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Measurement and modelling of ammonia exchange over arable croplands

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Abstract

Micrometeorological measurements of the exchange of atmospheric ammonia over arable land are reported. Measurements were made over bare soil and wheat canopies at early canopy closure, approaching anthesis and during early senescence. Bare soil showed a slow rate of deposition with a canopy resistance (R_c) of around 300 s m^{-1}, while fluxes over young wheat were still dominated by fertilizer urea soil emissions (up to 170 ng m^{-2} s^{-1}) nearly a month after fertilization. Summer measurements showed that vegetation processes dominated exchange, apart from immediately after fertilization with ammonium nitrate, which contributed around 5 ng m^{-2} s^{-1} to the net flux 1-2 days after application.

The Summer NH_3 fluxes have been interpreted using a new micrometeorological modelling approach. The R_c model is unable to simulate the mechanisms of bi-directional exchange, and a recently developed model that quantifies the 'canopy compensation point' (χ_c) for NH_3 was applied. In this model net fluxes are predicted as the resolution of competing leaf surface deposition and bi-directional stomatal fluxes. The model provides a simple approach to predict net NH_3 fluxes with the atmosphere, though sometimes underestimates morning NH_3 emissions. A possible explanation of this effect is that the leaf surface behaves as a capacitor for NH_3 adsorption. A revised capacitance model is developed that extends the analysis of the χ_c model. The capacitance model is able to reproduce the behaviour of morning emission, though further development of both models is required to provide a description valid over longer periods.

1. INTRODUCTION

Deposition of atmospheric ammonia (NH_3) and ammonium (NH_4^+) (collectively NH_x) is an important contributor to ecosystem acidification and eutrophication (*e.g.* Grennfelt and Thörnelöf 1992; Sutton *et al.* 1993d). It is necessary to quantify the inputs of these species to sensitive ecosystems, to be able to assess their environmental impact as well as the contribution of NH_x relative to other acidifying inputs. One of the main uncertainties in quantifying total inputs of NH_x is the magnitude of the gaseous NH_3 dry deposition term. The uncertainty is emphasized because NH_3 may be both emitted from and deposited to land surfaces. The atmospheric nitrogen inputs to arable land may be small compared with agricultural practice. However, because of the large area extent of arable land in Europe it becomes important to quantify the net fluxes (emission and deposition) in calculating atmospheric budgets and parametrizing atmospheric transport models (*e.g.* Sandnes and Styve 1992; Asman and van Jaarsveld 1992; Singles *et al.* 1995). In this way knowledge of crop-atmosphere exchange becomes important in understanding the N inputs to semi-natural ecosystems.

Measurements of NH_3 exchange over cereals have often implied that a 'compensation point' exists within plants and is important in controlling net fluxes (*e.g.* Farquhar *et al.* 1980; Schjørring 1991; Sutton *et al.* 1993c). It is known that ammonia plays a major role within the biochemical pathways of plants, so that for a particular intercellular NH_4^+ concentration, there is an equilibrium atmospheric gaseous NH_3 concentration. The term 'compensation point' is used to reflect the interpretation that this is the concentration at which metabolic consumption processes balance production, while the exchange is viewed as operating via stomata. This is referred to here as the 'stomatal compensation point' (χ_s). Against this physiological background, it is also known that ammonia is a very soluble gas and is frequently found in micrometeorological experiments to deposit rapidly to semi-natural vegetation and this is believed to be the result of leaf surface sorption processes (Duyzer *et al.* 1994; Sutton *et al.* 1993b; Erisman and Wyers 1993). Ammonia emission from a compensation point by therefore be short circuited by deposition to leaf cuticles.

Arable croplands to show evidence of both processes operating, resulting in the direction of the net atmospheric flux changing with environmental and plant conditions. In part, this may be related to the higher nitrogen status of these ecosystems, resulting in a larger compensation point and potential to overcome cuticular uptake. Until recently, model descriptions of these processes had taken one of two lines: either to assume a solely stomatal exchange with a compensation point (mostly the chamber experiments); or to treat the exchange with a deposition velocity (V_d) and canopy resistance (R_c) model, originally designed for parametrizing deposition processes (mostly the micrometeorological experiments). A combined model to reconcile these different interpretations was proposed by Sutton and Fowler (1993). In this model, calculation of R_c is replaced by its concentration analogue (χ_c), referred to as the 'canopy compensation point', the magnitude of which is defined by competition for exchange between the atmosphere, cuticle and stomata.

