Rapid nitrate reduction produces pulsed NO and $\text{N}_2\text{O}$ emissions following wetting of dryland soils

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Abstract Soil drying and wetting cycles can produce pulses of nitric oxide (NO) and nitrous oxide ($\text{N}_2\text{O}$) emissions with substantial effects on both regional air quality and Earth’s climate. While pulsed production of N emissions is ubiquitous across ecosystems, the processes governing pulse magnitude and timing remain unclear. We studied the processes producing pulsed NO and $\text{N}_2\text{O}$ emissions at two contrasting drylands, desert and chaparral, where despite the hot and dry conditions known to limit biological processes, some of the highest NO and $\text{N}_2\text{O}$ flux rates have been measured. We measured $\text{N}_2\text{O}$ and NO emissions every 30 min for 24 h after wetting soils with isotopically-enriched nitrate and ammonium solutions to determine production pathways and their timing. Nitrate was reduced to $\text{N}_2\text{O}$ within 15 min of wetting, with emissions exceeding 1000 ng N–$\text{N}_2\text{O}$ m$^{-2}$ s$^{-1}$ and returning to background levels within four hours, but the pulse magnitude did not increase in proportion to the amount of ammonium or nitrate added. In contrast to $\text{N}_2\text{O}$, NO was emitted over 24 h and increased in proportion to ammonium addition, exceeding 600 ng N–NO m$^{-2}$ s$^{-1}$ in desert and chaparral soils. Isotope tracers suggest that both ammonia oxidation and nitrate reduction produced NO. Taken together, our measurements demonstrate that nitrate can be reduced within minutes of wetting summer-dry desert soils to produce large $\text{N}_2\text{O}$ emission pulses and that multiple processes contribute to long-lasting NO emissions. These mechanisms represent substantial pathways of ecosystem N loss that also contribute to regional air quality and global climate dynamics.

Keywords Drylands · Nitrogen · Nitric oxide · Nitrous oxide · Nitrate · Pulse
Introduction

Soil drying–wetting cycles are widespread and can stimulate large emissions of both nitrous oxide (N\textsubscript{2}O) and nitric oxide (NO) (Scholes et al. 1997; Homyak et al. 2016; Eberwein et al. 2020) with profound implications for Earth’s climate, regional air quality, and ecosystem N retention. This is because N\textsubscript{2}O is a potent greenhouse gas (Ciais et al. 2013), NO is a precursor to tropospheric ozone (Crutzen 1979), and both NO and N\textsubscript{2}O represent important pathways for ecosystem N loss (Peterjohn and Schlesinger 1990). While the production of NO and N\textsubscript{2}O is governed by both biological and chemical processes upon wetting dry soil, the magnitude of the emissions varies as a function of aridity (Wang et al. 2014; Liu et al. 2017; von Sperber et al. 2017), with some drylands recording among the highest NO and N\textsubscript{2}O emission pulses globally (Eberwein et al. 2020). However, how these emissions vary across ecosystems experiencing drying–wetting cycles and the biogeochemical processes producing them are still not well characterized. Identifying the underlying processes producing pulsed NO and N\textsubscript{2}O emissions is necessary to predict how ecosystem N cycling may respond to global change factors including high rates of atmospheric N deposition (Fenn et al. 2006), rising temperatures, and changing precipitation regimes (Dai 2013).

Multiple biological and abiotic processes regulate NO and N\textsubscript{2}O emissions after dry soils are wetted. Biological processes include nitrification, the aerobic oxidation of ammonia (NH\textsubscript{3}) to nitrate (NO\textsubscript{3}\textsuperscript{−}) with NO and nitrite (NO\textsubscript{2}\textsuperscript{−}) as intermediates (Caranto and Lancaster 2017; Prosser et al. 2019), and denitrification, the sequential anaerobic reduction of NO\textsubscript{3}\textsuperscript{−} to N\textsubscript{2} gas with NO\textsubscript{2}\textsuperscript{−}, NO, and N\textsubscript{2}O as obligate intermediates (Knowles 1982); both of these processes can release NO and N\textsubscript{2}O as byproducts. In low oxygen environments, some nitrifiers use NO\textsubscript{2}\textsuperscript{−} as the electron acceptor during the oxidation of NH\textsubscript{3} and produce NO and N\textsubscript{2}O via nitrifier denitrification (Prosser et al. 2019). Chemodenitrification—an abiotic non-enzymatic process—can also produce NO and N\textsubscript{2}O through the chemical reduction of NO\textsubscript{2}\textsuperscript{−} and hydroxylamine (NH\textsubscript{2}OH) (Venterea and Rolston 2000; Zhu-Barker et al. 2015; Heil et al. 2016), which can accumulate in dry soils (Homyak et al. 2016). Because both biological and abiotic processes can occur simultaneously, it has been challenging to determine the contribution of individual processes to pulsed N emissions.

