Atmospheric ammonia at a moorland site. I: The meteorological control of ambient ammonia concentrations and the influence of local sources

By C. R. FLECHARD1,2 and D. FOWLER1

1Institute of Terrestrial Ecology, UK
2University of Nottingham, UK

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SUMMARY

Ammonia (NH₃) concentrations were continuously monitored at a moorland site in southern Scotland for 13 months from February 1995 to February 1996, providing about 13 500 half-hourly average measurements (71% of the time). Concentrations were found to be log-normally distributed (with a geometric mean of 0.43 µg m⁻³ and a geometric standard deviation of 3.35), and were strongly dependent on wind direction because of local agricultural point sources within 3 km of the site. These sources contributed approximately 60% of the NH₃ advected over the measurement site, while more distant sources accounted for the remaining 40%. Meteorological conditions also influenced the concentration of NH₃ because of their effects on emissions from vegetation, on dispersion by the atmosphere, and on rates of removal from the atmosphere. The largest concentrations were measured in warm (> 15 °C), dry, summer conditions and in cold (< 0 °C) weather, typically 1–5 µg m⁻³. Smaller concentrations, typically in the range 0.1–1 µg m⁻³ were found in intermediate (1–15 °C), humid and windy conditions. Ammonia concentrations generally decreased with increasing wind speed and were very variable at wind speeds < 3 m s⁻¹. Concentrations also decreased with increasing relative humidity, reflecting the partitioning of NH₃ toward the liquid phase at large (> 90%) relative humidities, while evaporation from aerosols seemed more likely at lower (40–90%) relative humidities. Seasonal variations in meteorological patterns resulted in marked seasonal variations in concentrations, with the largest mean-values observed during the warmer and drier summer months, and the smallest values measured in humid and windy, autumn and winter conditions. Measurements indicated a short atmospheric residence time for NH₃, of the order of 1–2 hours. The atmospheric residence time for dry deposition of gaseous NH₃ was estimated from these data and ranges from 2 to 20 hours depending on atmospheric and surface conditions, with a mean value of 3.5 hours for the 13 months of monitoring, which is equivalent to a mean transport distance of 50 km.

KEYWORDS: Ammonia Atmospheric chemistry Boundary layer Deposition Dispersion Surface emissions

1. INTRODUCTION

Interest in atmospheric ammonia (NH₃) has grown rapidly during the last decade as a result of its importance in atmospheric chemistry and the consequences of its deposition onto terrestrial and aquatic ecosystems. As the major base present in the atmosphere, it has the ability to neutralize acidic species such as H₂SO₄, HNO₃ and HCl, which result in the presence of ammonium (NH₄⁺) in aerosols, cloud droplets and precipitation. Because NH₄⁺ particles are largely present in the submicron size range, they experience much smaller dry deposition velocities than the reactive precursor gases and thus travel longer distances before dry or wet deposition (Fowler et al. 1991), and NH₃ influences the fraction of gaseous species entering long-range transport via gas-to-particle conversion. Ammonia has also been shown to play an important role in regulating SO₂ uptake and oxidation in clouds through the control of cloud water pH (Behra et al. 1989; Benner et al. 1992).

The deposition of NH₃ onto nutrient-poor, terrestrial and aquatic ecosystems, contributes significantly to nitrogen eutrophication† with the wet and dry deposition of NH₄⁺ ions and oxidized nitrogen collectively referred to as NOₓ (NO₂, HNO₃, NO₃⁻, HNO₂, PAN) (Grennfelt and Thörnlöf 1992). Nitrogen saturation of ecosystems may occur where the availability of inorganic N is in excess of total combined plant and microbial nutritional demand (Aber et al. 1989). Over moorland, the consequences of excess N availability

* Corresponding author: Institute of Terrestrial Ecology, Bush Estate, Penicuik, Midlothian EH26 0QB, UK.
† The enrichment of water with plant nutrients, which enter the water by leaching from the land drained by the water body. It can be accelerated by the leaching of agricultural fertilizers and the discharge of effluents containing nitrogen and phosphorus.
include the die-back of (e.g.) bryophytes and lichens as nitrophilous plants compete more successfully than these genera. Vegetation changes reported in the Netherlands include *Erica tetralix/Calluna vulgaris* dominated heathland to *Molinia caerulea/Festuca ovina* dominated grassland and have been attributed to increased N deposition (Heil and Dieumont 1983; Van Breemen and Van Dijk 1988; Bobbink *et al.* 1992). Direct effects of large atmospheric NH$_3$ concentrations on vegetation in the vicinity of intensively managed livestock units have also been reported, leading to the estimation of ‘critical levels’ for adverse effects (Van der Eerden *et al.* 1994), with a necessary distinction between ‘acute’ exposure to very high concentrations over short periods (hours) and ‘chronic’ exposure to lower concentrations over longer timescales (days to months).

In addition to these effects, microbial nitrification of NH$_4^+$ in soil produces acidity via an oxidation reaction (NH$_4^+$ + 2O$_2$ → 2H$^+$ + NO$_3^-$ + H$_2$O). Thus NH$_3$ produces one H$^+$ per molecule deposited and may also contribute to soil and groundwater acidification (Van Breemen *et al.* 1983, 1987; Skoffington and Wilson 1988; Van Breemen and Van Dijk 1988). Acidification in turn modifies the delicate ionic balance of nutrient-poor ecosystems, enhancing cation leaching (NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Al$^{3+}$) associated with high NO$_3^-$ concentrations in the soil solution, and altering cationic ratios (NH$_4^+/K^+$, NH$_4^+/Mg^{2+}$, Al$^{3+}$/Ca$^{2+}$). Such altered ratios may affect root uptake of plant nutrients (K$^+$ and Mg$^{2+}$) and may ultimately affect plant health (Nihlgård 1985; De Vries and Kros 1991; Bobbink *et al.* 1992; Fennema 1992). The eutrophication and acidification threats posed by excess nitrogen (and sulphur) deposition onto sensitive ecosystems led to the development of the ‘critical load’ concept (Nilsson and Grenefelt 1988; Grenefelt and Thörnelöf 1992; Hornung *et al.* 1995). Critical loads have since then provided the basis for abatement strategies for acidifying emissions in Europe.

Despite the importance of atmospheric NH$_3$ concentrations in determining the risk and extent of critical level/load exceedance, there has been little NH$_3$ concentration monitoring because of the difficulty associated with the continuous measurement of ambient concentrations, especially at background (< 0.5 µg m$^{-3}$) levels. The recent development of new measuring techniques (Wyer *et al.* 1993) has not only allowed dramatic improvements in detection limits for NH$_3$ concentrations, down to 0.02 µg m$^{-3}$, but also encouraged continuous monitoring. The new instruments provide ambient concentrations in the range 0.02 to 100 µg m$^{-3}$ for periods up to one week without the operator’s intervention (Erisman and Wyers 1993; Erisman *et al.* 1996; Burkhartd *et al.* 1998).

In this paper, long term (13 months) continuous measurements of ambient NH$_3$ concentrations at a rural site in southern Scotland are reported. Statistical properties of NH$_3$ concentrations and their variability are provided. Variations in NH$_3$ concentrations with wind direction are analysed to quantify the contribution of local and background sources of NH$_3$. The seasonal variability in concentrations is examined to quantify the influence of key meteorological variables such as wind speed, air temperature, relative humidity and surface wetness. An important focus of this paper is the residence time of NH$_3$ in the atmosphere; it is deduced from the monitoring data. However, this work forms part of a more intensive study of atmospheric NH$_3$ in which surface–atmosphere fluxes were continuously monitored at the same site and during the same period. These flux measurements are reported in an associated paper (Flechard and Fowler 1998).

