On the Gaseous Exchange of Ammonia between Leaves and the Environment: Determination of the Ammonia Compensation Point

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ABSTRACT

Whole shoots of *Phaseolus vulgaris* L. and other species were exposed to a range of partial pressures of gaseous ammonia in air and the resulting fluxes were measured. Net uptake is linear with partial pressure in the range 5 to 50 nanobars and is zero at a finite partial pressure, termed the ammonia compensation point. Below the compensation point, ammonia (or possibly other volatile amines) is evolved by the leaves. The compensation points in several species are near the low partial pressures found in unpolluted air and approximate to the K_m of glutamine synthetase *in vitro*. In *P. vulgaris* L., the compensation point increases with temperature.

Plants are regarded as sinks for atmospheric ammonia; Aneja (2) has reviewed this literature. This view stems largely from a number of experiments carried out at ammonia partial pressures in excess of those found naturally. However, Farquhar *et al.* (8) found that, at realistically low partial pressures (5 ± 3 nbar), no fluxes into or out of healthy leaves of *Zea mays* could be detected. An evolution of 0.6 nmol m^{-2} s^{-1} was observed from leaves showing senescence. They inferred that, even in healthy leaves, a finite partial pressure of ammonia must exist in the substomatal cavities. This is consistent with the large number of reactions involving NH_3/NH_4^+ in plant cells (6). An equation may be written for the molar flux density, J (nmol m^{-2} s^{-1}), of ammonia into the leaf through stomata:

$$J = g(n_a - n_i)/P \qquad (1)$$

where g (mol m^{-2} s^{-1}) is the conductance to diffusion of ammonia through stomata and the boundary layer surrounding the leaf, n_a (nbar) is the ambient partial pressure of ammonia (typically 1 to 8 nbar in unpolluted areas) (11), and P (bar) is the atmospheric pressure. Farquhar (6) suggested that, if the intercellular partial pressure, n_i, is less than the ambient partial pressure, n_a, there should be a net influx into the leaf, and vice versa. The diffusivity of ammonia in air is 0.92 times that of water vapor in air (pp 551–552 in ref. 1) and so g equals 0.92 times the conductance to the diffusion of vapor, g'. The cuticular conductance to ammonia transfer across the leaf epidermis is unknown.

Here, measurements of the net rate of uptake, J, are described, as n_a is varied over a range that includes naturally occurring partial pressures. The value of n_i that occurs naturally is also estimated.

MATERIALS AND METHODS

Phaseolus vulgaris L. var 'Hawkesbury Wonder' plants were grown in a glasshouse, in 5-liter pots containing sterilized soil, and flushed daily with 1 liter of a Hewitt nitrate-type nutrient solution. Plants used were 20 to 40 days old with a leaf area, typically, of 2540 cm^2.

The aerial portion of the plant was enclosed in a glass chamber, with a stainless steel base, measuring 64 × 64.5 × 49.5 cm. The chamber was sealed at the base of the stem using Terostat (Terosomwerke, GmbH, Heidelberg) to exclude the soil as a source of or sink for ammonia. The chamber was two-thirds surrounded by a bank of vertical fluorescent lights, and both the chamber and the lights were air-cooled with a 30-cm high-speed fan. The temperatures of two leaves were monitored using thermocouples constructed from 0.1-mm copper and 0.13-mm constantan wires. Air temperature was varied using an electric heater in the chamber, and the air was mixed by two small fans. The lights were surrounded by reflective aluminum sheeting, and the irradiance on one side of a vertical plane in the chamber was 250 μE m^{-2} s^{-1}. Air was drawn from outside the building through the chamber and into a 30-cm long, 1.8-cm diameter ammonia collector, similar to that of Denmead *et al.* (3), containing 38 cm^3 of 3-mm diameter glass beads and 5 ml 0.1 N H_2SO_4 with plugs of glass wool in the middle and at either end. Air was also drawn through a similar system in parallel but with no plant chamber interposed. The former collector tube is called the sample tube and the latter, the control tube. The flow rates into the collection tubes were measured using calibrated flowmeters (Duff and MacKintosh, Sydney) and were typically 36 liters min^{-1}. Air was drawn at 10 liters min^{-1} from both streams, before the collection tubes, through psychrometers to determine rate of transpiration, E (mol m^{-2} s^{-1}), and through the two cells of a Beckman 865 IR gas analyzer to determine rate of CO_2 assimilation.

