Fluxes of ammonia over oilseed rape
Overview of the EXAMINE experiment

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Abstract

An integrated field experiment was organized as part of the EC EXAMINE project to quantify surface–atmosphere fluxes of ammonia (NH₃). Fluxes of NH₃, NH₄⁺ aerosol, HNO₃ and HCl were measured using the gradient method with several continuous and batch sampling systems. Within-canopy NH₃ was determined to quantify the contribution of leaf cuticles, sub-stomatal apoplastic (intercellular) fluids and other sources and sinks to net fluxes. The campaign included the first field measurements of apoplastic pH and [NH₄⁺], providing independent estimates of the stomatal compensation point (χₛ) for comparison with micrometeorological results. The latter also compared fluxes before and after cutting.

Under the clean conditions of the experiment, [NH₃][HNO₃] and [NH₃][HCl] were much less than values required for aerosol formation, while the NH₄⁺ aerosol size distribution indicated that aerosol evaporation would be much slower than the time-scale of turbulent exchange. Nevertheless, the measurements suggest that aerosol production/growth as well as formation of HCl may have occurred within the canopy. Apoplastic [NH₄⁺] and pH of leaves showed no diurnal patterns, with the main control on χₛ being the temperature dependence of the solubility equilibria. Fluxes of NH₃ were bi-directional (−200 to 620 ng m⁻² s⁻¹), with deposition generally occurring when the canopy was wet and emission when it was dry, particularly during the day. Nocturnal emissions indicated a non-stomatal NH₃ source, while daytime emissions were larger than indicated by the apoplastic estimates of χₛ. The within-canopy data, together with an inverse Lagrangian source–sink analysis, showed decomposing litter to be a significant NH₃ source, explaining nocturnal NH₃ emissions and larger emissions following cutting. Daytime net fluxes were controlled by the top part of the canopy, due to χₛ for siliques apparently being larger than for leaves.

The measurements have been used to develop multi-layer resistance models of NH₃ exchange. A 3-layer ‘foliage–litter–silique model’ provides a detailed mechanistic treatment of the component fluxes, while a 2-layer ‘foliage–litter model’ is

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better suited to generalization in atmospheric transport models. Application of the new models should help improve estimates of regional atmospheric ammonia budgets. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The magnitude of ammonia (NH₃) exchange between ecosystems and the atmosphere is a central issue in the quantification of impacts of acidifying and nitrogen (N) containing pollutants (e.g. Sutton et al., 1998b). On a European scale, it has been estimated that NH₃ emissions amount to 6.4 Gg N yr⁻¹, which is a similar magnitude to emissions of nitrogen oxides, estimated at 6.3 Gg N yr⁻¹ (Barrett and Berge, 1996). The major fraction of NH₃ emissions (>80% on average in Europe) is estimated to arise from the volatilization of livestock wastes, although substantial emissions (5–30% of the national emissions) also occur from the application of mineral fertilizers to agricultural land and direct biological emissions from crops and crop residues (Asman, 1992). Such estimates, however, mask the complexity of the NH₃ exchange processes. In estimating ‘net emissions’ from agricultural land surfaces, it is essential to define the time-scale, since periods of net upward (emission) fluxes may alternate with periods of downward (deposition) fluxes on both seasonal and diurnal timescales.

In contrast to agricultural ecosystems, which characteristically show both emission and deposition fluxes, semi-natural ecosystems are generally more efficient sinks for NH₃ deposition (Duyzer, 1994; Sutton et al., 1993a,b; Schjoerring, 1997). This is largely related to the lower nitrogen status of unfertilized plant communities compared with intensive agricultural land. However, the divide is not sharp and, while net deposition dominates, short duration periods of NH₃ emission have also been observed from semi-natural ecosystems (Sutton et al., 1995a). For semi-natural ecosystems in agricultural regions, net dry deposition of NH₃ often represents the largest component of total N deposition (e.g. Sutton et al., 1993b). Quantification of NH₃ exchange is therefore critical in defining net N inputs.

An important use of information on NH₃ exchange is in atmospheric transport models (e.g. Asman and van Jaarsveld, 1992; Barrett and Berge, 1996; Singles et al., 1998), for which emissions estimates are compiled to provide spatial inventories (e.g. Buijsman et al., 1987; Asman, 1992; Sutton et al., 1995b). The emissions are advected across the model domain and removed from the model atmosphere by wet and dry deposition, the latter usually scaled by a deposition velocity (V_d). The bi-directional nature of NH₃ fluxes, however, means that this simplified approach needs to be refined to consider the temporal variability in direction and magnitude for different ecosystem types. This requires better quantification of NH₃ fluxes with all land surfaces, especially as these affect both atmospheric transport distances and inputs into remote sensitive ecosystems. Reliable quantification of these fluxes is essential as governments begin to develop strategies to limit acidification and eutrophication due to NH₃. Major commitments to NH₃ emission reductions are currently being developed under the UNECE Nitrogen Protocol and the EU Acidification Strategy (Bull and Sutton, 1998), while the EC Directive on Integrated Pollution Prevention and Control (IPPC) has already established a framework to limit emissions from intensive pig and poultry farms (EC, 1996).

In order to improve the understanding and quantification of NH₃ exchange, the EC project EX-AMINE (‘EXchange of atmospheric AMmonia IN European ecosystems’) was initiated, representing the first European project to address these issues (Sutton et al., 1997). The project focused on the development of a mechanistic understanding necessary for constructing models, and considered a wide range of European ecosystems including both agricultural and semi-natural land. As part of the project, an integrated field campaign was organized over oilseed rape (Brassica napus). A wide range of techniques was applied, including micrometeorological measurements of above-canopy fluxes of NH₃ (Sutton et al., 2000),
ammonium (NH$_4^+$) containing aerosol and acidic trace gases HNO$_3$, HCl, SO$_2$ (Nemitz et al., 2000c). These measurements were complemented by direct determination of the NH$_4^+$ concentration and pH of leaf apoplasts to provide estimates of the NH$_3$ 'compensation point' (Section 2.4) (Husted et al., 2000), together with an analysis of sources and sinks of NH$_3$ within the plant canopy (Nemitz et al., 2000a). The measurements and analyses have then been used to develop models of net NH$_3$ exchange (Nemitz et al., 2000b). The present paper summarizes the measurements and draws together the different components to highlight the key findings of the experiment. It shows how these advance the understanding of NH$_3$ exchange processes, and considers the implications for atmospheric budgets.

1.1. Objectives of the experiment

The specific objectives of the EXAMINE North Berwick experiment were:

1. To use micrometeorological methods to measure net fluxes of NH$_3$ above an oilseed rape canopy, including an assessment of the micrometeorological exchange parameters measured using several techniques.

2. To provide a comparison of several sampling methods used to measure NH$_3$ concentrations and concentration gradients above the canopy to estimate net NH$_3$ fluxes.

3. To provide parallel estimates of stomatal compensation points of NH$_3$ using (a) the micrometeorological flux estimates and (b) leaf apoplastic extraction and determination of plant apoplast NH$_4^+$ concentrations and pH in the field.

4. To establish source–sink relationships within the canopy and the relative contribution of rape plants and the soil to net fluxes above the canopy.

5. To measure aerosol NH$_4^+$ concentration gradients and fluxes above and within the canopy using two different techniques.

6. To estimate the interaction of NH$_3$ exchange fluxes with fluxes of HNO$_3$, HCl and SO$_2$ measured in parallel, including the possibility of gas–particle conversion interactions.

7. To apply the measurement data to develop and parametrize predictive models of net ammonia exchange with oilseed rape.

2. Measurement techniques

A summary of the different measurement techniques applied during the experiment is provided in Table 1. These fall into several groups, ammonia and acid gas sampling, aerosol sampling, micrometeorological measurements and plant/soil measurements.

2.1. Ammonia and acid gas sampling

The central NH$_3$ sampling technique was the AMANDA, of which two multi-point gradient systems were applied. For each of the AMANDA systems, NH$_3$ is captured in acidic solution in one of the three continuous wet annular denuders and analysed as NH$_4^+$ by a common detector. To allow intercomparison between the two systems, these were calibrated in parallel. The profile measurements were applied to compare estimates of the net NH$_3$ flux ($F_t$) above the canopy (Sutton et al., 2000) as well as to make six point measurements of NH$_3$ concentrations above and within the canopy (Nemitz et al., 2000a).