2. **Materials and methods**

   (a) **Site description**

The NH$_3$ concentration measurements reported in this study were obtained at a moorland site, Auchencorth Moss, from February 1995 through to February 1996. The monitor-
Figure 1. (a) Location of the flux monitoring site, Auchencorth Moss, southern Scotland; (b) frequency distribution of wind direction at Auchencorth Moss; (c) wind sector analysis of median ammonia concentration (µg m⁻³) at 3.37 m from February 1995 to February 1996. Key for (a): 1, Edinburgh; 2, Penicuik; 3, Pentland Hills; 4, monitoring site and instrumentation; 5, mixed farm; 6, Auchencorth Moss (blanket bog); 7, poultry farm; 8, 9, 10, 11, other mixed farms within a radius of 3 km of the monitoring site.

ing site is an extensive (> 1000 ha) area of ombrotrophic* (rain-fed) mire at an elevation of about 270 m a.m.s.l., approximately 18 km south-west of Edinburgh, southern Scotland (55°47′30″N, 3°14′20″W; National Grid reference NT221562) (Fig. 1). This site is located in an area of fairly low agricultural activity, with six farms within a radius of 3 km and none of them situated in the prevailing SW wind sector (Fig. 1). The largest agricultural point source among these six farms is an intensive poultry farm 2.7 km south of the site.

The site consists of semi-natural, unfertilized peatland vegetation and is grazed by sheep all year round with a fairly low stock density (< 1 sheep ha⁻¹). The peat layer is on average 60 cm deep. The ground is permanently damp to waterlogged in all seasons except summer, but very few pools of free water are present as a consequence of partial drainage undertaken about forty years ago. The vegetation is made up of a succession of hummocks and hollows (vertical range about 50 cm) that can be divided into sub-zones (for details see Lindsay (1995)). The low ridge and hollows (the lowest 30 cm) are the wetter parts and possess an almost continuous mixed carpet of Sphagnum species that are adapted to waterlogged and acidic conditions. Within this carpet, other bryophyte† species such as Polytrichum commune Hedw., and also a large community of sedges e.g. Carex nigra and C. ovalis, and monocotyledons such as Eriophorum angustifolium are present. The hummocks (the top 20 cm) are naturally drier, often Polytrichum-formed

† Mosses and liverworts.
TABLE 1. **VERTICAL DISTRIBUTION OF THE DOMINANT PLANT SPECIES AT AUCHENCORTH MOSS**

<table>
<thead>
<tr>
<th>Hummocks¹</th>
<th>Dominant vascular plants</th>
<th>Dominant bryophytes</th>
<th>Also present</th>
</tr>
</thead>
</table>
| Deschampsia flexuosa  
Molinia caerulea  
Eriophorum vaginatum  
Eriophorum angustifolium  
Festuca ovina  
Festuca rubra  
Agrostis stolonifera  
Anthoxanthum odoratum  
Nardus stricta | Polytrichum commune  
Polytrichum formosum  
Brachygoecium spp.  
Sphagnum tenellum | Vaccinium myrtillus  
Erica tetralix  
Potentilla erecta | |

| High ridge¹ | Deschampsia flexuosa  
Molinia caerulea  
Eriophorum vaginatum  
Festuca ovina | Polytrichum commune  
Sphagnum papillosum  
Brachygoecium spp. | Vaccinium myrtillus  
Erica tetralix  
Potentilla erecta  
Galium oratum | |

| Low ridge¹ and hollows | Eriophorum angustifolium  
Eriophorum vaginatum  
Festuca ovina  
Festuca rubra  
Trichophorum cespitosum | Sphagnum compactum  
Sphagnum papillosum  
Sphagnum cuspidatum  
Polytrichum commune  
Polytrichum urnigerum  
Rhytidophalus squarrosus  
Aulacomnium Palustre  
Brachygoecium spp. | Carex ovalis  
Carex nigra  
Scirpus cespitosus  
Juncus effusus  
Juncus squarrosus  
Calluna vulgaris  
Erica tetralix | |

¹The terminology hummocks/ridges/hollows is adapted from Lindsay (1995).

mound-like tussocks about 10–30 cm above the bog-moss carpet; they contain a lower density of *Sphagnum* species and more vascular plants than the hollows. Hummock tops and the high ridge are dominated by *Deschampsia flexuosa*, *Molinia caerulea*, *Eriophorum vaginatum*, *Eriophorum angustifolium* and *Festuca ovina*. Ericaceous dwarf-shrubs such as *Erica tetralix*, *Calluna vulgaris* and *Vaccinium myrtillus* are scarce and patchy in their occurrence at this site (Table 1).

The single-sided leaf area index (LAI) was difficult to measure because of the large structural diversity of the canopy and the very fine leaves of numerous plant species; estimates of about 4–6 m² m⁻² and 2–3 m² m⁻² were obtained for summer and winter respectively from collection of areas of foliage representative of this site. The site was generally greener and drier in summer than in winter but the exceptionally dry conditions of the 1995 summer led to early senescence of the annual species in August. However, the mildness and abundant rainfall of September and October revived a number of bryophytes and grasses before the winter.

(b) Ammonia concentration and micrometeorological measurements

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) (Fig. 2) with a detection limit of 0.02 μg m⁻³. Air was sampled at the three heights at 271 min⁻¹ through the wet denuders which consist of two concentric glass tubes about 40 cm long and 50 mm in diameter. Continuous rotation of each denuder around its axis ensured a thin, continuous coating of the tube walls with a slightly acidic solution (NaHSO₄, 3.6 mM) which was continuously pumped into and out of the denuder by two peristaltic pumps in counter flow with the air sample. Ammonia was captured as NH₄⁺ by the acidic film by molecular diffusion through the laminar air flow between
the two tubes. Subsequent mixing of the stripping solution with a sodium hydroxyde solution allowed \( \text{NH}_3 \) to diffuse selectively through a hydrophobic PTFE membrane into a flow of de-ionized water, the \( \text{NH}_4^+ \) concentration of which was determined continuously by conductivity of the water. The system was calibrated against aqueous \( \text{NH}_4^+ \) standard solutions. A common detector was used to measure solution \( \text{NH}_4^+ \) concentrations and to deduce air concentrations of \( \text{NH}_3 \) for the three heights (Wyers et al. 1993). Ammonia concentrations were measured at every height with a time resolution of two minutes in a 6-minute cycle, and then averaged over 30-minute intervals.

Vertical gradients of \( \text{NH}_3 \) concentrations were therefore continuously measured, and these data, together with wind speed, friction velocity and turbulence measurements pro-
vided by a Solent Research ultrasonic anemometer (Gill Instruments Ltd, Lymington, Hampshire, UK), were also used to calculate NH$_3$ fluxes by a combination of flux-gradient and eddy-covariance methods. These measurements of the surface–atmosphere exchange of NH$_3$ are beyond the scope of this paper and are reported elsewhere (Flechard and Fowler 1998). Additional measurements of temperature, rainfall and relative humidity (RH) were made using a Bowen-ratio system (Campbell Scientific, Loughborough, UK), which also provided measurements of global and net radiation, sensible- and latent-heat fluxes, and soil-heat fluxes.

3. Results

(a) Statistics of NH$_3$ concentrations

Ammonia concentrations were measured for about 71% of the time (i.e. 13 471 half-hourly concentrations) from February 1995 to February 1996 (Table 2). Statistics of measured NH$_3$ concentrations are presented here for the lowest sampling height of the monitoring tower (0.43 m above the ground) which provided the largest concentration-data coverage. It is especially relevant to provide statistics for NH$_3$ concentration at the canopy level when the effects of NH$_3$ on vegetation (critical levels) are considered. Large vertical gradients in NH$_3$ concentrations were observed; concentrations at the top of the tower (3.37 m) were on average 23% larger than those at 0.43 m (Table 2), providing evidence of NH$_3$ dry deposition to the surface (Flechard and Fowler 1998). Statistical patterns for the upper two sampling heights of the monitoring tower (1.38 and 3.37 m) were, however, found to be very similar to those for the lowest sampling height (0.43 m) which are presented hereafter.

Recorded individual six-minute concentration measurements of 0.43 m ranged from 0.00 to 76.7 µg m$^{-3}$; average half-hourly concentrations ranged from 0.00 to 26.7 µg m$^{-3}$ with a geometric mean of 0.43 µg m$^{-3}$ and a geometric standard deviation of 3.35 µg m$^{-3}$ (Table 2; Table 3). Statistics for daily and monthly, average and median NH$_3$ concentrations are also provided in Table 3, and show the importance of the averaging time interval (6 minutes, 30 minutes, day, month) and also the averaging procedure (arithmetic mean, geometric mean, median) in describing the population of NH$_3$ concentrations. This is due to the large spatial and temporal variability of NH$_3$ levels in rural areas where sources and sinks are not uniformly distributed and background levels are small relative to those in emission plumes.

