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Rapid nitrate reduction produces pulsed NO and N_2O 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 (N_2O) 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 N_2O 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 N_2O flux rates have been measured. We measured N_2O 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 N_2O within 15 min of wetting, with emissions exceeding 1000 ng N–N_2O 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 N_2O, 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 N_2O 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

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Introduction

Soil drying–wetting cycles are widespread and can stimulate large emissions of both nitrous oxide (N_2O) 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_2O is a potent greenhouse gas (Ciais et al. 2013), NO is a precursor to tropospheric ozone (Crutzen 1979), and both NO and N_2O represent important pathways for ecosystem N loss (Peterjohn and Schlesinger 1990). While the production of NO and N_2O is governed by both biological and chemical processes upon wetting dry soil, the magnitude of the emissions vary 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_2O 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_2O 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_2O emissions after dry soils are wetted. Biological processes include nitrification, the aerobic oxidation of ammonia (NH_3) to nitrate (NO_3^-) with NO and nitrite (NO_2^-) as intermediates (Caranto and Lancaster 2017; Prosser et al. 2019), and denitrification, the sequential anaerobic reduction of NO_3^- to N_2 gas with NO_2^-, NO, and N_2O as obligate intermediates (Knowles 1982); both of these processes can release NO and N_2O as byproducts. In low oxygen environments, some nitrifiers use NO_2^- as the electron acceptor during the oxidation of NH_3 and produce NO and N_2O via nitrifier denitrification (Prosser et al. 2019). Chemodenitrification—an abiotic non-enzymatic process—can also produce NO and N_2O through the chemical reduction of NO_2^- and hydroxylamine (NH_2OH) (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_2O, 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_2O 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_2O 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_2O 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_2O 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_2O (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 ^{15}N tracers into N_2O in-situ and at high resolution (e.g., one measurement per second). While similar instruments do not yet exist for NO, the incorporation of ^{15}N 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_2O is released (i.e. the holes in the pipe). Specifically, we ask: (1) what processes are contributing to pulsed NO and N_2O 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_2O emissions proportional to the amount of added N. To infer which processes contributed to NO and N_2O 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_2O 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_2O; if they were from denitrification, then added $^{15}N–NO_3^-$ would be captured as NO and/or N_2O; 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

Table 1 Soil chemical properties and meteorology prior to beginning experiments in the desert and chaparral sites (n = 8)

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 NO_3^- solution, while the other was wetted with NH_4^+ 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 NO_3^- or NH_4^+, 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 ^{15}N. The labeled NO_3^- was added to two of the collars underneath each shrub starting at approximately 9 am. Soil NO and N_2O 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 NH_4^+ label using the remaining collars underneath each shrub.

A separate group of four shrubs was used to measure the emission of NH_3 as well as the isotopic composition of NO. Emissions of NH_3 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 NO_x, NO_2, or NH_3 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 NO_2 on the NO_2 pads, indicating any N accumulation on the NO_x pads was mostly NO. Two collars underneath each of the shrubs were wetted with 500 mL of either NO_3^- or NH_4^+ solution (2 atom percent ^{15}N) 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 NH_3 during periods when we expected N emissions to be high.

NO and N_2O emissions

We used an automated chamber system to simultaneously measure NO and N_2O 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 N_2O 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, N_2O 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 N_2O 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/handr003/TraceGasArray). This timeframe was chosen to allow for even mixing of chamber air throughout the sample loop. The N_2O 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 ($R^2 = 0.96$). The change in N_2O concentration over time was close to linear for all measurements ($R^2 = 0.56$) and was highly linear when N_2O fluxes were greater than 10 ng N–N_2O m^{-2} s^{-1} ($R^2 = 0.97$).

Flux values were corrected for the volume in the sample loop, soil temperature, and chamber volume. The isotopic N_2O analyzer also recorded [δ^{15}N]N_2O, which requires five minutes of averaging time to report δ^{15}N 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 [δ^{15}N]N_2O values. Rather, we report *[δ^{15}N]N_2O as an index of when ^{15}N tracer was incorporated into N_2O after wetting dry soils. *[δ^{15}N]N_2O was calculated as the average δ^{15}N value during the final 10 s of each incubation—across all measurements the standard deviation of [δ^{15}N]N_2O during this 10 s interval averaged 4.95 ‰. We also refrain from reporting isotopomer values for these same reasons—two-minute chamber closures were not sufficient to ensure isotopic accuracy and precision. The isotope N_2O analyzer was referenced against a commercially available standard (Airgas, 5000 ppm N_2O, $\delta^{15}N = -0.3$ ‰) and a cylinder of medical grade air analyzed for N_2O and isotopic composition at the UC Davis Stable Isotope Facility (0.44 ± 0.02 ppm N_2O; $\delta^{15}N = 5.76 \pm 0.15$ ‰).

