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Estimate of annual NH₃ dry deposition to a fumigated ombrotrophic bog using concentration-dependent deposition velocities.

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Abstract

Estimates of the dry deposition of ammonia (NH₃) gas in a field fumigation experiment on an ombrotrophic bog have been made using the inferential technique, with measured wind speed at 2 m, and air concentrations at two heights above the vegetation. The parameters for a concentration-dependent surface resistance term have been derived from flux measurements over the same vegetation in a chamber study, separating stomatal from non-stomatal resistances.

Annual NH₃-N deposition in each of the 4 years 2003-2006 was estimated to increase from 3.0 ± 0.2 kg N ha⁻¹y⁻¹ in ambient air, with an NH₃ concentration at 0.5 m above the canopy of $0.7 \mu\text{g m}^{-3}$, to 50-70 kg N ha⁻¹y⁻¹ where annual average air concentrations were 70-90 $\mu\text{g m}^{-3}$ and concentrations during fumigation were up to 1600 $\mu\text{g m}^{-3}$. The equivalent deposition velocities (at $z=0.5$ m) were 0.016 m s^{-1} in ambient air and 0.003 m s^{-1} at $100 \mu\text{g m}^{-3}$. The differences between annual deposition estimates made from independent air concentration data at 0.1 m and 0.5 m above the canopy were small for distances more than 10 m from the source, after vertical mixing was complete. Over 4 years (2003 to 2006) and at 8 sampling points more than 10 m from the NH₃ source, the mean difference between the dry deposition estimates, using NH₃ concentrations measured independently at 0.1 m and 0.5 m above the canopy, was 2%.

Use of a constant surface resistance, with no concentration dependence, as commonly used in inferential models of dry deposition, would have predicted deposition up to 8 times too large.

1. Introduction

Ammonia (NH₃) is a trace gas primarily emitted from agricultural practices. Intensive rearing of poultry and animals leads to large point sources of NH₃ emission which can cause direct effects on sensitive vegetation (Cape, et al., 2008, Leith, et al., 2005, Pitcairn, et al., 2003) and lead to deposition of large amounts of nitrogen (N) downwind. Although it is relatively simple to measure the air concentrations of NH₃ by using passive diffusion samplers (Tang, et al., 2001), it is difficult to estimate the consequent dry deposition to the surface downwind, although such deposition is likely to be important in influencing ecological responses to the additional N, and may greatly exceed the wet deposition of N (Pitcairn, et al., 2002). Control of NH₃ emissions may be required where N deposition exceeds the Critical Load for ecosystems influenced by large point sources. However, simple attempts to estimate dry deposition from the

measured concentrations take no account of the possible effects of high NH_3 concentrations on the dry deposition process; direct measurements of NH_3 dry deposition fluxes have usually been made where air concentrations are (relatively) low ($< 10 \mu\text{g m}^{-3}$) and varying slowly with distance, e.g. (Erisman and Wyers, 1993, Flechard and Fowler, 1998, Rattray and Sievering, 2001, Sutton, et al., 1995, Sutton, et al., 1993a, Sutton, et al., 2000). The deposition of N is not well characterised in the vicinity of large point sources such as poultry or pig farms, where measured average NH_3 concentrations may be up to $60 \mu\text{g m}^{-3}$ (Pitcairn, et al., 2002), and hourly concentrations very much greater.

Estimates of the dry deposition of airborne gases and particles to the earth's surface are often made using an inferential method, whereby the air concentration (measured at a given height (z) above the surface) is multiplied by an appropriate height-referenced deposition velocity ($v_d(z)$) to give the deposition flux. For gases such as ozone, which are not emitted at the surface, the direction is downwards, and the deposition velocity can be estimated based on the measured or estimated turbulence of the atmosphere and the characteristics of the absorbing surface. Parameterisations of v_d are used, separating the different components of the overall transfer resistance ($R_t = 1/v_d$) into 'aerodynamic', 'boundary layer' and 'surface' terms. The deposition velocity is then expressed as: $v_d(z) = 1/R_t(z)$, where $R_t(z) = R_a(z) + R_b + R_c$ is the sum of the aerodynamic, boundary-layer and surface terms, respectively. Appropriate values for $R_a(z)$ can be estimated from vertical gradients in wind speed measured at the site, or from wind speed and surface roughness measurements, and R_b can be estimated for a particular surface vegetation type from measured wind speed. R_c can be parameterised in terms of vegetation type, stomatal opening, surface wetness, or any other factor which influences the reaction/deposition of the gas or particle of interest at the surface.

In its simplest formulation, the value of R_c is assumed to be independent of air concentrations. However, for some gases the surface may be a source as well as a sink, depending on the physical and physiological state of the vegetation, the wetness of the vegetation or soil surface, or the air concentration. Ammonia shows bi-directional transport (Sutton, et al., 1993b), which can be expressed in terms of an internal leaf concentration of ammonia which is in dynamic equilibrium with the air concentration; if air concentrations are greater than the equivalent leaf concentration then deposition occurs, but if the equivalent leaf concentration is greater than the air concentration, then the surface acts as a source rather than a sink.

The complexity of estimating ammonia deposition rates is further complicated by two other processes: (1) the surface sink for ammonia (i.e. to the outside of leaves rather than through stomata) has been shown to saturate at high concentrations, i.e. the surface resistance increases as concentrations increase (Jones, et al., 2007); and (2) the surface resistance depends upon the presence of acidic gases such as sulphur dioxide (SO_2) or nitric acid (HNO_3), which can effectively lower the surface resistance through chemical reaction with the deposited ammonia gas to form salts (Flechard, et al., 1999).

Such complexity makes it very difficult to estimate the dry deposition of ammonia to the landscape, particularly where there are many different plant species forming a varying canopy structure, where the different elements of the landscape may be sinks or

sources, and where conditions of surface wetness or the presence of acidic gases cause large temporal variations in surface resistance. Some of the same problems occur in field experiments, where although the air concentrations of ammonia may be measured, and the absorbing vegetation surface may be well characterised, the long-term deposition of ammonia is not simply estimated.

The objective of this paper is to take the detailed chamber measurements of the dependence of deposition rate on NH_3 concentration under controlled conditions (Jones, et al., 2007) and apply them to the field conditions of an open-air fumigation experiment over an ombrotrophic bog, in order to calculate the dry deposition of ammonia over the full range of measured NH_3 concentrations. The Whim bog nitrogen manipulation experiment in south-east Scotland is a unique field experiment comparing the effects of different forms of airborne nitrogen on an unmanaged ombrotrophic bog. The experiment (Leith, et al., 2004, Sheppard, et al., 2004) includes controlled additions of ammonium or nitrate in precipitation at 3 different levels of N deposition (some +/- potassium and phosphorus), and a gradient exposure to NH_3 gas. Ammonia is released from a cylinder of pure NH_3 gas into a 10 m x 0.2 m diameter perforated pipe when the wind direction is between 180 and 215° from north, and when wind speeds are greater than 2.5 m s⁻¹. Concentrations downwind of the source are measured using a combination of passive diffusion tube samplers and 'ALPHA' passive samplers, developed by CEH (Tang, et al., 2001) as used in the UK Ammonia Monitoring Network (www.cara.ceh.ac.uk). As part of the network operation, passive diffusion samplers are continuously compared against active denuder samplers at 12 sites to ensure accurate calibration (Sutton, et al., 2001, Tang, et al., 2007). In order to compare the relative response to wet and dry deposition, equivalent estimates of the total N deposition are required for each of the experimental treatments. For comparison with empirical Critical Loads for N (Bobbink, et al., 2003), values are required as an annual deposition rate. The site is well suited to a simplified approach in that there is no visible peat, but a complex canopy of mosses, lichens, sedges and ericaceous shrubs, with the water table close (< 10 cm) to the surface except during long drought periods. The site is also exposed to very low concentrations of acidic gases; measurements of SO_2 made at Auchencorth moss, approximately 2 km from the Whim site, indicate annual median concentrations of 0.44 $\mu\text{g m}^{-3}$ (average 2002-2006); this would represent an equivalent concentration of NH_3 to chemically neutralise the acidity from dissolved SO_2 of 0.43 $\mu\text{g NH}_3 \text{ m}^{-3}$. Measured HNO_3 concentrations in 2006, when monitoring started, were 0.46 $\mu\text{g HNO}_3 \text{ m}^{-3}$ (CEH, unpublished data); complete neutralisation would require 0.12 $\mu\text{g NH}_3 \text{ m}^{-3}$.