To advance understanding of the processes producing NO and N\textsubscript{2}O, the “hole-in-the-pipe” conceptual framework relates the factors that control N emissions to the processes that control N transformation rates (Firestone and Davidson 1989). Under this framework, N transformations are represented by changes in the diameter of the pipe—the diameter varies in proportion to process rates—whereas the factors controlling how much NO or N\textsubscript{2}O leak out of the pipe are represented by the holes (e.g., edaphic or environmental factors such as pH). In this sense, wetting soils could stimulate NO and N\textsubscript{2}O emissions by promoting nitrification, (Placella and Firestone 2013; Homyak and Sickman 2014), denitrification (Parker and Schimel 2011; Soper et al. 2016), or abiotic reactions (McCalley and Sparks 2009; Zhu-Barker et al. 2015; Homyak et al. 2017), thereby increasing the diameter of the pipe. However, the magnitude and timing of pulsed N emissions may vary as a function of environmental and edaphic factors that mediate which gaseous N intermediates are released to the atmosphere (i.e., the holes in the pipe). Understanding how process rates interact with the factors that control how much NO and N\textsubscript{2}O are emitted can help determine how N emissions may vary under future global change scenarios.

Two major challenges have limited progress identifying controls over soil NO and N\textsubscript{2}O emission pulses: (i) multiple biological and abiotic processes occur simultaneously making them difficult to separate, and (ii) traditional static chamber headspace experiments offer low temporal resolution, limiting understanding of the timing and magnitude of N trace gas emissions. To this end, isotope tracers are powerful tools that can help determine which N transformations produce NO and/or N\textsubscript{2}O (Van Groenigen et al. 2015). Moreover, isotope tracers can be coupled with laser-based isotope analyzers and automated soil chambers to detect the incorporation of 15N tracers into N\textsubscript{2}O in situ and at high resolution (e.g., one measurement per second). While similar instruments do not yet exist for NO, the incorporation of 15N tracers into NO can be detected using passive samplers (Homyak et al. 2016). By pairing high temporal resolution measurements of N emissions with stable isotopes, we assess the importance of increasing N availability (here used as a proxy for increasing the diameter of the pipe).
relative to the factors that control how much NO and N$_2$O is released (i.e. the holes in the pipe). Specifically, we ask: (1) what processes are contributing to pulsed NO and N$_2$O emissions after wetting dry soils, and (2) how does N availability (both the amount and chemical form) affect the magnitude of pulsed emissions?

To answer these questions, we monitored N emissions at two dryland sites (desert and chaparral) in Southern California characterized by pronounced and frequent transitions from dry-to-wet soils. We chose two sites with contrasting environmental conditions (Table 1) to understand whether meteorological and edaphic factors would overrule the effects of increasing N supply and the form of nitrogen added, nitrate (NO$_3^-$) or ammonium (NH$_4^+$). We hypothesized that N trace gas emissions are limited by soil N availability, resulting in pulsed NO and N$_2$O emissions proportional to the amount of added N. To infer which processes contributed to NO and N$_2$O emissions, we added $^{15}$N labeled NO$_3^-$ or NH$_4^+$ and used an automated chamber system connected to a NO and an isotope N$_2$O analyzer. We also measured NH$_3$ emissions using passive samplers as a relative index of the amount of NH$_3$ in soil pore space that may be available to nitrifiers. We predicted that if pulsed N emissions were from nitrification, then added $^{15}$N–NH$_4^+$ would be captured as NO and/or N$_2$O; if they were from denitrification, then added $^{15}$N–NO$_3^-$ would be captured as NO and/or N$_2$O; and if they were from the rapid transformation of accumulated nitrification intermediates (e.g., NO$_2^-$), then no $^{15}$N label would be incorporated in N emissions.

**Methods**

**Sites description**

We studied two drylands in Southern California in August 2018 (the end of the summer dry season) with contrasting soils and vegetation. Our chaparral site was located in the Box Springs Reserve (33° 58′ 16.4″ N, 117° 17′ 53.4″ W), a transitional zone between coastal sage scrub and chaparral dominated by chamise (*Adenostoma fasciculatum*). Our desert site was located in the Boyd Deep Canyon Desert Research Center (33° 38′ 54.7″ N, 116° 22′ 39.4″ W), and was dominated by creosote (*Larrea tridentata*). Both sites are part of the University of California Natural Reserve System. Since 1980, the chaparral site has received an average of 28 cm of rain per year with an average maximum August daily temperature of 35 °C. During this same time, the desert site received an average of 11.4 cm of rain per year with an average maximum August daily temperature of 39.3 °C. The chaparral soils are sandy loams classified as thermic Typic Haploxeralfs within the Fallbrook series. The desert soils are stony sands classified as hyperthermic Typic Torriorthents within the Carrizo series. Both sites received no rain in the month before our experiments.

