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Journal

Ecosystems, 17(7)

ISSN

1432-9840

Authors

Homyak, Peter M
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Publication Date

2014-11-01

DOI

10.1007/s10021-014-9792-2

Peer reviewed

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Ecosystems
DOI: 10.1007/s10021-014-9792-2

ECOSYSTEMS
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Assessing Nitrogen-Saturation in a Seasonally Dry Chaparral Watershed: Limitations of Traditional Indicators of N-Saturation

Peter M. Homyak,[1,2]* James O. Sickman,[2] Amy E. Miller,[3] John M. Melack,[1] Thomas Meixner,[4] and Joshua P. Schimel[1]

[1]*Department of Ecology, Evolution & Marine Biology, University of California, Santa Barbara, Santa Barbara, California 93106, USA;* [2]*Department of Environmental Sciences, University of California, Riverside, Riverside, California 92521, USA;* [3]*Inventory and Monitoring Program, National Park Service, 240 West 5th Avenue, Anchorage, Alaska 99501, USA;* [4]*Department of Hydrology and Water Resources, University of Arizona, Tucson, Arizona 85721, USA*

Abstract

To evaluate nitrogen (N) saturation in xeric environments, we measured hydrologic N losses, soil N pools, and microbial processes, and developed an N-budget for a chaparral catchment (Sierra Nevada, California) exposed to atmospheric N inputs of approximately 8.5 kg N ha^{-1} y^{-1}. Dual-isotopic techniques were used to trace the sources and processes controlling nitrate (NO_3^-) losses. The majority of N inputs occurred as ammonium. At the onset of the wet season (November to April), we observed elevated streamwater NO_3^- concentrations (up to 520 μmol l^{-1}), concomitant with the period of highest gaseous N-loss (up to 500 ng N m^{-2} s^{-1}) and suggesting N-saturation. Stream NO_3^- $\delta^{15}N$ and $\delta^{18}O$ and soil N measurements indicate that nitrification controlled NO_3^- losses and that less than 1% of the loss was of atmospheric origin. During the late wet season, stream NO_3^- concentrations decreased (to <2 μmol l^{-1}) as did gaseous N emissions, together suggesting conditions no longer indicative of N-saturation. We propose that chaparral catchments are temporarily N-saturated at $\leq$ 8.5 kg N ha^{-1} y^{-1}, but that N-saturation may be difficult to reach in ecosystems that inherently leak N, thereby confounding the application of N-saturation indicators and annual N-budgets. We propose that activation of N sinks during the typically rainy winter growing season should be incorporated into the assessment of ecosystem response to N deposition. Specifically, the N-saturation status of chaparral may be better assessed by how rapidly catchments transition from N-loss to N-retention.

Key words: N-saturation; drylands; chaparral; N deposition; N-budgets; xeric landscapes; *Adenostoma fasciculatum*.

Received 6 September 2013; accepted 22 May 2014

Author contributions PMH wrote the paper, analyzed data, collected and processed samples; JOS conceived the study, obtained funding, and collected and processed samples; AEM led field work and collected and processed samples; JMM conceived the study and obtained funding; TM conceived the study, obtained funding, and collected and processed samples; JPS conceived the study and obtained funding. All authors reviewed and edited the manuscript.

**Corresponding author; e-mail:* peter.homyak@email.ucr.edu

Published online: 24 June 2014

Introduction

In the United States, elevated rates of atmospheric nitrogen (N) inputs are altering terrestrial ecosystems through surface water and soil acidification, leaching of base cations from soils, imbalances in plant nutrients, changes in plant species composition, direct toxic effects on plants, and eutrophication (Galloway and others 2003). In an effort to understand how N additions adversely affect ecosystems, the concept of N-saturation was developed for temperate forests of the eastern United States (Aber and others 1989, 1998), a region receiving elevated rates of N deposition (NADP 2010). However, it remains unclear whether N-saturation concepts developed in mesic regions apply to xeric ecosystems such as chaparral, where deposition rates are among the highest in the United States (up to 71 kg N ha^{-1} y^{-1}; Fenn and others 2008).

N-saturation is defined as a condition where N availability exceeds soil and plant demand, and N first accumulates in live plants, litter, and soil, and then is increasingly lost from the ecosystem (Aber and others 1998). N-saturation progresses through a series of steps (Stoddard 1994; Aber and others 1998), each of which may be identified by indicators represented by ecological and hydrochemical signals. Stage 0 defines N-limited systems with low gaseous and hydrochemical N losses. In stage 1, increasing N inputs begin to alleviate N-limitation, but N continues to be cycled efficiently with minor increases in N export (Stoddard 1994). In stage 2, an ecosystem is nearing N-saturation and has elevated N-loss, high rates of soil nitrification, and foliar N-enrichment. N-saturation can be also assessed by decreases in the ratio of dissolved organic carbon (DOC) to dissolved organic N (DON) as elevated N inputs enrich the dissolved organic matter (DOM) pool with N, reducing the ratio (Brookshire and others 2007). Finally, in stage 3, ecosystem N sinks have exceeded their capacity to sequester N, resulting in substantial N-loss and decreased ecosystem productivity.

In the western United States, the concept of N-saturation has been used to examine risks posed to ecosystems exposed to elevated atmospheric N inputs (Fenn and others 1996). However, N-saturation theory may have to be modified for ecosystems in which significant N losses can occur before plants, litter, and soil components are saturated (Vourlitis and others 2009). Limits to applying N-saturation theory in chaparral likely stem from intrinsic differences between mesic and xeric landscapes; mesic sites are generally consistently moist and have relatively high soil C content which increases N-storage capacity (Taylor and Townsend 2010). Higher soil moisture allows for greater hydrological connectivity among N deposition and soil organic matter (SOM), roots, and microbes, even during winter (Judd and others 2007), which reduces the buildup of unassimilated atmospherically deposited N. In contrast, xeric soils have relatively low C content and high hydraulic conductivity, and can experience droughts of several months or longer. During these dry months, up to 95% of the atmospheric N inputs can be delivered as dry deposition (Bytnerowicz and Fenn 1996; Padgett and others 1999), favoring N accumulation on dry surfaces because of limited diffusion, during a period when chaparral vegetation is senesced and N uptake is low (Mooney and Rundel 1979). The first rain storms of autumn (wet-up), therefore create abrupt pulses of available N when the capacity of plants to use N is low (Mooney and Rundel 1979; James and Richards 2005, 2006), yielding elevated N losses in gas evasion from soil (Homyak and Sickman 2014) and streamflow (Bernal and others 2005), which are biogeochemical signals of advanced N-saturation (Fenn and others 1996; Meixner and Fenn 2004). Thus, in xeric environments, long periods of N accumulation when N sinks are inactive may complicate indicators of N-saturation.

As an alternative to using indicators of N-saturation, catchment N input–output budgets may be informative. In a N-limited system, N inputs should be greater than outputs, reflecting net N-retention. With increasing N supply, N outputs should begin to balance N inputs, eventually shifting to net N losses during ecosystem saturation (Stoddard 1994). Although this approach may be used to understand how much N was retained by an ecosystem on an annual basis (Fenn and others 2008; Vourlitis and Fernandez 2012), it requires intensive sampling of N fluxes. Annual N-budgets may also be sensitive to the episodic nature of fluxes in xeric landscapes, and may suggest N-saturation (that is, saturation of *all* N sinks) despite ecosystem components remaining N-limited.

Here, we use a headwater chaparral catchment, Chamise Creek (Sierra Nevada, California), previously identified to be at stage 2N-saturation (Fenn and others 2011), to evaluate whether traditional indicators of N-saturation (that is, increased soil nitrification, elevated nitrate (NO_3^-) in streamflow, N-enrichment of DOM) and watershed N-budgets are adequate tools for evaluating N-saturation in xeric ecosystems. In our approach, we use a small

catchment to evaluate close linkages between terrestrial processes and N export, while minimizing the influence of in-stream and riparian processes in our estimates of N-retention. We designed our study to address three questions: (i) Is the hydrologic flushing of biologically unprocessed dry deposition in the autumn, when plants are senesced, the major pathway for N-loss in xeric catchments? (ii) Are N outputs greater than inputs and if not, how is N-limitation being maintained under elevated N deposition regimes? and (iii) How can we best assess the N-saturation status of xeric ecosystems such as chaparral?

In this study, we measured atmospheric N inputs, hydrologic N losses, and belowground microbial processes and used a previous study from Chamise Creek for estimating gaseous N export (Li and others 2006; Homyak and Sickman 2014) as well as studies from other chaparral ecosystems in California for estimating N fixation and aboveground N cycling (Kummerow and others 1978; Mooney and Rundel 1979). We also used isotopic techniques ($\delta^{15}N$ and $\delta^{18}O$) to identify the sources and processes controlling NO_3^- losses. We hypothesized that if the watershed was N-saturated, we would observe (1) greater N outputs than inputs, sustained N-loss, and enhanced nitrification during both growing and non-growing seasons; (2) hydrologic N losses predominantly composed of unprocessed atmospheric NO_3^-; and (3) decoupled C and N cycling as expressed by decreases in the ratio of DOC:DON.

