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Plant-Atmosphere Exchange of Ammonia [and Discussion]

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Plant–atmosphere exchange of ammonia

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The results of recent controlled environment and micrometeorological measurements of NH_3 fluxes are presented to highlight the processes controlling NH_3 plant–atmosphere exchange. The presence of NH_4^+ in leaf tissues results in the existence of an NH_3 ‘compensation point’ concentration for substomatal tissues (χ_s), so that both emission and deposition are possible from stomata. In addition, NH_3 may deposit efficiently on to leaf cuticles, short-circuiting any stomatal emission, so that a ‘canopy compensation point’ (χ_c) may be defined that is smaller than χ_s. Ammonia is generally deposited to nitrogen limited ecosystems, indicating a small χ_s and small leaf cuticle resistance (R_w). In contrast, fluxes over croplands are typically bidirectional and may reflect a larger χ_s as a consequence of greater N supply. The paper discusses the processes defining R_w (humidity, acidic pollutants) and χ_s (plant phenology, species, N nutrition) and proposes a new resistance approach, which integrates χ_s and R_w into one model. Estimating long term bidirectional NH_3 fluxes is still uncertain, though it is now possible to apply a single model concept to a range of ecosystem types and satisfactorily infer NH_3 fluxes over diurnal time scales.

1. Introduction

Quantifying the magnitude of ammonia fluxes between vegetation and the atmosphere is of great interest in assessing the effects of regional atmospheric pollution. In continents with intensive agriculture such as Europe and eastern N. America, atmospheric inputs of reduced nitrogen (NH_x) as ammonia (NH_3) and ammonium (NH_4^+) by dry and wet deposition may represent a substantial contribution to the acidification and nitrogen eutrophication of semi-natural ecosystems (Fowler *et al.* 1989; Grennfelt & Thörnelöf 1992). Estimates of NH_3 dry deposition fluxes to semi-natural plant communities are therefore directly relevant as a component in comparing pollutant inputs with ‘critical loads’ for vegetation and soils (Grennfelt & Thörnelöf 1992). However, it is also important to quantify the net NH_3 flux over other vegetation types, such as arable croplands, even though these often show limited dry deposition or even emission (Dabney & Bouldin 1990; Sutton *et al.* 1993*c*; Schjørring *et al.* 1993*a*). This is necessary to quantify regional atmospheric budgets of NH_3, and as an input to atmospheric transport models (e.g.

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Asman & van Jaarsveld 1992). Since the whole atmospheric budget is considered, it is important to quantify the net NH_3 exchange over all major vegetation types (Sutton *et al.* 1993*d*).

The aim of this paper is to present the results of recent research on the plant–atmosphere exchange of NH_3 for a range of ecosystem types. The results of both micrometeorological and controlled environment studies are used to describe the environmental and biological factors controlling net NH_3 fluxes with the atmosphere. The measurements are used to identify limitations in existing models of NH_3 plant–atmosphere exchange and to highlight requirements for successfully predicting NH_3 fluxes. A newly developed, but simple, resistance model is proposed that allows the different processes controlling NH_3 fluxes to be distinguished and then combined to predict net NH_3 exchange.

Several recent papers have discussed measurements of NH_3 fluxes between the atmosphere and plant communities (e.g. Schjørring 1991; Langford *et al.* 1992; Sutton *et al.* 1993*e*, 1994; Holtan-Hartwig & Bøckman 1994). In the following section some of the main experimental findings are summarized together with a brief description of the approaches used. Subsequent sections consider the processes controlling NH_3 exchange with leaf cuticles and leaf tissues (via stomata), while the final sections discuss the modelling of NH_3 plant–atmosphere exchange.

2. Field and laboratory measurements of ammonia fluxes

Techniques that have been applied to measure trace gas fluxes to and from vegetation include enclosure and micrometeorological methods (Denmead 1983; Fowler & Duyzer 1989; Monteith & Unsworth 1990). Enclosure methods were the first to be applied to quantify NH_3 fluxes (Hutchinson *et al.* 1972). Most of these studies have used dynamic chambers, where air is drawn continuously through the chamber and the flux is related to the difference between the inlet and outlet concentrations and the air flow rate. Many of the measurements using dynamic chambers have shown that NH_3 is predominantly taken up by plant leaves through stomata (Hutchinson *et al.* 1972; Aneja *et al.* 1986). Rates of absorption have been related to photosynthetically active radiation intensity and CO_2 fluxes, with only limited deposition observed when stomata are closed. However, it should be noted that these experiments have frequently applied concentrations that are much larger (e.g. greater than $50\ \mu g\ NH_3\ m^{-3}$) than typically encountered in field conditions (e.g. $0.1–10\ \mu g\ m^{-3}$) (Sutton *et al.* 1993*e*), and at smaller air concentrations rates of exchange may differ.

At more typical air concentrations, chamber measurements have shown both NH_3 absorption and emission from plants (Farquhar *et al.* 1980; Schjørring 1991; Sutton *et al.* 1993*e*). Farquhar *et al.* explained this by proposing the existence of an NH_3 'compensation point' (χ_s), which is the air concentration at which no net in- or out-flux occurs through stomata. A compensation point is expected because of the presence of NH_x in plant metabolism and the Henry equilibrium with gaseous NH_3. Hence, at air concentrations larger than χ_s, absorption occurs, while at smaller air concentrations, emission occurs. An example of this is shown in figure 1, from controlled chamber measurements using two cultivars of barley (*Hordeum vulgare* L.), cv. Laevigatum and cv. Golf. For the two cultivars χ_s was 2.4 ± 0.4 and $2.8 \pm 0.4\ \mu g\ m^{-3}$, respectively (shown with standard errors). The larger χ_s of Golf may be a consequence of this being a modern high-yielding

