Sources and sinks of ammonia within an oilseed rape canopy

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Abstract

Within-canopy profiles of ammonia (NH₃) and measurements of the canopy turbulence characteristics were used to calculate the vertical source/sink density profile of NH₃ and sensible heat in a mature oilseed rape (Brassica napus) canopy. For the analysis, the inverse Lagrangian technique (ILT) based on localized near-field theory was used. Turbulence was measured with a standard ultrasonic anemometer, which, although not ideal for in-canopy work, is estimated to lead to a parameterization of the normalized standard deviation of the vertical wind component \( \sigma_w/u_w \), which is ±11% accurate for heights >0.16 m during the day.

The NH₃ profiles in the canopy consistently show largest concentrations at the ground caused by NH₃ release from decomposing litter leaves on the ground surface with values of up to 150 ng m⁻² s⁻¹ predicted by the ILT. The inverse Lagrangian source/sink analysis performs well for both sensible heat and NH₃, although it proves to be sensitive to the choice of the source/sink layers and becomes uncertain at the ground. Despite the large estimated ground level emission (26 g NH₃-N ha⁻¹ per day), the analysis indicates that for the runs considered all NH₃ is recaptured by the lowest 0.7 m of the 1.38 m tall canopy, and that the bi-directional net exchange with the atmosphere is governed by the top 0.5 m, leading to a net emission from the canopy of 12 g NH₃-N ha⁻¹ per day. Since measurements of apoplastic \([\text{NH}_₄^{+}]\) and pH indicate that no significant stomatal emission from foliage should have occurred, this suggests that the siliques were a further source of NH₃.

Keywords: Ammonia exchange; Inverse Lagrangian technique; Localized near-field theory; Brassica napus; Canopy layer turbulence; Within-canopy profiles; Source/sink distribution

1. Introduction

Ammonia has been recognized as one of the major atmospheric pollutants with impacts on atmospheric chemistry, soil acidification and eutrophication of ecosystems, as discussed in detail elsewhere (Pearson and Stewart, 1993; Sutton et al., 1993a). In
quantifying the net exchange with different ecosystem types it is an important pre-requisite to improve the mechanistic understanding of the exchange processes as well as to identify the main pathways of NH₃ exchange. Earlier studies have shown the NH₃ exchange above agricultural crops such as wheat and barley to be bi-directional, with absorption through leaf stomata and deposition to water films on the leaf cuticle (e.g., Sutton et al., 1995). Periods of daytime emission usually originate from an ammonium concentration ([NH₄⁺]) in the apoplastic intercellular fluid (Farquhar et al., 1980; Sutton et al., 1995). Knowledge of the physical sites of NH₃ exchange and the vertical distribution of sources and sinks within the plant canopy can greatly assist the characterization of the main pathways necessary for the development of generalized resistance models (Baldocchi et al., 1997; Sutton et al., 1995; Nemitz et al., 2000a).

The mechanisms of NH₃ exchange were studied during the North Berwick experiment carried out over oilseed rape (Brassica napus) in June 1995 as part of the EC ‘EXAMINE’ project. Both the set-up and objectives of the experiment were described by Sutton et al. (2000a), whereas the NH₃ fluxes were reported by Sutton et al. (2000b). As a component of this study, this paper examines the within-canopy cycling processes of NH₃ in an oilseed rape canopy. The vertical distribution of sources and sinks within the canopy is derived from direct measurements of both the NH₃ concentration profile and the turbulence within the canopy, using the inverse Lagrangian technique (ILT) by Raupach (1989a). Since the different height-layers may be identified with characteristic plant parts (leaf litter, senescent and live leaves, seed cases), this allows their role in the net exchange to be quantified, together with the origin of NH₃ emission frequently found during the campaign. The results were incorporated into multi-layer resistance models, which could be used then to quantify component fluxes during conditions when in-canopy profiles were not measured (Nemitz et al., 2000a; Sutton et al., 2000a). For this integrated field campaign, source/sink distributions can be compared with independent plant-physiological estimates of the stomatal emission potential, derived from extractions of the apoplastic fluid at different heights (Husted et al., 2000).

In a pioneering study, Denmead et al. (1976) derived source- and sink-densities of NH₃ within a grass-clover canopy from concentration profiles, using the simplification that the transport within canopies is purely diffusive. However, more recent research has led to a quantification of non-diffusive transport mechanisms within plant canopies (Finnigan, 1979; Raupach, 1987; Denmead, 1995). Raupach (1989a,b) has incorporated these effects into an ILT based on the ‘localized near-field’ (LNF) theory. This technique is employed here to derive the diffusion matrix that relates the (one-dimensional) scalar field of 4–14 measured concentrations (χ_i) in the canopy to that of the source (or sink if negative) densities (S_j). Diffusion within the plant canopy needs to be described based on the parameterization of the standard deviation of the vertical wind component (σ_w) and the Lagrangian time-scale (T_L). Whereas the latter was taken from existing parameterizations (Raupach, 1989a), the first was obtained from turbulence measurements at different heights in the plant canopy.

In the following section of this paper, the ILT is outlined with a detailed description of its implementation in Appendix A. The paper continues with a description of the measurements of NH₃ concentrations and canopy turbulence including quality assessment of the turbulence data. The results of the turbulence measurements and example profiles of NH₃ are then presented, before the ILT is first applied to sensible heat (as a performance test) and finally to NH₃. Uncertainties in both the measurements and the applicability of the ILT are discussed, together with the implications of the findings for the quantification of NH₃ exchange over oilseed rape.

2. Theory of the inverse Lagrangian technique using ‘localized near-field theory’

As a convention, single underlined symbols represent vectors, while matrices are underlined twice. For the ILT algorithm the canopy is divided into m height layers z_j^S (j = 1, . . . , m) of different source strengths (S_j) within the plant canopy, such that the upper limit of the top layer (z_m^Sn) coincides with the canopy height (h_c). A similar set of layers may be defined for the concentrations within the canopy (χ_i) at n different heights (z_i^X, where i = 1, . . . , n), as well as an additional reference height just above the plant canopy (χ_{n+1} = X(z_{n+1}) = X_{ref}). Source strengths and
concentrations can be related to each other by a dispersion matrix \( (D) \), which consists of the matrix elements \( D_{ij} \) that describe the contribution of source layer \( z_{i}^{j} \) to the concentration at \( z_{k}^{r} \). In vector format, this relationship can be written as a linear \((n, m)\)-system:

\[
\chi - \chi_{\text{ref}} = DS
\]  

(1)