Materials and Methods

Site Description

The Chamise Creek watershed, 4.2 ha in area, is *Adenostoma fasciculatum* dominated and located in the southwestern foothills of the Sierra Nevada, California, USA (680–700 m a.s.l.), within the Kaweah River drainage, in Sequoia and Kings Canyon National Park (SEKI) (36°30′47″N, 118°48′26″W). In California, chaparral ecosystems cover about 25,000 km^2, of which a significant proportion is found in this region (Keeley and Davis 2007). The climate is typical of Mediterranean regions with hot dry summers and cool wet winters. The average annual rainfall measured at the Ash Mountain meteorological station (approximately 3 km west of our site; 36°29′22″N, 118°49′22″W, 485 m a.s.l.) is 670 mm, most of which falls from November to April (Miller and others 2005). For water year (WY; October 1 to September 30) 2003 the total rainfall was 613 mm, for WY 2004 487 mm, and for WY 2010 777 mm. In California chaparral, the plant growing season occurs during the winter months (wet season) (Mooney and Rundel 1979). The average maximum and minimum air temperatures are 36.4 and 2.2°C. The slope of the catchment ranges from 10 to 17% and drains into a single ephemeral channel (Chamise Creek) fed by surface runoff that can reach flows of approximately 200 l s^{-1}.

Soils at the site are classified as Ultic Haploxeralfs, are well drained, have a sandy clay loam texture, a well-developed argillic horizon, a bulk density of about 1.2 g cm^{-3} in the upper 10 cm, and are derived from gabbro-dioritic parent material (Huntington and Akeson 1987). The soil pH is around 6, the C content is 2.3%, and the nitrogen content is 0.1% (Miller and others 2005). A thick closed canopy of *A. fasciculatum* dominates plant cover with annual grasses (*Bromus* spp.) occupying occasional open spaces. The watershed has not burned since 1960 (Li and others 2006) and represents a fully mature chaparral ecosystem (Rundel and Parsons 1979).

Watershed N-Budget: Atmospheric Inputs

Our annual N-budget was computed on a WY basis. Within our budget, we use measurements made in Chamise Creek during WY 2002–2004, along with literature values for ecosystem processes not measured in situ.

We measured bulk atmospheric N deposition from July 2002 to December 2003 using ion-exchange resin collectors (Fenn and Poth 2004). Collectors were deployed in open meadows (n = 3) from July 2002 to March 2003, to capture bulk atmospheric N deposition, and also under *A. fasciculatum* (n = 5) to measure throughfall. A second set of collectors was installed from March 2003 to December 2003 (Table 1). Atmospheric N deposition for WY 2003 was calculated as the average daily flux for each deployment period multiplied by the number of days corresponding to WY 2003. Resin extracts were analyzed for NO_3^- using the Griess–Ilovsay reaction after Cd reduction (Lachat method 12-107-04-1-B) and for ammonium (NH_4^+) using the diffusion method (Lachat method 31-107-06-5-A).

Nitrogen fixation was not measured at our site, so we relied on estimates from a 25-year-old chaparral stand with 30% cover of *Ceanothus greggii* (0.01 g N m^{-2} y^{-1}) (Kummerow and others 1978).

Table 1. Average (±Standard Error) Atmospheric N Inputs as Measured in Bulk Deposition and Throughfall Collectors During 2002 and 2003 in the Chamise Creek Watershed

Sampling period	# days sampled	Throughfall (g ha^{-1} d^{-1})			Bulk deposition (g ha^{-1} d^{-1})		
		NO_3^--N	NH_4^+-N	Total N	NO_3^--N	NH_4^+-N	Total N
07/28/02–03/04/03	219	7.1 ± 1.4	19.4 ± 3.2	26.6 ± 4.7	3.4 ± 0.6	7.8 ± 1.4	11.1 ± 1.9
03/06/03–12/01/03	270	5.0 ± 1.0	15.3 ± 0.8	20.3 ± 1.8	2.5 ± 0.4	12.2 ± 0.4	14.7 ± 0.6
		Throughfall (kg ha^{-1} yr^{-1})			Bulk deposition (kg ha^{-1} yr^{-1})		
		NO_3^--N	NH_4^+-N	Total N	NO_3^--N	NH_4^+-N	Total N
Water year 2003 (Oct 1, 2002–Sep 30, 2003)		2.2 ± 0.4	6.3 ± 0.7	8.5 ± 1.1	1.1 ± 0.1	3.8 ± 0.3	4.9 ± 0.4

Total N = NO_3^--N + NH_4^+-N.

Watershed N-Budget: Pools and Transformations

To estimate the N content and N uptake rate of *A. fasciculatum*, and N transferred in litterfall, we used values from a modeling study at our study site (Li and others 2006), and from measurements obtained in *A. fasciculatum*-dominated chaparral stands in Echo Valley near San Diego, California (Mooney and Rundel 1979).

We measured net N mineralization and nitrification using the intact soil core technique (DiStefano and Gholz 1986). In June 2002, two 50-m transects were established from which six sets of duplicate soil cores (10 cm depth, 4 cm diameter) were collected at six different locations along each transect. Gravimetric soil moisture (oven-drying at 104°C for 24 h) and initial (T_0) exchangeable NH_4^+ and NO_3^- concentrations were determined on one set of cores. To estimate net N mineralization and nitrification, the remaining cores were equipped with mixed bed ion-exchange resin (J.T. Baker, IONAC NM-60 H^+/OH^-) placed at the base of the core to capture N in leachate. The remaining cores were returned to their original holes for a 2- to 6-week incubation. Replicate sets of soil cores were harvested at roughly 3- to 4-week intervals between July 2002 and January 2004. All soil and resin extracts were filtered (2.5-µm porosity filters) and analyzed for NO_3^- and NH_4^+ as described for atmospheric inputs. Net N mineralization was calculated by subtracting total N at T_0 (exchangeable N) from total N at the end of the incubation (T_1) for each sampling date. Net nitrification was calculated by subtracting NO_3^- measured at T_0 from T_1. A bulk density of 1.2 g cm^{-3} (Huntington and Akeson 1987) and a depth of 10 cm were used to convert gravimetric to volumetric soil moisture, and to estimate soil N pools on an areal basis. Annual rates for net N mineralization and nitrification were estimated by linear interpolation of the measurements made between September 22, 2002 and October 6, 2003.

Nitrification potentials (an index of nitrifying population size) were determined on a second subsample of soils (n = 4) collected on two sampling dates in 2002 (July 15 and September 22) and 2003 (May 20 and November 5) using the chlorate-slurry method (Belser and Mays 1980).

The total C and N content of soils (upper 10 cm) were estimated from ten cores selected to represent the spatial heterogeneity of the catchment. We also sampled three pits at 15-cm vertical intervals to a depth of 100 cm. Finely ground soil subsamples were analyzed for %C and %N on a Thermo Flash EA 1112 analyzer.

Soil microbial biomass C and N (n = 8) were determined for each sampling date using a chloroform fumigation technique (Vance and others 1987). Soil extracts were analyzed for total C and N using a persulfate digestion technique (Doyle and others 2004), and biomass C and N calculated as the difference between fumigated and unfumigated C and N concentrations. A correction for extraction efficiency was applied to chloroform-labile C (K_{EC} = 0.4; Tessier and others 1998) and chloroform-labile N (K_{EN} = 0.54; Brookes and others 1985) to estimate microbial biomass.

Soil solution was sampled using six pressure/vacuum ceramic cup soil lysimeters (Soilmoisture Equipment Corp. Model 1920) installed at a 30 cm depth under *A. fasciculatum*. During sampling, lysimeters were first evacuated with a hand pump and allowed to fill for 1–3 h during major precipitation events. Samples were analyzed for NO_3^- and NH_4^+ as described for atmospheric samples.

Watershed N-Budget: Hydrologic and Gaseous Losses

During WY 2002–2004, a continuous record of stage was recorded with a vented pressure transducer and datalogger in an ''H'' flume installed at the Chamise Creek watershed outlet. Stream discharge was recorded at 15-min intervals and stream samples (NO_3^-, NH_4^+, DON, DOC) were collected at 30-min intervals during rainfall events using an ISCO automated sampler and manually. Chamise Creek was dry from May 2003 to December 2003. DOC samples were filtered through pre-baked (450°C) Whatman GFF filters, acidified (pH 2), and measured in a Shimadzu TOC-V CSH total organic carbon analyzer. All other stream samples were filtered (1.0 µm) and aliquots used for DIN (NO_3^- + NH_4^+) and DON analyses. DIN was measured as previously described. DON was measured as the difference between total dissolved N (TDN) and DIN, where TDN was measured as NO_3^- after persulfate oxidation (Valderrama 1981).

Hydrologic solute fluxes were computed as the integral of the product of discharge (Q) and concentration (C) between sampling intervals (dt)

$$L = \int_o^t Q \times C\mathrm{d}t, \tag{1}$$

where L is the total load in the time interval 0 to t. On days with no stream sampling, solute concentrations were estimated by linear interpolation of chemistry measurements made before and after the sampling gap (Cohn 1995). Uncertainty in hydrologic fluxes results from the combined errors in discharge measurements, analytical chemistry measurements, and error introduced by non-continuous measurements of stream chemistry. A 5% error was assigned to both discharge and analytical chemistry measurements. We used the ''jackknife'' approach (Sokal and Rohlf 1981) to estimate the error associated with interpolation of stream chemistry (that is, the sampling error). The total error (E_t) for annual solute fluxes was calculated as

$$E_t = (E_A^2 + E_B^2 + E_C^2)^{1/2}, \tag{2}$$

where E_A is the uncertainty in discharge, E_B the uncertainty in stream chemistry, and E_C the uncertainty introduced by the sampling error.

