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RESEARCH ARTICLE

Soil NH_3 emissions across an aridity, soil pH, and N deposition gradient in southern California

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Soil ammonia (NH_3) emissions are seldom included in ecosystem nutrient budgets; however, they may represent substantial pathways for ecosystem nitrogen (N) loss, especially in arid regions where hydrologic N losses are comparatively small. To characterize how multiple factors affect soil NH_3 emissions, we measured NH_3 losses from 6 dryland sites along a gradient in soil pH, atmospheric N deposition, and rainfall. We also enriched soils with ammonium (NH_4^+), to determine whether N availability would limit emissions, and measured NH_3 emissions with passive samplers in soil chambers following experimental wetting. Because the volatilization of NH_3 is sensitive to pH, we hypothesized that NH_3 emissions would be higher in more alkaline soils and that they would increase with increasing NH_4^+ availability. Consistent with this hypothesis, average soil NH_3 emissions were positively correlated with average site pH ($R^2 = 0.88$, $P = 0.004$), ranging between 0.77 ± 0.81 μg N-NH_3 m^{-2} h^{-1} at the least arid and most acidic site and 24.2 ± 16.0 μg N-NH_3 m^{-2} h^{-1} at the most arid and alkaline site. Wetting soils while simultaneously adding NH_4^+ increased NH_3 emissions from alkaline and moderately acidic soils ($F_{1,35} = 14.7$, $P < 0.001$), suggesting that high N availability can stimulate NH_3 emissions even when pH is less than optimal for NH_3 volatilization. Thus, both pH and N availability act as proximate controls over NH_3 emissions suggesting that these N losses may limit how much N accumulates in arid ecosystems.

Keywords: Ammonia, Drylands, Nitrogen, pH, Rewetting, Nitrogen limitation

1. Introduction

Soil ammonia (NH_3) emissions are seldom reported in nutrient budgets but may be an important nitrogen (N) loss pathway that contributes to ecosystem N limitation (Schlesinger and Peterjohn, 1991; Soper et al., 2016). In general, ecosystem N limitation is established when N inputs (e.g., biological N fixation or atmospheric N deposition) are outpaced by outputs (e.g., hydrologic and gaseous N losses; von Sperber et al., 2017; Vitousek et al., 2021). However, in N-limited ecosystems, high biological demand for N may constrain N losses, such that even small N inputs accumulate until primary productivity is no longer N limited (Vitousek and Field, 1999; von Sperber et al., 2017; Vitousek et al., 2022). Therefore, for ecosystem N limitation to persist, N losses must occur even when primary productivity is limited by N and biological N demand is high (von Sperber et al., 2017; Vitousek et al., 2022). In this sense, soil NH_3 emissions may operate as *demand-independent* N losses (i.e., N losses that are uncontrollable by biological processes; von Sperber et al., 2017; Vitousek et al., 2022) because NH_3 volatilization can rapidly convert NH_4^+ to gaseous NH_3 when dry soils wet up, exporting N before it can be assimilated by plants (Schlesinger and Peterjohn, 1991; Soper et al., 2016). While the emission of other N trace gases (e.g., nitric oxide [NO] and nitrous oxide [N_2O]) can also occur as demand-independent N losses (Homyak and Sickman, 2014; Eberwein et al., 2020; Krichels et al., 2022), the factors that control NH_3 emissions from natural ecosystems have been relatively less studied and it is less clear how interactions among these factors control them. Understanding which factors control NH_3 losses from soils can help understand why ecosystems become limited by N and help reconcile why some ecosystems may experience substantial N losses even when they remain N limited (Wang et al., 2014; von Sperber et al., 2017).