2. Theory

Measurements of the dependence of surface resistance on NH_3 concentrations were made using a large flux chamber at CEH Edinburgh, with a mixture of ombrotrophic bog vegetation including *Sphagnum* mosses, *Eriophorum vaginatum* L. and *Calluna vulgaris* (L.) Hull, to simulate the bog surface at Whim (Jones et al., 2007). Individual complete plants with their underlying peat were sampled from the bog and assembled inside the chamber, which was supplied with charcoal filtered air to which known concentrations of NH_3 up to 100 $\mu\text{g m}^{-3}$ were added. The results were divided into day-time and night-time to separate the responses to stomatal and non-stomatal uptake. Non-stomatal deposition was shown to be controlled by a surface resistance which

varied linearly with NH₃ concentration, following the expression $R_{ns} = 1.13 \chi + 4.6 \text{ s m}^{-1}$ at night, and $R_{ns} = 1.05 \chi + 3.6 \text{ s m}^{-1}$ during the day, where R_{ns} is the non-stomatal resistance; the day and night non-stomatal resistances were not significantly different. The stomatal resistance R_s was invariant with NH₃ concentration, at 112 s m^{-1} (Jones, et al., 2007).

The dependence of the overall surface resistance (R_c) on air concentration is not linear in daytime, because the stomatal and non-stomatal resistances act in parallel, so that $1/R_c = 1/R_{ns} + 1/R_s$. At night, $1/R_s$ is assumed to be zero, so that $R_c = R_{ns}$. The measured surface resistances in the flux chamber experiment cannot, however, be used directly to estimate deposition under field conditions, because the air concentration in the chamber experiment depends on the uptake rate, which in turn depends on the degree of mixing within the chamber – the problem can also be expressed in terms of identifying the equivalent surface concentration of ammonia in the chamber and in the field.

The transfer of NH₃ to the surface can be expressed using the normal resistance analogy:

Flux = $\chi * v_d$, where $v_d = 1 / (R_a + R_b + R_c)$ and both χ and v_d are referenced to a specific height, R_a and R_b refer to aerodynamic and boundary-layer resistance and R_c is the surface resistance. Separating the aerodynamic and surface terms, the flux can also be expressed in terms of a surface concentration χ_s : Flux = χ_s / R_c .

In the chamber the flux is calculated from the difference between measured outlet (χ_{out}) and inlet concentrations (χ_{in}). The overall transfer resistance between the air in the chamber and the surface comprises an ‘aerodynamic + boundary layer’ resistance term (R_{box}), that is a function of the fixed geometry and air flow through the chamber, and the surface resistance (R_c). The total flux can then be expressed as:

$$\text{Flux} = \chi_{in} / (R_{box} + R_c) = \chi_s / R_c \quad (1)$$

The effective surface concentration χ_s is the concentration driving the diffusive transfer across the surface resistance (R_c), after turbulent transport through the air and diffusion through the boundary-layer.

Case 1 – night-time (stomata assumed to be closed): $1/R_s = 0$

The assumption of closed stomata follows from the chamber experiments (Jones, et al., 2007) in which the variation of R_c with χ at night was made over similar vegetation to that growing at Whim. The same definition of day and night was used for the field data as in the chamber experiments, i.e. ‘day’ was when total solar radiation was greater than 50 W m^{-2} , and ‘night’ when less than 10 W m^{-2} .

In the chamber, the measured variation of NH₃ deposition with χ_{in} ($\mu\text{g m}^{-3}$) shows that:

$$R_c = R_{ns} = A * \chi_{in} + B, \quad (2)$$

where A and B are constants. A has units ($\text{s } \mu\text{g}^{-1} \text{ m}^2$); B has units (s m^{-1}). The surface concentration χ_s from eqn. 1 can therefore be written as:

$$\chi_s = R_c * \chi_{in} / (R_{box} + R_c), \quad (3)$$

and substituting for χ_{in} from eqn. 2,

$$\chi_s = R_c * (R_c - B) / [A*(R_{box} + R_c)] \quad (4)$$

which is the effective surface concentration of NH₃ in the chamber experiment.

In the field, for a particular reference height (z) at which χ and (R_a+R_b) are measured or calculated:

$$\text{Flux} = \chi(z) / (R_a(z) + R_b + R_c) = \chi_s / R_c \quad (5)$$

If the relationship between χ_s and R_c is the same in the field as in the chamber then we can substitute eqn. 4 into eqn. 5, to get:

$$\chi(z) / (R_a(z) + R_b + R_c) = (R_c - B) / [A*(R_{box} + R_c)] \quad (6)$$

Dropping the formal dependence on z for simplicity, rearranging gives a quadratic in R_c in terms of **measured (bold)** or *calculated (italics)* parameters:

$$R_c^2 + (R_a + R_b - \chi * A - B) * R_c - B * (R_a + R_b) + \chi * A * R_{box} = 0 \quad (7)$$

This can be solved for R_c:

$$R_c = -0.5 * (R_a + R_b - \chi * A - B) + 0.5 * [(R_a + R_b - \chi * A - B)^2 + 4 * (B * (R_a + R_b) + \chi * A * R_{box})]^{1/2} \quad (8)$$

As **A**, **B**, *R_a*, *R_b*, **R_{box}** and χ are known, then R_c, and hence the flux can be calculated.

The chamber data for night-time gave **A** = 1.13 m² s μg⁻¹, **B** = 4.59 s m⁻¹ and **R_{box}** = 180 s m⁻¹ (Jones, et al., 2007). R_c was calculated for a range of (R_a+R_b) and χ for the given values of **A** and **B**, and showed that to a good approximation, R_c is linear in both χ and (R_a+R_b) for $\chi > 50$ μg m⁻³.

During conditions without fumigation, when ambient NH₃ concentrations were small (< 5 μg m⁻³) a constant R_c of 20 s m⁻¹ was used, as in the algorithm used for mapping dry deposition of NH₃ across the UK (Smith, et al., 2000).

Case 2 – day-time (stomata open):

There are two parallel deposition pathways: to the leaf surface, and through the stomata into the leaf. The overall surface resistance (R_c) can therefore be expressed as:

$$1/R_c = 1/R_{ns} + 1/R_s \quad (9)$$

where R_{ns} is the non-stomatal resistance to the leaf surface, and R_s is the stomatal resistance. Experiments in the chamber showed that R_s was effectively constant over the concentration range used, at 112 s m⁻¹, suggesting that uptake and metabolism of absorbed NH₃ within the leaf occurred faster than the gas could be deposited through

the stomata. The external resistance R_{ns} showed similar behaviour to the night-time resistance, following a similar relationship to that in eqn. 2, but with $\mathbf{A} = 1.05 \text{ m}^2 \text{ s } \mu\text{g}^{-1}$, and $\mathbf{B} = 3.61 \text{ s m}^{-1}$ (Jones, et al., 2007).

