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Influence of soil moisture on the seasonality of nitric oxide emissions from chaparral soils, Sierra Nevada, California, USA

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ABSTRACT

Soil nitric oxide (NO) emissions are variable in both space and time, and are important pathways for N loss in seasonally dry ecosystems that undergo abrupt transitions from dry-to-wet soil conditions. We measured soil NO emissions from a chaparral catchment to characterize seasonal variability of, and triggers for enhanced NO losses. Pulses in NO emissions were observed in the summer and autumn when dry soils (soil water content (θ) < 6%) were wetted naturally and artificially (range: 97–513 ng NO–N m^{-2} s^{-1}). The rapidity and magnitude of these pulses suggest that abiotic processes may influence NO emissions. Outside of the observed pulses, NO emissions were highest during the dry season (θ < 6%; dry season mean = 3.4 ng NO–N m^{-2} s^{-1}) and lowest during the winter wet season (θ > 20%; wet season mean = 0.14 ng NO–N m^{-2} s^{-1}). These observed seasonal patterns contrast with previous DAYCENT simulations of NO emissions in our catchment, which predicted higher NO emissions during the wet season. Our field observations are consistent with sustained rates of nitrification, reduced plant N uptake, and high soil gas diffusivity observed during the dry season in arid environments.

1. Introduction

Soils are an important source of nitric oxide (NO) (Oswald et al., 2013; Su et al., 2011), a key compound in atmospheric photochemistry. In the troposphere, NO favors the production of ozone, and promotes reactions with hydroxyl radical and volatile organic compounds to produce HNO_3 and organic nitrates (Crutzen, 1979). Of the global NO production, dryland ecosystems account for approximately 25% of emissions (Davidson and Kingerlee, 1997), and may increasingly become hotspots for NO production both because of elevated rates of atmospheric N deposition in these areas (Fenn et al., 2003a; Sanz et al., 2002), and because the mechanisms that produce NO should be well suited to convert that extra N into NO (Firestone and Davidson, 1989).

In California, dryland ecosystems, such as chaparral, receive some of the highest rates of atmospheric N deposition in the U.S., averaging 30 kg N ha^{-1} yr^{-1} in the Los Angeles basin and as high as 70 kg N ha^{-1} yr^{-1} in downwind areas of the San Bernardino Mountains (Fenn et al., 2003a). Even in the more remote foothills of the western Sierra Nevada, large tracts of chaparral are exposed to N deposition rates that can exceed 10 kg N ha^{-1} yr^{-1} (Fenn et al., 2003b). In these seasonally dry ecosystems, atmospherically deposited N can accumulate in soils and plant surfaces (Padgett et al., 1999), and may quickly become bioavailable during rainfall events, potentially favoring processes that produce NO (Erickson et al., 2002; Fenn et al., 1996). For chaparral, however, it is unclear how increasing rates of atmospheric N deposition may influence N emissions (Vourlitis et al., 2009), limiting understanding of important feedbacks between the biosphere and the atmosphere.

In chaparral, seasonal changes in soil temperature and moisture likely regulate the production and consumption of NO and its rate of emission to the atmosphere. Soil moisture influences microbial activity and gas diffusivity, and therefore affects microbial processes (nitrification and denitrification) that produce and consume NO (Schindlbacher et al., 2004), while soil temperature can control the rate of chemical and biological reactions in soils (Firestone and Davidson, 1989; Saad and Conrad, 1993). The wet season generates favorable conditions for soil N cycling but these conditions may not optimize NO emissions: plant demand for N increases and may limit N supply to nitrifiers (Parker and Schimel, 2011), and high moisture content may constrict gas diffusivity—NO is rapidly cycled in wet soils (Schindlbacher et al., 2004). Thus, in seasonally dry ecosystems like chaparral, it is unclear how the balance between biological processes and edaphic factors control NO emissions from soils.