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Soil pH regulates NH_3 emissions by controlling the partitioning between ammonium (NH_4^+) and NH_3; alkaline conditions (pKa = 9.3) deprotonate NH_4^+ producing NH_3 (i.e., NH_3 volatilization; Avnimelech and Laher, 1977; Schlesinger and Peterjohn, 1991; McCalley and Sparks, 2008; Soper et al., 2016). At the landscape scale, soil pH is regulated by multiple state factors (Jenny, 1980), with precipitation playing a dominant role (Slessarev et al., 2016). In general, wet regions accelerate weathering of base cations, lowering soil buffering capacity and pH, whereas dry regions constrain weathering, favoring alkaline soils (Slessarev et al., 2016), and, therefore, increasing the potential for NH_3 volatilization. Indeed, among the highest NH_3 emissions from nonagricultural ecosystems have been measured in alkaline drylands (McCalley and Sparks, 2008), especially after dry soils are wetted (Peterjohn and Schlesinger, 1990; McCalley and Sparks, 2008). Wetting dry soil frees N from microbial biomass, minerals, and aggregates (Birch, 1958; Austin et al., 2004; Kim et al., 2012), thereby flushing soil pores with N-bearing substrates—including NH_4^+—that favor N emissions before the N can be biologically assimilated (Peterjohn and Schlesinger, 1990; Homyak and Sickman, 2014; Eberwein et al., 2020; Krichels et al., 2022). Yet, wetting-induced NH_3 emissions are seldom measured in dryland ecosystems, limiting our ability to understand the factors that control emissions and their potential to regulate ecosystem N limitation.

Besides pH, soil N availability can also control NH_3 volatilization, with NH_3 emissions increasing with increasing soil NH_4^+ concentrations (Avnimelech and Laher, 1977). NH_4^+ fertilization produces large NH_3 fluxes in agricultural systems (Pan et al., 2016; Ma et al., 2021), suggesting that NH_4^+ inputs, including those from atmospheric N deposition, may also increase soil NH_3 emissions in unfertilized systems so long as pH is optimal (Schlesinger and Peterjohn, 1991; McCalley and Sparks, 2008; Sun et al., 2014). However, atmospheric N deposition can also acidify soils (Falkengren-Grerup, 1989; Fenn et al., 1996), which can limit NH_3 volatilization and, therefore, how much N could be lost as NH_3. Because wetting-induced NH_3 emissions have been measured in only a handful of drylands, the effects of aridity, pH, and N availability on NH_3 emissions and overall N limitation status remain largely uncharacterized, leading us to ask: How do soil pH and NH_4^+ supply interact to control NH_3 emissions?

To address this question, we measured in situ NH_3 emissions in response to adding water and NH_4^+ to soils from 6 sites in southern California dryland ecosystems that vary in soil pH, aridity, and atmospheric N deposition. Extending a transect eastward from the edge of greater Los Angeles, CA, soil pH increases from moderately acidic conditions close to the city to more alkaline conditions further east (**Table 1**). Simultaneously, soils across this gradient are exposed to over 16 kg N ha^{-1} yr^{-1} near Los Angeles—with localized studies measuring up to 29 kg N ha^{-1} yr^{-1} (Sickman et al., 2019)—and as low as 3 kg N ha^{-1} yr^{-1} further inland (Schwede and Lear, 2014; National Atmospheric Deposition Program, 2022; **Table 1**). We hypothesized that NH_3 volatilization would increase with soil pH and that wetting alkaline soils with NH_4^+ solutions would reduce substrate limitation of NH_3 volatilization and lead to higher NH_3 emissions.

2. Methods

2.1. Sites description

We studied 6 sites spanning a soil pH gradient in southern California, labeled alphabetically in order of increasing pH (**Table 1**)—A was the most acidic and F was the most alkaline. Across the soil pH gradient, acidic soils generally had higher annual precipitation (Slessarev et al., 2016), with the site closest to Los Angeles averaging approximately 279 mm yr^{-1} and the most eastern site in Joshua Tree National Park averaging approximately 101 mm yr^{-1} (Daly et al., 2007). Vegetation at the most acidic site (site A) is dominated by chamise (*Adenostoma fasciculatum*), whereas creosote shrubs (*Larrea tridentata*) dominate the increasingly alkaline sites B, C, D, E, and F. At all sites, soils are relatively coarse-textured, characterized as sandy loams through gravelly sands covering a mix of taxonomies (see Table S1). Soil NH_4^+ concentrations were lowest in site E (1.62 $\pm$ 1.10 μg N g^{-1}) and highest in site F (12.2 $\pm$ 6.73 μg N g^{-1}); concentrations did not follow patterns in atmospheric N deposition (**Table 1**).