Specialized collectors (n = 3) were used to measure DIN concentrations in overland flow during large precipitation events between November 17, 2003 and March 26, 2004. These devices consisted of a trough (20 cm wide) laid flat against the ground surface underneath *A. fasciculatum* (10–20 m away from the stream), so that surface runoff was funneled into plastic bottles. Overland flow samples were analyzed for NO_3^- and NH_4^+.

Nitric oxide (NO) emissions were measured during WY 2010 in duplicate collars at four different locations representative of the spatial heterogeneity of the catchment (Homyak and Sickman 2014). N_2O emissions were measured using the static chamber technique (Homyak 2012). N_2 emissions were not measured at our site, but are presumed low, due to the low water content and coarse texture of soils that do not favor denitrification (Anderson and Levine 1987). Measurements of NO and N_2O were made at 4- to 6-week intervals, except during the dry-to-wet transition in which measurements were made every 1–3 weeks. The annual gaseous N-loss for the catchment was 0.13 ± 0.12 g N m^{-2} occurring mostly as NO. We also acknowledge DAYCENT simulations of annual NO + N_2O emissions at our catchment (0.4 g N m^{-2}), of which NO made up 98% of the combined flux (Li and others 2006). However, this model likely overestimates N emissions (Homyak and Sickman 2014) and was therefore not used for our N-budget calculations.

$\delta^{15}N$ and $\delta^{18}O$ of NO_3^-

To understand sources of NO_3^- in streamflow, we measured $\delta^{18}O$ and $\delta^{15}N$ of NO_3^- in: (i) bulk deposition and throughfall (atmospheric resin collectors), (ii) rainfall collected at Ash Mountain meteorological station, (iii) soil solution, (iv) overland flow, and (v) stream samples. Measurements for $\delta^{15}N$ and $\delta^{18}O$ were performed by the Facility for Isotope Ratio Mass Spectrometry (FIRMS) at the University of California, Riverside, using the bacterial denitrifier method (Sigman and others 2001). Fractionation effects on $\delta^{18}O$ and $\delta^{15}N$ were minimized by eluting the resins twice with 2 M KCl to ensure complete extraction of NO_3^- (Templer and Weathers 2011). *Pseudomonas aureofaciens* was used for the determination of $\delta^{18}O$ in all samples and for $\delta^{15}N$ determinations in soil and stream samples. *Pseudomonas chlororaphis* was used for the determination of $\delta^{15}N$ in atmospheric samples to avoid analytical artifacts introduced by excess ^{17}O. A two-component mixing model was used to estimate the average fraction of atmospheric NO_3^- in streamwater across all samples (f_{atm}). The two-component mixing model used the average $\delta^{18}O$–NO_3 of streamwater ($\delta^{18}O_{stream}$), soil solution ($\delta^{18}O_{soil}$), and throughfall ($\delta^{18}O_{throughfall}$) to calculate f_{atm}

$$f_{atm} = \frac{\delta^{18}O_{stream} - \delta^{18}O_{soil}}{\delta^{18}O_{throughfall} - \delta^{18}O_{soil}}. \quad (3)$$

Results

Atmospheric Deposition

One-year average throughfall N (NO_3^- + NH_4^+) deposition rates were 58% greater than bulk N deposition rates (Table 1). Our estimates likely underestimate atmospheric N deposition rates, due to unmeasured organic N inputs (Sleutel and others 2009), canopy retention and uptake (Lovett and Lindberg 1993), and uncertainties in measuring dry deposition (Fenn and others 2009). In California, dry N deposition represents a significant fraction of total atmospheric N inputs (up to 95%) (Bytnerowicz and Fenn 1996). At Lookout Point, a Clean Air Status and Trends Network (CASTNET) monitoring site located approximately 10 km south of Chamise Creek (36°25′45″N, 118°45′45″W; 1,225 m a.s.l.), dry N deposition contributed 58% of N inputs in 2002, 29% in 2003, and 64% in 2004 (CASTNET 2013). CASTNET does not measure throughfall or NH_3 (NPS 2001), an important contributor to N deposition at our site (Bytnerowicz and others 2002), and can underestimate rates of atmospheric N inputs.

Atmospheric N deposition varies in composition (NO_3^- vs. NH_4^+) relative to the influence of urban versus agricultural sources of N emissions (Grosjean and Bytnerowicz 1993; Bytnerowicz and others 2002; Cisneros and others 2010). At our site, NH_4^+ comprised 74% of throughfall and 78% of bulk N deposition (Table 1), suggesting that agricultural N emissions from the nearby San Joaquin Valley are an important N source to the western Sierra Nevada (Bytnerowicz and others 2002; Cisneros and others 2010). This high NH_4^+ contribution is consistent with measurements at Ash Mountain, in which the combined NH_3 and particulate NH_4^+ concentration during summer 1999 was about 4.5 μg m^{-3} and made up approximately 87% of nitrogenous compounds (particulate NH_4^+, particulate NO_3^-, HNO_2, HNO_3, and NH_3) (Bytnerowicz and others 2002).

Hydrologic Fluxes

Discharge and hydrologic N export was larger for WY 2003 (8,600 m^3; 0.7 ± 0.05 g N m^{-2}) than for WY 2004 (2,100 m^3; 0.1 ± 0.007 g N m^{-2}). During both years, streamwater DIN concentrations increased in response to the first discharge event of the dry-to-wet seasonal transition (November for WY 2003 and December for WY 2004), and NO_3^- was the dominant form of hydrologic N export (Figure 1). For WY 2003, 87% of the total hydrologic N-loss (DIN + DON) was exported during discharge events in November (dry-to-wet transition, Table 2). Similarly, for WY 2004, 70% of the total hydrologic N-loss was exported following the dry-to-wet transition, though the magnitude of the N-loss was substantially smaller (Table 2). Peak NO_3^- concentrations were 520 μM in WY 2003 and 442 μM in WY 2004. During these same rain events, stream NH_4^+ concentrations peaked at 5–7 μM (Figure 1). As the wet season progressed, the magnitude of the NO_3^- pulses in response to rainfall decreased (Figure 1) as did N export (Table 2). During consecutive rainfall events, when soils were consistently moist, NO_3^- concentrations pulsed only in response to the initial wetting of soil (Figure 2). By May 2003, NO_3^- pulses in response to rainfall did not rise above 32 μM and DIN concentrations remained low until the dry-to-wet seasonal transition of the following WY (Figure 1).

Concentrations of DOC and DON were generally higher at the onset of the dry-to-wet seasonal transition than during spring (Figures 2, 3). During early wet season rainfall, we observed pulses in DOC and DON concentrations in response to rising discharge (Figure 2), but similar to NO_3^-, this hydrochemical response diminished as the wet season progressed (Figure 3). In general, DON concentrations were positively correlated with DOC (Figure 3, inset). However, when DON concentrations were above 100 μM (following wet-up), proportional increases in DOC were not observed (Figure 3, gray oval). Overall, the molar ratio of DOC:DON ranged from 5.3 to 50.5 with an average (±SE) of 24.8 ± 0.69 (n = 135).

In soil lysimeters, pulses in NO_3^- were detected in response to wet-up in WY 2003 and 2004 (78–82 μM) and later in the wet season NH_4^+ became the dominant form of DIN (6–86 μM) (Figure 4). In overland flow, NH_4^+ was generally the dominant form of DIN, with concentrations reaching 1,100 μM during the first rainfall of WY 2004 (Figure 5).

Soil C and N Pools and Transformations

The average C content in the upper 10 cm of soil was 2% and for N was 0.14%. On average (±SE), the upper 10 cm of soil contained 163 ± 33 g N m^{-2}. Both C and N content gradually decreased with soil depth to a low of 0.06% C and <0.01% N at 90–100 cm.

The mean (±SE; n = 131) rate of net soil N mineralization measured from July 15, 2002 to January 28, 2004 was −0.04 ± 0.04 μg N g^{-1} d^{-1}

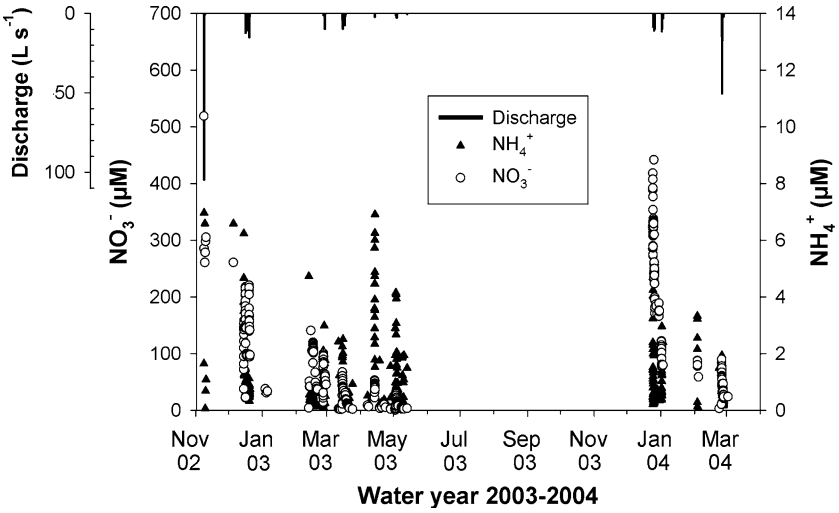

Figure 1. Streamwater NO_3^- and NH_4^+ concentrations and discharge during water years 2003–2004.