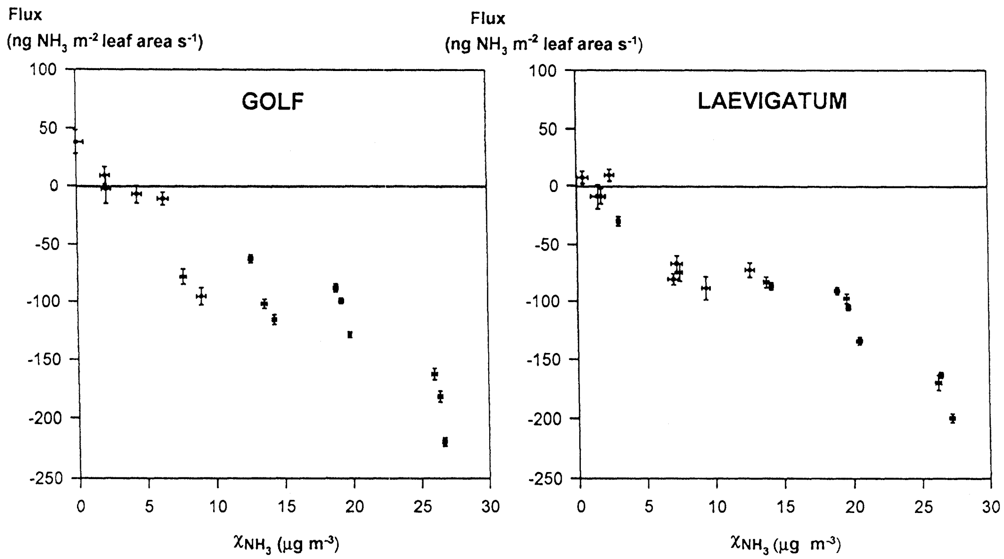

Figure 1. Relationship between NH_3 concentration and plant–atmosphere fluxes. Chamber measurements for two barley cultivars at 20 °C, 55% relative humidty and light intensity of $520\ \mathrm{mmol\ m^{-2}\ s^{-1}}$. Plants approaching anthesis. NH_3 determined using a modified Thermo-electron NO_x/NH_3 analyser (Husted & Schjørring 1995).

cutivar with a more active N metabolism. Enclosure methods are useful to examine the processes controlling NH_3 fluxes. However, it is difficult directly to extrapolate measured fluxes to the field.

In contrast to enclosure techniques, micrometeorological methods quantify net fluxes over plant canopies for large areas (e.g. 10^2–10^5 m^2) and do not disturb the canopy environment. The technique most frequently applied for NH_3 is the aerodynamic gradient method (Sutton *et al.* 1993*b*, Erisman & Wyers 1993; Duyzer *et al.* 1994). Above homogeneous plant canopies with extensive fetch, a trace gas flux may be determined from profiles of concentration, windspeed and temperature versus height above the ground. In management systems that give large NH_3 emission fluxes, an alternative approach is to quantify the horizontally advected flux of NH_3 emitted from a smaller area (e.g. 10^2–10^3 m^2). This has been used to measure NH_3 fluxes from grazed fields and following animal waste or urea fertilizer application. (Denmead 1983; Jarvis & Pain 1990). However, this method is less suitable for other plant canopies, as both emission and deposition occur and estimates become affected by fluxes over neighbouring land surfaces. A more recent approach measuring vertical gradients of the advection flux over extended homogeneous surfaces has been described elsewhere (Schjørring 1995).

Micrometeorological measurements of NH_3 fluxes have shown that both emission and deposition occur in relation to environmental conditions, ecosystem type and plant growth stage. Most measurements have been made in temperate climates and show bidirectional fluxes over intensively grazed pastures and arable land (Jarvis & Pain 1990; Schjørring *et al.* 1993*a*; Sutton *et al.* 1993*c*), whereas NH_3 deposition dominates for unfertilized semi-natural ecosystems (Duyzer *et al.* 1987, 1994; Sutton *et al.* 1993*e*; Erisman & Wyers 1993). This difference may be shown by a comparison of the results of Sutton *et al.* (1992, 1993*b*, *c*) who measured NH_3 fluxes over both unfertilized semi-natural ecosystems and fertilized

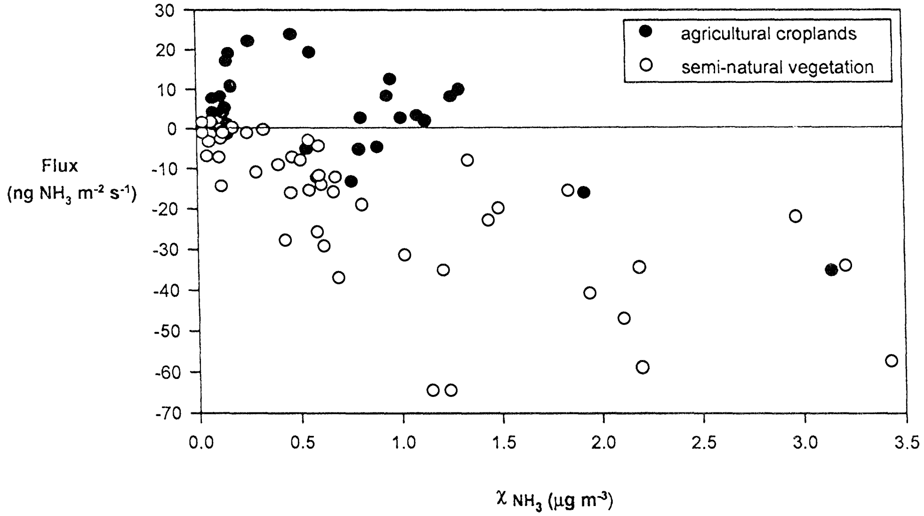

Figure 2. Comparison of micrometeorological gradient measurements of NH$_3$ fluxes over agricultural croplands and unfertilized semi-natural ecosystems. Ammonia determined by using filter packs.

croplands in the United Kingdom. The results are summarized in figure 2. The most likely reason for the difference between these vegetation types is that nitrogen fertilization raises χ_s, so promoting NH$_3$ emission. These data show a large variation and it is not easy to identify unique air concentrations at which there is a switch from emission to deposition. This is a result of the range of ecosystems types and sampling conditions (temperature, canopy wetness) combined in figure 2.