The soils at the two sites differed in several ways (Table 1). Soil NO$_2^-$ was over seven times greater in the desert (0.58 ± 0.64 µg N g$^{-1}$) than in the chaparral (0.08 ± 0.03 µg N g$^{-1}$, p < 0.05), while extractable NO$_3^-$ and NH$_4^+$ did not differ between sites (Table 1). Total C and N concentrations were

| Variable                  | Desert        | Chaparral     | n  | p value          |
|---------------------------|---------------|---------------|----|-----------------|
| pH                        | 8.4 ± 0.19    | 5.8 ± 0.50    | 8  | < 0.001***      |
| NH$_4^+$ (µg N g$^{-1}$)  | 8.5 ± 4.5     | 16 ± 11       | 8  | 0.10            |
| NO$_3^-$ (µg N g$^{-1}$)  | 28 ± 21       | 23 ± 29       | 8  | 0.75            |
| NO$_2^-$ (µg N g$^{-1}$)  | 0.58 ± 0.64   | 0.08 ± 0.03   | 8  | 0.04***         |
| Total C (%)               | 0.92 ± 0.50   | 2.03 ± 0.35   | 8  | 0.001**         |
| Total N (%)               | 0.08 ± 0.03   | 0.15 ± 0.02   | 8  | < 0.001***      |
| Relative Humidity (%)     | 10.7 ± 1.04   | 80.7 ± 15.0   | 8  | < 0.001***      |
| Soil Temperature (°C)     | 30.0 ± 0.68   | 16.5 ± 2.15   | 8  | < 0.001***      |
| Ambient NO efflux (ng N–NO m$^{-2}$ h$^{-1}$) | 0.39 ± 4.31 | 14.7 ± 9.27 | 8 | 0.01**         |

Statistical significance between the two sites was assessed using student’s t-test: *p < 0.10, **p < 0.05, ***p < 0.01. Errors represent standard deviation of the mean.
both higher in the chaparral (2.03 ± 0.35% C, 0.15 ± 0.02% N) than in the desert (0.92 ± 0.50% C, 0.08 ± 0.03% N). Desert soils were more alkaline (8.4 ± 0.19) than the chaparral (5.8 ± 0.50, p < 0.05). In the hour before starting our experiment, relative humidity was higher in the chaparral (80.7 ± 15.0%) relative to the desert (10.7 ± 1.04%, p < 0.001), while soil temperature was higher in the desert (30.0 ± 0.68 °C) than in the chaparral (16.5 ± 2.15 °C, p < 0.001).

Experimental design

We measured N trace gas emissions from underneath eight chamise shrubs in the chaparral and eight creosote shrubs in the desert. Interspace soils were not sampled as dryland shrubs are considered to be “islands of fertility” where soil nutrients are concentrated (Schlesinger et al. 1990). All shrubs were located within a 10-m radius and were separated from one another by at least one meter. Under each of the eight shrub canopies, we installed two pairs of PVC collars (4 collars, each 20 cm diameter × 10 cm height; inserted 5 cm into the ground) at least 48 h prior to the start of our measurements; the collar pairs were separated from each other by at least 50 cm to avoid cross contamination of isotope tracer and within 50 cm from the base of the shrubs. One pair of collars was wetted with NO₃⁻ solution, while the other was wetted with NH₄⁺ solution. Within each pair, one collar was used to measure N emissions, while the other was used to measure soil temperature, moisture, and inorganic N to minimize disturbances to the collars from which we measured emissions.

We wetted soils inside the collars with 500 mL of deionized water; this amount corresponds to about seven mm of rainfall, which is within the range of historically occurring rain events (Boyd Deep Canyon Desert Research Station, https://doi.org/10.21973/N3V66D). During wetting, we added eight levels of N spike corresponding to 0, 2, 4, 6, 8, 10, 12, or 15 kg-N ha⁻¹ as either NO₃⁻ or NH₄⁺, covering a range of annual N deposition in Southern California drylands (Eberwein et al. 2020, Fenn et al. 2006). The nitrogen added was isotopically enriched to 2 atom percent ¹⁵N. The labeled NO₃⁻ was added to two of the collars underneath each shrub starting at approximately 9 am. Soil NO and N₂O emissions were measured from one collar underneath each shrub every 30 min beginning 15 min prior to wetting. After 24 h, this process was repeated with the NH₄⁺ label using the remaining collars underneath each shrub.

A separate group of four shrubs was used to measure the emission of NH₃ as well as the isotopic composition of NO. Emissions of NH₃ were used as an index of substrate availability to nitrifiers. These measurements were made using passive samplers (Ogawa pads; Ogawa USA, Pompano Beach, FL) that required soil chambers to be permanently closed, prohibiting integration with our automated chambers. The passive sampling pads are chemically pretreated so that they would collect either NOₓ, NO₂, or NH₃ and have been demonstrated to work well under warm and humid conditions expected inside our soil chambers (Coughlin et al. 2017). We did not detect NO₂ on the NO₂ pads, indicating any N accumulation on the NO₂ pads was mostly NO. Two collars underneath each of the shrubs were wetted with 500 mL of either NO₃⁻ or NH₄⁺ solution (2 atom percent ¹⁵N) at a concentration corresponding to 15 kg-N ha⁻¹. The remaining two collars underneath each of the four shrubs were wetted with deionized water only. Chamber lids were installed immediately after wetting and pads were switched out at the following time intervals: 0 to 15 min, 15 min to 12 h, and 12 to 24 h post-wetting to capture NO and NH₃ during periods when we expected N emissions to be high.

