Atmospheric ammonia at a moorland site. II: Long-term surface–atmosphere micrometeorological flux measurements

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SUMMARY

Long term micrometeorological measurements of the net vertical exchange of atmospheric ammonia (NH3) over moorland vegetation at a site in southern Scotland from February 1995 through to February 1996 are reported. The measurements, made using a combination of eddy covariance and aerodynamic flux-gradient methods, provided satisfactory 30-minute average fluxes approximately 50% of the time using continuous annular wet denuders for NH3 sampling at three heights between 0.4 and 3.4 m above the ground.

The moorland vegetation was a net sink for atmospheric NH3 as 93.4% of all half-hourly measured fluxes indicated dry deposition to the surface with a mean flux of −5.2 ng m−2 s−1 and a mean deposition velocity Vd of 11.7 mm s−1 at (z−d) = 1 m. Despite the dominance of deposition to the moorland, emission fluxes were observed approximately 6.6% of the time with a median of +1.1 ng m−2 s−1, and most commonly resulting from drying water films on foliar surfaces.

The mean aerodynamic resistance at a reference height of (z−d) = 1 m and the mean viscous sub-layer resistance were 36.6 s m−1 and 11.6 s m−1 respectively, and of a similar magnitude to the mean canopy or surface resistance Rc of 37 s m−1. When the moorland surfaces were wetted by rain or dew, canopy resistances to NH3 deposition were generally smaller (averaging 23 s m−1) than in dry conditions (when Rc = 61 s m−1) or when surfaces were covered in snow (Rc = 56 s m−1). Therefore, moorland surfaces cannot be treated as perfect sinks for NH3 deposition.

Diurnal and seasonal patterns in rates of deposition and net fluxes to the moorland surface area were determined mainly by a combination of wind speed, surface wetness and ambient NH3 concentration. Thus, during winter, deposition rates expressed as a flux or deposition velocity were generally much larger than in summer by factors of 2 or 3 respectively, as a result of stronger winds and the presence of surface water for extensive periods which kept canopy resistances small except in frozen conditions. At temperatures below 0 °C, the surface became progressively dry and canopy resistances were large (50–100 s m−1).

The measurements provided direct estimates of the net annual gaseous NH3 input to the moorland, which was 2.5 kg NH3−N ha−1 a−1 and was almost identical to the measured wet deposition input at the site of 2.4 kg NH3−N ha−1 a−1.

KEYWORDS: Ammonia Atmospheric chemistry Boundary layer Dispersion Dry deposition Surface emissions

1. INTRODUCTION

The deposition of atmospheric nitrogen compounds including NH3, NH4+ and NO3− onto sensitive terrestrial and aquatic ecosystems has been shown to cause eutrophication† and to contribute to the acidification of soils and freshwater, leading to major changes in species composition (Heil and Diemont 1983; Nihlgård 1985; Van Breemen and Van Dijk 1988). Critical loads for nitrogen are now widely used to quantify the sensitivity of ecosystems to the deposition of atmospheric nitrogen (N) and to develop emission abatement strategies (Grennfelt and Thörnélöf 1992; Hornung et al. 1995). There is therefore a need to quantify wet and dry deposition inputs of atmospheric N at local, regional and national scales. Wet deposition of major ions is readily provided by monitoring networks (RGAR 1990). There are, however, no monitoring networks for dry deposition, and the long-term inputs of NH3 remain very uncertain, being dependent on the availability of monitored air concentrations and the current understanding and models of the processes.

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† See p. 733 of this issue.
regulating the land–atmosphere exchange of NH₃ (Sutton et al. 1995a,b; Sorteberg and Hov 1996). Such models have so far been developed on the basis of a very limited number of campaign-based field measurements, typically extending over periods of a few days.

The main problems associated with modelling NH₃ exchange between plant communities and the atmosphere arise from the bi-directional nature of NH₃ fluxes, and the very large temporal variability in the leaf cuticle NH₃ uptake. Arable crops can be a net source of NH₃ (Schjørring 1991; Sutton et al. 1995a,b), and the large extent of arable land in Europe and northern America is expected to influence the regional atmospheric NH₃ budgets significantly. Emission fluxes of NH₃ from plants have been interpreted as the consequence of a ‘stomatal compensation point’ resulting from the balance between consumption and production of NH₃ by plant metabolism (Farquhar et al. 1980; Schjørring 1991), or of a ‘canopy compensation point’ including the leaf cuticle as an additional site of exchange for NH₃ (Sutton et al. 1995b). In conditions when atmospheric concentrations of NH₃ are smaller than the compensation point, emission of NH₃ from the surface to the atmosphere is expected to prevail; conversely, when ambient NH₃ concentrations are larger than the compensation point, the surface is a sink for atmospheric NH₃ (Sutton et al. 1995a).

Field measurements over moorlands and heathlands have shown these surfaces to be net sinks for atmospheric NH₃. Large deposition velocities (typically 10–40 mm s⁻¹) have often been reported for moorlands and it has been suggested that such vegetation is a near-perfect sink for NH₃ with canopy resistances ₚ typically in the range 0–50 s m⁻¹ (Sutton et al. 1992; Sutton et al. 1993a; Duyzer 1994). However, the limited number of campaign measurements has so far hindered modelling efforts and the estimated inputs have generally been based on data sets representing a few tens of hours of flux measurements. This has highlighted the need for much more extensive measurements covering a wider range of environmental conditions over non-fertilized, semi-natural ecosystems, and from which the annual net surface–atmosphere exchange of NH₃ may be more accurately assessed. Long-term continuous monitoring of NH₃ exchange between moorland and the atmosphere is also required to develop a mechanistic understanding for inclusion in process-based models. The recent development of instrumentation capable of continuously measuring ambient NH₃ concentrations smaller than 0.05 μg NH₃ m⁻³ (Wyers et al. 1993a) has provided the necessary equipment for such long-term measurements.

In the present paper we report 13 months of continuous surface–atmosphere flux measurements using micrometeorological methods over a moorland site in southern Scotland from February 1995 to February 1996. A brief paper covering the first 7 months of measurements has been published as a part of the International Conference on Atmospheric Ammonia, Oxford (UK) in October 1995 (Fowler et al. 1998). An associated paper (Flechard and Fowler 1998) describes the influence of meteorology and local sources on NH₃ concentrations at this site for the same period of measurements. The data are here analyzed to quantify the role of atmospheric and surface processes in regulating the direction and magnitude of the surface fluxes. The development and application of a process-based model to simulate land-surface NH₃ exchange over vegetation are described elsewhere (C. R. Flechard, D. Fowler, M. A. Sutton and J. N. Cape, personal communication).

2. Materials and methods

The trace-gas flux measurements reported in this study were obtained using a combination of ammonia concentration gradients with eddy-covariance fluxes of momentum and heat. The literature provides theoretical descriptions and examples of applications of those methods in field micrometeorological measurements (Thom 1975; Fowler and Unsworth 1979; Monteith and Unsworth 1990; Sutton 1990).
(a) Flux-gradient theory

The deposition of a trace gas to or the emission away from a surface establishes a vertical gradient of concentration. The magnitude of the trace-gas flux $F_{\chi}$ is provided by the product of the turbulent-transfer coefficient $K_{\chi}$ for the trace gas (or eddy diffusivity) and the vertical gradient of trace-gas concentration; by convention a negative flux denotes deposition, so that

$$F_{\chi} = -K_{\chi} \frac{\partial \chi}{\partial z},$$

(1)

where $\chi$ is atmospheric gaseous concentration and $z$ is height above the surface. Given the similarity hypothesis (Thom 1975), the eddy diffusivities of heat and entrained properties ($K_{H}$ for heat; $K_{V}$ for water vapour; $K_{\chi}$ for trace gases or sub-micron aerosols) can, to a good enough approximation, be assumed to be equal to the turbulent diffusivity for momentum $K_{M}$ in stable and neutral conditions, while semi-empirical correction functions are necessary in unstable conditions. Further developments based on similarity theory (Thom 1975; Sutton 1990) lead to an expression of the vertical flux of a form similar to that of eddy covariance

$$F_{\chi} = -u_{*} \chi_{*},$$

(2)

where $u_{*}$ is the friction velocity, and $\chi_{*}$ the eddy concentration defined as

$$\chi_{*} = k \frac{\partial \chi}{\partial \left[\ln(z - d) - \Psi_{H}( (z - d)/L )\right]},$$

(3)

with $d$ the displacement height, $k$ the von Kármán constant and $L$ the Monin–Obukhov length (Thom 1975). The eddy concentration was calculated using a log–linear regression of a stability-corrected vertical profile of NH$_3$. The integrated stability function $\Psi\left( (z - d)/L\right)$ in stable conditions is equivalent for momentum and for heat and trace gases (Thom 1975):

$$\Psi_{M}\left( \frac{z - d}{L} \right) = \Psi_{H}\left( \frac{z - d}{L} \right) = -5.2 \left( \frac{z - d}{L} \right).$$

(4)

In unstable conditions, however, a discrepancy exists between $\Psi_{M}$ and $\Psi_{H}$ that accounts for the difference observed between $K_{M}$ and $K_{H}$ (Dyer and Hicks 1970; Paulson 1970):

$$\Psi_{M}\left( \frac{z - d}{L} \right) = 2 \ln \left( \frac{1 + x}{2} \right) + \ln \left( \frac{1 + x^2}{2} \right) - 2 \tan^{-1}(x) + \frac{\pi}{2},$$

(5)

$$\Psi_{H}\left( \frac{z - d}{L} \right) = 2 \ln \left( \frac{1 + x^2}{2} \right),$$

(6)

where

$$x = \left( 1 - 16 \frac{z - d}{L} \right)^{0.25}.$$  

(7)

The wind speed $u$ and concentration $\chi$ are then provided at a reference height $(z - d) = 1$ m from the integrated expressions

$$u(z - d) = \frac{u_{*}}{k} \left\{ \ln \left( \frac{z - d}{z_{0}} \right) - \Psi_{M}\left( \frac{z - d}{L} \right) \right\},$$

(8)

$$\chi(z - d) = \frac{\chi_{*}}{k} \left\{ \ln \left( \frac{z - d}{z_{\chi}} \right) - \Psi_{H}\left( \frac{z - d}{L} \right) \right\},$$

(9)
The constant of integration for concentration \( z_x \) is the analogue of the roughness length \( z_0 \), and represents the height above \( d \) at which the gas concentration is predicted to be zero.