The leaf conductance to the diffusion of water vapor, g', was estimated from measurements of the transpiration rate, E, and of water vapor pressures (mbar), using an equation analogous to equation 1. Thus

$$E = g'(e_i - e_a)/P \qquad (2)$$

where e_a is the ambient vapor pressure, and e_i (that in the intracellular spaces) was assumed equal to the saturation vapor pressure at the leaf temperature (7).

The partial pressure of NH_3 in the 92 liters min^{-1} supply was varied by changing the rate at which air, containing a 550 μbar partial pressure of NH_3 (mixture prepared by Commonwealth Industrial Gases), was bled into the supply. The required flows (0–3 cm^3 min^{-1}) were achieved using a reduction valve (Matheson model 14M) and were monitored by a Hastings Eall-5P mass-flow meter. After a change in partial pressure was imposed, at least 20 min equilibration was allowed before commencing collection.

After 90 min ammonia collection, the sample and control tubes were eluted with 25 ml distilled H_2O, and the ammonia concentration was determined by the indophenol method using a Tech-

nicon autoanalyzer, calibrated with standards at the same pH. Identical results were obtained with an Orion specific-ion electrode, but both techniques detect other amines and the possible contribution of these amines to the measured rates was unknown.

Variable results were obtained with the first 90-min experiment after inserting a plant, and first experiments were excluded from the data presented. Plants were normally in the chamber for 5 days.

From measurements of the NH_3 collected in both tubes and of the volumes of air that passed through both tubes, the partial pressures of ammonia in the air entering and leaving the chamber were determined. Together with measurements of the volume of air which flowed from the chamber through the psychrometer and the IR gas analyzer, determinations of the rate of assimilation (or evolution) of ammonia, J, were made possible.

RESULTS

The partial pressure of ammonia entering the chamber was varied in experiments with six different plants. For one such plant, the influx is plotted as a function of partial pressure in Figure 1. Influx is zero at a finite partial pressure of ammonia, and this partial pressure is termed the ammonia compensation point, γ. It is analogous to the CO_2 compensation point, Γ, at which the net assimilation of CO_2 is zero. Below the ammonia compensation point, ammonia, or some other amine, is evolved. The uncertainty in any particular determination of partial pressure was about 1 nbar. By determining the compensation point as the intersection with the abscissa of the line of best fit through points nearby, this uncertainty was reduced. The mean value of γ in six such experiments was 2.5 nbar with a standard error of ±0.13 nbar. The average temperature during these determinations was 26 C.

The compensation point increases with temperature. Figure 2 shows the results obtained at 33 C where γ has increased to 5.5 nbar. Note the evolution of ammonia at partial pressures below the compensation point. The partial pressure of ammonia in the
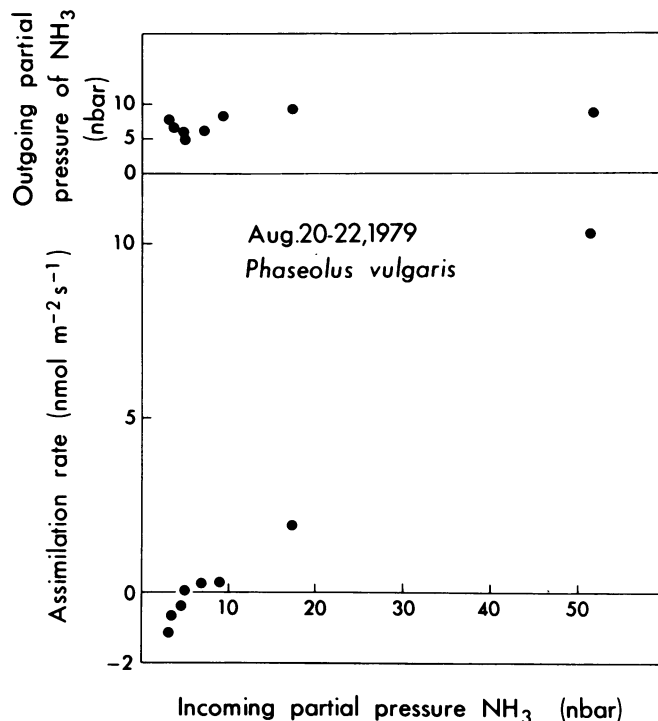
FIG. 2. Determination of the ammonia compensation point in *P. vulgaris* at 33.4 C: outgoing partial pressure and rate of uptake of ammonia *versus* incoming partial pressure.

