

Concentration-dependent NH₃ deposition processes for mixed moorland semi-natural vegetation

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Received 16 August 2006; received in revised form 31 October 2006; accepted 2 November 2006

Abstract

Dry deposition modelling typically assumes that canopy resistance (R_c) is independent of ammonia (NH₃) concentration. An innovative flux chamber system was used to provide accurate continuous measurements of NH₃ deposition to a moorland composed of a mixture of *Calluna vulgaris* (L.) Hull, *Eriophorum vaginatum* L. and *Sphagnum* spp. Ammonia was applied at a wide range of concentrations (1–100 $\mu\text{g m}^{-3}$). The physical and environmental properties and the testing of the chamber are described, as well as results for the moorland vegetation using the ‘canopy resistance’ and ‘canopy compensation point’ interpretations of the data.

Results for moorland plant species demonstrate that NH₃ concentration directly affects the rate of NH₃ deposition to the vegetation canopy, with R_c and cuticular resistance (R_w) increasing with increasing NH₃ concentrations. Differences in R_c were found between night and day: during the night R_c increases from 17 s m^{-1} at 10 $\mu\text{g m}^{-3}$ to 95 s m^{-1} at 80 $\mu\text{g m}^{-3}$, whereas during the day R_c increases from 17 s m^{-1} at 10 $\mu\text{g m}^{-3}$ to 48 s m^{-1} at 80 $\mu\text{g m}^{-3}$. The lower resistance during the day is caused by the stomata being open and available as a deposition route to the plant. R_w increased with increasing NH₃ concentrations and was not significantly different between day and night (at 80 $\mu\text{g m}^{-3}$ NH₃ day $R_w = 88 \text{ s m}^{-1}$ and night $R_w = 95 \text{ s m}^{-1}$). The results demonstrate that assessments using fixed R_c will over-estimate NH₃ deposition at high concentrations (over $\sim 15 \mu\text{g m}^{-3}$).

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Keywords: Canopy resistance; Compensation point; Cuticular resistance; Flux chamber; Dry deposition; Ammonia

1. Introduction

Ammonia is recognised to be an important atmospheric pollutant for semi-natural vegetation, causing eutrophication, nutrient imbalance and changes in species composition (Pearson and

Stewart, 1993; Sutton et al., 1993a). Quantifying and parameterising the deposition of NH₃ to vegetation is necessary to predict the likelihood of ecosystem change and for a mechanistic understanding of NH₃ deposition processes. There are several models of NH₃ deposition; the two models used in this paper are the canopy resistance (R_c) model (Sutton et al., 1992; Erisman and Wyers, 1993) and the canopy compensation point model

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(Sutton and Fowler, 1993; Sutton et al., 1995). Both models have been widely implemented and shown to work well in predicting NH_3 deposition to semi-natural vegetation (Sutton et al., 1993a; Nemitz et al., 2001). However, significant uncertainty still exists in modelling NH_3 deposition and in quantifying NH_3 deposition to the field. For example, determining R_c and the cuticular resistance (R_w), and how they respond to increasing NH_3 concentrations are among the most uncertain factors in understanding NH_3 deposition. Fowler et al. (1998) modelled increased resistance of the canopy to increasing NH_3 concentrations over moorland vegetation for low concentrations ($0.1\text{--}2\ \mu\text{g m}^{-3}$). However, little is known about concentration-dependant deposition over a wider concentration range ($0\text{--}100\ \mu\text{g m}^{-3}$). This range of concentrations covers the main areas of interest in air pollution research. The aims of this paper are to:

- Describe an innovative flux chamber that can accurately measure NH_3 deposition.
- Identify NH_3 concentration-dependent deposition rates for a mixed moorland vegetation canopy for a range of NH_3 concentrations ($1\text{--}100\ \mu\text{g m}^{-3}$).

2. Methods

2.1. Experimental design

To measure the exchange of NH_3 , an innovative flux chamber was constructed to accommodate a significant area of mixed moorland vegetation canopy. The chamber was tested extensively before flux measurements began, which allowed the results to be directly related to field conditions. The flux chamber was constructed inside an octagonal open-top chamber (OTC) with a floor area of $7\ \text{m}^2$ and a height of 2.3 m (Fowler et al., 1989) at Bush Estate near Edinburgh, Scotland ($55^\circ 51' \text{N}$, 198 m altitude) (Fig. 1) providing shelter, NH_3 fumigation and the air system.

The flux chamber design is shown in Fig. 2. The transparent polyethylene walls and roof were attached inside the wooden chamber framework (dimensions: $1.75 \times 1.75 \times 0.60\ \text{m}$). The flux chamber polyethylene walls were extended to produce a 0.3 m skirt allowing a seal to be formed with the polyethylene chamber floor. The total volume of the chamber was $1.8\ \text{m}^3$. The polyethylene minimised

deposition to internal surfaces of the flux chamber (in agreement with Mennen et al., 1995). The chamber was accessed, when necessary, by lifting one side of the flux chamber structure. Access was kept to a minimum because opening the chamber changed conditions temporarily ($\sim 20\ \text{min}$). Concentrations of NH_3 were determined at the inlet and the outlet which were at opposite ends of the chamber. Air in the flux chamber was mixed using a 1.7 m manifold on the inlet air with 14 inlets each of 10 mm in diameter. A 0.3 m fan (GF30 45 W ventilators) was positioned at each end of the inlet manifold; one 0.23 m fan (GF23 35 W ventilator) was placed in the centre of the manifold providing additional mixing of air in the chamber.

2.2. Air input system

Ambient air was pumped into the main OTC manifold (diameter 0.25 m) using a fan unit (Wolter GmbH EK31) which contained 10 activated charcoal filters, to remove ozone, sulphur dioxide, nitric acid and nitrogen dioxide. Air passed through the manifold at a positive pressure into an 11 cm flexible tube connected to the flux chamber inlet. Air passed through the flux chamber at a rate of $1.02\ \text{m}^3\ \text{min}^{-1}$. The ambient air was not filtered for NH_3 , but concentrations at the site provided a low background of typically $0.5\text{--}2\ \mu\text{g m}^{-3}$.