NO isotopes and soil NH_3 emissions

We used the bacterial denitrifier method to measure the [δ^{15}N]NO and [δ^{18}O]NO of NO captured on the NO_x pads (Coplen et al., 2012). Briefly, the Ogawa pads were extracted in 8 mL of deionized water and shaken overnight to extract NO as NO_2^-; no NO_3^- was detected in the filtered extracts. The NO_2^- was then converted to N_2O using *Pseudomonas aureofaciens* (Sigman et al. 2001). δ^{15} N and δ^{18}O values were measured using a Thermo Delta V isotope ratio mass spectrometer (Thermo Fisher Scientific, Woltham, 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 NO_2^- 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 [δ^{15}N]NO and [δ^{18}O]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 ^{15}N tracers added to soils are detected as NO (Homyak et al. 2016), altogether helping to preserve a [δ^{15}N]NO and [δ^{18}O]NO signal from the Ogawa pads, hereafter referred to as *[δ^{15}N]NO and *[δ^{18}O]NO. To help preserve the [δ^{18}O]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 NO_3^-—the NO was extracted as NO_2^-—reducing bias in the final isotope measurement (Casciotti et al. 2007).

We used Ogawa pads to measure NH_3 emissions as an index of NH_3 availability in soil pore space that may be available to nitrifiers. The NH_3 pads were extracted in 8 mL of deionized water and shaken overnight to extract NH_3 as NH_4^+. Extracted NH_4^+ 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 NH_4^+ and NO_3^- prior to wetting, two hours after wetting, and 24 h after wetting. NO_3^- and NH_4^+ 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 NO_2^- prior to wetting; NO_2^- 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 NH_4^+ (SEAL method EPA-126-A), NO_3^- (SEAL method EPA-129-A), and NO_2^- (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, N_2O emissions, and peak *[δ^{15}N]N_2O. This was accomplished by first calculating the cumulative NO or N_2O emissions measured at each shrub using the "trapz" function. Peak *[δ^{15}N]N_2O was calculated as the highest *[δ^{15}N]N_2O 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 N_2O emissions and peak *[δ^{15}N]N_2O. We report the R^2 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 NO_3^- ha^{-1}) and these data were omitted from our analyses.

We used mixed effects models to determine when ^{15}N tracers were detected in NO collected using passive samplers. The models included *[δ^{15}N]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 *[δ^{15}N]NO. We used the same approach to determine if *[δ^{15}N]NO and *[δ^{18}O]NO changed in collars that were amended with water only.

Results

Soil N_2O emissions

In the desert, peak N_2O emissions averaged 529 ± 469 ng N–N_2O m^{-2} s^{-1} after wetting soils with NO_3^- and NH_4^+ amended solutions, and returned to prewetting levels within four hours (Fig. 1a,c). However, desert N_2O emissions did not increase in proportion to adding more NO_3^- ($p = 0.12$) or NH_4^+ ($p = 0.89$, Table 2). In contrast to the desert, peak chaparral N_2O emissions averaged only 38.0 ± 72.0 ng N–N_2O m^{-2} s^{-1} after wetting with NO_3^- and NH_4^+amended solutions (Fig. 1b,d). As observed in the desert, N_2O emissions did not increase in proportion to adding NO_3^- ($p = 0.25$) or NH_4^+ ($p = 0.10$, Table 2).