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To understand this balance, the "hole-in-the-pipe" conceptual model developed by Firestone and Davidson (1989), may offer a model to understand how drylands might particularly favor NO emissions, and to explore how these emissions may vary in response to changes in processes that produce NO. Nitrogen-gas fluxes are controlled both by the overall rate of N-cycling (the pipe), and by the processes that regulate how much N is released in the side reactions that produce NO (the holes). In dryland ecosystems, long periods of summer drought are followed by abrupt wetting of soils, producing large pulses of NO (Davidson et al., 1993; Hall et al., 2008; McCalley and Sparks, 2009), through both biotic and abiotic pathways (Allison, 1963; Davidson, 1992; Harms and Grimm, 2012; Su et al., 2011; Venterea et al., 2005). Thus, during the seasonal transition period when dry soils are first wetted (wet-up), both the size of the conceptual pipe (rates of nitrification and denitrification) and the holes in the pipe (NO-producing reactions and gas permeability of soil) should be large. As the wet season progresses, moist soils should favor biological processes that produce NO (Stark and Firestone, 1995), and thus the size of the pipe should be largest. However, during the wet season (plant growing season), it is unclear how plant N uptake and edaphic factors affect the magnitude of NO fluxes: does an overall high rate of N-cycling outweigh intense biotic demand for N and poor diffusion for N-gases? Assessing the influence of plant N uptake and diffusion limitation on NO emissions requires understanding the seasonal patterns of NO flux.

For chaparral, our understanding of NO seasonal flux patterns stem from a single DAYCENT simulation study that assumes "pipe" control (Li et al., 2006). In the simulation, NO emissions are regulated by nitrification rates driven by soil moisture, and the model predicts greatest fluxes during the wet season. Other than this model, NO emissions have only been measured during two months of the year in chaparral: four times in July and one time in December (Anderson and Poth, 1989; Anderson et al., 1988), which not only preclude understanding of seasonal emission patterns, but also do not allow for validation of the DAYCENT model simulations.

Here, we sought to improve understanding of seasonal emission patterns of NO from drylands by focusing on chaparral. We designed our study to address two fundamental questions: 1) how do soil NO emission rates vary seasonally and 2) how are these emissions influenced by wetting events?

To answer these questions, we measured NO emissions in a chaparral catchment within Sequoia National Park over a one-year period, including the seasonal transition from dry-to-wet soils in the autumn. We also measured NO emissions following artificial wetting of soil to understand how antecedent moisture conditions influence NO emissions. We hypothesized that NO emissions would be highest during the dry season and during the dry-to-wet transition following wet-up, and lowest during the wet season (plant growing season). Our data represent the first full-year of NO field measurements in a chaparral ecosystem that can be used to validate earlier DAYCENT modeling of NO emissions.

2. Materials and methods

2.1. Site descriptions

Our study was conducted in the Chamise Creek watershed, a small 4.3 ha chaparral headwater catchment located along the western slope of the central Sierra Nevada, within the Kaweah River drainage of Sequoia and Kings Canyon National Parks, California, USA (36°30′47″N, 118°48′26″W; elevation 680–700 m a.s.l.). The Chamise Creek watershed has been the focus of ecological and biogeochemical research since the mid-1980s. The watershed was accessed by foot, via an unimproved trail, and backpacks were used to transport all equipment. The site is characterized by a Mediterranean climate, with strong seasonality in both precipitation and temperature (Fig. 1). Mean annual precipitation is 670 mm with most of the precipitation occurring as rain during the months of November through May, which comprise the main plant growing season (Mooney and Rundel, 1979). Typically, almost no precipitation falls during June through September and the first significant rain events usually occur in October. The average daily high temperature in the summer is 36.4 °C and the average daily low temperature in the winter is 2.2 °C. The watershed receives approximately 5–8 kg N ha^{-1} yr^{-1} from atmospheric deposition (Homyak, 2012).

Soils at the site are classified as Ultic Haploxeralfs and are sandy clay loams derived from gabbro-dioritic parent material with a well-developed argillic horizon and a bulk density of 1.4 g cm^{-3} (upper 15 cm) (Huntington and Akeson, 1987). Soil pH is about 6.0 with a C content of 2% and N of 0.14% in the upper 10 cm and declining to 0.06% C and <0.01% N at 100 cm depth (Homyak, 2012). Vegetation is dominated by thick stands of chamise (*Adenostoma fasciculatum*) with annual grasses (*Bromus* spp.) covering the interspaces between shrubs and the understory. The watershed has not burned since 1960 and therefore represents a mature chaparral ecosystem (Li et al., 2006).

2.2. NO emission measurements

Rates of NO emissions from soils were measured by soil chamber methodology. This approach was necessary due to the complex landscape of our site, which is dominated by steep slopes and sharp canyons, precluding eddy covariance methods (Baldocchi, 2003). The remoteness of the study site and National Park Service restrictions limited installation of permanent structures and we were unable to automate our chamber measurements, thus all measurements were made manually. Six months prior to measuring NO emissions, eight polyvinylchloride collars (PVC; 30.5 cm diameter × 10 cm height) were inserted, in pairs, 6 cm into the ground at four locations representative of the spatial heterogeneity of the Chamise Creek watershed. Four collars were placed under chamise, two collars were placed in interspaces between shrubs, and two collars were placed at the interface between chamise and California scrub oak. The placement of collars did not impede the growth of annual grasses within collars or exclude plant roots. Rates of soil NO emissions were determined by placing a PVC chamber (volume = 11 L) over the previously installed PVC collars and measuring the change in concentration of NO inside the chamber headspace for approximately seven minutes.