Because of the proximity of our sites to Los Angeles, the sites fall along an atmospheric N deposition gradient; the highest N deposition rates occur near Los Angeles in the most acidic soils (**Table 1**). Because atmospheric N deposition can acidify soils (Falkengren-Grerup, 1989; Fenn et al., 1996), it is possible that, together with the effect of aridity on soil pH (Jenny, 1980), this anthropogenic factor also contributes to the observed gradient in soil pH across our sites.

2.2. Experimental design

We measured NH_3 emissions after adding water or NH_4^+ to soils from sites A and F in August 2018 and from sites B, C, D, and E in June 2020. While environmental conditions likely differed between the 2 sampling periods, soils from all sites were dry prior to wetting (<3.6% gravimetric water content). Wetting-induced soil NH_3 emissions were measured from underneath 4 shrubs to capture the islands of fertility, where soil nutrients are concentrated (Peterjohn and Schlesinger, 1990) and where previous work has shown high gaseous N emission rates (Eberwein et al., 2020; Krichels et al., 2022). All 4 shrubs were within a 10-m radius and were separated from one another by at least 1 m. At each of the 4 shrubs, we installed 2 polyvinyl chloride collars (20-cm diameter × 10-cm height; inserted 5 cm into the ground) under each of the canopies. One collar underneath each shrub was wetted with 500-mL deionized water, corresponding to approximately a 7-mm rainfall event, within the range of historically occurring rain events at the sites (mean rain event in 2019 and 2020 at site F = 6.4 mm; https://doi.org/10.21973/N3V66D). The other collar was wetted with a solution of ammonium chloride corresponding to 15 kg NH_4^+-N ha^{-1}, an N input rate within the range of annual atmospheric N deposition in drylands in southern California

Table 1. Location, soil pH, annual precipitation (Daly et al., 2007), soil inorganic N, atmospheric N trace gas concentrations (see Supplemental Methods), and modeled atmospheric N deposition rates (Schwede and Lear, 2014; National Atmospheric Deposition Program, 2022) at each of the 6 sites from this study

Variable	A	B	C	D	E	F
Lat	33.9696	33.9221	33.8961	33.9440	33.9041	33.6487
Long	−117.2994	−116.7577	−116.6868	−116.3949	−115.7233	−116.3776
Mean annual precipitation (mm)	279	299	246	145	101	142
Soil pH	5.77 ± 0.50	6.65 ± 0.25	7.00 ± 0.36	7.19 ± 0.27	7.50 ± 0.34	8.36 ± 0.19
Soil NO_3^- (μg N g^{-1})	6.60 ± 3.73	5.48 ± 3.46	7.08 ± 3.95	2.75 ± 1.11	2.76 ± 1.81	17.4 ± 25.0
Soil NH_4^+ (μg N g^{-1})	10.7 ± 6.59	8.92 ± 5.67	8.37 ± 3.39	7.86 ± 8.34	1.62 ± 1.10	12.2 ± 6.73
Ambient NH_3 concentration (ppb)	6.3	4.2	3.6	2.4	1.4	NA
Ambient NO_x concentration (ppb)	19.7	9.9	4.2	2.2	1.5	NA
Modeled N deposition (kg N ha^{-1})	16.9	9.3	8.2	4.5	3.0	4.2

NA indicates that data are missing from a site.

(Fenn et al., 2006; Eberwein et al., 2020). The collars were separated from each other by at least 50 cm to avoid cross-contamination of wetting solutions.