2.3. NH_3 fumigation system

Elevated NH_3 concentrations in the flux chamber were generated through the volatilisation of 1% aqueous NH_3 solution into the OTC manifold air stream. Concentrations were manipulated by changing the rate and concentration of NH_3 solution released into the OTC manifold, using a peristaltic pump and different size tubing. NH_3 solution was added to the OTC manifold through an inverted sintered glass funnel ensuring complete volatilisation of the NH_3 solution into gas before entering the flux chamber. The system allowed fine and rapid adjustments of NH_3 concentrations, with chamber concentration changing within 10 min.

The environment in the flux chamber was inevitably modified from ambient conditions. Temperatures inside the chamber were slightly higher throughout the day and night; typically $0.3\text{--}3\ ^\circ\text{C}$ above ambient temperatures and humidity was

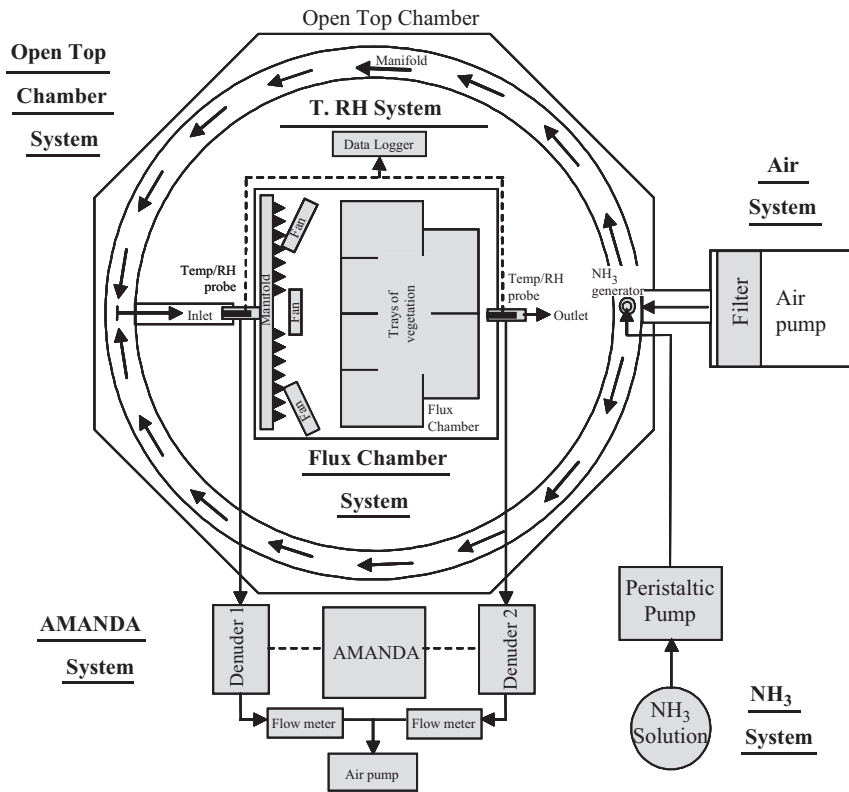


Fig. 1. Schematic diagram of the experimental setup, identifying the six component systems (not to scale). Arrows show air movements.

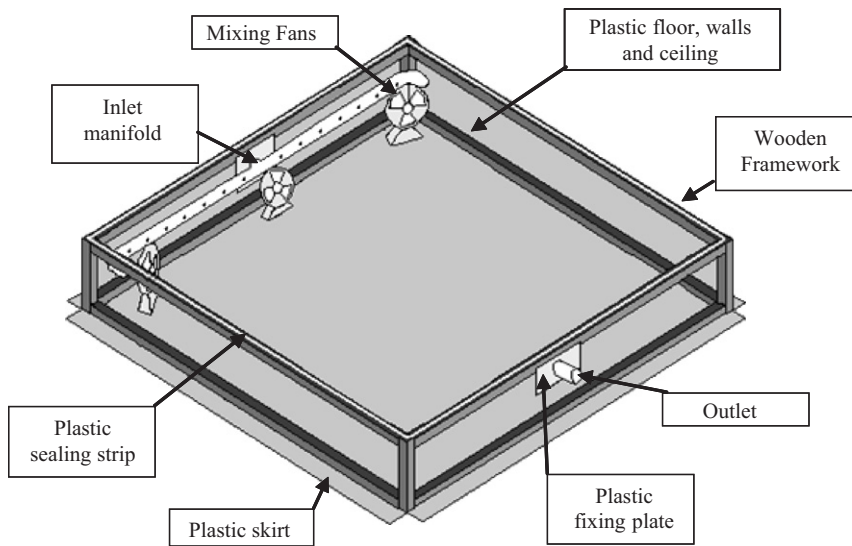


Fig. 2. Diagram showing the flux chamber design.

typically 5% higher than outside conditions. Solar radiation was 49.6% of that outside, due to shading by the plastic and wooden frame of the flux chamber and the glass walls and aluminium frame of the OTC.

2.4. Monitoring of chamber conditions

The NH₃ concentrations at the inlet and outlet of the flux chamber were sampled by two continuous flow denuders, and NH₃ concentrations were

determined by conductivity in a single detector box (response time: ~ 2 min). This dual channel AMANDA system (Ammonia Measurement by ANnular Denuder sampling with on line Analyser system) has been described in detail in Wyers et al. (1993). The denuders were connected to the inlet and outlet of the flux chamber via 10 mm PTFE tubing. Air was sampled through the denuder tube at a rate of $\sim 251 \text{ min}^{-1}$ using a suction pump (Becker suction pump regulated by a critical flow orifice). The air flow through the denuder tube was periodically inspected with a Dry-cal DC-lite flow meter. Denuder comparability was checked weekly by connecting the two denuders and sampling the air from the outlet, the difference between the denuders to be typically less than 3%. When differences exceeded 5%, the denuders were cleaned, checked for problems and then rechecked for comparability. Data were corrected for the denuder difference from these checks.

