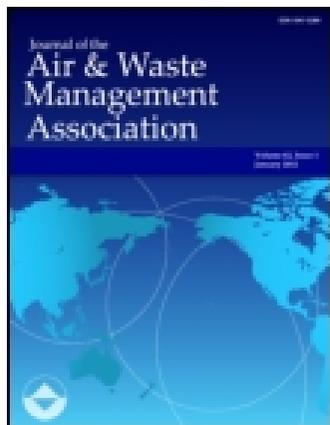


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Dry Deposition of Ammonia at Environmental Concentrations on Selected Plant Species

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TECHNICAL PAPERS

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Dry Deposition of Ammonia at Environmental Concentrations on Selected Plant Species

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The deposition velocity of NH_3 on six plant species at environmental concentrations has been studied in a dynamic plant gas exchange reactor. The total resistance to the transport of NH_3 was studied. The aerodynamic resistance was determined directly by NH_3 gas absorption in aqueous solutions at environmental concentrations in a two-phase gradientless reactor modeling the transfer processes through the stomata in a leaf. The concentration of NH_3 in the gas phase ranged from 50 to 1000 ppb and the temperature varied from 25 to 30°C. The results for the deposition velocity for NH_3 , during the day, varied from 0.3 to 1.3 cm/s. The deposition velocities at night were about one order of magnitude smaller. These results are compared with estimates from the Frössling equation which consistently yields higher values of the same order of magnitude. To determine accurate atmospheric transport models or global budget models, a variable deposition velocity should be used to account for the diurnal and seasonal variations in the surface resistance.

Nitrogenous gases from natural and man-made sources are responsible for a significant amount of air pollution. Man-made sources account for about 5.7×10^7 tons annually, principally as NO , NO_2 , and NH_3 , while natural sources contribute about 6.4×10^9 tons, mainly as NH_3 .¹

Atmospheric processes are extremely important in the circulation of nutrient nitrogen.² The delivery of nitrogen as ammonia and nitrate in rain has long been recognized as an important source of field nitrogen. Recent evidence suggests that the dry deposition of gaseous ammonia, ammoniated sulfate and ammoniated nitrate particles may constitute a quantitatively more significant exchange mechanism than the washout of nitrogen compounds in rain. However, there appears to be little or no data on the dry deposition of ammonia to vegetation or bare soils. Some workers³ have assumed NH_3 gaseous deposition velocity to equal that of SO_2 .

Ammonia is present as a gas in the atmosphere in quantities ranging from <5 to 100 ppb.^{1,4,5,6} Junge⁷ gives the tropospheric average near the surface as 10 ppb on the basis of measurements made mostly in the temperate zone. Pate *et al.*⁸ proposed 15 ppb as a tentative tropospheric average based in part on their measurements in tropical rain forests and Atlantic air. Dawson⁹ has summarized the results for ammonia concentrations in the remote areas of the United States.

Although small amounts of ammonia are introduced into the atmosphere from the burning of coal and from other industrial sources, the biosphere is the major source for what appears to be a large quantity of ammonia annually in circulation between the surface and the atmosphere.¹ The annual rates at which these compounds are exchanged with the surface are not known, and available estimates differ by an order of magnitude.

Removal of NH_3 at the Earth's surface is an important heterogeneous process and quantification of its removal rate by dry and wet deposition is lacking. It is therefore of considerable interest to measure dry deposition of NH_3 to vegetative surfaces since these types of surfaces constitute a large fraction of the U.S. continental surface. This will also help to refine the global budgets of the nitrogen cycle.

There are inherent difficulties in the measurement of dry deposition to a tall canopy, especially at a low ppb level. However, one possible way to overcome these difficulties (and which we have chosen) is to enclose plants in a chamber, expose them to uniform ambient atmospheric NH_3 concentrations, measure the deposition, and then calculate the dry deposition to the vegetative surface.^{10,11} Such an approach requires good knowledge of the variability within the canopy as well as localities. Temporal variations must be understood. Air resistance inside and slightly above and below the canopy must be parameterized. How the canopy responds when wetted by rain must also be understood. The surface resistance of a dry canopy (not wetted by rain) is, however, considered to be the key factor which controls the deposition of several trace gases, including NH_3 , to the vegetative surface.