The present paper reports measurements of ammonia surface-atmosphere exchange, made using the aerodynamic gradient technique. Fluxes were measured at several stages during the year, including over bare soil and over different wheat canopies at different stages. In addition to these main measurements, a short chamber study was made to provide an indication of the contribution of soil to the net atmospheric emission from a wheat canopy. Where the plant canopy was established as being the main site of ammonia surface-atmosphere exchange, particular attention was given to investigating the processes controlling the net ammonia flux. The results are interpreted using the canopy compensation point model of Sutton and Fowler (1993) and constraints of the model identified. In particular the possibility that the leaf surface may behave as a capacitor for NH_3 adsorption /dissolution is investigated and an initial framework to parametrize this effect suggested.

2. MICROMETEOROLOGICAL THEORY

A full description of the micrometeorology applied in this study and its restrictions has been given by Sutton *et al.* (1993a,b), so only an outline description is given here. The flux measurements were made using the aerodynamic gradient method. In this approach the net flux (F_t) (negative fluxes denote deposition) is determined from wind (u) and concentration (χ) profiles with height above a uniform surface with extensive fetch:

$$F_t = -k^2 \frac{du}{d[\ln(z-d)-\psi_M]} \frac{d\chi}{d[\ln(z-d)-\psi_H]} \qquad (1)$$

where z is height above ground, d is the displacement of ground level due vegetation, k is the von Karman constant (0.41) and ψ_M, ψ_H are corrections for atmospheric stability.

As noted in the introduction it is usual to interpret measured fluxes by calculating the deposition velocity (V_d) and canopy resistance (R_c). In principle this resistance approach is designed to describe deposition processes, since it assumes that the concentration at the absorbing surface ($\chi_{surface}$) is zero. In this case, by analogy with Ohm's law:

$$V_d\{z\text{-}d\} = 1/R_t\{z\text{-}d\} = F_t/(\chi_{surface} - \chi\{z\text{-}d\}) = -F_g/\chi\{z\text{-}d\} \qquad (2)$$

$$R_t\{z\text{-}d\} = R_a\{z\text{-}d\} + R_b + R_c \qquad (3)$$

where R_t is the total resistance to deposition, R_a the turbulent atmosphere resistance, R_b the quasi-laminar diffusion resistance. This approach is convenient since V_d is assumed to be independent of χ, and the flux may be modelled given estimates of R_c and χ, together with meteorological information. Nevertheless, it is not possible without manual switches to use the model to predict bi-directional exchange. The alternative stomatal model noted above describes bi-directional fluxes satisfactorily, but ignores any parallel deposition to leaf surfaces. Here χ_s is the stomatal compensation point and R_s the stomatal resistance:

$$F_t = (\chi_s - \chi\{z\text{-}d\})/(R_a\{z\text{-}d\} + R_b + R_s) \qquad (4)$$

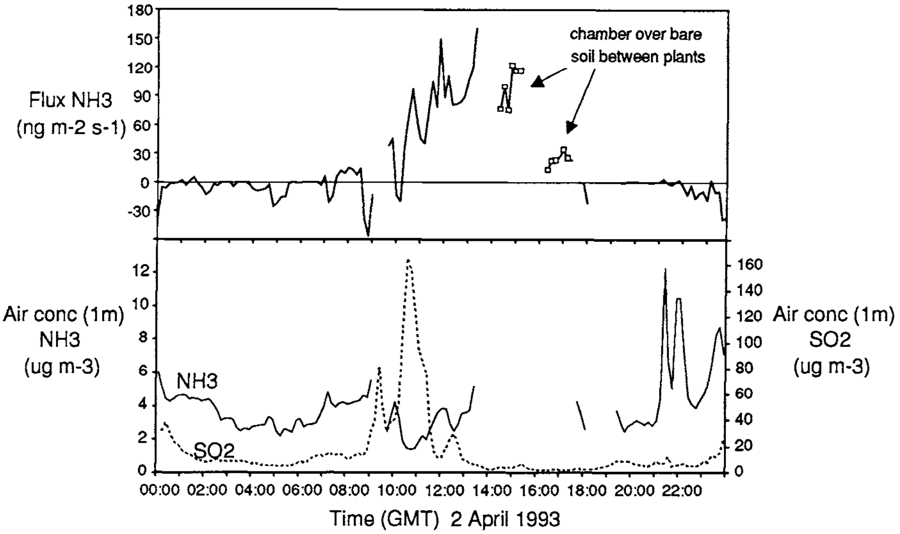

Figure 1. Micrometeorological ammonia flux measurements and air concentrations of NH_3 and SO_2 over a young wheat canopy (14 cm). Measurements made 1 month after fertilization with 35 kg N ha^{-1} as urea. Open squares are chamber measurements of soil emission.