air leaving the chamber is also plotted against that of the incoming air in Figures 1 and 2 and is seen to increase only slightly; the outgoing partial pressure is drawn towards the compensation point. In cases where the partial pressure of ammonia changes substantially as the air moves through the chamber, it is difficult to estimate an appropriate value for the ambient partial pressure, n_a. At the compensation point, of course, n_a and n_i and the incoming and exiting partial pressures are all equal to γ.

A low light intensity was used (one-tenth of full sunlight) to reduce rates of transpiration and avoid problems of condensation in the chamber. The resulting rates of CO_2 assimilation (typically, 5 μmol m^{-2} s^{-1}) and leaf conductances to the diffusion of water vapor (typically, 0.1 mol m^{-2} s^{-1}) were low. When measured in a conventional chamber (28) at 1500 μE m^{-2} s^{-1} (three-fourths of full sunlight), these plants had CO_2 assimilation rates of 25 μmol m^{-2} s^{-1} and leaf conductances of 0.4 mol m^{-2} s^{-1}. We do not know the effect of irradiance on the ammonia compensation point.

Compensation points were also determined in shoots of other species. These were (nbar): 2.1 (at 26 C) and 5.9 (at 25 C) in two *Z. mays* plants, 4.7 (at 32 C) in an *Amaranthus edulis* plant, and 3 (at 32 C) in an *Eucalyptus pauciflora* plant.

DISCUSSION

The results we present are unlikely to be due to surface absorption on the leaves, as it is known that plants can absorb ammonia from the air and metabolize it. Indeed, at high ambient partial pressures of NH_3, n_a, plants grow normally with no additional source of N (5). The rate of assimilation of NH_3 reaches a level, at 52 nbar (Fig. 2), similar to that observed by Hutchinson *et al.* (10). They measured uptake rates of 6 to 9 nmol m^{-2} s^{-1} by leaves of *Glycine max, Helianthus annuus, Z. mays*, and *Gossypium hirsutum* from air with n_a in the range 43 to 79 nbar.

In the present study, absorption of ammonia by leaves increased almost linearly with the partial pressure of ammonia in the air passed over the plants. Linear responses have been observed with *Z. mays* in the range 1,000 to 20,000 nbar (17) and with *Z. mays*,
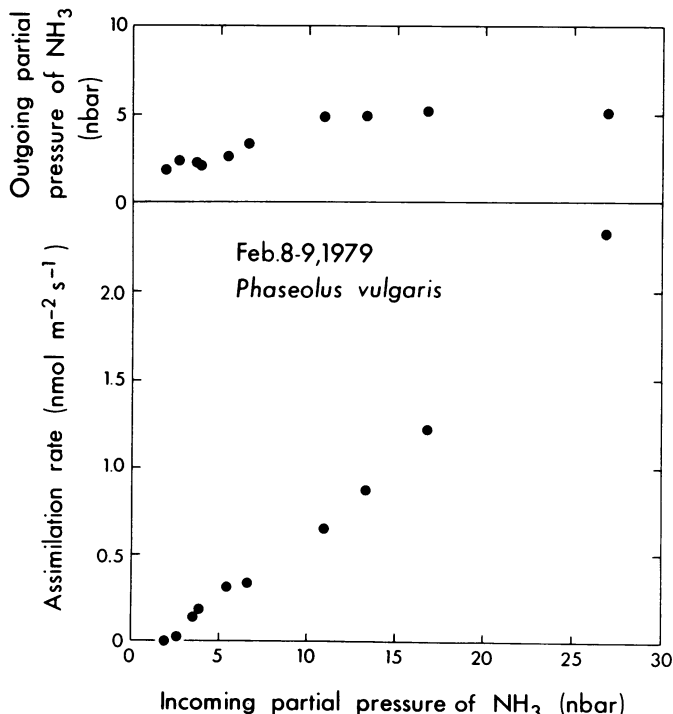
FIG. 1. Determination of the ammonia compensation point in *P. vulgaris* at 26.6 C: outgoing partial pressure and rate of uptake of ammonia *versus* incoming partial pressure.

