Natural Vegetation as a Source or Sink for Atmospheric Ammonia: A Case Study

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Measurements of gaseous ammonia above a montane-subalpine forest in the Colorado mountains show that the role of the forest as a source or sink depends on the atmospheric concentrations. The canopy appeared to be an ammonia source when exposed to air containing low concentrations, but a sink when exposed to air enriched by nearby agricultural sources. The forest-averaged compensation point was 0.8 part per billion by volume at 20°C. The net burden of ammonia and other nitrogen species of anthropogenic origin at this site was much less than at forest sites in the eastern United States and Europe and may provide a valuable resource for this nitrogen-limited ecosystem.

AMMONIA (NH_3) IS THE PRIMARY neutralizing agent for atmospheric acids and a ubiquitous component of the atmospheric aerosol. The predictive capacity of regional acid deposition models thus depends on detailed knowledge of NH_3 sources and sinks, but these remain poorly characterized in remote areas. Natural ecosystems are generally believed to be net sinks for NH_3 because uptake by growing plants is well documented (*1–6*) and NH_3 volatilized from agricultural sources has been implicated in the decline of European forests (*7–9*) and heathlands (*4*). However, several studies (*10–13*) have suggested that growing vegetation will emit NH_3 when exposed to air with concentrations below some "compensation point" related to the partial pressure of NH_3 in the substomatal cavities. As pointed out by Galbally *et al.* (*14*), these results imply that natural vegetation may be a net sink in the vicinity of agricultural sources but a net source in regions where unneutralized sulfate aerosols depress the gaseous NH_3 concentrations below the compensation point. In this report, we describe measurements from a montane forest in the western United States that support this hypothesis and derive an ecosystem-averaged NH_3 compensation point.

The measurements were made at sites near the western (Niwot Ridge) and eastern (Boulder) edges of a lodgepole-ponderosa pine, spruce-fir, and aspen forest (Roosevelt National Forest) situated between the High Plains and the Front Range of the Rocky Mountains (Fig. 1). Local transport is dominated by the prevailing westerlies (downslope), and during most periods the western edge of the forest is exposed to clean continental air containing background levels of NH_3 or ≤ 0.2 ppbv (parts per billion by volume) (*15*). However, easterly (upslope) flow induced by insolation of the mountain surfaces often occurs between midmorning and late afternoon during the summer, and the eastern edge is exposed to NH_3-enriched air masses from the heavily agricultural plains to the east. The role of the forest as source or sink for NH_3 thus depends on the prevailing wind direction and can be estimated by comparing the mean concentrations found at Boulder and Niwot Ridge for these two flow regimes.

The ambient concentrations near the canopy should approach the NH_3 compensation point in the absence of other sources or sinks (*16, 17*). Because the compensation point likely represents the vapor pressure of NH_3 above the water film on the mesophyllic walls of the substomatal cavities, it should increase with temperature according to Henry's law and the NH_3-NH_4^+ equilibrium. At both sites the mean NH_3 concentrations were temperature-independent when the sampled air masses had not passed over the forest (Fig. 2), that is, west winds at Niwot Ridge and east winds at Boulder. The mean mixing ratios under these conditions were ≈ 0.2 and 5.5 ppbv at Niwot Ridge and Boulder, respectively. However, the mean concentrations at the two sites converge and become temperature-dependent when the sampled air mass had recently passed over the forest. The correlation with air temperature suggests that the plant canopy and not the underlying soil is responsible. The ambient concentrations measured under these conditions are believed to represent the mean compensation point of the forest.

The measurements are consistent with the compensation points determined for individual snap bean (*Phaseolus vulgaris*) plants in the laboratory (*10*) and an alfalfa (*Medicago sativa*) field (*18*). The temperature dependence below ≈ 20°C agrees with the variation in NH_3 vapor pressure above a solution believed to be representative of the mesophyllic water film (*10*). The similarity between the forest results and the values extrapolated from the snap bean and alfalfa data to below ≈ 20°C suggests a common mechanism, namely, photorespiratory production and assimilation by way of the

Table 1. Estimated annual deposition of N to the eastern edge of Roosevelt National Forest; S, summer; W, winter.

