differences in soil moisture (Figure 1), which affect N mineralization and availability and/or nutrient acquisition by CSS shrubs.

Seasonal variations in the tissue ^{15}N for chaparral shrubs after summer 2003 were more

difficult to interpret owing to the fire. Fire causes significant mortality of surface roots (Neary and others 1999) and increases the $\delta^{15}N$ value of soil (Handley and Raven 1992), thus regenerating shrubs typically acquire available N from deeper soil horizons that are enriched in ^{15}N (Högberg 1997; Grogan and others 2000). Leaching losses of N also cause soil ^{15}N enrichment (Högberg 1991; Emmett and others 1998), and leaching losses were larger in the regenerating chaparral stand (Table 2). Both these fire-induced alterations to the chaparral N cycle could explain the substantial tissue ^{15}N enrichment observed for chaparral shrubs after summer 2003 (Figure 5). In contrast, *A. fasciculatum* is an evergreen chaparral shrub, and after the initial increase in tissue N following fire (Figure 4a), *A. fasciculatum* would presumably regenerate internal N more efficiently than CSS shrubs (Gray 1983), again causing tissue ^{15}N enrichment (Evans 2001). Unfortunately, neither explanation can be excluded given the data provided.

Added N significantly altered the tissue $\delta^{15}N$ natural abundance of chaparral and CSS shrubs (Figure 5); however, the response was not consistent between shrubland types. For example, CSS shrubs exposed to added N were significantly more enriched in ^{15}N than control shrubs, and when averaged for the year, the $\delta^{15}N$ of CSS shrubs exposed to added N (−0.6‰) was closer to the $\delta^{15}N$ of the NH_4NO_3 fertilizer (−0.8‰) than the control shrubs (−2.4‰) (Figure 5). Again, assuming that the tissue $\delta^{15}N$ natural abundance is broadly indicative of the source N (Nadelhoffer and Fry 1988; Handley and Raven 1992), these data suggest that the fertilizer N source deposited during the dry season was an important source of N for CSS shrubs exposed to added N. The N fertilizer response of regenerating chaparral shrubs is more difficult to interpret; however, the tissue ^{15}N of regenerating shrubs in control plots may be substantially enriched in ^{15}N if these shrubs acquired a larger proportion of available N from deeper soil horizons and/or were more efficient in recycling internal N reserves (Högberg 1997; Grogan and others 2000). In contrast, chaparral shrubs in added N plots would also have access to a NH_4NO_3 fertilizer source that was presumably depleted in ^{15}N ($\delta^{15}N = -0.8‰$) relative to the ambient source N, which may explain the relative tissue ^{15}N depletion of chaparral in added N plots (Högberg 1991; Handley and Raven 1992). Without information on the $\delta^{15}N$ natural abundance of the ambient source N this interpretation is clearly speculative.

Caveats, Limitations, and Implications

Our data suggest that a small portion of the N added during summer dry season was incorporated into chaparral and CSS available soil N pools following winter rainfall, which altered tissue chemistry of the dominant chaparral CSS shrubs. However, this research has many caveats that limit the potential for extrapolating our results to the anthropogenic N deposition regime of southern California. First, the use of NH_4NO_3 fertilizer as a surrogate atmospheric N source does not simulate N input from wet deposition and may not adequately simulate N input of gaseous and particulate N, which are important constituents of dry deposition in southern California (Bytnerowicz and Fenn 1996; Fenn and others 2003a). Secondly, the amount of N added (50 kg N ha^{-1}) is consistent with maximum N deposition observed in extremely polluted areas of southern California but is approximately two times higher than the average annual N deposition observed for most polluted chaparral and CSS shrublands (Riggan and others 1985; Fenn and others 2003a; Fenn and Poth 2004). Thirdly, the scale of our experiment, the divergent fire history, and the lack of replication for chaparral and CSS stands severely limit the potential for direct comparison of the chaparral and CSS response to added N and precludes the extrapolation of these results to other southern Californian chaparral and CSS ecosystems. Finally, many of the key N pools and fluxes, such as microbial immobilization, root and herbaceous annual N uptake and storage, and gaseous N emission are currently unknown but subject to ongoing research. Thus, the mechanisms of how N addition altered N storage and cycling are poorly understood making interpretation of these data speculative.

Given these limitations, our initial observations suggest that dry season N additions can significantly and rapidly alter N availability in Mediterranean-type chaparral and CSS shrublands of southern California. However, potentially significant but unsubstantiated losses of added N suggest that the semi-arid terrestrial ecosystems studied here were unable to sequester high dry season N inputs. Leaching losses of N, though not significantly different between added N and control plots, suggest substantial export of dry-season-derived N from recovering chaparral stands. Given the potential for large N losses from post-fire chaparral, groundwater and aquatic systems, which are critical sources for drinking water for urban, suburban, and rural populations of southern California, may be particularly vulnerable to high levels of

atmospheric N deposition. This interpretation is consistent with research conducted in southern Californian coniferous forests (Fenn and Poth 1999) and regenerating chaparral stands (Riggan and others 1994) exposed to chronic atmospheric N deposition. Continued N addition will provide the opportunity to assess the longer term response of Mediterranean-type shrublands to dry-season N inputs and the potential for these semi-arid shrublands to sequester and/or export added N.

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