In the simple case of \( m = n \), this linear system can be solved for concentrations (forward problem) or source strengths (inverse problem), whereas for \( m < n \) an approximation method can be used to find the best fitting values of \( S_{j} \) (see Appendix A). The dispersion matrix can be formed according to any transport theory that can be appropriately applied to plant canopies. Raupach (1987) showed that only a part of the concentrations measured within canopies is the result of diffusive transport and follows the classical flux–gradient relationship that is applied to derive the net exchange above canopies

\[
F_{\chi}(z) = -K_{H}(z, L) \frac{\partial \chi}{\partial z}
\]  

(2)

Here \( F_{\chi} \) is the flux of tracer \( \chi \), \( z \) the height and \( K_{H} \) the turbulent eddy diffusivity, which is a function of height and thermal stratification, expressed by the Monin–Obukhov length \((L)\). In canopies, where the length scale of the turbulent transport is of the order of \( h_{c} \) or larger, the transfer is determined through persistent coherent (non-diffusive) eddy motions as well as through diffusive transport by eddies small in comparison with \( h_{c} \). Following Raupach (1989a), this ‘near-field’ effect of persistence dominates as long as the travel time of a released entrained property is smaller than the Lagrangian integral time-scale \((T_{L})\). Hence in plant canopies, pure Eulerian (fixed-point) diffusive theory, as applied by Denmead et al. (1976), must be expected to lead to erroneous results. More accurate results are obtained using numerical Lagrangian (fluid following) stochastic dispersion models which track the motion of small quantities of the entrained property, visualized as ‘marked particles’ (e.g., Flesch and Wilson, 1992). Raupach (1989a,b) presented an analytical approximation to the Lagrangian approach, which is applied here.

The probability to find a ‘marked particle’ at \( z_{k}^{r} \) is subject to both a persistence governed ‘near-field contribution’ \( (\chi_{i}^{\text{near}}) \) and a diffusion governed ‘far-field contribution’ \( (\chi_{i}^{\text{far}}) \) so that the total concentration \( (\chi_{i}) \) can be written as the sum of both

\[
\chi_{i} = \chi_{i}^{\text{near}} + \chi_{i}^{\text{far}}
\]  

(3)

For the far-field, the classical flux–gradient relationship of Eq. (2) is a close approximation if the usual conditions (extensive horizontal homogeneity and stationarity) are fulfilled. The integration of Eq. (2) between the limits \( z_{i}^{r} \) and \( z_{\text{ref}} \) yields an expression for the far-field contribution:

\[
\chi_{i}^{\text{far}} = \chi(z_{\text{ref}}) - \chi^{\text{near}}(z_{\text{ref}}) + \int_{z_{i}^{r}}^{z_{\text{ref}}} \frac{F_{\chi}(z)}{K_{H}(z)} \, dz
\]  

(4)

The height dependent flux \( F_{\chi}(z) \) can be calculated as the integral over the source and sink layers:

\[
F_{\chi}(z) = \int_{0}^{z_{i}^{r}} S(z) \, dz
\]  

(5)

and the eddy diffusivity \((K_{H})\) within the canopy is given by

\[
K_{H} = \sigma_{w}^{2} T_{L}
\]  

(6)

Raupach (1989b) derived a ‘near-field kernel function’ of a variable \((\xi)\) which represents the non-diffusive ‘near-field’ contribution to the concentration as

\[
k_{\alpha}(\xi) = -0.39894 \ln(1 - \exp(-|\xi|))
\]

\[-0.15623 \exp(-|\xi|)
\]  

(7)

Using this function, it can be shown that the near-field concentration is given by

\[
\chi_{i}^{\text{near}} = \int_{0}^{\infty} S(z) \left[ k_{\alpha} \left( \frac{z_{i}^{r} - z}{\sigma_{w}(z) T_{L}(z)} \right) + k_{\alpha} \left( \frac{z_{i}^{r} + z}{\sigma_{w}(z) T_{L}(z)} \right) \right] \, dz
\]  

(8)

An approach by which Eqs. (3)–(8) can be turned into finite sums and used to calculate the diffusion matrix for Eq. (1) is demonstrated in Appendix A. Redundant concentrations \((m < n)\) can be used to obtain more stable solutions for the source profile (Raupach, 1989a), a concept that was adapted here. Comparisons of the LNF theory with random flight models and the assessment of the magnitude of the near-field contributions have been presented elsewhere (Raupach, 1989a,b;
van den Hurk and McNaughton, 1995). Raupach’s LNF theory has been successfully applied to fluxes of CO₂ and water vapour (Denmead, 1995; Katul et al., 1997).

Apart from the concentration profile, a description of the turbulence characteristics in the oilseed rape had to be obtained. Naturally, the Lagrangian time-scale ($T_L$) cannot be measured by one instrument fixed in space and here existing parameterizations had to be used. Below the canopy height, Raupach (1989a) suggested a height constant parameterization of $T_L = 0.3 h_c/u_*$, where $u_*$ is the friction velocity as measured well above the canopy. Since it appears that no parameterizations of the standard deviation of the vertical wind component ($\sigma_w$) have been presented in the literature, that are readily applicable or at least transferable to oilseed rape canopies, $\sigma_w(z)$ was directly measured in the rape canopy.

3. Methods

3.1. Measurements of gas concentrations within the canopy

The ammonia concentrations were measured with two independent techniques, continuous wet denuder systems (‘AMANDA’, ECN, Petten, NL; see Wyers et al., 1993) and filter-packs, which are described in more detail by Sutton et al. (2000b). Twice during the main 3-week campaign (14–15 and 21–22 June), four of the six denuder inlets were placed at heights of 0.04, 0.2, 0.5 and 1 m above ground within the oilseed rape canopy ($h_c = 1.38$ m), whereas two additional inlets were used to measure the net flux above the canopy (1.68 and 3.32 m above the ground). Although the AMANDA systems represent the state-of-the-art of high precision NH₃ air concentration measurements, the use of two separate conductivity cells to analyse the collection solution of the six denuder inlets on-line, made it necessary to cross calibrate the two three-point systems and to apply correction factors where necessary.

For individual runs (approximately 2 h) three-stage 90 mm filter-packs were used to yield the NH₃ concentration at another up to 10 heights. Seventeen within-canopy filter-pack runs were carried out during on 14 June (12:00–20:00 GMT), 15 June (05:00–20:00 GMT), 19 June (14:00–20:30 GMT) and 21 June (12:00 GMT) to 22 June (14:00 GMT). The filter-packs contained a PTFE particle filter, a basic filter for capturing HCl and HNO₃ as well as an H₃PO₄ impregnated filter for capturing NH₃ (see also Nemitz et al., 2000b).