N species	Mean mixing ratio (ppbv)*	ν_d (cm s^{-1})	N deposition (kg ha^{-1} $year^{-1}$) Dry†	Wet‡	Total
NH_3	5.5 (S)	0.4	0.42		0.42
	4.0 (W)		0.12		0.12
NH_4^+	1.5 (S) (*17, 29*)	0.2§	0.06	0.49	0.55
	1.0 (W) (*17, 29*)		0.01	0.35	0.36
NO_2	6.5 (S) (*31*)	0.2‖	0.25		0.25
	8.5 (W) (*31*)		0.13		0.13
HNO_3	1.0 (S) (*17, 29*)	2.0¶	0.38		0.38
	0.5 (W) (*17, 29*)		0.08		0.08
NO_3^-	0.15 (S) (*17, 29*)	0.1¶	<0.01	0.62	0.62
	0.25 (W) (*17, 29*)		<0.01	0.58	0.58
Total			1.5	2.0	3.5

*Estimated mean mixing ratios in Boulder during upslope events. †Assumes upslopes occur 25% of the time in summer and 10% of the time in winter (*21*). ‡Wet deposition data from NADP (Sugarloaf station) (*22*). §Deposition velocity from gradient measurements of (*30*). ‖Deposition velocity based on enclosure measurements and model of (*32*). ¶Deposition velocity based on field measurements of (*24*).

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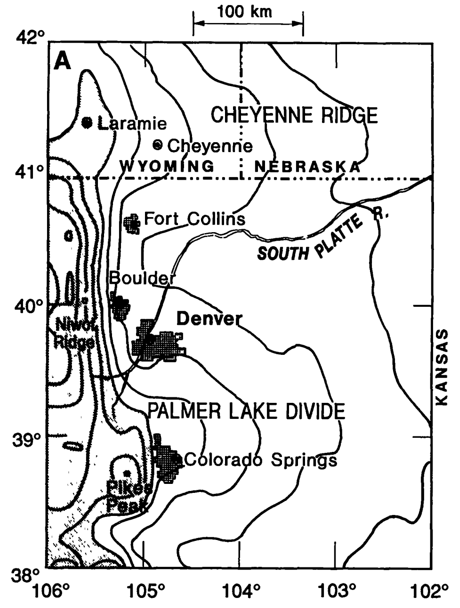

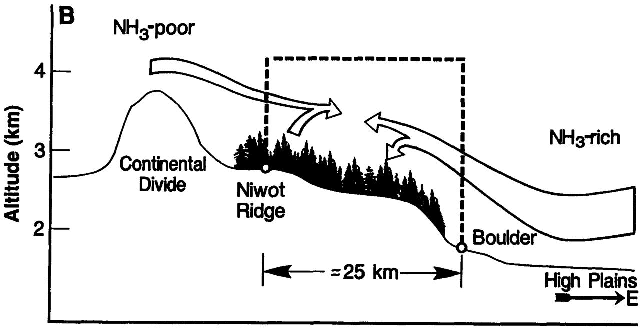

Fig. 1. (**A**) Location of the Roosevelt National Forest (shaded area) with respect to the Continental Divide, the Denver-Boulder urban corridor, and the High Plains. Measurements were made near the western edge of the forest at Niwot Ridge (3048 m) during the summer of 1987 and on the eastern edge near Boulder (1830 m) during the summer of 1986. In both cases, the molybdenum oxide annular denuder technique (*33*) was used to obtain continuous, half-hour samples at a height of ≈4 m above the ground (canopy height ≈6 to 8 m). Although not simultaneous, sufficient measurements were made at each site to be typical of late summer conditions (≥650 samples over 4 to 6 weeks). The NH_4^+ levels in precipitation (*22*) collected at Niwot Ridge during the summers of both years differed by ≤20%, suggesting no significant changes in the local sources or sinks. (**B**) Schematic diagram illustrating the transport of NH_3-poor air masses to the forest from the west and NH_3-rich air masses to the forest from the east. The forest is succeeded by alpine tundra within 2 km to the west, and no significant anthropogenic sources of NH_3 lie within 80 km in this direction. In contrast, the High Plains to the east of Boulder are heavily agricultural and more than 65 cattle feedlots lie within 80 km of Boulder in the South Platte River Valley.

glutamate synthase cycle (*19*). The reason for the less rapid increase in the forest compensation point at higher temperatures (Fig. 2) is unclear but may be associated with water stress; temperatures above ≈20°C occurred only during very dry mid-afternoon downslope conditions. No day-night variation was evident as would be expected if photorespiration were involved, but such an effect may have been obscured by the strong diurnal dependence of transport patterns and temperature; the diurnal variation of stomatal conductance would affect only the NH_3 exchange rate and not the compensation point.