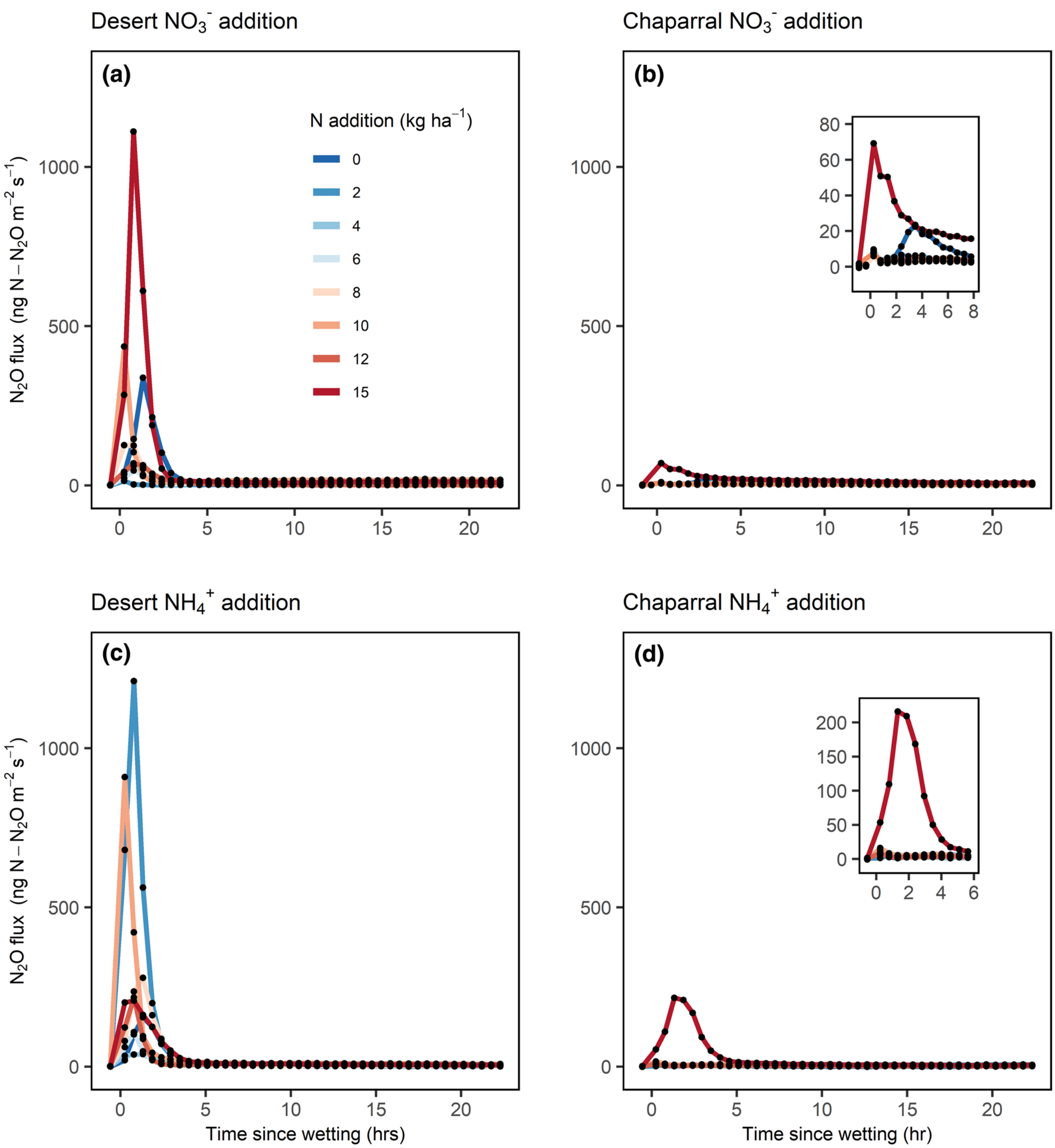

Fig. 1 Soil N_2O emissions (ng N–N_2O m^{-2} s^{-1}) over 24 h from the desert (**a**, **c**) and chaparral (**b**, **d**) following wetting of dry soils with nitrate (NO_3^-; **a**, **b**) or ammonium (NH_4^+; **c**, **d**) solutions. Each black dot represents flux measurements over a 2-min interval for each of the chambers

Rapid reduction of NO_3^- produced pulsed N_2O emissions at both sites. In response to 15 kg ha^{-1} equivalent NO_3^- addition, *[δ^{15}N]N_2O reached 1953 ‰ in the desert and 124 ‰ in the chaparral (Fig. 2a,b), whereas the *[δ^{15}N]N_2O of from soils amended with water only did not surpass 32.4 ‰ at either site. Peak *[δ^{15}N]N_2O 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 ‰

Table 2 Linear relationship between the added amount of NO_3^- or NH_4^+ and cumulative N_2O or NO emissions over the course of 24-h from either the desert or chaparral

Gas	N treatment	Site	Slope	Intercept	p-value	n	R^2
N_2O	NO_3^-	Desert	194	141	0.12	8	–
		Chaparral	50.4	94.1	0.25	6	–
	NH_4^+	Desert	– 20.6	2440	0.89	8	–
		Chaparral	86.1	– 101	0.10	8	–
NO	NO_3^-	Desert	1350	2940	0.28	8	–
		Chaparral	1370	– 1410	0.09*	6	0.56
	NH_4^+	Desert	1690	2520	0.07*	8	0.45
		Chaparral	779	2880	0.03**	8	0.58

Linear regression was performed to assess the relationship between the amount of N-added (kg N ha^{-1}) and cumulative N_2O or NO emissions (μg N m^{-2}). Coefficient of determination (R^2) and p-value of the linear regression are reported. Significance of the relationship is noted as: *$p < 0.10$, **$p < 0.05$, ***$p < 0.01$

(kg N $ha^{-1})^{-1}$, p = 0.089, Table S1). *[δ^{15}N]N_2O remained under 75 ‰ in NH_4^+-amended soils at both sites (Fig. 2c,d). Peak *[δ^{15}N]N_2O was positively correlated to NH_4^+ addition in the desert only ($R^2 = 0.50$, slope = 2.85 ‰ (kg N $ha^{-1})^{-1}$, p = 0.03), but the slope of this relationship was over 37 times smaller compared to NO_3^- addition (Table S1).

Soil NO and NH_3 emissions

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 NO_3^--amended soils (Fig. 3a) and 254 ± 200 ng N–NO m^{-2} s^{-1} in NH_4^+-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 NO_3^- amended soils (Fig. 3b) and 202 ± 154 ng N–NO m^{-2} s^{-1} in NH_4^+ amended soils (Fig. 3d).

In contrast to N_2O, isotopically labeled NH_4^+ and NO_3^- were both incorporated into the NO emitted at both sites. The ^{15}N labeled NO_3^- was rapidly converted to NO in the chaparral ($F_{3,9}$ = 93.8, p < 0.0001), enriching *[δ^{15}N]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 ^{15}N–NO_3^- label was detected in NO ($F_{3,9}$ = 1.7, p = 0.001) but not at 15 min (*[δ^{15}N]NO = 23.1 ± 7.33 ‰, p = 1.00); it was detected between 0.25 and 12 h, when *[δ^{15}N]NO reached 745 ± 202 ‰ (p = 0.003; Fig. 4a). The ^{15}N–NH_4^+ label took between 0.25 and 12 h to become incorporated into NO at both sites; *[δ-^{15}N]NO reached 949 ± 152 ‰ in the desert ($F_{3,9}$ = 12.1, p = 0.002; Fig. 4c) and 754 ± 132 ‰ in the chaparral ($F_{3,9}$ = 60.4, p < 0.001; Fig. 4d).