Given the limitations of both these approaches, in later sections the results are used to develop revised resistance models that treat both a compensation point and cuticular uptake.

3. SITE AND MEASUREMENTS

The measurements were made over bare soil and canopies of wheat at the field station of the University of Nottingham at Sutton-Bonington, Loughborough, UK. The site used provided extensive fetch of >200 m in most wind sectors and up to 500 m. Measurements were made in the surface layer up to 2 m above the wheat canopy. In May 1992, measurements were made above a wheat canopy (60-70 cm) approaching senescence. On May 20, 35 kg N ha^{-1} as ammonium nitrate was applied. A second campaign was made in March 1993, on the boundary between a bare field (harrowed soil) and a young wheat canopy (14 cm high). This wheat canopy had been fertilized with 35 kg N ha^{-1} as urea about 4 weeks prior to the measurements. A third campaign was made in June - July 1993, at the same site, when the wheat was approaching senescence (80 cm high), and sugar beet growing on the previously bare soil.

Ammonia concentration profiles were determined using a continuous wet annular denuder system described by Wyers *et al.* (1993). Measurements were made at two heights, and, to reduce possible bias between denuders, the collected NH_3 was brought (as NH_4^+ in the stripping solution) to a common detector for analysis. Analysis of the NH_4^+ in this system is by membrane diffusion of NH_3 at high pH into a counter flow of deionized water, with subsequent measurement by conductivity. Sulphur dioxide air concentrations were also determined though fluxes of SO_2 are not reported here. Windspeed was measured using 6 sensitive cup anemometers (Vector instruments), and temperature and water vapour profiles measured with a fine thermocouple and dewpoint meter system. Further details of the measurement methods and data treatment have been provided by Sutton *et al.* (1993a).

4. RESULTS

Figure 1 shows an example of the emissions detected during the Spring 1993 measurements, with fluxes up to 160 ng NH_3 m^{-2} s^{-1} and only limited net deposition occurring at night. Such large emissions are probably related to the fertilization of the soil with urea 1 month prior to the measurements. It is well known that substantial ammonia emissions occur from urea compared with other fertilizers (*e.g.* Whitehead and Raistrick 1990), however, it is generally

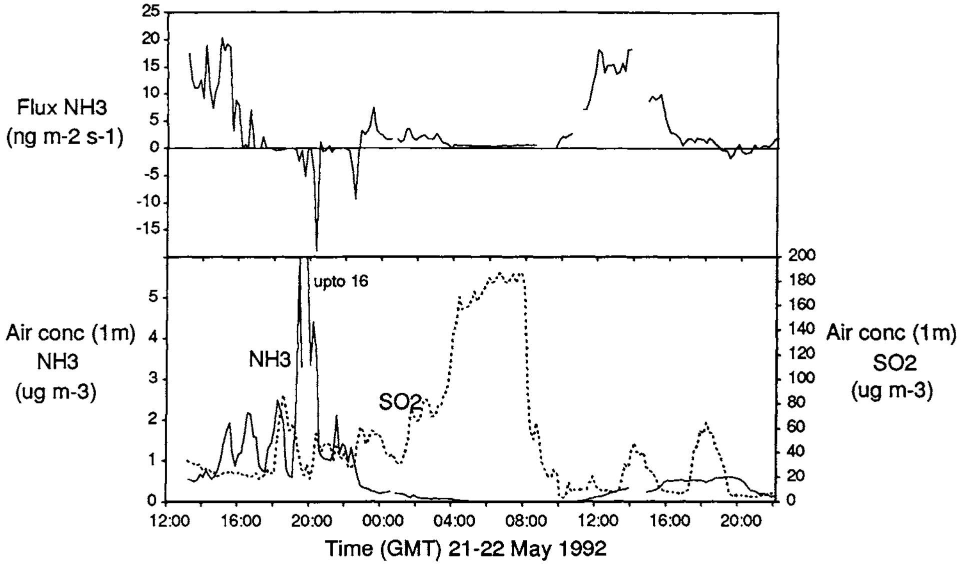

Figure 2. Micrometeorological ammonia flux measurements and air concentrations of NH_3 and SO_2 over a wheat canopy prior to anthesis. The soil was fertilized with 35 kg N ha^{-1} as ammonium nitrate on 20 May.