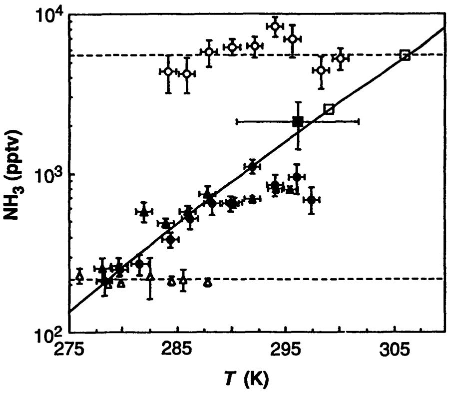

Fig. 2. Temperature dependence of the mean NH_3 mixing ratios at Niwot Ridge (triangles) and Boulder (circles) during periods of sustained (≥0.5 m s^{-1}) easterly and westerly flow. Open symbols correspond to air masses that have not passed through the forest (east winds at Boulder and west winds at Niwot Ridge), and the dashed lines represent the mean concentration at each site under these conditions. The filled symbols correspond to air masses that have passed through or over the forest. Each point represents the mean ± 95% confidence limits of all measurements within the temperature span represented by the horizontal bars. Also shown are the compensation points for *Phaseolus vulgaris* (snap bean) from (*10*) (open squares) and *Medicago sativa* (alfalfa) from (*18*) (filled square). The solid line corresponds to the calculated NH_3 vapor pressure above a solution with 46 μM [NH_4^+] and pH 6.8 (*10*).

The data in Fig. 2 suggest that the forest canopy will generally act as an NH_3 source during periods of westerly flow and as a sink during periods of easterly flow. The mean NH_3 emission and deposition rates can be estimated from

$$F = -g(p_a - \gamma)/P \qquad (1)$$

where p_a is the ambient partial pressure of NH_3, γ is the compensation point, g is the conductance of NH_3 through the stomatal openings and the boundary layer surrounding the leaf, and P is the atmospheric pressure. Laboratory studies suggest that the rate of NH_3 exchange will be limited by the stomatal conductance (*3, 4, 10*) if the forest is well ventilated. A value of $g = g_s \approx 0.17$ mol m^{-2} s^{-1} has been estimated for fully open lodgepole pine stomata by scaling the CO_2 conductance of $g_s = 0.27$ mol m^{-2} s^{-1} (*20*) by a factor of $(17/44)^{1/2}$. This conductance corresponds to a deposition velocity v_d of 0.40 cm s^{-1} and should be applicable to both uptake and emission because deposition to the leaf surfaces is probably negligible at the low (≤50%) relative humidities typical of the Front Range in summer (*5*).

During strong downslope conditions, the forest was a net source with a mean NH_3 emission rate of ≈1.2 ng m^{-2} s^{-1} (15°C) near Niwot Ridge. Farther east, the emission rate will depend on how well the forest is ventilated and will generally be smaller at low wind speeds. During upslope conditions, the forest became a net sink with a mean NH_3 deposition (uptake) rate of ≈10 ng m^{-2} s^{-1} (20°C) near Boulder. The deposition rate decreased rapidly from east to west as NH_3 was depleted from the surface layer through deposition and dispersion. Thus, at Niwot Ridge the mean mixing ratios rarely exceeded the compensation point, and NH_3 deposition appears to have been unimportant. Given that upslope conditions typically occur on ≈50% of summer days and ≈10% of winter days (*21*), the eastern edge of the forest between Cheyenne Ridge and the Palmer Lake Divide (see Fig. 1A) will be a net sink for NH_3 with a total

Table 2. Comparison of growing season N deposition (kg ha^{-1}) in three coniferous forests of the United States and Europe; Σ_d is the total dry N deposition; Σ_w is the total wet N deposition; $\Sigma_d + \Sigma_w$ is the total (dry and wet) N deposition.