The natural abundance δ^{15}N– and δ^{18}O–NO values emitted from soils amended with only deionized water decreased over the course of the experimental incubation (Fig. 5). The *[δ^{18}O]NO decreased from approximately 10 ‰ prior to wetting to – 15 ‰ 24 h after wetting in both the chaparral ($F_{3,21}$ = 7.35, p = 0.002) and the desert ($F_{3,21}$ = 11.5, p = < 0.001). Similarly, *[δ^{15}N]NO decreased from approximately – 10 ‰ to – 40 ‰ over the course of the incubation in both the chaparral ($F_{3,21}$ = 5.29, p = 0.007) and the desert ($F_{3,21}$ = 5.15, p = 0.01).

Soil NO emissions increased in proportion to incremental NH_4^+ additions in the chaparral (R^2 = 0.58, p = 0.03, Fig. 6d), whereas in the desert, the relationship was positive but weak (R^2 = 0.45, p = 0.07, Fig. 6c). Adding NO_3^- may have increased NO emissions in the chaparral, but the relationship was weak (p = 0.09, Table 2); adding NO_3^- did not increase NO emissions in the desert (p = 0.28, Table 2).

Soil NH_3 emissions increased immediately after wetting both sites but remained higher in the desert

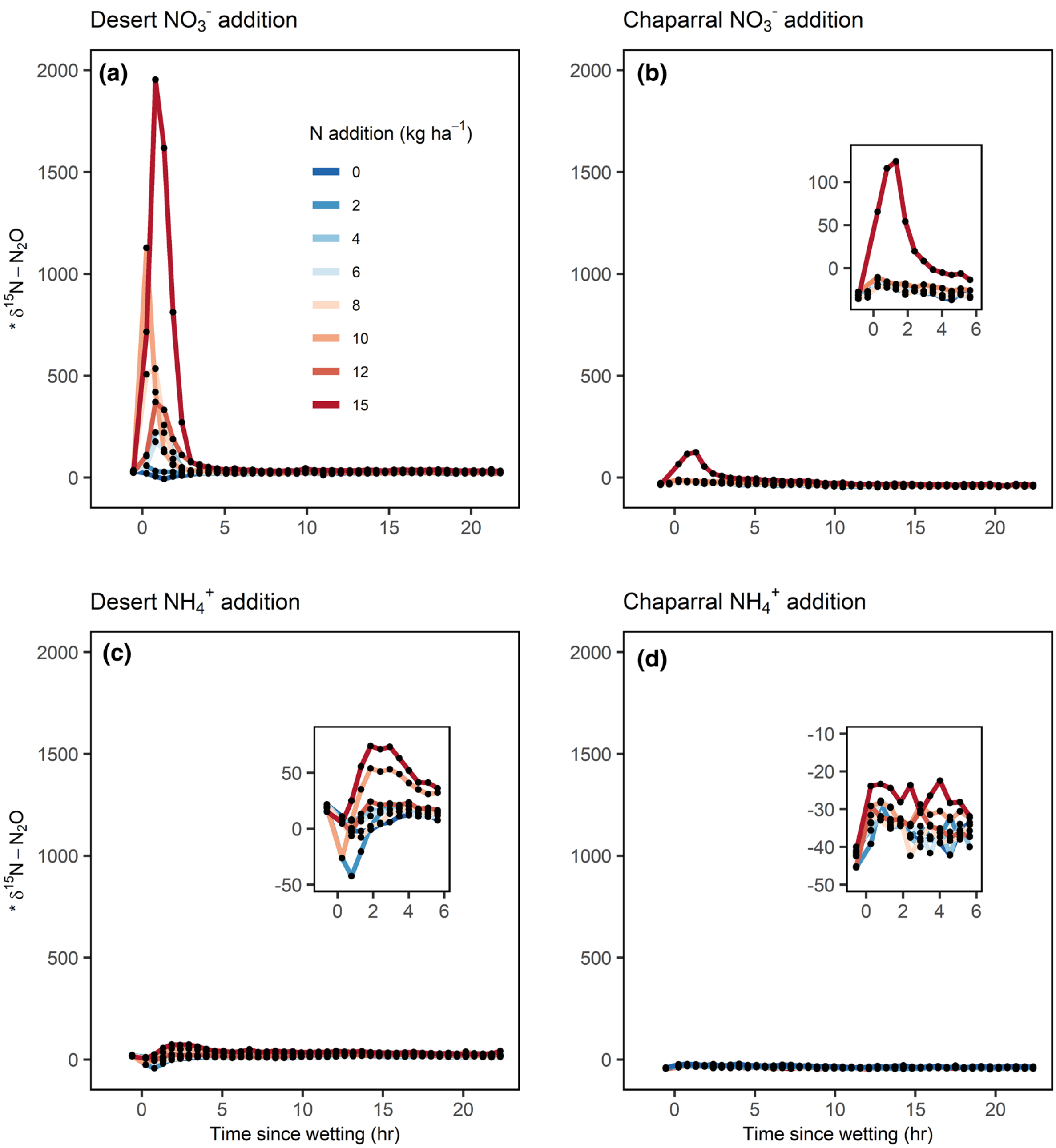

Fig. 2 Isotopic composition (*[δ-^{15}N]N_2O) of N_2O emitted over 24 h from the desert (**a**, **c**) and chaparral (**b**, **d**) following wetting of dry soils with nitrate (NO_3^-; **a**, **b**) or ammonium (NH_4^+; **c**, **d**) solutions. Each black dot represents the average isotopic composition of N_2O measured over the last 30 s from each chamber

relative to the chaparral (Fig S1). In the desert, NH_3 emissions averaged 27.3 ± 24.6 μg N–NH_3 m^{-2} h^{-1} between 0.25 and 12 h in NO_3^- amended soils; the NO_3^- treatment did not increase NH_3 emissions compared to soils amended with only water (Fig S1a). In NH_4^+ amended desert soils, NH_3 emissions averaged 52.5 ± 45.0 μg N–NH_3 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).