generally assumed that this soil emission is complete within 1-2 weeks of fertilization, after which vegetation processes dominate exchange. The hypothesis that the emissions derived from the soil was tested using a simple chamber placed over bare soil between the plants. The flux was derived from the difference of the inlet and outlet concentrations with a flow rate of 30 l min^{-1}. Given the small area of the chamber (0.07 m^2), possible patchiness in emissions over the field, and potential adsorption of NH_3 to chamber walls, this test was only expected to give a broad indication of the soil flux. The results, presented in Figure 1, show a very close agreement with the micrometeorological estimates. This high level of similarity is almost certainly fortuitous, though clearly demonstrates that the soil was the main source of emission. During the same campaign, measurements were made of the deposition rate to bare agricultural soil (pH 6-7). This showed a reasonably consistent pattern of deposition at a slow rate, with good data indicating an R_c of around 300 s m^{-1}.

The measurements in May 1992 were made before and after fertilization with ammonium nitrate. It is known from laboratory studies that emissions from this fertilizer are expected to be small (*e.g.* 1 % applied N). Measurements before fertilization (1 month after previous fertilization with ammonium nitrate) showed no detectable soil flux, with vegetation dominating the exchange process. In contrast to the April 1992 measurements, only a very small soil emission was detected following fertilization. The results are shown in Figure 2. In addition to day time emissions, they show a small but significant (5 ng m^{-2} s^{-1}) net emission during night time. Since stomata are closed during the night this is attributed to soil emission (supported by within-canopy concentration profiles).

In both Figures 1. and 2., SO_2 concentrations are plotted against the NH_3 concentrations. As previously shown by Sutton *et al.* (1993a), there is an inverse relationship between the concentrations of these 2 gases. This may be related to formation of ammonium sulphate aerosol depleting the concentration of one of the gases in the presence of an excess of the other.

5. INTERPRETATION OF RESULTS.

In order to simulate explain the bi-directional fluxes observed over the wheat canopy a modelling framework is required that can treat both NH_3 sources (compensation point, soil emission) and sinks (cuticular uptake, stomatal uptake) and their interaction. In particular,

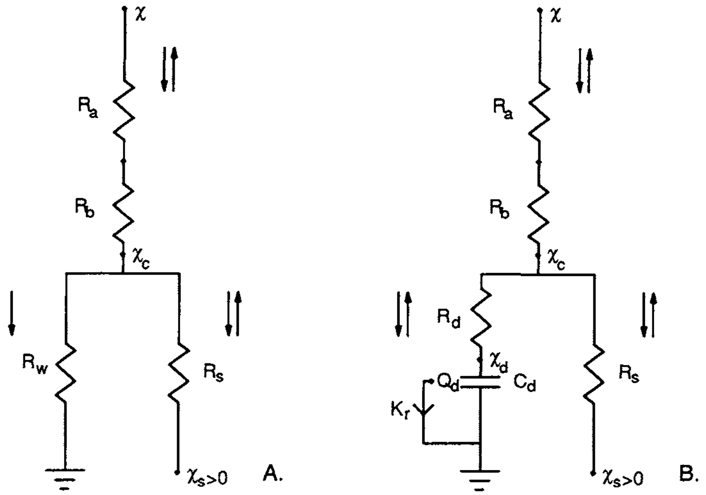

Figure 3. Model diagrams to describe the bi-directional exchange of ammonia between a plant canopy and the atmosphere. The net flux is described as the result of the exchange between the air concentration (χ) and the 'canopy compensation point' (χ_c), which is the result of competition between exchange to the leaf surface and transfer through stomata (R_s) with a stomatal compensation point (χ_s). Deposition to the leaf surface is treated in different ways: **A**, as a simple resistance (R_w); **B**. as an adsorption capacitance (C_d) of given charge (Q_d) with adsorption resistance (R_d) and a reaction rate (K_r). R_a and R_b are the resistances to atmospheric turbulence.

attention is given here to addressing the interaction between a stomatal compensation point, leaf cuticle uptake processes and atmospheric NH_3 concentrations.