2.3. NH_3 emissions

We used passive NH_3 samplers to estimate soil NH_3 emissions in soil chambers at our sites. Immediately after adding water or NH_4^+ solution to soil collars, a chemically pretreated NH_3 sampler (Ogawa pads; Ogawa USA, Pompano Beach, FL) was placed on the ground inside the chamber and sealed by fitting a rubber lid on top of the collar; the sampler was housed within a vented plastic container to prevent contact with the soil and contamination. Collar lids were then covered with aluminum foil to minimize heating from solar radiation. To minimize the chance that NH_3 would saturate our passive samplers and to capture discrete periods of NH_3 emissions, we replaced the NH_3 samplers with new ones at predetermined time intervals. In 2018, passive samplers were deployed to collect NH_3 from 0 to 15 min, 15 min to 12 h, and 12 h to 24 h postwetting. The chambers were open for approximately 10 s when new passive samplers were installed, which allowed some NH_3 to escape (based on our 15-min emission rates [Figure S1], we estimate less than 0.1% of the total NH_3 emitted escaped from site F while the chambers were open). Because the samplers did not saturate with NH_3 in 2018 (reaching as high as 50 μg N-NH_3 out of a theoretical maximum of 290–875 μg N-NH_3; Roadman et al., 2003), passive samplers were installed for 2 intervals in 2020: 0 to 15 min and 15 min to 24 h postwetting. All 8 collars within a given site were wet within a 30-min period starting at approximately 9:00 in the morning. For each site, 4 NH_3 samplers were used as blanks; they were placed adjacent to collars in sealed plastic bags to prevent the adsorption of atmospheric NH_3.

To measure how much NH_3 accumulated on each passive sampler, the samplers were extracted in 8 mL of deionized water overnight and analyzed for NH_4^+ at the University of California, Riverside, Environmental Sciences Research Laboratory (https://envisci.ucr.edu/research/environmental-sciences-research-laboratory-esrl). The NH_4^+ concentration of this solution was measured using a colorimetric assay (SEAL methods Environmental Protection Agency 126-A) with a SEAL AQ-2 discrete analyzer (SEAL analytical, Mequon, WI). To calculate total NH_3 fluxes for each chamber, we summed the amount of NH_3 collected on each NH_3 sampler (minus NH_3 from the blanks) incubated within each chamber. The sum of NH_3 was then divided by the time the chamber was closed (approximately 24 h) to estimate NH_3 emission rates. Because NH_3 may have been emitted throughout the 24-h incubation and rates of NH_3 absorption to the passive samplers are concentration-dependent, it is unlikely that the passive samplers collected all the NH_3 within a chamber for a given sampling period. However, passive samplers work well during short chamber incubations (Yu and Elliott, 2017) and have been successfully deployed to measure the fluxes of nitric oxide (Osborne et al., 2022). As such, while we acknowledge that our measurements likely underestimate NH_3 fluxes, they provide a reasonable estimate of how NH_3 emissions vary across sites and allow for comparisons among sites in response to adding N.

2.4. Statistical analyses

All statistical analyses were conducted using R 3.6.1 (R Core Team, 2019). We used analysis of variance to determine whether NH_3 emissions differed between sites and in response to adding NH_4^+; NH_3 emissions were the response variable, while site and N addition were the predictor variables. Model residuals were assessed for normality using Shapiro–Wilk's tests; log transformations were applied to NH_3 emissions. We used linear regression to determine whether soil pH was related to average NH_3 emissions in response to water addition from each site. Log-transformed average NH_3 emissions from each site were included as the response variable, and average soil pH at each site was included as the predictor variable.

3. Results

Over the 24 h after adding water to soils, NH_3 emission rates averaged 6.51 ± 10.9 μg N-NH_3 m^{-2} h^{-1} (± standard deviation) across all sites (**Figure 1**). Soil NH_3 emissions differed among sites ($F_{5,34} = 11.0$, $P < 0.001$); they were highest at the most alkaline site (site F; 24.2 ± 16.0 μg N-NH_3 m^{-2} h^{-1}) and lowest at the most acidic site (site A; 0.77 ± 0.81 μg N-NH_3 m^{-2} h^{-1}). Overall, site-averaged NH_3 emissions were positively correlated with soil pH (adjusted $R^2 = 0.88$, $P = 0.004$, **Figure 2A**). The positive relationship between NH_3 emissions and pH was also present when results from 3 other studies measuring NH_3 emissions from nonagricultural ecosystems were included in the model (adjusted $R^2 = 0.92$, $P < 0.001$, **Figure 2B**, Table S1).