Fagopyrum sagittatum, Pinus virginiana, G. max, and *Amaranthus retroflexus* using ^{15}N-labeled NH_3 in the range 39 to 607 nbar (13).

Denmead *et al.* (4), who measured ammonia uptake by a canopy of *Z. mays* using micrometeorological techniques, estimated that canopy conductances of 0.8 to 2 mol m^{-2} s^{-1} would have been necessary to account for the observed fluxes. These, they noted, seemed large for stomatal diffusion alone. However, in our experiments the leaf conductance, g, appeared sufficient. Conductance was estimated with some difficulty, as humidification occurred in the chamber and, although the transpiration rate (E) could be assessed accurately, the appropriate ambient humidity (e_a) could not. Further, leaf temperature varied over the plant surface, adding uncertainty via the estimate of e_i. Nevertheless, with *P. vulgaris* at 26 C, the leaf conductances were approximately 0.1 mol m^{-2} s^{-1}, as were the slopes of the plots of ammonia assimilation rate *versus* incoming partial pressure. Aneja (2) showed that rates of uptake of ammonia by leaves of *Z. mays, G. max,* snapbean, fescue grass, orchard grass, and *Avena sativa* varied with stomatal conductance in the predicted manner. He observed fluxes of 39 to 539 nmol m^{-2} s^{-1} from air containing 141 to 818 nbar.

We observed evolution of ammonia (or some other volatile amine) at low n_a. Porter *et al.* (17) indicated that *Z. mays* may leak small amounts of NH_3 or amide nitrogen into the atmosphere. However, these were isotopic and not net fluxes. Meyer (13) found that, when NH_3-free air was passed over plants in chambers, the exiting partial pressures were 2 nbar for *Z. mays,* 7 for *Medicago sativa,* 9 for *G. max,* 16 for *P. virginiana,* and 18 nbar for *A. retroflex.* (He concluded that absorption is predominant at the "normal atmospheric" partial pressures of 39 nbar but, over most of the globe, n_a is much lower.) Evolution of ammonia has also been observed occasionally in the field using micrometeorological techniques but, in such cases, the soil may have been the source (4).

Stutte and Weiland (23) and Stutte *et al.* (24) observed large gaseous losses of nonelemental N from the leaves of a variety of species grown under field conditions, when NH_3-free air was passed over them. The majority (typically 90%) of the collected N has since been shown to be in the reduced form (28). The volatilization was altered by several synthetic chemicals (27).

Our observation of a compensation point is consistent with micrometeorological data. Denmead *et al.* (3) found that a mixture of *Lolium perenne* and *Trifolium subterraneum* absorbed ammonia which had been released from the soil. Moving up the canopy, the partial pressure of ammonia declined from 24 to 2 nbar; the temperature at the top of the canopy was 24 C (O. T. Denmead, personal communication.).

A compensation point, γ, in *P. vulgaris* of 2.5 nbar at 26 C was observed. Knowing the Henry coefficient, one can determine to what γ corresponds in terms of a concentration of NH_3 at the wet surfaces of cells in the substomatal cavity. This coefficient, K_H (M/bar), is the ratio of the dissolved concentration (molar) of NH_3 and the partial pressure (bar) of NH_3 in equilibrium with the solution. K_H is 71 at 26 C (see under "Appendix") and so γ corresponds to a 177 nM solution of NH_3. This assumes that the Henry coefficient appropriate for distilled H_2O can be applied. In the same context, there is an equilibrium between $[NH_3]$ and $[NH_4^+]$ given by

$$[NH_3][H^+] = K_a[NH_4^+] \qquad (3)$$

and the pK_a is 9.21 at 26 C (see under "Appendix"). Thus, $\gamma = 2.5$ nbar corresponds to a $[NH_4^+]$ of $10^{2.46-pH}$. J. A. Raven (unpublished data) has equilibrated slices of our *P. vulgaris* leaves with aerated aqueous solutions in the light and has determined the resulting pH to be 6.8. Taking this to be the pH of the cell walls, γ corresponds to 46 μM $[NH_4^+]$. The last estimate is sensitive to the estimation of pH and would become 29 μM if the pH were estimated as 7.0.