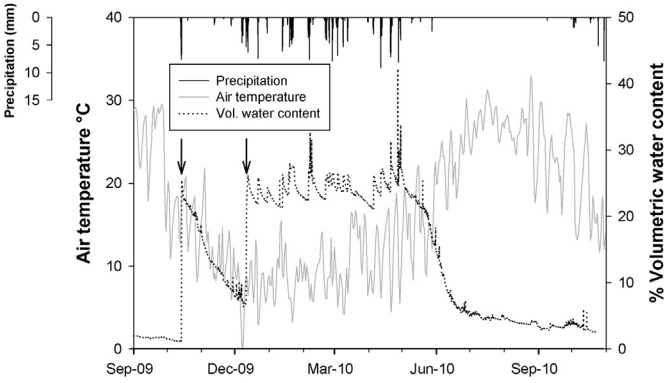

Fig. 1. Soil volumetric water content measured at a 5 cm depth along with air temperature and precipitation measurements from the nearby Ash Mountain meteorological station. The arrows denote the two time periods when NO pulses were assumed to occur after abrupt wetting of dry soils.

Chamber NO concentrations were measured with a Scintrex LMA-3 chemiluminescent NO_2 analyzer following methods described by Davidson et al. (1991), in which chamber air flowed into the analyzer and make-up ambient air flowed into the chamber through a vent. Because the LMA-3 analyzer only measures the concentration of NO_2, a CrO_3 in-line oxidizer (Drummond Technology Inc.; Bowmanville ON, Canada) was placed in-line to convert NO into NO_2. During sampling, NO_2 did not accumulate in the chambers, suggesting that increases in the instrument signal were due entirely to NO. A Nafion tube drier (Perma Pure DM-110-24) was used to remove moisture from the chamber air prior to entering the CrO_3 oxidizer, as humidity can limit the conversion of NO to NO_2 (Hutchinson et al., 1999). Although we did not measure O_3 directly, at NO_2 mixing ratios <1 ppb, 1 ppb of O_3 can induce a 0.003 ppb increase in the instrument signal (Kelly et al., 1990). Summer-time concentrations at Ash Mountain (approximately 3 km west of our site; 36°29′22″N, 118°49′22″W, 485 m a.s.l) average 5 ppb NO_2 and 60 ppb O_3 (Bytnerowicz et al., 2002), suggesting negligible impact of O_3 on our measurements. The ambient areal flux of NO was calculated based on the physical dimensions of the chamber, the rate of change in NO concentration inside the chamber, and air temperature:

$$F_{NO} = \frac{dC_{NO}}{dt} \times \frac{VN}{ART} \quad (1)$$

Where F_{NO} is the NO flux rate (ng NO–N m^{-2} s^{-1}); dC_{NO}/dt (ppbv NO–N s^{-1}) is the rate of NO concentration increase inside the chamber computed by linear regression; V is the chamber volume (L); N is the atomic weight of nitrogen (14.007 g $mole^{-1}$); A is the area of the PVC collar (730 cm^2); R is the gas constant (0.0821 L atm $mole^{-1}$ K^{-1}); and T is the chamber air temperature (K). The LMA-3 was calibrated in the field prior to and after each series of measurements. For calibration purposes, a standard curve was made by mixing an NO standard (0.0988 ppmv NO in N_2 gas; Scott Marrin, Riverside CA, USA) with zero-grade air. The method detection limit for NO measurements was 0.02 ppbv NO. Soil NO fluxes were measured from September 2009 through October 2010. During 2009, NO fluxes were measured on: October 11–12, October 16–17, November 8, November 25, and December 19. In 2010, we measured NO fluxes on: January 24–25, March 16–17, May 7–8, July 2–3, August 30–31, and September 15.

During NO emission measurements, air and soil (z = 10 cm) temperature was measured adjacent to the collars with a thermistor. Volumetric soil moisture, θ, was recorded hourly using a datalogger and two Decagon EC-5 dielectric moisture-sensors installed 5 and 30 cm below the soil surface nearby one pair of collars. The moisture sensors were calibrated using soil cores of known gravimetric water content. A continuous record of air temperature was obtained from the nearby Ash Mountain climate station operated by the National Park Service.