Ten minute-averaged temperature and humidity data were collected on a 21X datalogger (Campbell Scientific Inc.) at the inlet and outlet of the flux chamber using two RH/T sensor modules (MP100H/400H, Rotronic). The probes measured humidity from 0–100% ($\pm < 1\%$ RH) and temperatures from -40 to $+60$ °C (± 0.3 °C). The two probes were tested for their comparability, approximately monthly, by placing them together and comparing the output.

Solar radiation data were collected from a CEH fieldsite 350 m to the east of the OTC field-site. Reduction in radiation caused by the OTC and flux chamber was calculated by running a pyranometer (Single Channel Light Sensor, Skye Instruments Limited) for eight days inside the flux chamber and comparing it to the data from the CEH fieldsite: a high correlation was found (R^2 0.95, data not shown), with a 49.6% reduction.

The flow rate of air through the flux chamber was measured by pumping 500 ml of methane into the inlet, and sampling 10 ml of outlet air every 15 s for 195 s. Beforehand, six ambient 10 ml samples of chamber air were collected. Air samples were analysed for methane concentrations using a Hewlett Packard S890 series II gas chromatograph (porapax Q. $\frac{1}{4}$ in column) fitted with a flame ionisation detector. Flow rate was measured at the beginning of the experiment.

The flow rate was derived from the dilution of CH_4 in the chamber, which followed a logarithmic

decay:

$$\ln C = \ln C_{(0)} - kt, \quad (1)$$

where $\ln C$ is the natural log $[\text{CH}_4]$, $\ln C_{(0)}$ is a constant, k is the dilution rate constant (s^{-1}) and t is time (s).

The flow rate may be derived from the dilution rate constant:

$$f = kv, \quad (2)$$

where f is the flow rate ($\text{m}^3 \text{ min}^{-1}$) and v is the volume (m^3).

The averages of the experiments gave an overall average flow rate through the chamber of $1.02 \text{ m}^3 \text{ min}^{-1}$, s.e. $\pm 0.0021 \text{ m}^3 \text{ min}^{-1}$ (turnover = $0.56 \text{ chambers min}^{-1}$).

2.5. Atmospheric resistances

The total combination of atmospheric resistances in the flux chamber ($R_{\text{abt}} = R_{\text{a}} + R_{\text{b}} + R_{\text{trans}}$) were derived from NH_3 flux measurements when the vegetation canopy was fully saturated with water, R_{a} being the aerodynamic resistance, R_{b} the boundary layer resistance and R_{trans} the transfer resistance through the flux chamber. This assumed that a water saturated canopy had no canopy resistance and was a perfect sink for NH_3 , so that there were only atmospheric resistances. To achieve a saturated canopy for calculating the R_{abt} , the vegetation in the chamber was fully wetted with spray from a watering can. The total resistance in the chamber ($R_{\text{t}} = F_{\text{t}}/\chi_{\text{TN}}$) was then calculated and the lowest values after watering considered equivalent to R_{abt} . The value of R_{abt} calculated for the mixed moorland canopy was 182 s m^{-1} ($n = 18$, s.e. = 0.5).

2.6. Chamber physics

NH_3 flux within the chamber was derived from the difference between inlet and outlet NH_3 concentrations and the flow rate, based on the area of ground covered by the experimental vegetation in the chamber:

$$F_{\text{t}} = -\frac{((\chi_{\text{IN}} - \chi_{\text{OUT}}) \times f)}{A}, \quad (3)$$

where F_{t} is the flux ($\mu\text{g m}^{-2} \text{ s}^{-1}$), χ_{IN} is the inlet concentration ($\mu\text{g m}^{-3}$), χ_{OUT} is the outlet concentration ($\mu\text{g m}^{-3}$), f is the flow rate ($\text{m}^3 \text{ s}^{-1}$) and A is the ground area of the canopy (m^2).

Deposition velocity was then derived from the flux by

$$V_d = -\frac{F_t}{\chi_{IN}} = \frac{1}{R_t}, \quad (4)$$

where V_d is the deposition velocity (m s^{-1}) and R_t is the total resistance (s m^{-1}).

The canopy resistance was calculated from the canopy resistance model:

$$R_c = R_t - (R_{abt}). \quad (5)$$

Separately the compensation point model was used to calculate the cuticular and stomatal deposition components (R_w and R_s , respectively). Night data assumed that stomata were closed so that R_c was equivalent to R_w ; during the day, when stomata are open, R_c represents a combination of R_w and R_s .

The stomatal compensation point (Sutton and Fowler, 1993; Sutton et al., 1995) represents the relationship of apoplastic NH_4^+ concentrations and pH via the temperature response of the Henry equilibrium (K_{ha}), the equilibrium constant (K_b) and the dissociation constant for water (K_w) (Nemitz et al., 2000):

$$\chi_s = \frac{161\,500}{T} \exp(-10\,378T^{-1}) \frac{[\text{NH}_4^+]}{[\text{H}^+]}, \quad (6)$$

where T is the absolute temperature (K). The ratio of $[\text{NH}_4^+]$ to $[\text{H}^+]$ is termed Γ_s and was taken from flux measurements above a Scottish unpolluted moorland site as 180 (Flechard, 1998). The sensitivity of the R_w data to Γ_s was found to be minimal, when tested within a realistic range of values for semi-natural vegetation (Fig. 3).

When canopy was dry, parameterisation for stomatal resistance (R_s) was calculated from

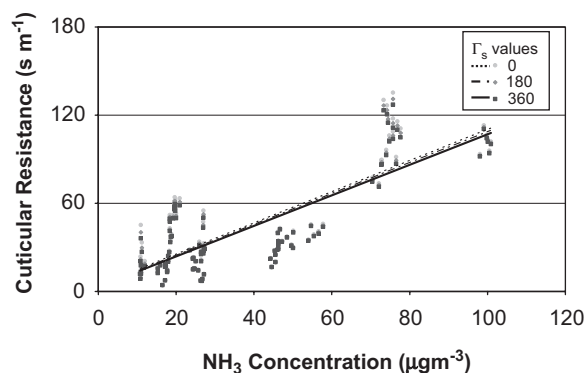


Fig. 3. Sensitivity of R_w to Γ_s values, comparing the Γ_s for 180 (as used) (dashed line, grey diamond), to Γ_s of 0 (dotted line, light grey circle), and Γ_s of 360 (solid line, black square).