An important property of an ammonium solution (at a fixed pH) is the temperature dependence of the partial pressure of ammonia in equilibrium with it. This relationship is derived under "Appendix" and an example is plotted in Figure 3. This example is valid for all combinations of $[NH_4^+]$ and pH, giving rise to γ = 2.5 nbar at 26 C. It is interesting that the $\gamma = 5.5$ nbar at 33 C fits on the same relationship. The ordinate may be rescaled linearly without affecting the shape. Thus, a combination of $[NH_4^+]$ and pH giving rise to 5 nbar at 26 C (= twice the present value) would cause a partial pressure of 2×5.5 (=11) nbar at 33 C, as indicated by the dashed line.

In this context, it is interesting that the losses of gaseous nonelemental N observed by Stutte *et al.* (23) increased with temperature and, at 28 and 35 C, respectively, were (in nmol m^{-2} s^{-1}): *Z. mays,* 2.5, 8; *G. hirsutum,* 6, 11; *Sorghum bicolor,* 5, 10; *G. max,* 2, 6; *Xanthium pensylvanicum,* 2.5, 7; *Ipomoea hederacea* var *integriuscula,* 5, 13; *Ipomoea hederacea,* 9, 16; *Datura stramonium,* 7, 21; *Sorghum halepense,* 4, 2; *Amaranthus palmeri,* 6, 27.

In other experiments (24), they observed volatilization from *G. max* leaves increasing from 1.4 to 18 nmol m^{-2} s^{-1} as the air temperature increased from 27 to 38 C. The intercellular partial pressure of the gaseous compound was apparently considerable at the higher temperatures.

Except at high NH_3 concentrations, where glutamate dehydrogenase may play a role, the majority of NH_3 fixation is probably via GS, which uses ATP to combine NH_3/NH_4^+ and glutamate to form glutamine (14). This reaction is important since, in leaf cells of C_3 species, there is a massive production and refixation of ammonia in the photorespiratory C cycle, stoichiometric with that of CO_2 (12, 30). For a plant with a CO_2 assimilation rate of 25 μmol m^{-2} s^{-1}, this internal flux of ammonia will be approximately

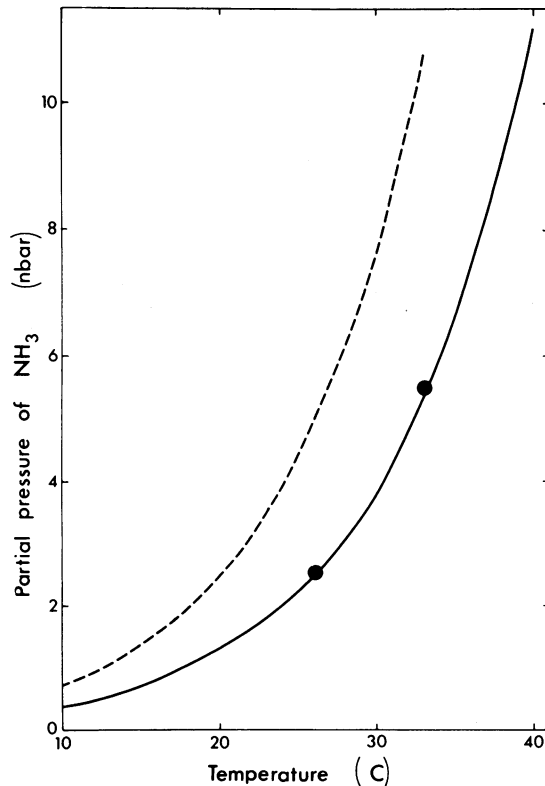FIG. 3. Effect of temperature on partial pressure of ammonia gas in equilibrium with an ammonium solution, at a fixed pH (here, 6.8). (———): $[NH_4^+]_{soln}$ = 46 μM; (– – –): $[NH_4^+]_{soln}$ = 92 μM (see under "Appendix" for derivation); (●): experimentally determined compensation points in *P. vulgaris.*

4,000 nmol m^{-2} s^{-1}. Further, since the N and C contents of plants are typically 2 and 40% of dry weight, respectively, a CO_2 assimilation rate of 25 μmol m^{-2} s^{-1} requires assimilation of N at approximately 1,070 nmol m^{-2} s^{-1}. Some of this flux will be via GS^4 in the leaf. Thus, the fluxes of ammonia into glutamine from internal sources, such as the decarboxylation of glycine, will dwarf the fluxes via stomata described here. This may explain why uptake shows no sign of saturation at the low partial pressures of NH_3 imposed in our experiments or even at the high values imposed by others (17).