Wetting with NH_4^+ solutions increased NH_3 emissions relative to adding only water over the 24 h post-wetting ($F_{1,34} = 14.7$, $P < 0.001$). In our most alkaline site (F), NH_3 emissions were 3 times higher in NH_4^+-amended soils (73.4 ± 39.7 μg N-NH_3 m^{-2} h^{-1}) than in soils wetted with only water (24.2 ± 16.0 μg N-NH_3 m^{-2} h^{-1}), but at our most acidic site (A) emissions were only 1.3 times higher in NH_4^+-amended soils (1.03 ± 1.71 μg N-NH_3 m^{-2} h^{-1}) than in soils wetted with only water (0.77 ± 0.81 μg N-NH_3 m^{-2} h^{-1}; **Figure 1**). NH_3 emissions from NH_4^+-amended soils were also positively correlated with average soil pH (adjusted $R^2 = 0.81$, $P = 0.009$, **Figure 2C**).

4. Discussion

By measuring NH_3 emissions in soils across a gradient in pH, aridity, and atmospheric N deposition, we show that NH_3 emissions generally increase in more alkaline and arid soils, supporting our hypothesis that NH_3 emissions would increase with soil pH. However, adding NH_4^+ increased NH_3 emissions in all but the most acidic site, suggesting that increasing N availability can overcome pH limitation of NH_3 emissions in slightly acidic soils. Below, we discuss how these controlling factors on soil NH_3 emissions may contribute to varying N losses from ecosystems that range in soil pH, atmospheric N deposition, and precipitation.

Soil NH_3 emissions were positively correlated with site pH whether soils were wetted with water or NH_4^+ solution, consistent with pH operating as a proximate control over NH^3 emissions (Avnimelech and Laher, 1977). However, these emissions varied substantially within each site (e.g., 0.77 ± 0.81 in site A and 24.2 ± 16.0 μg N-NH_3 m^{-2} h^{-1} in site F), likely due to microscale variation in soil and environmental factors known to govern trace gas emissions (e.g., soil moisture, temperature, texture, and substrate availability; Firestone and Davidson, 1989). While accounting for more soil and environmental factors could have improved the observed within-site variation in NH_3 emissions, we were still able to detect an effect of pH on NH_3 emissions across our landscape-scale pH gradient, suggesting it is a dominant control. Indeed, the most