The other active sampling technique for NH$_3$ was a set of 10 filter packs, capturing aerosols on a PTFE pre-filter and NH$_3$ on a subsequent acidified paper filter (Sutton et al., 2000). Although some artefacts have been suggested to be possible when sampling with such filter packs through capture of NH$_3$ on the pre-filter or volatilization of collected aerosol, such effects are often considered to be smaller than differences related to operator implementation, and good agreement with denuders has been shown to be possible (Harrison and Kitto, 1990). In order to minimize evaporative losses, the filter packs were run using low face velocity, sampling at 10–141 min$^{-1}$ using 90 mm diameter filters. A further filter in this system was coated with NaF in order to capture gaseous HNO$_3$ and HCl. These profile measurements were used to give independent values of net fluxes above the canopy, as well as to provide more detailed information on the structure of within-canopy concentration profiles. Other measurements of HNO$_3$, HCl and HNO$_2$ concentration gradients above the canopy were provided by three automatic wet rotating denuders, which were operated on an hourly cycle, including a 40 min sampling period (Nemitz et al., 2000c).

Two other passive measurement techniques were applied to measure NH$_3$ concentration. A passive
Table 1
Summary of key measurements made during the joint EXAMINE field campaign over oilseed rape near North Berwick, Scotlanda

<table>
<thead>
<tr>
<th>Approaches applied</th>
<th>Parameter (number of measurement heights)</th>
<th>Methodology</th>
<th>Sampling time</th>
<th>Contributing participant organization (method reference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical concentration profiles</td>
<td>NH₃ (6)</td>
<td>Continuous AMANDA denuders, with three inlet heights (×2 systems)</td>
<td>6 min</td>
<td>CEH, UPM (Wyers et al., 1993)</td>
</tr>
<tr>
<td></td>
<td>NH₃ (4)</td>
<td>Passive flux samplers (denuders and shuttles)</td>
<td>5 days</td>
<td>RVAU, ADAS (Schjoerring, 1995)</td>
</tr>
<tr>
<td></td>
<td>NH₃ (4)</td>
<td>Passive concentration samplers within the canopy</td>
<td>14 days</td>
<td>IUL (Blatter et al., 1992)</td>
</tr>
<tr>
<td></td>
<td>NH₃, HNO₃, aerosol NH₄⁺, SO₂²⁻, NO₃⁻, Cl⁻ (≤ 10)</td>
<td>Filter packs</td>
<td>1–3 h</td>
<td>CEH, University of Nottingham (Harrison and Katto, 1990)</td>
</tr>
<tr>
<td></td>
<td>Aerosol NH₄⁺ (2)</td>
<td>Steam jet aerosol collector</td>
<td>30 min</td>
<td>ECN (Khlystov et al., 1995)</td>
</tr>
<tr>
<td></td>
<td>HNO₃, HCl, HNO₂ (3)</td>
<td>Automatic batch wet annular denuder</td>
<td>40 min</td>
<td>ECN, University of Kiel (Keuken et al., 1988)</td>
</tr>
<tr>
<td></td>
<td>SO₂ (5)</td>
<td>Pulsed chemiluminescence analyser</td>
<td>10 min</td>
<td>CEH (Thermo Electron, model 43s, Franklin, MA, USA)</td>
</tr>
<tr>
<td>Concentrations at one height Micrometeorological measurements</td>
<td>Aerosol NH₄⁺, SO₂²⁻, NO₃⁻, Cl⁻</td>
<td>High volume sampler with cascade impactor inlet</td>
<td>2–12 h</td>
<td>UMIST/CEH (Series 230, Andersen Samplers, Atlanta, USA)</td>
</tr>
<tr>
<td></td>
<td>Horizontal mean wind speed (5)</td>
<td>Cup anemometers</td>
<td>10 min</td>
<td>CEH (Vector instruments, Clywd, UK)</td>
</tr>
<tr>
<td></td>
<td>Instantaneous wind speed and temperature fluctuations (3)</td>
<td>Ultrasonic anemometers</td>
<td>10 min</td>
<td>CEH, ECN (Solent Research 1012, Gill Instruments, Lymington, UK)</td>
</tr>
<tr>
<td></td>
<td>Instantaneous water vapour fluctuations (1)</td>
<td>Krypton hygrometer</td>
<td>10 min</td>
<td>ECN (KH₂O, Campbell Scientific, Shepshed, UK)</td>
</tr>
<tr>
<td></td>
<td>Mean humidity and temperature (1)</td>
<td>Thermistor and capacitance probe</td>
<td>10 min</td>
<td>ECN (Rhotonic Instruments, Lymington, UK)</td>
</tr>
<tr>
<td></td>
<td>Temperature and humidity gradients (2)</td>
<td>Fine thermocouples and dewpoint meter</td>
<td>10 min</td>
<td>CEH (Campbell Scientific, Loughborough, UK)</td>
</tr>
<tr>
<td>Plant measurements</td>
<td>Leaf apoplastic NH₄⁺ concentrations and pH</td>
<td>Pressure impregnation and extraction by cooled centrifugation</td>
<td>Daily or 2 h</td>
<td>RVAU (Husted and Schjoerring, 1995)</td>
</tr>
<tr>
<td></td>
<td>Bulk tissue NH₄⁺ concentrations</td>
<td>Bulk leaf extraction (living leaves and litter)</td>
<td>Daily or 2 h</td>
<td>RVAU (Husted and Schjoerring, 1995)</td>
</tr>
<tr>
<td></td>
<td>Leaf conductance to H₂O</td>
<td>Diffusion porometer</td>
<td>2 h (selected periods)</td>
<td>CEH/RVAU (ADC, Herts., UK)</td>
</tr>
<tr>
<td>Seals and leaf litter</td>
<td>NH₃ emissions</td>
<td>Dynamic chamber using AMANDA</td>
<td>10 min (selected periods)</td>
<td>CEH/UPM</td>
</tr>
<tr>
<td></td>
<td>Soil gas NH₃ concentrations</td>
<td>Passive samplers</td>
<td>14 days</td>
<td>IUL (Blatter et al., 1992)</td>
</tr>
<tr>
<td></td>
<td>Soil pH, bulk density, H₂O content, [NH₄⁺] and [NO₃⁻]</td>
<td>pH in CaCl₂</td>
<td></td>
<td>CEH (MacDonald et al., 1996)</td>
</tr>
</tbody>
</table>

a CEH: Centre for Ecology and Hydrology; ECN: Netherlands Energy Foundation; UMIST: University of Manchester Institute of Science and Technology; RVAU: Royal Veterinary and Agricultural University; IUL: Institute for Environmental Protection and Agriculture; UPM: Technical University of Madrid; AMANDA: Ammonia Measurement by ANnular Denuder sampling with online Analysis.
NH₃ denuder, which samples air in proportion to wind speed, has recently been applied in vertical gradient formation to measure long-term net NH₃ fluxes above crop canopies (Schjoerring, 1995). The normal principle of the aerodynamic flux gradient method is to couple mean gradients of concentration with diffusivity estimates over periods of 10 min–3 h. The assumption is that the sampling period is short enough that atmospheric stability and diffusivity do not change substantially during a run, since this would confound the mean estimate of the flux. In the passive flux sampling approach, sampling periods are typically 5 days–2 weeks and thus integrate over a wide range of stabilities. However, since the passive denuders sample in proportion to wind speed, it has been argued that the confounding due to changing diffusivity is largely cancelled out. Several runs using the passive approach were made during the experiment using the AMANDA NH₃ fluxes as a reference (Sutton et al., 2000).

Ammonia concentrations were also measured within the canopy and in the surface layer of soil using passive diffusion samplers (Blatter et al., 1992). Given the variability expected in soil NH₃ concentrations, a network of 40 samplers was established covering an area of 16 m × 16 m (Nemitz et al., 2000a).

2.2. Aerosol sampling

Three techniques were applied successfully to measure aerosol ion concentrations during the experiment, a steam jet aerosol collector (SJAC, Khlystov et al., 1995), filter packs and a high volume Andersen impactor. Each of these provided measurements of aerosol NH₄⁺ concentrations, and in addition the filter pack filters and Andersen impactor substrates were analysed for SO₄²⁻, NO₃⁻ and Cl⁻ (Nemitz et al., 2000c). The field experiment here represented the first use of the SJAC to measure vertical profiles and fluxes of NH₄⁺ aerosol. Inlet tubes were used together with a switching valve to provide 15 min NH₄⁺ concentrations at two different heights (Nemitz et al., 2000c).

An attempt was also made to deploy two active scattering aerosol spectrometer probes (ASASP-X) to measure particle fluxes by eddy covariance in the size range 0.1–1 μm. By applying eddy covariance with two probes at different heights, it was planned to investigate the possibility of aerosol flux divergence as a consequence of gas–particle conversion. Unfortunately, this implementation was not successful due to sampling problems associated with the isokinetic sampling inlets and resonant interference from the sampling pump.