In the conventional flux–gradient theory (Sutton et al. 1993a), the friction velocity \( u_* \) is provided by an expression analogous to Eq. (3) using a linearized logarithmic vertical wind-profile. In this study, the friction velocity \( u_* \), wind speed \( u \) and sensible-heat flux \( H \) were measured directly using a sonic anemometer, obviating the empirical nature of important aspects of the wind-profile methodology. Thus

\[
\begin{align*}
    u_* &= (-u'w')^{1/2} \\
    H &= \rho C_p w'T',
\end{align*}
\]

where \( u' \), \( w' \) and \( T' \) are the instantaneous fluctuations about the mean horizontal and vertical wind-speeds and temperature respectively. These measurements also provided the Monin–Obukhov length \( L \) needed for the calculation of the stability corrections in Eqs. (4), (5) and (6).

\( b \) Resistance analysis

The trace-gas flux, assumed to be constant with height in a fully-developed surface-layer, may be regarded as analogous to an electrical current flowing through a network of resistances, in order to identify the processes that regulate the gaseous exchange. Three resistances to trace-gas transfer in series can be identified (Garland 1977; Fowler and Unsworth 1979): the atmospheric aerodynamic resistance to turbulent diffusion of heat and trace gas in the surface layer \( R_{ah}(z - d) \); \( R_b \), the resistance to gaseous transfer in the viscous sub-layer at the immediate vicinity of the surface, where turbulent diffusion is damped and molecular diffusion becomes the dominant transfer mechanism; the canopy resistance \( R_c \) is relevant only in the case of dry deposition and represents the affinity of the surface for gaseous uptake. The flux normalized for gaseous concentration yields the deposition velocity \( V_d(z - d) \) which is also the reciprocal of the sum of the three aforementioned resistances

\[
V_d(z - d) = \frac{-F_x}{\chi(z - d)}
\]

\[
V_d(z - d) = \{ R_{ah}(z - d) + R_b + R_c \}^{-1}.
\]

In this study, \( R_{ah}(z - d) \) is calculated using the method of Garland (1977) and \( R_b \), using the method of Owen and Thomson (1963) and Garland (1977) as

\[
R_{ah}(z - d) = \frac{u(z - d)}{u_*^2} \left\{ \psi_M((z - d)/L) - \psi_M((z - d)/L) \right\}
\]

\[
R_b = (Bu_*)^{-1}.
\]

\( B \), the sub-layer Stanton number, is a function of the Schmidt number and the roughness Reynolds number (Garland 1977). The canopy resistance \( R_c \) is calculated as the residual between \( R_l(z - d) \) and \( \{ R_{ah}(z - d) + R_b \} \).

In practice, \( NH_3 \) may be emitted by the surface in response to a decrease in concentration in the air above, or an increase in surface concentration, e.g. when water films on cuticles evaporate. In these conditions, \( R_c \) is not appropriate to quantify processes at the surface. The other objection to the use of \( R_c \) is that, by calculating its value, there is an implied assumption that the concentration at the surface is zero. The presence of a residual resistance term when \( R_s(z - d) \) and \( R_b \) have been removed from the total resistance \( R_l(z - d) \) can be expressed either as a resistance or a concentration. A large value of
$R_c$ may reflect either a large physico-chemical resistance to deposition or an increase in surface concentration, or both. We recognize that there can be an effective surface concentration which may be presented as an alternative to $R_c$. In the case of dry-deposition fluxes in this paper, we have presented surface resistances simply as a measure of the affinity of the absorbing surface for NH$_3$ uptake. The same approach has been widely applied for other pollutants such as SO$_2$ (Fowler and Unsworth 1979). This simplification in the analysis may partly be overcome by introducing a more complex treatment of the surface, with two routes for NH$_3$ exchange (Sutton et al. 1997), namely stomata and leaf-surface water-films with their respective transfer-resistances $R_s$ and $R_w$. However, this so-called two-leg approach is also subject to major uncertainties, and would not help to communicate the main findings of this study, in which a simple canopy-resistance approach applied to deposition fluxes obviates the need for a more detailed and complex modelling.

In the case of gaseous emission by the surface, however, there is a need to estimate the surface concentration in an attempt to develop a mechanistic understanding of the processes involved. For NH$_3$, the surface concentration, referred to here as $\chi(z_0')$, has been termed the 'canopy' compensation point $\chi_0$, which results from the combination of a 'stomatal' compensation point $\chi_0$ and epicuticular* gaseous-exchange processes (Sutton et al. 1995a,b). Following Sutton et al. (1993a), the surface concentration $\chi(z_0')$ may be defined as

$$\chi(z_0') = \chi(z - d) + F_\chi \{R_{ah}(z - d) + R_0\}. \quad (16)$$

Similarly, the vertical profile of air temperature in the surface boundary-layer can be extrapolated down to the surface as a function of the sensible-heat flux $H$ and the atmospheric resistances for heat transfer

$$T(z_0') = T(z - d) + \frac{H}{\rho C_p} \{R_{ah}(z - d) + R_{sh}\}. \quad (17)$$

(c) Site description and experimental set-up

Continuous measurements of vertical NH$_3$ fluxes were made during the 13 months from February 1995 to February 1996 at a moorland site, Auchencorth Moss, in southern Scotland. The site is situated 18 km SW of the City of Edinburgh, at an elevation of 270 m a.m.s.l. (55°47’30”N, 3°14’20”W). The site and experimental set-up for the monitoring of NH$_3$ concentrations at three heights above the vegetation have been described in detail in an associated paper (Flechard and Fowler 1998).

The monitoring site is an extensive area (> 1000 ha) of peatland with an average peat depth of 60 cm and is usually damp to very wet all year round except during warm, dry summers such as that of 1995. Few pools of surface water remain because the site was drained 40 years ago. The vegetation is of a tussocky nature and consists of a compact, humid, peat-forming moss carpet at the bottom of the canopy, with undulating, drier hummocks of taller, vascular species. The moss carpet is mainly made up of Sphagnum sp. and Polytrichum sp. with occasional rough grasses and Carex sp. The hummocks are dominated by Deschampsia flexuosa, Molinia caerulea and Eriophorum sp. The single-sided leaf-area-index varied between about 2–3 m$^2$ m$^{-2}$ in winter to 4–6 m$^2$ m$^{-2}$ in summer. The site, generally sheep-grazed (< 1 animal ha$^{-1}$), is located in an area of fairly low agricultural activity with only six farms within a radius of three kilometres from the instrumentation enclosure on the moor.

* The epicuticle is the layer of waxes including long-chain (> C$_{20}$) alkanes, alcohols, acids and esters on the surface of the cuticle of a plant.
The homogeneous, flat, undisturbed-moorland fetch provided for the micrometeorological flux measurements varied from 500 m to 4 km in the upwind directions between 170° through north to 60°. Flux measurements were therefore discarded for wind directions between 60° and 170°, where the monitoring cabin and instrumentation interfered with the air flow. An analysis of the frequency distribution of the wind direction showed that winds were in this unacceptable sector for 15% of the period from February 1995 to February 1996. During the same period, the wind directions between 180° and 240° accounted for 50% of the time. The other micrometeorological restrictions leading to rejection of flux data included large stability or instability (data rejected whenever \(-5 \text{ m} < L < 5 \text{ m}\)) and low horizontal wind speeds (data rejected whenever \(u(1 \text{ m}) < 0.8 \text{ m s}^{-1}\)).

Concentrations of NH₃ were measured at three heights above the canopy (0.43 m, 1.38 m and 3.37 m) using a continuous-flow wet annular denuder gradient system (ECN, Petten, The Netherlands) with a detection limit of 0.02 \(\mu g \text{ m}^{-3}\) (Wyers et al. 1993a; Flechard and Fowler 1998). Wind speed, friction velocity (Eq. (10)) and sensible-heat flux (Eq. (11)) were measured using a Solent Research ultrasonic anemometer (Gill Instruments Ltd, Lymington, Hampshire, UK) mounted on a mast at a height of 3.6 m above ground level, situated 10 m to the west of the NH₃ measuring tower. In addition, measurements of global radiation \(St\) and net radiation \(Rn\), temperature, relative humidity (RH), precipitation, soil heat fluxes and sensible and latent heat fluxes, were made using a Bowen-ratio system (Campbell Scientific, Loughborough, UK). Canopy wetness was measured using two independent methods, a Campbell Scientific wetness sensor and a set of leaf-wetness sensors built on the design by Burkhardt and Gerchau (1994). All measured parameters were then averaged and logged at half-hourly intervals, providing 30-minute average NH₃ concentrations, fluxes and related micrometeorological variables.