Table 2. Average Hydrologic N-Loss for Water Years 2003 and 2004

Major discharge events (dates)	Discharge (m^3)	DIN export (kg ha^{-1})	DON export (kg ha^{-1})	Total N export (kg ha^{-1})
Water year 2003				
Nov 8–Nov 19, 2002	5,685	5.5	0.6	6.1
Dec 5–Dec 20, 2002	772	0.3	0.1	0.4
Feb 12–Feb 28, 2003	216	0.04	0.03	0.07
Mar 11–Mar 24, 2003	692	0.08	0.08	0.16
Apr 7–May 2, 2003	833	0.1	0.1	0.2
May 3–May 13, 2003	157	0.01	0.02	0.03
	8,355	6.03	0.93	6.96
Water year 2004				
Dec 24–Jan 3, 2004	951	0.6	0.1	0.7
Feb 3–Feb 27, 2004	1,023	0.2	0.1	0.3
	1,974	0.8	0.2	1.0

NH_4^+ contributed to 2% of total DIN export in water year 2003 and 0.8% in 2004.
DIN = dissolved inorganic nitrogen (NO_3^- + NH_4^+); DON = dissolved organic nitrogen; Total N = DIN + DON. Catchment area = 4.3 ha.

and, with one exception, varied between −0.12 to 0.15 µg N g^{-1} d^{-1}. On November 9, 2002, strong net N immobilization was measured in response to wet-up of soils (−0.88 µg N g^{-1} d^{-1}) (Figure 6).

The significant net N immobilization event of November 9, 2002 strongly influenced annual net N mineralization estimates (−0.001 ± 2.0 g N m^{-2} y^{-1}). Because a similarly large N immobilization event was not observed in WY 2004, we also calculated an annual rate for net N mineralization that excluded this event (1.4 ± 1.3 g N m^{-2} y^{-1}), which may best represent the N mineralization rate for WY 2004.

The average (±SE; n = 131) rate of soil net nitrification was −0.02 ± 0.03 µg N g^{-1} d^{-1} (July 15, 2002 to January 28, 2004), and ranged from 0.13 to −0.09 µg N g^{-1} d^{-1}, except during the November 9, 2002 net N immobilization event (−0.59 µg N g^{-1} d^{-1}) (Figure 6). Changes in net mineralization were synchronous with changes in net nitrification and of similar magnitude (Figure 6). The N immobilization event of November 2002 strongly influenced the annual estimate for nitrification (0.4 ± 1.5 g N m^{-2} y^{-1}); excluding the November 9, 2002 measurement yielded a net nitrification rate of 1.4 ± 0.9 g N m^{-2} y^{-1}.

As soils dried during the summer of 2002, average (±SE) nitrification potentials increased from 7 ± 3 µg N g^{-1} d^{-1} in July to 19.5 µg N g^{-1} d^{-1} in September (data not graphed). In 2003, nitrification potentials were 0.3 ± 0.01 µg N g^{-1} d^{-1} when measured in May and 7.4 ± 1 µg N g^{-1} d^{-1} when measured in November.

Extractable soil NH_4^+ pools were generally greater than NO_3^-, except for a few occasions in which increases in soil moisture reversed this pat-

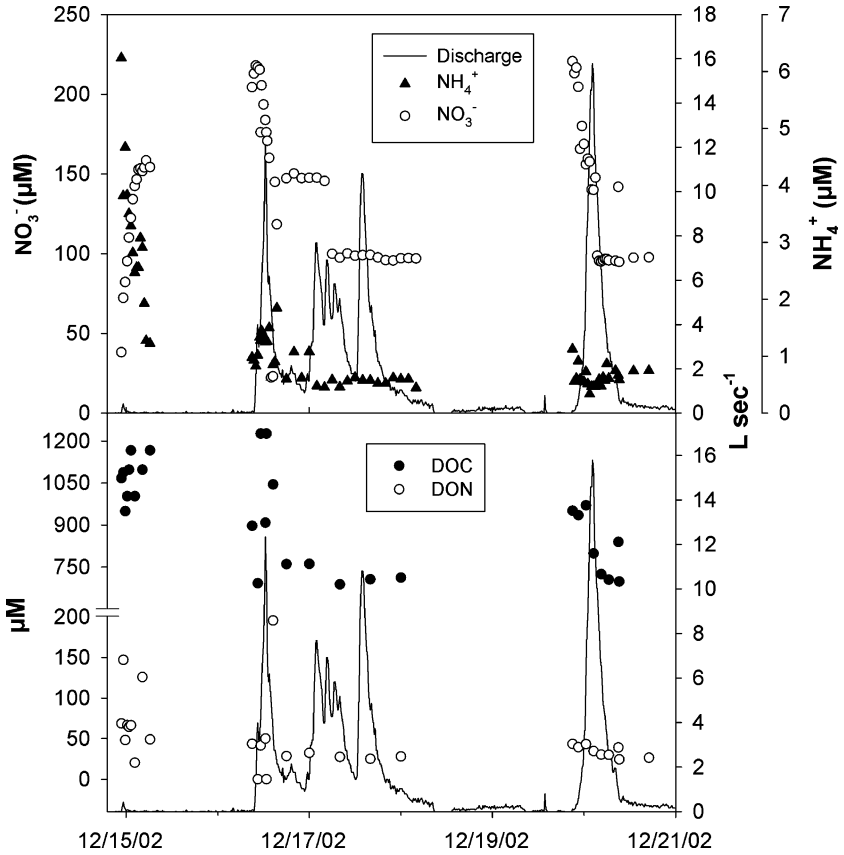

Figure 2. Streamwater NO_3^-, NH_4^+, DOC, DON concentrations, and discharge during an early wet season rainfall event recorded on December 15–21, 2002.

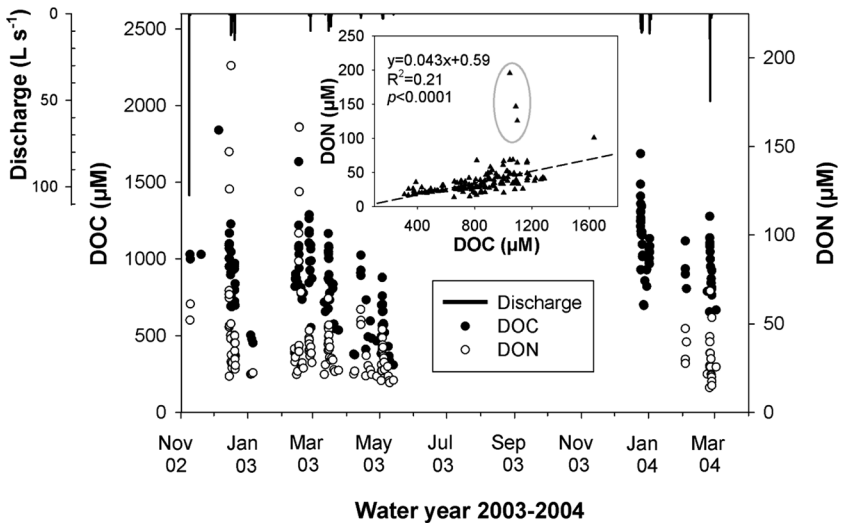

Figure 3. Streamwater DOC and DON concentrations and discharge during water years 2003–2004. *Inset* relationship of DON as a function of DOC for water years 2003–2004. The *gray oval* encloses samples collected during the dry–wet seasonal transition following soil rewetting.

tern (Figure 6). The highest NO_3^- and NH_4^+ concentrations occurred during the dry-to-wet seasonal transition in 2002, during which NH_4^+ concentrations declined with a concomitant increase in NO_3^-. These observations correspond to periods in which NO_3^- concentrations in streamwater (Figure 1) and the soil solution (Figure 4) were highest.

Microbial biomass C and N generally decreased in the 2002 dry season and varied during the 2003 wet season, during which both microbial biomass C and N had among the highest values recorded (Figure 6). At the onset of the 2003 dry season, as soil moisture declined, so did microbial biomass C and N. However, unlike the 2002 dry season, both microbial biomass C and N increased as soil mois-

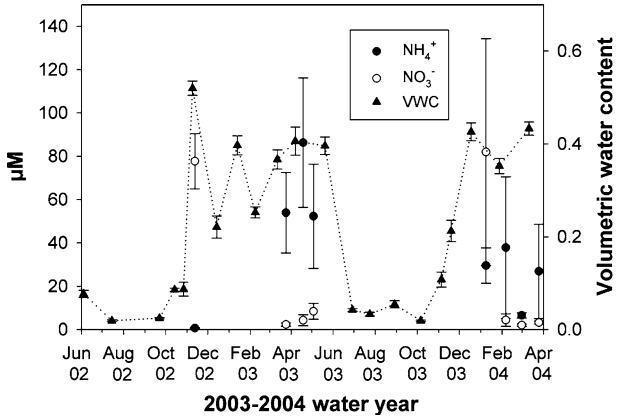

Figure 4. Average soil solution NO_3^- and NH_4^+ concentrations extracted from soil lysimeters (30 cm depth) during water years 2003–2004. Soil volumetric water content (VWC) was estimated from soil cores (10 cm depth). *Error bars* denote standard errors.

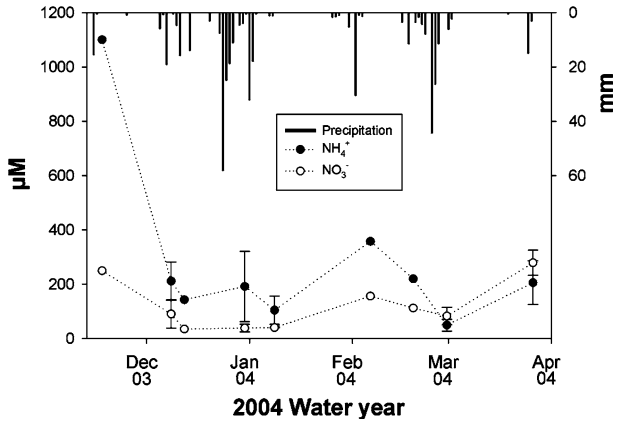

Figure 5. Average NO_3^- and NH_4^+ concentrations (±standard error) in overland flow collectors during the 2004 water year.