2.3. Micrometeorological measurements

Measurements of eddy diffusivity and fluxes of sensible heat (H) and latent heat (λE), as well as related parameters such as surface temperature, surface humidity and canopy stomatal resistance, were made to interpret the trace gas/aerosol gradients and fluxes. Three eddy covariance systems and one profile system (Sutton et al., 2000) were used to provide estimates of eddy diffusivity and friction velocity (u*). The profile determination was made using five sensitive cup anemometers set at 0.2–2 m above the canopy, together with a two point temperature profile from a ‘Bowen ratio system’ (Campbell Scientific) applying the aerodynamic gradient method. Gradient determination of u* and the roughness length (z₀) was made by calculating atmospheric stability from the Richardson number (Ri), from which the Monin–Obukhov length (L) was derived and used to apply integrated stability corrections to the wind and temperature profiles (Sutton et al., 1993a).

The range of techniques provided the facility to compare independent estimates and establish more reliable estimates of both u* and H. During part of the experiment, one of the Gill ultrasonic anemometers was placed at different heights within the rape crop to investigate within-canopy turbulence for an inverse Lagrangian analysis of NH₃ sources and sinks (Nemitz et al., 2000a).

Latent heat fluxes were estimated using three methods, two direct and one inferred (Sutton et al., 2000). Direct measurements were made by eddy covariance using a krypton hygrometer, which was referenced using a Rhotronic temperature and humidity sensor. The Bowen ratio system was also used to provide two point profile determinations of λE again by applying the aerodynamic gradient method. Indirect estimates of λE were also made assuming closure of the surface energy balance from the fluxes provided by the Bowen ratio system.
2.4. Plant physiological measurements

The central measurements at the plant scale were determination of leaf apoplastic \([\text{NH}_4^+]\) and pH (Husted et al., 2000). This is of interest since these values may be used to estimate the air concentration of \(\text{NH}_3\) at equilibrium with the leaf tissues, according to the Henry and dissociation equilibria. This concentration is referred to as the \(\text{NH}_3\) ‘stomatal compensation point’ \(\left(\chi_s\right)\), since it is expected to be the concentration at which plant \(\text{NH}_4\) production balances consumption in the sub-stomatal leaf tissues (Farquhar et al., 1980). When the air concentration of \(\text{NH}_3\) above stomata equals the compensation point, the net gaseous flux though the stomata is expected to be zero; with smaller air concentrations, emission is expected, and at larger air concentrations deposition is expected. Bulk estimates of \(\chi_s\) may be made from a top-down approach, applying micrometeorological measurements of \(F_t\) for \(\text{NH}_3\) and resistance models (Sutton et al., 2000; Nemitz et al., 2000b). In contrast, apoplastic measurements provide a valuable independent bottom-up estimate.

The principle of the extraction procedure is to impregnate an isotonic solution into the apoplast of a leaf segment, which is then extracted using cooled centrifugation. Although conceptually simple, the method involves several additional steps to calculate apoplastic concentration, including the estimation of the air content of the apoplast (using silicone infiltration) and the calculation of dilution coefficients using an inert dye (Husted and Schjoerring, 1995). The application of this technique here represents its first use in the field and the first comparison of \(\chi_s\) from apoplastic and micrometeorological estimates. In addition to the apoplastic assays, whole leaf extracts were made for leaves, siliques (oilseed rape seed cases) and decomposing abscised leaves.

3. Site description and experimental conditions

3.1. The North Berwick field site

The measurement campaign took place on a large oilseed rape (\(B. \text{napus}\) var. ‘Express’) field 2.5 km south of North Berwick in southern Scotland and 35 km east of Edinburgh. The field had received 285 kg N ha\(^{-1}\) since the previous autumn, mainly as ammonium nitrate. This is a rather high N input compared with other arable crops, but reasonably typical for oilseed rape. A plan of the field site and location of the main equipment is shown in Fig. 1. A track was cut into the field from the northern side to allow access for a caravan and mobile laboratory. Micrometeorological equipment was located to the south of...
the mobile laboratory, with sampling generally up to 2 m above the canopy. Electricity was provided by a diesel generator on the northern edge of the field. The site provided a fetch over the oilseed rape exceeding 200 m for wind sectors from 46° to 293°, with fetch in the west (209–278°) exceeding 350 m. The site is 65 m above sea level in an area of gently undulating intensive mixed farming, but only 3 km from the river Forth estuary in the north, and 7 km from the open North Sea in the east.

On the basis of national gridded estimates provided by Dragosits et al. (1998), the site is in an area of rather modest NH$_3$ emissions. For the 10 km × 10 km area surrounding the site, the following estimates apply: 909 cattle (0.96 kg N ha$^{-1}$ yr$^{-1}$), 23,453 poultry (0.66 kg N ha$^{-1}$ yr$^{-1}$), 2620 pigs (0.89 kg N ha$^{-1}$ yr$^{-1}$) and 652 sheep and goats (0.02 kg N ha$^{-1}$ yr$^{-1}$), together with an estimated crop/fertilizer emission of 1.47 kg N ha$^{-1}$ yr$^{-1}$ and a non-agricultural emission of 0.20 kg N ha$^{-1}$ yr$^{-1}$. Overall estimated NH$_3$ emission totals 4.2 kg N ha$^{-1}$ yr$^{-1}$.

The measurements took place in two periods during summer 1995. The main sampling period involved most EXAMINE groups and provided measurements from 6 to 27 June, while the crop was at the late flowering stage and 1.38 m tall. The second sampling period (21 July–3 August) included micrometeorological measurements by CEH only, with the objective of considering NH$_3$ fluxes immediately before and after cutting the rape canopy. However, as the field was cut earlier than had been planned (22 July), the results from these measurements are almost exclusively for the period after cutting. The rape was cut by swathing at 0.3 m, while the siliques were still partly green, with the cut crop resting in east–west oriented bands approximately 0.8 m high and 1.9 m wide. The intervening bands of exposed cut stems were approximately 1.5 m wide. In order to be above the roughness sub-layer in the second experiment, measurements were made with a minimum height of 1.5 m above the ground. The second period covered seed ripening with the measurements terminated to allow the farmer to harvest the seed. A view of the field site during the second campaign is provided by Sutton et al. (1996, cover photograph).

The soils of the field are of the Kilmarnock association, being a brown forest soil with gleying. Soil measurements were made by MacDonald et al. (1996) for 8–23 June. These measurements provided a bulk density of 1.3 g cm$^{-3}$ and a soil moisture of 19.9% dry weight (average of five samples taken during 8–23 June 1995). The soil pH (measured in CaCl$_2$) was 5.1, with a free NH$_4^+$-N content of 3.6 μg g$^{-1}$ DW and a NO$_3^-$-N content of 1.5 μg g$^{-1}$ DW. Methane oxidation and nitrous oxide emission rates for the soil were also presented by MacDonald et al. (1996).

3.2. Meteorology during the experiment

The first part of the experiment took place during several weeks in summer with daytime air temperatures reaching 20–25°C and night-time temperatures down to 5–10°C. The weather was fine and sunny with light showers on several days and dewfall on several nights. The wind direction in this part of Scotland is generally dominated by E–W flow patterns and this is reflected in Fig. 2A, which shows the number of NH$_3$ determinations from the AMANDA for the first phase of the experiment in relation to wind direction. The most frequent winds were from the west, and only about 15% provided unacceptable wind fetch for the purposes of flux calculation. For the second phase of the experiment, there were more easterly winds and some periods with low cloud or sea fog. Overall, the range of conditions was quite typical for Scotland in summer.

3.3. Concentrations of ammonia, acid gases and inorganic aerosol

A summary of the pollutant concentrations ($\chi_a$) measured during the experiment is shown in Table 2. The AMANDA analysers measured NH$_3$ for 31 days, equivalent to 3700 means for 10 min averaging periods. During the intensive first part of the experiment, the mean $\chi_a$ for NH$_3$ was 1.03 μg m$^{-3}$ with a range 0–21 μg m$^{-3}$. The values of $\chi_a$ for NH$_3$ were larger in the post-cutting period with a mean of 2.48 and a range 0.3–12.6 μg m$^{-3}$. These represent reasonably clean air conditions, and indicate that the site was not strongly affected by advection from point sources. This is reflected in the geometric standard deviation of 1.8–2.1, which is much smaller than the value of 2.9 derived from monitoring in a mixed agricultural area reported by Burkhardt et al. (1998).
The concentrations of the other pollutants are reported only for the first measurement period. Concentrations of SO$_2$ were on average 2.8 $\mu$g m$^{-3}$, which is larger than the mean NH$_3$ concentration on an equivalent basis (SO$_2$/NH$_3$: 1.5). This feature is of interest as it may affect the efficiency of deposition of NH$_3$ to leaf cuticles as compared with other sites. For example, for NH$_3$ and SO$_2$ flux measurements over cropland in central England (Sutton et al., 1998a), the mean equivalent ratio was 1.74. The concentrations of HNO$_3$, HCl and HNO$_2$ were small throughout the experiment with mean concentrations of 0.68, 0.32 and 0.10 $\mu$g m$^{-3}$, respectively. Aerosol NH$_4^+$ concentrations provided by the SJAC were similarly small with a mean of 0.42 $\mu$g m$^{-3}$. From the limited number of filter pack samples, the mean concentrations of SO$_4^{2-}$, NO$_3^-$ and Cl$^-$ were 1.35, 0.89 and 2.31 $\mu$g m$^{-3}$, respectively. The larger concentration of Cl$^-$ is attributable