For one 7-day run, 40 passive NH₃ samplers (Blatter et al., 1992) were buried 0.02 m deep into the soil and long-term canopy profiles were measured at three heights within the canopy (0.02, 0.64 and 1.32 m). The concentration at each height was obtained at two different locations with sets of four passive samplers that were placed in a common housing with a membrane at the bottom. The passive samplers in the ground were individually covered by membranes to prevent intruding soil from reducing the diffusion distance. The passive samplers themselves consist of a pool of 0.5 mM HCl with 20% ethyleneglycol, which is separated from a 7.0 mm diffusion path by a polypropylene membrane. Analysis of the passive samplers was carried out on a flow injection analyser (FIA) using the method by Genfa and Dasgupta (1989).

3.2. Measurements of profiles of turbulence and temperature: time series analysis

Above the canopy, meteorological parameters were measured as described by Sutton et al. (2000b). In order to obtain a parameterization of the within-canopy turbulence, an ultrasonic anemometer (asymmetric Solent research 1012 anemometer, Gill Instruments, Lymington, UK) was placed inside the canopy. The system was operated at 20.83 Hz in calibrated mode and the raw data were logged for spectral analysis. A similar system has been successfully applied to turbulence measurements within forest canopies (e.g. Gardiner, 1994). It was expected that the large cage size of a height of 11 cm and the low sampling frequency might lead to severe low pass filtering and an underestimation of the turbulence in the dense oilseed rape canopy. However, for this study more suitable sensors were not available. Profile measurements of the turbulence characteristic were carried out at three different occasions at different sites in the canopy to estimate the dependence on micrometeorological conditions and the horizontal variability of the canopy structure.
The adequacy of the turbulence measuring system was estimated by the assessment of the power spectra of the vertical wind component for the measurement at different heights. Data conditioning included coordinate rotation such that the arithmetic means of the vertical ($u$) and lateral ($v$) wind components vanished, linear detrending of 214 data points (approximately 13 min) and windowing using a Welch window (e.g. Stull, 1988). Discrete energy spectra were calculated from overlapping 13 min periods by 'fast Fourier transform' (Press et al., 1989) and subsequent energy spectra were averaged. The energy spectra were examined and the variance of the vertical wind component ($\sigma_w^2$) calculated as the sum of the discrete values.

To assess the performance of the ILT with an entity easier to measure than NH$_3$, a temperature profile was recorded on 22 June at four heights within the canopy using standard K-type thermocouples and at two heights above the canopy, using ultra-fine 0.3 mm E-type thermocouples to minimize radiative heating (Campbell Scientific, Loughborough, UK).

4. Results and interpretation

4.1. The turbulence in an oilseed rape canopy

The cross-section through the canopy as well as the normalized single sided leaf area density (LAD) are presented in Fig. 1. The siliques (seed cases) of the upper part of the canopy were interwoven with each other and formed a dense and rigid structure. In contrast, the lowest part of the canopy consisted of virtually leafless stems and the leaf area index declined rapidly towards the ground. Hence the profile of $\sigma_u/u_a$ should be expected to differ significantly from that of cereal crops (e.g. Raupach, 1989b). Fig. 2 shows the power spectral density (PSD) of the vertical wind component ($\chi_w(n)$) as a function of non-dimensional frequency ($n$), normalized by the natural frequency ($f$) and $\sigma_w^2$. The power spectra show the expected behaviour:

1. As expected from similarity theory (e.g. Stull, 1988), above the canopy, PSD is proportional to $f^{-2/3}$. For heights below $h_c$ the slope becomes increasingly steeper for $n > 0.8$, consistent with energy dissipation in the dense canopy.

2. Up to a height of $z/h_c = 0.7$ the peak frequencies ($n_p$) scaled by $h_c$ are fairly constant (not shown), while the value $n_p$ was at 0.36 smaller than the value of 0.45 ± 0.05 reported by Kaimal and Finnigan (1994), probably due to an underestimation of $u(h_c)$, which was not measured directly, but derived from extrapolation of the wind profile above the canopy.

3. The spectra obtained close to the ground ($z = 0.26$ and 0.45 m) become flatter for high frequencies. Considering the low wind speed and variance of the measurements at the bottom heights (typical values: $u(z) = 0.15$ m s$^{-1}$, $\sigma_u^2 = 0.003$ m$^2$ s$^{-2}$), here measurements must be expected to be affected by the limited resolution of the analogue-to-digital converter of the ultrasonic anemometer (0.02 m s$^{-1}$).

Despite the very reasonable shape of the power spectra, it is possible that the steep roll-off of the spectra within the canopy was partly due to spatial averaging of small eddies, associated with high frequencies, over the large sampling volume of the standard ultrasonic anemometer used during this study (Kaimal, 1968). Conversely, white noise could have contributed to the flat spectra measured at the bottom of the canopy, although the expected linearity in $f$ was not observed. A sensitivity analysis can help estimating the maximum effects of both errors. For this purpose a $-\frac{2}{3}$ line was fitted to the maximum of the PSD and subsequent summing over the area under the curve should lead to an upper estimate of the variance which was typically 10% (max. 15%) larger than the unmodified value. Similarly, a lower limit can be found by eliminating possible white noise by extrapolation of the actually measured slope towards higher frequencies (Fig. 3). This procedure led to values that were reduced by mainly less than 1% (4% for lowest height).

Possibly due to the inhomogeneity of the canopy, as well as effects of thermal stratification, the relative standard deviation of the values $\sigma_u/u_a$ for subsequent measuring intervals at one height was typically 11%. It is therefore concluded that over the height range of the measurements the error was in general within 11%, and possibly much less, because the deviation from the $-\frac{2}{3}$ line can probably be attributed partly to real damping effects.

The measured profiles of $\sigma_u$, $\sigma_v$ and $\sigma_w$ normalized by $u_a$ are presented in Fig. 4, together with the mean wind speed profile, normalized by the lowest wind speed measured above the canopy ($u(1.68 \text{ m})$).
Although slight systematic differences can be found between the measurements at the different locations and different wind directions, the agreement is reasonably good.

Probably owing to the density of the rape canopy, the decrease of $\sigma_w/u_s$ just below the canopy height is much more pronounced than it would be for other crops as exemplified by the parameterization Raupach.
(1989b) proposed for wheat (dotted line in Fig. 4). The values of $\sigma_w$ showed good linearity with $u_w$ over the time periods the ultrasonic anemometer was placed at a particular height within the canopy (data not shown). The quality of the turbulence parameterization can indirectly be assessed by the performance of the ILT and of resistance models using a within-canopy resistance based on $\sigma_w$ (Nemitz et al., 2000a).