NO and N₂O emissions

We used an automated chamber system to simultaneously measure NO and N₂O emissions from one of the collars under each of the eight shrubs sequentially over a 24-h period post-wetting. Collars were equipped with automated chambers (8100-104/C, LI-COR Biosciences, Lincoln, NE) connected to a multiplexer (LI-8150, LI-COR Biosciences) to sequentially measure emissions from each of the eight collars. We measured gas concentrations for two minutes, during which time gas from the chamber was recirculated through a sample loop connecting the multiplexer, an infrared gas analyzer (IRGA; LI-8100, LI-COR Biosciences), an isotope N₂O analyzer (Model 914-0027, Los Gatos Research, Inc., Mountain View, CA), and a NO analyzer (Model 410 and Model 401, 2B Technologies, Boulder CO). The IRGA, N₂O analyzer, and NO analyzer all sampled air from the recirculating sample loop, and each instrument, except for the NO
analyzer, returned air back into the sample loop. Since the NO analyzer consumed NO, this air was vented to the atmosphere at a rate of 0.75 L min⁻¹. While this open system dilutes the concentration of trace gases emitted from the soil with atmospheric air, flux rates are not appreciably affected after accounting for our chamber volume (~ 6 L) and the short incubation period (Davidson et al. 1991). All instruments were housed inside an air-conditioned box made of five cm thick housing insulation (5 × 2 × 2 m). To prevent condensation in the lines, the sample loop included a water trap to remove moisture by cooling the hoses with ice water. Soil temperature (Model 8150-203, LI-COR Biosciences) and moisture sensors (Model 8150-205, LI-COR Biosciences) were installed under each shrub and were connected to the IRGA, which also measured relative humidity.

Fluxes of NO and N₂O were calculated as the linear change in trace gas concentrations inside the chamber headspace over the last 90 s of the two-minute incubation (script available on https://github.com/hand003/TraceGasArray). This timeframe was chosen to allow for even mixing of chamber air throughout the sample loop. The N₂O analyzer recorded concentrations once every second and the NO analyzer recorded every ten seconds. If the linear correlation between time and trace gas concentration was not statistically significant (p > 0.1), the net flux was reported as zero. The change in NO concentration over time was highly linear over the 90 s window for all measurements (R² = 0.96). The change in N₂O concentration over time was close to linear for all measurements (R² = 0.56) and was highly linear when N₂O fluxes were greater than 10 ng N–N₂O m⁻² s⁻¹ (R² = 0.97).

Flux values were corrected for the volume in the sample loop, soil temperature, and chamber volume. The isotopic N₂O analyzer also recorded [δ¹⁵N]N₂O, which requires five minutes of averaging time to report δ¹⁵N values within 1-sigma precision. Given the short incubation period of our measurements (2 min) and the fact that our measurements were diluted with ambient air, we do not attempt to calculate absolute [δ¹⁵N]N₂O values. Rather, we report *[δ¹⁵N]N₂O as an index of when ¹⁵N tracer was incorporated into N₂O after wetting dry soils. *[δ¹⁵N]N₂O was calculated as the average δ¹⁵N value during the final 10 s of each incubation—across all measurements the standard deviation of [δ¹⁵N]N₂O during this 10 s interval averaged 4.95 ‰. We also refrain from reporting isopomer values for these same reasons—two-minute chamber closures were not sufficient to ensure isotopic accuracy and precision. The isotope N₂O analyzer was referenced against a commercially available standard (Airgas, 5000 ppm N₂O, δ¹⁵N = − 0.3 ‰) and a cylinder of medical grade air analyzed for N₂O and isotopic composition at the UC Davis Stable Isotope Facility (0.44 ± 0.02 ppm N₂O; δ¹⁵N = 5.76 ± 0.15 ‰).

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NO isotopes and soil NH₃ emissions

We used the bacterial denitrifier method to measure the [δ¹⁵N]NO and [δ¹⁸O]NO of NO captured on the NOx pads (Coplen et al., 2012). Briefly, the Ogawa pads were extracted in 8 mL of deionized water and shaken overnight to extract NO as NO₂⁻; no NO₃⁻ was detected in the filtered extracts. The NO₂⁻ was then converted to N₂O using Pseudomonas aureofaciens (Sigman et al. 2001). δ¹⁵ N and δ¹⁸O values were measured using a Thermo Delta V isotope ratio mass spectrometer (Thermo Fisher Scientific, Waltham, MA) at the Facility for Isotope Ratio Mass Spectrometry (FIRMS; https://ccb.ucr.edu/facilities/firms) at the University of California, Riverside. Due to isotopic fractionation associated with NO collection with passive samplers, isotopic fractionation associated with the denitrifier method, exchange of oxygen atoms between NO₂⁻ and water (Casciotti et al. 2007; Dahal and Hastings, 2016; Yu and Elliott 2017), and potential interactions between volatile organic compounds (VOC) with NO (Walters and Michalski 2016) it is unlikely we measured the actual [δ¹⁵N]NO and [δ¹⁸O]NO emitted from soil. However, these fractionation and oxygen exchange effects are generally uniform across samples (Dahal and Hastings, 2016) and even if NO and VOCs interacted within our chambers, the passive samplers can still inform when ¹⁵N tracers added to soils are detected as NO (Homyak et al. 2016), altogether helping to preserve a [δ¹⁵N]NO and [δ¹⁸O]NO signal from the Ogawa pads, hereafter referred to as *[δ¹⁵N]NO and *[δ¹⁸O]NO. To help preserve the [δ¹⁸O]NO signal from the Ogawa pads, we used the same water source
to prepare all isotope tracers and analyzed all samples in a single batch. Furthermore, our samples did not have NO₃⁻—the NO was extracted as NO₂⁻—reducing bias in the final isotope measurement (Casciotti et al. 2007).