Table 2
Summary of measured pollutant concentrations during the North Berwick experiment

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Mean ($\mu$g m$^{-3}$)</th>
<th>S.D. ($\mu$g m$^{-3}$)</th>
<th>Median ($\mu$g m$^{-3}$)</th>
<th>Geo S.D.</th>
<th>Min. ($\mu$g m$^{-3}$)</th>
<th>Max. ($\mu$g m$^{-3}$)</th>
<th>Data coverage (days)</th>
<th>Averaging time (min)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gases</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_3$ (pre-cutting)</td>
<td>1.03</td>
<td>0.90</td>
<td>0.90</td>
<td>2.11</td>
<td>0.00</td>
<td>21.0</td>
<td>20</td>
<td>10</td>
<td>2268</td>
</tr>
<tr>
<td>NH$_3$ (post-cutting)</td>
<td>2.48</td>
<td>1.52</td>
<td>2.21</td>
<td>1.85</td>
<td>0.38</td>
<td>12.6</td>
<td>11</td>
<td>10</td>
<td>1247</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>2.84</td>
<td>5.58</td>
<td>1.68</td>
<td>2.33</td>
<td>0.00</td>
<td>111</td>
<td>19</td>
<td>10</td>
<td>2515</td>
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<td>HNO$_3$</td>
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<td>0.50</td>
<td>0.56</td>
<td>1.79</td>
<td>0.18</td>
<td>3.97</td>
<td>6</td>
<td>40</td>
<td>109</td>
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<td>HONO</td>
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<td>0.09</td>
<td>1.93</td>
<td>0.03</td>
<td>0.70</td>
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<td>1.854</td>
<td>0.07</td>
<td>0.91</td>
<td>6</td>
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<td><strong>Aerosols</strong></td>
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<tr>
<td>NH$_4^+$</td>
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<td>0.34</td>
<td>2.36</td>
<td>0.02</td>
<td>1.55</td>
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<td>235</td>
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<td>1.30</td>
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<td>7</td>
<td>120</td>
<td>12</td>
</tr>
</tbody>
</table>

aData are for the pre-cutting period, unless otherwise noted. The concentrations of the different species are not directly comparable, since they were partially measured at different times or only during a part of the campaign. S.D.: arithmetic standard deviation; Geo S.D.: geometric standard deviation; $n$: number of observations.

b Data as measured by the steam jet aerosol collector, including correction or estimated capturing efficiency.
to the importance of marine air masses at this site, and
is reflected by the significant HCl concentration.

The dependence of $x_a$(NH$_3$) on wind direction is shown in Fig. 2B. The largest $x_a$ occurred during WSW and NE winds. The location of the sources providing these peak values is not certain, although there are several livestock farms at around 5–10 km distance to the SW. In the NE, the most likely source is the Bass Rock, a sea bird colony 7 km away with $\approx$50 000 breeding pairs of gannets (Sula bassana).

4. Intercomparison of turbulent exchange parameters

The intercomparison of several techniques provided reliable estimates of both $u_s$ and $H$. The median relative standard deviation of the filtered values for $u_s$ and $H$ measured with the four independent systems was 14 and 26%, respectively. Given the inherent uncertainty in measuring these terms, especially during night-time, when absolute values are small, this agreement is considered very encouraging. An example of the different estimates of $H$ for 2 days is shown in Fig. 3. Both the overall magnitude and the fluctuations at a 10 min level are reproduced by each of the methods. On the evening of the 20 June, the smaller value determined by the profile method may be due to uncertainty in the semi-empirical stability correction applied to these results as a consequence of stable atmospheric conditions. The agreement for $\lambda E$ between the Krypton hygrometer and closure of the energy balance was also very encouraging (Sutton et al., 2000). However, the dewpoint gradient system underestimated $\lambda E$ by approximately 50% as a consequence of an inadequate time response coupled to the channel switching between two heights. Subsequent analysis of NH$_3$ fluxes was performed using means of the different estimates of $u_s$, $H$ and $\lambda E$, excluding the gradient estimate of $\lambda E$.

5. Surface exchange of ammonia and interacting chemical species

5.1. Above-canopy ammonia fluxes with the rape canopy

The net flux of NH$_3$ was found to be bi-directional, with the largest emission fluxes during the day and

![Fig. 3. Comparison of sensible heat flux (H) measured with three ultrasonic anemometers and a profile of cup anemometers for an example period (20–22 June). Ultrasonic anemometers are denoted by their height above ground. For clarity, an additional estimate by the ultrasonic anemometer at 4.74 m using the signal analogue output is not shown. The weighted mean of the relative standard deviation for the whole dataset is 26%.](image-url)
Fig. 4. Example diurnal course of NH$_3$ fluxes (top) and concentrations (bottom) as measured with two AMANDA systems (CEH and UPM), each measuring at three heights above the canopy, as well as filter packs at five heights. Data are for 15 June 1995. Positive fluxes denote emission.

smaller deposition fluxes mostly occurring at night. The availability of the two gradient AMANDA systems together with the filter packs provided the opportunity for intercomparison between the different methods (Sutton et al., 2000). This showed that reliable measurement of NH$_3$ concentration gradients is still the major uncertainty in determining NH$_3$ fluxes despite the availability of the sensitive continuous denuder technology. Another major constraint was malfunctioning of the equipment, which, together with the need for frequent inter-calibrations, resulted in many periods when only one of the AMANDA systems provided reliable data. A typical example of the diurnal variation of the NH$_3$ flux is shown in Fig. 4, which also demonstrates the intercomparison between flux estimates. For the period where both the CEH and UPM systems were working and the filter pack measurements took place, the agreement for $\chi_a$ is very close (<15% relative S.D.). The agreement of $F_t$ is still encouraging, but not as close since the estimates derive from smaller changes in the vertical NH$_3$ profile.

Fig. 4 illustrates an interaction between $\chi_a$ and the direction of $F_t$ that was observed for much of the experiment and which has implications for modelling NH$_3$ exchange. Generally, deposition occurred at night often with small fluxes as a consequence of stable conditions and limited atmospheric turbulence. During these periods of deposition, increases in $\chi_a$ couple with larger deposition fluxes. This behaviour is well established for pollutants which are generally deposited (e.g. SO$_2$, HNO$_3$, O$_3$) and underpins the classical ‘inferential’ application of the resistance modelling approach, where $F_t$ is inferred from estimated transfer resistances ($R$) and pollutant concentrations which are provided from monitoring at a reference height ($z$), e.g.

$$F_t = \frac{-\chi_a(z)}{R_a(z) + R_b + R_c}$$

with $R_a(z)$, $R_b$ and $R_c$ being the aerodynamic, quasi-laminar boundary-layer and canopy resistances, respectively. During the daytime over the oilseed rape (Fig. 4), however the occurrence of emission clearly indicates the existence of a non-zero NH$_3$ concentration at the canopy surface. Defining this average surface concentration as the ‘canopy compensation point’ ($\chi_c$), the resistance analogy may be expressed as (Sutton et al., 1993a)

$$F_t = \frac{[\chi_c - \chi_a(z)]}{R_a(z) + R_b}$$

Whereas Eq. (1) is only applicable for deposition, Eq. (2) describes both emission and deposition situations. For a constant value of $\chi_c$, a similar response
of \( F_t \) to increasing \( \chi_a \) is expected as in Eq. (1) with a larger value of \( \chi_a \) providing either enhanced deposition or reduced emission. Fig. 4, however, shows the opposite to occur during the day, with \( F_t \) becoming more positive in relation to larger \( \chi_a \). This is counter-intuitive if \( F_t \) is considered as a consequence of the concentration potential difference driven by changes in \( \chi_c \). A likely explanation is that the change to emission during the day is driven primarily by variation in \( \chi_c \), so that the increased emission results in larger \( \chi_a \). Although not universally clear in the data with other factors affecting \( \chi_a \), this pattern is also seen on several other days in the experiment (Sutton et al., 2000). The positive effect of emissions on air concentrations is a basic principle seen in dispersion modelling. However, it is a new step to consider this in relation to bi-directional NH3 exchange linked to a compensation point. The consequence is that while the bi-directional model (Eq. (2)) may, in principle, be applied in an inferential approach as used with Eq. (1), the coupling with monitored \( \chi_a \) is expected to result in errors in estimated \( F_t \). Ideally, resistance modelling of bi-directional NH3 exchange should be built directly into atmospheric dispersion models, thereby allowing the feedback between \( \chi_a \) and \( F_t \).