**4.2. Sources and sinks of sensible heat within the canopy**

Despite new technological developments, measurements of ammonia at atmospheric concentration are still prone to errors. Furthermore, as discussed below, the NH$_3$ concentration within the rape canopy is heavily influenced by the ground level emission from...
litter leaves, and the performance of the ILT must be expected to be poorest close to the ground. As a performance test, the ILT was therefore applied to temperature profiles measured within the canopy in order to obtain the vertical source/sink distribution of sensible heat. Fig. 5 shows the temperature measured at three heights within and two heights above the canopy, together with the source/sink strengths of three canopy layers and the flux at the top of each layer.

During daytime, radiative heating of the canopy from above led to the temperature being highest at the top part of the canopy and decreasing towards both ground and atmosphere. With sunset (20:00 GMT) the above-canopy gradient reversed and radiative cooling was strongest in the top layer of the canopy, whereas heat stored in the canopy and released from the ground led to slightly higher temperatures at lower canopy layers. This is also reflected in the source/sink distribution: the top layer was a source during daytime and a sink at night; the middle layer became a sink during daytime, which can be explained by heat storage and by plant transpiration (transformation of sensible into latent heat). The lowest part of the canopy was virtually inactive with some emission periods, while the flux at the top of the lowest layer (Fig. 5c) was much smaller than the ground heat flux measured with the Bowen ratio system (\( G \)). Despite the limited number of measurement heights, the sensible heat flux predicted by the ILT at the top of the canopy agrees well with the flux measured by the micrometeorological method, also shown in Fig. 5c (Sutton et al., 2000b). Deviations were found around 18:00 GMT, possibly due to processes that were confined to a shallow height layer at the top of the canopy and therefore not resolved by the ILT. Even with the small number of input heights the ILT can reproduce the main features of the flux above the canopy.

4.3. Within-canopy profiles of \( \text{NH}_3 \)

Fig. 6a shows the \( \text{NH}_3 \) profile measured at three heights within the canopy using the passive samplers
averaged over the period from 14 June to 21 June 1995. The results of the passive samplers placed within the soil, at a depth of about 0.02 m, are presented in Fig. 6b. The NH$_3$ concentration measured within the top layer of the soil was smaller than the one just above the ground at all the sites measured, indicating that the NH$_3$ originated from the decomposing leaf litter on the ground surface and that the measured average concentration at $-0.02$ m of $1.8 \mu g \cdot m^{-3}$ was more probably caused by downward diffusion. This also explains the high scatter in the ground concentration, which is likely to be caused by the variability of the soil permeability and possibly the spatial 'patchiness' of the litter distribution.

Fig. 7a shows a diurnal cycle for 14–15 June of the NH$_3$ concentration as measured by the AMANDA
systems at 0.04, 0.20 and 1.00 m within the canopy, as well as above the canopy at 3.32 m. Micrometeorological information about this period is given in Fig. 7b. For most of the time, the concentration at the lowest height was by far the largest, increasing with temperature on 15 June, indicating a flux away from the ground surface. The concentration at 0.20 m was the second largest, except for the period between 04:00 and 07:00 GMT, when the concentrations above the canopy rose. Before 06:00 this rise could have been caused by advection, while between 06:00 and 07:00 GMT the emission gradient above the canopy together with a lower concentration at 1 m, suggested a source at the very top of the canopy.

Additional profiles of single runs including both filter-packs and denuders are presented in Fig. 9 in more vertical detail with up to 14 heights. Whereas there was net emission of NH$_3$ during the daytime runs (a) and (b), the runs (c) and (d) represent nighttime NH$_3$ deposition situations.

4.4. Sources and sinks of NH$_3$ within the canopy

The ILT was applied to two daily cycles of AMANDA measurements and 16 runs of combined filter-pack and AMANDA measurements. Fig. 7 shows some of the input concentrations for 14–15 June 1995, together with the theoretical NH$_3$ gas concentrations ($\chi_6$) in equilibrium with the [NH$_4^+$] concentrations of the water pool in the litter leaves, using a constant [NH$_4^+$] of 16.2 mM and a pH of 5.25, the averages of all values measured by Husted et al. (2000). The source/sink strength and flux profiles predicted by the ILT are shown in Fig. 8. The lowest canopy layer that contained the ground litter leaves acted as a continuous source, which was much larger during day than during nighttime (see Section 4.5). The next (stem-) layer appeared to absorb most of the NH$_3$ emitted from below; negative values of the flux at the top of this layer (0.33 m) were probably not real but errors due to the limited resolution of the model. The layer of the lower leaves (0.33–0.85 m) showed some emission during daytime, whereas the main emission originated from the upper leaves or the siliques, which was correlated with the net radiation ($R_n$) and can be attributed to stomatal exchange with plant tissue.

The agreement between the net exchange inferred from within-canopy gradient using the ILT and the flux calculated from gradients above the canopy...
Fig. 7. (a) High temporal resolution daily cycle of the NH$_3$ concentration as measured by the AMANDA analysers of CEH and UPM at three heights within and one height above the canopy on 14–15 June 1995. Also shown for comparison are the NH$_3$ gas concentration in equilibrium with the leaf litter tissue [NH$_4^+$] concentration, calculated as a function of temperature ($T$) only ($\chi_d(T)$) as well as in a dynamic approach ($\chi_d$ dynamic). (b) Micrometeorological conditions during this period $T(z_0)$: temperature at the canopy height; $h$: relative humidity; $u_z$: friction velocity.

with the aerodynamic gradient method (Sutton et al., 2000b) is encouraging. Although both techniques use the same values of $u_z$ and the NH$_3$ concentration at $z_{ref} = 1.68$ m, the function of both parameters is very different in each framework, and hence the two methods must be taken as mainly independent. The agreement between the two techniques is similar to that between micrometeorological flux systems (Sutton et al., 2000b). The main period with poor agreement is from 06:00 to 07:00 GMT, when net emission was measured by the micrometeorological method, whereas the ILT still predicted deposition. A morning emission peak coinciding with the sunrise has been found in other studies and this phenomenon has been attributed to the release of NH$_3$ in combination with the evaporation of dew and water layers from the leaf cuticle (e.g. Sutton et al., 1998). This morning emission appears to be related to the increase in solar radiation in the morning. Since canopies heat up from the top (compare Section 4.2), the evaporation started in the topmost layer, which was outside the range of the within-canopy measurements and therefore not taken into account in the ILT. By contrast, the increase in $\chi_{ref}$ as a consequence of this emission (Fig. 7a) may have caused the ILT method to predict enhanced deposition. Once the NH$_3$ originated from lower layers in the canopy (after 07:30 GMT), the emission was contained in the within-canopy profile. An alternative explanation for the poor agreement in the early morning would be the persistence of nighttime free convection in the canopy, which is not treated in the ILT (see Section 4.6).