2.3. Artificial wetting of chaparral soils

To understand the effects of soil wet-up on NO fluxes, we performed artificial wetting experiments on each sampling date in four of the eight PVC collars. Over the course of these experiments, four collars were wetted and four served as controls (denoted “ambient” measurements).

NO fluxes were measured at three time points during a wetting experiment: (i) one hour before artificial wetting (measurements are denoted “pre-wetting”) to capture a baseline in NO emissions, (ii) within one minute following artificial wetting (denoted “wetting”) to capture NO pulses that could be attributed to rapid chemical transformations, and (iii) approximately 16 h following artificial wetting (denoted “post-wetting”) to gain understanding about the duration of the NO pulse. Due to weather and logistical constraints we did not collect post-wetting measurements from all experiments. During a wetting experiment, deionized water (1 L) was added slowly (ca. 45–60 s) and evenly to the soil within the collars simulating a 1.4 cm rainfall event. In all experiments, water was quickly absorbed by the soil, without signs of hydrophobicity, and NO flux measurements were begun within 20 s after water addition. Mean NO emissions for pre-wetting and wetting measurements were analyzed by a two-way repeated measures analysis of variance (ANOVA). Tukey post-hoc tests were used to discern significant effects of watering and time on NO emissions ($\alpha = 0.05$). Post-wetting measurements were not included in our analysis due to missing values. To understand seasonal effects on ambient NO emissions, we used a one-way repeated measures ANOVA with Tukey post-hoc tests on ambient collars ($\alpha = 0.05$). Linear and non-linear regression models were used to develop empirical relationships between ambient NO measurements and temperature and θ.

3. Results

3.1. Ambient NO emissions

Ambient NO emissions exhibited strong seasonal and spatial variability at Chamise Creek (Fig. 2 and S1). Across the four ambient collars, the relative standard error (standard error (s.e.) divided by mean) for individual sampling dates (Fig. 2) ranged from 23% to 80%. The highest NO emission rates occurred during the dry-to-wet seasonal transition of 2009 (Fig. 2). Prior to rainfall, ambient NO emissions (white bars in Fig. 2) were 9.2 ± 1.7 ng NO–N m^{-2} s^{-1} (mean ± s.e.) in dry soils. Rain fell at the study site on October 13 and 14, and on October 16, 2009, ambient emission rates were 13.0 ± 3.7 ng NO–N m^{-2} s^{-1}. These higher emissions presumably reflect enhanced NO fluxes stimulated by natural wetting of dry soil by the first rainfall following the summer dry season.

During the subsequent wet season (November 2009–May 2010) θ typically ranged between 20 and 30% (Fig. 1), and ambient NO

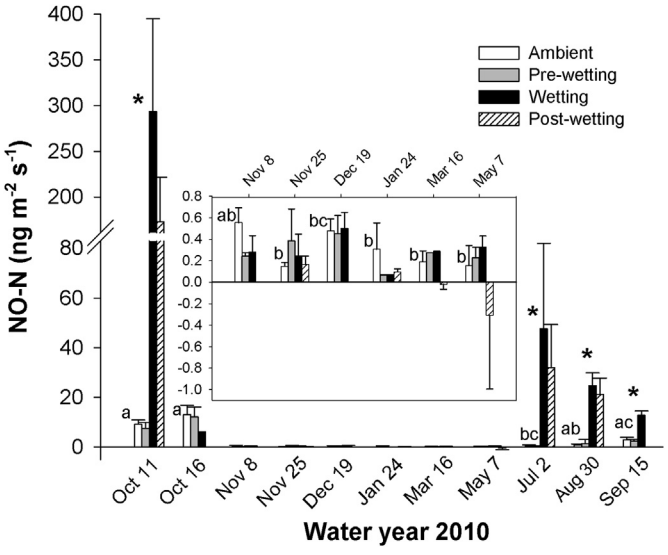

Fig. 2. Fluxes of NO measured under ambient conditions and at three time points following artificial water addition: prior to wetting (pre-wetting), immediately following wetting (wetting), and approximately 16 h post-wetting (post-wetting). Error bars represent standard errors (n = 4). Significant differences between pre-wetting and wetting treatments are denoted by * (α = 0.05). Lowercase letters denote significant effects of sampling time on ambient NO emissions (α = 0.05).

emissions remained below 1 ng NO–N m^{-2} s^{-1} (Fig. 2). Except for fluxes measured in 8 November 2009, all wet season measurements were significantly lower than dry season measurements made in October 2009 ($p < 0.026$). The wet season mean (±s.e.) NO emission rate was 0.14 ± 0.09 ng NO–N m^{-2} s^{-1}.