Sources of tropospheric NH$_3$ have been shown to be mainly agricultural (Buijsman et al. 1987; Asman 1992) (agriculture is the source of about 90% of UK emissions (Sutton et al. 1995a)). Large point-sources, such as intensively managed livestock or poultry units, highly increase the variability of NH$_3$ concentrations within a radius of up to a few kilometres as concentrations near a point source are very sensitive to wind direction (Bencala and Seinfeld 1976). By contrast, concentrations near the centre of a uniform source area would be much less sensitive to changes in wind direction and thus less variable. The temporal variability of NH$_3$ concentrations is described by the geometric standard deviation ($\sigma_G$) (Table 3) which is used here in preference to the arithmetic standard deviation, since the two-parameter log–normal distribution proved a reasonable fit for the measured frequency distribution (Fig. 3), irrespective of the averaging time interval (Fig. 4) (Bencala and Seinfeld 1976). Averaging times of minutes up to one hour retain the plume nature and variability of NH$_3$ concentrations, whereas daily or monthly means fail to capture this variability. This is demonstrated in Table 3 where there are no significant differences in median, arithmetic mean, geometric mean, geometric standard deviation, 90 percentile and 99 percentile between the 6-minute and 30-minute average concentrations, while for
<table>
<thead>
<tr>
<th>$x_{NH_3}$ (0.43 m)</th>
<th>N</th>
<th>Data coverage</th>
<th>Median $\mu g$ m$^{-3}$</th>
<th>$\mu_A$ 1 $\mu g$ m$^{-3}$</th>
<th>$\mu_G$ 1 $\mu g$ m$^{-3}$</th>
<th>$\sigma_G$ 1 $\mu g$ m$^{-3}$</th>
<th>Min $\mu g$ m$^{-3}$</th>
<th>90%ile 2 $\mu g$ m$^{-3}$</th>
<th>99%ile 2 $\mu g$ m$^{-3}$</th>
<th>Max $\mu g$ m$^{-3}$</th>
<th>$\chi_{3.37} - \chi_{0.43}$</th>
<th>$\chi_{1.38} - \chi_{0.42}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feb 95</td>
<td>1149</td>
<td>87</td>
<td>0.25</td>
<td>0.53</td>
<td>0.25</td>
<td>3.20</td>
<td>0.00</td>
<td>0.94</td>
<td>5.53</td>
<td>18.49</td>
<td>28.9</td>
<td>13.7</td>
</tr>
<tr>
<td>Mar 95</td>
<td>938</td>
<td>63</td>
<td>0.43</td>
<td>0.66</td>
<td>0.41</td>
<td>2.63</td>
<td>0.01</td>
<td>1.43</td>
<td>4.27</td>
<td>9.94</td>
<td>16.1</td>
<td>4.3</td>
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<tr>
<td>Apr 95</td>
<td>1059</td>
<td>74</td>
<td>0.44</td>
<td>1.16</td>
<td>0.49</td>
<td>3.65</td>
<td>0.01</td>
<td>3.14</td>
<td>12.47</td>
<td>23.78</td>
<td>25.8</td>
<td>11.1</td>
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<tr>
<td>May 95</td>
<td>1375</td>
<td>92</td>
<td>0.57</td>
<td>0.94</td>
<td>0.55</td>
<td>2.95</td>
<td>0.00</td>
<td>2.03</td>
<td>5.37</td>
<td>23.43</td>
<td>25.4</td>
<td>11.4</td>
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<tr>
<td>Jun 95</td>
<td>1246</td>
<td>87</td>
<td>0.49</td>
<td>0.65</td>
<td>0.43</td>
<td>2.66</td>
<td>0.01</td>
<td>1.28</td>
<td>2.76</td>
<td>12.70</td>
<td>14.8</td>
<td>10.8</td>
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<tr>
<td>Jul 95</td>
<td>1217</td>
<td>82</td>
<td>0.78</td>
<td>1.20</td>
<td>0.72</td>
<td>2.85</td>
<td>0.02</td>
<td>2.53</td>
<td>7.59</td>
<td>18.45</td>
<td>15.1</td>
<td>10.3</td>
</tr>
<tr>
<td>Aug 95</td>
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<td>82</td>
<td>0.88</td>
<td>1.39</td>
<td>0.85</td>
<td>2.73</td>
<td>0.06</td>
<td>3.03</td>
<td>8.01</td>
<td>22.45</td>
<td>18.5</td>
<td>11.2</td>
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<tr>
<td>Sep 95</td>
<td>1166</td>
<td>81</td>
<td>0.23</td>
<td>0.43</td>
<td>0.26</td>
<td>2.33</td>
<td>0.05</td>
<td>0.71</td>
<td>3.59</td>
<td>20.54</td>
<td>25.0</td>
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<td>Oct 95</td>
<td>804</td>
<td>54</td>
<td>0.27</td>
<td>0.45</td>
<td>0.26</td>
<td>2.76</td>
<td>0.00</td>
<td>1.05</td>
<td>2.92</td>
<td>16.80</td>
<td>22.1</td>
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<td>Nov 95</td>
<td>1024</td>
<td>72</td>
<td>0.55</td>
<td>1.00</td>
<td>0.45</td>
<td>3.84</td>
<td>0.00</td>
<td>2.08</td>
<td>10.31</td>
<td>16.59</td>
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<tr>
<td>Dec 95</td>
<td>748</td>
<td>50</td>
<td>0.32</td>
<td>0.50</td>
<td>0.29</td>
<td>2.79</td>
<td>0.01</td>
<td>0.88</td>
<td>3.07</td>
<td>20.96</td>
<td>22.9</td>
<td>15.8</td>
</tr>
<tr>
<td>Jan 96</td>
<td>572</td>
<td>38</td>
<td>0.28</td>
<td>0.97</td>
<td>0.34</td>
<td>4.63</td>
<td>0.01</td>
<td>2.79</td>
<td>6.39</td>
<td>12.84</td>
<td>22.2</td>
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<tr>
<td>Feb 96</td>
<td>946</td>
<td>68</td>
<td>0.60</td>
<td>1.58</td>
<td>0.54</td>
<td>5.06</td>
<td>0.00</td>
<td>4.07</td>
<td>11.22</td>
<td>26.68</td>
<td>25.7</td>
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<tr>
<td>Total</td>
<td>13471</td>
<td>71</td>
<td>0.42</td>
<td>0.89</td>
<td>0.43</td>
<td>3.35</td>
<td>0.00</td>
<td>2.06</td>
<td>7.16</td>
<td>26.68</td>
<td>22.8</td>
<td>12.7</td>
</tr>
</tbody>
</table>

1 $\mu_A$, arithmetic mean; $\mu_G$, geometric mean; $\sigma_G$, geometric standard deviation.
2 90%ile and 99%ile denote the ninetieth and ninety-ninth percentiles.
3 Monthly-mean vertical gradients in NH$_3$ concentration are expressed as a percentage difference between concentrations at the lowest (0.43 m) and the highest (3.37 m) or middle (1.38 m) measurement heights on the tower, e.g. $\chi (0.43$ m) was on average 25.4% smaller than $\chi (3.37$ m) in May 1995.
Figure 3. Frequency distribution of half-hourly ammonia concentrations at 0.43 m above ground level (Auchen- corth Moss, from February 1995 to February 1996). The probability density function of the two-parameter log-normal distribution \( P(\mu_0, \sigma_0) \) is given by \( f(x) = \frac{1}{\sqrt{2\pi x} \sigma_0} \exp\left(-\frac{(\ln x - \ln(\mu_0))^2}{2\ln(\mu_0)^2}\right) \) (Seinfeld 1986) with \( \mu_0 = 0.43 \mu g \text{ m}^{-3} \), the geometric mean ammonia concentration, and \( \sigma_0 = 3.35 \), the geometric standard deviation \( (N = 13471) \).