The mean values and variability of NH3 fluxes during the experimental periods are summarized in Table 3. Net fluxes were 3.5 times larger for the post-cutting period than during the main part of the experiment for the ripening canopy. Considering the components of Eq. (2), this could have been either due to a larger value of \( \chi_c \) or smaller exchange resistances, but not due to smaller \( \chi_a \), since this was larger in the second measurement period (Table 2). While the rougher surface of the cut canopy would promote increased turbulence (reducing \( R_a \) and \( R_b \)), the main change is almost certainly due to an increased contribution of leaf litter emissions (Section 5.3) to \( \chi_c \), which for the first measurement period are largely recaptured by the overlaying canopy. In addition the onset of the decomposition of the cut crop, resting on the stubble, may have contributed to the NH3 volatilization.

Sutton et al. (2000) report the intercomparison between the passive flux samplers and AMANDA flux estimates. Although close agreement (within 25%) was found, the degree of scatter suggests that this was partly fortuitous and that much longer inter-comparisons (>2 months) are required to validate the method. A linked implication is that this method would provide a minimum time resolution of 1–2 weeks for typical fluxes over arable croplands.

### Table 3

<table>
<thead>
<tr>
<th>Period</th>
<th>Coverage</th>
<th>Mean</th>
<th>Standard deviation</th>
<th>Min.</th>
<th>Max.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-cutting</td>
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<td>16.4</td>
<td>25.4</td>
<td>−148.2</td>
<td>178.5</td>
<td>2270</td>
</tr>
<tr>
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<td>56.8</td>
<td>81.8</td>
<td>−197.0</td>
<td>622.2</td>
<td>1244</td>
</tr>
</tbody>
</table>

a The field was cut on 22/7/1995. Positive fluxes denote emission. \( n \): number of observations.

5.2. Leaf apoplastic ammonium and pH as determinants of NH3 exchange

The measurements of rape apoplastic concentrations which were made throughout the experiment showed relatively stable values, although there was a possible small increase toward the end of measurement period (Husted et al., 2000). The canopy leaves were considered in three different fractions, low, mid and high canopy, with Husted et al. (2000) showing a trend of increasing apoplastic NH4+ and decreasing pH lower down in the canopy.

The net interaction between pH, NH4+ and temperature may be expressed with a range of different parametrizations (e.g. Farquhar et al., 1980; Sutton et al., 1993b; Husted and Schjoerring, 1995). Nemitz et al. (2000b) provide the following simplified empirical form:

\[
\text{NH}_3(g) = \frac{161512}{T}10^{-4507.11/T}\frac{[\text{NH}_4^+]}{[\text{H}^+]} \tag{3}
\]

where all concentrations are in mol l\(^{-1}\) and \( T \) is the temperature in Kelvin. From this it can be seen that, for
a given temperature, the equilibrium NH$_3$ concentration is proportional to the ratio [NH$_4^+$]/[H$^+$], which is here termed $\Gamma$. NH$_3$(g) is a strong function of temperature and doubles approximately every 5°C. From Eq. (3), it can be seen that spatial and temporal variation in $\chi_s$ will result both from changes in apoplastic chemical composition through $\Gamma$ and from changes in temperature. For the profile of live leaves within the canopy reported by Husted et al. (2000), the decreasing pH with decreasing height more than compensates for the increase in NH$_4^+$, so that $\chi_s$ is smaller for the lower leaves (0.5 m) compared with the higher leaves (0.75, 1.25 m).

A key question for developing models of NH$_3$ exchange is whether $\Gamma$ might vary diurnally in response to altering metabolic activity, e.g. respiration, photosynthesis and photorespiration. In addition to the twice daily measurements throughout the experiment, two 24 h campaigns of intensive sampling were made to address this (Husted et al., 2000). The results of one of these periods are shown in Fig. 5. Typical apoplastic [NH$_4^+$] was 0.2–0.4 mM with pH 5.9–6.2 and $\Gamma$ in the range 220–460. There was no clear change in these values during the day, and the scatter was probably due to measurement uncertainties and natural variability. The lack of a diurnal pattern in $\Gamma$ is important as it makes modelling much simpler. The major diurnal control on $\chi_s$ is therefore temperature. According to Eq. (3) with $\Gamma = 350$, the value of $\chi_s$ increases from 0.41 $\mu$g m$^{-3}$ NH$_3$ at 10°C to 1.43 $\mu$g m$^{-3}$ at 20°C and 4.30 $\mu$g m$^{-3}$ at 30°C.

The measurement of apoplastic conditions focused on live leaves since the extraction techniques have been developed for these. A large part of the plant surface area was, however, accounted for by developing siliques. Although it was of interest to measure the silique apoplastic concentrations, lack of a developed protocol prevented this. A sound procedure is important since incorrect extraction can result in errors in the calculations as well as contamination from the cytoplasm (Husted and Schjoerring, 1995). A similar constraint applied to dead and decaying leaves lying on the soil surface, which were implicated as being a source of NH$_3$ emission (Section 5.3). For decomposing leaves the distinction between apoplast and symplast is largely removed due to cell breakdown. For these plant parts a guide to the values of $\chi_s$ was provided by measurement of pH and NH$_4^+$ concentration in whole tissue extracts. These confirmed the very high concentrations in decaying leaves, with $\Gamma$ up to 14 300, which probably result from fungal decay and proteolysis in the decomposing leaves (Husted et al., 2000; Nemitz et al., 2000a,b). Data reported by Husted (1997) indicate that $\Gamma$ for whole tissue extracts of siliques is 3–5 times larger than for living leaves. This suggests that the siliques may have acted as an additional source of NH$_3$ emission.
5.3. Sources and sinks of ammonia within the rape canopy

It is clear that the canopy compensation point ($\chi_c$) defined in Eq. (2) is a composite term, which is influenced by a wide range of component sources and sinks within the canopy. In addition to exchange with a stomatal compensation point, NH$_3$ may exchange with leaf surfaces (cuticles and surface water), different parts of the rape plant (leaves, siliques) or with the ground surface. For many vegetation types, however, stomatal and cuticular exchange at the aerodynamically exposed top of the canopy is central to defining fluxes (e.g. Sutton et al., 1995c).

The initial measurements of within-canopy NH$_3$ profiles using an AMANDA were made to confirm this expected pattern. The results, however, showed unexpected large NH$_3$ concentrations of 3–15 $\mu$g m$^{-3}$ near the ground surface. Since the AMANDA denuders provide a result immediately in the field, it was possible to focus subsequent measurements to address the within-canopy source strength. These included the cuvette measurements of litter NH$_3$ emissions, detailed within-canopy concentration profiles, and determination of within-canopy turbulence for an inverse Lagrangian source–sink analysis.

The AMANDA cuvette measurements demonstrated that decomposing leaf litter was the source of the ground surface NH$_3$ emission rather than the soil itself, and this picture was later confirmed by the results from the sampling network of soil NH$_3$ concentrations (Nemitz et al., 2000a). Soil NH$_3$ (at 20 mm depth) was typically 1–2 $\mu$g m$^{-3}$, indicating that the soil would most likely have acted as a sink for NH$_3$ emitted by the decomposing leaf litter.

In all cases the within-canopy NH$_3$ profiles showed the largest concentrations to occur at the ground surface. During daytime the profile decreased to a minimum above the canopy (e.g. Fig. 6), while for the night-time runs, the minimum concentration occurred at mid-canopy. While the latter indicates that the foliage was a sink for both nocturnal litter emission and atmospheric deposition, during the day it is not immediately clear whether the net emission was the result of leaf litter or the overlaying canopy.

To quantify the sources and sinks within the canopy, the inverse Lagrangian technique (ILT) of Raupach (1989) was applied (Nemitz et al., 2000a). The ILT combines profiles of turbulence structure ($\sigma_w/\mu_a$) and Lagrangian time-scale with mean scalar (e.g. NH$_3$) profiles to estimate source and sinks strengths for different canopy layers. While this technique has been investigated elsewhere for transport of heat, water vapour and CO$_2$ (e.g. Denmead, 1995), Nemitz et al. (2000a) provide the first known application to NH$_3$ fluxes.
The ILT provided estimates of litter NH$_3$ emission in the range 0–150 ng m$^{-2}$ s$^{-1}$ for the periods analysed, but indicated that this emission was fully recaptured by the overlaying canopy (Fig. 6). For daytime runs, net emission above the canopy is estimated to derive from the top of the canopy, where the canopy consists mainly of growing siliques. For the analysed night-time runs, the ILT indicated complete recapture of soil NH$_3$ emissions. However, while this pattern may hold for much of the experiment, it does not explain some periods of nocturnal net NH$_3$ emission. These occurred during windy nights (not covered by the ILT) when increased turbulence and absence of dew would have allowed the litter emissions to escape the canopy.