The non-linear variation of R_c with χ in the field, based on the data obtained in the chamber and illustrated in Figure 1, makes a simple parameterisation more complex than for the night-time case. Details are given in the Appendix.

A parameterisation has been used during times of fumigation based on fitting the curves in Figure 1 with a rectangular hyperbola:

$$R_c = R_{c0} + a.\chi/(b+\chi) \quad (10)$$

where R_{c0} , a and b show a weak dependence on (R_a+R_b) as given in the Appendix. Values of R_c during daytime fumigation are calculated every 15 minutes from eqn. 10.

3. Calculations of fluxes at the Whim experimental field site

NH_3 is emitted in the field as pure gas diluted in a flow of air that is released from a perforated tube (10 m x 0.2 m) mounted 0.5 m above the ground surface. Air concentrations of NH_3 at Whim are measured at several locations, both upwind of the NH_3 release point and downwind along the experimental field transect, using passive diffusion samplers exposed over one month, mounted at 0.1 and 0.5 m above the vegetation surface, which is on average 0.3 m above the ground surface. At some locations measurements are made at other heights. Details of the exposure and measurement techniques have been reported elsewhere (Leith, et al., 2004). Wind speed at the two measurement heights is calculated from measurements made at a height of 2 m above the ground surface, reported as an average every 15 minutes, from:

$$u(z_1+h-d) = u(z_2-d) \cdot [\ln(z_1+h-d)-\ln(z_0)] / [\ln(z_2-d)-\ln(z_0)] \quad (\text{m s}^{-1}) \quad (11)$$

where:

z_1 (NH_3 measuring height above vegetation) = 0.1 or 0.5 m,

h (vegetation height) = 0.3 m,

z_2 (wind speed measurement height) = 2 m,

d (zero plane displacement of the ground caused by the vegetation) = 0.2 m,

z_0 (roughness length) = 0.03 m

The friction velocity (u^*) is calculated every 15 minutes from:

$$u(z_2-d) = u^* \cdot [\ln(z_2-d)-\ln(z_0)] / k \quad (\text{m s}^{-1}) \quad (12)$$

where k is von Karman's constant = 0.4

Values for the aerodynamic resistance (R_a) are calculated every 15 minutes from:

$$R_a(z-d) = u(z-d)/(u^*)^2 \quad (\text{s m}^{-1}) \quad (13)$$

for $z = 0.1$ and $z = 0.5$ m

Values for the boundary layer resistance (R_b) are calculated every 15 minutes (Garland, 1977, Sutton, et al., 1993a) from:

$$R_b = 1.45 (\text{Re}^{*0.24} \cdot \text{Sc}^{0.8}) / u^* \quad (\text{s m}^{-1}) \quad (14)$$

where Re^* is the Reynolds number = $z_0 \cdot u^* / \nu$,

and ν is the kinematic viscosity of air = $1.42 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ at 10°C ;

and Sc is the Schmidt number = $\nu / D = 0.68$

where D is the diffusion coefficient of NH_3 in air = $2.09 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$

For every 15 minute period, the total resistance at $z = 0.1 \text{ m}$ and $z = 0.5 \text{ m}$ is calculated from $R_t = R_a + R_b + R_c$ where R_c is given by eqn. 8 (night) or eqn. 10 (day), using the monthly average measured NH_3 concentration at that height. The deposition velocity $v_d(z) = 1 / R_t(z)$ calculated for each 15 minute period during fumigation is then multiplied by the average NH_3 concentration during fumigation $\chi(z)$ at each point along the transect, to give the deposition, and summed over the month. Deposition during periods without fumigation is calculated using the monthly average ambient concentration and the monthly average ($R_a + R_b$) at each height, with a constant value of R_c (20 s m^{-1}), and is the same at all points across the site.

Comparison of the deposition calculated from the independent concentration measurements at 0.1 m and 0.5 m provides an estimate of the overall uncertainty. Divergence is mostly caused by large concentration differences with height close to the NH_3 source, where the influence of the emission height (0.5 m) is evident, and the NH_3 gas is not well mixed vertically. The good agreement further from the source (Table 1) suggests that the overall uncertainty in the calculation is relatively unimportant in estimating the dry deposition flux.

4. Results from Whim bog site monitoring data (monthly)

A typical pattern of air NH_3 concentration along the transect is shown in Figure 2 (left-hand axis) for the annual average at both sampling heights (0.1 m and 0.5 m) in 2006. The concentration measured at 0.1 m above canopy close to the source is less than that at 0.5 m because the emitted NH_3 is not yet well mixed vertically. The number of minutes of NH_3 release is known for each month, so the average concentration during fumigation can be calculated, and is also shown in Figure 2 (right-hand axis). In 2006 NH_3 was released over 535 h, or 6% of the time. This pattern of exposure would be typical of a situation downwind of a major point source of NH_3 such as an intensive poultry unit. Air concentrations at 0.1 m above the vegetation are still elevated at 80 m downwind (one-tailed paired t-test over 11 monthly data, Feb - Dec 2006; $p=0.04$), but are not significantly different from ambient at 105 m ($p=0.17$). The lateral extent of the emission plume can be judged from measurements made at 60 m downwind of the source (Figure 3).

This pattern of average air concentration is reflected in the deposition pattern for 2006 (Figure 4), using the methods outlined above, corresponding to the data in Figure 2. It can be seen that the deposition estimated from the independent measurements at 0.1 m and 0.5 m are the same (as they should be) despite the small differences in NH_3 concentrations at the two heights (Figure 2 and Table 1). Figure 5 shows the deposition based on measurements at a height of 0.5 m for each of the 4 years; the pattern is the

same from year to year, although the absolute deposition varies, depending on the fraction of time that NH_3 is released, and the consequent differences in annual average concentrations (Table 1).

The average deposition velocities ($v_d = \text{flux}/\text{concentration}$) are shown in Figure 6 for 2006 only, as a function of distance downwind of the source, and in Figure 7 as a function of air concentration (note the logarithmic concentration scale).

A summary of the estimated deposition for each full year of treatment to date (2003-2006) at each of the sampling points is shown in Table 1. The differences between annual deposition estimates made from the independent air concentration data at 0.1 m and 0.5 m above the canopy were small for distances more than 8 m from the source, after vertical mixing was complete. Over 4 years (2003 to 2006) and at 8 sampling points more than 10 m from the NH_3 source, the mean difference between the two NH_3 deposition estimates was 2%.

5. Discussion

The approach used here relies on data gathered from the chamber experiment using reconstructed vegetation canopies, which could not reproduce completely the spatial complexity or overall species composition observed in the field. The chamber measurements were also made at least an hour after watering, avoiding the presence of surface water on the vegetation. These artificial conditions compared to the field situation may have led to systematic differences in deposition which cannot be quantified.

The uncertainty involved in using eqn. 10 is described in the Appendix. However, this begs the question as to whether the daytime stomatal resistance R_s remains constant as concentration increases, or at different phenological stages. Evidence from studies of similar semi-natural species (*Luzula sylvatica*) suggests no saturation of stomatal uptake of NH_3 when plants were exposed to concentrations up to $400 \mu\text{g m}^{-3}$ (Hill, 1999). The measurements on which the value of 112 s m^{-1} were based (Jones, et al., 2007) were made using well-watered vegetation at temperatures between 1°C and 20°C , typical of the range observed in the field, and showed no discernible variation with temperature. However, it may be that under very dry conditions, or at freezing temperatures, stomatal uptake of NH_3 is inhibited, so that the estimates provided above may be too high at some times of the year.