5.1. Canopy compensation point - cuticular resistance model

A resistance diagram of the model of ammonia canopy exchange proposed by Sutton and Fowler (1993) is shown in Figure 3a. The model may be used as a tool either to interpret measured net fluxes or to infer the net flux given particular conditions. The difference between this and the of model Eq. (3) is that here the canopy compensation point (χ_c) is calculated rather than the canopy resistance (R_c). As with R_c (Eq. 3), χ_c may be directly estimated from micrometeorological measurements:

$$\chi_c = \chi\{z\text{-}d\} + F_t(R_a\{z\text{-}d\} + R_b) \qquad (5)$$

In principle the total flux F_t must be conserved in its component fluxes to the cuticle/water layers (F_w) and with stomata (F_s) so that:

$$F_t = F_w + F_s \qquad (6)$$

$$F_w = -\chi_c/R_w; \quad F_s = (\chi_s - \chi_c)/R_s \qquad (7a, 7b)$$

Hence, having determined F_t and χ_c from measurements, and from measured (or modelled) R_s, the value of R_w may be determined given different assumed values of χ_s. Alternatively, given an estimate of R_w, χ_s may be found. The presence of two unknowns points to the need for independent laboratory determinations of these parameters (*e.g.* χ_s).

In contrast, the model may be used in an inferential manner to explicitly estimate χ_c and F_t. Substitution of Eqs. (7a,b) into Eq. (6) and rearrangement provides:

$$F_t = (\chi_s\text{-}\chi_c)/R_s - \chi_c/R_w \qquad (8)$$

This may then be combined with Eq. (5) to eliminate F_t:

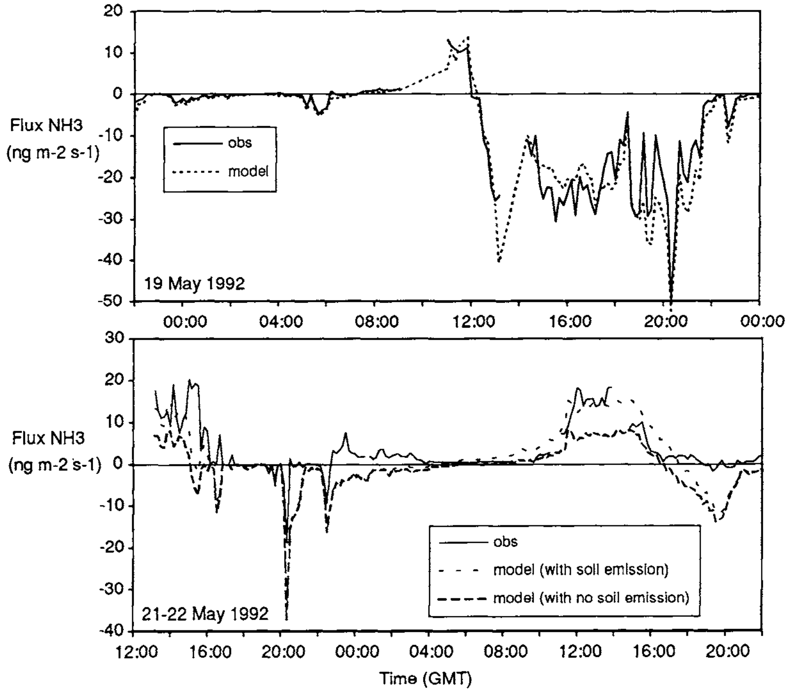

Figure 4. Comparison of measured ammonia flux over wheat and that predicted by the simple (R_w) canopy compensation point model. R_w calculated according to Eq. (12) and assuming plant intercellular pH 6.8 and 100 µmol NH_4^+ l^{-1}. Model soil emission in the χ_c calculation (Eq. 13) for 21-22 May set at 10 ng m^{-2} s^{-1}.

$$\frac{\chi_s/\chi_c - 1}{R_s} - \frac{1}{R_w} = \frac{1-\chi\{z-d\}/\chi_c}{R_a\{z-d\}+R_b} \qquad (9)$$

$$\frac{\chi_s}{\chi_c R_s} - \frac{1}{R_s} - \frac{1}{R_w} = \frac{1}{R_a\{z-d\}+R_b} - \frac{\chi\{z-d\}}{\chi_c(R_a\{z-d\}+R_b)} \qquad (10)$$

From which the canopy compensation point may be given as:

$$\chi_c = \frac{[\chi\{z-d\}/(R_a\{z-d\}+R_b)+\chi_s/R_s]}{\left[(R_a\{z-d\}+R_b)^{-1}+R_s^{-1}+R_w^{-1}\right]} \qquad (11)$$

and the flux found from Eq. (5).