Fig. 9 shows individual profiles obtained as 2 h runs with two AMANDA systems and up to
Fig. 8. Results of the inverse Lagrangian source/sink analysis performed for 14–15 June 1995 on the data presented in Fig. 7: (a) fluxes from (>0) or into (<0) the four source/sink layers as defined in Fig. 1; (b) the integrated flux ($F_{\text{NH}_3}$) at the top of each layer; (c) the net radiation ($R_n$).

10 filter-packs. Also shown are the source/sink densities in the different layers (Fig. 9b) and the resulting flux profiles (Fig. 9c). For example, two daytime runs (Runs 8 and 29) and two nighttime runs (Runs 24 and 26) are presented, and the fluxes as measured with the aerodynamic gradient technique are also indicated. Depending on the number of measuring points and quality of the measurements, different numbers of source/sink layers were chosen. In this case the choice of the height layers did not affect the results as much as during the analysis of the daily cycle measured at only five heights with the AMANDA systems (Figs. 7 and 8). All runs showed a large emission at the ground, most of which was recaptured by 0.3 m. At about 0.7 m the flux was close to zero. During daytime the canopy layers above provided a further source causing the emission flux to increase with height within the top source/sink layer. The nighttime runs showed net deposition at the top of the canopy that gradually decreased with lower heights. The NH$_3$ from the atmosphere was deposited to the canopy above 0.85 m. Whereas during daytime the agreement with the flux derived from micrometeorological methods is fairly good, the ILT overestimates deposition at nighttime. As discussed in more detail in Section 4.6, this might be caused by low turbulence or the stable
Fig. 9. (a) Example in-canopy gradients measured with filter-packs (○), the CEH AMANDA (■) and the UPM AMANDA (▲) on four occasions. (b) The source/sink distribution within the canopy, which is assumed to be homogeneous over each height layer. (c) The resulting flux as a function of height assuming only diffusive transport (■ and dashed line) and including near-field effects according to the ILT (● and solid line). Also shown are the reference concentrations above the canopy in (a) and the micrometeorological flux measurement (▲) in (c).
stratification not treated by the ILT. Moreover, the ILT often produces negative fluxes at about 0.3 m, which are probably an artefact caused by errors in the turbulence parameterization of the lowest canopy layers.

4.5. Ground level emission of NH$_3$

A short series of chamber measurements was carried out in the field, using two AMANDA denuders and a simple stirred dynamic cuvette to further investigate the emission of NH$_3$ from decomposing oilseed rape litter. The ground level emissions of typically 10–50 ng m$^{-2}$ s$^{-1}$ measured with the cuvette system were smaller than predicted by the ILT (up to 150 ng m$^{-2}$ s$^{-1}$). This may be due to (i) the impact of the cuvette or (ii) the spatial variability of the leaf litter emission. After removing all litter leaves from the chamber the measured flux virtually dropped to zero, which can be taken as a further indication that soil emission was not significant. In contrast, increasing the mass of leaves in the chamber by factor 3.3 led to a rise in the emission flux by factor 4.1. Although the mineralization rate of plant litter incorporated into soils has been investigated in a number of studies (e.g. Nicolardot et al., 1995), little is known about processes within detached leaves lying on the ground surface. Schjørring et al. (1998) have shown that [NH$_4^+$] production by mineralization is tightly linked to degradation of chlorophyll and to the degradation of soluble proteins in senescent leaves. The NH$_3$ gas concentration at the surface of the litter leaves ($\chi_\text{g}$) must be expected to be in equilibrium with the [NH$_4^+$] and pH of the decomposing leaf litter tissue, where little is known about the compartmentation of the water in these leaves. It must be assumed that [NH$_4^+$] is regulated by the water content of the litter, mineralization and nitrification rates as well as the amount of [NH$_4^+$] released to the atmosphere as NH$_3$. These processes were implemented here in a first dynamic model adapting: (a) the mineralization and nitrification rates of Dawson (1977) and (b) the response of the leaf water content to relative humidity ($h$) proposed by van Hove and Adema (1996). The values of $\chi_\text{g}$ predicted by this model (‘$\chi_\text{g}$ dynamic’ in Fig. 7a) matched concentrations measured near the ground much more closely than the only temperature dependent $\chi_\text{g}(T)$ in Fig. 7a. In addition, preliminary controlled chamber measurements carried out under lab conditions have shown the NH$_3$ emission from decomposing B. napus leaves to increase with humidity (Nemitz et al., 2000a).

4.6. Uncertainties associated with the inverse Lagrangian technique

This section discusses the main uncertainties expected to affect the performance of the ILT.

4.6.1. Concentration measurements

At atmospheric concentrations, NH$_3$ is still difficult to measure and the use of three independent analysers (filter-packs and two AMANDA systems) is bound to lead to some differences in concentrations, although cross checks were carried out and, where necessary, systematic differences ($\pm$20%) between systems were corrected.

4.6.2. Parameterization of $\sigma_w/u_*$ near the ground

During daytime the parameterization of $\sigma_w/u_*$ was estimated to be accurate to $\pm$11% over the height range of the measurements (Section 4.1). However, turbulence could not be measured directly close to the ground. For $z < 0.16$ m, the so-called ‘unresolved basal layer’ (Wilson and Flesch, 1993), parameterizations of $\sigma_w$ had to be estimated by extrapolation. The lowest 0.05 m layer of the rape canopy is a strong source and measurements of NH$_3$ concentrations were carried out close to the ground. Table 1 shows the flux at different heights in the canopy for various parameterizations of $\sigma_w$ below the measurement range ($z < 0.2$ m). Different parameterizations of $\sigma_w$ result in different flux profiles, in particular, in very different estimates of the ground level emission. By contrast, the effect on the net flux is small and mid-canopy fluxes vanish in all scenarios. Acknowledging that Fig. 4 makes a lower limit of $\sigma_w \geq 2u_*$ unlikely, case 4 in Table 1 may nevertheless be taken as a scenario that reflects the small possibility of the in-canopy turbulence being systematically underestimated by the anemometer.