Most studies utilizing the chamber technique to estimate the deposition velocity of gases on vegetative surfaces of interest have used indirect measures to compute both the total resistance, R , and the gas phase (aerodynamic) resistance, r_g . The surface resistance, r_s , is then estimated by the difference. The total resistance is determined by estimating the rate of transpiration and the water vapor density differences between the leaf and the air.^{12,13} The value of r_g is estimated from the semi-empirical Frössling equation.¹⁴ Bennett *et al.*¹⁵ present various important resistances involved for the transport of gas into the leaf. However, in this paper we present NH_3 deposition velocity computed such that r_g is determined directly by NH_3 gas absorption in aqueous solutions at atmospheric conditions in a two-phase gradientless reactor. A Teflon plate with holes drilled in it rides at the gas-liquid interface, thus experimentally modeling the transfer of gas through stomata in leaves. R is determined by estimating the rate of transpiration and the water vapor density differences between the leaf and air. Then r_s is

estimated by difference. This technique, we believe, will give a more realistic understanding of the various resistances comprising R , and hence, v_d (deposition velocity). The detailed results of the two-phase reactor are presented elsewhere.¹⁶

Materials and Methods

Resistance Measurement

The exposure system, housed in a controlled room, consisted of two CSTRs designed for gas exchange studies.¹⁷ Each 200-L exposure reactor was cylindrical and consisted of a Teflon-coated steel frame covered by 5-mil Teflon (FEP) film (Figure 1). The configuration of each exposure unit along with an impeller (120 rpm) produced uniform composition, which was corroborated by tracer experiments, which showed a reasonable approach to phase uniformity.¹⁷ All internal surfaces were made of Teflon or glass to minimize wall losses.

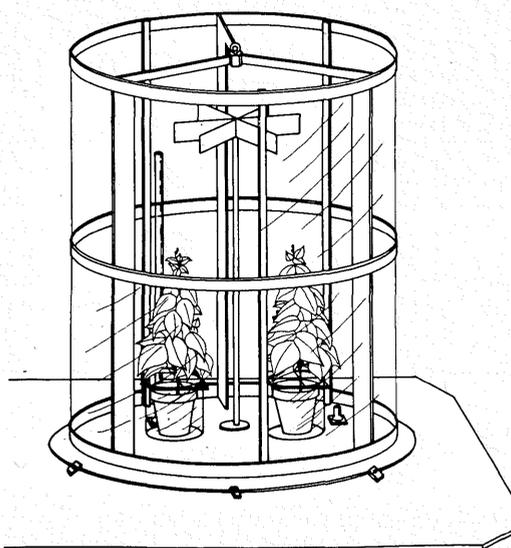


Figure 1. A single unit of the dual CSTR system during exposure of two snap bean plants. The glass inlet near the impeller, the outlet near the bottom of the right plant, and the glass enclosures around the pots are shown.

Plant pots were inserted into glass containers with split plate-glass lids, the interfaces of which were sealed with a fluorocarbon grease. Plants were then placed inside the exposure system by lifting the units from gasketed bases. These containers permitted uptake of NH_3 and loss of water vapor by plant tops only, thus allowing calculation of NH_3 sorption rates by leaves and total diffusion resistance (stomatal plus aerodynamic), and dry deposition. Experimental blank runs without plants provided correction factors for minor wall and chamber effects.

Ammonia was supplied to the system from a permeation tube using N_2 as a carrier. The flow rate into each exposure unit was 10 L/min. The level of NH_3 was controlled by using different sizes and numbers of permeation tubes. The common inlet to both chambers and separate outlets were sampled in sequence for 5 minutes each. A timer, which actuated Teflon solenoids, controlled sampling through 0.635-cm Teflon tubing. The tubing fed into a heated glass manifold that supplied the analyzers. The NH_3 was continually monitored with a Monitor Labs Model 8440 Oxides of Nitrogen Analyzer equipped with a catalytic converter that maintained at 800°C to oxidize NH_3 to NO .¹⁸

Injection of NH_3 began as soon as plants were placed in the exposure unit. Total diffusion resistance was computed from measurements of transpiration, leaf area, (i.e., outline area of leaf profile), temperatures and water vapor concentrations of leaves and air. The following instruments were used: EG&G Model 880 Dew Point Hygrometer for dew point temperature, 44203 Yellow Springs Thermistors for air temperature, No. 36-gauge Type T thermocouples for leaf temperature, and a Lambda 3200 Area Meter for leaf area.

The following diverse species were chosen for the survey portion of this experiment because they represent six economically important and widely distributed agricultural crops: corn (*Zea mays* L. "Pioneer Brand 3369A"), fescue (*Festuca arundinacea* Schreb. "Kentucky 31 Tall Fescue"), oat (*Avena sativa* L. "Carolee"), orchard grass (*Dactylis glomerata* L. "Potomac"), snap bean (*Phaseolus vulgaris* L. "Bush Blue Lake 290), soybean [*Glycine max* (L.) Merr. "Davis"].