As to temporal variations, the dependence of fumigation on wind direction and wind speed means that NH_3 is released at Whim bog for periods as short as 1 minute, up to several hours. The variation in air concentration is the main driving factor determining the temporal variation in deposition, as seen even in the annual data (Figure 5 and Table 1). The non-stomatal resistances derived from eqn. 8 are based on the chamber results (Jones, et al., 2007) obtained once equilibrium had been established. During initial fumigation, before saturation occurs, uptake is likely to be greater than estimated from the equilibrium data; however, when fumigation ceases, there will be release of absorbed NH_3 back to the ambient air. Any discrepancy between initial uptake and final release can be attributed to the 'fixing' of NH_3 on the vegetation surface in an involatile form. The estimates above assume that there is no net deposition related to this

‘capacitance’ effect during intermittent fumigation, so may underestimate the true deposition. This effect is expected to be small in relation to the overall deposition rate, particularly for the low concentrations of acidic gases at this site, but the uncertainty cannot be quantified.

The uncertainty arising from use of monthly-averaged NH_3 concentrations is also difficult to assess. At night-time, the linear dependence of R_c on concentration means that the monthly mean of the 15-minute R_c values based on monthly mean concentrations would not differ from the monthly mean of the 15-minute R_c values based on the 15-minute average concentration values, had these been available. However, the 15-minute derived deposition velocity $v_d = 1/(R_a + R_b + R_c)$ does not scale linearly with concentration, so that the monthly dry deposition based on 15-minute v_d and a monthly mean concentration will not in general be the same as the monthly dry deposition based on 15-minute v_d and 15-minute concentrations. An estimate of the uncertainty introduced from this averaging process can be gained by comparing the difference in predicted deposition by changing concentration from 0.5χ to 1.5χ for a typical value of $(R_a + R_b)$ of 40 s m^{-1} ; this introduces a range in deposition of $\pm 10\%$ at $600 \mu\text{g m}^{-3}$ and $\pm 30\%$ at $100 \mu\text{g m}^{-3}$, but if within a month the concentration fluctuates between fumigation episodes so that one-third of the time it is at 0.5χ , χ and 1.5χ , the overall effect on the monthly deposition is $\pm 3\%$ or less.

The more complex relationship between R_c and χ during daytime fumigation (Figure 1), which dominates the deposition flux over a month, also introduces uncertainty caused by variation in concentration during different fumigation periods within the monthly timescale of the ammonia concentration measurements. However, for concentrations above $100 \mu\text{g m}^{-3}$ the variation in R_c with concentration is $< 20\%$, so the largest relative uncertainties in R_c will occur in the region where the concentration during fumigation is less than $100 \mu\text{g m}^{-3}$, which is at distances of more than 40 m from the release point (Figure 2). Even at $50 \mu\text{g m}^{-3}$ a similar calculation to that for night time (above) yields a range of deposition of $\pm 40\%$ between 0.5χ and 1.5χ , but an overall uncertainty in deposition of around $\pm 1\%$.

All the data on which these estimates are based were obtained in well-watered conditions but with dry leaf surfaces, using a chamber with charcoal-filtered air (Jones, et al., 2007). It is to be expected that in regions with higher concentrations of acidic gases such as SO_2 or HNO_3 the capacity for NH_3 uptake by surfaces would be enhanced, i.e. the surface resistances for non-stomatal uptake would be less than used in the above calculations. For the Whim bog site the comparison with charcoal-filtered air is a reasonable approximation, given the very low air concentrations of acidic gases present, but the values and parameterisations used in this study to calculate effective surface resistances and deposition velocities cannot safely be extrapolated to other sites where there may be much higher concentrations of acidic gases. Deposition during rain, and after rainfall to wet surfaces, would also be expected to be greater than to dry surfaces, but NH_3 that dissolved in surface water on the vegetation would (mostly) be released to the atmosphere as water evaporated. The methods used here would systematically underestimate dry deposition of NH_3 in such conditions.

Use of an inferential method for estimating dry deposition relies on the assumption that fluxes are not greatly affected by advection and storage terms which arise from measurements being made at a fixed height above the vegetation surface at which gas exchange occurs. The use of independent concentration measurements at two heights (0.1 and 0.5 m) above the canopy suggests (Table 1) that any such errors are small relative to the errors introduced by the method of calculation, at least for distances more than 8 m from the source, with no consistent bias from year to year.

The net effect of all these assumptions and uncertainties, the approximations used in calculating R_a and R_b , and the measurement error in NH_3 concentrations cannot be easily quantified; an estimate of $\pm 30\%$ for the uncertainty in annual dry deposition can be made based on 'expert judgement' with a potential bias towards underestimating deposition. This needs to be set in the context of the currently used methods for estimating NH_3 dry deposition, which assume a value of R_c that is independent of concentration (e.g. 20 s m^{-1} ; (Smith, et al., 2000)). Figure 8 shows the comparison between the methods used here and a simple constant value of $R_c = 20 \text{ s m}^{-1}$ for the Whim site in 2006, which would predict a very large overestimate, up to 8 times too large. The calculated annual average values for R_c varied between 30 and 330 s m^{-1} depending on distance from the source (highest values closer to the source and at night-time); this compares with values up to 140 s m^{-1} measured in the chamber experiments (Jones, et al., 2007).

6. Conclusions

The effect of including a concentration-dependent R_c in the calculation of dry deposition of NH_3 using the inferential method is to radically reduce the estimated dry deposition of N at the high NH_3 concentrations observed close to sources of NH_3 . Where high concentrations of NH_3 exist, either in experimental exposures, or close to major sources, any estimates of the consequent dry deposition of NH_3 need to take account of the likely dependence of non-stomatal uptake rates on concentration. The site at Whim bog is unique in that the parameters needed for using a concentration-dependent deposition rate have been measured under controlled conditions. Such data are not available for other vegetation types, for conditions where water availability might restrict stomatal uptake, or where the presence of acidic gases might enhance surface uptake of NH_3 . This means that estimates of the local contribution of large point sources of NH_3 to total N deposition cannot be made with confidence unless some information is available on the concentration dependence of the surface resistance for NH_3 deposition of the exposed vegetation. The evaluation of potential ecological responses close to large NH_3 sources may therefore be difficult using the Critical Loads approach (UNECE, 2003), which requires an accurate assessment of deposited N. In such cases, use of the average NH_3 concentrations (the Critical Levels approach (Cape, et al., 2008)) may be more robust as regards effects on vegetation, but does not address the long-term effects on soils and freshwaters.

In rural areas, where concentrations of acidic gases are low, the parameterisations of the deposition process used in this study may give a better indication of actual N deposition than the use of a constant non-stomatal resistance, or constant deposition velocity. However, the requirement to calculate explicitly the surface resistance as a function of NH_3 concentration applies only where concentrations occasionally exceed $100 \mu\text{g m}^{-3}$.

For regional-scale estimates of NH₃ deposition, which rely on the spatially-averaged air concentrations applicable at the km scale, a concentration-independent non-stomatal resistance is appropriate because the average NH₃ concentrations will be small (usually < 10 µg m⁻³), and non-stomatal resistances will not be greatly affected.