We used Ogawa pads to measure NH₃ emissions as an index of NH₃ availability in soil pore space that may be available to nitrifiers. The NH₃ pads were extracted in 8 mL of deionized water and shaken overnight to extract NH₃ as NH₄⁺. Extracted NH₄⁺ was quantified using a colorimetric assay (SEAL methods Environmental Protection Agency (EPA)-126-A) using a SEAL AQ-2 discrete analyzer (SEAL analytical, Mequon, WI).

Soil chemical properties

We measured soil extractable NH₄⁺ and NO₃⁻ prior to wetting, two hours after wetting, and 24 h after wetting. NO₃⁻ and NH₄⁺ were measured by extracting soils (5 g) in 2 M KCl (30 mL). Soil solutions were shaken for one hour, filtered (Whatman 42 filter paper; 2.5 µm pore size), and frozen until analysis. We also measured NO₂⁻ prior to wetting; NO₂⁻ was extracted in deionized water to minimize its loss via gaseous N products (Homyak et al. 2015). We used colorimetric assays to measure soil extractable NH₄⁺ (SEAL method EPA-126-A), NO₃⁻ (SEAL method EPA-129-A), and NO₂⁻ (SEAL method EPA-137-A). Additionally, we measured total C, total N, and pH in dry soils (0–10 cm depth) collected from underneath each shrub prior to adding water or N. Soil total C and total N was measured in an elemental analyzer (Flash EA1112; Thermo Scientific, Woltham, MA) at the Environmental Sciences Research Laboratory at the University of California, Riverside (https://envisci.ucr.edu/research/environmental-sciences-research-laboratory-esrl). Soil pH was measured in a 1:1 soil to water ratio with a pH meter (Orion VersaStar Pro; Thermo Scientific, Woltham, MA).

Statistical analyses

All statistics were conducted in R version 3.6.1 (R core development team, 2019). We used linear regression to evaluate the relationship between the amount of added N and soil NO emissions, N₂O emissions, and peak *[δ¹⁵N]N₂O. This was accomplished by first calculating the cumulative NO or N₂O emissions measured at each shrub using the “trapz” function. Peak *[δ¹⁵N]N₂O was calculated as the highest *[δ¹⁵N]N₂O value recorded from underneath each shrub. We then used the “lm” function to determine the linear relationship between the amount of added N and cumulative NO or N₂O emissions and peak *[δ¹⁵N]N₂O. We report the R² of each linear regression where p < 0.10 to avoid type II error associated with high spatial variation in field experiments. However, we consider linear regressions with p > 0.05 as “weak” and include alternative explanations for these relationships. A block in the sample loop prevented us from measuring fluxes from two of the collars in the chaparral (2 and 10 kg-N NO₃⁻ ha⁻¹) and these data were omitted from our analyses.

We used mixed effects models to determine when ¹⁵N tracers were detected in NO collected using passive samplers. The models included *[δ¹⁵N]NO as the response variable, collection time as the predictor variable, and a random effect to account for measuring the same collar repeatedly. Models were run using the “nlme” package in R. We used the anova.lme function to determine if time was a significant model term and Tukey corrected multiple comparisons to determine which times differed compared to ambient *[δ¹⁵N]NO. We used the same approach to determine if *[δ¹⁵N]NO and *[δ¹⁸O]NO changed in collars that were amended with water only.

Results

Soil N₂O emissions

In the desert, peak N₂O emissions averaged 529 ± 469 ng N–N₂O m⁻² s⁻¹ after wetting soils with NO₃⁻ and NH₄⁺ amended solutions, and returned to prewetting levels within four hours (Fig. 1a,c). However, desert N₂O emissions did not increase in proportion to adding more NO₃⁻ (p = 0.12) or NH₄⁺ (p = 0.89, Table 2). In contrast to the desert, peak chaparral N₂O emissions averaged only 38.0 ± 72.0 ng N–N₂O m⁻² s⁻¹ after wetting with NO₃⁻ and NH₄⁺ amended solutions (Fig. 1b,d). As observed in the desert, N₂O emissions did not increase in proportion to adding NO₃⁻ (p = 0.25) or NH₄⁺ (p = 0.10, Table 2).