$R_s(\text{H}_2\text{O})$ (s m^{-1}), which was derived from evapo-transpiration (Eq. (7)). A seven day period when the canopy had not been watered and the relative humidity was lower than 75% was used—this excluded evaporation from the plant surfaces. R_s for the mixed vegetation during the day could then be calculated from a simple parameterisation (Wesley, 1989; Erisman et al., 1994; Nemitz et al., 2004) (Eq. (8)):

$$\begin{aligned} R_s(\text{NH}_3) &= \frac{D_{\text{H}_2\text{O}}}{D_{\text{NH}_3}} R_s(\text{H}_2\text{O}) \\ &= -\frac{D_{\text{H}_2\text{O}} e_w(z'_0) - e_{\text{sat}}(T(z'_0))}{D_{\text{NH}_3} E}, \end{aligned} \quad (7)$$

where $D_{\text{H}_2\text{O}}$ and D_{NH_3} are the diffusivities of H_2O and NH_3 . e_w is the water vapour pressure (kPa) and T is the temperature ($^{\circ}\text{C}$) at the mean canopy height (z'_0), and the water vapour flux (E) (kPa m s^{-1}) is calculated from the flux of temperature and humidity through the flux chamber. $e_{\text{sat}}(T(z'_0))$ is the saturated water vapour pressure at the mean T of the canopy ($T(z'_0)$),

$$R_s = \left(1 + \frac{\alpha}{2 \times S_t}\right) \times \beta, \quad (8)$$

where R_s is the stomatal resistance (s m^{-1}), α is 25 (W m^{-2}), S_t is the solar radiation (W m^{-2}) and β is 100 (s m^{-1}). Data was shown to closely match the parameterisation over the seven day period (data not shown).

χ_c (canopy compensation point) can then be calculated using

$$\chi_c = \chi_{IN} + (F_t \times (R_{abt})), \quad (9)$$

where χ_c is the canopy compensation point ($\mu\text{g m}^{-3}$).

R_w can then be calculated during the day (Eq. (10)), which is derived from Eq. (10) in Sutton and Fowler (1993),

$$R_w^{-1} = \frac{(\chi_{IN}/R_{abt}) + (\chi_s/R_s)}{\chi_c} - (R_{abt})^{-1} - R_s^{-1}. \quad (10)$$

2.7. Development of the system

2.7.1. Empty chamber testing

Extensive measurements were made prior to experimental flux measurements to determine the influence of the chamber on NH_3 deposition and to ensure that the experimental vegetation was the only depositing surface. The flux chamber and internal instrumentation were assessed as a potential source

or sink for NH_3 by running the flux chamber when empty of vegetation. Inlet concentrations of NH_3 were varied between 1 and $100 \mu\text{g m}^{-3}$ so that deposition to the internal artificial surfaces could be tested at a range of NH_3 concentrations. No difference between the inlet and the outlet concentrations were observed, indicating that no emission or deposition occurs to the empty chamber. Over the test period the outlet averaged $0.18 \mu\text{g m}^{-3}$ less than the inlet. The agreement between the inlet and the outlet concentrations over the experiment is displayed in Fig. 4, clearly showing that there is no adsorption to the 'empty' chamber.

2.7.2. Chamber air turbulence

Uniformity in the chamber conditions and effective air mixing are fundamental to the measurements of NH_3 exchange with vegetation in the flux chamber. Poorly mixed air causes spatially heterogeneous deposition and, generates data that are unrepresentative of the vegetation in the chamber.

A short path length-ultrasonic anemometer was used to measure air turbulence at 12 heights (between 10 and 35 cm) and spatial positions around the chamber. Turbulence was sampled at 5 min intervals for ~ 30 min. Data were analysed using a 3D-interpolation program (written in IDL 6.0). This provided a visual image of the spatial conditions and variability throughout the chamber. For these investigations the effect of the different fans on air mixing was tested with 0, 2 and 3 fans running.

Fig. 5(a) and (b) shows that with no fans and two fans running there are large areas of unmixed air, represented by the red/yellow areas. Fig. 5(c) shows

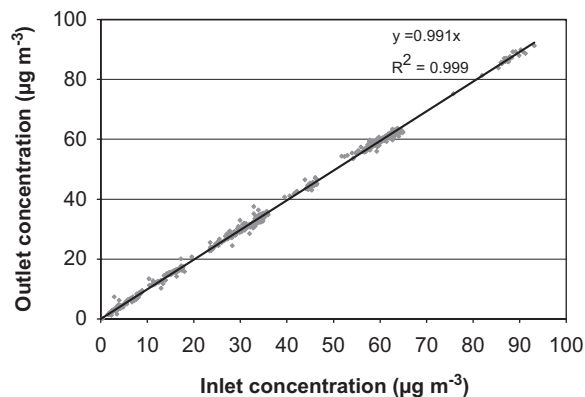


Fig. 4. Relationship between the inlet and the outlet NH_3 concentration when the flux chamber is empty.

that with three fans running; the air is completely mixed and stationary areas of air have been eliminated; three fans were used in all the flux chamber experiments.

2.8. Vegetation source and procedure

Calluna vulgaris (L.) Hull, *Eriophorum vaginatum* L., *Sphagnum capillifolium* (Ehrh.) Hedw. and *Sphagnum papillosum* Linb. were collected and placed on capillary matting in plastic trays: $0.60 \text{ m} \times 0.40 \text{ m}$ and 0.12 m deep. The vegetation was collected at Whim Moss, Peeblesshire which is $\sim 12 \text{ km}$ south of CEH Edinburgh $3^\circ 16' \text{ W}$ and $55^\circ 46' \text{ N}$ at 280 m asl. It is an ombrotrophic bog (NVC M19) which receives a low ambient N deposition of $8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, of which half is from dry deposition (Leith et al., 2004). The mean annual atmospheric NH_3 concentration at Whim Moss is $1.7 \mu\text{g m}^{-3}$ (1.5 m above the ground). Average canopy compensation point of the vegetation is $> 0.4 \mu\text{g m}^{-3}$.