\((d)\) Uncertainties in measured fluxes and related variables

Uncertainties in individual half-hourly flux measurements by the aerodynamic flux-gradient method may be estimated on the basis of both random and systematic errors (see appendix). Earlier studies have shown random errors in flux estimates to be dominated by errors in the concentration measurements, namely the log-linearity of vertical concentration-profiles (Sutton 1990; Duyzer 1994). Systematic errors arise from various artefacts inherent in the gradient method which lead to vertical fluxes being height-dependent (Fowler and Duyzer 1989). Non-stationarity and horizontal concentration-gradients introduce systematic storage- and advection-errors in the flux respectively (Sutton and Fowler 1992), and chemical production or consumption of NH₃ in the surface layer where the gradients are measured may lead to a divergence between the measured flux and the ‘true’ surface flux of NH₃ (Brost et al. 1988; Huebert et al. 1988; Allen et al. 1989).

Systematic advection-errors were not calculated in this study owing to the absence of measurements of horizontal gradient; however, a discussion of advection errors in gradient fluxes, based on theoretical horizontal gradients, has been provided by Sutton et al. (1993b). They found that close to strong NH₃ sources, advection errors were likely to provide an apparent enhancement to deposition. Therefore, if advection errors were important at Auchencorth Moss, their effect would be an overestimation of fluxes and deposition velocities. Errors resulting from storage effects were maximum at low ambient concentrations, up to 50% in fluxes, and decreased exponentially with increasing concentrations. The overall average error in fluxes due to storage was small, however, less than 5%, the median error being about 2%. Chemical reactions between NH₃, HNO₃ and HCl were assumed not to have had any significant quantitative influence on NH₃ fluxes as median measured air-concentrations of HNO₃ and HCl at Auchencorth Moss were very small,
<table>
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<tr>
<th></th>
<th>N fluxes</th>
<th>% data coverage</th>
<th>NH₃ flux (ng m⁻² s⁻¹)</th>
<th>XNH₃ (1 m) (μg m⁻³)</th>
<th>Vd (1 m) (mm s⁻¹)</th>
<th>Rₛ(H1 m) (s⁻¹)</th>
<th>Rₒ (s⁻¹)</th>
<th>Vₘₐₓ (1 m) (mm s⁻¹)</th>
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Ammonia concentrations at 1 m were calculated after simple linear regression of concentrations measured at three heights against stability-corrected ln(z - d); a data selection was performed on all measured variables on the basis of fetch requirements, stability and wind speed.

0.19 and 0.18 μg m⁻³ respectively. It was therefore unlikely that they contributed to the total error in fluxes significantly.

The mean relative standard error in measured NH₃ fluxes was typically 30–40% and was dominated by the random scatter in the three-point concentration-gradient. The analysis of errors in the concentration regression-slopes (Sokal and Rohlf 1969; Sutton and Fowler 1992) showed that the relative error in interpolated concentrations (1 m) was typically < 5% whereas the error in extrapolated surface concentrations (zₒ) was between 40% and 50%. The uncertainty in the deposition velocity at 1 m was virtually the same as the uncertainty in the flux (30–40%) since the error in the concentration at 1 m was small. Standard errors for canopy resistances were typically 10–50 s⁻¹.

3. Results

Concentrations were measured about 71% of the time during the period from February 1995 to February 1996 (Flechard and Fowler 1998). Coverage for fluxes was less, 53% (Table 1), as the measurements had to meet the criteria defined in subsection 2(c). Thus, there were about 13 500 half-hourly concentration-measurements and 10 000 half-hourly valid flux-measurements. For most months during the monitoring period, the data coverage was sufficient to obtain representative mean values for concentrations, fluxes and the exchange parameters deposition velocity and canopy resistance. Clear seasonal and diurnal trends in the data were observed and interpreted in relation to meteorological, physiological and morphological variations at this site. In this section, a general description of the variations in measured NH₃ fluxes at Auchencorth Moss for the whole monitoring period is presented. Case studies are then used to identify the processes that regulate the surface–atmosphere exchange of NH₃ and quantify the influence of surface conditions, e.g. leaf wetness, temperature and snow cover, on measured fluxes.

A statistical description of atmospheric NH₃ concentrations, the seasonal variations in NH₃ concentrations and the influence of meteorological variables such as temperature, wind speed and humidity on NH₃ are reported in an associated paper (Flechard and Fowler 1998).
(a) Ammonia fluxes: trends, mechanisms and variability

Over the whole monitoring period, NH₃ was generally found to be deposited to the moorland. Measured fluxes ranged from $-269.2$ (deposition) to $+17.8$ ng NH₃ m⁻² s⁻¹ (emission) with an overall median flux of $-5.2$ ng m⁻² s⁻¹ of the population of $10^4$ measured fluxes. NH₃ was found to be emitted by the moor for only about 6.6% of the time and the magnitude of the integrated emission-flux over the whole monitoring period represented only about 1.3% of that of the deposition flux. It is therefore appropriate in this study to describe the diurnal and seasonal variations in measured fluxes at this site in terms of concentrations, deposition velocity and canopy resistance. Median canopy-resistances for given periods were calculated from the corresponding median fluxes, median air-concentrations, median $R_a$ and median $R_b$.

- **General trends.** Mean monthly fluxes were generally larger in winter than in summer (Table 1), ranging from $-2.5$ ng NH₃ m⁻² s⁻¹ in September 1995 to $-11.5$ ng m⁻² s⁻¹ in January 1996, even though mean concentrations were higher in summer than in winter, because of larger surface resistances in summer. The moor was generally an efficient sink for atmospheric NH₃ in winter, cool (2–10 °C), wet and windy conditions, with small canopy-resistances, typically in the range 0–20 s m⁻¹. Canopy resistances for NH₃ deposition were, however, significantly larger over ‘dry’ snow and frozen surfaces at temperatures < $-1$ °C, with $R_c$ values generally in the range 50–100 s m⁻¹. The largest mean values for $R_c$ were found in summer in dry and warm conditions, typically $R_c > 100$ s m⁻¹ in daytime, when cuticular uptake of NH₃ was reduced; $R_c$ was found to decrease with increasing RH after sunset.

Warm summer weather occasionally provided the necessary conditions for NH₃ emission from the canopy into the atmosphere. Upward fluxes were assumed to result from two processes occurring at the canopy level: firstly, NH₃ emission from apoplasm* NH₄⁺ when NH₃ air concentrations fell below a ‘stomatal’ compensation point $\chi_s$; secondly, NH₃ desorption from water films, e.g. an evaporating dew-layer on plant cuticles, controlled by a ‘canopy’ compensation point $\chi_c$. Both processes were dependent on surface temperature and RH. Emission fluxes were of scientific interest but quantitatively they were negligible at this site relative to deposition fluxes.

The frequency distribution of the 9961 measured NH₃ fluxes (Fig. 1) was seen to be strongly skewed towards negative values with a small number of positive (emission) fluxes (6.6% of the total number of measurements). Of the measured fluxes, 82% were within the range $-20$ to 0 ng NH₃ m⁻² s⁻¹.

The frequency distribution of measured deposition-velocities (Fig. 2) also reflected the bidirectional nature of the exchange, with negative deposition velocities denoting emission fluxes. Figure 2 also shows the difference between actual rates of exchange ($U_d$) and those expected for a perfect sink (zero canopy resistance) expressed here as the maximum deposition-velocity allowed by turbulence, $V_{max}(1 \text{m}) = 1/(R_{diff}(1 \text{m}) + R_b)$. The frequency distribution of $V_d(1 \text{m})$ shows a distinct peak with a large proportion of the measurements in the range 0–20 mm s⁻¹; by contrast, the distribution of $V_{max}(1 \text{m})$ was broader with a smaller kurtosis (0.8) and values generally in the range 5–35 mm s⁻¹.

A median deposition-velocity of 11.7 mm s⁻¹ was calculated for the whole monitoring period from the median flux ($-5.2$ ng m⁻² s⁻¹) and the median NH₃ concentration at 1 m above $d (0.44 \mu g \text{ m}^{-3})$. The median $V_{max}(1 \text{m})$, which represents the ‘potential’ $V_d(1 \text{m})$, was 20.8 mm s⁻¹ (Table 1). A significant canopy-resistance, accounting for the difference between $V_d$ and $V_{max}$, therefore limited the rates of NH₃ dry-deposition over the moorland to

* See p. 749 of this issue.
Figure 1. Frequency distribution of the 9961 30-minute average NH$_3$ fluxes measured at Auchencorth Moss (from February 1995 to February 1996). The class width for NH$_3$ fluxes on the x-axis is 0.2 ng m$^{-2}$ s$^{-1}$.

Figure 2. Frequency distribution of deposition velocity for NH$_3$, $V_d$ (1 m) and maximum deposition velocity allowed by turbulence $V_{\text{max}}$ (1 m) = ($R_{\text{all}}$ (1 m) + $R_b$)$^{-1}$ at Auchencorth Moss (from February 1995 to February 1996). Negative deposition velocities denote emission fluxes. The class width for deposition velocities on the x-axis is 0.2 mm s$^{-1}$.

about half the maximum allowed by turbulent transfer. The median $R_c$ (37 s m$^{-1}$), measured over the 13 months of the monitoring period, was very similar to the median atmospheric aerodynamic resistance $R_{\text{all}}$ (1 m) (36.6 s m$^{-1}$). Earlier studies (Duyzer et al. 1987; Sutton et al. 1992) had suggested that moorlands were efficient sinks for atmospheric NH$_3$ with minimal surface resistances, and rates of dry deposition were limited only by atmospheric turbulence, except in frozen conditions. These new measurements at Auchencorth Moss
show that moorland surfaces are not perfect sinks for NH$_3$, with median canopy-resistances in summer larger than 100 s m$^{-1}$ (Table 1) and even occasional NH$_3$ emission-fluxes.