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APPENDIX

Case 2 – day-time:

There are two parallel deposition pathways, to the leaf surface, and through the stomata into the leaf. The overall surface resistance (R_c) can therefore be expressed as:

$$1/R_c = 1/R_{ns} + 1/R_s \quad \text{or} \quad R_{ns} = R_c \cdot R_s / (R_s - R_c) \quad (\text{A1})$$

where R_{ns} is the non-stomatal resistance to the leaf surface, and R_s is the stomatal resistance. R_s is taken to be constant, with a value appropriate to this vegetation type of 112 s m^{-1} , and the non-stomatal resistance varies with concentration (Jones et al., 2007):

$$R_{ns} = \alpha \cdot \chi_{in} + \beta \quad (\text{A2})$$

where $\alpha = 1.05 \text{ m}^2 \text{ s } \mu\text{g}^{-1}$ $\beta = 3.61 \text{ s m}^{-1}$

In the chamber, the concentration at the point where transfer is determined only by the surface resistance, $\chi_s = R_c \cdot \chi_{in} / (R_{box} + R_c)$, as before, and can be equated to the equivalent concentration in the field (eqn. 4):

$$\chi_s = R_c \cdot \chi(z) / (R_a(z) + R_b + R_c) \quad (\text{A3})$$

Combining eqn. A1 and A2 gives an expression for χ_{in}

$$\chi_{in} = \frac{R_c \cdot R_s}{\alpha \cdot (R_s - R_c)} - \beta / \alpha \quad (\text{A4})$$

The term β/α is small ($3.4 \mu\text{g m}^{-3}$) relative to the values of χ_{in} , so can be neglected.

From eqn. 1, Flux = $\chi_{in} / (R_{box} + R_c)$, and substituting for χ_{in} from eqn. A4 gives

$$\text{Flux} = \frac{R_c \cdot R_s}{\alpha \cdot (R_s - R_c)(R_{box} + R_c)} \quad \text{in the chamber} \quad (\text{A5})$$

$$= \chi(z) / (R_a(z) + R_b + R_c) \quad \text{in the field} \quad (\text{A6})$$

Inverting these equations gives a quadratic in R_c

$$(\alpha \cdot \chi + R_s) \cdot R_c^2 + [(R_a + R_b) \cdot R_s - \alpha \cdot \chi \cdot (R_s - R_{box})] \cdot R_c - \alpha \cdot \chi \cdot R_s \cdot R_{box} = 0 \quad (\text{A7})$$

which can be solved to give values for R_c for a range of χ and $(R_a + R_b)$, given the measured values of α , R_s and R_{box} from the chamber experiment. The relationship between field R_c and χ for different values of $(R_a + R_b)$ in the range observed at Whim bog ($10\text{-}150 \text{ s m}^{-1}$) is shown in Figure 1, and can be approximated by eqn. 10.

With the measured values of α , R_s and R_{box} from the chamber experiment, the parameters of eqn. 10 can be well described by:

$$R_{c0} = 26.7 e^{-0.0234 (R_a+R_b)} \quad (A8)$$

$$a = 7.39 \ln(R_a+R_b) + 74.1 \quad (A9)$$

$$b = 44.2 e^{0.0051(R_a+R_b)} \quad (A10)$$

$$\text{where } R_c = R_{c0} + a.\chi/(b+\chi) \quad (10)$$

This set of parameters provides estimates of R_c in terms of $(R_a+ R_b)$ and χ that are within 1% of those calculated from eqn. A7, and can be used directly from the field estimates of $R_a(z)$, R_b and measured $\chi(z)$ every 15 minutes to calculate R_c and thence $R_t(z)$ and $v_d(z)$.

For values of (R_a+R_b) in the range measured in the field, at the small values of χ typically used for regional modelling NH_3 deposition, the second term of eqn. 10 is less than $2.\chi \text{ s m}^{-1}$, i.e. $R_c \sim R_{c0}$. For $\chi = 1 \mu\text{g m}^{-3}$ this means that the surface resistance is predicted to be less than 20 s m^{-1} , the value assumed in area-scale modelling of deposition (Smith et al., 2000), only for values of $(R_a+ R_b) > 16 \text{ s m}^{-1}$, leading to only a weak dependence of R_t (and v_d) on the value of R_c as calculated from eqn. 10.

Table 1. Annual average measured concentrations and calculated deposition at each point along the transect.

Measurements were made at 0.1 m and/or 0.5 m above the canopy.

The last 4 columns give data for measurements across the line of the transect; 12W = 12 m to west of the centre line, etc.

| Concentrations at 0.5m above vegetation ($\mu\text{g NH}_3 \text{ m}^{-3}$) | | | | | | | | | | | | | | | | | | | |
|--|-----|-----|-----|-----|-----|----|----|----|----|----|-----|-----|-----|-----|---------|------------|------------|------------|------------|
| distance (m) | 1 | 2 | 4 | 6 | 8 | 12 | 16 | 20 | 24 | 32 | 48 | 60 | 80 | 105 | ambient | 60: 12W | 60: 12E | 60: 15W | 60: 15E |
| 2002(May-Dec) | 354 | 232 | 169 | 137 | 132 | 84 | 59 | | | 21 | | 6.7 | | | 0.6 | | | | |
| 2003 | 194 | 140 | 108 | 93 | 84 | 67 | 49 | | | 19 | | 6.1 | | | 0.8 | | | | |
| 2004 | 132 | 98 | 77 | 71 | 68 | 57 | 46 | | | 17 | | 6.1 | | | 0.7 | 2.4 | 2.4 | 2.0 | 1.9 |
| 2005 | | 102 | | 72 | 63 | 56 | 34 | | | 14 | | 5.0 | | | 0.6 | 2.1 | 2.2 | 1.6 | 1.8 |
| 2006 | | 103 | | 71 | 60 | 45 | 31 | 22 | 18 | 13 | 5.2 | 3.5 | | | 0.7 | 2.0 | 3.2 | 2.0 | 2.5 |
| Concentrations at 0.1m above vegetation ($\mu\text{g NH}_3 \text{ m}^{-3}$) | | | | | | | | | | | | | | | | | | | |
| distance (m) | 1 | 2 | 4 | 6 | 8 | 12 | 16 | 20 | 24 | 32 | 48 | 60 | 80 | 105 | ambient | 60: 12W | 60: 12E | 60: 15W | 60: 15E |
| 2002(May-Dec) | 48 | 115 | 115 | 112 | 123 | 88 | 59 | | | 21 | | 6.0 | | | 0.5 | | | | |
| 2003 | 28 | 74 | 82 | 82 | 84 | 63 | 48 | | | 18 | | 5.2 | | | 0.5 | | | | |
| 2004 | 20 | 56 | 61 | 60 | 69 | 53 | 51 | | | 16 | | 5.0 | | | 0.5 | 1.8 | 2.1 | 1.4 | 1.5 |
| 2005 | | 57 | | 67 | 67 | 48 | 34 | | | 13 | | 3.8 | | | 0.5 | 1.8 | 1.8 | 1.4 | 1.4 |
| 2006 | | 63 | | 72 | 65 | 49 | 30 | 21 | 16 | 13 | 5.0 | 2.8 | 1.5 | 0.9 | 0.5 | 1.7 | 2.5 | 1.5 | 2.0 |
| Deposition based on concentrations at 0.5m above vegetation ($\text{kg N ha}^{-1}\text{y}^{-1}$) | | | | | | | | | | | | | | | | | | | |
| distance (m) | 1 | 2 | 4 | 6 | 8 | 12 | 16 | 20 | 24 | 32 | 48 | 60 | 80 | 105 | ambient | 60: 12W | 60: 12E | 60: 15W | 60: 15E |
| 2003 | 167 | 123 | 98 | 85 | 80 | 64 | 52 | | | 26 | | 13 | | | 3.2 | | | | |
| 2004 | 114 | 89 | 71 | 67 | 64 | 55 | 47 | | | 22 | | 13 | | | 3.1 | 7.7 | 7.7 | 6.9 | 6.8 |
| 2005 | | 73 | | 54 | 47 | 46 | 32 | | | 18 | | 11 | | | 2.8 | 6.8 | 6.7 | 5.8 | 5.7 |
| 2006 | | 72 | | 49 | 44 | 33 | 27 | 21 | 19 | 16 | 9.7 | 7.9 | | | 2.9 | 5.4 | 7.7 | 5.3 | 6.7 |
| Deposition based on concentrations at 0.1m above vegetation ($\text{kg N ha}^{-1}\text{y}^{-1}$) | | | | | | | | | | | | | | | | | | | |
| distance (m) | 1 | 2 | 4 | 6 | 8 | 12 | 16 | 20 | 24 | 32 | 48 | 60 | 80 | 105 | ambient | 60: 12W | 60: 12E | 60: 15W | 60: 15E |
| 2003 | 34 | 75 | 80 | 82 | 82 | 65 | 51 | | | 26 | | 12 | | | 2.5 | | | | |
| 2004 | 26 | 55 | 60 | 62 | 67 | 54 | 54 | | | 22 | | 12 | | | 2.7 | 6.8 | 7.4 | 5.9 | 6.1 |
| 2005 | | 45 | | 51 | 52 | 41 | 33 | | | 18 | | 9.3 | | | 2.3 | 6.2 | 5.9 | 5.3 | 5.0 |
| 2006 | | 50 | | 53 | 47 | 37 | 26 | 21 | 18 | 16 | 9.5 | 7.1 | 5.2 | 3.4 | 2.4 | 5.2 | 6.7 | 4.6 | 6.1 |