While the inverse Lagrangian technique is clearly very helpful, there are still many uncertainties. Nemitz et al. (2000a) show how the calculations are most uncertain closest to the ground (the location of the litter emissions) and also more uncertain in night-time conditions, since the within-canopy turbulence was derived from daytime measurements. A further issue addressed by Nemitz et al. (2000a) is the importance of near-field effects related to transport by eddies large in comparison with the canopy structure, which is treated with the ILT, but not by earlier within-canopy gradient diffusion theory (e.g. Denmead et al., 1976). Inclusion of near-field effects improves the estimate of the above-canopy flux (Fig. 6), but only by a small amount — typically <30%. This is probably related to the dense silique layer, which promotes energy dissipation from large to smaller eddies.

5.4. Interactions of ammonia exchange with acidic species and aerosols

An important uncertainty in the quantification of atmospheric NH$_3$ fluxes with ecosystems is the potential for interaction with acid gases and aerosols. The reactions of NH$_3$ with both HNO$_3$ and HCl to form NH$_4$NO$_3$ or NH$_4$Cl are reversible and the time constants to reach equilibrium are poorly known. Enrichment of the air at the canopy surface with NH$_3$ as a consequence of NH$_3$ emission or high relative humidities near the canopy/ground may result in exceedance of the equilibrium concentration product ($K_e$) leading to formation or growth of NH$_4^+$ containing aerosol. Alternatively, with deposition of HNO$_3$, HCl and NH$_3$, depletion of concentration products near the surface might lead to aerosol evaporation. Where attainment of the equilibrium occurs on a similar or shorter time-scale as turbulent exchange, this provides an error in the classical flux gradient measurements due to production or consumption in the measurement layer. This could also be important for NH$_3$ and aerosol exchange budgets, modifying the total fluxes with the ground (Nemitz et al., 1996).

While some studies have suggested these effects to be important (e.g. Brost et al., 1988; Kramm and Dlugi, 1994), other authors have not detected any effect (e.g. Harrision et al., 1989). Allen et al. (1989) argued that thermodynamic constraints limit attainment of the equilibrium, although this may only apply for cool (<10°C) and humid conditions.

To address the extent of these interactions, parallel measurements of HNO$_3$, HCl, and aerosol gradients were determined, which also provided information on fluxes of each component (Nemitz et al., 2000c). The results showed small concentrations, with [NH$_3$][acid gas] concentration products ($K_m$) at 1 m being much less than $K_e$. Under these conditions any NH$_4$NO$_3$ and NH$_4$Cl would tend to form the component gases. For measured aerosol size distributions and small aerosol concentrations during the experiment, Nemitz et al. (2000c) show that chemical time-scales for reaching equilibrium ($\tau_c$, Wexler and Seinfeld, 1990) would have been much longer than the time-scale of turbulent exchange above the canopy ($\tau_t$). During the experiment typically, $\tau_t > 0.1\tau_c$ only where $u_s < 0.02$ m s$^{-1}$. Hence the effect would have only been significant in calm conditions where stability corrections are uncertain and net fluxes small.

The flux measurements of the atmospheric acids were unexpected in suggesting bi-directional exchange for HCl. While the HNO$_3$ gradients were highly uncertain, with HNO$_3$ concentrations being at the limits of detection, the HCl measurements were more consistent, with mostly HCl emission from the canopy (Nemitz et al., 2000c). Measurements have often indicated efficient deposition of HNO$_3$ and HCl, with $V_d$ approaching $1/(R_a + R_b)$ (e.g. Huebert and Robert, 1985; Harrision et al., 1989), and this observation has been taken as reasonable given the ‘stickiness’ and high water solubility of these gases. Nevertheless, bi-directional gradients of HNO$_3$ have
been observed elsewhere (Neftel et al., 1996). The mechanism of the HCl emission here is not certain, but Nemitz et al. (2000c) provide a detailed consideration of the possible sources (leaf litter, apoplastic Cl\(^-\), cuticular reactions with HNO\(_3\), reaction from emitted CH\(_3\)Cl). A key finding of Nemitz et al. (2000c) is that the within-canopy sources of HCl and NH\(_3\) result in \(K_m > K_e\) permitting aerosol formation within the canopy, particularly in warm, high humidity conditions. \(\tau_t\) is also much longer within the canopy, which would permit more reaction than immediately above the canopy. While this effect would not violate the applicability of micrometeorological techniques to measure above-canopy fluxes, it would mean that the net fluxes are not just a result of direct exchange with plant tissues and surfaces. Given the available concentrations, 100% reaction of the HCl would have affected NH\(_3\) emissions by up to 30%. Hence, the actual effect on NH\(_3\) fluxes was probably rather small (<5%). However, the within-canopy effect would explain parallel observations of NH\(_4\)\(^+\) aerosol emission for some runs (Nemitz et al., 2000c), even though above the canopy \(K_m < K_e\).

6. Modelling component and net fluxes of ammonia

The bi-directional fluxes of NH\(_3\) measured here represent a substantial challenge for modelling. From the measurements, it is clear that key sites of NH\(_3\) exchange include the following:

1. leaf cuticles by adsorption/desorption,
2. apoplast surfaces in sub-stomatal cavities with a compensation point, \(\chi_s\), which may differ between leaves and siliques,
3. fallen abscised leaves in relation to decomposition rates and capacity to store NH\(_4\)\(^+\).

This is more complicated than for many other canopies, both because of the contribution of each of these processes and because they take place at different heights within the canopy. On the other hand, the additional complexity of modelling fluxes including above-canopy gas–particle reactions is avoided for the clean conditions here, while within-canopy reactions, although potentially significant for aerosol NH\(_4\)\(^+\) budgets, would have only a small effect on the NH\(_3\) fluxes.

For semi-natural canopies with low nitrogen status and hence small \(\chi_s\), the net flux is generally dominated by exchange with plant cuticles (e.g. Sutton et al., 1993a; Duyzer, 1994), and the resistance model of Eq. (1) is often sufficient. Emissions from the ground surface are not expected to be significant for many systems, especially where litter is acidic such as for moorlands. Complexity arises in modelling such fluxes where occasional emission fluxes occur, which may result from cuticular desorption as well as some stomatal emission (Erisman and Wyers, 1993; Sutton et al., 1995a).

Over agricultural vegetation the exchange pattern is clearly bi-directional with both emission and deposition regularly occurring. The higher N status of plant leaves is related to increased apoplastic concentrations of NH\(_4\)\(^+\) leading to a significant value of \(\chi_s\). Controlled measurements under laboratory conditions have demonstrated that exchange may be related to \(\chi_s\) (e.g. Farquhar et al., 1980; Schjoerring et al., 1998), particularly where low humidity, steady-state conditions are used to limit exchange with plant cuticles. By contrast, in the field cuticular exchange processes are clearly recognized as important (Sutton et al., 1995a, 1998a). However, apart from immediately after fertilization when soil emissions may be important, exchange appears to be regulated by the plant foliage including both stomatal and cuticular exchange (Schjoerring et al., 1993; Sharpe and Harper, 1995; Neftel et al., 1998; Sutton et al., 1998a). A simple 1-layer model has been introduced to describe the exchange process accounting for both cuticular adsorption and stomatal exchange with a compensation point (Sutton et al., 1995c, 1998a), and this is illustrated in Fig. 7a. The model depends on the calculation of the canopy compensation point, \(\chi_c\), of Eq. (2), and has been successfully applied to describe bi-directional fluxes of NH\(_3\) for a range of canopies (e.g. Sutton et al., 1995c, 1998a, 1999; Wyers and Erisman, 1998).

For the oilseed rape canopy here, Nemitz et al. (2000b) show that the \(\chi_c\) model of Fig. 7a reproduced daytime emissions, but failed to give any emissions at night (Fig. 8). It is clear that the 1-layer model fails where leaf litter emissions escape the canopy in windy nocturnal conditions (after midnight on 13 June). The model value of \(\chi_s\) needed to provide agreement with the measurements shows another limitation. Using \(\Gamma = 350\) from the apoplastic measurements of
Fig. 7. Two example resistance models of ammonia exchange with plant canopies: (a) 1-layer canopy compensation point model according to Sutton et al. (1995c), (b) 2-layer foliage–litter canopy compensation point model of Nemitz et al. (2000b). $F$, flux; $R$, resistance; $\chi$, NH$_3$ concentration in air. The subscripts are: a, aerodynamic; b, boundary-layer; ac, in-canopy turbulent; s, stomatal; w, leaf cuticle; l, litter. $\chi_s$ and $\chi_c$ are the stomatal and canopy compensation points, respectively, and $F_t$ is the net flux.