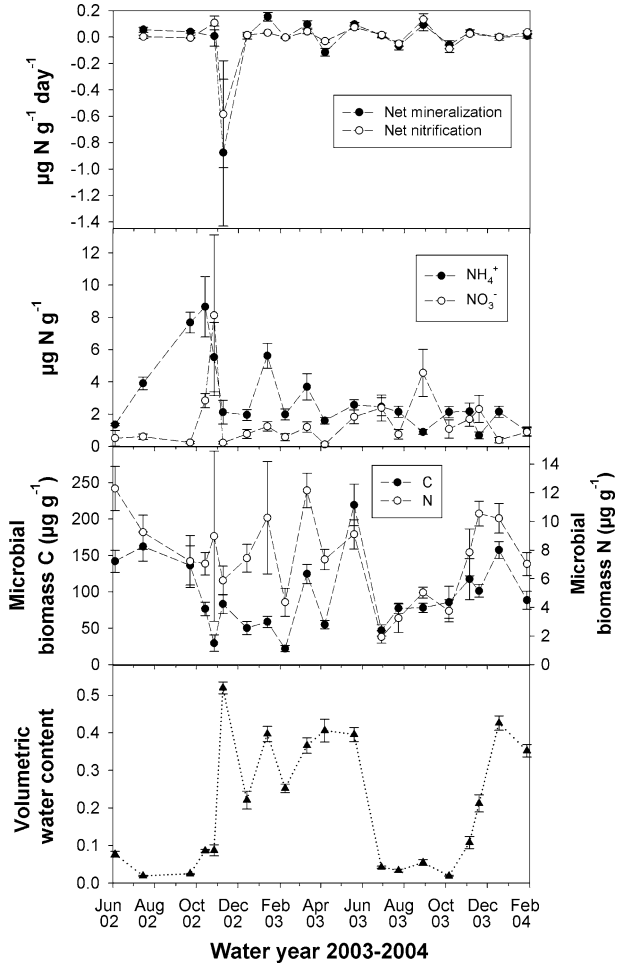

Figure 6. Average rates of soil net N mineralization (NO_3^- + NH_4^+) and nitrification (NO_3^-) for 3- to 4-week incubations, average soil NO_3^--N and NH_4^+-N concentrations, average microbial biomass C and N, and soil volumetric water content during water years 2002–2004. *Error bars* denote standard errors.

ture remained limited (Figure 6). Increases in both microbial biomass C and N continued well into the dry-to-wet transition of 2003 (December 18, 2003) after which both microbial biomass C and N declined following increases in moisture (Figure 6).

Isotope Tracing of NO_3^- in Streamflow

End member averages for $\delta^{15}N$–NO_3^- ranged from −2.69 to −6.87 ‰ (Table 3; Figure 7). Throughfall $\delta^{15}N$–NO_3^- was the most enriched in ^{15}N and water from the overland flow collectors was most depleted (Table 3). For $\delta^{18}O$–NO_3^-, the separation between potential sources of streamflow NO_3^- was large (Figure 7), with average values ranging from 1.31 ‰ for soil solution to 81.06 ‰ for throughfall (Table 3). The average $\delta^{18}O$–NO_3^- of overland flow was intermediate to both atmospheric and terrestrial sources (21.26 ‰). The $\delta^{18}O$–NO_3^- of streamflow was well constrained (typically between −10 to 10 ‰; Table 3), and remained relatively constant through WY 2003–2004 (Figure 8). However, during the first precipitation event in November 2002, a $\delta^{18}O$ value of 53 ‰ was recorded in streamflow NO_3^- indicating an atmospheric source (Figure 8). On average, only 0.9 ± 3% of the NO_3^- in streamwater was of direct atmospheric origin (equation 3).

Watershed N-Budget

Evaluation of atmospheric N inputs (this study), N fixation (Kummerow and others 1978), and hydrologic (this study) and gaseous (Homyak 2012) N losses, indicates that during a wet year (WY 2003), the watershed retains 0.03 ± 0.17 g N m^{-2} y^{-1} or 3% of N inputs (Figure 9). In contrast, during a dry year

Table 3. Average $\delta^{15}N$ and $\delta^{18}O$ (±Standard Error, SE) of NO_3^- in Precipitation, Atmospheric Bulk Deposition, Throughfall, Streamwater, Overland Flow, and Soil Solution During Water Years 2003–2004

Component	*n*	$\delta^{15}N$ (‰)		$\delta^{18}O$ (‰)	
		Average	SE	Average	SE
Ash Mt. rainfall	20	−2.75	±0.42	76.93	±1.71
Bulk deposition	47	−4.76	±0.50	60.92	±2.51
Throughfall	16	−2.69	±0.70	81.06	±1.70
Overland flow	11	−6.87	±1.50	21.26	±6.65
Soil solution	18	−3.92	±1.33	1.31	±1.27
Streamwater	66	−3.02	±0.41	2.06	±1.03

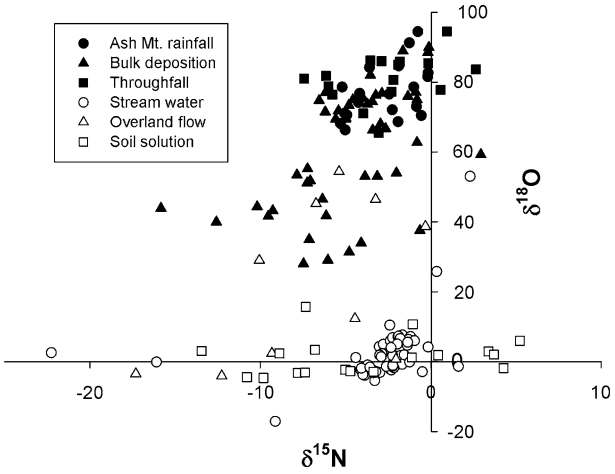

Figure 7. $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- from precipitation, atmospheric bulk deposition, throughfall, streamwater, surface runoff water, and soil solution during water years 2003–2004.

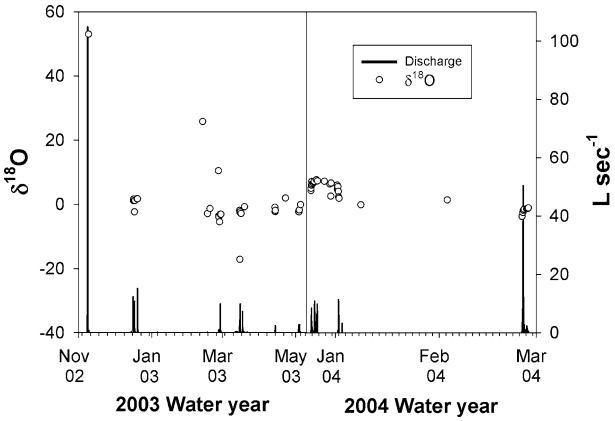

Figure 8. Streamwater $\delta^{18}O$–NO_3^- and discharge during the wet season of water year 2003 (*left panel*) and 2004 (*right panel*).

(WY 2004), the watershed retains 0.6 ± 0.16 g N m^{-2} y^{-1} (73% of N inputs). Our estimates of N-retention are consistent with the overall negative rate of N mineralization measured at our site, suggesting N sequestration in soils. However, we likely underestimate atmospheric N inputs, suggesting that N-retention could be higher.

Differences in hydrologic N export between wet and dry years highlight the importance of incorporating gaseous N emissions in N-budgets, as well as constraining uncertainty in these measurements. For example, DAYCENT modeling suggests gaseous N losses of up to 0.4 g N m^{-2} y^{-1} (Li and others 2006), whereas field measurements suggest 0.13 g N m^{-2} y^{-1} (Homyak 2012) (Figure 9). In the Chamise Creek watershed, large NO pulses (up to 500 ng NO-N m^{-2} s^{-1}) were observed when dry soils were wetted (Homyak and Sickman 2014). Besides these pulses, NO emissions were highest during summer, when soils were dry, and lowest during the wet growing season (<1 ng NO-N m^{-2} s^{-1}) (Homyak and Sickman 2014). Thus, during a dry year, some of the perceived N-retention can be exported via gaseous pathways (Homyak and Sickman 2014).