The mixed bog species comprised four trays of *Sphagnum* (50% *S. papillosum* and 50% *S. capillifolium*), two trays of *E. vaginatum* and three trays of *C. vulgaris* giving proportions of species similar to Whim Moss. Intact, healthy plants of *C. vulgaris* and tussocks of *E. vaginatum* were extracted from the ground together with a volume of peat to minimise root disturbance. The plants and peat were then packed tightly into the trays with no exposed peat, which is a potential depositing or emitting surface. The *C. vulgaris* plants were approximately 4–8 yr old in the pioneer phase, with an average height of 0.14 m (max. height 0.24 m). The *E. vaginatum* plants were also 4–8 yr old, and averaging 0.22 m tall (max. height 0.35 m). *S. capillifolium* and *S. papillosum*, were removed in intact clumps to minimise disturbance. *Sphagnum* trays contained $\sim 50\%$ of each *Sphagnum* species. The *Sphagnum* clumps were approximately level with the top of the trays. During the experiment the plant surfaces were kept moist but not waterlogged.

Plants were watered every 3–5 days from overhead using a spray watering can containing rainwater ($\text{pH} \sim 5$) collected at the OTC site. After watering, a period of up to an hour was left before collection of further data, preventing excess surface waters from affecting flux measurements. Trays were replaced with fresh plants between experimental data sets, reducing possible effects of plant experimental history.

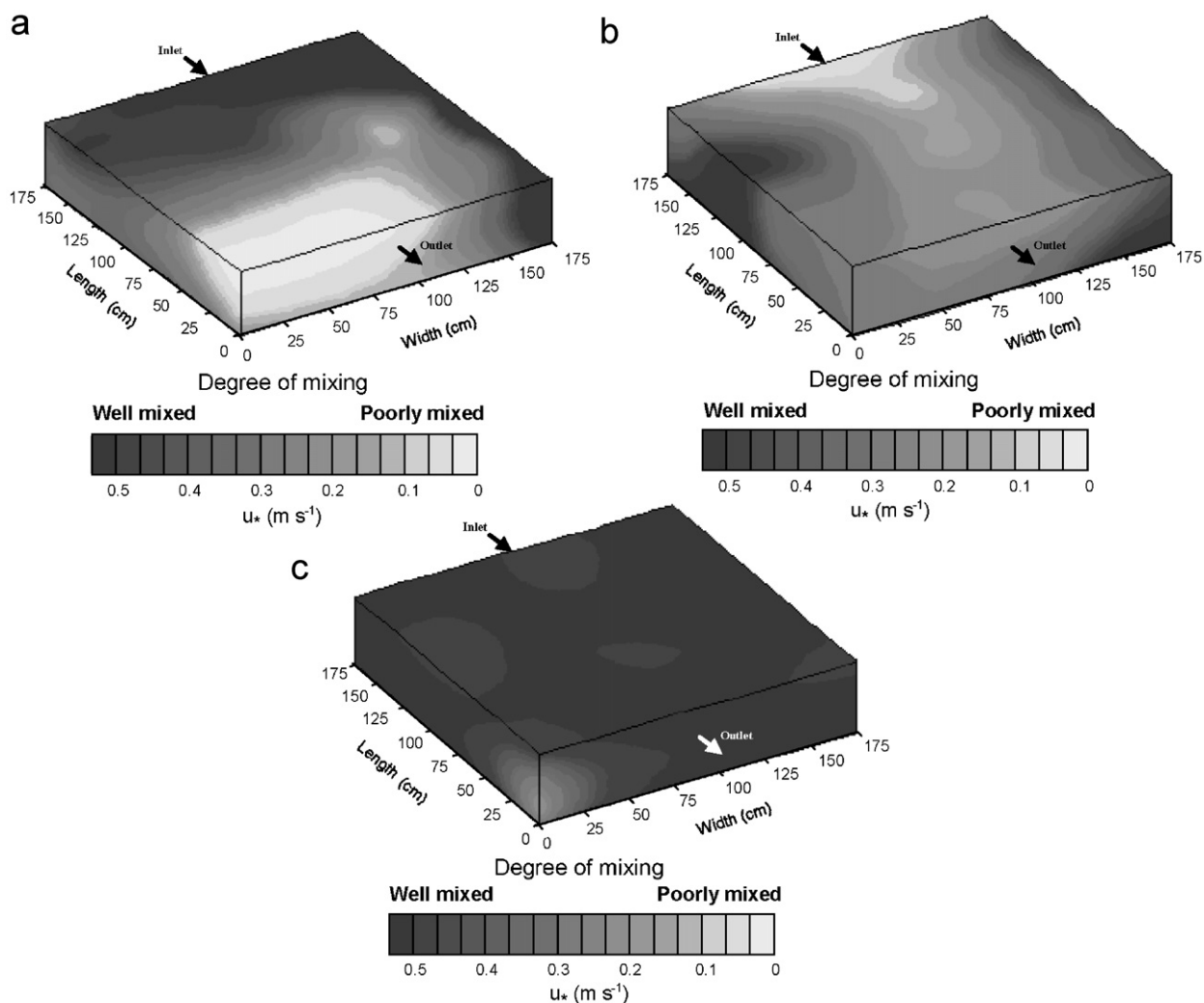


Fig. 5. Turbulence measurement: (a) without fans; (b) two fans; and (c) three fans; well mixed areas are shown in black, poorly mixed areas are light grey and white.