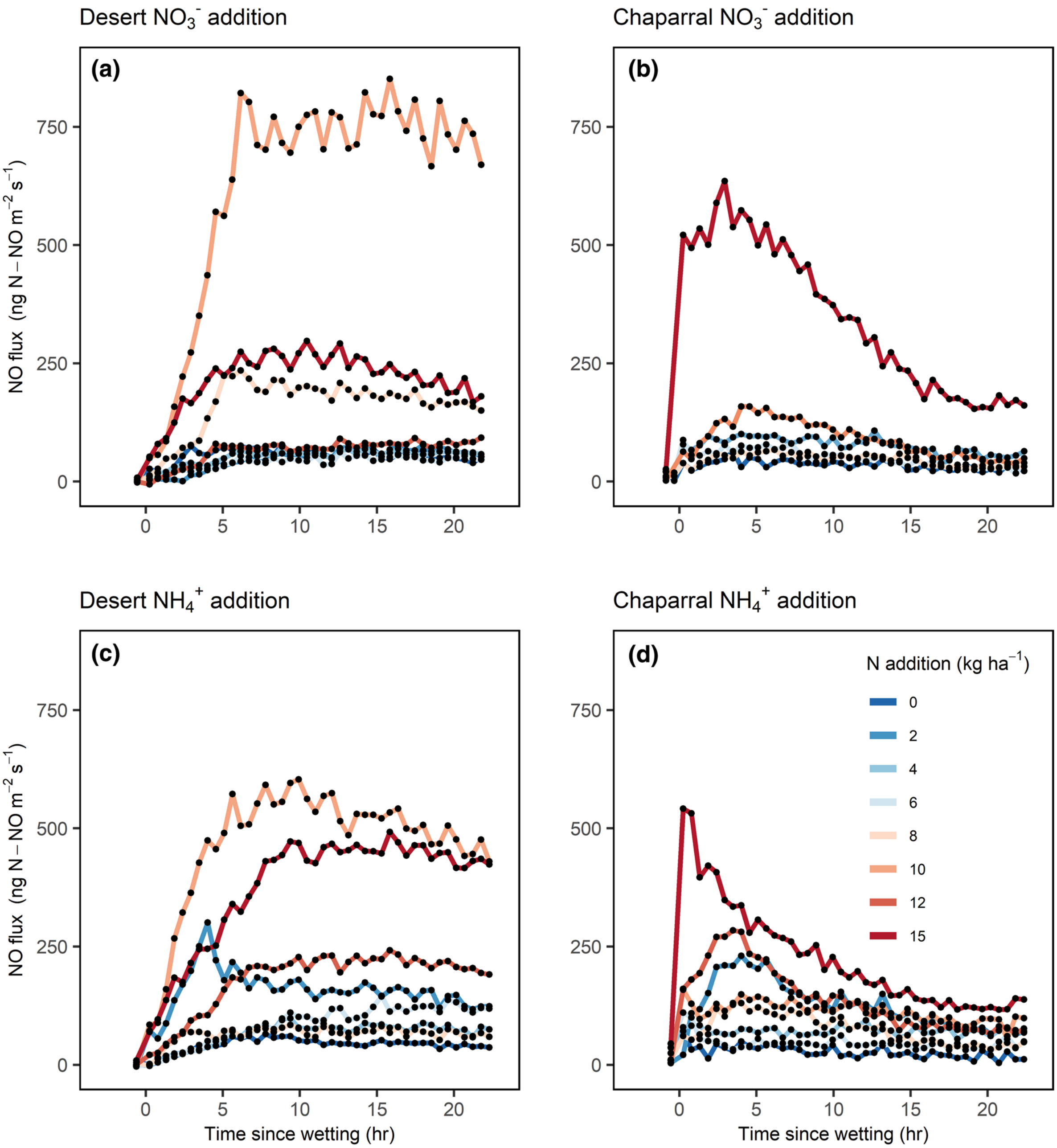

Fig. 3 Soil NO emissions (ng N–NO m^{-2} s^{-1}) over 24 h from the desert (**a**, **c**) and chaparral (**b**, **d**) following wetting of dry soils with nitrate (NO_3^-; **a**, **b**) or ammonium (NH_4^+; **c**, **d**) solutions. Each black dot represents flux measurements over a 2-min interval for each of the 8 chambers

Discussion

We investigated the dynamics of and mechanisms driving pulsed NO and N_2O 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