Figure 4. Log-probability plot of ammonia concentrations at 0.43 m for various averaging times and methods. Note the nonlinearity of the plot at low ammonia concentrations \((< 0.01 \mu g \text{ m}^{-3})\) reflecting the uncertainty in measurements below the detection limit \(< 0.02 \mu g \text{ m}^{-3}\) of the instrumentation.
TABLE 3. \textit{Statistical properties of measured NH\textsubscript{3} concentrations in relation to the averaging mode used.}

| \(\chi_{\text{NH}_3} (0.43 \text{ m})\) | N \(\mu g \text{ m}^{-3}\) & Median \(\mu g \text{ m}^{-3}\) & \(\mu A \) & \(\mu G \) & \(\sigma G \) & Min \(\mu g \text{ m}^{-3}\) & 90\%ile\textsuperscript{2} & 99\%ile\textsuperscript{2} & Max \(\mu g \text{ m}^{-3}\) |
|--------------------------------------|-----------------|-----------------|----------|--------|--------|-----------------|-----------------|-----------------|-----------------|
| 6-min average                        | 72976 \(0.42\)  | 0.88 \(0.43\)   | 3.38 \(0.00\) | 1.97 \(7.22\) | 76.69 |
| 30-min average                       | 13471 \(0.42\)  | 0.89 \(0.43\)   | 3.35 \(0.00\) | 2.06 \(7.16\) | 26.68 |
| Daily median                         | 327 \(0.42\)    | 0.70 \(0.43\)   | 2.68 \(0.03\) | 1.60 \(4.03\) | 5.67 |
| Daily average                        | 327 \(0.59\)    | 0.90 \(0.56\)   | 2.75 \(0.03\) | 2.10 \(4.13\) | 6.02 |
| Monthly median                       | 13 \(0.44\)     | 0.47 \(0.43\)   | 1.55 \(0.23\) | 0.75 \(0.87\) | 0.88 |
| Monthly average                      | 13 \(0.94\)     | 0.88 \(0.81\)   | 1.56 \(0.43\) | 1.35 \(1.56\) | 1.58 |

\textsuperscript{1} \(\mu A\), arithmetic mean; \(\mu G\), geometric mean; \(\sigma G\), geometric standard deviation.

\textsuperscript{2}90\%ile and 99\%ile denote the ninetieth and ninety-ninth percentiles.

daily and monthly means, substantially smaller geometric standard deviations and narrower concentration ranges were found, as well as departures from annual mean values, compared with the distribution of 6-minute average concentrations.

Log-probability plots of NH\textsubscript{3} concentrations are presented in Fig. 4 for averaging intervals ranging from six minutes (individual measurements) to one month, also showing the differences between average (arithmetic mean) and median, daily and monthly values. The geometric standard deviations for the six cumulative frequency distributions shown in Fig. 4 can be graphically provided by the slopes of individual regression lines of the six plots (Seinfeld 1986), the slopes clearly decreasing as averaging time increases from six minutes to one month.

The geometric standard deviation of NH\textsubscript{3} concentration was also found to vary with time of year (Table 2), with the largest monthly values in winter, up to 5 \(\mu g \text{ m}^{-3}\) in February 1996, and the lowest values in summer, typically 2.5 to 3 \(\mu g \text{ m}^{-3}\). Micrometeorological measurements of the surface–atmosphere exchange of NH\textsubscript{3} were made at this site from February 1995 to February 1996 (Flechard and Fowler 1998) and showed large seasonal variations in the NH\textsubscript{3} deposition velocity \(V_d\) (1 m). Although these measurements are beyond the scope of this paper, they show that monthly geometric standard deviations of NH\textsubscript{3} concentration increase exponentially with monthly-median deposition velocity (Fig. 5). As the removal of atmospheric NH\textsubscript{3} by dry deposition increases linearly with \(V_d\), the tropospheric residence time \(\tau\) of NH\textsubscript{3} is expected to decrease with increasing \(V_d\) and therefore to decrease with the geometric standard deviation of NH\textsubscript{3} concentration. These findings are in accordance with previous theoretical considerations by Junge (1974) who demonstrated that temporal and spatial variability of tropospheric trace constituents, and thus the geometric standard deviation of their tropospheric concentration, should be approximately inversely proportional to their tropospheric residence time, provided that the source and sink distributions are similar. Though the assumption of uniform distribution of sources and sinks is not entirely valid for NH\textsubscript{3} in rural areas, the data are consistent with the arguments of Junge (1974).

The geometric standard deviation of NH\textsubscript{3} of 3.35 \(\mu g \text{ m}^{-3}\) was similar to that of other pollutants measured at this site with a short atmospheric residence time, e.g. NO \(\sigma G = 3.97 \mu g \text{ m}^{-3}\) or SO\textsubscript{2} \(\sigma G = 3.4 \mu g \text{ m}^{-3}\), and is considerably larger than that for NO\textsubscript{2} (2.73 \(\mu g \text{ m}^{-3}\)) which has a much longer atmospheric residence time.

Critical levels for effects of NH\textsubscript{3} on vegetation at this site were never found to exceed values suggested by Van der Eerden \textit{et al.} (1994) for semi-natural vegetation; they found that 95\% of heathland species including bryophytes were protected from adverse effects.
at P > 0.95 for hourly and yearly average concentrations of 3300 μg m⁻³ and 8 μg m⁻³, respectively.

(b) Vertical gradients

Ammonia concentrations were generally found to increase with height, denoting dry deposition to the surface. Yearly-mean gradients showed a 23% difference in concentration between the lowest and the highest measurement heights of the tower (0.43 m and 3.37 m respectively) with monthly-mean differences varying between 15% and 30% (Table 2). The mean difference in concentration between the lowest and the middle sampling heights (0.43 m and 1.38 m) was about 13% (Table 2). The influence of sheep emissions on vertical gradients and concentrations of NH₃ was assumed to be negligible given the very low animal density (< 1 sheep ha⁻¹) and the extensive nature of the moorland site (> 1000 ha).

Vertical gradients were larger at night-time and in cold winter conditions, and more generally in stable atmospheres when a temperature inversion in the surface boundary-layer reduced or suppressed turbulent mixing. This, coupled with depletion of NH₃ at the surface, resulted in a rapid increase in concentration with height above the vegetation. By contrast, high wind-speeds and warm, unstable, summer conditions resulted in small vertical gradients in concentration by enhancing turbulent mixing through surface friction and free convection (buoyancy) respectively. The turbulent fluxes resulting from (or pro-
duc ing) the vertical NH₃ gradients and measured at this site using flux-gradient techniques are reported elsewhere (Flechard and Fowler 1998).

(c) Wind-direction dependence of NH₃ concentration at Auchencorth Moss

The importance of agricultural emissions to regional atmospheric NH₃ budgets has been widely recognized (Buijsman et al. 1987; Asman 1992; Sutton et al. 1995a). However, the spatial distribution of farms in the countryside is also important in dictating the areas which are likely to be affected by high NH₃ concentrations and deposition, depending on the prevailing wind direction. This is particularly important with respect to critical levels for direct effects of NH₃ on vegetation (Van der Eerden et al. 1994). In Great Britain, the mean distance between farms is smaller than 1 km, so that most rural sites are likely to be within 1 km of a significant NH₃ source except in purely arable or remote moorland areas.

Ammonia concentrations at Auchencorth Moss were found to vary strongly with wind direction as a consequence of the presence of a number of local agricultural sources on different bearings relative to the site, there being one poultry farm and five mixed farms within a radius of 3 km of the site. Even though Auchencorth Moss is situated in an area of low agricultural activity, local agricultural emissions dominated NH₃ concentrations and their variations at this site. The poultry farm on the bearing of 190° is an intensive unit but the mixed farms to the east and north-east of the site are much smaller sources of NH₃ (Fig. 1(a)).

The wind-sector dependence of NH₃ concentration can readily be seen on Fig. 1(c) where median concentrations at the top of the tower (3.37 m above ground level) are plotted for each 10° wind sector; no agricultural point-source is present within 3 to 5 km of open moorland to the west and west-south-west of the monitoring site (220°–360°), and this sector provides the lowest mean concentrations, generally below 0.3 µg m⁻³. The influence of the poultry farm on NH₃ concentrations was indicated by the presence of a large plume centred on the bearing of 180°, extending from 150° to 210°, where mean concentrations for 10° wind sectors reached 2.5 µg m⁻³ (Fig. 1(c)). The small mixed farm on the bearing of 160° is not believed to have made any significant contribution to this large plume. Two other wind-sectors were found to have significantly larger mean concentrations than the background level seen to the north-west: one 60°-wide plume to the north-east, centred on the bearing of 30° and reaching mean concentrations of 0.65 µg m⁻³; a smaller plume on the bearing of 100°. The north-easterly plume is influenced by three small mixed farms, primarily the farm labelled ‘5’ on Fig. 1(a), about 500 m from the site, and two other farms labelled ‘10’ and ‘11’ about 3 km away; the easterly plume was produced by the farm labelled ‘8’ on Fig. 1(a). There was no evidence that the small town of Penicuik (pop. 17 000), 4 km to the north-east of the site, contributed significantly to the NH₃ at Auchencorth Moss.