A key finding of the field measurements over semi-natural ecosystems that is not so clearly seen in the chamber measurements is the importance of cuticular deposition. This may be a result of smaller concentrations and higher humidities encountered in the field. The existence of cuticular uptake may be shown by applying a resistance analogy to the measured fluxes. The usual approach assumes that the air concentration at the surface (χ_0) is zero, in which case the total resistance for deposition from a height (z) above the zero plane of the vegetation is

$$R_t\{z\} = [\chi_0 - \chi\{z\}]/F_g = -\chi\{z\}/F_g = 1/V_d\{z\}, \qquad (2.1)$$

where F_g is the vertical flux (positive fluxes denote emission), $\chi\{z\}$ is the air concentration at the reference height. The reciprocal of R_t is the deposition velocity, V_d. The total resistance may be considered as the sum of several component resistances in series:

$$R_t\{z\} = R_a\{z\} + R_b + R_c. \qquad (2.2)$$

The resistance for turbulent transfer from z to the surface is given by R_a, and an additional resistance for diffusion through the quasi-laminar boundary-layer around leaves by R_b, both of which may be estimated from wind and temperature profiles. The remaining term, R_c, represents the resistance due to the canopy itself, and is found by difference from the other terms. The canopy resistance is a composite term, and includes resistances for transfer through stomata (R_s) as well as uptake on leaf surfaces (R_w). Since the field measurements of NH$_3$ deposition

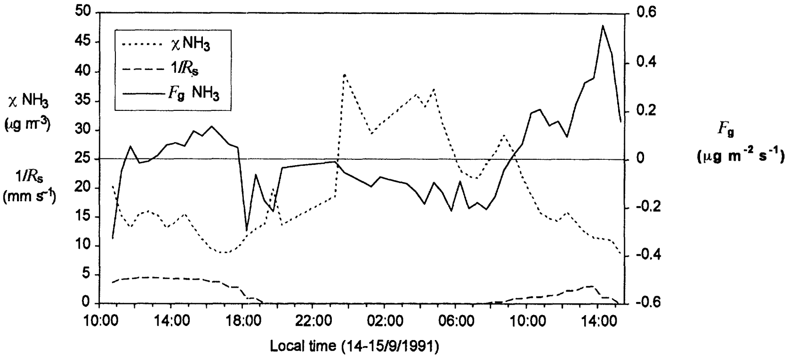

Figure 3. Example of NH_3 fluxes over dry heathland in The Netherlands (Eslpeetsche Veld). Bi-directional fluxes are observed, with emission occurring during daytime when stomata are open.

to unfertilized vegetation cited above have frequently shown values of R_c in the range 0–30 $\mathrm{s\,m^{-1}}$, this implies substantial cuticular uptake. Typical daytime R_s over such vegetation are much larger than this (e.g. 50–400 $\mathrm{s\,m^{-1}}$ (Miranda *et al.* 1984)), so that such uptake rates would not be possible solely by absorption through stomata.

The co-occurrence of both stomatal exchange and leaf surface deposition obviously complicate the interpretation of NH_3 plant–atmosphere exchange. Hence, deposition to leaf cuticles may re-capture NH_3 emitted from stomata reducing net emission to the atmosphere. As an example, figure 3 shows the time-course of measured NH_3 exchange above a heather (*Calluna vulgaris* (L.) Hull) canopy. Measurements of NH_3 fluxes are generally limited by the capabilities of the NH_3 detection system. Until recently, the required precision and necessity to distinguish between gaseous NH_3 and aerosol NH_4^+ has only been possible using batch sampling of 1–3 h periods, such as by filter pack systems (Harrison *et al.* 1989; Sutton *et al.* 1992; figure 2) and simple denuders (Duyzer *et al.* 1987). However, much progress has been made in continuous NH_3 sampling. The NH_3 measurements shown in figure 3 were made using continuous wet annular denuders, with online determination of NH_4^+ in solution by conductivity (Wyers *et al.* 1993*b*). Maintaining the system is labour intensive, but it has a detection limit of 0.02 $\mathrm{\mu g\,m^{-3}}$ and a time resolution of 2 min, making it suitable for precise determination of NH_3 fluxes. The flux measurements summarized in figure 3 were made in the Netherlands, in an area with unusually large air concentrations. Figure 3 shows that significant NH_3 emission from the heathland was observed during daytime, probably related to NH_3 release from stomata. In contrast, periods of deposition during humid conditions during evening and early morning were consistent with $V_d = 10$–$20\ \mathrm{mm\,s^{-1}}$ and $R_c = 0$–$50\ \mathrm{s\,m^{-1}}$. It should be noted that the R_c model (equations (2.1) and (2.2)) is less suited to describing the emission periods, since it assumes $\chi_0 = 0$. In this case R_c is apparently negative. Since a negative R_c also indicates $V_d > (1/(R_a + R_b)$, it is difficult to use these values predictively.

Other periods of emission were also observed by Sutton *et al.* (1992) and Erisman & Wyers (1993) over Dutch heathland, though the average flux was net deposition. A possible explanation of these surprisingly large emissions for semi-natural vegetation is that the large atmospheric nitrogen inputs to these sites result in a 'nitrogen saturation' for NH_3 exchange, raising χ_s and limiting net deposition (Sutton *et al.* 1993*e*). Such a negative feedback would have important consequences for the comparison of inputs with critical loads, since the existence of emission might itself be an ecosystem response indicating exceedance of the critical load.

Clearly it is a challenge for the interpretation of data such as these to quantify the net effect of the different processes controlling NH_3 fluxes. To do this it is necessary to distinguish the component processes of NH_3 exchange with leaf surfaces, stomata and with soils.

3. Ammonia exchange with leaf surfaces

Deposition of NH_3 on to leaf surfaces appears to be closely related to the presence of water on the cuticle. This is to be expected due to the large solubility of ammonia in water. Both laboratory (Adema *et al.* 1986) and field measurements (Sutton *et al.* 1993*b*; Erisman & Wyers 1993; Duyzer *et al.* 1994) have shown rapid NH_3 uptake by wet surfaces. However, there is also clear evidence that the presence of microscale water in or on 'dry' leaf cuticles may affect the rate of deposition. Van Hove *et al.* (1988, 1989) applied cuvette techniques to examine the response of NH_3 adsorption on leaf surfaces to atmospheric humidity. They found a strong increase in NH_3 adsorption capacity of the cuticle between 45–95% relative humidity (H), which they attributed to the presence of bound water layers. More recently, Benner *et al.* (1992) have provided direct measurements of water adsorption to glass surfaces, and found a similar response to H.

It would be useful to relate these humidity responses to the expected plant cuticle resistance to deposition (R_w). The subscript 'w' is used here because of the possible roles of water and surface waxes. The chamber measurements noted above estimated total adsorption and are therefore not directly comparable with estimates of R_w. However, the response to H might be expected to be similar for adsorption and $1/R_w$. By comparing these laboratory results with micrometeorological measurements, Sutton & Fowler (1993) estimated R_w at 100% H as $2\,\mathrm{s\,m^{-1}}$, with the following simplified humidity response:

$$R_w = 2\exp[(100 - H)/12]. \tag{3.1}$$

This relationship is shown in figure 4, alongside the reciprocal of adsorption from the laboratory studies (arbitrary units). The laboratory measurements of van Hove *et al.* (1988) were conducted by using more than $50\,\mu\mathrm{g\,m^{-3}}$ of NH_3, which simplifies the results as there would be little interaction with a compensation point. Micrometeorological estimates of R_c may also show a relationship with H, however, this may be complicated at small air concentrations because of competing stomatal emissions. Where soil emissions are unimportant, this effect may be avoided at night-time, because of stomatal closure, and it may be asssumed that $R_c \approx R_w$. Measurements of NH_3 fluxes over at Speuld Forest in the Netherlands (Wyers *et al.* 1993*a*) were analysed to provide median night-time R_c for different humidity classes (figure 4). It is encouraging that these data show a very similar humidity response to the other estimates.