Examples of the application of this model are shown in Figure 4. On the basis of comparison with laboratory studies of the relative humidity (*RH*) response of adsorption, a simple parametrization of R_w (s m^{-1}) was used (Sutton and Fowler 1993):

$$R_w = 2 \exp([100\text{-RH}]/12) \qquad (12)$$

The stomatal compensation point was calculated based on the temperature dependent Henry equilibrium using pH of 6.8 (Farquhar *et al.* 1980) and assuming 100 µmol NH_4^+ l^{-1} in the leaf intercellular fluid. The latter was chosen to fit the data in Figure 4a, and is consistent with other published estimates (Farquhar *et al.* 1980; Sutton *et al.* 1993c). Applying these values to the measurements after fertilization with ammonium nitrate (Figure 4b) significantly underestimated the flux. This may be due to daily variations in R_w but is also likely to be related to the presence of an additional soil emission, as indicated by the night time measurements. It is possible to provide to provide a simple treatment of soil emission in the canopy model:

$$\chi_c = \frac{\left[\chi\{z-d\}/(R_a\{z-d\}+R_b)+\chi_s/R_s+F_{soil}\right]}{\left[(R_a\{z-d\}+R_b)^{-1}+R_s^{-1}+R_w^{-1}\right]} \qquad (13)$$

The effect of adding a soil flux in this manner is shown in Figure 4b, indicating that the daytime emissions would be consistent with an additional emission into the canopy space of 10 ng m^{-2} s^{-1}. The difference between the two model estimates is not constant because of varying recapture by leaf surfaces and stomata. It should be noted, however, that introducing a soil emission in this simple way is unlikely to give precise results, because of the different physical location of the soil to the vegetation canopy. As a single layer model, it is assumed that all the exchange occurs at a single hypothetical height, which would be expected to provide errors for soil exchange processes.

5.2. Canopy compensation point - cuticular capacitance model

Although it is possible to provide reasonable agreement with the measured data using the simple canopy compensation point model, the measured results sometimes show much larger emission in the morning than predicted from a temperature dependent compensation point, while emission in the evening may be smaller than be expected. Two effects that may explain this are that the concentration of NH_4^+ in leaves is not constant throughout the day, and/or that the leaf cuticle acts more like a capacitor for adsorption of ammonia. There is some recent support from laboratory studies that the concentration of NH_4^+ may vary diurnally, with larger values in the early morning (Schjørring, 1994, pers. comm.), and further work is required to examine this possibility and its cause. However, it is equally possible that during increasing humidity conditions the leaf surface will be able to absorb more NH_3 than when the surface is drying. In the latter case, if deposited NH_4^+ is not 'fixed' by reaction to form salts with low vapour pressure (*e.g.* $[NH_4]_2SO_4$), it may be released back as NH_3 and contribute to net emission.

An model to explore this behaviour ammonia on leaf surfaces is shown in Figure 3b. A number of studies have investigated the link between relative humidity and thickness of notional 'water-films' on leaf surfaces (Van Hove *et al.* 1988; Benner *et al.* 1992; Burkhardt and Eiden 1994), which, for a given pH, would be expected to have a defined capacitance according to Henry's law. The relation defining the capacitance (C_d) may be expressed as:

$$C_d = Q_d/\chi_d \qquad (14)$$

where Q_d is the adsorption charge (µg m^{-2}) and χ_d the adsorption concentration (µg m^{-3}) associated with the capacitor. By analogy to this relationship, an estimate of C_d may be found from the Henry equilibrium constant and an equivalent water-film thickness (M_{H2O}). Using the solubility equilibria provided by Sutton *et al.* (1993d) gives:

$$C_d = M_{H_2O}\frac{[NH_4^+]+[NH_3.H_2O]}{[NH_3]_{(g)}} = M_{H_2O}\left[[H^+]/(10^{1.6035-4707.6/T})+(10^{1477.7/T-1.6937})\right] \qquad (15)$$

