

## Chapter (non-refereed)

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# Application of a NH<sub>3</sub> gas-to-particle conversion model to measurement data

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## Summary

A dataset of simultaneous gradient measurements of gaseous NH<sub>3</sub>, HNO<sub>3</sub>, HCl and SO<sub>2</sub> together with particulate NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> was used to investigate the quantitative effect of gas-to-particle conversion (GPC) on NH<sub>3</sub> flux measurements. The measurement data show periods of apparent NH<sub>4</sub><sup>+</sup> aerosol emission, as well as HNO<sub>3</sub> and HCl deposition with both  $R_c > 0$  and  $< 0$ , indicating that GPC took place. From these data, input values at two heights were extracted and used in a numerical first-order-closure model. The model allows simultaneous treatment of the reaction of NH<sub>3</sub> with both HNO<sub>3</sub> and HCl. It also accounts for gradients of the dissociation constants, due to changes in temperature and relative humidity with height, and extrapolates the calculated profiles of concentrations and fluxes down to the surface. The model can simulate the observed phenomena quantitatively, but more measurement data of increased accuracy are necessary to enable statistically valid model assessments.

## Introduction

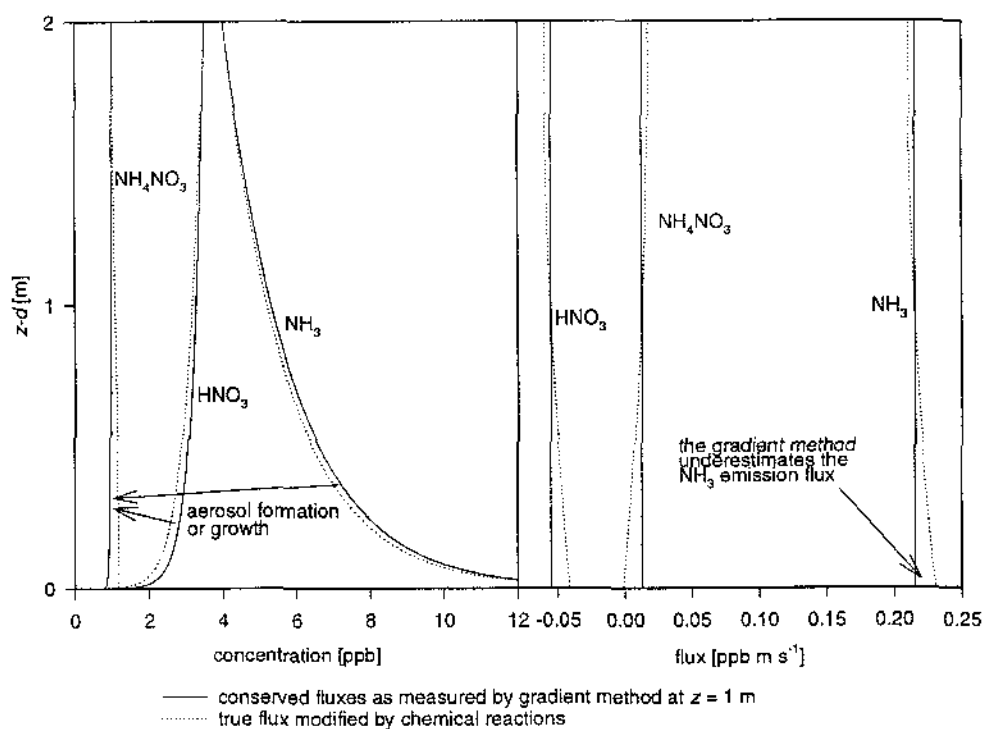
Ammonia fluxes are usually measured by gradient techniques, which require the flux to be invariant within the height range in which the measurements are carried out. Over a homogeneous area a layer is expected to form in which fluxes are in equilibrium with the surface (e.g. Monteith and Unsworth, 1990). However, only fluxes of heat and chemically inert tracers are constant with height. Ammonia (NH<sub>3</sub>) as the major atmospheric base reacts reversibly with nitric and hydrochloric acid forming ammonium aerosol and can also be neutralised by sulphuric acid. The reactions with HNO<sub>3</sub> and HCl may be given by:



where  $k_1$ ,  $k_2$ ,  $k'_1$  and  $k'_2$  represent the reaction rate coefficients. In dis-equilibrium situations this gas-to-particle conversion (GPC) can provide sources and sinks in the atmosphere resulting in height dependent fluxes and non log-linear concentration profiles of NH<sub>3</sub>, acids and NH<sub>4</sub><sup>+</sup> aerosol. Where these reactions occur at rates similar to those of turbulent exchange, gradient techniques assuming a constant flux layer are, strictly speaking, not applicable for NH<sub>3</sub>, as these methods would not derive the surface flux but a mean value for the flux in the height of the measurements (see Figure 1).