Further evidence of a humidity response to cuticular adsorption was observed in studies of Burkhardt & Eiden (1994). They measured leaf surface conductivity and found this to increase with H, indicating the importance of microscale water. There has been some debate as to whether such 'water-films' are more closely connected with epicuticular waxes or to pre-existing hygroscopic salts on the leaf

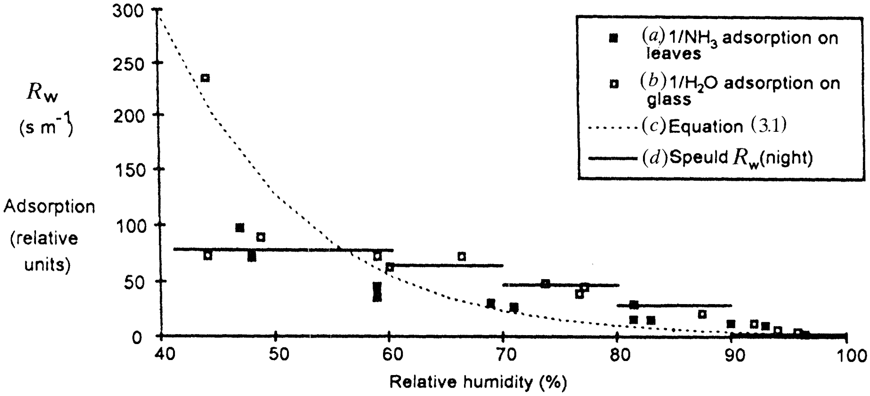

Figure 4. Relationship of the resistance to cuticular deposition (R_w) to relative humidity. The model estimate (*c*) of R_w (equation (3.1)) was based on a simple fit to the humidity response of (*a*) the reciprocal of NH_3 adsorption on leaves (van Hove *et al.* 1988), and (*b*) the reciprocal of H_2O adsorption on to glass (Benner *et al.* 1992). (*d*) Median nighttime R_c from measurements over Speuld forest (Wyers *et al.* 1993*a*) to approximate R_w.

surface, from deposited trace gases and aerosols (van Hove *et al.* 1989; Sutton *et al.* 1993*e*). Burkhardt & Eiden (1994) measured the change in conductivity following addition of elevated NH_3 for both washed and unwashed leaves. They found a large increase in conductivity for unwashed leaves, but little effect for clean leaves, suggesting that cuticular NH_3 uptake is largely mediated by the presence of hygroscopic salts on the leaf surface.

(*a*) *Interactions with other pollutants*

In addition to the effect of humidity, R_w is also expected to be controlled by the chemistry of leaf surfaces. This may be influenced both by ion-exchange with plant tissues and by the simultaneous deposition of other pollutants (Draaijers 1993). The solubility of NH_3 in leaf surface water is controlled largely by solution pH, so that buffering of leaf surface pH by CO_2 or leaching of base cations may affect deposition rates. A frequently discussed interaction is the possible effect of SO_2 deposition and subsequent oxidation to SO_4^{2-}, enhancing deposition rates of NH_3. This effect has been termed ‘co-deposition’, because it would affect both NH_3 and SO_2 uptake rates in parallel. Measurements of forest throughfall fluxes have sometimes shown molar ratios of 2:1 for NH_4^+:SO_4^{2-}, and this has been explained assuming equivalent co-deposition of SO_2 and NH_3 (van Breemen *et al.* 1982). However, other ratios (up to 4:1) have also been measured (Draiijers 1993; Wyers, unpublished data), while canopy ion-exchange and NH_3 emission would complicate such simplistic interpretations.

Expressed using the resistance analogy, SO_2 deposition might be expected to reduce R_w and R_c for NH_3. While this effect is supported by the results of laboratory experiments (Adema *et al.* 1986; van Hove *et al.* 1989), there is debate as to whether this is seen in micrometeorological measurements (Sutton *et al.* 1993*a*; Erisman & Wyers 1993). Sutton *et al.* (1993*a*) have, however, noted that any such effect for NH_3 may be offset because of competing emission from plant stomata, particularly for agricultural plants with large χ_s. Larger concentrations of SO_2 are expected to form more acidic SO_4^{2-} aerosol in the atmosphere. This may react with and deplete gaseous NH_3 concentrations to less than χ_s, so promoting

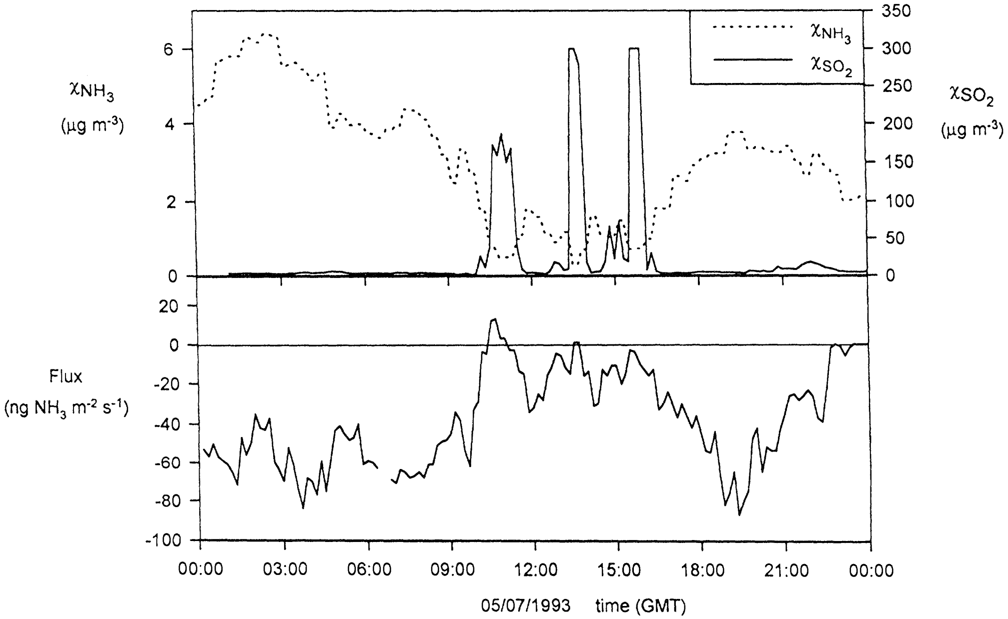

Figure 5. Observed interaction between NH_3 and SO_2 air concentration and NH_3 flux over a wheat canopy at Sutton-Bonington in central England.