4.6.3. Conceptual limitations of the ILT

The parameterization of $\sigma_w$ was obtained as an average over various unstable daytime conditions, and its application to stable nocturnal stratification and low wind-speeds is therefore problematic. Here, free convection may become the dominant transport mechanism within the canopy, especially close to the ground.
where turbulence is lowest. During free convection $\sigma_w$ scales with a velocity ($u_a$) that is related to the sensible heat flux rather than with $u_a$ (Jacobs et al., 1994). Indeed, there was evidence that, for small values of $u_a$, the linearity of $\sigma_w$ in $u_a$ might not hold. For stable nighttime runs, the disagreement between ILT and micrometeorological method was larger than between the ILT with and without ‘near-field’ contribution, indicating that in-canopy stability effects on the net flux might be more important than the near-field contribution itself (Fig. 9c). Hence in the current form the ILT should only be applied to nighttime conditions if the effect of turbulence (parameterized by $u_a$) is much larger than that of free convection.

Closely related is the simplification that the ILT is based on a Gaussian distribution of the turbulent parameters (Raupach, 1989a). Within plant canopies and especially close to the ground, free convection and intermittency of the turbulence lead to skewness in turbulent parameters. Intermittency and non-Gaussianity appear to be unimportant for source-concentration relationships (Sawford, 1993; Flesch and Wilson, 1992), but since model validation studies have been restricted to mid-canopy sources, it is possible that the effect is larger for a ground-level source. A contribution of free convection to the vertical transport near the ground would have the same effect as larger values of $\sigma_w$ (Table 1, cases 3 and 4), and its inclusion in the modelling would therefore lead to a prediction of larger leaf litter emission.

As a net result, while the magnitude of the leaf litter emission derived with the ILT is highly uncertain, the net flux above the canopy appears to be stable. At present there is no available alternative concept that could be applied more reliably.

### 4.6.4. Number of input values

A further error is induced by the number of input values and the resolution of the measurements. Some exchange processes, such as the desorption of NH$_3$ by top leaves, probably take place in a very shallow height range, which might not be resolved by the measured profile. Also, the need to implement the ILT as finite sums, results in a sensitivity to the choice of the heights $z_j$, especially when only few input concentrations are used. Table 2 shows the NH$_3$ flux at the top of the canopy calculated from the same input concentrations at eight heights using different values of $z_j$. Since in the present analysis, $S_j$ is expected to be constant over the whole height layer $j$, the $z_j$ were chosen to represent physical plant parts (e.g. leaf litter, stems, lower leaves, upper leaves and siliques — compare Fig. 1). Thus good results were achieved without choosing the heights arbitrarily.

### Table 1

The NH$_3$ fluxes ($F$) at the top of the four source layers (0.05, 0.33, 0.85 and 1.38 m), estimated by the ILT, as a function of the parameterization for the normalized standard deviation of the vertical wind component ($\sigma_w/u_z(z)$) chosen for the lowest 0.2 m of the canopy$^a$

<table>
<thead>
<tr>
<th>Case</th>
<th>Additional conditions for turbulence parameterization</th>
<th>$F(0.05\text{ m})$</th>
<th>$F(0.33\text{ m})$</th>
<th>$F(0.85\text{ m})$</th>
<th>$F(1.38\text{ m})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Original parameterization; see Run 8, Fig. 9</td>
<td>59.5</td>
<td>−6.6</td>
<td>8.6</td>
<td>63.2</td>
</tr>
<tr>
<td>2</td>
<td>$T_L$ decreasing exponentially (Raupach et al., 1992)</td>
<td>29.8</td>
<td>−6.3</td>
<td>9.6</td>
<td>77.1</td>
</tr>
<tr>
<td>3</td>
<td>$\sigma_w/u_z \geq 0.1$</td>
<td>63.7</td>
<td>−7.6</td>
<td>9.7</td>
<td>66.3</td>
</tr>
<tr>
<td>4</td>
<td>$\sigma_w/u_z \geq 0.2$</td>
<td>172.9</td>
<td>−6.0</td>
<td>9.1</td>
<td>67.5</td>
</tr>
<tr>
<td>5</td>
<td>$\sigma_w/u_z \rightarrow 0.05$ for $z \rightarrow 0$</td>
<td>42.5</td>
<td>−2.9</td>
<td>6.3</td>
<td>65.2</td>
</tr>
<tr>
<td>6</td>
<td>$\sigma_w/u_z \rightarrow 0$ for $z \rightarrow 0$</td>
<td>8.8</td>
<td>10.4</td>
<td>−4.4</td>
<td>75.0</td>
</tr>
<tr>
<td>7</td>
<td>Aerodynamic gradient technique</td>
<td>52.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All runs are based on the parameterization according to the solid line in Fig. 4 and a Lagrangian time-scale ($T_L$) that is constant over the height range of the canopy (Raupach, 1989a), with the additional condition given in the second column. Fluxes are given in ng m$^{-2}$ s$^{-1}$.

### Table 2

The values of the net flux of NH$_3$ ($F_{\text{NH}_3}$) at the canopy height ($h_c$) calculated from the same input values using different values of the source layers ($z_j^S$). The data are taken from Fig. 9, Run 8 and case 1 represents the standard values of $z_j^S$.

<table>
<thead>
<tr>
<th>Case</th>
<th>$z_j^1$ (m)</th>
<th>$z_j^2$ (m)</th>
<th>$z_j^3$ (m)</th>
<th>$z_j^4$ (m)</th>
<th>$F_{\text{NH}_3}(h_c)$ (ng m$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>0.33</td>
<td>0.85</td>
<td>1.38</td>
<td>63.2</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>0.33</td>
<td>0.85</td>
<td>1.38</td>
<td>60.7</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>0.33</td>
<td>0.85</td>
<td>1.38</td>
<td>61.2</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>0.20</td>
<td>0.85</td>
<td>1.38</td>
<td>75.3</td>
</tr>
<tr>
<td>5</td>
<td>0.05</td>
<td>0.50</td>
<td>0.85</td>
<td>1.38</td>
<td>53.3</td>
</tr>
<tr>
<td>6</td>
<td>0.05</td>
<td>0.75</td>
<td>0.85</td>
<td>1.38</td>
<td>41.3</td>
</tr>
<tr>
<td>7</td>
<td>0.05</td>
<td>0.33</td>
<td>0.65</td>
<td>1.38</td>
<td>62.4</td>
</tr>
<tr>
<td>8</td>
<td>0.05</td>
<td>0.33</td>
<td>1.10</td>
<td>1.38</td>
<td>101.4</td>
</tr>
</tbody>
</table>

