PROCESSES CONTROLLING AMMONIA VOLATILIZATION FROM CHIHUAHUAN DESERT SOILS

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Summary—Ammonia volatilization was measured at three sites in the Chihuahuan Desert of southern New Mexico, U.S.A. In dry soils, ammonia volatilization ranged from 9 to 11 μg N m^{-2} day^{-1}, but rates increased to 95 μg N m^{-2} day^{-1} in a shrubland site after an experimental addition of water. Ammonia volatilization also increased with experimental additions of NH$_4$Cl and decreased with additions of sucrose. Competition by nitrifiers for available NH$_4^+$ had little effect on NH$_3$ volatilization; N-Serve, added to inhibit nitrification, decreased NH$_3$ volatilization in a grassland site and had little effect at other sites. We suggest that NH$_3$ volatilization is controlled by the rate of mineralization of NH$_4^+$ from soil organic matter, and mineralization is stimulated by rainfall. Overall rates of NH$_3$ volatilization from undisturbed desert ecosystems appear to be much lower than those reported for rangeland and agricultural soils.

INTRODUCTION

When soil pH exceeds 7.0, NH$_3$ gas is formed by the deprotonization of NH$_4^+$, viz.:

$$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O.$$
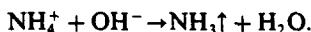
This reaction accounts for the loss of significant amounts of NH$_3$ and urea fertilizers applied to agricultural soils in arid and semi-arid regions (Terman, 1979). Losses of NH$_3$ from fertilized agricultural soils and from vertebrate excretion are thought to account for most of the NH$_3$ in the atmosphere (Buijsman *et al.*, 1987). Since NH$_3$ is highly soluble in water, volatilization from moist soils is minimal. The loss of NH$_3$ is greatest from coarse, dry soils with limited cation exchange capacity (Nelson, 1982; Freney *et al.*, 1983; Fleisher *et al.*, 1987).

Little is known about the loss of NH$_3$ from non-agricultural soils (Warneck, 1988). Many native soils in arid regions have alkaline pH and may be a significant source of NH$_3$ to the atmosphere (Dawson, 1977). In the absence of exogenous inputs, NH$_4^+$ in soils is derived from the mineralization of soil organic N. Loss of NH$_3$ is affected by the rate of nitrification, cation exchange and biotic immobilizations that compete for NH$_4^+$ (Fig. 1). Plant growth in many desert ecosystems is limited by available N during the wet season (Fisher *et al.*, 1988), and gaseous losses of N represent an important potential loss of soil fertility (Peterjohn and Schlesinger, 1990). We have examined the processes controlling the loss of gaseous NH$_3$ from Chihuahuan Desert soils.

We hypothesized that if the rate of nitrification limits the loss of NH$_3$ from desert soils, then the rate of NH$_3$ volatilization should increase when nitrification is inhibited experimentally (Fig. 1). Similarly, if microbial immobilization of NH$_4^+$ inhibits the loss of NH$_3$, then the loss of NH$_3$ should decline when labile organic C is added. If the availability of NH$_4^+$ determines the loss of NH$_3$, then losses should increase when NH$_4^+$ is added or when added water stimulates the rate of N mineralization from native organic matter.

MATERIALS AND METHODS

Field investigations were made on the New Mexico State University Ranch, 40 km NNE of Las Cruces, N.M. in the Jornada Del Muerto Basin. The experimental plots were established at three sites along the desert Long Term Ecosystem Research (LTER) transect that crosses the alluvial piedmont of Mount Summerford in the Doña Ana Mountains. One site was located in a grassland dominated by *Bouteloua eriopoda* in the upper reaches of the piedmont. A second site was in a mid-slope position in a shrubland dominated by *Larrea tridentata*, an invasive desert species (Buffington and Herbel, 1965). The third site was located in an ephemeral dry lake, or *playa*, dominated by *Panicum obtusum*, at the base of the piedmont. Mean annual rainfall is 23 cm, with roughly 50% falling during July, August, and September.

Soils in the grassland and shrubland sites are derived from the quartz monzonite bedrock of Mount Summerford; soils in the playa are derived from ancestral Rio Grande river deposits with smaller amounts of Mount Summerford alluvium. Soils are described by Wierenga *et al.* (1987) and Lajtha and Schlesinger (1988), and basic soil characteristics are given in Table 1. Grassland and shrubland soils contain 70–80% sand, whereas playa soils are 57% clay in the < 2 mm fraction. Playa soils also had much higher concentrations of NH$_4^+$ and NO$_3^-$ at the beginning of this study. At the shrubland site, erosion of the upper horizons of the soil has exposed a Pleistocene-age calcic horizon near the surface, accounting for the high soil pH at that site.