Site	Dry deposition					Wet deposition			Total
	NH_3	NH_4^+	HNO_3	NO_3^-	Σ_d	NH_4^+	NO_3^-	Σ_w	$\Sigma_d + \Sigma_w$
Niwot Ridge	0.4	0.06	0.4	≈0	1.3	0.5*	0.6*	1.1	2.4
Oak Ridge†	0.3‡§	0.2	2.4	0.1	2.5	1.2*	1.7*	2.9	5.4
Göttingen†	3.6‡	0.9	6.4	1.1	12.0	1.1	3.9	7.0	19.0

*Wet deposition data from (*22*). †Oak Ridge and Göttingen data are from (*24*). ‡Deposition rates based on estimated NH_3 concentrations from (*24*). §The present hypothesis and unpublished results of Langford and Fehsenfeld suggest an NH_3 emission rate of 0.3 kg ha^{-1} at this site.

annual N burden of ≈0.5 kg ha^{-1} deposited primarily during the summer. This burden represents ≈40% of the total N dry deposition and ≈15% of the total atmospheric N input (≈3.5 kg ha^{-1} $year^{-1}$) estimated by similar methods and wet deposition data (*22*) (Table 1). The total N deposition is equivalent to ≥25% of the total N translocated through the roots (12.5 kg ha^{-1} $year^{-1}$) of a similar forest 150 km to the north (*23*) and represents a sizable nutrient input to this N-limited ecosystem.

The total deposition of all N species to Roosevelt National Forest is much less than that in other coniferous forests in the eastern United States and Europe (*24*) (Table 2) and is well below the estimated threshold for forest damage (≈10 to 20 kg ha^{-1} $year^{-1}$) (*25*). Table 2 contrasts the N burdens in forests near sources of high agricultural and low industrial emissions (Roosevelt), low agricultural and high industrial emissions (Oak Ridge, Tennessee), and high agricultural and high industrial emissions (Göttingen, Germany). Forests in areas with high (SO_2 + NO_x)/NH_3 emission ratios (for example, Oak Ridge and the eastern United States) may simultaneously act as net sinks for anthropogenic N in the form of NO_x, HNO_3, NO_3^-, and NH_4^+ while emitting gaseous NH_3 to the atmosphere. This results from the presence of unneutralized sulfate aerosols that scavenge NH_3 and depress the ambient NH_3 mixing ratios to well below the compensation point [≤0.05 ppbv (*26, 27*)]. These emissions can account for both the presence of NH_3 in regions with no known anthropogenic sources at mixing ratios greater than predicted from the NH_3-H_2SO_4-NH_4HSO_4-$(NH_4)_2SO_4$ equilibrium and the ubiquity of ammonium sulfate and bisulfate aerosols in the atmosphere (*28*).

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Topographic and Magnetic-Sensitive Scanning Tunneling Microscope Study of Magnetite

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The topographic and magnetic surface structure of a natural single crystal of magnetite (Fe_3O_4), a common mineral, has been studied from the submicrometer scale down to the atomic scale with a scanning tunneling microscope having nonmagnetic tungsten as well as ferromagnetic iron probe tips. Several different (001) crystal planes were imaged to atomic resolution with both kinds of tips. A selective imaging of the octahedrally coordinated Fe B-sites in the Fe–O planes, and even a selective imaging of the different magnetic ions Fe^{2+} and Fe^{3+}, has been achieved, demonstrating for the first time that magnetic imaging can be realized at the atomic level.

THE SCANNING TUNNELING MICROSCOPE (STM), developed by Binnig, Rohrer, Gerber, and Weibel (*1*), is already well known for its ability to image surface structures of conducting samples down to the atomic scale. The most significant contributions of STM have initially been made in the field of semiconductor surfaces (*2, 3*) and, more recently, in the fields of metal surfaces (*4*), superconductivity (*5*), charge-density wave systems (*6*), and atomic-scale writing (7) and switching (*8*). We demonstrate that the STM can also be a

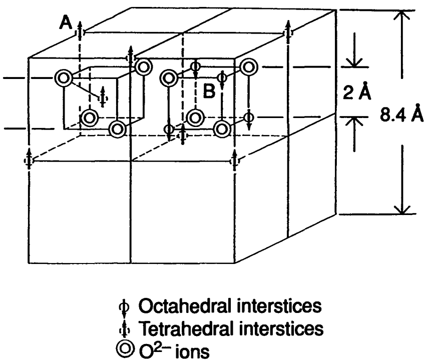

Fig. 1. Simplified picture of the conventional unit cell of magnetite, including its spin structure. There are (001) planes built up by the Fe A-sites, as well as other (001) planes (C_a and C_b) that are built up by Fe B-sites and O-sites.

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