(d) Quantifying the contribution of local agricultural sources to NH₃ concentrations

The relative contribution of local agricultural sources—in relation to background—to NH₃ concentrations monitored at this site depended on a number of factors including: seasonal variations in the source strengths of the different farms; seasonal variations in wind direction and its frequency distribution; other meteorological factors affecting the local and long-range transport of NH₃ and processes of NH₃ emission and removal (e.g. wind speed, stability, temperature, gas-to-particle conversion, precipitation, surface wetness and physiological status of the vegetation). For a given ‘point’ source such as the poultry farm, the contribution to NH₃ concentration at Auchencorth Moss 2.7 km downwind from the farm over a monthly period was determined by its monthly emission, the percentage of
the time the wind direction was southerly, the rates of advection and turbulent diffusion, and the fraction of the emitted NH$_3$ that was deposited between the poultry farm and the monitoring site.

To estimate the relative contributions of background and local agricultural sources to the NH$_3$ concentrations at Auchencorth Moss, advection fluxes of NH$_3$ at 3.5 m above ground were calculated for the whole monitoring period. The products of NH$_3$ concentrations (µg NH$_3$ m$^{-3}$) and horizontal wind-speeds (m s$^{-1}$) were integrated to provide long-term (13-month) horizontal fluxes of NH$_3$ over the monitoring site, expressed as the mass flux of NH$_3$ per vertical square metre centred on the measuring height (3.5 m).

For each 10° sector of the wind rose, the total integrated advection flux $F_{\text{adv, total}}^{(i)}(z)$ was calculated by integrating all products (wind speed times concentration) over the whole monitoring period (February 1995 to February 1996) (Eq. (1)). The advection flux attributed to background sources $F_{\text{adv, background}}^{(i)}(z)$ was calculated (Eq. (2)) using a constant ‘background’ concentration $\chi_{\text{background}}$ arbitrarily chosen as the mean NH$_3$ concentration measured for wind directions between 270° and 310° where no agricultural sources were present in the nearest 3 km from the site. The contribution of local agricultural sources $F_{\text{adv, local}}^{(i)}(z)$ was given as the difference between the total measured advection flux and the background advection flux (Eq. (3)) for each of the 36 (10°) wind-direction sectors.

$$F_{\text{adv, total}}^{(i)}(z) = \int \{ \chi_{\text{NH}_3}(z, t).u(z, t) \} \, dt \quad i = 1, \ldots, 36 \quad (1)$$

$$F_{\text{adv, background}}^{(i)}(z) = \int \{ \chi_{\text{background}}(z).u(z, t) \} \, dt \quad i = 1, \ldots, 36 \quad (2)$$

$$F_{\text{adv, local}}^{(i)}(z) = F_{\text{adv, total}}^{(i)}(z) - F_{\text{adv, background}}^{(i)}(z) \quad i = 1, \ldots, 36. \quad (3)$$

Results are shown in Fig. 6 for a background concentration of 0.36 µg m$^{-3}$ at 3.5 m above ground. Local sources (within 3 km of the site) contributed about 60% of the NH$_3$ advection flux over the site for the 13-month monitoring period, and background sources
the remaining 40%. The poultry farm 2.7 km to the south may have contributed as much as 50% to the total even though the prevailing wind direction was not southerly but south-westerly (Fig. 1(b)). The three mixed farms north-east of the site had a small influence on \( \text{NH}_3 \) (10% of the advection flux) at Auchencorth Moss even though one of these farms was within 500 m of the site.

The contributions of local agricultural sources to \( \text{NH}_3 \) at this site were not constant with time as the frequency distribution of wind direction varied throughout the monitoring period, with, for example, a larger frequency of easterlies from December 1995 to February 1996, and also because agricultural emissions of \( \text{NH}_3 \) are not constant with time. This accounts for some of the variability observed in monthly-mean concentrations (Table 2).

(e) Seasonal variations; influence of wind speed, air temperature and humidity

Ammonia concentrations were generally larger in summer than in winter, with monthly-mean concentrations at 0.43 m above ground in the range 0.25–0.88 \( \mu \text{g m}^{-3} \) (Table 2; Fig. 7), but there was a close coupling between daily weather and \( \text{NH}_3 \) concentration. Windy, rainy conditions favoured low concentrations; warm and dry, or cold and calm conditions were generally characterized by larger concentrations. The steady increase in median \( \text{NH}_3 \) air concentration observed between February 1995 (0.25 \( \mu \text{g m}^{-3} \)) and August 1995 (0.88 \( \mu \text{g m}^{-3} \)) (Fig. 7) was consistent with the increase in mean temperature from 2.5 °C to 14.5 °C. The sudden decline in \( \text{NH}_3 \) concentration from August to September and October 1995 was coupled with a large increase in rainfall (from 37 mm in August to 164 mm in September). From October 1995 to February 1996, however, the patterns of monthly-concentration changes in relation to air temperature and precipitation were less straightforward.

Quantifying the influence of weather variables on ambient \( \text{NH}_3 \) concentrations was difficult, as many of these variables are intercorrelated. For example, high wind-speeds were often associated with intermediate temperatures in the range 2–10 °C and rain and wet surfaces in autumn and winter, the combination of these factors generally producing low \( \text{NH}_3 \) concentrations. On the other hand, low wind-speeds were more frequently observed in summer, warm weather (> 20 °C), and also during cold (–10 °C–0 °C), calm spells of winter weather, and this often coincided with low precipitation and dry or frozen surfaces.
This analysis was further complicated by the presence of significant agricultural NH$_3$ sources within a radius of 3 km of the monitoring site, a large poultry-farm and 5 mixed farms whose influence was wind direction dependent (Fig. 1; see also subsections 3(c) and 3(d)).

To study the effects of air temperature, wind speed and RH on NH$_3$ concentration, the data were first divided arbitrarily into three subsets corresponding to three main sectors of wind direction, namely north-east (010°–130°; N = 3351 half-hourly measurements), south (130°–230°; N = 5809) and north-west (230°–000–010°; N = 3486), thereby isolating the weather-induced variability from the wind-direction-induced variability associated with local sources. The NW sector may then be considered as the ‘background’ uninfluenced by local agricultural sources, whereas the NE and S sectors are influenced by local sources with the largest influence found in the S sector owing to the poultry farm’s emissions (Fig. 1). The variations of NH$_3$ concentration with air temperature, wind speed and atmospheric RH are presented in Fig. 8 for the three sectors of the wind rose.

Ammonia concentrations generally increased exponentially from about 0.1–0.3 μg m$^{-3}$ to 2–5 μg m$^{-3}$ with air temperature from 0°C to 25°C, but concentrations were also found to increase up to 1–2 μg m$^{-3}$ with decreasing temperatures in freezing (≤ 0°C) conditions (Fig. 8(a)). The scatter in the relationship between air temperature and NH$_3$ concentration was considerably larger for the NE and S sectors where the influence of local sources was larger than for the NW sector. Ammonia concentrations decrease with wind speed (Fig. 8(b)); the relationship is almost linear for winds in the NW and NE sectors. In the S sector, however, NH$_3$ concentrations increased rapidly and linearly from 0.5 to 3 μg m$^{-3}$ with wind speed increasing from 0.5 m s$^{-1}$ to 2 m s$^{-1}$, and then decreased exponentially down to 0.1 μg m$^{-3}$ with wind speed increasing up to 14 m s$^{-1}$. The effect of RH on NH$_3$ is shown in Fig. 8(c), with a clear decrease in concentration with increasing RH from 30 to 100%. For the S sector, the form of the relationship between RH and NH$_3$ was not as straightforward as for the other two domains (exponential decay for the NW and linear decrease for the NE), showing larger scatter and also a very steep decrease in NH$_3$ concentration from about 1.5 μg m$^{-3}$ down to 0.2 μg m$^{-3}$ for RH increasing from 90% to 100%.