As the exchange of NH<sub>3</sub> is bi-directional and generally governed by an unknown canopy resistance ( $R_c$ ) the fluxes of acids and NH<sub>4</sub><sup>+</sup> aerosol provide better means to detect GPC. HNO<sub>3</sub> and HCl can be expected to deposit with  $R_c=0$  (e.g. Müller *et al.*, 1992) whereas particles in the prevailing size range of ammonium aerosol (0.01-0.1  $\mu\text{m}$ ) deposit with a deposition velocity ( $V_d$ ) of about 1  $\text{mm s}^{-1}$ . Significant deviation from the expected deposition velocities may be taken to indicate that GPC takes place. These deviations have been found during measurements (e.g. Huebert *et al.*, 1988; Sutton *et al.*, 1993; Zhang *et al.*, 1995).

The problem of the influence of GPC has been increasingly acknowledged over the past five years. The error that GPC induces for both individual  $\text{NH}_3$  flux measurements and estimation of the net deposition/emission of  $\text{NH}_3$  with ecosystems needs to be quantitatively assessed. GPC is also likely to effect the physical processes of the surface/atmosphere exchange themselves. For example, evaporation of particulate  $\text{NH}_4^+$  into fast depositing gaseous  $\text{NH}_3$  would potentially enhance the total deposition of reduced nitrogen in highly polluted areas. This would obviously have important consequences for the exceedance of critical loads of nitrogen. If  $\text{NH}_3$  is emitted in the presence of a high background concentration of  $\text{HNO}_3$ , aerosol formation can deplete  $\text{NH}_3$  near the surface resulting in bigger gradients and increased  $\text{NH}_3$  emission. Although the produced  $\text{NH}_4^+$  is expected to deposit mainly onto existing aerosol resulting in particle growth, the generation of new ultrafine  $\text{NH}_4^+$  particles is also likely to occur.



**Figure 1.** Schematic outline of the principle of gas-to-particle conversion. In this example, emission of  $\text{NH}_3$  in the presence of a considerable  $\text{HNO}_3$  concentration leads to formation or growth of  $\text{NH}_4^+$  aerosol which is highest at the ground.

### Field measurements

Unexpected surface exchange rates of gaseous  $\text{HNO}_3$  and  $\text{HCl}$  as well as particulate  $\text{NH}_4^+$  can be seen in previously unpublished data from measurements carried out in a joint field campaign in September 1989 as a part of the BIATEX project near Halvergate, Norfolk, UK. A site description of the experiment has been provided by Hargreaves *et al.* (1992) and Dollard *et al.* (1990). The data of four out of twelve runs are shown in Figure 2.

The average of the night-time runs (10 - 12) shows expected deposition fluxes for  $\text{NH}_4\text{NO}_3$  and  $\text{HNO}_3$  which indicate that GPC did not effect the  $\text{NH}_3$  fluxes. In contrast, runs 1 and 5 show high apparent emission of  $\text{NH}_4^+$  aerosol and deposition of  $\text{HNO}_3$  and  $\text{HCl}$  faster than permitted by turbulence,  $V_{\text{max}} = (R_a + R_b)^{-1}$ , indicating aerosol formation or growth close to the surface. The opposite process, enhanced evaporation of aerosol near the surface, may be the cause of the apparently slow acid and too rapid  $\text{NH}_4^+$  deposition in Run 8.

As the measurements included simultaneous gradients of  $\text{NH}_3$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  they provide a unique dataset for model assessment. However, some other runs (data not included in Figure 2) show inconsistent data, e.g. deposition of all chemical species faster than permitted by turbulence, observation which cannot be explained in terms of GPC. A large contribution of  $\text{SO}_4^{2-}$  to the  $\text{NH}_4^+$  concentration was also found during some runs requiring the inclusion of  $\text{H}_2\text{SO}_4$  into the modelling which was beyond the scope of the first model tests presented here.