Here C_d and M_{H2O} are given in metres and T in Kelvin. On the basis of measurements on polluted leaves it is estimated that a typical value of M_{H20} would be 20 nm at 60% (Burkhardt, unpublished data). Using a similar humidity response to Eq. (12) and accounting for the canopy leaf area index (*LAI*), an initial estimate of M_{H2O} was found as:

$$M_{H2O} = LAI * 20 \exp([RH\text{-}60]/10) \qquad (16)$$

Unlike straightforward resistance models, treating the leaf surface exchange process as a capacitance results in the flux at a given time being time dependent on previous fluxes. Hence calculation of the modelled is linked over different model time steps. It is necessary to set an initial value of either Q_d or χ_d, so that for an initial time (i):

$$\chi_{d\{i\}} = Q_{d\{i\}}/C_d \qquad (17)$$

The flux into or out of the adsorption capacitor (F_d) is then:

$$F_d = (\chi_{d\{i\}} - \chi_{c\{i\}})/R_d \tag{18}$$

where R_d is the charging resistance of the capacitor. The value of $\chi_{c\{i\}}$ may be found by applying the canopy compensation point equation (Eq. 11) in slightly modified form:

$$\chi_c = \frac{[\chi\{z-d\}/(R_a\{z-d\}+R_b)+\chi_s/R_s+\chi_d/R_d]}{\left[(R_a\{z-d\}+R_b)^{-1}+R_s^{-1}+R_d^{-1}\right]} \tag{19}$$

The new capacitance charge ($Q_{d\{i+t\}}$) after t seconds is then found as:

$$Q_{d\{i+t\}} = Q_{d\{i\}} - (F_d.t) \tag{20}$$

Given the new value of Q_d a revised value of χ_d is found according to Eq. (17), and the process repeated for the next time step. While this parametrization will treat adsorption and desorption to cuticular water-layers, it does not provide for any net removal of NH_3 from the air by leaf surfaces. This may be accounted for by proposing a reaction flux (F_r) of the stored NH_4^+ (*e.g.* to form ammonium sulphates) with a rate constant K_r (s^{-1}):

$$F_r = Q_d.\, K_r$$

where a negative value of K_r indicates deposition. Inclusion of F_r into Eq. (20) provides:

$$Q_{d\{i+t\}} = Q_{d\{i\}} - (F_d.t) + F_r \tag{21}$$

In running this model it is found that the value of R_d defines the rate of charging of Q_d and provides the time constant of the adsorption/desorption process. It is anticipated that R_d should be larger in dry conditions (reduced access to the water layer), and this is also required to make the model run, since the model requires smaller time steps to remain stable with decreasing values of R_d and C_d. The initial results presented here are calculated using R_d (s m^{-1}) = $5000/C_d$ (m). This is equivalent to a time constant of 83 minutes.

An example of the application of this model is shown in Figure 5, for the measurements on 3-4 July 1993 over mature wheat (early leaf senescence). The measured fluxes on the 4 July showed a larger emission in the morning and less in the evening than would be expected by a compensation point emission through stomata. In this case the capacitance model is run assuming a leaf surface pH of 4.5 and an adsorbed NH_4^+ reaction rate (K_r) of -0.01 s^{-1}. The effect of including K_r is shown on the value of Q_d. Estimates of the modelled flux are provided, one just accounting for the capacitance effect, and the second linking this with the compensation point exchange. The model is able to predict successfully the peak of emission on the morning of 4 July, though daily differences related to untreated factors also occur since the flux on 3 July is not well represented. The comparison between the two model flux estimates in Figure 5, shows that stomatal uptake of NH_3 desorbed by the cuticle reduces the peak emission, while later on in the day stomatal exchange contributes to the modelled net emission.

6. DISCUSSION AND CONCLUSIONS

Measurements of NH_3 surface atmosphere-exchange over arable croplands show that each of stomatal, leaf surface and soil exchange processes are important in defining net fluxes. Where fertilizer nitrogen is added as ammonium nitrate, soil emissions are small and contributed here about 5 ng m^{-2} s^{-1} to the net flux 1-2 days after fertilization. In contrast, fertilization with urea provides much larger ammonia emissions. Chamber measurements made here supported the interpretation that the emissions were soil rather than vegetation related. An important finding was that the enhanced ammonia flux following urea fertilization may continue long after fertilization (4 weeks). Previous studies have often considered soil emissions complete after 1-2 weeks and may have underestimated urea emissions. Emission of ammonia from urea is a result of its hydrolysis to by urease producing ammonia and raising solution pH. In the example reported there had been little rain between fertilization and the measurements reported, suggesting that hydrolysis was slow. In contrast to these results, measurements over