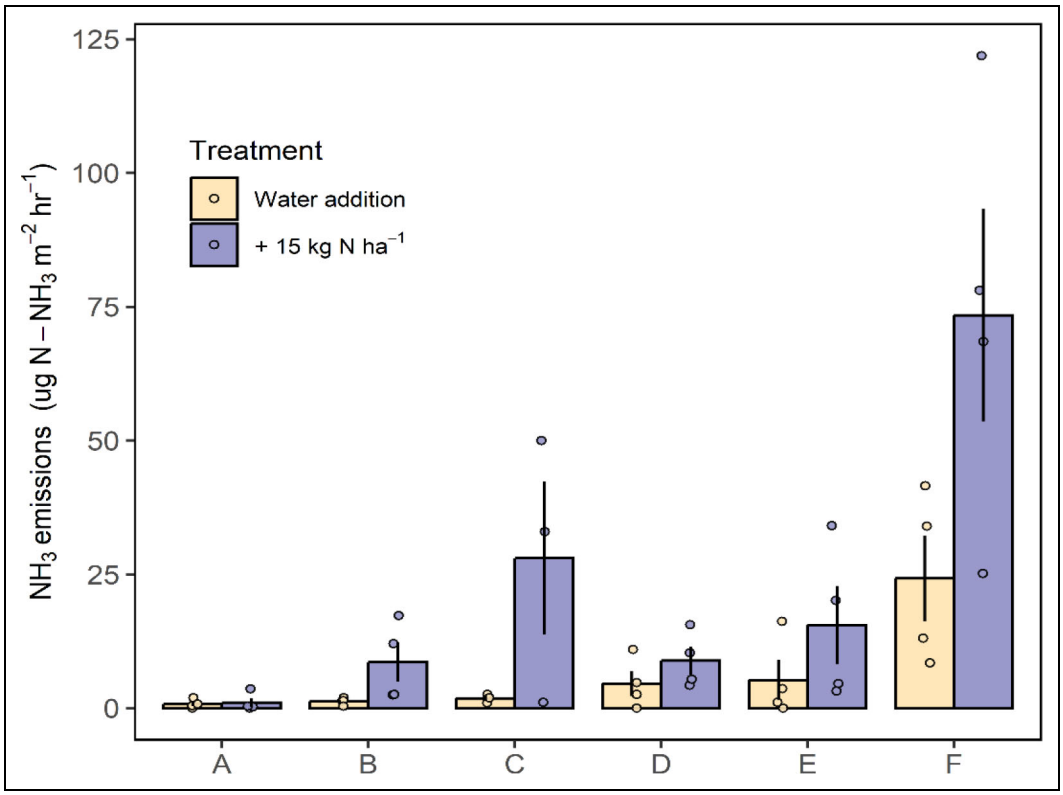

Figure 1. Average soil ammonia (NH_3) emissions at each site after adding water or 15 kg N-NH_4^+ ha^{-1} addition. Bars represent the mean NH_3 emissions, lines the standard error of the mean ($n = 4$ per site), and dots represent individual measurements. Sites are arranged in order of pH, with site A being the most acidic and site F the most alkaline.

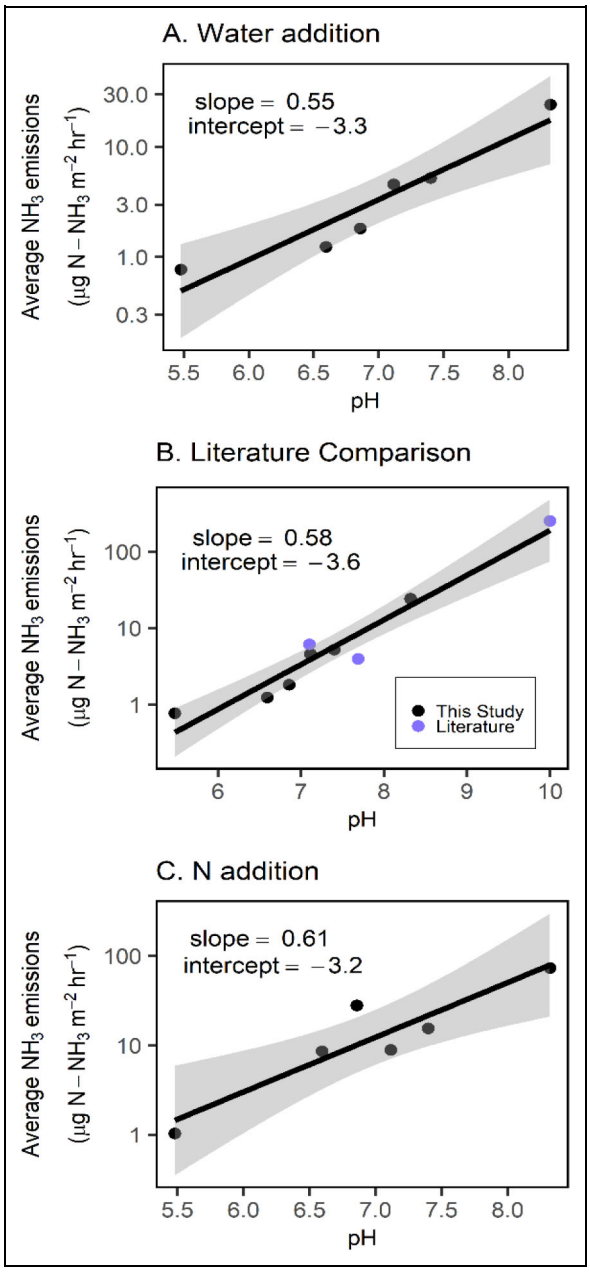

Figure 2. Relationship between mean soil pH and mean log-transformed ammonia (NH_3) emissions over the 24 h after wetting (A and B) or 15 kg N-NH_4^+ ha^{-1} addition (C) at each site. Lines show the linear regression between mean soil pH and mean log-transformed NH_3 emissions at each site. Shaded gray areas represent the 95% confidence interval for statistically significant linear regressions ($P < 0.05$). Panel B includes NH_3 emissions and soil pH from 3 studies conducted in nonagricultural ecosystems (Table S1). We used pH 10 as the average pH for the study by McCalley and Sparks (2008) that reported a range in pH from 9 to 11.