2.9. Experimental procedures

A range of NH_3 concentrations ($1\text{--}100\ \mu\text{g m}^{-3}$) was supplied, with each level maintained for typically 2–6 h, which was the time taken to attain a stable concentration. The vegetation was analysed over a period of a month inside the flux chamber, from 27.2.03 to 26.3.03. Temperatures ranged from $4\text{--}20\ ^\circ\text{C}$ during the day and $1\text{--}16\ ^\circ\text{C}$ during the night, relative humidity varied from 45–75% during the day and 43–78% during the night and solar radiation varied from $50\text{--}276\ \text{W m}^{-2}$ during the day.

Data were split into night and day; periods where the S_t exceeded $50\ \text{W m}^{-2}$ were classified as day data assuming stomata are open above this limit; periods below $10\ \text{W m}^{-2}$ were classified as night data (Jarvis

and Mansfield, 1981; Willmer and Fricker, 1983). Data collected immediately after NH_3 concentration changes or watering events were excluded, as the chamber required time to reach a stable equilibrium (20–120 min depending on the level of disturbance). Periods where there was co-sampling of the denuders, general maintenance or breakdowns of the AMANDA were also removed.

2.10. Statistical analysis between day and night R_c and R_w

Statistical analysis was carried out using Genstat 8. For the statistical analysis, the individual data runs, i.e. a series of measurements conducted at a set concentration, were averaged. Data in each run formed

clusters of points because there were only small differences in the inlet NH_3 concentration. In order to realistically assess statistical differences between the linear fits for day and night R_c and R_w , the cluster of points were averaged. The differences in the day and night data for R_c and R_w , for each species, were tested using a General Linear Model (GLM) procedure.

3. Results

3.1. Flux and deposition velocity

The flux and deposition velocity are chamber specific parameters, as they include the influence of atmospheric variables occurring inside the chamber at the time the measurements were made. This means the flux and the deposition velocity cannot be related directly to the outside world. They do, however, demonstrate the overall trends in NH_3 deposition that are occurring in the chamber system. A highly significant relationship can be seen for both day and night flux (Fig. 6), showing an increase in deposition of NH_3 with increasing concentration. However, a slight curvature can be seen for both day and night, demonstrating that the rate of increase in deposition declines with increasing concentration. The deposition velocity decreases with increasing concentration both night and day (Fig. 7). However, there is also a difference between the night and day, with night data being 7.1% lower at $60 \mu\text{g m}^{-3}$.

3.2. Canopy resistance

Calculation of the R_c component through the canopy resistance model is critical, because the

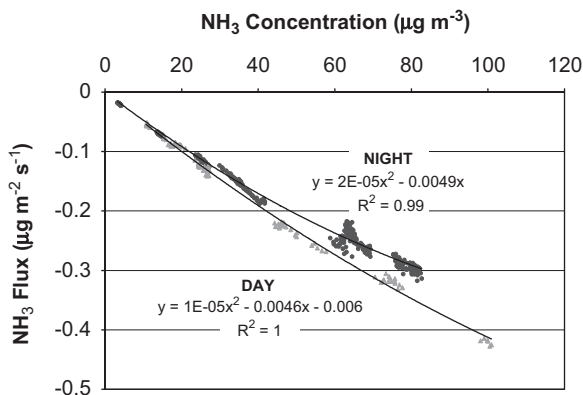


Fig. 6. Relationship between NH_3 concentrations ($\mu\text{g m}^{-3}$) and daytime flux ($\mu\text{g m}^{-2}\text{s}^{-1}$) (light grey triangles) and night-time flux ($\mu\text{g m}^{-2}\text{s}^{-1}$) (dark grey circles) for a mixed vegetation canopy.

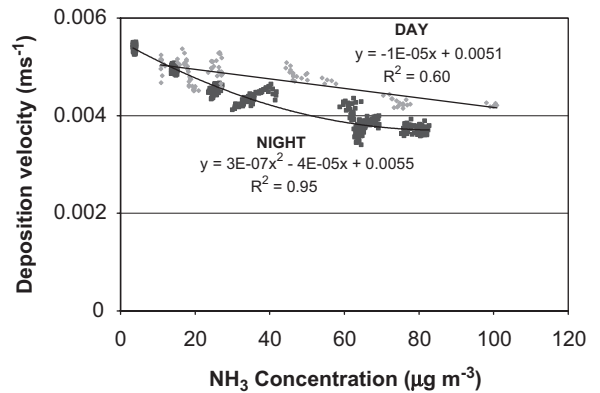


Fig. 7. Relationship between NH_3 concentrations ($\mu\text{g m}^{-3}$) and daytime deposition velocity (m s^{-1}) (light grey diamonds) and night-time deposition velocity (m s^{-1}) (dark grey squares) for a mixed vegetation canopy.

chamber specific atmospheric resistance component has been removed. This allows R_c values to be related directly to conditions in the real world. The R_c data for day and night can be seen in Fig. 8. R_c in the day and night increases, with increasing concentration. In the day R_c increases from 13.4 s m^{-1} at $5 \mu\text{g m}^{-3}$ to 47.6 s m^{-1} at $80 \mu\text{g m}^{-3}$. At night, R_c increases more rapidly from 10.3 s m^{-1} at $5 \mu\text{g m}^{-3}$ to 95.1 s m^{-1} at $80 \mu\text{g m}^{-3}$, and R_w approximates to R_c during the night as deposition can only occur to the cuticle.

3.3. R_w day and R_s day

Canopy resistance during the day is a combination of R_w , stomatal resistance (R_s) and stomatal compensation point (χ_s) and is calculated through the compensation point model. R_s was stable at 112.4 s m^{-1} (Eq. (8)) at all concentrations under the conditions of the experiment, as it is dependant on whether the stomata are open or closed and is calculated from solar radiation measurements.

R_w can be seen to increase with increasing concentration from 8.9 s m^{-1} at $5 \mu\text{g m}^{-3}$ to 87.7 s m^{-1} at $80 \mu\text{g m}^{-3}$ (Fig. 9). R_w at low NH_3 concentrations is small compared with R_s , and will therefore be the major sink for NH_3 . R_s and R_w have similar values at $101.8 \mu\text{g m}^{-3}$. Concentrations above this will result in more deposition to the stomata than the cuticle.