- **Seasonal variations in stomatal uptake and epicuticular absorption of NH$_3$.** From February to August 1995, there was a gradual rise in NH$_3$ concentration, but during this period, the monthly median fluxes decreased from about $-8$ to $-4$ ng NH$_3$ m$^{-2}$ s$^{-1}$ (Table 1; Fig. 3). During the same period, median $V_{\text{max}}$ (1 m) steadily decreased from 33 mm s$^{-1}$ to 18 mm s$^{-1}$ as mean wind-speeds decreased, while median $V_d$ (1 m) showed a similar decline from 26 mm s$^{-1}$ to only 6 mm s$^{-1}$ and the canopy resistance rose from 10–20 to above 100 s m$^{-1}$. March 1995 was an exception to the general trend with a significantly larger median canopy-resistance and lower median flux and deposition-velocity than February, April and May 1995, as a result of the vegetation being covered in snow for about 15 days in March. At the end of the summer 1995 and into the 1995–1996 winter, a sharp decline in canopy resistance was seen, down to median monthly values of 10 to 20 s m$^{-1}$. An increase in monthly canopy-resistances was observed in December 1995 and January 1996, up to 40 s m$^{-1}$, which, like March 1995, coincided with the occurrence of long periods of snow and cold easterly weather.

Rates of NH$_3$ deposition were generally larger in cool, wet conditions with canopy resistances often not significantly different from zero. These conditions were generally found in winter, spring and autumn, with high wind-speeds, and temperatures in the range 2–10 °C. Monthly rainfall did not vary much between March and August 1995, fluctuating between 30 and 60 mm; however, large differences were found between monthly-mean canopy-resistances, the largest mean values being observed in June, July and August 1995 (> 100 s m$^{-1}$) (Fig. 3) whereas the surface behaved as an efficient sink during the spring months. The differences in $R_c$ are unlikely to have resulted from effects of rainfall amount, but are more likely to have resulted from the duration of leaf surface wetness following rain or dew, which is related to saturation deficit and air temperature. The increase in rainfall between August and September 1995 was coupled with a sharp decline in mean air temperature by 4 deg C and resulted in significantly smaller surface resistance in September and the following months. The main difference between warm months and cool months, precipitation rates being equal, was the duration of wetness on the surfaces of leaves from rain or dew. Evaporation rates were larger in summer than in winter, spring or autumn, which meant that the reduction in cuticular resistance $R_w$ associated with wet films on plant surfaces would last for shorter periods. By contrast, the canopy remained wet longer in cool, overcast conditions, with small latent-heat fluxes and reduced evaporation rates, favouring small cuticular resistances.

Seasonal variations in the canopy resistance were not dictated by canopy wetness alone. Physiological changes in the vegetation also contributed to the variations in $R_c$; annual and perennial vascular plants present at this site followed vegetative and reproductive cycles starting in May and ending in November 1995. The upper canopy was green and photosynthesizing during this period, and was senescent or dormant for the rest of the year. The lower part of the canopy was made up of bryophytes and was almost always wet or moist, except during the exceptionally dry summer months of 1995. Water-vapour-flux measurements and O$_3$-flux measurements, made at this site at the same time as NH$_3$, indicated summer daytime bulk stomatal resistance $R_b$ in the range 150–200 s m$^{-1}$ with clear evidence of a diurnal cycle as a consequence of stomatal opening and closing, and night-time values in the range 500–1000 s m$^{-1}$. Winter bulk stomatal resistances were large, typically 500 s m$^{-1}$ in daytime, with little evidence of a diurnal cycle.

With dry leaf-surfaces during daytime in June, July and August 1995, stomatal uptake of NH$_3$ is likely to have represented a significant part of the overall flux during these months.
Figure 3. Monthly median NH$_3$ fluxes, deposition velocities, canopy resistances, and monthly rainfall and mean air temperatures. Note that median values of $R_c$ were calculated from monthly median fluxes, concentrations and atmospheric resistances as median $R_c = (\text{median } \chi(1 \text{ m})/\text{median } F_{\chi}) - \text{median } R_{\text{alt}}(1 \text{ m}) - \text{median } R_0$.

and in dry conditions. This is strongly supported by mean measured canopy-resistances for NH$_3$ in the range 100–150 s m$^{-1}$ for these three months (Table 1). The plant cuticle, which would otherwise bypass stomatal uptake, would not act as an efficient sink for NH$_3$ under warm and dry conditions when $R_\text{w}$ was larger than $R_c$. The moss carpet beneath the vascular-plant canopy may have provided an alternative sink to stomata within the canopy as bryophyte surfaces generally remained wet, even when the upper part of the canopy
was dry in summer, daytime conditions. However, reduced turbulence at the bottom of the canopy greatly limits turbulent transport to these bryophyte surfaces.

- **Ammonia uptake by frozen surfaces.** Rates of NH$_3$ deposition over frozen or snow-covered surfaces were considerably smaller than over wet surfaces in milder weather. The moorland vegetation was covered in snow for about 50% of March 1995, and about 30% of the period December 1995 to February 1996 inclusive. Measured deposition-velocities were smaller than for the other winter months for two reasons: firstly, $V_{\text{max}}$ was smaller as a consequence of reduced turbulence in a cold, stable boundary-layer, and also because of the small roughness of the snow cover ($z_0$ was typically 3.0 to 3.5 mm over snow); secondly, the canopy resistance was larger than over a wet surface, as the frozen surface or the ice or snow crystals were effectively dry. $R_c$ was found to increase as surface temperature decreased below 0 °C. Fresh snow was found to have a lower surface-resistance than older snow because it usually had a near-zero surface-temperature and a larger surface-area per square metre of ground than older compacted snow.

The monthly median values of fluxes, deposition velocities and canopy resistances for December 1995 and January 1996 should, however, be treated with care because they were based on significantly fewer data than in summer (Table 1), owing to difficulties in operating the flux-measurement instrumentation in cold ($T < -5$ °C) conditions as the solutions are liable to freeze in the wet denuders and the sample lines. The flux-data coverage was reduced to 25% and 14% in December 1995 and January 1996, respectively. The reduction in concentration-data coverage for the months of the 1995–96 winter (Flechard and Fowler 1998) may have also introduced some bias in median monthly-concentrations, as NH$_3$ concentrations tend to build up in the surface boundary layer in stable, cold conditions, owing to suppressed turbulent mixing and reduced dry deposition onto frozen or snow-covered surfaces. Minimum monthly values for $V_{\text{max}}$ were obtained in December 1995 (median $V_{\text{max}}(1 \text{ m}) = 15.0 \text{ mm s}^{-1}$) and January 1996 (median $V_{\text{max}}(1 \text{ m}) = 15.5 \text{ mm s}^{-1}$) as a result of low wind-speeds and high stability. The reported median $V_{\text{max}}(1 \text{ m})$ for these two months may have been overestimated because large parts of the flux data-set were lost because of extreme stability (Table 1).

- **Seasonal variability in surface resistance.** The variability in $R_c$ was smaller in winter than in summer, except over snow when fluxes were controlled by snow temperature at the surface. In wet, non-frozen winter conditions, variations in $R_c$ were small and few values exceeded 50 s m$^{-1}$. Figure 4 shows the contrast between the frequency distributions of $R_c$ for two selected months, February 1995 and August 1995, and for the whole monitoring period; 75% of the measured canopy resistances in February 1995 were below 20 m s$^{-1}$, whereas 75% of those in August exceeded that value. The frequency distribution of surface resistances measured in February was strongly peaked around zero and the fraction of the time that canopy resistances were not significantly different from zero was approximately 60%. This contrasts sharply with August 1995 which showed a much flatter distribution owing to a high frequency of surface resistances in the range 50–200 s m$^{-1}$.

- **Diurnal variations.** Ammonia concentrations at 1 m above $d$ generally underwent more pronounced diurnal cycles in spring and summer than in autumn and winter. Daytime median concentrations reached maximum values above 1 μg m$^{-3}$ in June, July and August 1995 with nocturnal median minima in the range 0.3–0.7 μg m$^{-3}$ (Fig. 5). During the windy, wet months of February and October 1995, the diurnal cycle in concentration was suppressed by turbulence (Fig. 5).

The diurnal cycles observed in concentrations for the summer months can be interpreted as a consequence of strong diurnal cycles in canopy resistance and temperature. The
median diurnal cycles in $R_c$ during the summer months (Fig. 5) produce night-time minima in $R_c$ (50–100 s m$^{-1}$) which enhance NH$_3$ depletion at the surface on the one hand, and on the other hand daytime maxima in $R_c$ (150–250 s m$^{-1}$) reduce dry deposition, presumably limiting NH$_3$ deposition to stomatal uptake. Strong diurnal temperature-cycles in summer are expected to favour NH$_3$ emission and large NH$_3$ concentrations during the warmer daytime conditions as NH$_3$ emission fluxes from vegetation increase exponentially with temperature (Husted and Schjøerring 1996).

The absence of a strong surface-heating in autumn and winter time, with increased cloud cover and higher wind-speeds, generally produced neutral stability, except for those months (March and December 1995 and January and February 1996) when very cold conditions and low wind-speeds generated large stability at this site. Thus, diurnal variations in air temperature in autumn and winter were much smaller at this site than in summer. More importantly, daytime temperatures were much lower in winter than in summer, with surfaces almost permanently wet and senescent vegetation. Ammonia emissions and concentrations were therefore much less dependent on temperature and vegetation, and more at this site on wind speed, wind direction and dispersion from local agricultural point sources (Flechard and Fowler 1998).