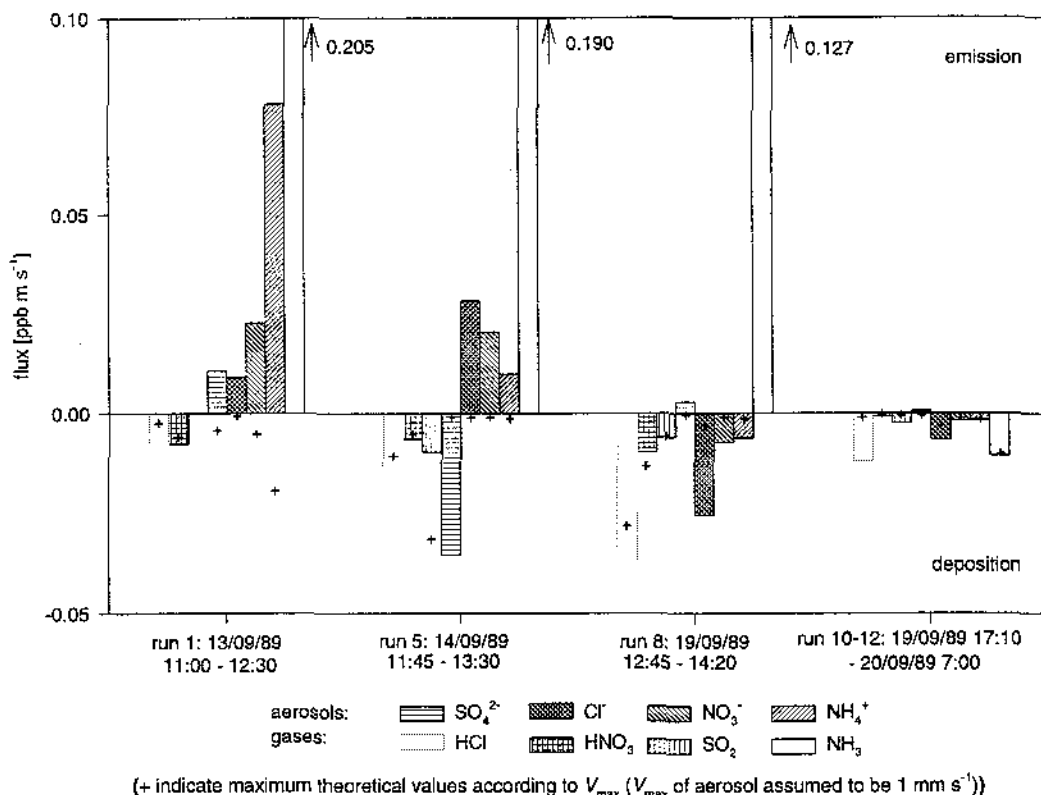


Figure 2. Fluxes of four out of twelve runs during the Halveragate '89 campaign as calculated with the aerodynamic gradient method (bars) and maximum deposition fluxes (+). Fluxes of both aerosol and acids show high deviation from the expected values.

### The model

If the gradients of  $\text{HNO}_3$  and  $\text{NH}_3$  are obtained in the same way, i.e. if the concentrations are measured at the same heights, the error due to GPC for both fluxes should be expected to be similar, assuming the effect of  $\text{HCl}$  is negligible. Since the error in the  $\text{HNO}_3$  flux can be estimated using the expected value for  $V_d = V_{max}$  a first order correction of the  $\text{NH}_3$  flux is given by:

$$F_{\text{NH}_3, \text{real}}(z'_n) = F_{\text{NH}_3, \text{meas}}(1 \text{ m}) + \Delta F_{\text{NH}_3} \quad (2)$$

with

$$\Delta F_{\text{NH}_3} = [\text{HNO}_3]_{\text{meas}}(1 \text{ m}) \times (V_{d, \text{HNO}_3}(1 \text{ m}) - V_{\text{max}, \text{HNO}_3}(1 \text{ m})) \quad (3)$$