alkaline site in our gradient (F) produced the most NH_3 over 24 h postwetting (**Figure 1**) with the emissions being over 20 times higher than in woody clusters within a remnant grassland (pH = 7.1; Soper et al., 2016) and 4 times higher than in deserts (pH = 7.69; Schlesinger and Peterjohn, 1991; **Figure 2B**; Table S2). However, emissions at our most alkaline site were 10 times lower than wetting-induced emissions from the highly alkaline Mojave Desert (pH = 9–11; Table S2; McCalley and Sparks, 2008), consistent with increasingly alkaline soils driving higher rates of NH_3 volatilization. Furthermore, our results align well with other studies measuring NH_3 emissions, illustrating a consistently positive relationship between soil pH and NH_3 emissions (**Figure 2B**), and reinforcing the role of pH as a major control over NH_3 emissions. This consistent positive relationship between pH and NH_3 emissions may also be most pronounced in coarse-textured desert soils—like those in our study sites—that are often characterized by low cation exchange capacity, favoring deprotonation of NH_4^+ to NH_3 over the binding of NH_4^+ to soil surfaces (Schlesinger and Peterjohn, 1991). Altogether, our measurements suggest that arid and alkaline soils with low cation exchange capacity are particularly susceptible to losing N via NH_3 volatilization.

While NH_3 emissions were highest in the most alkaline and arid site, adding NH_4^+ still increased NH_3 emissions in all but the most acidic site, where low pH (5.8) likely constrained NH_3 volatilization (Avnimelech and Laher, 1977). However, adding NH_4^+ still increased NH_3 emissions in moderately acidic soils (pH = 6.7), suggesting that adding NH_4^+ can shift the equilibrium between dissolved NH_4^+, NH_3, and H^+ in soil pore water to produce more NH_3 so long as H^+ concentrations are not exceedingly high (Avnimelech and Laher, 1977; Sun et al., 2014). Our data show that adding N shifted this equilibrium when soil pH was somewhere between 5.8 and 6.7, suggesting that in sites with high rates of atmospheric N deposition, NH_3 may be emitted even in moderately acidic soils if excess N overcomes pH restrictions on NH_3 volatilization.

Relative to the emission of other N-bearing trace gases, NH_3 emissions (between 0.77 ± 0.81 and 24.2 ± 16.0 μg N-NH_3 m^{-2} h^{-1}) were smaller than nitrogen oxide losses measured at nearby sites. Peak NO emissions from some drylands can exceed 700 μg N-NO m^{-2} h^{-1} (Homyak and Sickman, 2014; Eberwein et al., 2020), and peak N_2O emissions can exceed 2,100 μg N-N_2O m^{-2} h^{-1} (Eberwein et al., 2020; Krichels et al., 2022). In contrast, average NH_3 emissions did not surpass 25 μg N-NH_3 m^{-2} h^{-1} in any of our sites, though some of our passive samplers exposed for only 15 min postwetting exceeded 80 μg N-NH_3 m^{-2} h^{-1} (Figure S1). While these rates are low compared to NO and N_2O emissions, NH_3 emissions increased after adding NH_4^+, suggesting that NH_3 emissions may become increasingly important in systems, where NH_4^+/NH_3 atmospheric inputs are increasing (Decina et al., 2020).

5. Conclusions

We show that in situ NH_3 emissions were highest in the most arid and alkaline soils. While soil pH is a well-established control on NH_3 volatilization, we found that increasing N availability can help overcome pH limitation of NH_3 volatilization even in moderately acidic soils. These demand-independent NH_3 losses upon wetting dry soils are particularly large in alkaline drylands, where they may

allow ecosystem N limitation to persist despite anthropogenic N inputs.

Data accessibility statement

All data presented in this study are available in the Dryad database (Krichels, 2023).

Supplemental files

The supplemental files for this article can be found as follows:

SI_Material.Docx

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Competing interests

PMH is an associate editor at *Elementa* but did not have a role in the reviewing or handling of this manuscript. The authors declare no other competing interests.

Author contributions

Contributed to conception and design: AHK, PMH, ELA, JOS, JB, ACG, HMA, HS, SP, GDJ.

Contributed to acquisition of data: AHK, PMH, ELA, JOS, JB, ACG, HMA, HS, SP, GDJ.

Contributed to analysis and interpretation of data: AHK, PMH, GDJ.

Drafted and/or revised this article: AHK, PMH, GDJ.

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