NH_3 emission from the plants. Hence the net flux with the atmosphere would be expected to be a result of competition between enhanced cuticular uptake and enhanced stomatal emission. A case study of this effect is shown in figure 5 for a wheat canopy at grain filling stage. The data show a clear anti-correlation between the NH_3 and SO_2 concentrations, with brief periods of NH_3 emission occuring when the NH_3 concentration was low.

4. Ammonia exchange with plant tissues

The primary pathway for gaseous NH_3 exchange with plant tissues is via stomata, with the compensation point expected to be the substomatal NH_3 concentration at equilibrium with aqueous NH_3 in the apoplastic (intercellular) solution. The dissociation equilibrium of ammonia provides that aqueous NH_3 is a function of the ratio $[NH_4^+]/[H^+]$. In addition, the effect of temperature on the combined Henry and dissociation equilibria (Sutton *et al.* 1994) results in an exponentially larger χ_s at increasing temperature, given fixed solute concentrations. The resulting flux of NH_3 through stomata depends on the relative magnitude of the χ_s, $\chi\{z\}$ and R_s.

It should be noted that more than one compensation point concentration may be defined. The 'stomatal compensation point' (χ_s) in the leaf is not necessarily equal to net the value for the whole canopy. The 'canopy compensation point' has, for micrometeorological reasons, been referred to previously as $\chi\{z_0'\}$ (Sutton *et al.* 1992, 1993*a*, *b*) though this is given here as χ_c, both to simplify the notation and to reflect the fact that it is the concentration analogue of R_c. The difference between χ_c and χ_s is a result of the competing fluxes within the canopy. Thus, where deposition to leaf cuticles occurs, $\chi_c < \chi_s$.

Farquhar *et al.* (1980) did not account for leaf cuticle deposition and estimated

Table 1. *Gaseous* NH_3 *exchange and* NH_4^+ *concentrations in leaf tissues and xylem sap of 35-day old barley plants growing in either* NO_3^- *or* NH_4^+ *nutrient solutions*

(Ammonia fluxes determined by controlled chamber experiments with measurements of NH_3 by continuous flow denuder. Values are means ±SE of four independent experiments (M. Mattsson & J. K. Schjørring, unpublished data).)

growth conditions	plant component	plant dry weight (g plant^{-1})	NH_3 emission (ng m^{-2} leaf area s^{-1})	tissue NH_4^+ (µmol g^{-1} fresh weight)	xylem NH_4^+ (mmol l^{-1})
NH_4^+	shoot	3.9 ± 0.3	13.8 ± 1.87	40 ± 8	0.60 ± 0.05
	root	1.7 ± 0.3		96 ± 19	
NO_3^-	shoot	4.0 ± 0.6	0.68 ± 0.09	16 ± 5	0.38 ± 0.03
	root	2.2 ± 0.1		24 ± 1	

χ_s at 1–4 µg m^{-3} for several plant species. The values in figure 1 are similar, and since here chamber H was only 55%, cuticular deposition was probably small. Morgan & Parton (1989) reported a much larger χ_s of 13 µg m^{-3} for spring wheat during early grain filling, increasing to more than 25 µg m^{-3} at the end of the growing period. In contrast, Kesselmeier *et al.* (1993) estimated values of 0.3 µg m^{-3} for spruce in a German forest. Estimates of χ_s have also been made from micrometeorological measurements over other crops using simple models assuming negligible cuticular deposition, and providing values in the range 1–7 µg m^{-3} (Dabney & Boulding 1990; Sutton *et al.* 1993*c*). In addition, Sutton *et al.* (1993*c*) estimated the canopy compensation point (χ_c) to be in the range 0-2 µg m^{-3} depending on canopy wetness. The estimates of Langford *et al.* (1992) over a mixed pine, spruce-fir and aspen forest of less than 1 µg m^{-3} would also be analogous to χ_c, though for their low H conditions it is likely that $\chi_c \approx \chi_s$.

Typical pH values of the apoplast are estimated to be in the range 6–7 (Farquhar *et al.* 1980; Pfanz & Dietz 1987; Hoffmann *et al.* 1992). Thus given a value of χ_s of 2 µg m^{-3} at 20 °C and applying solubility equilibria, would provide an apoplastic $[NH_4^+]$ of 46–460 µmol l^{-1}. The existence of large pH and $[NH_4^+]$ gradients in leaf tissues make it difficult to measure apoplastic concentrations. However, leaf apoplast concentrations will depend on the transpiration stream $[NH_4^+]$ in xylem. Examples of xylem $[NH_4^+]$ for barley plants are shown in table 1, with values in the region 500 µmol l^{-1}. Larger values were found for plants supplied with NH_4^+ compared with NO_3^-, and this is consistent with results of Cramer & Lewis (1993). In contrast, the effect of nutrition on χ_s may not be so simple. The form of nitrogen (N) nutrition is expected to have different effects on leaf pH (Raven 1988) and there is evidence that plants supplied with NH_4^+ may have reduced apoplastic pH compared with those receiving NO_3^- (Hoffmann *et al.* 1992), an effect that would reduce χ_s. Nevertheless, the results in table 1 show that NH_4^+ fertilized plants emitted more NH_3 compared with plants supplied with NO_3^-. Effects such as this could alter the magnitude of χ_s between native plants growing on acidic soils (largely NH_4^+ nutrition) and agricultural crop species (largely NO_3^- nutrition).