Deposition velocities were largest in autumn and winter and lowest in spring and summer but no diurnal cycles were clearly seen in $V_d$ (Fig. 5). There was, however, strong evidence of diurnal cycles for the maximum deposition velocity $V_{\text{max}}$ in spring and summer because its fluctuations are coupled with those of $R_{\text{air}}$ and $R_0$, themselves functions of $u_z$ and stability (Eqs. (14) and (15)), but the variations in $V_{\text{max}}$ were consistently overwhelmed by the magnitude and variations in $R_c$ in controlling total resistance to deposition, resulting in little diurnal change in $V_d$.

- Ammonia emission fluxes. The moorland at Auchencorth Moss was found to be a net sink for atmospheric NH$_3$, with emission fluxes observed only 6.6% of the time; the monthly frequency of emission reached 16% during the summer 1995. The overall
importance of emission fluxes was minor, however, representing only about 1.3% of the integrated deposition-flux; this was because the canopy compensation point was generally small at this site, typically in the range 0–0.3 μg m⁻², resulting in emission fluxes never exceeding 20 ng NH₃ m⁻² s⁻¹ and being usually short-lived (1 to 3 hours) as atmospheric concentrations of NH₃ rapidly rose again above $\chi_c$.

Upward NH₃ fluxes from the moorland were often observed during the drying of dew and rainwater from foliar surfaces and resulted in the desorption of NH₃ from the
liquid phase, and also whenever the phase equilibrium between atmospheric NH$_3$ and NH$_3$/NH$_4^+$ in solution was disrupted because of a decrease in air concentration above the surface. This is best described by the temperature response (Eq. (18)) of the equilibrium partial pressure $p_{NH_3}$ for a given ammonium–hydronium molar-ratio in solution, resulting from the combined effects of Henry’s Law for NH$_3$ (Dasgupta and Dong 1986) and its dissociation constant in water $pK_a$ (Bates and Pinching 1950):

$$
p_{NH_3} = 10^{4.1218 - 4507.05/T} [\text{NH}_4^+]/[\text{H}^+].
$$

This relationship not only governs the NH$_3$ fluxes from or into water films on plant cuticles, but also the exchange of NH$_3$ within the stomatal cavities of plants where gaseous NH$_3$ is in equilibrium with apoplast NH$_3$ and NH$_4^+$ as a function of pH and temperature (Farquhar et al. 1980; Husted and Schjøerring 1996).

The animal density on the moor was very small (<1 sheep ha$^{-1}$) and while the animals could have contributed to the emission fluxes, the data are more consistent with the vegetation as the source of the NH$_3$ on the occasions when air concentrations were small enough for emission to occur (i.e. below the compensation point of the vegetation). Such conditions are very unlikely to have been caused by the presence of sheep in the vicinity of the measuring instrumentation.

(b) Case studies

Meteorological conditions were shown to have a strong influence on both NH$_3$ concentrations (Flechard and Fowler 1998) and rates and net direction of NH$_3$ exchange between moorland and the atmosphere. To illustrate these links and identify the processes which regulate NH$_3$ exchange, four case-studies are presented which encompass a wide range of meteorological and environmental conditions: ammonia exchange in cool, wet and windy conditions (26 and 27 September 1995); ammonia exchange in summer, warm and moderately dry conditions (19, 20 and 21 June 1995; 03 July 1995); ammonia exchange over frozen and snow-covered surfaces (14 and 15 March 1995).

- Cool, wet and windy conditions. The moorland surface was generally an efficient sink for atmospheric NH$_3$ in winter, cool, wet and windy conditions i.e. for air temperatures in the range 0–10 °C, RH typically 90–100%, and wind speeds from 4 to 15 m s$^{-1}$. Measured canopy-resistances over Auchencorth Moss were generally in the range 0–30 s m$^{-1}$, often not significantly different from zero, allowing deposition velocities close to the maximum provided by atmospheric turbulence and surface roughness. This is exemplified by two days in September 1995 (Fig. 6); the canopy resistance fluctuated between near-zero values during night-time and 30 s m$^{-1}$ during daytime. $R_c$ was, however, seen to gradually increase on 27 September 1995 as surface temperature $T(z_0)$ fell below 0 °C after 2000 GMT; the deposition of NH$_3$ was most probably uptake into a water film on cuticular surfaces. It was also likely that the decreased mobility of water molecules and ions in solutions at the surface of plants below freezing accounted for the increase in canopy resistance after sunset on 27 September as the leaves rapidly cooled below −2 °C. When temperatures were not close to 0 °C, $R_c$ was seen to increase slightly in daytime as the RH at the surface RH($z_0$) dropped from 100% to about 85% on 26 and 27 September, and there was then a significant difference between $V_d$ and $V_{max}$. Rates of deposition were nevertheless fairly large with $V_d$(1 m) almost constantly in the range 15–30 mm s$^{-1}$ until 1600 GMT 27 September. Ammonia fluxes remained small, however, oscillating about a mean value of $-3$ ng m$^{-2}$ s$^{-1}$, with a peak of $-12$ ng m$^{-2}$ s$^{-1}$ between 2100 GMT 26 September and 0100 GMT 27 September as NH$_3$ concentration increased from 0.20 to 0.45 µg m$^{-3}$. 
Figure 6. Surface-atmosphere exchange of NH₃ in wet conditions and at fairly low temperatures for two example days (26 and 27 September 1995, Auchencorth Moss).
This rise in concentration coincided with a shift in wind direction from about 230° back to 180° that occurred between 1800 GMT 26 September and 0200 GMT 27 September; during this period, the influence of a large poultry farm 2.7 kilometres to the south of the monitoring instrumentation was visible. A subsequent fall in concentration was observed as wind direction returned to 230° and rain started falling at 2400 GMT 26 September. During the rain event, from 0000 GMT to 0700 GMT 27 September, $V_d$ was found to be very close to $V_{\text{max}}$ with minimal canopy-resistances, but after precipitation stopped, $R_e$ gradually increased from near-zero to 50 s m$^{-1}$, limiting $V_d$ to about half the $V_{\text{max}}$ value.

- **Summer, warm and moderately dry conditions.** Patterns of surface–atmosphere exchange of NH$_3$ over Auchencorth Moss during the 1995 summer contrasted sharply with those of the wet, winter conditions. With air temperatures typically ranging from 6 to 22 °C, RH from 50 to 100%, and ambient NH$_3$ concentrations from 0.2 to 2 $\mu$g m$^{-3}$, deposition velocities were frequently in the range 0–10 mm s$^{-1}$ with daytime minima and night-time maxima; significant periods of emission fluxes were observed. The data presented in Fig. 7 and Fig. 8 show the bidirectional nature of NH$_3$ fluxes in warm conditions for selected days in June and July 1995. For these two occasions, measured emission-fluxes were the result of NH$_3$ desorption from water films on plant cuticles (Fig. 7) and the release of NH$_3$ from apoplastic NH$_4^+$ into the air through stomata (Fig. 8). The sign of the NH$_3$ flux was clearly dependent on the NH$_3$–air concentration, with emission fluxes only possible when air concentrations were smaller than the canopy compensation point. The “canopy” compensation point $\chi_c$ was found to vary with temperature, surface wetness, RH and the stomatal compensation point $\chi_s$.

- **Ammonia uptake by plant cuticles and stomata; NH$_3$ emission as a result of desorption from water films.** Emission fluxes of NH$_3$ were measured from 0430 to 1100 GMT 20 June 1995 (Fig. 7) at atmospheric (1 m) NH$_3$ concentrations smaller than about 0.5 $\mu$g m$^{-3}$; the exchange switched to deposition again as $\chi_{\text{NH}_3}(1 \text{ m})$ increased above the threshold level of 0.5 $\mu$g m$^{-3}$ at 1100 GMT. However, emission was not observed on the night of 20 June 1995 nor the following day (21 June 1995) when the air concentration fell below 0.4 $\mu$g m$^{-3}$; $\chi_e$ was therefore lower than than when emission was seen on the morning of 20 June. This was partly because large deposition-fluxes (from $-5$ to $-35 \text{ ng NH}_3 \text{ m}^{-2} \text{ s}^{-1}$) occurred during the hours preceding the morning of 20 June along with precipitation (3.4 mm from 2200 GMT to 0400 GMT); during this period, the bulk of the deposition was onto wet leaf-surface cuticles, increasing the NH$_4^+$ concentration in the water film. The emission fluxes observed thereafter were mainly desorption fluxes from the water film, in order to re-establish phase equilibrium according to Henry’s Law (Eq. (18)), as atmospheric NH$_3$ concentrations fell below an increased $\chi_c$. Emission was promoted in the following hours by the evaporation of the liquid film as the surface temperature increased and the RH declined from 100% at 0400 GMT to 70% at 1100 GMT. Larger NH$_4^+$ concentrations reached in the liquid film in the early hours of the morning of 20 June raised $\chi_e$ up to 0.4–0.5 $\mu$g m$^{-3}$. This was not repeated on 21 June because no large NH$_3$-deposition fluxes occurred in the night-time hours preceding the morning increase in temperature and evaporation of the dew layer. It was then $\chi_s$ that controlled the exchange at a somewhat lower value, preventing emission. Surface temperatures were also 5–8 deg C higher on 20 June, when emission occurred, than the following morning; this was also important in regulating $\chi_c$ as NH$_3$ is less soluble at higher temperatures (Eq. (18)).