Ambient NO emissions during the dry season of 2010 (July to September measurements) began to trend above wet season measurements in July and reached a maximum in September 2010 (Fig. 2 and S1). Except for NO emissions measured on 8 November and 19 December 2009, ambient NO emissions observed at the end of the 2010 dry season (15 September 2010; $\theta < 5\%$) were significantly greater than during the wet season ($p \leq 0.001$; Fig. 2 and S1). During the 2009–2010 dry seasons, the mean (±s.e.) ambient NO emission was 3.4 ± 1.1 ng NO–N m^{-2} s^{-1}.

The range in ambient NO emissions measured at Chamise Creek, −0.5–16 ng NO–N m^{-2} s^{-1}, span the emission rates measured in other arid and semiarid ecosystems. NO emissions averaged 2.1 ng NO–N m^{-2} s^{-1} in a chaparral site in the San Gabriel Mountains (southern California) (Anderson and Poth, 1989), 0.2–2.8 ng NO–N m^{-2} s^{-1} in semiarid grassland and scrubland (Smart et al., 1999), 0.3–21.9 ng NO–N m^{-2} s^{-1} in South African savannas (Parsons et al., 1996), and 0–2.9 ng NO–N m^{-2} s^{-1} in a Mediterranean scrubland in Israel (Gelfand et al., 2009).

3.2. Artificial wetting experiments

The artificial wetting of dry chaparral soils ($\theta < 2\%$) on October 11, 2009 enhanced the emission of NO 32-times above pre-wetting levels (Fig. 2; $p < 0.001$). Peak emissions averaged (±s.e.) 294 ± 101 ng NO–N m^{-2} s^{-1} across the collars (Fig. 2). The mean (±s.e.) post-wetting NO emission rate was 173 ± 48.5 ng NO–N m^{-2} s^{-1} 16 h after artificial wetting (October 12). Rain fell on October 13 and 14 and pre-wetting values on October 16 (gray bars in Fig. 2) showed that NO emission rates had returned back to the pre-wetting levels of October 11 (12.1 ± 3.9 ng NO–N m^{-2} s^{-1}). Between November 2009 and May 2010, artificial wetting of soils did not significantly enhance NO fluxes (Fig. 2 inset; $p > 0.8$).

During the summer of 2010, NO emissions after artificial wetting were up to two orders of magnitude greater than pre-wetting or ambient rates, but were lower than emission rates measured during the artificial wetting experiment of October 10, 2009 (Fig. 2). Differences between pre-wetting and wetting measurements were significantly different in July ($p < 0.001$), August ($p < 0.001$) and September ($p = 0.005$) (Fig. 2). Soil θ during summer 2010 ranged from 3 to 5% and was higher than during the summer of 2009 (Fig. 1). Interestingly, the stimulation of NO emission with wetting decreased during the summer of 2010 with each additional wetting experiment while ambient NO emission rose (Fig. 2; July 2, 2010 – September 15, 2010).

Similar to our findings, artificial soil wetting experiments produced peak emission rates of 140 ng NO–N m^{-2} s^{-1} in seasonally dry tropical forest in Mexico (Davidson et al., 1991, 1993), 150–250 ng NO–N m^{-2} s^{-1} in tropical savanna, and 160 ng NO–N m^{-2} s^{-1} in an urban desert in Phoenix, AZ (Hall et al., 2008).

3.3. Relationships between NO emissions and soil temperature and moisture

The relationship between ambient NO emissions and air and soil temperature was best described by linear models, but the relationships had low predictive power (Fig. 3). The relationship between NO emissions and soil θ was "*U*-shaped" (Fig. 4). The highest ambient NO emissions occurred during periods with low soil θ near the end of the dry season, and during the dry-to-wet seasonal transition (October 2009), when rainfall abruptly increased θ from