Husted et al. (2000) significantly underestimated daytime emissions, with a value of $\Gamma = 1200$ being required to reproduce the measured flux. At $\approx 3.5$ times the measured $\Gamma$, this is consistent with the larger values expected for the siliques (Section 5.2).

As a first stage to describe the leaf litter emissions, Nemitz et al. (2000b) present a 2-layer canopy compensation point model (Fig. 7b). The key new terms are $\Gamma$ for the decomposing litter ($\Gamma_l$) and the in-canopy turbulent and boundary-layer resistances ($R_{ac}$, $R_b$). The performance of this model, as shown in Fig. 8, is very encouraging, particularly since for this period $\Gamma_l$ was set to a constant of 13,000, only slightly larger than the values measured for bulk litter extracts. It should be noted, however, that this model (using measured $\Gamma_s$) could not reproduce the vertical

Fig. 8. Application of the models shown in Fig. 7 to exchange over the oilseed rape field at late flowering (12–13 June). The measured net flux is compared with two models assuming (a) 1-layer canopy compensation point model ($\chi_s$–$R_w$ model) with $\Gamma_s$ according to either the measured leaf apoplastic concentrations ($\Gamma_s = 350$) or an assumed value for siliques ($\Gamma_s = 1200$), (b) 2-layer ‘foliage–litter model’ with leaf litter emissions based on $\Gamma_l$ for bulk litter extraction ($\Gamma_l = 13,000$) together with measured $\Gamma_s$ for leaf apoplasts.
source–sink structure indicated by the inverse Lagrangian technique: although the ILT indicated that daytime emissions resulted from emissions at the top of the canopy (the siliques), all net emissions in the 2-layer model derive from the leaf litter.

Nemitz et al. (2000b) advance this position through the development of a 3-layer ‘foliage–litter–silique’ model. This represents a major increase in complexity, and necessitates partitioning the bulk canopy values of $R_s$ and $R_w$ into estimates dependent on canopy leaf area and stomatal density. Nemitz et al. (2000a,b) also developed an initial dynamic model to predict $\Gamma_l$, incorporating temperature and humidity effects on water content, mineralization and volatilization, and they test a simplified parameterization of $\Gamma_l$ as a function of relative humidity for the inclusion in the 3-layer model. The 3-layer model provides a much closer description to that shown by the ILT, and provides a helpful tool both to predict net fluxes and quantify component fluxes. To illustrate the cycling of NH$_3$ within the canopy, Fig. 9 contrasts the mean day- and night-time component fluxes for the first experimental campaign as predicted by this model. Night-time $\Gamma_l$ is larger than during the day (due to increased humidity and mineralization), and despite cooler temperatures the litter compensation point ($\chi_l$) is therefore larger at night. However, with larger $R_{ac}$ and $R_b$ at night, the mean litter emission is estimated to be the same as during the day. The mean modelled night-time fluxes indicated that all the litter emission is recaptured, mostly onto leaf and silique cuticles. This permits a small modelled net NH$_3$ deposition of $-3$ ng m$^{-2}$ s$^{-1}$, which is close to the measured mean of $+2$ ng m$^{-2}$ s$^{-1}$. During the day the canopy is a source, with the model estimating a net flux of $22$ ng m$^{-2}$ s$^{-1}$, compared with a measured mean of $25$ ng m$^{-2}$ s$^{-1}$; most of the litter emission is recaptured, with the net flux largely due to emission from silique stomata.

Fig. 9. Three-layer ‘foliage–litter–silique model’ of ammonia exchange with a maturing oilseed rape canopy showing: component resistances ($R$), fluxes (ng m$^{-2}$ s$^{-1}$, bold numbers), and NH$_3$ concentrations ($\chi$, µg m$^{-3}$, italic numbers). The values are mean model estimates for the period 6–27 June (Nemitz et al., 2000b), with arrows indicating the direction of the flux. The resistances are: a, turbulent atmospheric; b, boundary-layer; ac, in-canopy turbulent; s, stomatal; w, leaf cuticle. Different parts of the canopy are indicated by: q, siliques; f, foliage and l, litter. $\chi_s$ and $\chi_c$ are the stomatal and canopy compensation points, respectively.
7. Implications for estimation of regional ammonia budgets

7.1. Modelling approaches

The bi-directional exchange of NH$_3$ measured over oilseed rape demonstrates the need for models which take account of compensation points within the plant canopy. As a result, atmospheric transport models (ATMs) using the simplified deposition velocity approach are expected to provide inaccurate estimates of transport distances and regional budgets.

The 1-layer canopy compensation point model has been shown to be adequate for many canopies. However, for oilseed rape the occurrence of significant leaf litter emissions results in it only being able to reproduce part of the flux. Both the 2- and 3-layer models are, nevertheless, able to explain the fluxes, with the 3-layer model being mechanistically most accurate. Potentially, the 3-layer model could be incorporated into ATMs. However, this is much more complex to parametrize than the 2-layer model, and it would be a major effort to extend it to other canopies. The most suitable surface exchange model to implement in ATMs should provide a balance between simplicity and adequate process description.

It is considered here that the 2-layer ‘foliage–litter’ model best meets this balance — both for oilseed rape and for other canopies. As the canopy foliage is treated as a single layer and the resistances $R_a$ and $R_b$ are large, the model automatically simplifies to the 1-layer $\chi_c$ model of Sutton et al. (1995c), wherever $\Gamma_1$ is small. Hence the parametrization of each of the terms $\chi_c$, $R_w$, $R_s$, $R_a$ and $R_b$ remains identical in both models. The 2-layer model simply has the advantage that it can also deal with emissions from the ground surface.

Although inferential models may be applied for NH$_3$, estimating fluxes from monitored $\chi_d$, component resistances and compensation points, the results here indicate that this is best restricted to estimating inputs to semi-natural land, where deposition dominates. In the case of bi-directional fluxes, it is seen that $\chi_d$ may become positively correlated to the emission flux, rather than the other way round. This clearly points to the need to incorporate the bi-directional resistance models directly into ATMs.

It is recognized that ATMs must include a full description of the atmospheric cycle of ammonia and therefore exchange of NH$_3$ with agricultural croplands, as illustrated here by oilseed rape, is only part of the analysis. Information on the dynamics of all emissions, together with cloud processing and wet deposition are also needed. However, estimation of net exchange fluxes of NH$_3$ and NH$_4^+$ containing aerosol has long been recognized as highly uncertain. Inclusion of bi-directional exchange and compensation points in ATMs will affect the linearity of relationships between emission, concentrations and deposition. Hence inclusion of these effects is relevant in establishing atmospheric budgets, as well as the relationship between emission abatement policies and expected changes in concentrations and deposition.

The 2-layer model proposed here has general relevance to most vegetation canopies including semi-natural land, agricultural grasslands and arable land. In order to take this approach further forward, information needs to be collected on the seasonal values of $\Gamma_1$, $\Gamma_1$ and $R_w$ for different canopies, together with basic information on canopy structure and regional landcover.

7.2. Consequences for regional budgets

As noted above, the NH$_3$ fluxes measured in the North Berwick experiment and the derived models both have consequences for estimation of regional atmospheric budgets of NH$_3$. Most simply, the results indicate that foliar–litter NH$_3$ emissions may have been underestimated in generalized emission inventories. Similarly, persistent emissions of HCl from oilseed rape is a new finding, and this would for example permit increased formation of NH$_4^+$ containing aerosol. Although above-canopy gas-to-particle conversion can largely be ruled out for the clean conditions here, within-canopy reactions are possible and could also enhance regional aerosol production.

The bi-directional nature of NH$_3$ exchange will have a major effect on the atmospheric residence time ($r_d$) of NH$_3$. Over regions dominated by semi-natural land, where removal rates are large, $r_d$ will be much shorter than in arable regions, where crop emissions add to the atmospheric NH$_3$ load (Sutton et al., 1994). A further key issue is the coupling between the direction of the NH$_3$ flux with agricultural land and environmental conditions (e.g. light, wetness, temperature). As a result $r_d$ will not just vary spatially, but also with time. In
warm, dry conditions, large crop emissions may couple with a lack of precipitation allowing a substantial regional export of NH₃. By contrast, in wet conditions, the residence time of point source NH₃ emissions will be much smaller both because of precipitation scavenging and more efficient deposition to agricultural and non-agricultural vegetation. The non-linearity inherent in averaging these conditions for different times will result in simplified ATMs incorrectly estimating net transport over the longer term. For example, as $\tau_d$ is expected to correlate positively with emissions, mean values of $\tau_d$ may be larger than estimated in current models, indicating longer average transport distances.