Ammonia tissue concentrations may be closely coupled to plant N metabolism. Assimilation of NH_3/NH_4^+ is mediated by the enzymes glutamine synthetase (GS)

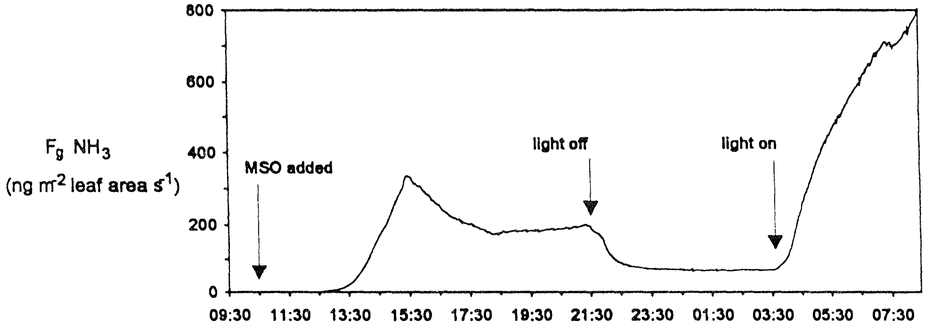

Figure 6. Effect of inhibition of glutamate synthetase (GS) activity by methionine sulphoxime (MSO) on NH_3 emission from 30-day-old barley plants. Controlled chamber measurements with online determination of NH_3 by continuous flow denuder (M. Mattsson & J. K. Schjørring, unpublished data).

and glutamate synthase (GOGAT), while processes releasing NH_4^+ in plants include nitrate reduction, photorespiration and senescence-induced proteolysis (Joy 1988). In agricultural cereals GS and GOGAT activities decrease rapidly as the leaves senesce (Schjørring *et al.* 1993*b*). Coupled to increased proteolysis for remobilization of N to seeds, this may be followed by an increase in $[NH_4^+]$ and NH_3 emission (Parton *et al.* 1988; Schjørring 1991; Schjørring *et al.* 1993*a*). It appears that plant source–sink relations are therefore important in controlling NH_3 emissions. For example, unfavourable growth conditions during the grain-filling stage of crop growth may limit the sink capacity for N, giving larger emissions (Schjørring 1991).

The importance of GS in re-assimilating NH_3/NH_4^+ produced by plant metabolism is shown by the fact that inhibition of GS dramatically increases NH_3 emission (figure 6). Before adding the GS inhibitor methionine sulphoxime (MSO), NH_3 emission per unit leaf area from these NO_3^- fed barley plants was less than $1\ \mathrm{ng\ m^{-2} s^{-1}}$. Application of MSO increased this to more than $200\ \mathrm{ng\ m^{-2} s^{-1}}$ as NH_3 production was not balanced by re-assimilation. It is notable that large NH_3 emissions occurred even in dark conditions, which may result from NH_3 accumulation limiting stomatal closure. By 0400 hours the plant metabolism became severely disrupted, with secondary protein breakdown producing even larger NH_3 emissions.

It should be evident from this section that the stomatal compensation point (χ_s) is by no means a constant. For a known leaf temperature, apoplastic pH and $[NH_4^+]$, χ_s may be predicted from chemical solubility. However, both pH and $[NH_4^+]$ vary greatly with plant nutrition, growth stage and species, and it is a challenge to future measurements to provide sound estimates of χ_s.

5. Modelling the plant–atmosphere exchange of ammonia

Though the focus of this paper is the plant–atmosphere exchange of NH_3, it should be noted that for agricultural systems soil emissions may occur following fertilizer application. However, NH_3 emitted from soils may be recaptured by leaf cuticles and stomata (Denmead *et al.* 1976). Where recapture is efficient or the soil flux small, the net flux with the atmosphere may be quantified on the basis of the plant canopy processes, and this simplification is made here. However,

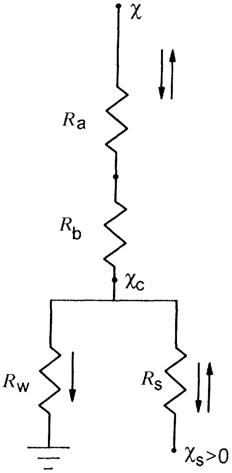

Figure 7. Proposed resistance model of NH_3 exchange with plant canopies, accounting for parallel deposition on to leaf cuticles (R_w) and exchange through stomata (R_s) with a stomatal compensation point (χ_s). The canopy compensation point is given by χ_c.

where soil emission cannot be ignored there is a need for improved integration in modelling plant–soil–atmosphere exchange.

The most usual resistance model used to describe pollutant deposition is the V_d and R_c approach of equations (2.1) and (2.2). While this may adequately describe NH_3 dry deposition to unfertilized ecosystems, as has been discussed, it is less suited to modelling bidirectional fluxes. Wyers *et al.* (1993*a*) have parametrized NH_3 emission/deposition using R_c estimates. However, external criteria were required (e.g. H, light intensity) to impose the required switch from deposition to emission. An alternative to the R_c model is to assume that NH_3 is exchanged solely through stomata with a compensation point, χ_s. In this case the flux is

$$F_g = (\chi_s - \chi\{z\})/(R_a\{z\} + R_b + R_s). \tag{5.1}$$

However, this model is also limited, since it ignores the parallel deposition to leaf cuticles, controlled by the resistance R_w.

Figure 7 illustrates a revised model that accounts for both R_w and χ_s (Sutton *et al.* 1993*a*). The inclusion of χ_s and R_w means that leaf surface deposition may short-circuit stomatal emission, and it is therefore not possible to sum R_s and R_w in parallel, as done in models for SO_2 (Fowler *et al.* 1989). The key to the present model is that the canopy compensation point (χ_c) is calculated instead of R_c, and this allows inference of both emission and deposition fluxes. The model may be used to interpret measured fluxes, by examining the sensitivity of R_w to imposed χ_s, or vice versa. Altenatively, it may be used to predict χ_c and the net atmospheric flux (F_g) given estimates of χ_s and R_w. It may be shown that (Sutton & Fowler 1993):

$$\chi_c = \frac{\chi\{z\}/(R_a\{z\} + R_b) + \chi_s/R_s}{(R_a\{z\} + R_b)^{-1} + R_s^{-1} + R_w^{-1}}, \tag{5.2}$$

$$F_g = (\chi_c - \chi\{z\})/(R_a\{z\} + R_b). \tag{5.3}$$

An example application of this model to predict measured fluxes is shown in figure 8 using the data from figure 5. The measurements were fitted using a