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Rapid reduction of NO$_3^-$ produced pulsed N$_2$O emissions at both sites. In response to 15 kg ha$^{-1}$ equivalent NO$_3^-$ addition, *[δ$^{15}$N]N$_2$O reached 1953 ‰ in the desert and 124 ‰ in the chaparral (Fig. 2a,b), whereas the *[δ$^{15}$N]N$_2$O of from soils amended with water only did not surpass 32.4 ‰ at either site. Peak *[δ$^{15}$N]N$_2$O increased in proportion to NO$_3^-$ addition in the desert ($R^2 = 0.62$, slope = 107 ‰ (kg N ha$^{-1}$)$^{-1}$, $p = 0.013$) and to a smaller degree in the chaparral ($R^2 = 0.31$, slope = 6.2 ‰).
Prior to wetting, NO emissions were greater in the chaparral (14.7 ± 4.31 ng N–NO m−2 s−1) than in the desert (0.39 ± 9.27 ng N–NO m−2 s−1) (Table 1). In the desert, NO emissions steadily increased for 10 h post-wetting, and remained elevated for the remainder of the experiment (Fig. 3a); peak NO emissions averaged 221 ± 269 ng N–NO m−2 s−1 in NO3−-amended soils (Fig. 3a) and 254 ± 200 ng N–NO m−2 s−1 in NH4+ amended soils (Fig. 3c). In contrast to the desert, chaparral NO emissions reached their peak within only 5 h of wetting and decreased at faster rates; NO emissions averaged 114 ± 204 ng N–NO m−2 s−1 in NO3−-amended soils (Fig. 3c). In contrast to N2O, isotopically labeled NH4+ and NO3− were both incorporated into the NO emitted at both sites. The 15N labeled NO3− was rapidly converted to NO in the chaparral (F3,9 = 93.8, p < 0.0001), enriching *[δ15N]NO from −13.2 ± 1.82 ‰ to 388 ± 27.8 ‰ within 15 min of tracer addition (p < 0.0001, Fig. 4b). In the desert, the 15N–NO3− label was detected in NO (F3,9 = 1.7, p = 0.001) but not at 15 min (*[δ15N]NO = 23.1 ± 7.33 ‰, p = 1.00); it was detected between 0.25 and 12 h, when *[δ15N]NO reached 745 ± 202 ‰ (p = 0.003; Fig. 4a). The 15N–NH4+ label took between 0.25 and 12 h to become incorporated into NO at both sites; *[δ15N]NO reached 949 ± 152 ‰ in the desert (F3,9 = 12.1, p = 0.002; Fig. 4c) and 754 ± 132 ‰ in the chaparral (F3,9 = 60.4, p < 0.001; Fig. 4d).

The natural abundance δ15N– and δ18O–NO values emitted from soils amended with only deionized water decreased over the course of the experimental incubation (Fig. 5). The *[δ18O]NO decreased from approximately 10 ‰ prior to wetting to −15 ‰ 24 h after wetting in both the chaparral (F3,21 = 7.35, p = 0.002) and the desert (F3,21 = 11.5, p = < 0.001). Similarly, *[δ15N]NO decreased from approximately −10 ‰ to −40 ‰ over the course of the incubation in both the chaparral (F3,21 = 5.29, p = 0.007) and the desert (F3,21 = 5.15, p = 0.01).

Soil NO emissions increased in proportion to incremental NH4+ additions in the chaparral (R2 = 0.58, p = 0.03, Fig. 6d), whereas in the desert, the relationship was positive but weak (R2 = 0.45, p = 0.07, Fig. 6c). Adding NO3− may have increased NO emissions in the chaparral, but the relationship was weak (p = 0.09, Table 2); adding NO3− did not increase NO emissions in the desert (p = 0.28, Table 2).

Soil NH3 emissions increased immediately after wetting both sites but remained higher in the desert...
relative to the chaparral (Fig S1). In the desert, NH₃ emissions averaged 27.3 ± 24.6 µg N–NH₃ m⁻² h⁻¹ between 0.25 and 12 h in NO₃⁻ amended soils; the NO₃⁻ treatment did not increase NH₃ emissions compared to soils amended with only water (Fig S1a). In NH₄⁺ amended desert soils, NH₃ emissions averaged 52.5 ± 45.0 µg N–NH₃ m⁻² h⁻¹ between 0.25 and 12 h, compared to 16.7 ± 10.6 µg N m⁻² h⁻¹ in soils amended with only water (Fig S1c).

Fig. 2 Isotopic composition ([δ₁⁵N]N₂O) of N₂O emitted over 24 h from the desert (a, c) and chaparral (b, d) following wetting of dry soils with nitrate (NO₃⁻; a, b) or ammonium (NH₄⁺; c, d) solutions. Each black dot represents the average isotopic composition of N₂O measured over the last 30 s from each chamber.
Discussion

We investigated the dynamics of and mechanisms driving pulsed NO and N$_2$O emissions during drying–wetting cycles in two contrasting drylands. We found that soil NO emissions increased in proportion to the amount of NH$_4^+$ added in both sites, although this relationship was weaker in the desert, partially supporting the hypothesis that increasing biological process rates would increase N emissions and

Fig. 3  Soil NO emissions (ng N–NO m$^{-2}$ s$^{-1}$) over 24 h from the desert (a, c) and chaparral (b, d) following wetting of dry soils with nitrate (NO$_3^-$; a, b) or ammonium (NH$_4^+$; c, d) solutions. Each black dot represents flux measurements over a 2-min interval for each of the 8 chambers.
suggesting that nitrification may control NO emission magnitude in these coarse-textured soils. In contrast, increasing N supply did not increase N$_2$O emissions at either site, which does not support the hypothesis that N$_2$O emissions are limited by NO$_3^-$ or NH$_4^+$. While N addition did not stimulate N$_2$O emissions, N$_2$O was produced in part by the near-instantaneous reduction of NO$_3^-$, raising questions as to the

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**Fig. 4** Isotopic signature ($^*$δ-15N(NO) of NO emitted from the desert (a, c) and chaparral (b, d) over 24 h after wetting dry soils with nitrate (NO$_3^-$; a, b) or ammonium (NH$_4^+$; c, d) solutions. Lines represent the mean $^*$δ-15N(NO (n = 4) from each treatment within each site. Dots represent individual measurements using passive Ogawa samplers. Asterisks indicate if the mean for a given time differed from the control ($^*$p < 0.1, **p < 0.05, ***p < 0.01)
mechanisms driving \( \text{NO}_3^- \) reduction in these dryland soils and how factors controlling these emissions could help explain variation in N emissions across ecosystems.