4. Discussion

Ammonia concentrations at Auchencorth Moss were strongly dependent on meteorological conditions and also extremely variable, reflecting the short residence time τ of NH$_3$ in the atmospheric boundary-layer. The residence time of NH$_3$ is determined by the efficiency of atmospheric removal processes, including wet and dry deposition, gas-to-particle conversion and incorporation into cloud droplets; yet, τ has not been determined precisely by any field measurements to date. A study by Möller and Schieferdecker (1985), however, suggested a short residence time for NH$_3$, of the order of 0.8 d (19 h) and Sutton (1990) estimated a mean characteristic time for NH$_3$ dry deposition τ$_d$ of 15 h, based on estimates of dry deposition velocities from Duyzer et al. (1987), and a mixing height of 1000 m, leading to an estimate for τ of 10 h. To provide a mechanistic understanding of the behaviour of NH$_3$ in the atmosphere and to assess the effects of NH$_3$ at local and regional scales, it is necessary to quantify the major removal processes by dry and wet deposition and the gas-to-particle conversion rates, and thus determine the residence time for NH$_3$ in the atmosphere.

The measurement difficulties for ambient NH$_3$ have, until recently, limited field concentration measurements to long-period averages, e.g. 1-week to 4-week averages. The high temporal resolution and low detection threshold of the concentration measurements
Figure 8. Ammonia concentrations (μg m⁻³) in relation to air temperature (°C), wind speed (m s⁻¹) and atmospheric relative humidity (%) for three wind direction sectors at Auchencorth Moss: (a) mean half-hourly ammonia concentrations versus mean air temperature at 3.4 m above ground; (b) mean half-hourly ammonia concentrations versus mean wind speed at 3.4 m above ground; (c) mean half-hourly ammonia concentrations versus mean relative humidity at 1 m above the displacement height d (data are medians of 50 half-hourly measurements sorted by ascending order of air temperature, wind speed and relative humidity).

reported in this paper have allowed the statistical properties of NH₃ and the influence of key meteorological variables on ambient NH₃ concentrations to be studied. Seasonal and meteorological effects on ammonia emissions, dispersion and removal rates are thereafter examined in order to identify major influences on ambient concentrations and on the residence time of NH₃ in the boundary layer.
Figure 9. Variations of interpolated half-hourly NH$_3$ concentrations (µg m$^{-3}$) at 3.4 m with air temperature (°C) and wind speed (m s$^{-1}$) for three sectors of the wind rose at Auchencorth Moss. Key: NE, 0°-130° (N = 3351); S, 130°-230° (N = 5809); NW, 230°-000°-010° (N = 3486).

(a) Seasonal effects

Seasonal changes in meteorology and, more specifically, the systematic variations with time of year of the key variables (air temperature, wind speed, rainfall and RH) led to seasonal changes in air concentrations of ammonia. Larger NH$_3$ concentrations occurred in both cold (< 0 °C) and stable winter conditions, and warm (> 15 °C), dry and unstable summer conditions, generally coupled with low (< 3 m s$^{-1}$) wind-speeds. In contrast, small concentrations were generally associated with higher wind-speeds (> 5 m s$^{-1}$) and intermediate (1-15 °C) temperatures (Figs. 8, 9). Such conditions frequently occur in winter, spring and autumn in the British Isles and often coincide with pronounced zonal weather with south-westerly airflows. Seasonal trends in NH$_3$ concentrations, however, were not as straightforward as might have been expected purely on the basis of the relationships shown in Fig. 8 between NH$_3$ and air temperature, wind speed and humidity. Local sources contributed about 60% of the NH$_3$ measured at Auchencorth Moss (Fig. 6) and there were marked changes in prevailing wind directions with time of year, with frequent periods of very cold and stable north-easterly weather between December 1995 and February 1996.
As a result, changes in monthly concentrations (Fig. 7) were not always entirely consistent with observed changes in the key meteorological variables mentioned above. It appeared from Fig. 8 and Fig. 9 that the scatter in the relationships between NH$_3$ concentration and air temperature, wind speed and RH was considerably smaller for the background sector (NW) than for the sectors with local sources (NE and S). This variability may well result from local agricultural point sources of NH$_3$ such as intensive livestock and poultry and cannot readily be predicted from standard meteorological measurements.

The NH$_3$ concentrations in air masses which have passed over extensive areas of uniform emission-density, such as fertilized cropland or unfertilized, semi-natural vegetation, are considerably less variable and more easily predicted from factors known to influence emission, such as temperature, RH and plant nitrogen status (Farquhar et al. 1980; Sutton et al. 1993b; Husted and Schjøerring 1996). The meteorological variables which influence ground-level NH$_3$ emissions also affect dispersion from sources and removal processes, both in the atmosphere and at terrestrial surfaces. For example, NH$_3$ emissions from vegetation are expected to increase exponentially with temperature (Husted and Schjøerring 1996), but the canopy resistance to NH$_3$ dry deposition onto plant communities has also been shown to increase with ambient air temperature (Duyzer 1994; Flechard and Fowler 1998), thereby increasing the mean characteristic time for dry deposition $\tau_d$ and the residence time $\tau$ of NH$_3$ in the boundary layer. Large values of wind speed were found to yield smaller ambient NH$_3$ concentrations (Figs. 8, 9) by increasing advection and diffusion away and upward from ground-level sources, while also providing larger friction velocities and therefore enhanced removal by dry deposition. In addition, these meteorological variables which influence emission and the residence time of NH$_3$ in the atmosphere are clearly interrelated; for example, low wind-speeds, small relative humidities and, by extension, dry surfaces often coincide with either very low (freezing) or high temperatures. Individual meteorological influences on NH$_3$ concentrations are thus difficult to separate quantitatively.

(b) Air temperature

Air temperature exerts a number of indirect controls over atmospheric concentrations of NH$_3$, being the driving force behind numerous physico-chemical, physiological and microbiological processes. Ammonia is a highly soluble gas in water, but its solubility depends strongly on temperature, this being clear in Henry’s Law (Dasgupta and Dong 1986). Air temperature is thus expected to drive the partitioning of NH$_3$ between the liquid phase and the gas phase, both on terrestrial and aquatic surfaces, and around liquid-phase NH$_4^+$ aerosols and cloud droplets in the atmosphere. Changes in air temperature with time, all things otherwise remaining equal, must imply transfer fluxes of NH$_3$ from one phase to the other in order to maintain phase equilibrium. This phenomenon is clearly important in regulating both emission and deposition fluxes at the earth’s surface. Ammonia emissions from plants have been shown to increase exponentially with temperature (Husted and Schjøerring 1996), which can be explained on the basis of the effects of the thermodynamic equilibrium between gas phase NH$_3$ and solution NH$_3$ and NH$_4^+$ within the plant’s apoplast*. This relationship is described in Eq. (4) and results 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)

$$p_{NH_3} = 10^{4.1218 - 4507.05/T} ([NH_4^+]/[H^+]).$$

(4)

* That part of the plant body which is external to the living parts of plant cells, such as the cell walls, the spaces between cells, and, in some contexts, the water-filled parts of these spaces.
where $T$ is absolute temperature (K), $p_{\text{NH}_3}$ the partial pressure of gaseous NH$_3$ (atm), and [NH$_3^+$] and [H$^+$] are the concentrations of ammonium and hydronium ions in solution (mol l$^{-1}$) respectively. For given apoplastic values of pH and NH$_3^+$, it can be shown that the partial pressure of NH$_3$ in equilibrium with the apoplastic solution increases exponentially with temperature, thus generating an exponential rise in the emission flux. In addition, air temperature drives the evaporation of layers of free water on terrestrial surfaces, such as dew or rain on plant cuticles, in a way which is similar to transpiration from plants through stomata. During the process of evaporation, concentrations of solutes progressively increase in the liquid film, but species like NH$_3$ are volatile enough to evaporate in order to maintain phase equilibrium. The temperature effects on NH$_3$ emission are in this case twofold: firstly, the decrease in NH$_3$ solubility with increasing temperature; secondly, the evaporation of water at high temperatures and subsequent evaporation of NH$_3$. Similarly, NH$_3$ is more likely to be released from aqueous-phase aerosols at high temperatures (> 20 °C), especially as they are often associated with low relative humidities (< 60%) in the British Isles. The same mechanisms apply for terrestrial sources of NH$_3$ other than living plant tissues whenever evaporation of NH$_3$ from the liquid phase is involved. Ammonia emissions from slurry patches broadcast over bare soil, and more generally emissions from animal excreta, are expected to be largest during warm and dry weather. The quasi-exponential temperature response of NH$_3$ concentrations observed in Fig. 9 for wind speeds in the range 4–14 m s$^{-1}$ for the three wind-sectors is consistent with increased emission at high temperatures for lower wind-speeds (< 4 m s$^{-1}$), this relationship is less clear and the variability much larger. For the S sector, largest concentrations are found for wind speeds < 3 m s$^{-1}$ and temperatures below 0 °C. The influence of the poultry farm in the S sector is reflected in Fig. 9 as variations in concentration levels with temperature as expected on the basis of Eq. (4) are overshadowed by local emissions, whereas this is less clear for the NE and SW sectors.