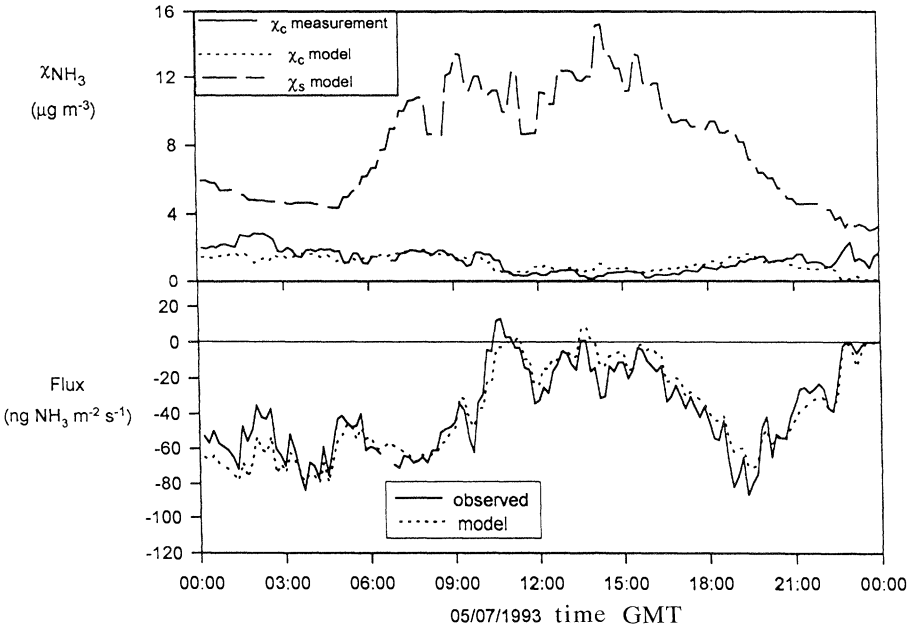

Figure 8. Comparison of measured NH_3 flux and canopy compensation point (χ_c) over a wheat canopy, with model estimates of the stomatal compensation point (χ_s). Modelled χ_s based on canopy temperature, pH 6.8 and 600 μmol l^{-1} NH_4^+. Model R_w set to 20 m s^{-1}.

constant R_w of 20 s m^{-1} and apoplastic NH_4^+ of 600 μmol l^{-1}. The large [NH_4^+] for these data is comparable with the xylem measurements in table 1. Figure 8 shows the clear difference between χ_s and χ_c, which is a result of the small value of R_w. In figure 9 the model is applied to fluxes measured over Speuld forest (Wyers *et al.* 1993*a*) in the Netherlands, which is located in an agricultural area with very large NH_3 concentrations. In this case the model was fitted to the measurements by applying the R_w from measured night-time R_c (figure 4) together with pH 6.8 (Farquhar *et al.* 1980) and [NH_4^+] of 550 μmol l^{-1}. It may seem surpising that this forest could have apoplastic [NH_4^+] similar to the agricultural canopy. It is possible that these large [NH_4^+] for the Speuld forest may be linked to the negative feedback discussed by Sutton *et al.* (1993*e*), as intense long-term N deposition at this site alters the biology of the trees. Typical χ_s at this site would be approximately 10 μg m^{-3} at 15 °C, a factor of 30 larger than the estimates of Kesselmeier *et al.* (1993) for a forest subject to much cleaner air.

The model outlined above provides the simplest treatment of competing stomatal, leaf cuticle and atmospheric NH_3 exchange processes. In practice cuticular uptake may behave more like a capacitance. For example, periods of NH_3 emission may be expected following a drop in NH_3 air concentrations or during evaporation of dew. Nevertheless, the model provides a first step that would enable the importance of this effect to be tested, since emissions not predicited by stomatal fluxes may point to NH_3 release from leaf surfaces. A further limitation of the present model is the exclusion of soil fluxes. In principle a soil flux may be added to (5.2). However, since the model is essentially a ‘big leaf’ model of the canopy, the results would be imprecise because of different source sink locations. In this instance, multilayer models might be helpful to integrate plant– and soil–atmosphere fluxes.

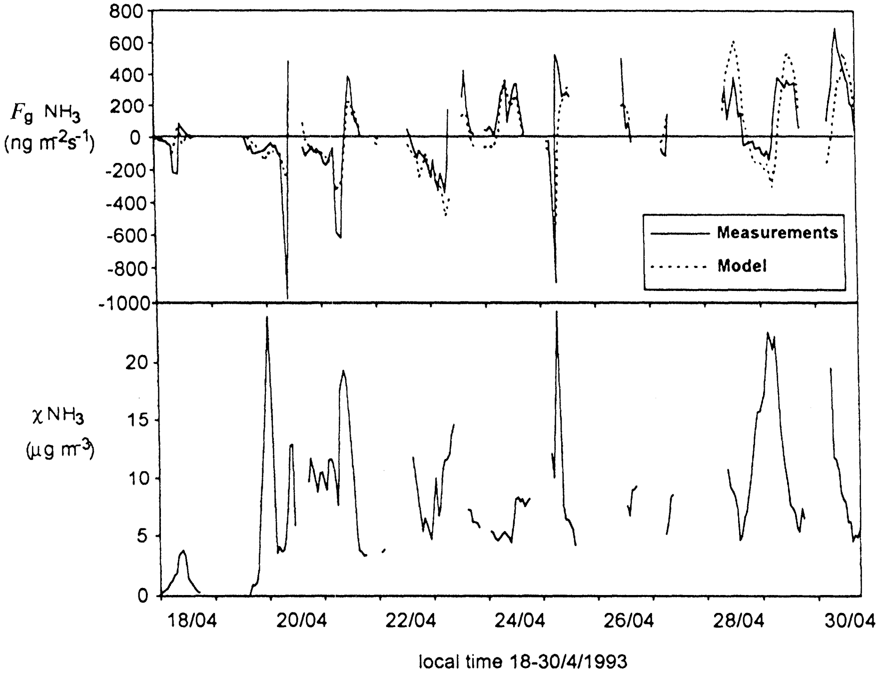

Figure 9. Air concentrations and comparison of measured and modelled NH_3 flux over Speuld forest in The Netherlands. Model assumes leaf apoplast pH 6.8 and 550 μmol l^{-1} NH_4^+. R_w from figure 4*d*.

6. Conclusions

Controlled environment and micrometeorological studies have both provided useful information on NH_3 plant–atmosphere exchange. Chamber measurements have demonstrated the existence of a compensation point concentration for NH_3 exchange with plant stomata (χ_s). Cuticular uptake was probably negligible in these studies because of the use of low relative humidity conditions. By contrast, micrometeorological studies have shown that cuticular deposition is often large in the field. The competition between stomatal exchange and cuticular uptake may result in the net NH_3 compensation point for the canopy (χ_c) being much smaller than χ_s.