During the latter part of 20 June and 21 June 1995, NH$_3$ was deposited to the vegetation but deposition rates were small during the day because of substantial canopy-resistances, frequently in the range 50–200 s m$^{-1}$. The cuticular uptake is likely to have been influenced by leaf-surface water-films as suggested by Burkhardt and Eiden (1994), thus the change
Figure 7. Surface-atmosphere exchange of NH$_3$ in summer conditions (19 to 21 June 1995, Auchencorth Moss).
Figure 8. Bidirectional exchange of NH$_3$ and sensible and latent heat at Auchencorth Moss over the course of a warm, dry summer day (3 July 1995).
in $R_e$ from the daytime 50–200 s m$^{-1}$ at RH < 60% to night-time values < 50 s m$^{-1}$ at RH > 90% is consistent with uptake on cuticular surfaces regulated by leaf-surface wetness.

- **Ammonia emission from stomata in summer conditions.** Measured emission-fluxes of NH$_3$ at Auchencorth Moss in summer often resulted from desorption processes on leaf cuticles, and sometimes from the combination of both cuticular desorption and stomatal emission. To obtain evidence of stomatal emission by moorland plants, upward-flux data were selected for periods when leaf surfaces were as dry as possible. By selecting data this way, desorption fluxes would contribute a minor fraction to the total emission-flux. It is also important to recognise that NH$_3$ emitted by plant stomata can be recaptured by surface-cuticular water.

Assessing the degree of dryness or wetness of the vegetation was difficult, however, because of the complexity of the plant canopy, with almost permanently moist or wet mosses at the bottom of the moor canopy, and 30 to 40 cm-tall vascular plants, mainly grasses and sedges, arranged in a better ventilated and generally drier upper canopy. The RH of air surrounding individual leaves was therefore expected to be very variable within the canopy. The relative humidity at $z_0$ was extrapolated from vertical water-vapour and temperature profiles measured in the lowest 2.5 m of the surface layer, and RH($z_0$) provides a "big leaf" estimate of the surface humidity. Hence leaf-wetness sensors built to the design of Burkhardt and Gerchau (1994) were used to measure the conductance of thin waterfilms on leaf surfaces and provide additional information on the humidity at the surface. Conditions when RH($z_0$) was small (< 60%), and when the leaf-surface conductance was lowest, were assumed to be 'dry' conditions, for which an upward flux gave substantial evidence of stomatal emission. Such conditions were for instance found on 03 July 1995 from 1200 to 1430 GMT (Fig. 8); before 1200 GMT, the surface was still drying out from dew, and desorption fluxes from cuticles were measured; after 1200 GMT, a decrease in air concentration of NH$_3$ from about 0.5 down to 0.2 $\mu$g m$^{-3}$ occurred as wind direction veered from north-easterly to south-westerly. As the air concentration of NH$_3$ was smaller than $x_0$, NH$_3$ emission was observed for about 3 hours, before the wind direction turned more southerly, bringing in larger NH$_3$ concentrations at 1600 GMT and a return to deposition fluxes.

- **Frozen and snow-covered surfaces.** Small rates of NH$_3$ deposition were measured over snow-covered surfaces, and more generally in conditions when temperatures fell below 0 °C. In the example described in Fig. 9, deposition velocities ranged between 5 and 15 mm s$^{-1}$ over a 10-cm snow cover with surface resistances between 30 and 150 s m$^{-1}$. Yet, despite the high surface-resistances, the measured fluxes over snow were typically 4 to 5 ng NH$_3$ m$^{-2}$ s$^{-1}$, i.e. close to the yearly-mean flux, because air concentrations were higher than average as a consequence of the restricted vertical mixing of NH$_3$ from local ground sources in stable air over the aerodynamically smooth snow-surface. The surface resistance increased rapidly from 20 to above 100 s m$^{-1}$ as snow started falling from 1830 GMT 14 March 1995 and the surface temperature fell below −1 °C. When surface temperature rose above 0 °C at 1000 GMT 15 March, the surface resistance declined to 60 s m$^{-1}$, and then increased above 100 s m$^{-1}$ at 1400 GMT as temperature dropped again below 0 °C. The NH$_3$ concentration at $z_0$ was found to increase when surface temperature fell below 0 °C, and to decrease for temperatures rising above the melting point of the snow surface. Surface concentrations of NH$_3$ as high as 0.5 $\mu$g m$^{-3}$ were measured for surface temperatures of about −2 °C at 0700 GMT 15 March as a result of decreased solubility of NH$_3$ in the snow crystals. The increase in NH$_3$ surface-concentrations over snow cover and at very low temperatures, down to −7 °C, was frequently observed at Auchencorth.
Figure 9. Surface–atmosphere exchange of NH₃ in wintry conditions (14 and 15 March 1995). Recorded snow showers are indicated by vertical arrows; the depth of the snow cover was 10 cm at 1200 GMT 15 March 1995.
TABLE 2. Effects of surface conditions on NH₃ exchange (values are median measured parameters)

<table>
<thead>
<tr>
<th>Condition</th>
<th>(x_{\text{NH}_3}(1 \text{ m})) (\mu g \text{ m}^{-3})</th>
<th>NH₃ flux (\text{ng m}^{-2} \text{s}^{-1})</th>
<th>(V_q(1 \text{ m})) (\text{mm s}^{-1})</th>
<th>(V_{\text{max}}(1 \text{ m})) (\text{mm s}^{-1})</th>
<th>(R_c) (\text{s m}^{-1})</th>
</tr>
</thead>
<tbody>
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<td>All conditions</td>
<td>0.44</td>
<td>-5.2</td>
<td>11.7</td>
<td>20.8</td>
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<tr>
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<td>-5.0</td>
<td>13.1</td>
<td>19.2</td>
<td>23</td>
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<tr>
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<td>-5.3</td>
<td>9.4</td>
<td>22.1</td>
<td>61</td>
</tr>
<tr>
<td>Snow cover</td>
<td>0.47</td>
<td>-4.3</td>
<td>9.1</td>
<td>18.5</td>
<td>56</td>
</tr>
</tbody>
</table>

Moss, occasionally leading to small emission-fluxes if the air concentration fell below that at the surface.

4. Discussion

The continuous monitoring of NH₃ fluxes at Auchencorth Moss over a period of 13 months yielded both representative long-term and seasonal rates of NH₃ exchange over moorland surfaces. The measurements provided better insight into mechanisms which regulate the exchange than short-term campaign measurements which have been reported previously (Sutton et al. 1992; Sutton et al. 1993a; Duyzer 1994). They also overcame the bias introduced through selection of suitable days for the measurements. The large number of measurements (≈10⁴ half-hourly runs) provides statistical weight to the observed trends and the mechanistic studies that have been made possible. The influence of meteorological and other environmental parameters on NH₃ concentrations and fluxes can now be assessed with more confidence and accuracy, and provide better estimates of annual fluxes to terrestrial ecosystems. Modelling and mapping studies which have been hampered by the lack of field measurements can now be validated against a substantial set of measured data.

(a) Seasonality of NH₃ fluxes and canopy resistance; effects of wetness and temperature

Seasonal variations in deposition fluxes are controlled by seasonal changes in air concentrations, rates of turbulent mixing (\(V_{\text{max}}\)) and canopy resistance. These parameters are closely coupled with the meteorological variables, viz. wind speed, temperature, stability, precipitation and canopy wetness. Wet surfaces were consistently found to be more efficient sinks for atmospheric NH₃ with a mean canopy-resistance of 23 s m⁻¹ than dry surfaces (mean \(R_c = 61 \text{ s m}^{-1}\)) (Table 2). The mean fluxes, however, were similar for wet and dry conditions, -5.0 and -5.3 ng m⁻² s⁻¹ respectively, because air concentrations were larger in dry conditions. Mean canopy-resistances were found to be much larger in summer than in winter; a positive correlation between surface temperature and canopy resistance was also found for temperatures above 0 °C (Fig. 10(b)). By promoting evaporation of surface-water films, high temperatures partially suppressed the cuticular uptake of NH₃ which would otherwise provide an efficient sink. Duyzer (1994) also reported a positive correlation between air temperature and canopy resistance in both wet and dry conditions over heathland, and suggested that the temperature effect was probably related to the reduced solubility of NH₃ at higher temperatures. However, this effect did not seem to be of great importance in the overall NH₃ budget in his study and rates of NH₃ deposition were generally very high; season, time of day or NH₃ concentration appeared to have no influence on either \(V_q\) or \(R_c\). This may have been because of the limited number of
measurements available and the detection limit of the equipment used. The increase in $R_c$ with temperature shown in Fig. 10(b) is the consequence of two independent processes: partitioning of NH₃ towards the gas phase at leaf surfaces induced by the action of Henry’s Law, and the resulting increase in $\chi(z')$ at high temperatures (Fig. 10(b)); the decrease in surface water on foliage with temperature as the vapour-pressure deficit increases.

Frozen and snow-covered surfaces at Auchencorth Moss showed large canopy-resistances, typically 50–150 s m⁻¹; this is consistent with limited measurements made by Sutton et al. (1992) in frozen conditions over Eriophorum-dominated vegetation (201 s m⁻¹) and over Calluna (53 s m⁻¹). For winter months with substantial snow cover, mean surface-resistances were significantly larger than for wet and windy months, but the larger air concentrations that frequently occurred at low ($<-1^\circ$C) temperatures may have compensated for larger surface-resistances, giving substantial mean deposition-fluxes (−4.3 ng m⁻² s⁻¹, see Table 2). Snow cover at low temperatures indeed behaved like dry surfaces with little adsorption capacity, because of the reduced availability of liquid water.
There was also substantial evidence of larger surface-concentrations of NH$_3$ over frozen and snow-covered surfaces at temperatures below $-1$ °C (Fig. 10(a)). Values of $R_b$ used in Eq. (16) for the estimation of $\chi_{NH_3}(z_b)$ may be subject to considerable uncertainty because the roughness and aerodynamic properties of a snow-covered canopy are different from those of fibrous surfaces for which the $R_b$ formulation used was best suited (Garland 1977). This formulation probably underestimates $R_b$ over snow, and therefore $\chi_{NH_3}(z_b)$ for deposition onto snow-covered vegetation may be overestimated. Emission fluxes from snow (7% of the time for fluxes measured over snow) were probably the result of the existence of a compensation point which depended on the temperature and the NH$_3$/NH$_4^+$ concentrations of the snow.