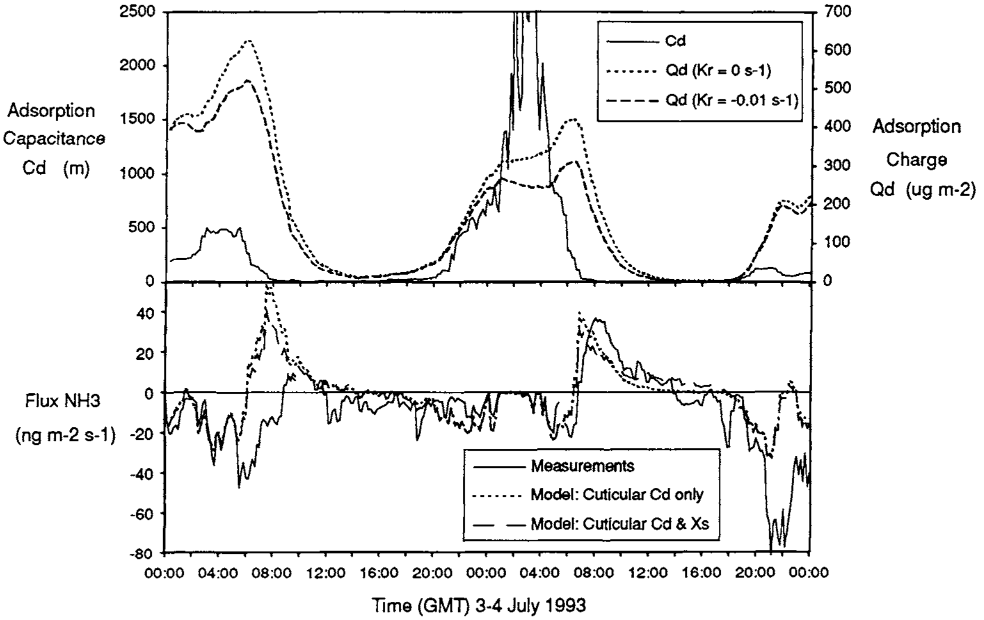

Figure 5. Comparison of measured ammonia flux over a ripening wheat canopy (78 cm, early senescence) with model estimates parametrized using the capacitance only (C_d) description of NH_3 uptake onto leaf surfaces, and the full model allowing for both C_d and stomatal exchange (R_s, χ_s). The model flux assumes leaf intercellular pH 6.8 and 50 µmol NH_4^+ l^{-1}, leaf surface pH 4.5, with an equivalent water-film thickness and C_d according to Eqs. (15-16). The model fluxes are calculated applying an adsorption reaction rate (K_r) of -0.01 s^{-1}, the effect of which is shown on the adsorption charge (Q_d), alongside the modelled value of C_d.

bare soil (pH 6-7) suggested a slow rate of dry deposition with canopy resistances of the order 300 s m^{-1}.

Apart from immediately after fertilization with ammonium nitrate, Summer measurements over a growing wheat crop, , showed no significant soil emissions. In these cases a recently developed model for estimating NH_3 fluxes was tested. In contrast to usual models, which calculate canopy resistances (R_c), the present model calculates the canopy compensation point (χ_c), which is found from the resolution of competing leaf cuticle and stomatal emission fluxes. Using a simple function of humidity to describe cuticular uptake, and assuming a stomatal compensation point dependent on leaf NH_4^+, provided a reasonable estimate of the net flux. Inclusion of a soil emission in the model provided a better fit to the measurements made after ammonium nitrate fertilization, though in principle such a single-layer model would be expected to be uncertain here because source-sink locations differ.

One limitation of the simple canopy compensation point model is that it sometimes underestimates emissions in the morning and overestimates emission in the evening. This may be due to either temporal variability in the stomatal compensation point, or to the leaf surface behaving as a capacitor for NH_3 adsorption. A revised capacitance model was developed to provide an initial investigation into the second possibility. Modelled fluxes in the capacitance model are dependent on previous fluxes, which regulate the value of the adsorption charge (µg m^{-2}) of NH_3. By itself the capacitance treatment does not result in a net removal of ammonia from the atmosphere, though this effect may be treated by allowing for reaction of the adsorbed NH_4^+ to form fixed salts. The model is only at a preliminary stage, and yet is able to predict accurately the elevated morning emission of ammonia. Other subtleties of the chemical processes and physiological controls will require further development of these approaches. The simple canopy compensation point model has fewer unknowns than the capacitance model, and is therefore to be preferred in principle. However, an examination of the fluxes in more detail using the capacitance model provides a useful aid to understanding the processes which regulate the net exchange of ammonia between soil/vegetation and the atmosphere.

7. ACKNOWLEDGEMENTS

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