\( \text{N}_2\text{O} \) emissions: controls and dynamics

While we expected \( \text{N}_2\text{O} \) to increase within minutes after wetting to produce large emission pulses (Eberwein et al. 2020), the incorporation of \( ^{15}\text{N}-\text{NO}_3^- \) tracer into \( \text{N}_2\text{O} \) within 15 min of adding water was unexpected (Fig. 2a, b)—denitrification is an anaerobic process not thought to dominate in well-aerated coarse-textured soils during dry summer months (Werner et al. 2014). Possibly, rapid onset of microbial respiration (Birch 1958; Jenerette and Chatterjee 2012) consumed sufficient \( \text{O}_2 \) to stimulate \( \text{N}_2\text{O} \) production via denitrification immediately after adding water, or soil aggregates may have sustained a viable denitrifier population within anoxic microsites throughout the hot and dry summer (Sexstone et al. 1985). Indeed, laboratory studies show denitrification enzyme activity can be maintained in dry soils (Peterjohn 1991; Parker and Schimel 2011), perhaps suggesting this process is viable in deserts. However, because \( \text{NO} \) is produced as an obligate intermediate during denitrification, and our \( ^{15}\text{NO}_3^- \) tracer was not incorporated into \( \text{NO} \) within 15 min post-wetting in the desert (Fig. 4a), denitrification may not have contributed to rapid \( \text{N}_2\text{O} \) emissions. Besides biological processes, chemodenitrification can produce \( \text{N}_2\text{O} \) (Zhu-Barker et al. 2015; Heil et al. 2016; Harris et al. 2021), but the abiotic reduction of \( \text{NO}_3^- \) has only been reported under manipulated laboratory settings (Davidson et al. 2003; Matus et al. 2019) and is yet to be demonstrated to occur in-situ (Colman et al. 2007, 2008). The detection of the \( ^{15}\text{N}-\text{NO}_3^- \) label in \( \text{N}_2\text{O} \) within 15 min of wetting dry soils at our site shows that dryland soils have the capacity to reduce \( \text{NO}_3^- \) immediately after wetting and argues for additional work identifying which processes contribute to rapid \( \text{N}_2\text{O} \) emissions.

Even though \( ^{15}\text{N}-\text{NO}_3^- \) was rapidly reduced to \( \text{N}_2\text{O} \), adding more \( \text{NO}_3^- \) did not increase the magnitude of pulsed \( \text{N}_2\text{O} \) emissions. This suggests that the processes reducing \( \text{NO}_3^- \) to \( \text{N}_2\text{O} \) are not limited
by soil N availability (i.e., the size of the pipe), and that other factors regulate the magnitude of N\textsubscript{2}O emissions. For example, more \textsuperscript{15}N–NO\textsubscript{3}\textsuperscript{−} tracer was reduced to N\textsubscript{2}O in the desert (Fig. 2; Table S1), where soils had higher pH and warmer temperature compared to the chaparral (Table 1). These soil properties and environmental conditions can determine which N intermediates are released to the atmosphere,
potentially explaining variation in the magnitude of N₂O emissions between sites. For example, higher pH desert soils may have increased denitrification rates (Knowles 1982), or warmer temperatures in the desert may have favored abiotic reactions that can produce N₂O (McCalley and Sparks 2009; Zhu-Barker et al. 2015). Average peak N₂O emissions from the desert were slightly higher compared to emissions measured in tropical forests (66.4 ng N–N₂O m⁻² s⁻¹; Hall and Matson 2003) and temperate agricultural systems (355 ng N–N₂O m⁻² s⁻¹; Smith et al. 1994), which are thought of as denitrification hotspots. In addition to differences in pH and temperature between sites, variation in soil properties underneath each shrub could override any effect of experimental N addition on N₂O emissions. Indeed, N₂O emissions are notoriously difficult to predict since they are often driven by high rates of microbial activity within microsites where soil C and N are concentrated (Sey et al. 2008; Harris et al. 2021). As such, greater replication may be needed to detect effects of N addition over the inherent variability in N₂O emissions. Despite this variation, documenting the rapid reduction of NO₃⁻ to form N₂O is an important step in identifying controls over dryland N₂O emissions.