Our compensation point, γ, is close to the K_m in vitro of GS (12–22 μM [NH_4^+]; refs. 15 and 22). However, it need not be associated with the kinetics of GS and may reflect the operating concentration of a cellular transport system. Such transport systems for NH_4^+ exist in fungi (19), algae (20) and in charophyte plants (26).

Regardless of whether γ is controlled by a cellular transport system or by the kinetics of GS, the small fluxes added via stomata in normal conditions are unlikely to affect the internal metabolism in the short term. The linear response of absorption to ambient partial pressure in the range up to 600 nbar (13) and even from 1,000 to 20,000 nbar (10) supports this notion. Thus, in natural conditions the partial pressure of ammonia in the substomatal cavity, n_i, is likely to be very nearly equal to γ and equation 1 becomes

$$J = g(n_a - \gamma)/P. \qquad (4)$$

Studies of the fate of atmospheric ammonia have assumed a mean deposition velocity acting on a mean ambient partial pressure to estimate the uptake by vegetation and soil. This is equivalent to assuming that n_i and γ are zero. The mean deposition velocity, assumed by Robinson and Robbins (18), was 1 cm s^{-1}, which would be mimicked by a canopy conductance of 0.4 mol m^{-2} s^{-1}. Estimates which ignore the compensation point are likely to be in error.

The results presented here may have implications for the study of NH_3 in the atmosphere. Volatilization of ammonia from vegetation may contribute to the huge, but unknown, terrestrial source of ammonia (21). Such losses are likely to be greatest when temperature is highest, stomatal conductance greatest, and ambient partial pressure least. In turn, stomatal conductance is greatest in conditions favoring CO_2 assimilation: high light, ample moisture, and high levels of nutrition, in particular that of N (29). That atmospheric levels are affected by the underlying vegetation may explain in part observations (9) that the atmospheric partial pressure of ammonia is higher on warm days.

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APPENDIX: PROPERTIES OF DILUTE AMMONIA SOLUTIONS

$$[NH_3]_{solution} = K_H p_{NH_3} \qquad (A1)$$

The Henry coefficient, K_H (M/bar) is the ratio of the dissolved concentration (molar) of NH_3 and the partial pressure (bar) of NH_3 in equilibrium with the solution. Its value is quoted as 56 M/bar (16). However, the Subcommittee on Ammonia, Committee on Medical and Biologic Effects of Environmental Pollutants (25) uses an expression for the Henry constant H (M/M), the ratio between the dissolved concentration and the gaseous concentration, which leads to a different value. The Subcommittee (25) uses the expression

$$\log_{10} H = 1477.7/T - 1.6937 \qquad (A2)$$

where T is the absolute temperature. The relationship between K_H and H may be expressed as

$$K_H = H \cdot \frac{\text{mol } NH_3/1 \text{ air}}{p_{NH_3}} = H/RT \qquad (A3)$$

where R (liter bar/K) is the gas constant (0.0831). At 26 C, $K_H = 70.8$.

At equilibrium, the relationship between [NH_3] and [NH_4^+] in solution is given by

$$[H^+][NH_3]_{solution} = K_a[NH_4^+]_{solution} \qquad (A4)$$

The Subcommittee (25) uses the following expression for the temperature dependence of the pK_a of NH_4^+:

$$pK_a = 0.09018 + 2729.92/T(K) \quad \text{(A5)}$$

for a value equalling 9.21 at 26 C. Combining equations (A1) and (A4) gives

$$p_{NH_3} = \frac{K_a}{K_H} \cdot \frac{[NH_4^+]_{\text{solution}}}{[H^+]} \quad \text{(A6)}$$

Using equations A2, A3, and A5, this becomes

$$p_{NH_3} = RT(10^{1.60352 - 4207.62/T}) \cdot \frac{[NH_4^+]_{\text{solution}}}{[H^+]} \quad \text{(A7)}$$

This relationship is plotted in Figure 3 with $[NH_4^+] = 46\ \mu M$ and $[H^+] = 10^{-6.8}$.

For the dashed line, $[NH_4^+] = 92\ \mu M$ and $[H^+] = 10^{-6.8}$.