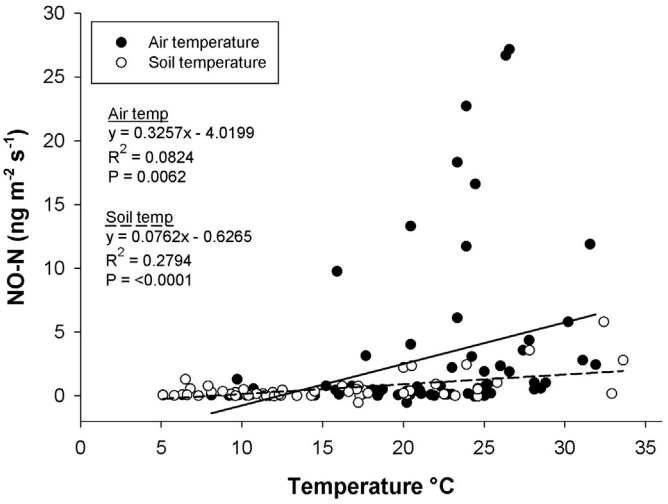

Fig. 3. Relationships among chaparral NO fluxes and air and soil temperature.

below 6% to above 20% (points in gray box in Fig. 4). Outside of the dry to wet seasonal transition, emissions of NO were best described by an exponential decay function using soil θ at a 5 cm depth ($R^2 = 0.60$; $p < 0.0001$; all points in Fig. 4 except those inside the gray box). Although the relationship between soil θ at a 30 cm depth and NO flux was statistically significant, it had lower predictive ability ($R^2 = 0.21$; $p < 0.0001$).

4. Discussion

We measured soil NO fluxes in chaparral to determine seasonal patterns and to assess whether antecedent soil moisture conditions influenced NO emissions. Here, we highlight important implications for NO emissions in chaparral and draw comparisons to previous DAYCENT modeling of NO emissions at our study watershed

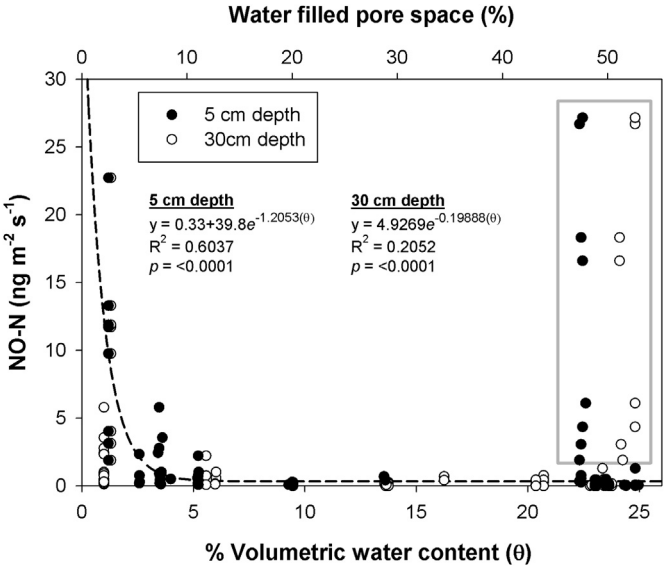

Fig. 4. Relationships between chaparral NO fluxes and soil volumetric water content (θ) at both a 5 and 30 cm depth. Values inside the gray box represent NO pulses measured within two days following the first precipitation event of the wet season and are not included in the soil θ regression models. Water filled pore space is provided as secondary *x*-axis calculated as $\theta^{*}100/(1-(\rho_b/\rho_p))$, where ρ_b = bulk density (1.4 g cm^{-3}) and ρ_p = particle density (2.65 g cm^{-3}).

(Li et al., 2006). Within our discussion, we elaborate on three important findings: i) ambient NO emissions were highest during the dry season and lowest during the wet season (plant growing season), ii) large NO pulses were only observed during brief periods when dry soils ($\theta < 6\%$) were wetted, and iii) DAYCENT-modeled seasonal NO emissions patterns for chaparral do not reflect the seasonal variation observed in our field study.

4.1. Seasonal patterns of NO emissions

Our field observations conflict with DAYCENT modeling of NO emissions from chaparral, which predicted greater NO fluxes during the wet season than during the dry season (Li et al., 2006). Outside of high NO pulses observed during the dry-to-wet seasonal transition (early autumn), we observed the highest NO emissions during the dry season ($\theta < 6\%$), and the lowest during the wet season (θ consistently above 20%). DAYCENT calculates NO emissions in proportion to nitrification and denitrification rates (pipe control) (Parton et al., 2001). At the Chamise Creek watershed, it was assumed that nitrification rates during the dry season were smaller than during the wet season (Li et al., 2006), which yielded relatively low NO emissions when soils were dry. However, measurements of soil net nitrification over two years (3–4 week intervals) at our small catchment generally ranged between −0.03–0.1 μg N g^{-1} day^{-1} during the wet season and from −0.05–0.13 μg N g^{-1} day^{-1} during the dry season ($\theta \leq 7\%$) (Homyak, 2012), and do not support the assumption that these rates substantially decrease in dry soils. Instead, field measurements show that nitrification potentials increase as soils dry, suggesting an increase in nitrifier populations that may explain greater NO emissions during the dry season (Homyak, 2012). It is also possible that atmospheric N inputs subsidize dry season N processes and maintain active N cycling rates. In coniferous forests of southern California, NO emissions were greater at high N than at low N deposition sites (Fenn et al., 1996). Similar patterns in soil N cycling have been observed in California annual grasslands (Parker and Schimel, 2011), and suggest that nitrifiers can remain active during the dry season, a period that may be conducive to elevated NO flux because of high gas diffusivity in soils.