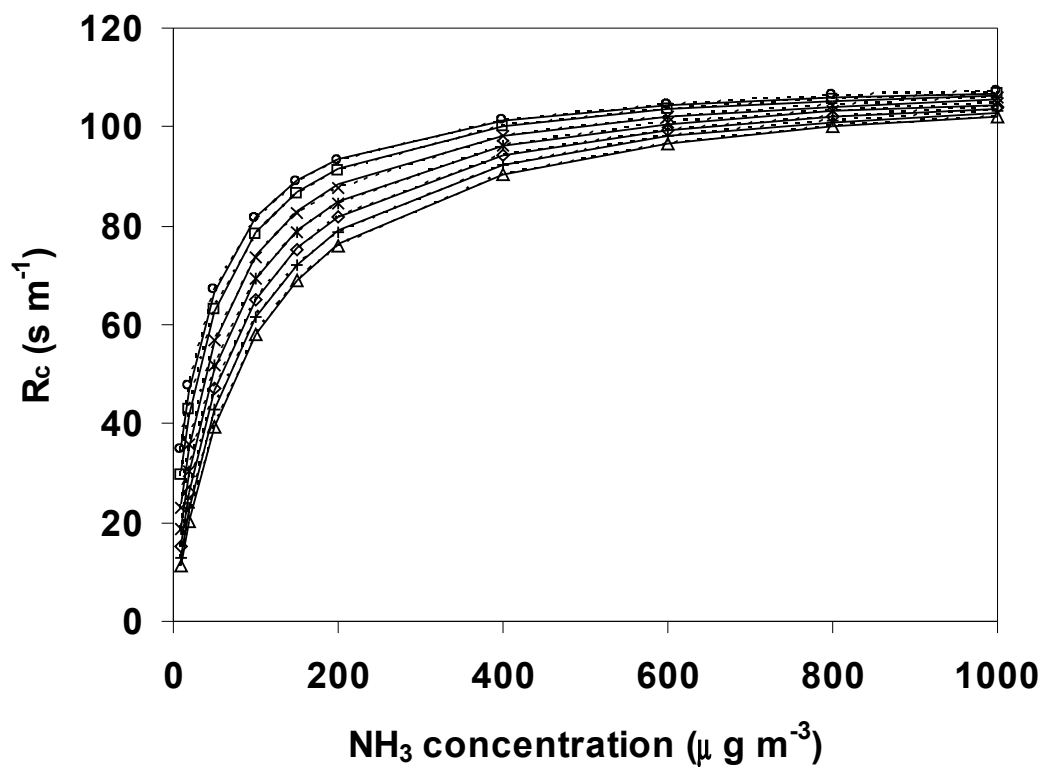


Figure 1. Variation in R_c with concentration during daytime fumigation. The top curve is for $(R_a + R_b) = 10\ s\ m^{-1}$ and the bottom curve for $(R_a + R_b) = 150\ s\ m^{-1}$, with intermediate curves at intervals of $25\ s\ m^{-1}$. The solid lines are calculated from the parameterisation of rectangular hyperbolae (see eqn. 10 and Appendix), and the data points are connected by dashed curves.

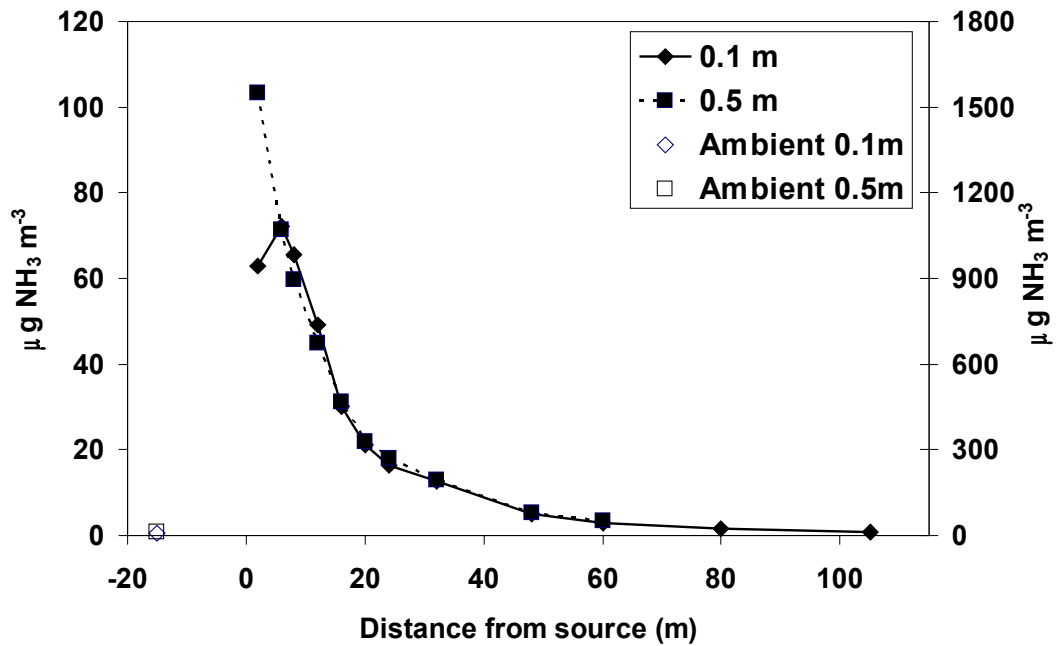


Figure 2. Annual average concentration (left-hand axis) of NH₃ at Whim bog during 2006, measured at 0.1 m and 0.5 m above the canopy, as a function of distance downwind of the release point. The right-hand axis shows average concentrations during fumigation.