Five experimental plots (= blocks) were located at each site. The blocks were chosen subjectively to include the range of local soil and vegetation conditions at each site. Each block contained 16 tubes
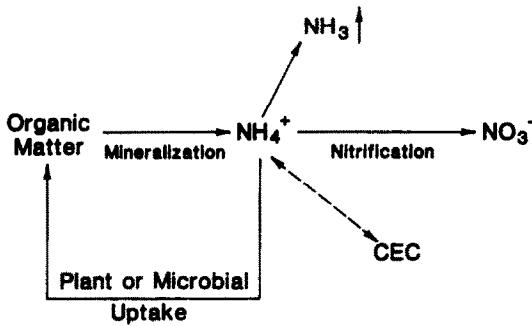
Fig. 1. Processes regulating the availability of NH_4^+ in the soil.

that were used to collect NH_3 lost from *in situ* soil columns subjected to one or more experimental treatments. Tubes, made of 30-cm lengths of 10-cm diam PVC pipe, were pounded into the soil for half their length on 8–10 June 1988.

After a 10-day equilibration period, NH_3 was collected in each tube for 24 h using 10 ml of 2% H_2SO_4 in a small open vial. During the collection the tubes were covered with aluminum foil held with a rubber band. Silicon grease was used to ensure a tight seal between the tube and the foil covering. This initial collection was made to compare natural rates of NH_3 volatilization from all soils before experimental manipulations. To further characterize the initial conditions, soils collected from each plot were measured for water content (% mass loss after 48 h at 110°C), pH in 10 mM $CaCl_2$, and concentrations of NH_4^+ and NO_3^- in 2 M KCl extracts.

On 20 June 1988, four experimental treatments, comprising a full factorial design with one replicate per block, including an unmanipulated control, were imposed on each block. Wet tubes received 220 ml distilled water (2.75 cm), chosen to bring the 15-cm soil column to field capacity (0.01 MPa potential) as determined from the moisture tension release curves of Schlesinger *et al.* (1987). Fertilized tubes received 10 ml of water containing 70 mg of N as NH_4Cl, to achieve $10\times$ the typical NH_4^+ pool found in the surface soils at this site (Lajtha and Schlesinger, 1986). Tubes with added organic C received 10 ml of water containing 26 g sucrose, chosen to add approx-

imtely $10\times$ the natural amount of labile organic C to the soil. Finally, N-serve® (Nitrapyrin) was added to tubes, using 10 ml of a solution of 3.67 g l^{-1} mixed in acetone to achieve the field concentration of 20 mg kg^{-1} recommended by Bundy and Bremner (1973) to inhibit nitrification. In each block, treatments were randomly assigned to tubes, and all solutions were applied to the surface, except for N-serve, which was injected to *ca.* 5-cm depth using a 0.89-mm dia needle. NH_3 was collected during 24-h periods beginning on 21 June and 23 June and a 7-day period beginning on 29 June, using the procedures described above. The tubes were left uncovered between collection times to allow the normal course of soil drying.

A second set of experiments was established in the grassland in June 1989. Water, N-serve and CaC_2-generated C_2H_2 were applied in a full 3-way factorial design in 8 tubes in each of 10 blocks, each of which included an unmanipulated control tube. Water and N-serve were applied as in 1988. C_2H_2 was applied by covering these tubes with a PVC cap and injecting 30 ml C_2H_2 into the headspace through a rubber septum. The volume was chosen to greatly exceed the 10 Pa level, which is found, in short-term exposures, to cause a persistent inhibition of nitrification in soils (Berg *et al.*, 1982; Hyman and Wood, 1985). The syringe was pumped several times to ensure mixing of the C_2H_2 into the soil pore space. After 10 min the cap was removed, and all tubes were allowed to equilibrate in the field for 24 h. NH_3 was collected during the subsequent 24 h using the 1988 procedures. Following gas collections, the columns were removed, the soil was homogenized and sieved (<2-mm), and subsamples were extracted with 0.5M K_2SO_4 to determine NH_4^+ concentrations.