Plants were grown in a controlled environment room under 9-h light periods with a photosynthetically active radiation (PAR) level of 440 $\mu\text{E}/\text{m}^2/\text{s}$ with temperatures of 26°C (day) and 22°C (night). Each plant was grown in a 177-mL Styrofoam cup containing a 1:2 mixture of peat-lite and gravel and watered in the morning with deionized water and in the afternoon with nutrient solution.¹⁹ Plant age at time of exposure ranged from 2 to 41 days from seed, depending upon germination and development rate.

Results and Discussion

Dry deposition is a mass transfer process whereby NH_3 is first transported to surfaces by turbulent and molecular diffusion and then removed by adsorption or absorption at the surface. This mass transfer rate can be characterized by a mass transfer coefficient (v_d). The inverse of v_d is the overall resistance to transport and is expressed by $R = 1/v_d$. Since the units of v_d are length per time, it is called "deposition velocity"; even though it has no simple physical interpretation that is equivalent to a velocity in the hydrodynamic sense. Conceptually, it is also convenient to utilize the overall resistance to mass transfer, R , which is the sum of gas phase resistance, r_g ($= 1/v_g$), and surface resistance, r_s . Hence, $R = r_s + r_g$.

The surface resistance (r_s) incorporates adsorption and desorption. In the case of vegetation, r_s is believed to be dominated by the size of the stomatal openings. The gas

Table I. NH_3 total resistance, R , on crop species. $\text{PAR} = 440 \mu\text{E}/\text{m}^2/\text{s}$.

Species	No. of plants N	Age (days)	Leaf area (cm^2)	Characteristic length (cm)	NH_3 concentrations (ppb)	R (s/cm)
Corn	4	15	781 \pm 5	15.8	250	3.2 \pm 0.1
Snap bean	4	15	548 \pm 1	13.2	100	2.5 \pm 0.1
Soybean	4	16	510 \pm 2	12.7	75	1.65 \pm 0.2
Orchard grass	4	2	84 \pm 1	5.2	576	1.04 \pm 0.1
Oats	5	25	340 \pm 1	10.4	200	1.0 \pm 0.1
Fescue	4	22	50 \pm 1	4.0	603	0.86 \pm 0.05

phase resistance or the aerodynamic resistance (r_g) is due to turbulent diffusion in the atmospheric surface layer.

The total diffusion resistance to gaseous NH_3 on six crop species was experimentally determined by a dynamic chamber technique (Table I) at a temperature of 26°C. Since there is the possibility that the value of R is a function of NH_3 concentration, it was systematically measured at a light intensity of 440 $\mu\text{E}/\text{m}^2/\text{s}$ for corn, snap beans, and soybeans (Tables II, III, and IV) for NH_3 concentration ranging from

Table II. Total resistance, R , of corn at varying NH_3 concentrations. $PAR = 440 \mu\text{E}/\text{m}^2/\text{s}$.

NH_3 concentrations (ppb)	R (s/cm)
63	2.54
77	2.90
104	3.90
268	2.91
556	3.90

50 ppb to 1000 ppb. It is observed that there is no recognizable change in the value of R within the plant species at the 95 percent confidence level (corn, $R = 3.23 \pm 0.6$ s/cm; snap bean, $R = 2.40 \pm 0.27$ s/cm; soybean, $R = 1.64 \pm 0.21$ s/cm). It seems reasonable to conclude that the value of R is independent of the NH_3 concentration over the range of concentrations investigated (i.e., atmospheric NH_3 concentrations).

It is interesting to compare these results from a biotic system (i.e., plant species) with an abiotic system (i.e., aqueous solutions) for similar gaseous NH_3 concentrations, and we observe that R for the abiotic system is ~ 0.4 s/cm, much less than the values presented for biotic systems (Table I).¹⁶

Table III. Total resistance, R , of snap bean at varying NH_3 concentrations. $PAR = 440 \mu\text{E}/\text{m}^2/\text{s}$.

NH_3 concentrations (ppb)	R (s/cm)
50	2.20
397	2.28
576	2.88
636	2.33
1150	2.31

The effect of light intensity on total diffusional resistance was determined by stepping the light through two levels on corn, snap beans, and soybean, and the results are presented in Table V. We observe that the resistance to the transport of NH_3 into or out of a leaf is a strongly light-dependent phenomenon. This is because stomatal opening is a strong

Table IV. Total resistance, R , of soybean at varying NH_3 concentrations. $PAR = 440 \mu\text{E}/\text{m}^2/\text{s}$.

NH_3 concentrations (ppb)	R (s/cm)
70	1.80
80	1.73
146	1.58
501	1.30
549	1.79

light-dependent function. Hence NH_3 flux to vegetation in the field would be heavily influenced by solar radiation and dominates the magnitude of the total diffusion resistance. We therefore suggest that a variable deposition velocity should be used in atmospheric transport models or global budget model to account for the diurnal and seasonal variations in the surface resistance of a canopy.