Similar expressions can be derived for the correction for the reaction with  $\text{HCl}$  if appropriate. However, a potentially more accurate correction can be obtained by modelling the profiles of the concentrations and fluxes of the different chemical species. Here a first-order-closure model according to Brost *et al.* (1988), and also used by Kramm and Dlugi (1994), was applied. The divergence of the flux ( $F$ ) with height ( $z$ ) is given by the chemical source and sink term ( $Q$ ):

$$\frac{\partial F_{\text{NH}_3}}{\partial z} = Q_{\text{NH}_3} \quad (4)$$

which for  $\text{NH}_3$  can be written as

$$Q_{\text{NH}_3} = -[\text{NH}_3] \{k_1[\text{HNO}_3] + k_2[\text{HCl}]\} + (k'_1[\text{NH}_4\text{NO}_3] + k'_2[\text{NH}_4\text{Cl}]) \quad (5)$$

Closure of the model is provided by the classical flux gradient relationship:

$$F_{\text{NH}_3} = -K_H \frac{\partial [\text{NH}_3]}{\partial z}; \quad K_H \approx \frac{z K u_*}{\Phi_H \left( \frac{z}{L} \right)} \quad (6)$$

Here  $K_H$  represents the eddy diffusivity;  $\kappa$ , the von Karman constant (0.41);  $u_*$ , the friction velocity, and  $\Phi_H(z/L)$ , the stability correction (Sutton *et al.*, 1993). Although  $K_H$  is modified in the presence of chemistry, Fitzjarrald and Lenschow (1983) found that the standard expression of equation (6) is a sufficiently accurate approximation. The equations of the form of equation (4) and (6) together with equation (5) form a set of three (five if the reaction with HCl is included) coupled second order differential equations which have to be solved simultaneously calculating the source/sink terms for each height after each iteration step. Here three features were added compared with the models of former authors:

- 1) The equilibria of  $\text{NH}_3$  with both  $\text{HNO}_3$  and  $\text{HCl}$  were dealt with simultaneously as some runs show a high contribution of  $\text{NH}_4\text{Cl}$ .
- 2) The dissociation constants of  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  ( $k_p$ ), which form the link between  $k_1$ ,  $k_1'$  and  $k_2$ ,  $k_2'$ , respectively, were calculated as functions of temperature and relative humidity. In this way the model is no longer limited to relative humidities below the deliquescence point and also allows vertical gradients of relative humidity and temperature to be accounted for. The expressions from Stelson and Seinfeld (1982) and Pio and Harrison (1987) were used to calculate the equilibrium constants.
- 3) Like for the model by Brost *et al.* (1988), the concentrations at two heights are required as input parameters. These were obtained by interpolating the measured gradients in order to account for scatter in the data. The model calculates the profiles between the two input heights. The values of the concentrations and fluxes at the lower boundary height were here used to extrapolate the profiles down to the surface, the roughness length ( $z_0$ ), so that the surface fluxes can be found.

## Results and discussion

The model described is applied to two different measurement examples as presented in Figures 3 and 4. Figure 3 shows a case in which the concentration product  $[\text{NH}_3][\text{HNO}_3]$  does not obtain its theoretical value ( $k_p$ ) at any height. This leads to aerosol evaporation which is highest close to the ground, where the  $\text{HNO}_3$  concentration is smallest. The magnitude of the dis-equilibrium is governed by the concentration of  $\text{HNO}_3$  rather than  $\text{NH}_3$ .