NH_4^+ was determined in the H_2SO_4 solutions using a TrAAcs® 800 autoanalyzer and Industrial Method NO 786-86T for total N (Bran and Luebbe, 1986). Standards were mixed in aliquots of the same H_2SO_4 solution used in the field collections. Anomalous high values were found in 30 vials (3%) that were contaminated by ants; these were deleted from subsequent statistical treatments. Concentrations of NH_4^+ and NO_3^- in the KCl and K_2SO_4 extracts were determined following standard procedures on the autoanalyzer.

Table 1. Soil and vegetation characteristics at the study sites

Site	Grassland	Shrubland	Playa
Dominant vegetation	*Bouteloua eriopoda*	*Larrea tridentata*	*Panicum obtusum*
Soil classification	Ustollic Haplargid*	Typic Haplargid*	Typic Torrerts[a]
Surface soil characteristics			
Physical			
% sand[a]	76	80	10
% clay[a]	7	8	57
% $CaCO_3$[b]	0.68	1.06	3.36
% organic C[b]	0.48	0.19	2.91
Chemical			
pH (in 10 mM $CaCl_2$)[b]	7.02	7.69	7.57
NH_4-N (mg kg^{-1})[c]	1.13	2.15	10.24
NO_3-N (mg kg^{-1})[c]	0.57	0.61	6.75
Moisture (% of fresh mass)[c]	0.95	1.06	5.65

*Lajtha and Schlesinger (1988).
[a]Wierenga *et al.* (1987), 0–30 cm depth.
[b]W. T. Peterjohn, unpublished Ph.D. thesis, Duke University (1990), 0–5 cm depth.
[c]This study on 20 June 1988, 0–15 cm depth.

Table 2. NH₃ volatilization from Chihuahuan Desert soils. All values are $\mu g \, N \, m^{-2} \, day^{-1}$ (± 1 SE), averaged across all treatments. For 168 h, values are daily mean for the 7-day period

Time (h)	Grassland	Shrubland	Playa	Mean
Pretreatment	9.02 (2.51)	9.90 (2.59)	11.02 (2.85)	9.97 (1.52)
24	205.54 (32.60)	668.28 (107.27)	375.79 (69.40)	417.59 (45.67)
48	98.56 (13.97)	271.47 (56.91)	202.67 (33.27)	190.96 (22.82)
168	124.21 (22.64)	397.04 (71.76)	222.59 (32.77)	251.05 (29.16)
Mean	109.18	340.02	204.40	

RESULTS

Spatial and temporal variation, 1988

Before experimental manipulations were applied, losses of NH₃ were small, and there was no significant difference among the sites (Table 2). These soils were dry (Table 1), the most recent rainfall having delivered 7.1 mm of water on 13 June 1988. When averaged over all treatments and times, loss of NH₃ was greatest from the shrubland and least from the grassland. When averaged over all treatments and vegetation zones, losses were greatest immediately after the experimental manipulations. With the deletion of the initial collections, which showed no differences, analysis of variance (ANOVA) shows that time and vegetation zone are significant main effects (Table 3). There were no significant block effects, and in all subsequent considerations, the blocks within each vegetation zone are composited, so that $n = 5$ for each treatment during each collection period.

Treatment effects, 1988

All experimental treatments had significant main effects on the rate of NH₃ volatilization in one or more vegetation zones (Table 4). Additions of water and NH₄⁺ always stimulated the rate of NH₃ loss. The addition of sucrose always retarded the rate of NH₃ loss. N-serve also retarded the rate of volatilization, but only in the grassland.

Significant 2-way interactions were seen for some treatments. Addition of both water and NH₄⁺ produced a greater release of NH₃ than either treatment alone. When sucrose was added to tubes that also received water or NH₄⁺, the rate of volatilization was always lower than from tubes not receiving sucrose. However, when sucrose was added to tubes without water or NH₄⁺, it had little effect.

In the grassland, N-serve always retarded the loss of NH₃, and the effect was greatest when NH₄⁺ was added. In the shrubland, N-serve stimulated the rate of NH₃ volatilization when water was added, but reduced the loss of NH₃ without water (Fig. 2). Significant 3-way interactions were also seen for some treatments, but the 4-way interaction was never sig-

nificant. The higher-order responses are not discussed in this paper.