Ammonia emissions from vegetation generally occur during daytime and have been measured and reported for coniferous forest and heathland (Sutton et al. 1995b), fertilized agricultural crops (Sutton et al. 1993b) and slurry patches over bare soil (Genermont et al. 1998). On the other hand, the maximum rates of dry deposition generally occur in cool and humid conditions, typically during the night (Flechard and Fowler 1998). Such radiation- and temperature-driven diurnal cycles in surface–atmosphere exchange tend to increase ground-level concentrations of NH$_3$ during the day and reduce these during the night. Diurnal cycles in NH$_3$ concentration at 1 m above vegetation level were indeed found at Auchencorth Moss for the warm summer months only (May to August 1995) when diurnal cycles in temperature and daytime temperatures were large enough to significantly promote NH$_3$ emission during the day (Flechard and Fowler 1998). During the remaining months, temperature effects were less important in the control of atmospheric NH$_3$ than wind speed. Simultaneous measurements of surface–atmosphere fluxes of NH$_3$ at this site showed that there were also diurnal cycles in canopy resistance $R_c$ to dry deposition, with $R_c$ largest during daytime and smallest during night-time, but again only during the summer months. The canopy resistance increased from 20 s m$^{-1}$ at 0 °C to 200 s m$^{-1}$ at 30 °C, with values ranging from 20 s m$^{-1}$ to 100 s m$^{-1}$ at temperatures below freezing (Flechard and Fowler 1998). These findings were consistent with those of Sutton et al. (1993a) and Duyzer (1994) for semi-natural vegetation.

(c) Relative humidity, surface wetness and chemistry

The dry deposition of NH$_3$ onto terrestrial surfaces, the incorporation of NH$_3$ into acidic aerosols and cloud droplets, and the scavenging by precipitation—rain or snow—make up the bulk of removal processes for atmospheric NH$_3$. The combined efficiency of
all these concurrent processes determines the atmospheric residence time of NH₃. While temperature provides an important control over emissions from vegetation, removal processes, and hence the residence time of NH₃ in the atmosphere, are largely controlled by atmospheric and surface humidity.

As air temperature and atmospheric or surface humidity are closely coupled, separating the effects of humidity from those of temperature on NH₃ concentrations is not a straightforward matter. For these field measurements, this separation is not possible. Yet, these variables control the chemistry of the removal processes for NH₃. It has been suggested, for example, that in NH₃-polluted atmospheres such as in the Netherlands, interactions between NH₃ and SO₂ on wet leaf surfaces may regulate rates of dry deposition (Erisman and Wyers 1993). The rate of uptake of NH₃ by leaf cuticular surfaces has been shown to increase with atmospheric relative humidity (Van Hove et al. 1989; Sutton et al. 1995b) while dew- or rain-wetted surfaces show substantially smaller canopy-resistances (Flechard and Fowler 1998). In the atmosphere, the removal of NH₃ by gas-to-particle conversion is also more likely to occur at significant rates when the air is cool and moist, and these conditions are generally associated with wet plant surfaces and reduced canopy-resistances to NH₃ dry deposition. Conversely, the evaporation of NH₃ from aerosols is expected to occur mainly in warm weather at lower relative humidities when emission from ground-level sources and surface resistance to dry deposition are both largest.

Measurements obtained during the monitoring period at Auchencorth Moss show the influence of RH on the partitioning of NH₃ between the gas phase and the aerosol aqueous phase. Nitric acid (HNO₃) and hydrochloric acid (HCl) concentrations were measured on an hourly basis, one day a week, during the NH₃ monitoring period. Concentrations of HNO₃ and HCl were determined using a wet annular denuder (ECN, The Netherlands) in which two rotating, concentric glass tubes are coated with a slightly alkaline solution (0.1M K₂PO₃) that captures acidic gases from a laminar sample air flow (30 l min⁻¹) (Keuken et al. 1988). Hourly liquid-samples were then refrigerated before analysis by HPLC anion chromatography ( Dionex DX-100 system using a Dionex Ionpac AS4A 10-32, 4 × 250 mm column and a self-regenerating suppressor ASAR-1).

Hourly concentration-products (Kₘ) of NH₃ and HNO₃ and also NH₃ and HCl were calculated at 1 m above the vegetation and compared with the dissociation constants (Kₚ) of pure ammonium nitrate (NH₄NO₃) and ammonium chloride (NH₄Cl) salts respectively (see also Stelson and Seinfeld (1982); Harrison and Pio (1983); Pio and Harrison (1987); Erisman et al. (1988)). The variations with relative humidity of the ratio Kₘ/Kₚ between the measured concentration product and the theoretical equilibrium value for NH₄NO₃ are presented in Fig. 10. The theoretical dissociation constants for pure NH₄NO₃ aerosol were calculated after Mozurkewich (1993). The field data presented in Fig. 10 suggest that phase equilibrium (i.e. Kₘ/Kₚ = 1) seldom occurred at this site during the period when these measurements were made (May to September 1995). Below relative humidities of about 90%, NH₄NO₃ aerosol evaporation is more likely to occur in the atmosphere as most Kₘ/Kₚ ratios are smaller than unity, causing a partitioning of NH₄ toward the gas phase.

This is considered to have favoured larger NH₃ concentrations in dry atmospheric conditions. Above 90%, however, there was considerable scatter in the data, with Kₘ/Kₚ ratios found equally on both sides of the equilibrium line (Fig. 10), even though the data are consistent with an exponential increase with relative humidity, the largest values (> 10) being exclusively found above 97%. The implications of these findings are that, if gas-to-particle conversion of NH₃ was important over Auchencorth Moss during the monitoring period, it occurred primarily during the time that relative humidities were larger than 90%, and was highly unlikely to occur at humidities below 80%.

While a discussion on the conditions affecting the equilibration of NH₃ and acid
gases between gaseous and aerosol phases is beyond the scope of this paper and has been treated in detail in numerous studies (e.g. Allen et al. 1989; Pandis and Seinfeld 1990; Meng and Seinfeld 1996), it is important to note that there are considerable restrictions on the interpretation of the previous results. Firstly, the concentration product concept is valid only when dealing with ‘pure’ aerosols, i.e. those composed of particles containing only salts of the ionic forms of the gases considered. This ideal situation seldom occurs in polluted atmospheres where aerosols contain a mixture of numerous chemical species including ammonium, nitrate, chloride, sulphate, base cations and heavy metals. Secondly, the timescales of the gas–particle processes are largely unknown, as are the size distributions of aerosols. As the chemical timescale necessary to achieve equilibrium must be short compared with that of turbulent mixing (Meng and Seinfeld 1996), using concentration products as indicators of gas-to-particle conversion or aerosol evaporation may not always be appropriate because potential time constraints are ignored. The fact that most concentration products measured at Auchencorth Moss did not equate to the theoretical equilibrium value suggest the existence of important time constraints which led to non-equilibrium aerosol-gas concentrations. Given these restrictions, the question of whether RH affects NH\textsubscript{3} concentrations by controlling gas-to-particle conversion and aerosol evaporation remains unanswered. However, it remains the most plausible explanation for the observed sharp decline in NH\textsubscript{3} concentration for values of RH above 90\% (Fig. 8(c)) in both sectors (NE and, especially, S) where local agricultural influences were largest.