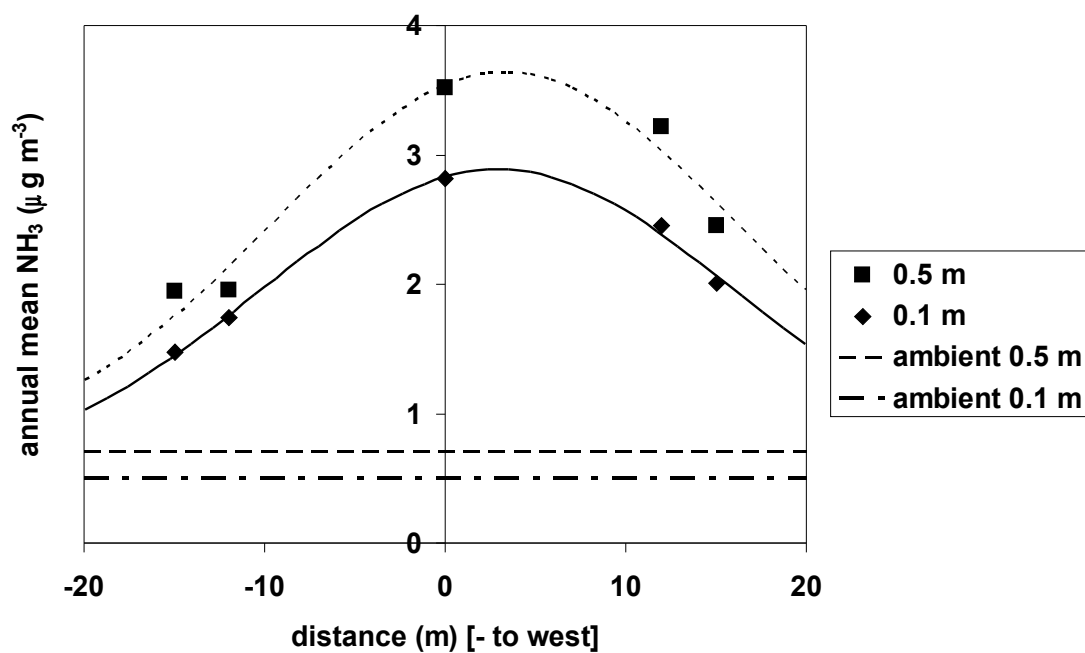


Figure 3. Annual average concentration of NH₃ at Whim bog during 2006, measured at 0.1 m and 0.5 m above the canopy, as a function of distance across the plume at 60 m downwind of the release point.

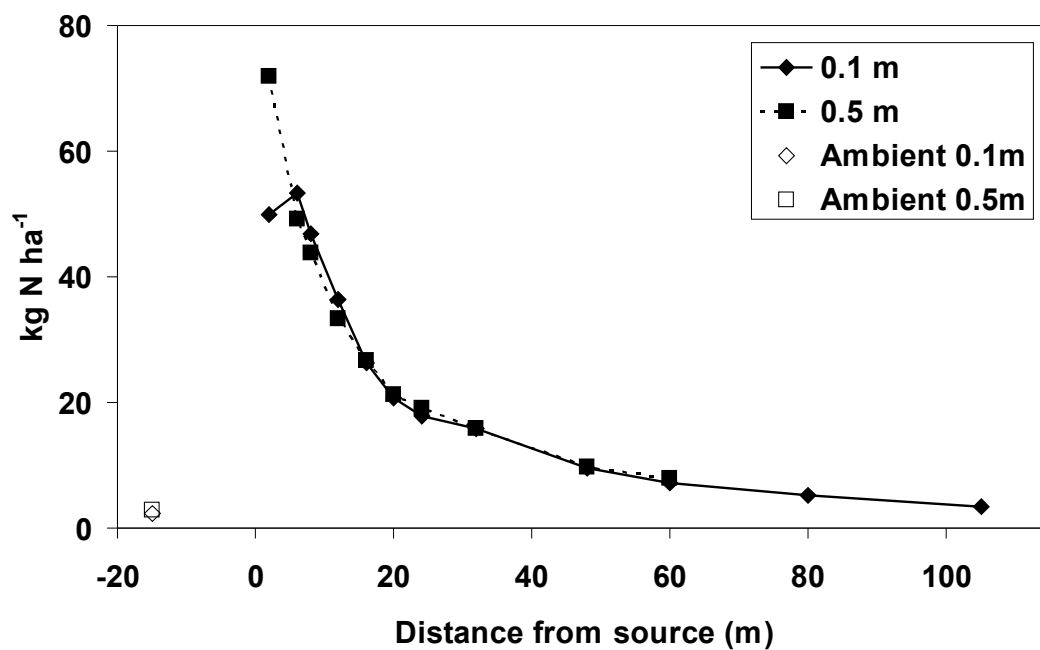


Figure 4. Calculated dry deposition of NH₃ to Whim bog in 2006 (kg N ha⁻¹ y⁻¹) as a function of distance downwind of the source, from independent concentration measurements at 0.1 m and 0.5 m above the canopy.

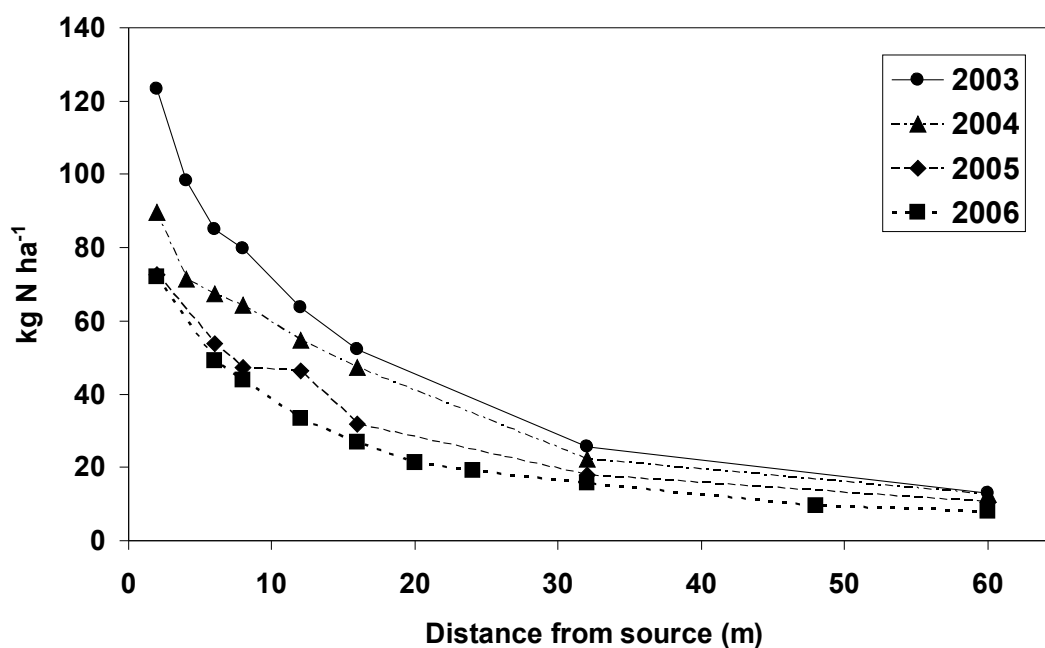


Figure 5. Calculated dry deposition of NH_3 to Whim bog in 2003-2006 ($\text{kg N ha}^{-1} \text{ y}^{-1}$) as a function of distance downwind of the source, from concentration measurements at 0.5 m above the canopy, showing annual variation (see Table 1).