(b) Leaf surface processes

Ammonia deposition-fluxes over moorland could not be clearly explained by stomatal uptake alone, especially in wet conditions. Had stomatal uptake controlled deposition, mean canopy-resistances for the whole period would have been of the order of the bulk stomatal resistance to gaseous diffusion, typically 150–200 s m$^{-1}$ in daytime and 500–1000 s m$^{-1}$ at night. Values reported in Table 2 indicate mean surface-resistances of 23 and 61 s m$^{-1}$ in wet and dry conditions respectively; this suggested that NH$_3$ was deposited efficiently to leaf surfaces, bypassing the stomatal pathway.

Wet surfaces were better sinks for NH$_3$ than dry surfaces, yet they were not perfect sinks as suggested earlier (Sutton et al. 1992; Sutton et al. 1993a; Duyzer 1994). The mean surface-resistance in wet conditions for the whole monitoring period was 23 s m$^{-1}$, only allowing a mean deposition velocity of 13.1 mm s$^{-1}$, i.e. about 2/3 of the mean maximum deposition velocity ($V_{max} = 19.2$ mm s$^{-1}$).

The adsorption capacity of leaf surfaces increased with wetness of the cuticle; this was found after rain events, at night with dewfall and during fog episodes. The humidity effect was also visible during daytime, ‘dry’ conditions, when the canopy resistance was inversely related to RH at the surface. This demonstrated the important roles of both macroscale and microscale wetness in regulating the capacity of adsorption of cuticles, as previously highlighted by Van Hove et al. (1989), Wyers et al. (1993b), Burkhardt and Eiden (1994) and Duyzer (1994). It was suggested (Burkhardt and Eiden 1994) that at moderately low surface RHs (60–70%), the deliquescence of pre-deposited salts on hydrophobic waxy cuticles creates thin water films which provide a sink for atmospheric water-soluble gases such as NH$_3$ or SO$_2$, even though the vegetation appears ‘dry’. This may account for small canopy-resistances occasionally observed in summer, daytime, moderately dry conditions, and for much of the variability in $R_c$.

The resistance to NH$_3$ adsorption on cuticular surfaces varies with the thickness of the water film, but perhaps equally importantly with the chemical composition of the solution. Considering NH$_3$/NH$_4^+$ only, the partial pressure of NH$_3$ in air immediately above, and in equilibrium with, a solution containing aqueous NH$_3$ and NH$_4^+$ ions is determined by the pH of the solution and the temperature which imposes values for the Henry coefficient and the $pK_a$ of NH$_4^+$ (Eq. (18)). As NH$_3$ is readily taken up by water films on plant surfaces, it either remains as aqueous NH$_3$ or is reduced to NH$_4^+$ depending on pre-existing concentrations in solution, temperature and pH. The solution acts as a capacitor charging up with NH$_3$ so long as the concentration of air above the surface is larger than that of the air immediately in equilibrium with the solution and so long as saturation of the water film is not reached. The fate of ammoniacal-N in the solution is rather uncertain; some will be washed to the ground by subsequent rain; aqueous NH$_3$ can be released to the atmosphere if air concentrations drop below the concentration in equilibrium with the surface; NH$_4^+$ can combine with anions in solution to form salts on evaporation and remain on the leaf surface.
There is scope for some of the \( \text{NH}_4^+ \) ions in solution to reach the sub-stomatal cavity, and the adjacent apoplast, if there is continuity between the film on the leaf surface and the internal solution as suggested by Burkhartd and Eiden (1994). The mechanism involved would be migration of ions along a concentration gradient between external and internal leaf-surfaces. Continuous measurements of \( \text{SO}_2 \) fluxes were also made at Auchencorth Moss at the same time as \( \text{NH}_3 \), but a detailed investigation of \( \text{NH}_3/\text{SO}_2 \) interactions on leaf surfaces (Van Hove et al. 1989; Erisman and Wyers 1993) is beyond the scope of the present paper.

(c) Stomatal and canopy compensation-points

The measurements reported here show that, although moorlands are net sinks for atmospheric \( \text{NH}_3 \) and that emission fluxes are quantitatively negligible, they cannot be regarded nor treated as perfect sinks as suggested earlier (Sutton et al. 1992). This would lead to an overestimation of annual fluxes to semi-natural ecosystems in models currently used for atmospheric deposition in Europe by 50–100%. Instead, the roles of canopy wetness and temperature on surface concentrations and canopy resistances must be quantified. The way forward may be the use of canopy compensation points \( (\chi_c) \) in models to predict the direction and magnitude of fluxes (Sutton et al. 1995a; Sorteberg and Hov 1996), even though stomatal emission of \( \text{NH}_3 \) at this site, and possibly over moorland in general, is of little practical significance in countries with significant agricultural sources.

Figure 10(a) allows a comparison to be made between the measured temperature-response of \( \text{NH}_3 \) concentration at \( z_0 \) above \( d \) (or canopy compensation point) at Auchencorth Moss and the theoretical temperature-response of \( \text{NH}_3 \) concentration in equilibrium with an \( \text{NH}_4^+ \)-containing solution. The theoretical curve was fitted according to Eq. (18) and the best fit was obtained for a ratio \( [\text{NH}_4^+]/[\text{H}^+] = 132.1 \). For a given pH value, one can then predict the \( \text{NH}_4^+ \) concentration of the solution and, at a given temperature, the \( \text{NH}_3 \) concentration in air in equilibrium with the solution. A solution pH of 6.8, for instance, would yield an \( \text{NH}_4^+ \) concentration of 21 \( \mu \text{M} \) and a canopy compensation point of 0.15 \( \mu \text{g m}^{-3} \) at 10 °C.

This analysis was obtained on the basis of all measured flux-data at Auchencorth Moss, regardless of the wetness and physiological status of the canopy. Data measured in dry, summer conditions over a green photosynthesizing canopy were pooled together with winter data measured over a dead, wet canopy. The effects of humidity and plant metabolism were therefore averaged to produce a curve that presents "mean" variations in concentrations at the notional height of the surface \( (z_0) \). The mean ratio \( [\text{NH}_4^+]/[\text{H}^+] = 132.1 \) contains the yearly combined and averaged variations in pH and \( \text{NH}_4^+ \) concentrations of both leaf-surface water-films and internal apoplast.

Because \( \chi_c \), or \( \chi(z_0) \), is calculated from Eq. (16), it increases with air concentration at a reference height \( z - d \). The concentration \( \chi_c \) is therefore expected to increase with air temperature purely on the basis of the positive correlation between air concentration and air temperature above 0 °C (Flechard and Fowler 1998). Thus, the present analysis could not distinguish between a rise in \( \chi_c \) due to larger air concentrations of \( \text{NH}_3 \) and a rise in \( \chi_c \) due to enhanced plant metabolic production of \( \text{NH}_3 \) in summer warmer weather. At Auchencorth Moss, ambient \( \text{NH}_3 \) concentrations were also wind-direction dependent; the yearly mean \( \chi(z_0) \) in upwind sectors with local agricultural point sources was in the range 0.5–0.8 \( \mu \text{g m}^{-3} \) as a result of the larger air concentrations, but it was only about 0.1–0.15 \( \mu \text{g m}^{-3} \) for sectors with no upwind sources in the nearest 5 km. Such discrepancies did not indicate significant differences in vegetation for the various sectors over which the fluxes were measured, but probably merely that \( \chi_c \) is a positive function of ambient concentration. The concentration dependence of \( \chi_c \) may hamper modelling based on this
approach. Furthermore it could be argued that, strictly speaking, $\chi (z_0)$ can be considered a 'compensation' point only if the $\text{NH}_3$ flux is zero (Sutton et al. 1998).

(d) Annual flux of ammonia at Auchencorth Moss

Deposition dominated the surface–atmosphere exchange of $\text{NH}_3$ at Auchencorth Moss. The moorland was a net sink for $\text{NH}_3$ with fluxes directed toward the surface 93.4% of the time at a median rate of $-5.2 \text{ ng m}^{-2} \text{ s}^{-1}$. The sinks were strongest in winter, autumn and spring as a result of extended periods of wet canopies, even though the largest $\text{NH}_3$ concentrations were measured in warm, summer weather. Over the year, the input of $\text{NH}_3$ to the site was estimated to be 2.5 kg ha$^{-1}$ a$^{-1}$ directly from monthly means of the net deposition-flux. This dry deposition-input is similar in magnitude to the measured annual wet-deposition of $\text{NH}_4^+$ at this site (2.4 kg $\text{NH}_3$–N ha$^{-1}$ a$^{-1}$) (Fig. 11).

The unusually warm and dry summer of 1995 may be unrepresentative of the longer-term climate at this site. However, the mechanistic information provided by the large quantity of detailed measurements provides the basis for the development of process-based models of land–atmosphere $\text{NH}_3$ exchange over semi-natural vegetation which can be used to predict $\text{NH}_3$ deposition-fluxes in a wide range of environmental conditions. This work will form the basis of a subsequent paper.