NO emissions: controls and dynamics

Nitrification produced NO at our sites as supported by the detection of ¹⁵N–NH₄⁺ in NO (Fig. 4c,d) and the positive response of NO emissions to adding NH₄⁺ (Fig. 6c,d). In addition to nitrification, denitrification also produced NO at both sites; ¹⁵N–NO₃⁻ was reduced to NO 12 h after wetting dry soils in the desert, and within 15 min in the chaparral (Fig. 4a,b). Denitrifiers can initiate NO₃⁻ reduction within hours of decreasing soil O₂ concentrations (Liu et al. 2019) and maintain this activity once aerobic conditions return (Roco et al. 2016). We also observed a simultaneous decrease in ³²⁰¹⁸O]NO and ³¹⁵N]NO over the course of the incubation at both sites, perhaps suggesting other processes produced NO (Fig. 5). While changes to ³¹⁸O]NO and ³¹⁵N]NO could have been caused by interactions between NO and VOCs (Walters and Michalski 2016), these observations may also indicate nitrifier denitrification activity as observed in a Mediterranean grassland (Homyak et al. 2016). Nitrifier denitrification produces NO from NO₂⁻, which contains O from both water and air, whereas nitrification produces NO from NH₄OH, which contains only O from air (Andersson and Hooper 1983; Buchwald et al. 2012; Medinet et al. 2015; Boshers et al. 2019). As such, the change in ³¹⁸O]NO may reflect incorporation of ¹⁸O from the NO₂⁻ produced prior to and after wetting these dry soils (Homyak et al. 2016). Furthermore, biological NO production pathways—including nitrifier denitrification and nitrification—fractionate against ¹⁵N by 28–60 ‰ (Robinson 2001), consistent with the simultaneous decrease in ³¹⁸¹⁵N]NO observed throughout the incubation. Abiotic reactions may have also contributed to soil NO efflux by converting nitrification intermediates—such as NO₂⁻ or NH₂OH—to NO (McCalley and Sparks 2009; Heil et al. 2016; Homyak et al. 2017). Regardless of the mechanism, our work suggests that multiple pathways, including those requiring anaerobic conditions, produce NO after wetting these dry coarse-textured soils.

Soil NO-producing pathways were likely limited by soil N availability, since adding more N was associated with higher NO emissions. The positive response of cumulative NO emissions to adding NH₄⁺ is consistent with N limitation of N trace gas production via nitrification (Davidson et al. 2000; Vourlitis et al. 2015; Prosser et al. 2019), as has been observed in other drylands (Hartley and Schlesinger 2000; Eberwein et al. 2020). However, other factors besides N limitation likely contributed to the magnitude of the NO pulse since NO emissions diverged between sites; the tracers were reduced to NO more quickly in the chaparral (Fig. 4), while cumulative NO emissions had a larger positive relationship with NH₄⁺ addition in the desert (Fig. 6). These differences between sites may be explained by background microbial activity. For example, chaparral soils were exposed to fog (Table 1) and were already producing NO before we added water, whereas desert soils were not (Fig. 3b,d). In this sense, non-rainfall water inputs via fog (McHugh et al. 2015) may have influenced the magnitude of pulsed N emissions by resuscitating microbes and priming them for the N we added, helping to explain the rapid NO emission pulse (Fig. 3b,d) and the rapid incorporation of ¹⁵N–NO₃⁻ into NO (Fig. 4b). In contrast to chaparral, microorganisms in the relatively drier desert took hours to activate before producing the more delayed, but relatively long-lasting, NO emission pulse (Fig. 3a,c). In the desert, we measured higher NH₃ emissions relative
to the chaparral (Fig S1), consistent with higher soil pH favoring NH₃ production from the equilibrium between NH₄ and NH₄⁺ (pKa = 9.25; Avnimelech and Laher 1977). This suggests the longer NO emission pulse in the desert could have been sustained by greater NH₃ diffusion through soil pore space and supply to nitrifiers even as drying soils may have limited nitrifier access to NH₄⁺ in soil pore water (Stark and Firestone 1995). The role of NH₃ diffusion to nitrifiers may also help explain why the relationship between NH₄⁺ addition and NO emissions was weaker in the desert; variable background NH₄⁺ concentrations may have supplied NH₃ to nitrifiers even when little N was added to soils. Taken together, our observations support the hypothesis that wetting-induced NO emissions are limited by soil N availability but suggest that environmental and edaphic factors contribute to variation in NO production among ecosystems.

Conclusion

We demonstrate that rapid NO₃⁻ reduction (within 15 min) can occur even in coarse summer-dry desert soils under temperature extremes to produce N₂O. However, the N₂O emissions produced were insensitive to experimentally adding N. Identifying the processes that govern the rapid NO₃⁻ reduction pathway will help constrain variation in N emissions across dryland soils as these ecosystems expand with expected changes in climate (Huang et al. 2016). In contrast to N₂O, NO emissions were governed by N limitation of multiple N cycling processes, suggesting that N-limited NO production pathways may increase in response to higher rates of atmospheric N deposition (Fenn et al. 2006). These wetting induced N trace gas production pathways appear widespread across ecosystems that experience repeated drying–wetting cycles and will likely become increasingly important sources of atmospheric NO and N₂O as global precipitation regimes become more variable.

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Data availability The datasets generated during this study are available in the Dryad repository, https://doi.org/10.6086/DIC39X.

Code availability Custom code used for calculating trace gas fluxes is available at https://github.com/handr003/TraceGasArray

Declarations

Conflict of interest The authors have no conflicts of interest to declare that are relevant to the content of this article.

Ethical approval Not applicable.

Informed consent Not applicable.

Consent for publication Not applicable.

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