The aerodynamic resistance, r_g , was obtained by absorbing NH_3 from NH_3 and N_2 mixture into sulfuric acid solution in a dynamic gradientless gas-liquid reactor. The gradientless reactor is fabricated such that there is an interfacing Teflon plate riding on the liquid surface with holes of known configuration corresponding to open stomates in a plant. This experimental model for determining the aerodynamic resistance over the plant leaves is a more realistic approximation for aerodynamic resistance estimation than conducting studies on a flat plate or using the semi-empirical Frössling correlation, as has been done in previous investigations. Since the dissolved NH_3 reacts infinitely fast with respect to mass transfer and with a large excess of H_2SO_4 at the gas-liquid interface, the liquid phase mass transfer resistance is considered to be negligible. Detailed results are published elsewhere.¹⁶

Table V. Total resistance, R , and deposition velocity, v_d , for NH_3 sorption for corn, snap bean, and soybean at changing light intensity (PAR) levels.

Species	PAR level ($\mu\text{E}/\text{m}^2/\text{s}$)	R (s/cm)	v_d (cm/s)
Corn	0	35.4	0.03
Corn	440	3.2	0.3
Snap bean	0	69.7	0.02
Snap bean	440	2.5	0.4
Soybean	0	90.8	0.01
Soybean	440	1.65	0.6

The following relationship for v_g was obtained:

$$v_g = 0.069 \sqrt{Re_g} - 0.394 \quad (1)$$

where: Re_g is the gas phase Reynolds number.

It was also found that the effect of the concentration of NH_3 in the gas phase (90–1400 ppb) or that of temperature (12–30°C) on the v_g value was negligible in the experimental range investigated.

Table VI. NH_3 gas phase mass transfer coefficient, v_g , and aerodynamic resistance, r_g , over the leaf determined from the Frössling correlation.

Species	Mass transfer coefficient $v_g = v_d$ (cm/s)	Aerodynamic resistance $r_g = R$ (s/cm)
Corn	0.85	1.17
Snap bean	1.02	0.98
Soybean	1.06	0.94
Orchard grass	2.59	0.39
Oats	1.30	0.77
Fescue	3.37	0.30

The Reynolds number for gas phase in the plant exposure chamber was $Re_g \approx 48,000$. This corresponds with aerodynamic conditions in the atmosphere.²⁰ This would yield $v_g = 14.72$ cm/s (or $r_g \approx 0.07$ s/cm) based on Equation 1. The mass transfer coefficient, v_g obtained from the Frössling correlation:

$$v_g = \frac{D_{\text{NH}_3}}{R} \left[1 + 0.3 \left(\frac{2Ru}{v} \right)^{1/2} \left(\frac{v}{D_{\text{NH}_3}} \right)^{1/3} \right] \quad (2)$$

Table VII. NH₃ deposition velocities, v_d , for atmospheric conditions on crop species during day. $PAR = 440 \mu E/m^2/s$.

Species	v_d	v_d
	Present work (cm/s)	Estimated using Frössling correlation (cm/s)
Corn	0.3	0.85
Snap bean	0.4	1.02
Soybean	0.6	1.06
Orchard grass	1.0	2.59
Oats	1.0	1.30
Fescue	1.2	3.37

where: D_{NH_3} = diffusion coefficient for ammonia, 0.234 cm²/s

R = characteristic length, cm

u = air velocity above plant, cm/s

ν = kinematic viscosity of ammonia, 0.15 cm²/s

is presented in Table VI for similar Re_g .

Table VII presents the results for NH₃ deposition velocity for the crop species. We observe that v_d varies from 0.3 cm/s for corn to 1.3 cm/s for fescue in the presence of light. These results compared with v_d determined from the Frössling correlation (Table VII) and we observe that, in general, consistently higher values for v_d are obtained by the Frössling correlation.

During the night, there may be a one order of magnitude decrease in v_d for NH₃ (Table V). It is interesting to compare these results with the deposition velocities for SO₂ over vegetation. For SO₂, v_d varies between 0.1 to 1.5 for grass and crops (Table VIII).²¹ While results are sketchy, values are of the same order of magnitude, supporting rough estimates as suggested in the literature. These approaches offer, however, a direct, sensitive, experimentally valid method of measuring such velocities.

Table VIII. SO₂ deposition velocities over vegetation. Source: [ISSA] Workshop, 1978.²¹

Vegetation		Height (m)	Range of deposition velocity, v_d (cm/s)	Typical deposition velocity, ^a v_d (cm/s)
Height	Example			
Short	Grass	0.1	0.1–0.8	0.5
Medium	Crops	1.0	0.2–1.5	0.7
Tall	Forest	10.0	0.2–2.0	Uncertain

^a These values were obtained in a humid climate. Much smaller values are likely in arid climates.

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