Field measurements have also shown a difference between unfertilized ecosystems and fertilized croplands, with the latter showing bidirectional NH_3 fluxes, while deposition usually dominates for the lower nitrogen (N) status ecosystems. However, more recent measurements have also shown NH_3 emission from native ecosystems, particularly where atmospheric N inputs are large. This may be due to a negative feedback, where N deposition raises χ_s, limiting deposition. This effect would have important consequences for comparisons with critical loads, as reduced NH_3 deposition may be a consequence of having exceeded the critical load.

Resistance to NH_3 uptake by plant cuticles (R_w) may be a function of the chemical composition of deposits on leaves, with the presence of SO_2 enhancing NH_3 cuticular uptake. However, reactions with atmospheric SO_2 or SO_4^{2-} may also deplete NH_3 air concentrations to less than χ_c, which would promote NH_3 emission.

At present further work is required to establish the quantitative importance of these processes.

A new resistance model of NH_3 exchange has been developed to account for the competing effects of R_w and χ_s. The model calculates χ_c, from which net fluxes with the atmosphere may be inferred. At present it is possible to predict short term NH_3 fluxes, though there is a need to provide a better link between χ_s, plant phenology, species and N supply to allow longer term estimates for different ecosystems. Current estimates of NH_3 inputs are extremely uncertain, but show that NH_3 represents a major fraction of the total atmospheric N loading to temperate ecosystems in agricultural regions. The present development of a more mechanistic description of NH_3 exchange is therefore an important component in quantifying the impact of regional pollutant deposition.

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Discussion

J. H. DUYZER (*TNO, Delft, The Netherlands*). How sensitive to the choice of the compensation point is the performance of the model which predicts NH_3 fluxes? Are there independent methods to determine this compensation point?

M. A. SUTTON. The model estimates of NH_3 fluxes are sensitive both to the choice of stomatal compensation point (χ_s) and the leaf cuticle resistance (R_w). The predicted canopy compensation point (χ_c) is the most sensitive parameter, though because net exchange is scaled by the atmospheric resistances, the net flux with the atmosphere is much more stable. Specifically, the sensitivity to χ_s

depends on the values of R_w and R_s; where R_w is small, the value of χ_s has little effect as any emitted NH_3 is recaptured by leaf surfaces. Equally, where R_s is large (night), χ_s has little effect on fluxes.

The interaction between χ_s and R_w obviously points to the need for more independent estimates of these quantities. Independent estimates of χ_s may be made by chamber gas exchange measurements and from tissue NH_4^+ concentrations, as reported in the paper, and these provide an important check on the model values. Clearly, the early estimates made here need to be refined by more extensive comparisons with these other methods.

P. Ineson (*Merlewood Research Station, Grange-over-Sands, Cumbria, U.K.*). If NH_3 is released at about 0.5 km upwind of a forest and co-deposition of $(NH_4)_2SO_4$ to the canopy is observed, will most of the $(NH_4)_2SO_4$ have been formed as an aerosol before reaching the trees, on the leaf surfaces in the canopy, or in stomatal cavities? Can a wet sheet of glass be said to have a compensation point for NH_3 deposition?

M. A. Sutton. The rate of formation of ammonium sulphate aerosol in the atmosphere downwind of an ammonia source will depend on the air concentrations of SO_2 and acidic SO_4^{2-} aerosol. In a polluted environment with sufficient acidic aerosol, such as H_2SO_4, reaction to form ammonium sulphates will be rapid, limited by rates of mass transfer between the NH_3 and aerosol. However, the ammonium sulphate aerosols produced (e.g. NH_4HSO_4), $(NH_4)_2SO_4$), typically exist in a size range (0.1–1 μm) that is dry deposited slowly so that this mechanism is expected to increase long-range transport, and only contribute a small fraction of the local deposition. Atmospheric reaction of NH_3 and SO_2 is limited by rates of SO_2 oxidation to SO_4^{2-}, so that aerosol formed by this reaction are expected to contribute even less to local deposition. It is more likely that enhanced concentrations of ammonium sulphate observed in forest throughfall are the result of SO_2 and NH_3 dry deposition to leaf surfaces. Measurements show significant uptake of these gases on to leaf cuticles, so that oxidation to SO_4^{2-} would proceed after dry deposition. The importance of the reaction occurring in stomata followed by leaching of $(NH_4)_2SO_4$ is less clear.

The term 'compensation point' refers to the offsetting of two (or more) opposing processes. Hence the compensation point of ammonia is the air concentration at which processes consuming ammonia balance those releasing it. In the case of a 'stomatal compensation point' this depends on metabolic production and consumption at a cellular scale. For a 'canopy compensation point', the processes would be the stomatal versus leaf cuticular fluxes. Evaporation of ammonium from a wet sheet of glass may result in a concentration potential for ammonium emission, but this is the result of only one chemical equilibrium, and would be exhausted once the glass is dry. This is therefore not the same as a compensation point.

D. S. Powlson (*Institute of Arable Crops Research, Rothamsted, Hertfordshire, U.K.*). Results suggesting substantial loss of ammonia – of about 30–40 kg N ha^{-1} a^{-1} – from the foliage of arable crops have been published. Are such values consistent with modern understanding of the subject, or are they likely to be 'special cases'? Are there opportunities to manipulate plant process, by management or breeding, to alter plant compensation points and decrease the possibility of NH_3 loss?

M. A. Sutton. The only measurements I am aware of that have indicated foliar ammonia emissions from arable crops of the magnitude mentioned were indirect measurements, based for example on dilution of N^{15} applied to experimental plants. Most of the direct micrometeorological ammonia flux measurements of ammonia emissions from crops indicate emissions in the range 0–5 kg N ha^{-1} a^{-1}, with values up to 15 kg N ha^{-1} a^{-1}. There is certainly evidence that larger ammonia emissions may be associated with poor growing conditions, resulting in poor grain filling and a low fraction of N in the grain compared with the rest of the plant. However, differences of this magnitude between the micrometeorological measurements and indirect experiments do beg the question of the reliability of the indirect estimates.

There are few data on ammonia compensation points for different crop cultivars. Nevertheless, the results presented in figure 1 of this paper indicate that an old-fashioned, low N cultivar of barley had a lower compensation point than a modern, high yielding variety. This suggests that plant breeding for higher yields may actually have resulted in larger ammonia emissions from crops.