Discussion

Although seasonally induced changes in N cycling are common to a variety of ecosystems, including those in mesic sites, the mechanisms controlling episodic N losses during seasonal transitions are different. For example, in mesic systems such as temperate forests, N flushing episodes occur primarily during snowmelt, when soil N is mobilized during a period when plant N uptake is low (Lovett and others 2000; Burns and Kendall 2002; Burns and others 2009); soil microbes, however, can remain active and mineralize N under the snow (Schimel and others 2007). In contrast, in xeric landscapes the majority of N inputs occur during the dry season when hydrologically disconnected soils temporarily decouple catchment biogeochemical processes (Meixner and Fenn 2004) and favor the accumulation of atmospherically deposited N on soil and plant surfaces (Padgett and others

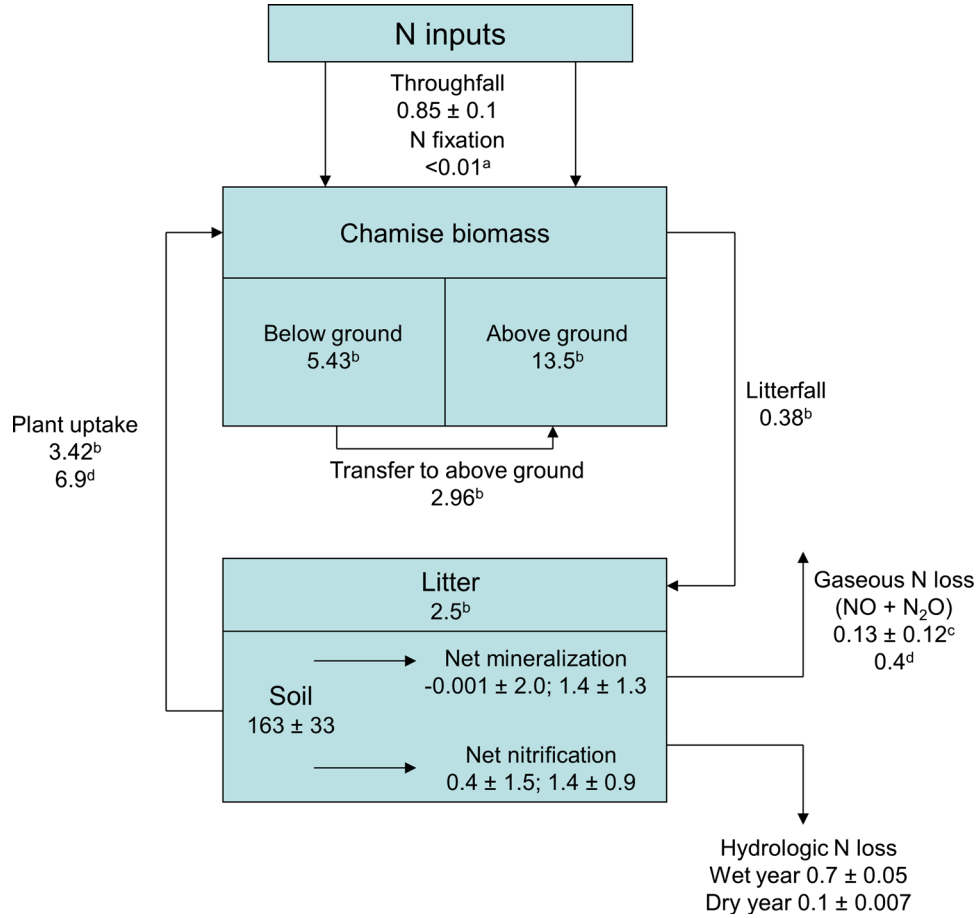

Figure 9. Watershed N-budget (average ± standard error; g N m^{-2}) for chaparral ecosystems as calculated from this study, from pools and fluxes measured by [a]Kummerow and others (1978), [b]Mooney and Rundel (1979), [c]Homyak and Sickman (2014) and Homyak (2012), and DAYCENT modeling by [d]Li and others (2006). *Boxes* represent pools (g N m^{-2}) and *arrows* represent fluxes (g N m^{-2} y^{-1}). Rates of N mineralization and nitrification were calculated using two different approaches (see ''Results'': Nitrogen pools and transformations in soils). Atmospheric N inputs represent water year 2003 (see Table 1) and hydrologic losses represent water year 2003 (wet year) and 2004 (dry year).

1999). Upon wetting, accumulated N can be rapidly exported through hydrologic and gaseous pathways, suggesting advanced N-saturation. Here, we used a chaparral catchment to evaluate the effectiveness of traditional N-saturation indicators in xeric ecosystems where atmospheric N inputs are temporarily decoupled from ecosystem processes.

Is the Hydrologic Flushing of Biologically Unprocessed Dry Deposition the Major Pathway for N-Loss in Xeric Catchments?

Because atmospheric NO_3^- has been shown to accumulate on land surfaces during the dry season and to contribute to stream NO_3^- export in N-polluted catchments of southern California (Michalski and others 2004), we had hypothesized the Chamise Creek watershed would show similar patterns. However, the low $\delta^{18}O$–NO_3^- values in most streamwater samples (mean 2.06 ‰; Figure 8) suggested that atmospheric NO_3^- made up less than 1% of annual NO_3^- losses, and was not the major pathway for N-loss. The single exception was the November 2002 storm where the $\delta^{18}O$–NO_3^- measurement suggested that about 50% of the NO_3^- was atmospheric in origin. Although biological processes controlled NO_3^- losses, these observations do not imply long-term N sequestration in microbial biomass or SOM (Lovett and Goodale 2011); short-term microbial cycling (rapid nitrification) could have generated the $\delta^{18}O$–NO_3^- signal.

Our mass balance and $\delta^{18}O$–NO_3^- data suggest that much of the NO_3^- carried in streamflow was atmospheric NH_4^+ that underwent nitrification either in soils or surface water—a processes consis-

tent with other chaparral (Fenn and others 1993; Vourlitis and others 2007b) and mesic catchments (Curtis and others 2011). Although low moisture limits microbial processes (Stark and Firestone 1995), soil microbes can be adapted to drought-induced stress (Schimel and others 2007), so that NH_4^+ accumulated during the dry season can diffuse to surviving nitrifiers once soil hydrologic connectivity is re-established (Parker and Schimel 2011). We hypothesize that atmospheric NH_4^+ moved along shallow surface flowpaths (Swarowsky and others 2012) where rapid nitrification occurred (Vourlitis and Zorba 2007). It is also possible that atmospheric NH_4^+ that escaped nitrification in soils was nitrified in the riparian stream-zone; in-stream nitrification has been shown to occur within short distances (10–100 m; Curtis and others 2011).

At Chamise Creek, DON losses accounted for 13% of the N export in WY 2003 and 29% in WY 2004. In catchments with low N deposition, hydrologic N losses occur primarily as DON (Hedin and others 1995; Perakis and Hedin 2002), and may serve as an indicator of N-saturation status (Goodale and others 2000). Because the slow turnover of SOM controls DON leaching (Perakis and Hedin 2002), DON concentrations in unpolluted catchments are expected to be in strict stoichiometric proportion with DOC (Passive Carbon Vehicle Hypothesis; Brookshire and others 2007). At Chamise Creek, DON concentrations were generally proportional to DOC (Figure 3), suggestive of a nutrient-limited system. However, exceptions to the strict stoichiometry between DON and DOC occurred at wet-up (Figure 3, gray oval), suggesting N-saturation as well as highlighting inconsistencies when using indicators of N-saturation in xeric landscapes.

As an alternative to the Passive C Vehicle Hypothesis, the ''stoichiometric enrichment hypothesis'' proposes that in N-polluted systems, the ratio of DOC:DON decreases through two potential mechanisms: (i) enrichment of the SOM pool with N or (ii) direct enrichment with N of the dissolved organic matter (DOM) pool (Brookshire and others 2007). We hypothesize that SOM enrichment with N was unlikely; N-rich SOM should have yielded consistently N-enriched DOM beyond the three samples collected after wet-up, but it did not (Figure 3, gray oval). In contrast, direct DOM enrichment with N could have occurred through several pathways. First, in N-polluted catchments, atmospheric inputs of organic matter can account for 20–30% of N deposition, and this material generally has a low C:N ratio (~2.5; Sleutel and others 2009), potentially enriching the DOM pool with N. Second, N additions could have enhanced the production and leaching of hydrophilic compounds of low molecular weight (amino acids and amino sugars), increasing the N content of DOM (McDowell and others 2004). Last, decreases in soil hydrologic connectivity can promote NH_4^+ accumulation (Figure 6; Parker and Schimel 2011), as well as nitrite (NO_2^-) buildup in soils (Gelfand and Yakir 2008). At wet-up, NO_2^- could have been incorporated into DOM, thereby lowering the DOC:DON ratio (Thorn and Mikita 2000; Fang and others 2009; Isobe and others 2012). At our site, we observed accumulation of NH_4^+ during the 2002 dry season (Figure 6), suggesting that NO_2^- could have accumulated as well. Together, our observations suggest that the evaluation of N-saturation in xeric landscapes is complicated by dry season processes (accumulation of N) that can produce temporary N export patterns indicative of saturation.

How is N-Limitation Maintained and What Mechanisms Control N-Retention in Chaparral?

The episodic pulses of N availability in chaparral ecosystems are controlled by strong shifts in soil moisture (Fenn and others 1996; Miller and others 2005; Parker and Schimel 2011), in which elevated stream NO_3^- losses (Riggan and others 1985; Fenn and Poth 1999; Meixner and Fenn 2004) and enhanced gaseous N emissions (Gelfand and others 2009; McCalley and Sparks 2009; Harms and Grimm 2012; Homyak and Sickman 2014) occur following the first rainfall event of the dry-to-wet seasonal transition (autumn). Our field measurements suggest that the dry-to-wet transition is a critical period characterized by substantial N losses that contribute to the maintenance of N-limitation in xeric ecosystems (Vitousek and Field 2001; Vourlitis and others 2009).