During the wet season, despite moist soil conditions that should optimize N-cycling rates, we observed low or negative NO fluxes presumably due to several interacting mechanisms: (i) when soil $\theta > 20\%$ (Fig. 1), NO diffusivity decreases (Conrad, 1996) and processes that consume NO, such as consumption by nitrifying or denitrifying bacteria could have been intensified (Chapuis-Lardy et al., 2007; Davidson and Schimel, 1995; Kim et al., 2012); (ii) lower soil temperature could have reduced the rate of microbial N transformations (Ludwig et al., 2001); (iii) repeated drying-rewetting episodes may have increased C supply to microbes, promoting net N retention (Miller et al., 2005; Navarro-Garcia et al., 2012), and thereby limited substrate supply to nitrifiers; and (iv) increased N uptake by chaparral during the wet season (Mooney and Rundel, 1979) likely limited the pool of N available to nitrifiers (Parker and Schimel, 2011) and thus reduced NO production.

Of these mechanisms, plant N uptake may be an important control on gaseous N emissions from dryland ecosystems. For example, in chaparral watersheds of southern California, plant N uptake regulates hydrologic N losses, where N export peaks during periods of low plant N demand and fast hydrologic flushing (dry-to-wet seasonal transition), but decreases during the plant growing season (wet season) when plant N uptake is high (Meixner and Fenn, 2004). In other semiarid catchments, changes in vegetation cover have been shown to exert strong control on N cycling and nitrate leaching (Meglioli et al., 2013). Because the asynchrony between N availability and plant N demand can control hydrologic N losses, it may also influence seasonal patterns of NO emission from soil.

Wetting of dry soils during the dry-to-wet transition produced NO pulses that were up to 44 times greater than pre-wetting levels. Measurements made during October 2009 and the summer of 2010, suggest that wetting produces NO pulses when antecedent soil θ is roughly 6%. We note that production of NO pulses coincides with periods during which plant N uptake is low in chaparral (Mooney and Rundel, 1979) and during which abrupt wetting of soils could stimulate NO-producing reactions (McCalley and Sparks, 2009) as well as processes that produce NO (nitrification and denitrification) (Davidson, 1992). Based on the rapid production of NO pulses, we speculate that chemodenitrification could have contributed to NO emissions measured within one minute of irrigating dry soils, since biological processes require more than a few seconds to recover from drought-induced stress (Placella et al., 2012). During the dry season, NO_2^- can accumulate in soils (Davidson et al., 1993; Gelfand et al., 2009) in hydrologically disconnected sites (Parker and Schimel, 2011). During soil wet-up, NO_2^- may then become protonated to produce HNO_2 followed by disproportionation to NO (Su et al., 2011; Venterea and Rolston, 2000).

Repeated wetting of soils during summer 2010 produced progressively smaller pulses of NO despite the fact that ambient NO emissions generally increased over the same period. Similar emission patterns have been observed in other studies (Kim et al., 2012), and suggest that substrates necessary for NO-producing reactions became progressively depleted during the wetting experiments. Substrate limitation may also help explain why artificial wetting experiments conducted during the wet season of 2009–2010 produced no statistically significant stimulation of NO emissions (inset box in Fig. 2). Future studies that incorporate soil sterilization treatments, and that investigate the control of plant N uptake on soil NO emissions, are needed to better understand substrate-limitation of N emissions from dryland ecosystems.

4.2. Temperature and θ effects on NO emissions

The relationships among soil temperature, soil θ, and NO emissions are typically described by optimum functions, where peak NO production occurs at temperatures and moisture contents that favor biological processes (e.g., ~20–25 °C for nitrification (Saad and Conrad, 1993; Schindlbacher et al., 2004)). At our field site, we did not observe an optimum temperature at which NO emissions peaked, but we did observe a weak positive relationship between temperature and NO emissions. In the field, weak relationships between temperature and NO emissions have been observed (Cardenas et al., 1993) likely due to confounding factors not easily controlled outside the laboratory (e.g., changes in θ and plant N uptake). It is also possible that an optimum temperature was not observed simply because chemical transformations controlled NO emissions (Saad and Conrad, 1993; Schindlbacher et al., 2004), a potential scenario given the rapid production of NO pulses observed at our site.