3.4. R_w day vs R_w night

Day and night R_w data are compared in Fig. 10; R_w values are similar in the night and day. This has

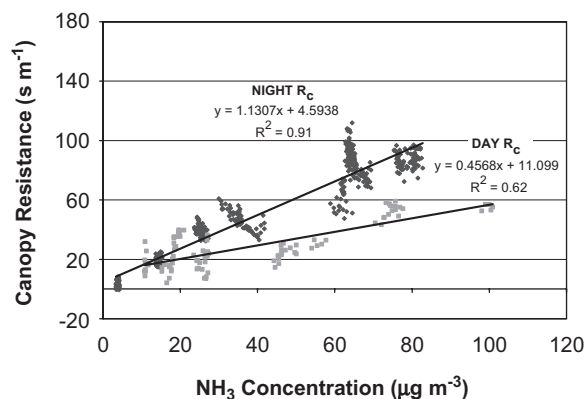


Fig. 8. Relationship between NH_3 concentrations ($\mu\text{g m}^{-3}$) and R_c (s m^{-1}) for night-time (dark grey diamonds) and R_c (s m^{-1}) for daytime (light grey squares).

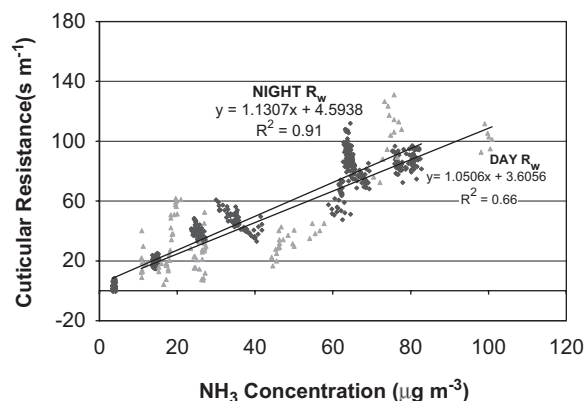


Fig. 10. Relationship between NH_3 concentrations ($\mu\text{g m}^{-3}$) and daytime R_w (s m^{-1}) (light grey triangles) and night-time R_w (s m^{-1}) (black diamonds) for a mixed vegetation canopy.

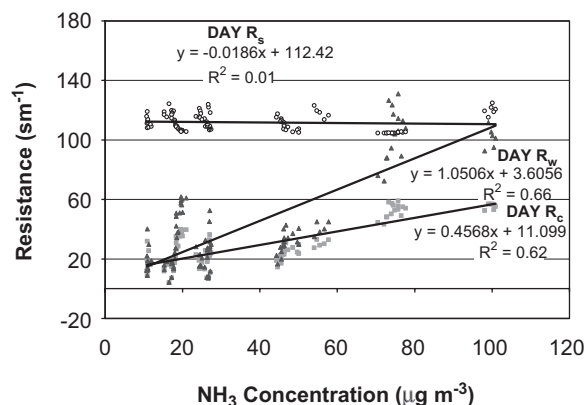


Fig. 9. Daytime relationship between NH_3 concentrations ($\mu\text{g m}^{-3}$) and R_s (s m^{-1}) (hollow black circles), R_w (s m^{-1}) (dark grey triangles) and R_c (s m^{-1}) (light grey squares) for a mixed vegetation canopy. R_c is calculated according to the canopy resistance model, and R_w and R_s from the compensation point model.

been supported by a GLM, which has shown that the lines are not significantly different (t -probability 0.657, d.f. 12), so there is no evidence of differential NH_3 uptake to the cuticle between day and night for the canopy tested.

4. Discussion

4.1. Changes in NH_3 deposition with increasing concentration

Many papers report that the flux of NH_3 from the atmosphere to a vegetation canopy changes linearly

with increasing NH_3 concentration. This is seen in studies as far back as Farquhar et al. (1980) who conducted a chamber experiment using *Phaseolus vulgaris* L. and found linear uptake of NH_3 with increasing NH_3 concentration, above the value of the stomatal compensation point and up to concentrations of $\sim 20 \mu\text{g m}^{-3}$. Gessler et al. (2002) conducted a chamber experiment for *Picea abies* needles and showed a linear relationship between concentrations 0 and $\sim 115 \mu\text{g m}^{-3}$. Linear relationships in NH_3 flux have also been reported and demonstrated in chamber experiments by Gessler et al. (2000) on *Fagus sylvatica* twigs and seedlings for concentrations between 0 and $\sim 190 \mu\text{g m}^{-3}$, Husted and Schjoerring (1995) on *Hordeum vulgare* for concentrations between 0 and $\sim 30 \mu\text{g m}^{-3}$ and Whitehead and Lockyer (1987) on *Lolium multiflorum* Lam. for concentrations between 14 and $709 \mu\text{g m}^{-3}$. These studies suggest a linear increase in the uptake of NH_3 with increasing concentration.

However, in some of the published literature, uptake of NH_3 is not linear with NH_3 concentration, although the authors still describe the flux as linear. Schjoerring et al. (1998) concluded that there was an approximately linear relationship of increases in NH_3 flux with increasing NH_3 concentrations, in a chamber experiment using *C. vulgaris* and *D. flexuosa* for concentrations ranging between 0 and $\sim 20 \mu\text{g m}^{-3}$. However, closer inspection of their graphs (Figs. 2 and 3 of Schjoerring et al., 1998), shows that *C. vulgaris* display curvature in both experiments and that the *D. flexuosa* data also show evidence of curvature. A linear interpretation with evidence of curvature can be observed in other data,

e.g. Huber et al. (2002) (their Fig. 1) in a chamber experiment for forest floor vegetation for concentrations between 0 and $60 \mu\text{g m}^{-3}$, Husted and Schjoerring (1995) (their Fig. 4) for a chamber experiment on *Brassica napus* L. at concentrations between 0 and $\sim 20 \mu\text{g m}^{-3}$, Schjoerring and Husted (1997) (their Fig. 6) for a chamber experiment for *H. vulgare* between 0 and $\sim 18 \mu\text{g m}^{-3}$ and Duyzer (1994) (their Fig. 2) for a field experiment on *Pseudotsuga menziesii* for concentrations between 0 and $30 \mu\text{g m}^{-3}$. This simplified linear interpretation instead of a non-linear function was also recognised by Sutton et al. (1993b)—data of Sommer and Jensen (1991) have a non-linear increase in flux with increasing concentrations, although the originators assumed that the flux to the surface is controlled by a constant affinity with the plant surface, i.e. R_c is constant with NH_3 concentration.