Although we observed elevated N-loss during the dry-to-wet transition, these patterns were not observed during the wet growing season. We attribute the observed reduction in N export to two mechanisms: (1) substrate limitation of nitrifiers as the atmospherically deposited (mainly NH_4^+ in this study) or mineralizable soil N pool was nitrified and exported from the catchment and/or (2) N uptake by plants (estimated to be 3–7 g N m^{-2} y^{-1}; Figure 9) and immobilization within stable soil organic matter pools and microbial biomass. Because the concentration of NO_3^- in streamwater steadily declined during the growing season (Figure 1), it is

possible that both substrate limitation and N immobilization occurred. Indeed, net N immobilization was observed, presumably as microbes degraded C from previously protected SOM (Navarro-Garcia and others 2012) or C-rich litter (Miller and others 2005), but it was temporary. A reduction in N export due to substrate limitation is consistent with the observed decrease of NH_4^+ in runoff (Figure 5) and with the sharp decline in soil NH_4^+ during WY 02 after wet-up (Figure 6). However, because we observed net N mineralization during spring, neither net N immobilization in soil nor substrate limitation can fully explain the reduction in N export as the wet season progressed.

Long-term soil N-storage requires a stable soil organic matter pool (Curtis and others 2011), but in xeric landscapes soils can be relatively C-poor (Garcia and others 1994; Miller and others 2005). Elevated N losses are typical of C-limited ecosystems, in which stream DOC:NO_3^- molar ratios between 2.2 and 2.5 mark a threshold at which NO_3^- leaching is observed (Taylor and Townsend 2010). During the dry-to-wet seasonal transition at Chamise Creek, DOC:NO_3^- ratios were as low as 2.7, consistent with a period of elevated NO_3^- export. During the spring, however, when DOC:NO_3^- ratios were as high as 970, negligible N losses occurred, suggesting that N export may be controlled by C availability.

Nitrogen-storage in chaparral may also be controlled by the timing of N inputs and interactions with plant N uptake and water availability (Huxman and others 2004; Vourlitis 2012). For example, in arid and semiarid regions, N is supplied to plants mostly as pulses following precipitation events, where plant growth rates control N uptake (James and Richards 2005, 2006). In a 4-year fertilization study of chaparral (50 kg N ha^{-1} y^{-1}), in which N was applied yearly in October (end of dry season), N additions failed to stimulate ecosystem N-storage in soils and plant biomass, while the majority of the added N was lost via hydrologic and presumably gaseous pathways (Vourlitis and others 2007a, 2009). In comparison, when a 50 kg N ha^{-1} y^{-1} fertilizer application extended into the growing season at a mixed conifer/California scrub oak site in the San Bernardino Mountains, California (background atmospheric N deposition $\approx$ 35 kg N ha^{-1} y^{-1}), N was retained in plant biomass (Grulke and others 2005). In chaparral ecosystems, plant N demand peaks in the spring (March–April) (Mooney and Rundel 1979), likely explaining why, in the absence of plant N uptake, we observed substantial hydrologic N losses following wet-up (Table 2). In these seasonally dry ecosystems, N losses are strongly influenced by the asynchrony between N availability and plant demand (Meixner and Fenn 2004; Ochoa-Hueso and others 2011), whereby N-limitation may prevail in ecosystems exposed to elevated rates of atmospheric N deposition (Vourlitis and others 2009).

The role of plant N uptake in regulating N losses from chaparral may be analogous to N export in mesic sites following disturbance, where N uptake and N mineralization are decoupled (Burns and Murdoch 2005). For example, in northern hardwoods, forest harvesting can temporarily elevate exchangeable soil N pools (Homyak and others 2008) and increase stream NO_3^- concentrations to above 1,400 μM (Likens and others 1970; Burns and Murdoch 2005). In seasonally dry systems, the onset of the wet season may function as a temporary ''disturbance;'' senesced plants are unable to take up N deposited during the dry season as soils wet-up. At our site, we did not observe abrupt increases in rates of net N mineralization and nitrification following wet-up, suggesting that the asynchrony between N availability and plant N demand influenced hydrologic (Meixner and Fenn 2004) and gaseous N losses (Homyak and Sickman 2014).

Fire may also represent an important pathway for N-loss in chaparral (Meixner and others 2006). A stand-replacing fire (40- to 60-year return interval) can remove 14 g N m^{-2} through volatilization and leaching (DeBano and others 1979). However, based on our rates of atmospheric N deposition, it may take only 16–28 years to replace the N lost to fire, suggesting that over the long term, fire alone cannot maintain N-limitation in chaparral. Our budget also shows that although 14 g N m^{-2} is an appreciable amount of N, this loss is much smaller than the N pool in the upper 10 cm of soil (180 g N m^{-2}). Thus, although fire may help maintain N-limitation in chaparral, it is not surprising that it does not reverse symptoms of N-saturation (Meixner and others 2006)—soil N pools remain relatively intact, supporting mechanisms of hydrologic and gaseous N-loss. Other studies have also shown relatively small N losses due to fire when compared to ecosystem N stocks (Wan and others 2001). Therefore, although N losses due to fire can be significant over short-time scales, increases in the frequency of fire would be required to significantly impact ecosystem N-storage over longer time periods.

Supporting Evidence for N-Loss Mechanisms in Chaparral Soils

In the Chamise Creek watershed, soil N dynamics were consistent with rapid nitrification of atmo-

spheric NH_4^+ and with observations in stream chemistry (this study) and gaseous N emissions (Homyak and Sickman 2014). At the onset of the wet season, we observed net nitrification following wet-up, consistent with the isotopic analysis of streamwater NO_3^-, as well as with the significant export of NO_3^- and NO measured at the site (byproducts of nitrification; Figure 1; Homyak and Sickman 2014).

We observed greater nitrification potentials in dry soils than in moist soils, suggesting that nitrifier populations were adapted to drought-induced stress. This observation is consistent with increases in NO emissions as soils dried (Homyak and Sickman 2014), relatively stable or increasing microbial biomass C pools during dry season periods, and with the rapid nitrification of NH_4^+ during wet-up, suggesting that hydrologically disconnected sites could have maintained active nitrifier populations during summer (Parker and Schimel 2011). Except for a pronounced net N immobilization period observed in November 2002, rates of N mineralization and nitrification were relatively constant and support our supposition that the significant N-loss following wet-up was not entirely due to faster rates of N cycling when compared to pre-wet-up conditions, but to inactive or weaker N sinks (for example, C-limitation and reduced plant N uptake).

Application of Indicators of N-Saturation and N-Budgets to Xeric Landscapes

Recent studies have shown that the hypotheses developed by Aber and others (1998) are in need of revision (Lovett and Goodale 2011). For example, it has been argued that hypotheses developed for N-polluted sites have limitations when applied to ecosystems that are naturally N-rich (Perakis and Sinkhorn 2011); that is, systems where net N mineralization should decline when N availability is above soil and plant demand, but it does not. In other ecosystems, elevated N inputs do not always result in increased rates of N mineralization and nitrification or higher foliar N content (Lovett and Goodale 2011), and in xeric systems, significant N losses occur in catchments where the vegetation remains N-limited (Vourlitis and others 2009). In an attempt to describe N-saturation in xeric ecosystems, the original conceptual model (Aber and others 1989) was modified to better reflect N losses prior to a peak in net primary productivity in spring, as observed in N-polluted catchments downwind from Los Angeles (see Figure 1 in Fenn and others 1998). However, our study underscores the need for additional refinement: specifically, the use of indicators of saturation and annual N-budgets for assessing the N-status of xeric landscapes.

We propose that the use of indicators of N-saturation may result in conflicting assessments of the stage of N-saturation of chaparral watersheds. For example, if streamwater NO_3^- concentrations are used as the sole criterion, then samples collected during the dry-to-wet transition at Chamise Creek would suggest stage 2 or 3, whereas stream samples collected in the spring would suggest stage 1. Similarly, the use of DOC:DON and DON:NO_3^- ratios or temporal patterns of gaseous N emissions would yield different assessment of N-saturation. Although the N-saturation hypothesis of Stoddard (1994) differentiates between N export during the growing and non-growing seasons, it predicts small N losses during the non-growing season for stages 0 and 1 (for example, unlike the 400–500 μM stream NO_3^- concentrations and high N flux (Table 2) observed in Chamise Creek.

As an alternative to using indicators of N-saturation, N-budgets have been shown to be useful (Fenn and others 2008), particularly when estimating N-retention in N-fertilizer addition studies (Vourlitis and Fernandez 2012). However, we raise two concerns regarding the ability of N-budgets, based on an annual timescale, to signal when Mediterranean-type ecosystems reach N-saturation (that is, saturation of all sinks). First, we show that significant N-retention can occur during a dry year, while nearly balanced N-budgets can occur during a wet year (Figure 9), suggesting the need for multi-year N-budgets. More importantly, annual N-budgets may fail to describe the *total* capacity of Mediterranean-type ecosystems to sequester N. Because up to 95% of N inputs can occur during the dry season (Bytnerowicz and Fenn 1996; Padgett and others 1999), and substantial N losses occur during the dry-to-wet transition before ecosystem N sinks are active (Table 2; Riggan and others 1985; Meixner and Fenn 2004; Bernal and others 2005; Homyak and Sickman 2014), N outputs may frequently balance inputs. Whether a chaparral watershed receives N inputs of only 5 to over 50 kg N ha^{-1} y^{-1}, the majority of this N is nitrified and exported upon wet-up (Vourlitis and others 2009). Thus, annual N-budgets would incorrectly suggest that an ecosystem has exceeded its capacity to assimilate N. Although N-budgets can indicate how much N was retained by an ecosystem on an annual basis, they may not describe the *total* capacity of an ecosystem to sequester N—this assessment must use N-budgets on a seasonal timescale, along with experimental N additions during the wet season, when N sinks are active.

How Can We Best Assess N-Saturation in Xeric Environments?