Temporal variations in treatments, 1988

The main effects of sucrose and NH₄⁺ showed no change during the course of the experiment, but the effects of other experimental manipulations diminished through time (Table 5). For example, the stimulation of NH₃ volatilization by water was lost after 1 week of soil drying. Significant main and interaction effects of N-serve were only seen for 24 h after treatment of the soil.

Treatment effects, 1989

The processes controlling the loss of NH₃ from grassland soils in 1989 were identical to those observed in 1988. Low rates of NH₃ volatilization were observed in all tubes not receiving water (Fig. 3). Water stimulated the rate of NH₃ volatilization, and the rate was slightly higher with added C_2H_2 ($P < 0.13$ for the main effect in a 3-way ANOVA). All tubes with water had significantly higher concentrations of NH₄⁺ in the soil ($P < 0.0001$ in 3-way ANOVA). Tubes receiving N-serve had the highest concentrations of NH₄⁺ in the soil ($P < 0.0001$), but slightly lower rates of NH₃ volatilization than tubes receiving water and no N-serve ($P < 0.11$).

DISCUSSION

Field collections in closed chambers introduce a number of changes in the natural rate of gas exchange between the soil and the atmosphere (Fenn and Hosser, 1985; Reynolds and Wolf, 1988). Our estimates of NH₃ volatilization are best used for comparisons among experimental treatments and not for areal extrapolations of NH₃ lost from the soil surface.

Before the experimental treatments, there were no significant differences in the rate of NH₃ loss among sites, and the NH₃ flux from dry soils was small (Table 2). The highest rate was found in the playa, which had relatively high soil pH, soil NH₄⁺ and soil moisture. Losses of NH₃ increased markedly after

Table 3. Analysis of variance for time and space effects over all vegetation zones and all times after experimental treatment

Source of variation	d.f.	Sums of squares	Probability
Vegetation	2	7.02	0.001
Time	2	4.17	0.001
Block	4	0.96	0.22
Time × vegetation	4	1.21	0.13
Time × block	8	0.48	0.94
Vegetation × block	8	0.98	0.67
3-way interaction	16	0.43	0.99
Error	653	109.98	

Table 4. Analysis of variance for experimental treatments over all times. Data are the probability of an insignificant effect

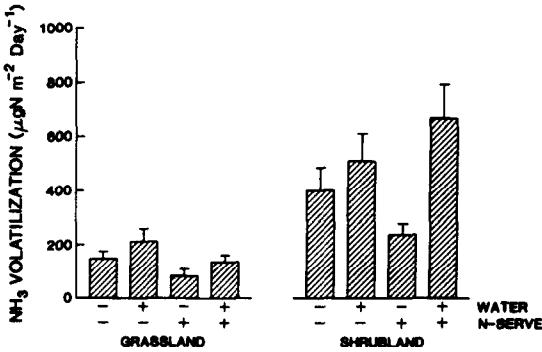| Treatment	Grassland	Shrubland	Playa
Water	0.0071	0.0001	0.0001
NH₄	0.0001	0.0001	0.0001
Sucrose	0.0001	0.0001	0.0001
N-Serve	0.0007	0.9705	0.6429
Water × NH₄	0.0293	0.0355	0.0001
Water × sucrose	0.0010	0.0001	0.0001
NH₄ × sucrose	0.0001	0.0001	0.0002
NH₄ × N-serve	0.0089	0.1279	0.8279
Water × N-serve	0.6344	0.0158	0.8041
Sucrose × N-serve	0.5836	0.0276	0.2699

Fig. 2. NH$_3$ volatilization from grassland and shrubland soils in the Chihuahuan Desert, June 1988, in response to additions of water and N-serve. Values are the daily means, shown with one standard error, from collections beginning 24, 48 and 168 h after application, averaged across all other treatments.
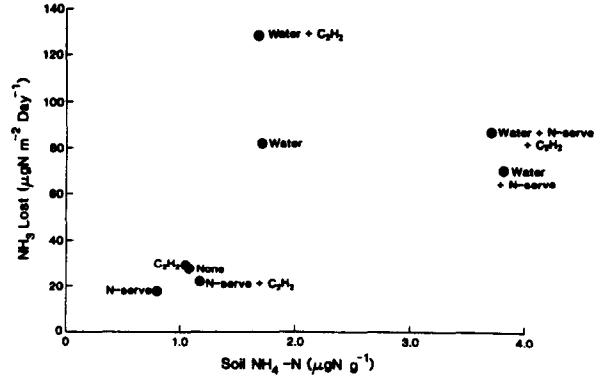