Fowler et al. (1998) showed, for moorland, evidence of a non-linear relationship in flux by demonstrating a variable R_c for low NH_3 concentrations, ranging from $\sim 20 \text{ s m}^{-1}$ for $0.1 \mu\text{g m}^{-3}$ to 80 s m^{-1} for $2 \mu\text{g m}^{-3}$. This suggested that as concentration increased the canopy took up relatively less NH_3 , i.e. the relative deposition decreased. There were, however, limitations with this study; for example, the concentrations measured in these observations were very small, so the data do not apply to the full range of concentrations found in the field.

The work described in this paper has significantly advanced the study of the effects of concentration, by reliably identifying non-linear relationship in the flux, showing a decrease in the increment of uptake per unit increase in concentration at higher NH_3 concentrations in all species tested. This demonstrates a reduction in the fraction of atmospheric NH_3 depositing to the vegetation at higher NH_3 concentrations. This concept is fundamental to understanding NH_3 deposition to vegetation and crucial in applying deposition data for NH_3 modelling and for application to field experiments.

The concentration-dependent canopy resistances and NH_3 fluxes are most probably the result of saturation of the cuticle and cuticular surface water by depositing NH_3 , i.e. a decrease in surface conductance to NH_3 at higher NH_3 concentrations, a conclusion also reached by Fowler et al. (1998). The concentration dependence of R_c to the dry cuticle surface could be the response of the NH_3/SO_2 ratio on the leaf surface (Nemitz et al., 2001). However, saturation of transport through the

stomata, inter-cellular gas spaces, plasmalemma and symplast, including ‘acid trapping’ in acidic vacuoles and assimilation by glutamine synthetase and subsequent enzymes could also be important. Husted and Schjoerring (1995) and Nielsen and Schjoerring (1998) demonstrated that transport from the stomata, through the plasmalemma into the symplast is sufficient to remove all the NH_3 deposited into the plant via the stomata. This will allow more deposition to occur through the stomata, as they will not become saturated if the transport into (and assimilation by) the rest of the plant exceeds the input into the stomata. Hill (1999) calculated for *Luzula sylvatica* that atmospheric NH_3 concentration in excess of $400 \mu\text{g m}^{-3}$ would be needed to exceed the transport of $\text{NH}_3/\text{NH}_4^+$ through the plasmalemma. In this experiment concentrations did not exceed $100 \mu\text{g m}^{-3}$, so it can be assumed that saturation of the stomatal pathway will not occur.

4.2. Diurnal differences in NH_3 deposition

Diurnal variations in NH_3 deposition have been studied before. Duyzer et al. (1987a, b) failed to identify a difference between day and night data for heathland or pine forest. However, Sutton et al. (1993b) found that diurnal change is a factor influencing NH_3 deposition. This has also been observed by Hutchinson et al. (1972), who showed a considerable difference in uptake between day and night (*Glycine max*), and by Wyers and Erisman (1998) who found diurnal variations in R_w for a coniferous forest, showing higher uptake rates and smaller R_w during the day. The results presented in this paper also support the importance of diurnal influences of NH_3 exchange. As can be seen (Fig. 7), R_c is significantly lower during the day compared to the night, indicating that during the day uptake in vascular plants occurs by both stomatal and cuticular uptake.

4.3. Changes in the cuticular and stomatal resistance with increasing NH_3 concentrations

The cuticle is recognised as a sink for NH_3 in the compensation point model (Sutton and Fowler, 1993). However, much previous literature considers that under the majority of conditions the cuticular deposition is less than stomatal deposition (Gessler et al., 2000, 2002). Gessler et al. (2000) and Wyers and Erisman (1998) do, however, recognise that

cuticular deposition is an important influence under high humidity and where the cuticle is fully saturated with water. Few previous studies have examined the changes in cuticular and stomatal deposition with increasing concentration, and how the two interact.

By examining the daytime data for mixed moorland vegetation it can be seen that there is a strong linear increase in R_w as the cuticle saturates. R_s remains stable for all the concentrations measured due to its relationship to whether the stomata are open or closed, and has also been related to solar radiation data. The stomatal pathway is stable because transport and assimilation in the stomata does not become saturated within the range of concentrations used in this study and due to the low χ_s of the vegetation.

4.4. Difference in the cuticular resistance in the daytime and night-time

Wyers and Erisman (1998) proposed that during the day transpiration from the open stomata resulted in a wetter cuticle, leading to greater deposition. However, the work from this paper has shown that night R_w and day R_w are not statistically different for the species tested.

5. Conclusions

Flux chamber measurements revealed that for NH_3 concentrations between 1 and $100 \mu\text{g m}^{-3}$ that there were increases in R_c with increasing NH_3 concentration for a mixed moorland canopy both during the day and night. Furthermore, results showed that there was a lower R_c during the day than at night due to uptake through the stomata. R_w increases with increasing NH_3 concentration, both in the day and night, due to saturation of the cuticle. Furthermore, R_w in the day was the same as at night, demonstrating no changes in surface chemistry or surface water between day and night. These results have large implications for field scale manipulation studies, atmospheric transport models and critical loads, all currently calculated based on a R_c value that is fixed with increasing NH_3 concentrations.

This paper shows that it is important for NH_3 concentration effects to be investigated on a greater range of species and vegetation communities, including stomatal and non-stomatal species. Species specific responses will be published in a

future paper. This will test the findings from this paper and identify any interspecies differences in deposition.

Acknowledgement

We acknowledge the funding of The Natural Environment Research Council (NERC).

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