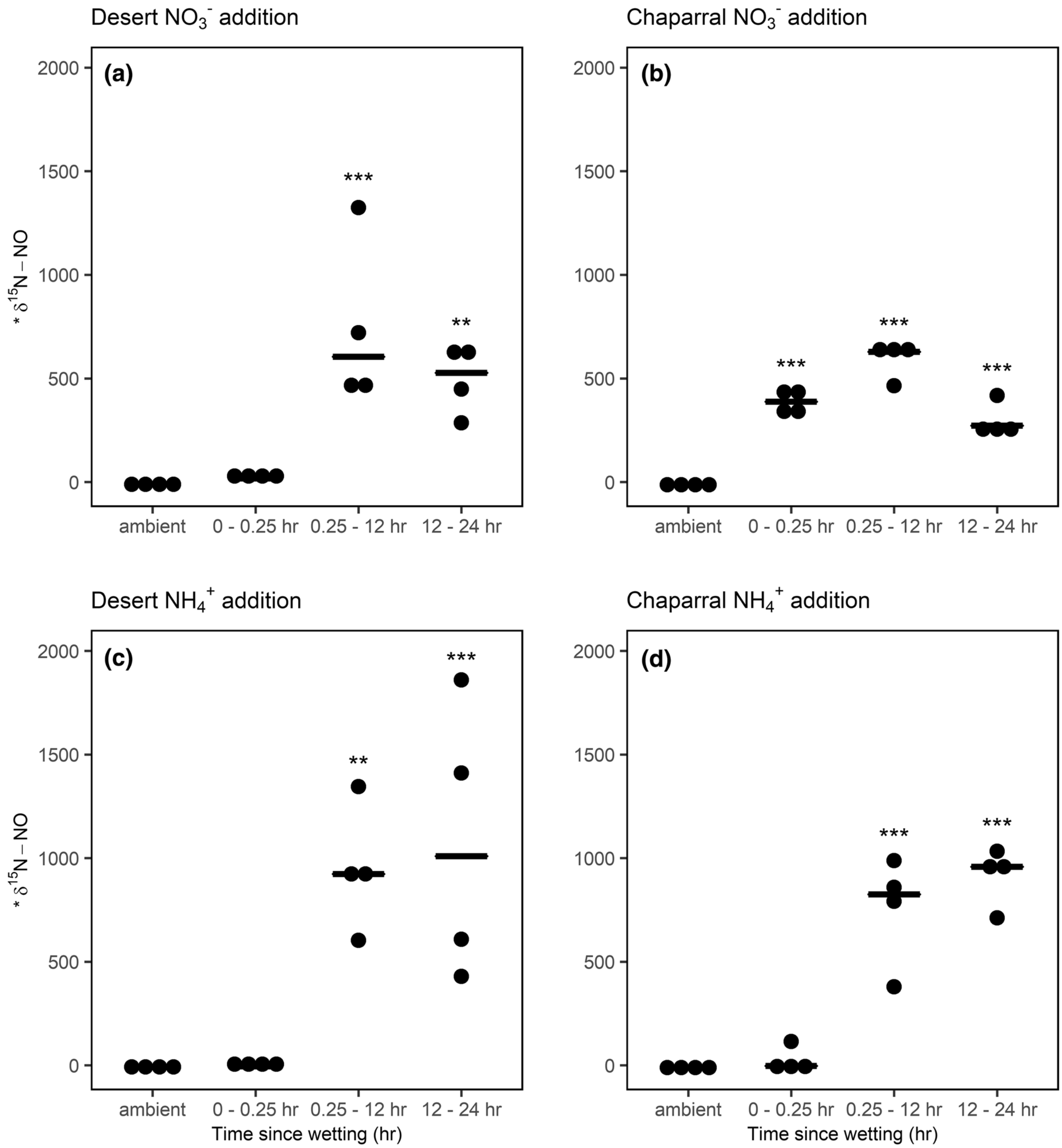

Fig. 4 Isotopic signature (*[δ-^{15}N]NO) of NO emitted from the desert (**a**, **c**) and chaparral (**b**, **d**) over 24 h after wetting dry soils with nitrate (NO_3^-; **a**, **b**) or ammonium (NH_4^+; **c**, **d**) solutions. Lines represent the mean [*δ-^{15}N]NO (n = 4) from each treatment within each site. Dots represent individual measurements using passive Ogawa samplers. Asterisks indicate if the mean for a given time differed from the control (*$p < 0.1$, **$p < 0.05$, ***$p < 0.01$)

suggesting that nitrification may control NO emission magnitude in these coarse-textured soils. In contrast, increasing N supply did not increase N_2O emissions at either site, which does not support the hypothesis that N_2O emissions are limited by NO_3^- or NH_4^+. While N addition did not stimulate N_2O emissions, N_2O was produced in part by the near-instantaneous reduction of NO_3^-, raising questions as to the