Fig. 3. NH$_3$ volatilization from grassland soils of the Chihuahuan Desert in June 1989, plotted as a function of extractable NH$_4^+$ in the soil column at the end of the collection period. Mean values for each treatment ($n = 10$) are derived from a 3-way factorial experiment.

application of simulated rainfall, with the greatest change occurring in the shrubland (Table 6). Losses of NH$_3$ declined as the soils dried during the next 7 days. Others have observed that NH$_3$ volatilization from dry soils is small, since the microbial production of NH$_4^+$ is limited in these conditions. The greatest rates of loss accompany the evaporation of water after irrigation or rainfall (Nelson, 1982).

Our results indicate that the concentration of NH$_4^+$ in the soil solution limits the rate of NH$_3$ volatilization in desert soils. NH$_3$ loss increased with experimental additions of NH$_4$Cl. Despite the high solubility of NH$_3$ in water, additions of water also stimulated the loss of NH$_3$, presumably by stimulating the mineralization of organic N to NH$_4^+$ (Milchunas et al., 1988) and raising soil concentrations of NH$_4^+$ (Fig. 3). Other studies have shown that microbial biomass in dry soils responds rapidly to wetting by rainfall (Kieft et al., 1987), but our results differ from those of Fisher et al. (1987), who found that additions of water to dry soils reduced the rate of net mineralization. Inhibition of NH$_3$ loss by the addition of sucrose is consistent with our suggestion that NH$_4^+$ limits the rate of NH$_3$ volatilization. Sucrose provided a large quantity of labile C to stimulate microbial immobilization of NH$_4^+$ from the soil solution.

We expected that the addition of N-serve would stimulate the loss of NH$_3$ from Chihuahuan Desert soils, in which high rates of nitrification are observed (Lajtha and Schlesinger, 1986; Fisher et al., 1987).

Applications of nitrification inhibitors are frequently observed to increase NH$_3$ volatilization from agricultural soils (Sahrawat, 1989). We were surprised to find lower rates of NH$_3$ volatilization when N-serve was added to the grassland soils. Initially, we thought that the acetone used to apply N-serve might have acted as a source of labile C for soil microbes, which immobilized available NH$_4^+$ during a subsequent growth phase (cf. Shen et al., 1984). Jenkinson and Powlson (1976) observed an analogous effect during soil fumigations with CHCl$_3$ containing small amounts of ethanol. Following reinoculation, the growth of a new population of bacteria using ethanol as a substrate immobilized all available N. Our observation of high NH$_4^+$ in grassland soils treated with N-serve in 1989 (Fig. 3) suggests that immobilization did not limit the loss of NH$_3$ from those soils. We suspect that these high NH$_4^+$ concentrations reflect the inhibition of nitrification by N-serve or an inadvertent extraction of microbial biomass-N by the acetone, analogous to the action of a CHCl$_3$ fumigation (Brookes et al., 1985). The inhibition of NH$_3$ volatilization by the application of N-serve and acetone needs further investigation. We found that N-serve and acetone had no effect on soil pH in the laboratory.

In the shrubland, N-serve showed no main effect, but there was a significant two-way interaction with water. N-serve stimulated the release of NH$_3$ when water was added, indicating that nitrification is an important competitive reaction consuming NH$_4^+$ when soil microbes are active (Fig. 1). These were the only soils in which the rate of nitrification appeared to control the rate of NH$_3$ volatilization. In dry soils,

Table 5. Analysis of variance showing changes in the significance of main effects and 2-way interactions as a function of time. Data are composited across vegetation zones

Effects	Time (h)		
	24	48	168
Water	0.0001	0.0001	0.4541
N-serve	0.0252	0.9773	0.3504
NH$_4$	0.0001	0.0001	0.0001
Sucrose	0.0002	0.0001	0.0001
Water × N-serve	0.7954	0.2647	0.0580
Water × NH$_4$	0.0001	0.0001	0.5111
Water × sucrose	0.0001	0.0001	0.0085
N-serve × NH$_4$	0.0231	0.7918	0.3455
N-serve × sucrose	0.5562	0.5260	0.3042
NH$_4$ × sucrose	0.0022	0.0001	0.0001