8. Uncertainties and directions for further work

In addition to the major advances in quantifying NH₃ exchange, the work has highlighted the key uncertainties in both flux measurements and modelling. Estimation of accurate NH₃ fluxes still dominates the measurement uncertainties and continued work is needed on the continued development of sampling systems. Similarly, the apoplastic bioassay is a helpful complement to the micrometeorological estimates; here further work is required to extend it to reproductive plant parts and decomposing vegetation. The inverse Lagrangian analysis also proved powerful in identifying within-canopy sources and sinks and key advances needed here are treatment of stability effects, as well as improved input data to reduce uncertainties in estimating within-canopy turbulence close to the surface.

For the modelling NH₃ exchange, the 1-, 2-, and 3-layer resistance models have been shown to be robust in predicting fluxes. The key issues for further work here are to improve the parametrizations of the model terms, such as $R_w$, $\Gamma_s$ and $\Gamma_1$ and to generalize them for a wide range of crops and ecosystems. For $\Gamma_1$, Nemitz et al. (2000a) have developed an initial dynamic model, however it is clear that much more work is required to improve the simulation of decomposing litter emissions. The challenge for $R_w$ is to improve the relationships to wetness (either relative humidity or vapour pressure deficit) and leaf surface chemistry (e.g. in relation to other pollutant depositions). Having established that most of the short term temporal variability of $\chi_s$ is due to the temperature response, work is needed to build datasets of $\Gamma_s$ for different plant growth stages, as well as different ecosystem types, such as grasslands and semi-natural land (Sutton et al., 1999). So far, ongoing work is focusing on the application of the apoplastic bioassay, as well as long-term flux measurements. However, there is a clear need for linking functional ecosystem modelling of plant nitrogen fluxes to $\Gamma_s$. If progress can be made here, important possibilities will open up for considering the effects of different management practices on NH₃ fluxes with agricultural crops.

Finally, it is clear that further work is required on the exchange processes of aerosols and acid gases with which NH₃ interacts. The mechanistic basis for HCl emissions from oilseed rape and other agricultural vegetation, as well as potential HNO₃ should be investigated. In addition, work at polluted locations, where the concentration products of NH₃ with these acid gases are exceeded, is still required to quantify the interaction of gas–particle inter-conversion and exchange fluxes, both within and above plant canopies. Even where effects on NH₃ fluxes are secondary, this may be important in relation to budgets of NH₄⁺ containing aerosol, with implications for transport distances and radiative scattering.

9. Conclusions

The North Berwick field experiment has provided continuous measurements of net NH₃ fluxes for approximately 30 days over oilseed rape, together with periods of NH₄⁺ aerosol, HCl and HNO₃ fluxes. Attention has been given to quantifying the different components contributing to net fluxes, to assessing the importance of gas–particle reactions on the measured fluxes, and to applying the measurements to model the NH₃ exchange process. It is concluded that the following holds:

1. Application of continuous AMANDA denuders has provided a major database of the time course of NH₃ fluxes over oilseed rape with over 3000 10 min mean values. By using replicated AMANDA systems together with filter packs, it was possible to screen the measured values for inconsistencies as well as determine within-canopy
NH₃ gradients. Use of a range of methods to estimate friction velocity, sensible and latent heat fluxes allowed reliable determination of the turbulent exchange parameters driving NH₃ fluxes. Passive sampler estimates of NH₃ fluxes were consistent with the AMANDA measurements, although the large uncertainties indicate that longer intercomparisons are required.

2. Above-canopy exchange of NH₃ over the oilseed rape was bi-directional, with mostly daytime emission and small deposition at night. The emissions were generally larger than previously measured over crops in UK, with periods of emission also occurring at night. Ten minute mean fluxes during late flowering were in the range -150 to +180 ng m⁻² s⁻¹, and following cutting -200 to +620 ng m⁻² s⁻¹, where positive fluxes denote emission. The larger fluxes are consistent with a relatively high fertilizer input of 285 kg N ha⁻¹ compared with other arable crops, although such values are typical for oilseed rape.

3. Net emissions of NH₃ over the whole measurement period totalled 0.7 kg N, and were larger following cutting. Separating the up and down fluxes for the measurement period provided a total emission of 0.8 kg N ha⁻¹ and a total deposition of 0.1 kg N ha⁻¹. Extrapolation to the months of May–August suggests a net emission of around 2.5 kg N ha⁻¹.

4. Temporal variability of the fluxes for individual days was related to canopy wetness, friction velocity and the surface energy balance which affected the magnitude of the NH₃ canopy compensation point (χₛ). Larger emission fluxes during daytime periods were positively correlated with air concentrations (χₐ) at 1 m, while larger air concentrations during the post-cutting period are also consistent with increased net emissions. This implies a feedback on χₛ, with net fluxes controlled more by variation in χₖ than χₛ.

5. A major determinant of χₖ for croplands is the compensation point within the sub-stomatal cavity (χₛ), and the experiment included the first parallel estimates of χₛ by apoplastic extraction in the field and micrometeorological measurements. The apoplastic extraction gave typical values of pH 5.9–6.2 and NH₄⁺ concentrations of 0.2–0.4 mM. This provided values of Γ = [NH₄⁺]/[H⁺] in the range 220–460. The average value of Γ is equivalent to χₛ of 0.4, 1.4 and 4.3 μg m⁻³ at 10, 20 and 30°C, respectively. The temperature dependence indicates the potential for larger NH₃ emissions in conditions warmer than experienced here for southern Scotland.

6. Estimates of χₛ for the canopy as a whole by the micrometeorological approach suggested much larger values than by the apoplastic bioassay for the live leaf fraction. This may be explained by the presence of additional sources in the canopy, including siliques (seed cases) and the ground surface. Although it was not possible to measure siliques apoplastic concentrations, whole tissue measurements suggested higher NH₄⁺ concentrations in siliques than in leaves. Within-canopy measurements showed large concentrations near the ground (3–15 μg m⁻³), indicating a surface source of NH₃. Cuvette measurements showed that the source was decomposing abscised rape leaves. By contrast, soil gas NH₃ concentrations of typically 1–2 μg m⁻³ indicated that the soil was a sink for NH₃.

7. The inverse Lagrangian technique was applied for the first time to quantify NH₃ source/sink strength of different layers within a plant canopy. The technique showed NH₃ emissions from the rape litter layer of 3–60 ng m⁻² s⁻¹. During daytime, litter emissions were estimated to be recaptured in the canopy, with net emission being controlled by the siliques. The night-time runs showed deposition to the dew wetted canopy from both the atmosphere and the leaf litter. Night-time net emissions occurred especially on windy nights when litter emission would be less efficiently recaptured by the overlying canopy.

8. Concentrations of NH₄⁺ aerosol as well as HNO₃ and HCl were rather small during the campaign so that little effect of gas–particle inter-conversion on the measured fluxes should be expected. This finding can be extended widely to NH₃ fluxes in clean, cool-temperate air masses. However, gradients of HCl indicated bi-directional exchange fluxes, with mostly emission from the canopy. The latter observation is contrary to the usual assumption in models, and may result from either a physiological source of HCl, decomposition of...
liberated CH₃Cl, or leaf cuticle reactions with deposed NaCl.

9. The increased concentrations of HCl and NH₃ together with longer turbulent residence times in the canopy would have been sufficient to permit in-canopy production of NH₄Cl aerosol, even though the above-canopy concentration product was less than the equilibrium value. Such in-canopy effects would allow increased production/growth of fine aerosol. This is a relevant issue for estimating atmospheric aerosol loadings, with potential consequences for global radiative forcing.

10. A 1-layer canopy compensation point model, incorporating χ₈ based on measured apoplastic values, was unable to reproduce measured fluxes. A larger value of χ₈ (with Γ = 1200) would be required to fit typical daytime emissions and be consistent with expected values for the siliques. However, the 1-layer model cannot explain the nocturnal NH₃ emissions. These fluxes can be explained using 2- and 3-layer models incorporating emissions from the abscised decomposing leaves, based on the measured values of Γ for bulk litter, and for the 3-layer model a separate Γ for siliques and leaves. The current major uncertainties in applying the models more widely are the parametrization of litter NH₄⁺ and pH dynamics, and estimates of G for siliques.

11. The 3-layer model is mechanistically most accurate and may be used to estimate the component fluxes of NH₃ in different parts of the rape canopy. However, for generalized application in atmospheric transport models (ATMs), the 2-layer model is sufficient, and this model is therefore recommended for general application.

12. Given the feedbacks between bi-directional fluxes and NH₃ concentrations, the compensation point resistance models are best applied directly into ATMs, rather than as inferential models. Averaging fluxes to give simplified deposition velocity estimates in ATMs is expected to have a non-linear effect on regional NH₃ budgets. For example, a positive correlation between air concentration and residence time would indicate longer mean atmospheric transport distances for NH₃ than estimated using average values.

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