(d) Dispersion of NH\textsubscript{3} from local sources

Dispersion and mixing processes are major factors controlling NH\textsubscript{3} concentrations at the vegetation level when, as is the case in the UK landscape, the spatial source distribution is not uniform and point agricultural sources contribute a large fraction of the
overall NH$_3$ emission (Asman and Van Jaarsveld 1992). Because NH$_3$ is mainly emitted from agricultural, ground level sources, NH$_3$ tends to accumulate at the earth’s surface in conditions of reduced turbulent mixing. Thus, low wind-speeds and small radiative surface heating or even night-time radiative cooling associated with a temperature inversion in the lower troposphere lead to larger NH$_3$ concentrations by limiting both frictional drag on the surface and free convection. Similar findings by Burkhardt et al. (1998) showed a marked diurnal cycle for wind speeds less than 1 m s$^{-1}$ and NH$_3$ concentrations smallest during the day and higher at night. They argued that NH$_3$ emitted by local sources is trapped at ground level in stable atmospheric conditions at night and that greater turbulent mixing during the day leads to smaller ground-level concentrations.

These purely mechanical effects tend to counteract the diurnal cycles of emission from vegetation and dry deposition which both reduce surface concentrations at night and to increase these during the day (see subsection 4(b)). Because the strong diurnal cycles in air temperature and wind speed are closely related, particularly in summer, the periods of maximum NH$_3$ emission, i.e. daytime, match those of maximum wind-speed, surface friction and turbulent mixing; on the other hand, wind-speed and turbulence minima (night-time) occur simultaneously with the emission minima, making predictions of ground-level concentrations rather uncertain.

Wind speed, surface friction and stability determine the horizontal and vertical spread of a plume from a source (Pasquill 1974; Asman and Van Jaarsveld 1992), and this, combined with wind direction, is the major factor regulating the concentration field within a few kilometres from the source. With regard to critical levels and critical loads of NH$_3$ for vegetation close to large sources, it is necessary to assess the fraction of NH$_3$ which has been removed from the atmosphere as a function of distance downwind from the source. There is a great deal of uncertainty about the mean residence time of NH$_3$ in the atmosphere because most of the processes that determine its value, such as gas-to-particle conversion, occur at unknown rates. The residence time also varies with time of year as indicated by systematic variations in the deposition velocity (Fig. 5) caused by the seasonal meteorological variability.

If the reciprocal of $\tau$ is seen as the sum of the reciprocals of individual characteristic times, such as $\tau_d$ (dry deposition), $\tau_w$ (wet deposition) (Möller and Schieferdecker 1985) and $\tau_c$ (gas-to-particle conversion) (Erisman et al. 1988), it appears that the residence time for dry deposition $\tau_d$ provides an upper limit for the overall residence time $\tau$. Estimates of $\tau_d$ (s) have often been obtained by dividing the depth $h$ (m) of the boundary layer (typically 1000 m in daytime, unstable conditions) by the dry deposition velocity $V_d$ (m s$^{-1}$) at a reference height (1 m above the vegetation) (Garland 1978; Möller and Schieferdecker 1985; Sutton 1990). This application of a simple box-model is based on the assumption that the gas is uniformly mixed throughout the entire depth $h$ of the boundary layer which can thus be treated as a box with an average depletion rate of the gas, $V_d$

$$\tau_d = \frac{h}{V_d}.$$  

(5)

This assumption may not be entirely valid in the case of NH$_3$ because of gas-to-particle conversion of NH$_3$ at the top of the boundary layer. A more realistic approach is probably the use of the vertical spread $z_p$ of an emission plume at a given distance downwind from a point source when this source is known to contribute most of the NH$_3$ in the air column at this location. Such conditions were assumed to apply at Auchencorth Moss for winds blowing from the poultry farm on the bearing of 190o and at a distance of 2.7 km from the measurement site. The vertical spread of the ammonia plume $z_p$ was estimated from the vertical standard deviation of concentration $\sigma_z$ using an empirical power-law
approximation for the growth of $\sigma_z$ (km) with distance $x$ (km) from a ground level source (Pasquill 1974) such that

$$\sigma_z = ax^s,$$

(6)

the parameters $a$ and $s$ being given for different Pasquill stability categories and roughness lengths (Pasquill 1974). Atmospheric stability at Auchencorth Moss typically ranged from ‘slightly stable’ (E, $z_p = 90$ m) through ‘neutral’ (D, $z_p = 150$ m) to ‘moderately unstable’ (B, $z_p = 350$ m). Measured deposition-velocities at this site generally ranged from 5–10 mm s$^{-1}$ in cold and stable, winter conditions or dry and unstable, summer conditions, to 25–30 m s$^{-1}$ in windy, neutral and wet conditions (Flechard and Fowler 1998). Typical estimates of the residence time of NH$_3$ for dry deposition therefore ranged from two to three hours in neutral, wet and windy conditions, to 3–5 hours in cold and stable, winter conditions and up to 9–20 hours in warm and dry, summer conditions. A mean deposition-velocity of 12 mm s$^{-1}$ as measured at this site over a period of 13 months (Flechard and Fowler 1998) combined with a vertical spread of the poultry-farm plume of 150 m in typically neutral conditions at this windy, cool and overcast site, provide a mean $\tau_d$ of about 3.5 hours.

An important restriction on the use of Eq. (5) in obtaining estimates of $\tau_d$ is that deposition velocities at 1 m above the vegetation were used although $V_d$ is known to vary with height. Assuming dry-deposition fluxes to be height-independent and vertical concentration profiles to be logarithmic, a zero surface-concentration implies an infinitely large $V_d$ at the surface and an exponential decrease of $V_d$ with height. The problem lies in the choice of a ‘mean’ representative value of $V_d$ for the whole plume. However, a sensitivity analysis showed that estimates of $\tau_d$ obtained using deposition velocities at 0.2 m, 5 m and 20 m above the vegetation were generally within 50% of those obtained using $V_d$ at 1 m, typically in the range 1–8 hours. Because $\tau_d$ provides an upper limit for $\tau$, the values of mean residence times of NH$_3$ in the atmosphere presented here contrast sharply with those published earlier by Söderlund and Svensson (1976) (1–4 days), Möller and Schieferdecker (1985) (19 hours) and Sutton (1990) (10 hours). The main reason for the very short residence times observed in this study is the use of smaller mixing heights (90 to 350 m) than those used earlier (1000 m; Möller and Schieferdecker 1985; Sutton 1990). However, since all agricultural NH$_3$ sources are characterized by low (< 10 m) emission-heights, the atmospheric residence times obtained from this study are considered to be appropriate for agricultural NH$_3$ emissions in northern Europe. In warmer, drier climates, residence times for NH$_3$ may be much longer.

Removal rates of NH$_3$ by gas-to-particle conversion measured in The Netherlands, and published by Erisman et al. (1988), were of the order of 0.01% s$^{-1}$ during daytime and 0.005% s$^{-1}$ during night-time, equivalent to chemical lifetimes $\tau_c$ of 2 hours and 4 hours respectively. These figures, combined with the above estimates of lifetimes for dry deposition, may yield more realistic estimates of the overall lifetime of NH$_3$ in the troposphere, typically 2 hours in stable, night-time conditions and 1.7 hours in unstable, daytime conditions. However, these estimates remain rather speculative given the uncertainty and the variability in the rates at which gas-to-particle conversion proceeds.

Although the mean residence time for atmospheric NH$_3$ as a result of dry deposition was found to be as short as 3.5 hours over the 13 months, a mean wind-speed of 4 m s$^{-1}$ measured at this site implied a mean transport-distance before dry deposition of 50 km. Other removal processes, such as gas-to-particle conversion and removal in precipitation, also contribute to the overall residence time of ammonia $\tau$ which may be as short as 1–2 hours, equivalent to transport distances of the order of 15–30 km. The consequence of the very short residence time for NH$_3$, its large rate of deposition and the characteristics
of the numerous low-level sources is that the most acute problems of NH₃ are likely to
occur close to livestock units where ambient NH₃ levels lead to large dry-deposition inputs
within 1 km.

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