The results of continuous flux-measurements at Auchencorth Moss are summarized in Fig. 11 which provides the annual net $\text{NH}_3$ exchange at the site, and mean canopy and boundary-layer parameters associated with the $\text{NH}_3$ flux. For comparison, the measured wet-deposition flux of $\text{NH}_4^+$ and measured net dry and wet inputs of oxidized nitrogen ($\text{NO}_x$) are also shown. The detailed description of oxidized nitrogen exchange (e.g. $\text{NO}_x$, $\text{NO}_2$, $\text{HNO}_3$, HONO) at this site is reported elsewhere (Fowler et al. 1996).
The dry deposition of NH₃—N represented about 30% of the total atmospheric-nitrogen input (8.2 kg N ha⁻¹ a⁻¹) and the total reduced-nitrogen deposition (NH₃—N) was about 5.2 kg N ha⁻¹ a⁻¹, i.e. 63% of the total nitrogen input.

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APPENDIX

ANALYSIS OF THE UNCERTAINTIES IN MEASURED FLUXES AND RELATED PARAMETERS

Uncertainties in individual half-hourly flux measurements by the aerodynamic flux-gradient method may be estimated on the basis of both random and systematic errors. Earlier studies have shown random errors in flux estimates to be dominated by errors in the concentration measurements, namely the log-linearity of vertical concentration profiles (Sutton 1990; Duyzer 1994); systematic errors arise from various artefacts inherent in the gradient method (Sutton and Fowler 1992).

Quantification of random errors

For quantities calculated from combinations involving several parameters, and therefore several different sources of errors, an approximation of the combined error is the square root of the sum of the squares of the individual errors where the combinations involve addition or subtraction; if multiplication or division are involved, relative (or fractional) errors (i.e. error in value/value) are used instead of actual errors (Sutton 1990).

In the case of the flux given by Eq. (2), the standard errors and confidence limits may be given by the combination of fractional errors in the regression slopes, i.e. χₛ/k and uₛ/k, since k is a constant (Sokal and Rohlf 1969; Sutton 1990; Sutton and Fowler 1992). However, the small number of NH₃ sampling heights (3) leads to only one degree of freedom, and thus a very large Student’s t value (12.7 at 95%). This gives unrealistically large 95% confidence limits for flux measurements, and therefore standard errors (SE) are preferred in this paper. The relative standard error in the flux is given as

$$\text{SE}(F_x) = \sqrt{\left(\frac{\text{SE}(u_x/k)}{u_x/k}\right)^2 + \left(\frac{\text{SE}(\chi_x/k)}{\chi_x/k}\right)^2}.$$  \hspace{1cm} (A.1)

Since the friction velocity in this study is not computed from a log-linearized stability-corrected wind-profile, but from a sonic anemometer, the relative standard error in uₛ/k is taken as a constant depending on the manufacturer’s specifications, e.g. 5%, instead of being calculated from the standard error of the slope as for χₛ/k.
The random error in the deposition velocity may be calculated according to Eq. (A.2)

\[
\frac{\text{SE}(V_d(1 \text{ m}))}{V_d(1 \text{ m})} = \frac{\text{SE}(R_t(1 \text{ m}))}{R_t(1 \text{ m})} = \sqrt{\left(\frac{\text{SE}(F_x)}{F_x}\right)^2 + \left(\frac{\text{SE}(\chi(1 \text{ m}))}{\chi(1 \text{ m})}\right)^2},
\]

(A.2)

where \( R_t(1 \text{ m}) \) is the total resistance to deposition, i.e. the sum of \( R_{sh}(1 \text{ m}) \), \( R_b \) and \( R_c \) in series, and consequently

\[
\text{SE}(R_c) = \sqrt{\text{SE}(R_t(1 \text{ m}))^2 + \text{SE}(R_{sh}(1 \text{ m}))^2 + \text{SE}(R_b)^2}.
\]

(A.3)

However, the upper and lower standard errors in \( R_t \) and \( R_c \) should differ since the major source of error in \( R_t \) (the flux) is as a reciprocal. To account for this, the reciprocals of the upper and lower limits of \( V_d \) are taken as the lower and upper limits for \( R_t \) respectively, and the limits for \( R_c \) are calculated accordingly (Eq. (A.3)).

Standard errors for interpolated and extrapolated NH\(_3\) concentrations vary with the square of the distance to the mean measurement height (Sokal and Rohlf 1969), so that error bars for estimated concentrations are much smaller at the reference height (1 m) than those for the surface concentrations (\( z_0 \)) (Fig A.2).

Sources of systematic errors

The flux-gradient method assumes that in a fully-developed surface-layer the vertical flux is constant with height and thus the flux measured at a reference height above the surface (here 1 m) equals the flux at the surface. This, however, is strictly true only if a number of prerequisites are satisfied; these include stationarity (no change of concentration with time), the absence of a horizontal gradient in concentration, and the absence of chemical production or consumption of the measured gas in the surface layer where the gradients are measured (Fowler and Duyzer 1989).

Non-stationarity results in a change in storage of the trace gas in the air between the surface and the measurement heights; the storage error in the flux may be estimated on the basis of \( \Delta \chi/\Delta t \) (Sutton et al. 1993b). Horizontal gradients result in advection errors which are especially important when measuring NH\(_3\) fluxes close to a large source, and farms in the vicinity of Auchencorth Moss may have introduced a significant bias in fluxes at large ambient concentrations from upwind agricultural sources. Advection errors are, however, difficult to estimate when horizontal gradients are not measured. Chemical reactions relevant to NH\(_3\) fluxes include the gas-to-particle conversion of NH\(_3\) in the presence of HNO\(_3\) or HCl or the evaporation of NH\(_3\) from ammonium nitrate or ammonium chloride aerosols (Broost et al. 1988; Huebert et al. 1988; Allen et al. 1989). There is still, however, a great deal of uncertainty regarding the rates of the reactions involved and the extent of the influence of these reactions on measured (or apparent) fluxes.

Other sources of systematic errors include the uncertainty in the estimation of the sub-layer resistance \( R_b \), which is based on empirical relationships and the semi-empirical stability corrections applied to the concentration profile. The latter has been assessed by comparing the standard errors in the regression slopes of concentration versus stability-corrected and stability-uncorrected \( \ln(z - d) \) (Sutton and Fowler 1992); the authors concluded that a 10% error in the stability corrections would yield a very small contribution to the total error in the flux (\(<3\%\)). A discussion was also provided by Sutton (1990) on the errors associated with different formulations for \( R_b \), with the conclusion that they are likely to be small compared to random errors.
Figure A.1. Time course of ammonia exchange and uncertainties in measured ammonia fluxes, deposition velocities (1 m) and canopy resistances at Auchencorth Moss on 30 June 1995. Error bars are standard errors of individual half-hourly runs calculated from standard errors in the log-linear regression of ammonia concentration versus height and standard errors in friction velocity and atmospheric resistances to turbulent transfer.
Figure A.2. Uncertainties in estimated ammonia concentrations at the reference height (1 m above the displacement height $d$), and concentrations at the surface ($z'_{0}$) on 30 June 1995. Error bars are standard errors of individual half-hourly runs calculated from the linear regression of concentrations versus stability-corrected $\ln(z - d)$.

**Combined errors in the flux measurements at Auchencorth Moss**

The mean relative standard error in measured NH$_3$ fluxes was typically 30–40% (Fig. A.1) and was dominated by the random scatter in the three-point concentration-gradient. The relative standard error in the concentration gradient was generally much larger than that of the friction velocity measured by the sonic anemometer by a factor ranging from three to eight. The relative error in interpolated (1 m) concentrations was typically < 5% whereas the error in extrapolated surface concentrations ($z'_{0}$) was between 40 and 50% (Fig. A.2), which made the compensation-point estimates fairly uncertain. The uncertainty in deposition velocity at 1 m was virtually the same as the uncertainty in the flux (30–40%) since the error in the concentration at 1 m was small. The median width of standard error bars for canopy resistances (Fig. A.1) was about 50 s m$^{-1}$. Even though errors in individual half-hourly measurements of exchange parameters were fairly large, the observed differences from run to run and the diurnal and seasonal variations in response to environmental conditions could generally be seen as significant.

Random errors in $\chi_{r}$ were smallest when concentration gradients were largest, i.e. in stable conditions (night-time and winter) but this was also when systematic errors resulting from stability corrections were large. By contrast, the scatter in concentration gradients
was relatively larger in a well-mixed, unstable surface-layer and systematic errors arising from semi-empirical corrections for instability were also large. Errors in fluxes and canopy resistances may therefore have been largest in summer, daytime, unstable conditions.

Systematic advection errors were not calculated in this study because of the absence of measurements of horizontal gradient; however, a discussion of advection errors in gradient fluxes, based on theoretical horizontal gradients, has been provided by Sutton et al. (1993b). They found that, close to strong NH₃ sources, advection errors were likely to provide an apparent enhancement to deposition. Therefore, if advection errors were important at Auchencorth Moss, their effect would be an overestimation of fluxes and deposition velocities.

Errors resulting from storage effects were maximum at low ambient concentrations, up to 50% in fluxes, and decreased exponentially with increasing concentrations. The overall average error in fluxes as a result of storage, however, was small (less than 5%, the median error being about 2%).

Chemical reactions between NH₃, HNO₃ and HCl were assumed not to have had any significant quantitative influence on NH₃ fluxes as median measured air-concentrations of HNO₃ and HCl at Auchencorth Moss were very small (0.19 and 0.18 μg m⁻³ respectively). It was, therefore, unlikely that they significantly contributed to the total error in fluxes.

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