Aerodynamic gradient technique 52.7
5. Discussion

Within-canopy profiles and canopy cycling processes of NH₃ have been investigated in a very limited number of studies (Denmead et al., 1976; Lemon and van Houtte, 1980; Harper et al., 1987; Sutton et al., 1993b; Meixner et al., 1996). In accordance with the concept that NH₃ emissions above cereal crops often originate from NH₃ concentrations within the substomatal cavity (e.g. Farquhar et al., 1980), emission profiles of NH₃ within canopies often show the largest concentration at mid-canopy, at the height of the greatest leaf density (Sharpe and Harper, 1995; Meixner et al., 1996; Sutton et al., 1996). In canopies of grass-clover pasture as well as soybeans and quackgrass NH₃ emissions have been observed, while within-canopy profiles showed the highest concentrations at ground level (Denmead et al., 1976; Lemon and van Houtte, 1980; Sutton et al., 1993b). This has been attributed to leaf litter decomposition and NH₃ emission from the soil. In contrast, deposition profiles (e.g. during nighttime when the stomata are closed) often show concentration minima at mid-canopy (Sutton et al., 1996), owing to the depletion of NH₃ by cuticular adsorption at the height of maximum LAD. Low turbulence allows NH₃ concentrations to build up above the ground, even if the ground level emission of NH₃ is very small, and counter-gradient–fluxes are also possible (Denmead and Bradley, 1985).

The oilseed rape canopy showed the largest NH₃ concentration at the ground surface. This was found to be caused by N mineralization from fallen leaf litter that led to NH₃ release of up to 150 ng m⁻² s⁻¹, depending on humidity, temperature and turbulence. A major contribution of soil emission could be ruled out on grounds of NH₃ concentration measurements within the soil as well as chamber measurements over bare soil. Under these conditions the net exchange cannot be expected to be purely governed by stomatal and cuticular exchange, and here the source/sink analysis offers further insight in the exchange process and the contribution of ground level emission.

The ILT based on the LNF theory developed by Raupach (1989a,b) proved to be a useful tool for the source/sink analysis for both heat and NH₃. For both entities the net flux above the canopy as derived by the ILT agrees well with the micrometeorological method. However, the analysis turns out to be sensitive to the choice of the source/sink layers as well as the parameterization of the turbulence close the ground surface, which could not be measured directly but had been estimated by extrapolation. The effect of the turbulence close to the ground on the estimation of the leaf emissions is especially pronounced in the present case, since due to the leaf litter emission, the NH₃ gradient is particularly large in the lowest part of the canopy. Above z = 0.2 m and during daytime the accuracy of the profile of σ_w/υₘ, although measured with a standard ultrasonic anemometer that is not ideal for measurements in canopies as dense as oilseed rape, is expected to be within ±11%. This is similar to the accuracy at which NH₃ concentrations can be measured. Here σ_w was only obtained as an average over daytime conditions. Especially at night, the performance of the ILT might be substantially improved if σ_w could be parameterized as a function of stability, and scaled with υ₈ rather than υₙ at night. Similarly, estimates and measurements of the turbulence characteristics of canopy layers very close to the ground (z/h_c < 0.1) need to be improved. The profiles of the standard deviations of the different wind components showed a sharper decline in the top canopy than measurements in other plant canopies (e.g. Raupach, 1989b; Kaimal and Finnigan, 1994), which is probably due to the large LAD and the rigid mesh formed by the silique layer (Fig. 1).

For the apoplastic liquid in the rape leaves, Husted et al. (2000) reported values of [NH₄⁺] and pH, which, according to the Henry and solubility equilibrium, correspond to NH₃ gas concentrations lower than the concentrations measured. They therefore concluded that the net NH₃ emission above the canopy could not have originated from the leaf stomata, but that a part of the emission from the litter leaves on the ground might have penetrated through the canopy. Hence it is surprising that the inverse Lagrangian analysis indicates that all NH₃ emitted from the ground level was recaptured within the lowest 0.7 m of the canopy and that the daytime emission originated from the top 0.5 m of the canopy, where the top leaves and the siliques were located. On a daily average, the emission from the leaf litter at the ground surface (26 g NH₃-N ha⁻¹ per day) was recaptured in the lowest 0.33 m of the canopy (−26 g ha⁻¹ per day), whereas the layer between 0.33 and 0.85 m was on average virtually inactive (1.5 g ha⁻¹ per day) and the net emission of the
canopy originated from the top layer above 0.85 m (12 g ha⁻¹ per day). Therefore, the N loss from the plant as gaseous NH₃ was more than balanced by uptake from NH₃ emitted by decomposing leaves. Following the discussion of errors, the actual magnitude of the ground level emission, however, is rather uncertain (see Table 1). Nemitz et al. (2000a) have developed and applied a range of resistance models to the NH₃ surface exchange with the B. napus canopy at North Berwick. A three-layer resistance model, differentiating between litter leaves, foliage and siliques, is required to reproduce the source/sink distribution reported here.

Both the continuous measurements of the net NH₃ exchange above the canopy (Sutton et al., 2000b) and the modelling study (Nemitz et al., 2000a) show significant NH₃ emissions during some windy nights. Unfortunately, no in-canopy profiles were measured during these particular periods, but it can be assumed that here the NH₃ emitted by the leaf litter did penetrate through the canopy due to increased turbulent mixing.

Since at present the apoplastic liquid extraction cannot be applied to B. napus siliques, no [NH₄⁺] measurements could be carried out on the siliques themselves. More recent measurements by Husted (1997) have shown the bulk tissue [NH₄⁺] concentration of the siliques to be 3–5 times the value of attached leaves. Emission of NH₃ by cuticular desorption as observed by Sutton et al. (1998) can contribute to a part of the emission in the morning hours, when dew and water films evaporate, but it is unlikely to be the main process over the whole day. Both apoplastic [NH₄⁺] and pH from bioassay as well as the ILT modelling indicate that the low canopy acted as a sink for the leaf litter emission. Unless the apoplastic measurements significantly underestimate leaf compensation points, these results point to the siliques being the main source of the measured daytime net NH₃ emission above the canopy.

6. Concluding remarks

The present study is the first application of the ILT to estimate the source/sink distribution of NH₃ within a plant canopy. The net flux above the oilseed rape canopy at North Berwick predicted by the ILT agreed well with the micrometeorological measurements during daytime for both sensible heat and NH₃, but nighttime deposition of NH₃ was underestimated. The source distribution predicted by the ILT indicates that significant NH₃ emission from leaf litter at the ground surface occurred, but the absolute magnitude is currently rather uncertain. During daytime the litter emission was almost certainly fully recaptured by the canopy, while the net emission originated from the top of the canopy, probably from the siliques.