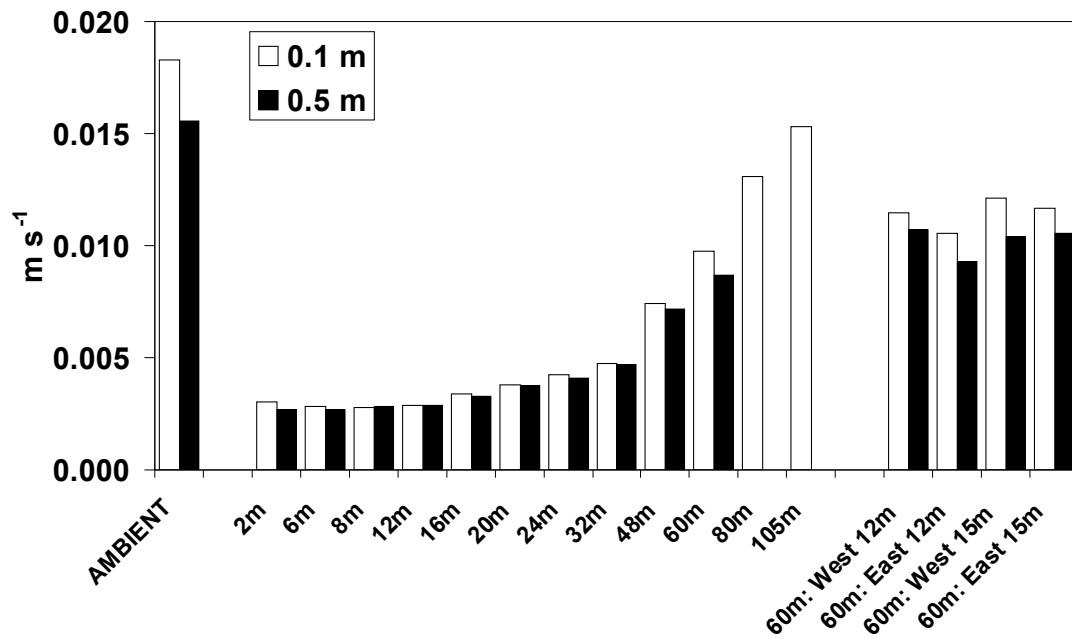


Figure 6. Average deposition velocity (v_d , $m s^{-1}$) at each measurement distance downwind from the source; Whim bog, 2006. The data at 60m West and East refer to measurements made across the plume (Figure 3).

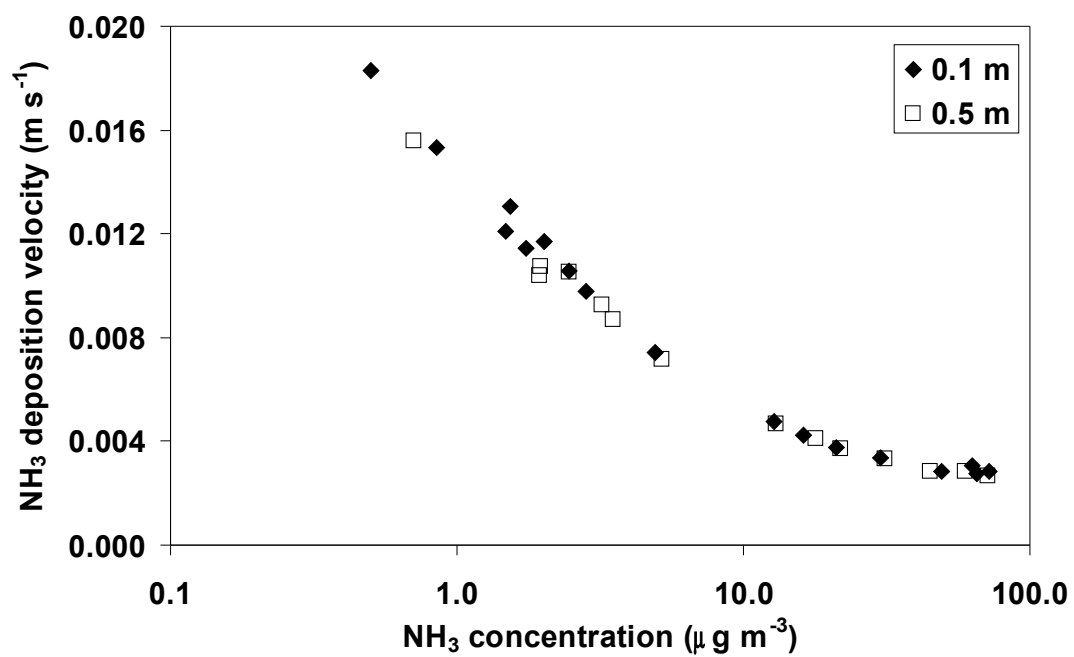


Figure 7. Average deposition velocity (v_d , m s^{-1}) as a function of NH₃ concentration; Whim bog, 2006.

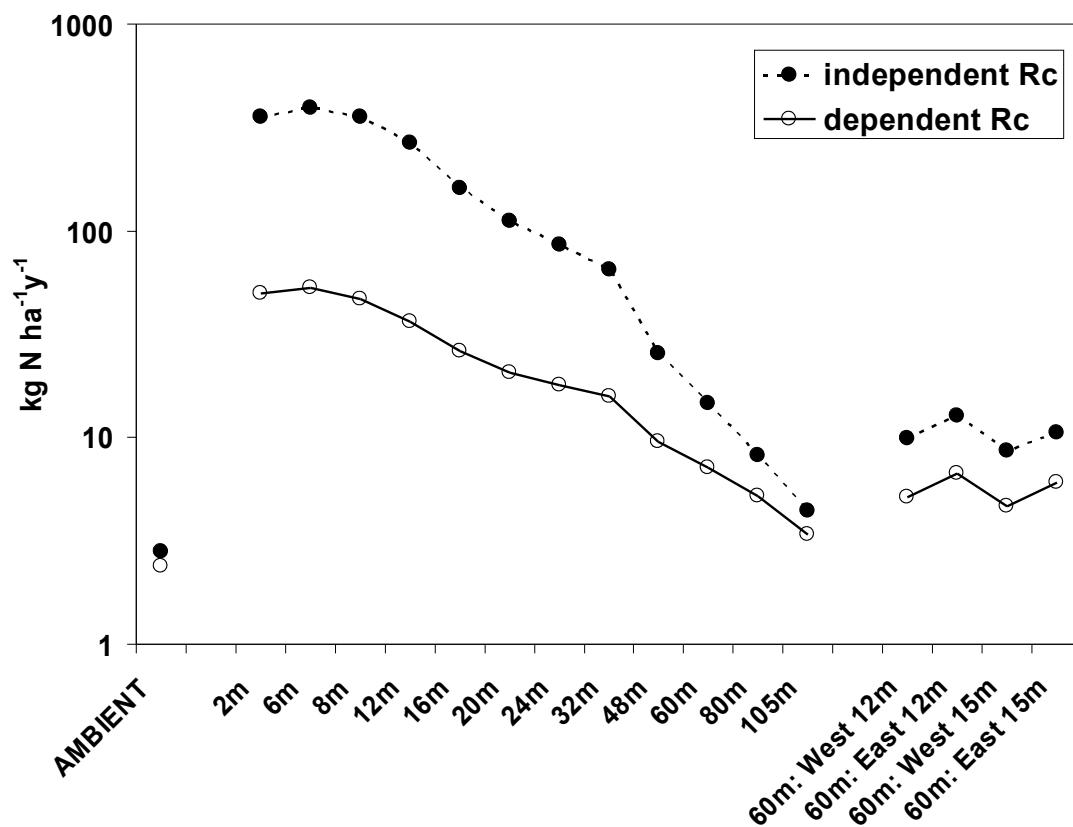


Figure 8. Dry deposition of NH₃ as a function of distance from source, calculated using measured NH₃ concentrations at 0.1 m above canopy and a constant value of $R_c = 20 \text{ s m}^{-1}$ (dashed line) or with the concentration-dependent R_c derived here (solid line). Note the logarithmic vertical scale; Whim bog, 2006.