In an effort to refine the concept of N-saturation, Lovett and Goodale (2011) introduced the concept of ''kinetic'' and ''capacity'' N-saturation. Kinetic N-saturation occurs when the N input rate temporarily exceeds the soil and vegetation consumption rates (temporary N-saturation), and capacity N-saturation, when the system can no longer assimilate N irrespective of the N input rate (Lovett and Goodale 2011). The model proposes that, rather than expecting a stepwise sequence of N-saturation moving from vegetation to litter to soil, to eventually elevated N losses, N-saturation should be envisioned as a simultaneous flow of N to all four possible fates: vegetation, detritus and SOM, leaching, or gaseous loss (Lovett and Goodale 2011). The application of this new model explains why annual N-budgets may not fully describe capacity N-saturation; annual N-budgets are sensitive to substantial N losses observed during kinetic N-saturation (dry-to-wet transition). The model is also useful for understanding how elevated NO_3^- losses can occur even when the vegetation remains N-limited. We propose the incorporation of C-limitation and asynchrony between N availability and plant N demand as additional controlling factors determining the flow of N to leaching and gaseous N-loss fates (see Figure 6 in Lovett and Goodale 2011).

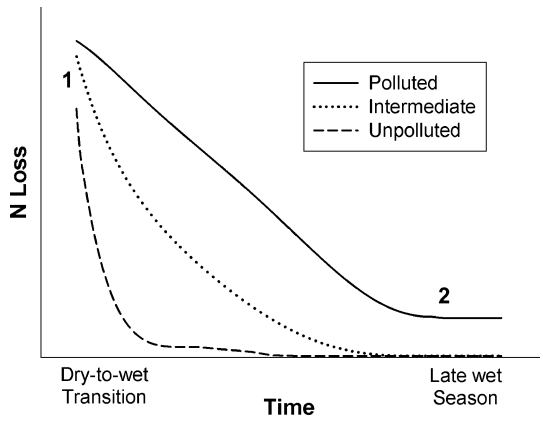

Figure 10. Conceptual model for N-loss in xeric catchments. Elevated N losses during the dry-to-wet transition are intrinsic to xeric catchments regardless of the degree of N inputs. N-saturation may be best assessed by how rapidly ecosystems shift from N-loss to N-retention as they transition into the wet growing season. Kinetic N-saturation is represented by the elevated N-loss during the dry-to-wet transition. For the N-polluted catchment, capacity N-saturation is represented by the sustained N-loss during the late wet season (plant growing season).

The revised model suggests future work in xeric ecosystems should focus on kinetic rather than on capacity N-saturation; capacity N-saturation may be delayed in ecosystems, like chaparral, that naturally leak N by way of pulses following wet-up. Because wetting a dry soil increases N availability (Miller and others 2005; Xiang and others 2008; Parker and Schimel 2011; Navarro-Garcia and others 2012) and plants are not actively consuming N during the dry non-growing season (Mooney and Rundel 1979; James and Richards 2005), it must be recognized that elevated hydrologic and gaseous N losses are intrinsic properties of xeric ecosystems following wet-up (Meixner and Fenn 2004; Bernal and others 2005; Vourlitis and others 2009; Homyak and Sickman 2014). For example, in a relatively N unpolluted Mediterranean deciduous woodland in northeastern Spain (bulk N deposition ≈ 4 kg N ha^{-1} y^{-1}), stream NO_3^- concentrations reached approximately 250 μM during the dry-to-wet transition (Bernal and others 2005), suggesting that N export patterns from Chamise Creek ($\sim$8.5 kg N ha^{-1} y^{-1}) and this unpolluted catchment may be of similar magnitude during the dry-to-wet transition. Thus, we propose that the key distinction between N-affected and unaffected catchments is the rate at which the ecosystem transitions toward N-retention.

We hypothesize that unpolluted catchments should shift toward strong N-retention at a faster rate than N-polluted catchments (Figure 10). In our model, kinetic N-saturation is represented by elevated N losses intrinsic to both N-polluted and unpolluted catchments during the dry-to-wet transition (point 1, Figure 10), whereas capacity N-saturation is represented for N-polluted catchments by sustained N-loss during the late wet season (point 2, Figure 10). We propose that (i) reduced N losses as the wet season progresses represent the period when N-retention mechanisms become active (for example, release of C-limitation and plant N uptake), and that (ii) the transition from N-loss toward N-retention is a better indicator of N-saturation; differences between N-polluted and unpolluted landscapes may be magnified during this transition (area between points 1 and 2, Figure 10). For example, evaluating N-saturation indicators during the late wet growing season (point 2, Figure 10) may not differentiate between unpolluted and intermediately polluted catchments.

Although we lack the measurements to test this conceptual hypothesis for assessing N-saturation in xeric ecosystems, we speculate that Chamise Creek may be representative of an intermediately N-polluted catchment. At Chamise Creek, NO_3^- con-

centrations during the late wet season ranged from 0.7 to 42 μM, and fell in between concentrations for N-polluted (35–581 μM) and unpolluted chaparral streams (0.14–14 μM) (Riggan and others 1985), suggesting an intermediate stage of N pollution (Figure 10). However, we argue that information on how rapidly these catchments transitioned from N-loss to N-retention could have further distinguished degrees of N pollution, especially considering that NO_3^- concentrations for Chamise Creek overlapped with both N-polluted and unpolluted catchments.

Our study is based on a small headwater catchment where hydrology is strongly influenced by surface runoff. Because watershed N-retention is also controlled by catchment characteristics (for example, slope and watershed area) (Creed and Band 1998a, b; Meixner and Fenn 2004), we acknowledge limitations to our conceptual model. In particular, our measurements presumably ignore in-stream and riparian processes that affect N-retention in larger catchments (Meixner and Fenn 2004), and do not account for situations in which groundwater inputs may be important. We also acknowledge uncertainty in our N-budget, where we likely underestimate atmospheric N inputs and where uncertainty in our measurements limits understanding of whether N-retention occurred at our site. For instance, it is unclear whether the average negative N mineralization rates are indicative of long-term soil N-storage. However, our findings highlight the importance of terrestrial processes in controlling N losses from arid and semiarid regions (Meixner and Fenn 2004; Bernal and others 2005; Vourlitis 2012), validate studies suggesting a limited capacity for these ecosystems to sequester N (Austin and Vitousek 1998), and can frame a better understanding of dryland ecosystem response to increasing rates of atmospheric N deposition.

N-Saturation and Ecosystem Decline in Xeric Environments

Under elevated rates of N deposition, C-limitation, asynchrony between N availability and plant demand, and fire may delay the onset of capacity N-saturation in chaparral. However, we stress that xeric landscapes are not insensitive to chronic N inputs. Although direct effects on the vigor of chaparral stands have not been reported, elevated N inputs have led to elevated NO_3^- concentrations in streams (Meixner and Fenn 2004), soil N-enrichment with concomitant increases in soil N mineralization and nitrification (Vourlitis 2012), soil acidification (Wood and others 2007), leaching of base cations from soils (Fenn and Poth 1999), and loss in the productivity and species richness of arbuscular mycorrhizal fungi (Egerton-Warburton and others 2001; Ochoa-Hueso and others 2011). Importantly, as N deposition rises, additional stressors can push xeric landscapes toward ecosystem decline (Allen and others 2009). In N-impacted regions of southern California, chronic N fertilization has favored the invasion of exotic grasses, which through increases in fine fuel biomass, have altered the frequency and intensity of fires, leading to large-scale vegetation type conversions and loss of native plant species (Allen and others 1998, 2011; Rao and others 2010). Under these conditions, coastal sage scrub and desert shrub communities have been replaced by exotic grasslands (Minnich and Dezzani 1998; Talluto and Suding 2008; Rao and others 2010), and may serve as an example of how chronic N fertilization may affect chaparral ecosystems that may have not yet reached capacity N-saturation. Thus, development of critical loads for xeric ecosystems should consider the kinetic N-saturation of these landscapes, as efforts based on capacity N-saturation may do little to mitigate the adverse effects of elevated rates of atmospheric N deposition.

Summary and Conclusions

Atmospheric N inputs to chaparral ecosystems of southern California can be quickly exported through hydrologic and gaseous pathways. Coupled with C-limitation of N-storage and asynchrony between N availability and plant demand, we hypothesize that chaparral vegetation can remain N-limited despite elevated rates of N deposition. Our observations suggest that the transition from dry-to-wet soil conditions significantly affects microbial N-processing and regulates N-loss, contributing to the maintenance of N-limitation in chaparral. Given the ''leaky'' nature of chaparral catchments with respect to N (Austin and Vitousek 1998), we highlight issues that may influence interpretations of N-saturation using traditional saturation indicators and annual N-budgets. We conclude that the Chamise Creek watershed is temporarily N-saturated (kinetic N-saturation), but that the N-assimilation capacity of chaparral and other xeric ecosystem is difficult to determine because these ecosystems intrinsically leak N (Austin and Vitousek 1998). Thus, N-saturation in xeric landscapes may be more accurately assessed by how rapidly ecosystems transition from N-loss to N-retention.

ACKNOWLEDGMENTS

We thank the National Park Service and Annie Esperanza for facilitating access to the study sites and for other logistical support. We are indebted to Kevin Skeen, Delores Lucero, Jennifer Quach, and Amanda James for help in the field and laboratory and thank Gary Lovett and three anonymous reviewers for their insightful comments. This research was funded by the National Science Foundation (DEB-0089839, DEB-0614207, and DBI-1202894 post-doctoral research award) and fellowship support from a Graduate Mentorship award at UCR.

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