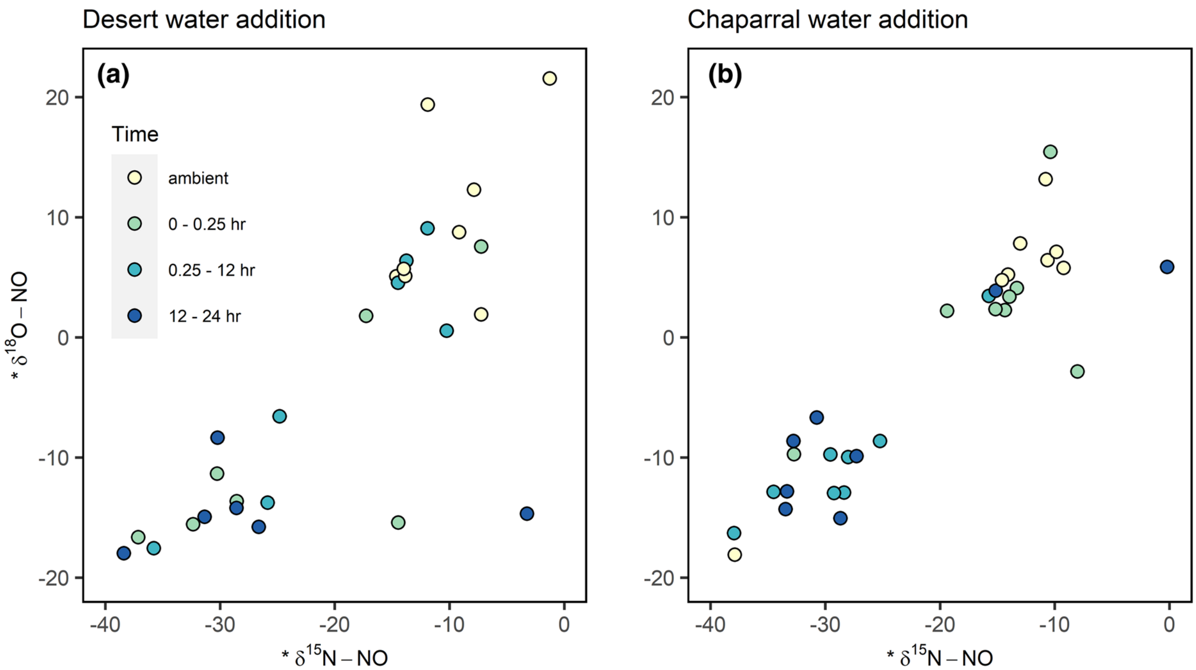

Fig. 5 Dual isotope plot of NO (*[δ-^{15}N]NO and *[δ-^{18}O] NO) produced after wetting dry soils from the desert (**a**) and chaparral (**b**) with 500 mL water. Colors correspond to timing of the isotopic signature of NO collected from ambient air and from soils after wetting. Each dot represents the isotopic composition of NO measured at each of the shrubs (n = 8). Isotopic NO composition is presented from shrubs receiving water-only additions

mechanisms driving NO_3^- reduction in these dryland soils and how factors controlling these emissions could help explain variation in N emissions across ecosystems.

N_2O emissions: controls and dynamics

While we expected N_2O to increase within minutes after wetting to produce large emission pulses (Eberwein et al. 2020), the incorporation of $^{15}N–NO_3^-$ tracer into N_2O 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 O_2 to stimulate N_2O 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 NO is produced as an obligate intermediate during denitrification, and our $^{15}NO_3^-$ tracer was not incorporated into NO within 15 min post-wetting in the desert (Fig. 4a), denitrification may not have contributed to rapid N_2O emissions. Besides biological processes, chemodenitrification can produce N_2O (Zhu-Barker et al. 2015; Heil et al. 2016; Harris et al. 2021), but the abiotic reduction of 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 $^{15}N–NO_3^-$ label in N_2O within 15 min of wetting dry soils at our site shows that dryland soils have the capacity to reduce NO_3^- immediately after wetting and argues for additional work identifying which processes contribute to rapid N_2O emissions.

Even though $^{15}N–NO_3^-$ was rapidly reduced to N_2O, adding more NO_3^- did not increase the magnitude of pulsed N_2O emissions. This suggests that the processes reducing NO_3^- to N_2O are not limited