Some uncertainties of the ILT remain: to improve the performance of the ILT at the ground surface and at nighttime it will be necessary to derive parameterizations of the standard deviation of the vertical wind component (σₚₙ) (i) close to the ground and (ii) for the full range of in-canopy stabilities, especially for the free convection regime. In addition, more measurement heights would be needed to desensitize the technique with respect to the choice of the height layers. However, this only affected the prediction of the source distribution, while the net flux remained stable.

Acknowledgements

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Appendix A. An implementation of the inverse Lagrangian technique

Since Raupach (1989a,b) presented his novel technique to infer the source/sink distribution of tracers within plant canopies from measurements of vertical profiles of concentrations (χ) and turbulence (σₚₙ, Tₚ), it does not seem to have been frequently applied. This may be because although Raupach explains the theory in mathematical detail, he does not describe
how the presented integrals may be turned into finite sums, a fact that might deter the mathematically less confident reader. It is therefore helpful to outline a practical way to implement the ILT, and in particular how to calculate the diffusion matrix \( D = (\delta_{ij})^{(m,n)} \) of Eq. (1), which is here repeated in non-vector format:

\[
\chi_i = \chi_{\text{ref}} = \sum_{j=1}^{m} \delta_{ij} S_j
\]  

(A.1)

It is assumed that continuous parameterizations for \( \sigma_w(z) \) and \( T_L(z) \) have been found and that the height divisions for concentrations \( (z_j^S) \) and source/sink layers \( (z_j^S) \) are taken as defined above with \( z_j^S > 0 \) and \( \Delta z_j^S = z_j^S - z_{j-1}^S \). Note that, unlike by Raupach (1989a,b), the values of \( \Delta z_j \) are incorporated into \( \delta_{ij} \) and that the ground flux \( (F_g) \) is not dealt with explicitly. In general \( F_g \) can be incorporated into the source/sink density of the lowest source layer as in the case of the leaf litter in the oilseed rape canopy.

In order to limit the uncertainties caused by the small number of layers and to account for the strong height dependence of \( \sigma_w, T_L, K_H \) and \( k_n \), each source/sink layer is sub-divided into \( r \) sub-layers \( z_{jl}^S (j = 1, \ldots, n; l = 1, \ldots, r) \), where \( z_{jl}^S \) is defined as

\[
z_{jl}^S = z_{j,l-1}^S + l \Delta z_j^S, \quad \Delta z_j^S = \frac{z_j^S - z_{j-1}^S}{r}
\]  

(A.2)

To obtain a similar resolution the distance between a concentration height \( (z_i^X) \) and \( z_{\text{ref}} = z_{n+1} \) is sub-divided into \( s_i = r(n+1-i) \) sub-layers:

\[
z_{ik}^X = z_{i-1}^X + l \Delta z_i^X, \quad \Delta z_i^X = \frac{z_{i}^X - z_{i-1}^X}{s_i}
\]  

(A.3)

Eq. (8) can be directly turned into a finite sum to yield an expression for the matrix elements of the near-field contribution \((\alpha_{ij})\):

\[
\alpha_{ij} = \Delta z_j^S \sum_{l=1}^{r} \sigma_{wl}^{-1}(z_{jl}^S) \left[ k_n \left( \frac{z_i^X - z_{jl}^S}{\sigma_w(z_{jl}^S)T_L(z_{jl}^S)} \right) + k_n \left( \frac{z_i^X + z_{jl}^S}{\sigma_w(z_{jl}^S)T_L(z_{jl}^S)} \right) \right]
\]  

(A.4)

where \( k_n(z) \) is given by Eq. (7).

In order to evaluate the expression for the far-field contribution to the concentration \((\beta_{ij})\) it has to be substituted according to Eq. (5). This substitution leads to a double integral which can be evaluated to yield the matrix elements of the far-field contribution \((\beta_{ij})\) as

\[
\beta_{ij} = \sum_{k=1}^{s_j} \gamma_{i,j,k},
\]

\[
\gamma_{i,j,k} = \begin{cases} 
0, & \text{if } z_{ik}^X \leq z_{j-1}^S \\
(z_{ik}^X - z_{j-1}^S)K_H^{-1}(z_{ik}^X), & \text{if } z_{j-1}^S < z_{ik}^X \leq z_j^S \\
\Delta z_j^S K_H^{-1}(z_{ik}^X), & \text{if } z_{ik}^X > z_j^S
\end{cases}
\]  

(A.5)

Adding the expressions for the near- and far-field contributions according to Eqs. (3), (4) and (8) and sorting them for the dependency on \( S_j \) yields

\[
\chi_i - \chi_{\text{ref}} = \sum_{j=1}^{m} \alpha_{i,j} S_j - \sum_{j=1}^{m} \alpha_{n+1,j} S_j + \sum_{j=1}^{m} \beta_{i,j} S_j
\]

(A.6)

Hence it is established that the matrix elements \( \delta_{ij} \) of Eq. (A.1) are given by

\[
\delta_{i,j} = \alpha_{i,j} - \alpha_{n+1,j} + \beta_{i,j}
\]  

(A.7)

Despite the complexity of the expression, the diffusion matrix can be easily calculated on basis of the turbulence parameterization within the canopy and the height spacing. Since Eq. (A.1) represents a linear system of \( n \) equations in \( m \) unknowns it can uniquely be solved if \( m = n \). However, in order to obtain a more stable (non-oscillating), smooth solution for the source/sink strengths, it is necessary to include redundant concentrations \( (m > n) \). In this case the linear system becomes over-determined and is in general not solvable. Raupach (1989b) therefore suggested the calculation of the \( m \) values of \( S_j \), which lead to the \( m \) concentrations that best approximate the \( n \) measured concentrations. In this case Raupach delivers the concrete procedure of how to turn the \((n,m)\)-system of equation into an \((m,m)\)-system:
\[ \sum_{k=1}^{n} \tau_{j,k} S_k = t_j, \quad \tau_{j,k} = \sum_{i=1}^{n} \delta_{i,j} \delta_{i,k}, \]
\[ t_j = \sum_{i=1}^{n} (\chi_i - \chi_{ref}) \delta_{i,j} \quad \text{(A.8)} \]

Note that the summations in Eqs. (A.5) and (A.6) can be calculated more accurately using numerical integration procedures such as Simpson’s rule or the Trapezoidal rule (e.g. Press et al., 1989).

References