We observed the highest NO emissions when soils were dry ($\theta < 6\%$) and following the first rainfall event of the dry-to-wet transition when θ increased to >20%. We note that both of these periods of high NO emission occurred during periods of low N uptake by chaparral (Mooney and Rundel, 1979), supporting our argument in favor of plant N demand as an important control on gaseous N emissions from soils. At our site, we attribute the elevated NO emissions observed at $\theta > 20\%$ as a response to soil wet-up, during which moist soils stimulated NO-producing reactions and processes, rather than to an optimum θ that consistently yields high NO emissions in chaparral. We base this conclusion on observations made during the wet season, during

which similarly high θ did not stimulate NO emissions. At $\theta < 6\%$, however, it may be argued that an optimum θ was reached, likely resulting from interactions between sustained rates of N mineralization and nitrification during summer (Homyak, 2012; Parker and Schimel, 2011), reduced plant N uptake (i.e., increased substrate availability) (Mooney and Rundel, 1979), NO-producing reactions (McCalley and Sparks, 2009; Su et al., 2011), and well-aerated soils conducive to high gas diffusivity (Conrad, 1996).

4.3. Annual NO flux rate

Based on our observations, we estimate an annual NO flux from Sierra Nevada chaparral of between 0.35 ± 0.48 and 1.41 ± 1.21 kg N ha^{-1} yr^{-1} (Online supplementary materials). In comparison, DAYCENT simulations of NO + N_2O emissions at our catchment predicted an annual flux of 4 kg N ha^{-1} yr^{-1}, of which NO made up 98% of the combined flux (Li et al., 2006). Our estimates are a first approximation and are influenced by the relatively low temporal resolution of our measurement technique and the substantial spatial variability in all seasons (23–80% relative standard errors for NO emission rates across collars). Despite these shortcomings, our data suggest that the DAYCENT model overestimates the annual flux of NO from Chamise Creek. We draw this conclusion from the fact that if we unrealistically based our annual flux estimates solely on measurements from artificially wetted collars (Wetting values in Fig. 2) we would predict a flux of 4.1 kg N ha^{-1} yr^{-1}.

At Chamise Creek, during 2002–2003, total direct N ($NH_4^+ + NO_3^-$) deposition was 4.9 kg ha^{-1} yr^{-1} and throughfall was 8.5 kg ha^{-1} yr^{-1}, of which NH_4^+ comprised roughly 74–78% of the total (Homyak, 2012). At Ash Mountain, total N deposition estimated by the Clean Air Status and Trends Network ranges from 3 to 4.5 kg ha^{-1} yr^{-1}, and was 3.7 kg ha^{-1} yr^{-1} during 2009–2010 (CASTNET, 2013). CASTNET, however, does not calculate throughfall rates or include deposition of NH_3 (NPS, 2001), which at our chaparral site represents a significant proportion of N inputs (Bytnerowicz et al., 2002). As a first approximation, average annual NO emissions could represent 4–47% of atmospheric N inputs to our chaparral watershed. During dry years, however, surface runoff does not exit the catchment (Fenn et al., 2003b), implying that gaseous N fluxes can be the principal route for ecosystem N loss.

5. Conclusions

We found that seasonal patterns in NO emissions at our site were opposite to those previously predicted by DAYCENT simulations; NO emissions were highest during the dry season and during wet-up events following dry antecedent conditions. Our data suggest that, outside of wet-up events, NO emissions were favored when $\theta < 6\%$, a period during which plant N uptake is low and soil gas diffusivity is high. In chaparral ecosystems, N emissions from soils are likely influenced by dry season processes that maintain active rates of N cycling and that favor NO-producing reactions. In reference to the "hole-in-the-pipe" conceptual model, the size of the conceptual pipe may not substantially decrease during the dry season, and may be subsidized by atmospheric N inputs that favor NO emissions from soils (Fenn et al., 1996). We highlight that NO emissions may represent as much as 47% of atmospheric N inputs in our catchment, suggesting that gaseous N losses are important to ecosystem N-dynamics and that ecosystem models must accurately capture dry season processes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jaridenv.2013.12.008.

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