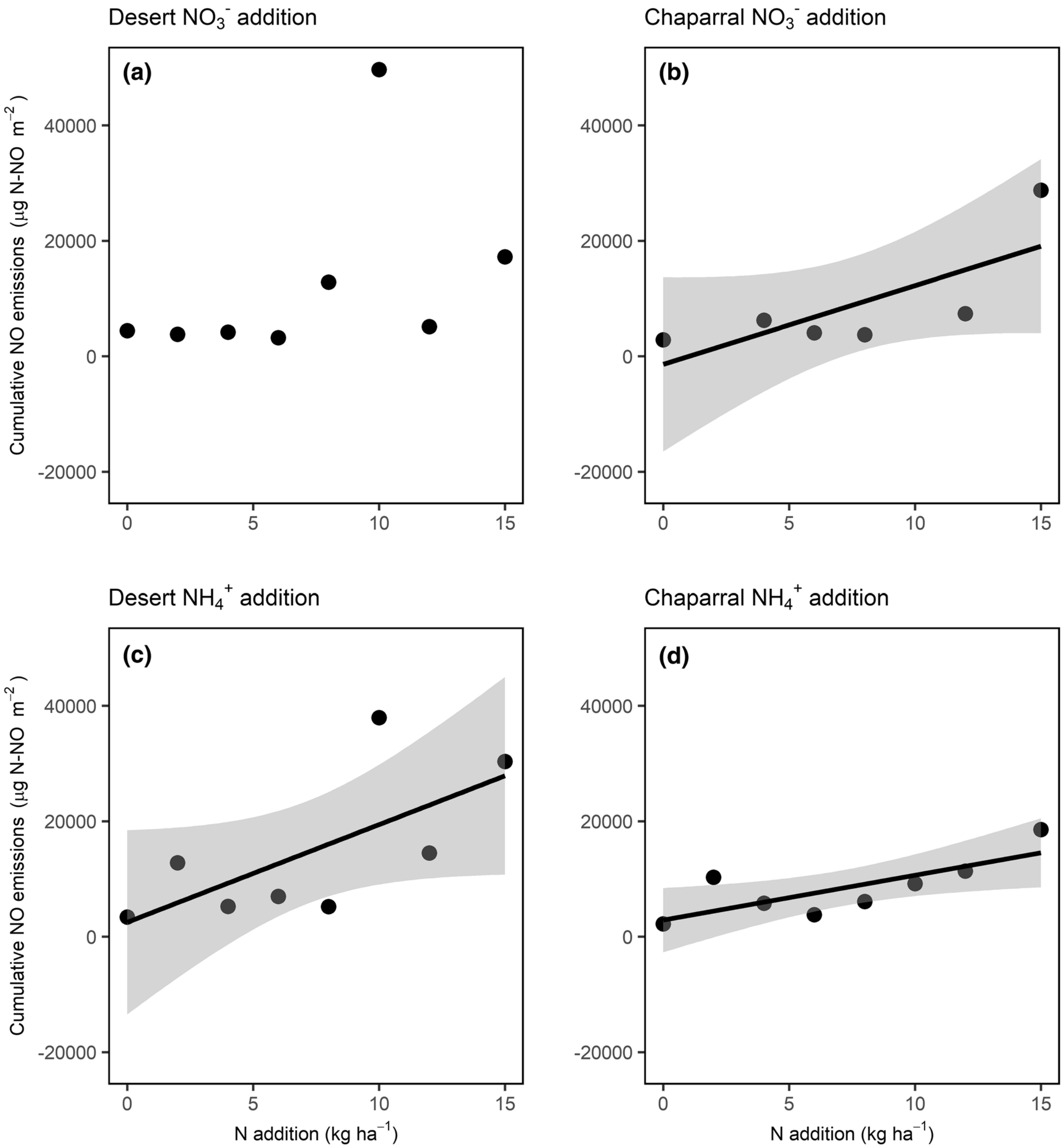

Fig. 6 Cumulative soil NO emissions (μg N–NO m^{-2}) from the desert (**a**, **c**) and chaparral (**b**, **d**) over 24 h after wetting dry soils with nitrate (NO_3^-; **a**, **b**) or ammonium (NH_4^+; **c**, **d**) solutions. Lines show the linear regression between added N and cumulative NO emissions. Shaded gray areas represent the 95% confidence interval for statistically significant linear regressions ($p < 0.1$)

by soil N availability (i.e., the size of the pipe), and that other factors regulate the magnitude of N_2O emissions. For example, more $^{15}N–NO_3^-$ tracer was reduced to N_2O 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 N_2O 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 N_2O (McCalley and Sparks 2009; Zhu-Barker et al. 2015). Average peak N_2O emissions from the desert were slightly higher compared to emissions measured in tropical forests (66.4 ng N–N_2O m^{-2} s^{-1}; Hall and Matson 2003) and temperate agricultural systems (355 ng N–N_2O 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 N_2O emissions. Indeed, N_2O 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 N_2O emissions. Despite this variation, documenting the rapid reduction of NO_3^- to form N_2O is an important step in identifying controls over dryland N_2O emissions.

NO emissions: controls and dynamics

Nitrification produced NO at our sites as supported by the detection of ^{15}N–NH_4^+ in NO (Fig. 4c,d) and the positive response of NO emissions to adding NH_4^+ (Fig. 6c,d). In addition to nitrification, denitrification also produced NO at both sites; ^{15}N–NO_3^- 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 NO_3^- reduction within hours of decreasing soil O_2 concentrations (Liu et al. 2019) and maintain this activity once aerobic conditions return (Roco et al. 2016). We also observed a simultaneous decrease in *[δ^{18}O]NO and *[δ^{15}N]NO over the course of the incubation at both sites, perhaps suggesting other processes produced NO (Fig. 5). While changes to *[δ^{18}O]NO and *[δ^{15}N]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 NO_2^-, which contains O from both water and air, whereas nitrification produces NO from NH_2OH, which contains only O from air (Andersson and Hooper 1983; Buchwald et al. 2012; Medinets et al. 2015; Boshers et al. 2019). As such, the change in *[δ^{18}O]NO may reflect incorporation of ^{18}O from the NO_2^- 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 ^{15}N by 28–60 ‰ (Robinson 2001), consistent with the simultaneous decrease in *[δ^{15}N]NO observed throughout the incubation. Abiotic reactions may have also contributed to soil NO efflux by converting nitrification intermediates—such as NO_2^- or NH_2OH—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 NH_4^+ 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 NH_4^+ 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 ^{15}N–NO_3^- 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 NH_3 emissions relative to the chaparral (Fig S1), consistent with higher soil pH favoring NH_3 production from the equilibrium between NH_3 and NH_4^+ (pKa = 9.25; Avnimelech and Laher 1977). This suggests the longer NO emission pulse in the desert could have been sustained by greater NH_3 diffusion through soil pore space and supply to nitrifiers even as drying soils may have limited nitrifier access to NH_4^+ in soil pore water (Stark and Firestone 1995). The role of NH_3 diffusion to nitrifiers may also help explain why the relationship between NH_4^+ addition and NO emissions was weaker in the desert; variable background NH_4^+ concentrations may have supplied NH_3 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 NO_3^- reduction (within 15 min) can occur even in coarse summer-dry desert soils under temperature extremes to produce N_2O. However, the N_2O emissions produced were insensitive to experimentally adding N. Identifying the processes that govern the rapid NO_3^- 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 N_2O, 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 N_2O 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/D1C39X.

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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