Table 6. Ammonia volatilization from the Chihuahuan desert of southern New Mexico during a drying sequence after application of simulated rainfall. All data are in μg N m^{-2} day^{-1} (± 1 SE), and means are calculated from tubes receiving only water. From Schlesinger et al. (1990)

Time (h)	Grassland	Shrubland	Playa
Pretreatment	15 (12.7)	15 (7.3)	43 (28.9)
24	45 (10.9)	95 (18.4)	50 (13.7)
48	35 (9.2)	30 (8.5)	34 (7.9)
168	21 (6.2)	24 (6.8)	20 (4.7)

Table 7. Some comparative rates of NH_3 volatilization. All values μgN m^{-2} day^{-1}

Study area	Rate	Notes	Reference
Global	720	Average surface flux calculated by modeling	Dawson (1977)
Tanzania	490–1780	Tropical grassland Natural grazing	Reuss and McNaughton (1988)
Canada	220	Marshland Natural grazing by migratory geese	Reuss et al. (1989)
Colorado (U.S.A.)	30	Temperate grassland	Schimel et al. (1986)
New Mexico (U.S.A.)	15–95	Temperate desert	This study
Australia	26,000	Grazed pasture Aerodynamic calculation	Denmead et al. (1974)
Great Britain	4060	Regional estimate from agriculture	Kruse et al. (1989)
Europe	450–9020	Regional estimate of anthropogenic releases	Buijsman et al. (1987)

nitrification is unimportant, and the rate of NH_3 loss showed a slight decline when N-serve was added.

NH_3 volatilization in the shrubland was greater than in the grassland. When shrubland replaces grassland in the process of desertification (Buffington and Herbel, 1965), soil erosion can expose buried calcic horizons that buffer soil pH at ca. 8.3. Thus, during desertification, rates of NH_3 volatilization may increase (Schlesinger et al., 1990).

Despite high soil pH, NH_3 volatilization from the playa was not significantly different from that in the grassland in tubes receiving only water (Table 6). However, playa soils had nearly twice the NH_3 volatilization of the grassland soils, when averaged over all treatments (Table 2). The positive response to additions of water and NH_4^+ suggest that the main process regulating NH_3 loss in the playa is the production of NH_4^+ through mineralization. N-serve showed no main or interaction effects in the playa. Martens and Bremner (1989) found that NH_3 volatilization was negatively correlated with soil clay content and CEC. Ammonia volatilization in the playa may also have been limited by the retention of NH_4^+ on the cation exchange complex contributed by the large clay fraction (Table 1).

Volatile losses of NH_3 from soils are greatest in fertilized agricultural soils and grazed pastures (Table 7). One of the highest rates, 26 mgN m^{-2} day^{-1}, was reported for a grazed pasture in Australia (Denmead et al., 1974). Losses under intensive, natural grazing by ungulates and birds are largely due to the mineralization of excrement deposited on the soil surface (Reuss and McNaughton, 1988; Reuss et al., 1989). Despite the problems associated with measurements of NH_3 flux in closed chambers, our measurements of loss, 15–95 μgN m^{-2} day^{-1} from soils receiving amendments of water (Table 6), probably represent the natural range of NH_3 volatilization from Chihuahuan Desert soils. These values are similar to the loss of 30 μgN m^{-2} day^{-1} for a shortgrass prairie ecosystem in Colorado (Schimel et al., 1986), in which most NH_3 volatilization was associated with patches of cattle urine. These losses are much lower than the global average rate for NH_3 volatilization from undisturbed soils, 720 μgN m^{-2} day^{-1}, calculated by Dawson (1977). Thus, soils in natural ecosystems, even those with high pH, are minor contributors to atmospheric NH_3 compared to agricultural soils and livestock (Dawson and Farmer, 1984).

Measurements of denitrification in soils of the Chihuahuan Desert show that the potential rate of N loss during a 24-h period after rainfall is nearly

8 mgN m^{-2} day^{-1} (Peterjohn and Schlesinger, unpublished). This is about 150 × higher than the rate of NH_3 volatilization under similar conditions (Table 6). Desert soils typically have low concentrations of N (Post et al., 1985; Peterjohn and Schlesinger, 1990), and we believe that the major process contributing to the gaseous loss of N from desert soils is denitrification (Klubek and Skujins, 1981; Peterjohn and Schlesinger, unpublished).

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