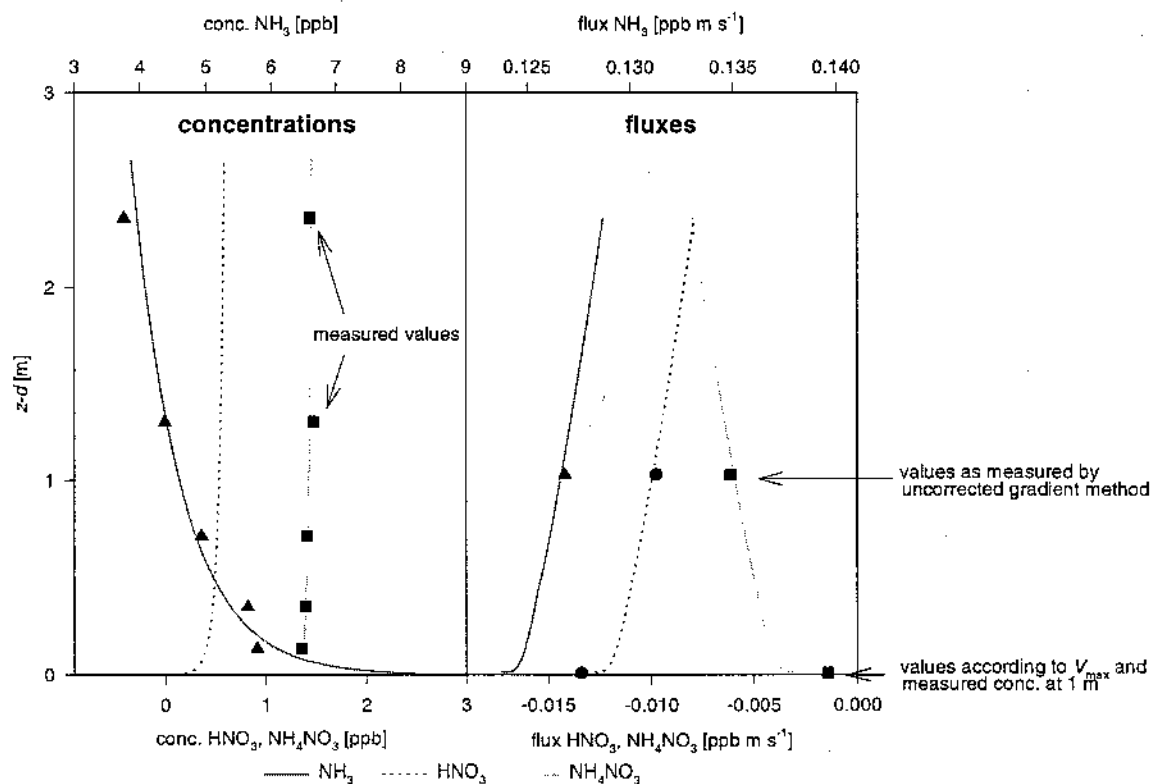


Figure 3. Model application to data from Halvergate, Run 8, when aerosol evaporation occurred close to the surface. The reaction with HCl is neglected as  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations balance.

A comparison of the concentrations of the aerosol species suggested that for Run 8 the  $\text{NH}_4^+$  is mainly present as  $\text{NH}_4\text{NO}_3$ . Hence the reaction with HCl was ignored. The high deposition velocity of the Cl<sup>-</sup> aerosol could be explained by the chloride mainly consisting of sea salt which usually shows a larger mass median diameter than  $\text{NH}_4^+$  aerosol leading to deposition faster than  $V_d = 1 \text{ mm s}^{-1}$ .

In contrast to Run 8, Figure 4 demonstrates the case of aerosol formation or growth which was more frequently observed during the Halvergate experiment, as shown for Run 5. In addition to gradients and fluxes Figure 4 also shows flux divergences ( $dF/dz$ ), which vanish in equilibrium conditions (Kramm and Dlugi, 1994) and thus indicate the magnitude of the dis-equilibria. The relative humidity approaches 100% near the ground which leads to a small value of  $k_p$ . Because of the large emission of  $\text{NH}_3$ , the equilibrium product exceeds its theoretical value ( $[\text{NH}_3][\text{HNO}_3] > k_p$ ) leading to aerosol formation or growth to be largest close to the surface, where the smallest value for  $k_p$  and the largest for  $[\text{NH}_3]$  can be found. In order to balance the  $\text{NH}_4^+$  concentration measured, the reaction with HCl has to be included in the model. As the  $\text{NO}_3^-$  and  $\text{Cl}^-$  gradient measurements show high scatter, the  $\text{NH}_4^+$  gradients were used as input and arbitrarily split into  $\text{NO}_3^-$  and  $\text{Cl}^-$ .

In modelling both runs 8 and 5, the reaction rate coefficient,  $k_1$  (and in Run 5 also  $k_2$ ), was altered for the surface flux of  $\text{HNO}_3$  (or HCl) to match the predicted value (see Figure 3), i.e.  $-\text{[HNO}_3\text{]}(z_0)/R_b$ , with  $R_b$  being the resistance of the laminar boundary layer. A value of  $k_1 = 8 \text{ ppb}^{-1} \text{ s}^{-1}$  was found for Run 8 which results in a mean  $\text{NH}_4^+$  formation rate of about  $0.32 \text{ ng m}^{-3} \text{ s}^{-1}$ . The good match of the surface flux of the aerosol indicates data consistency (see Figure 3). However, matching the fluxes at  $z_0$  assumes no flux divergence to occur within the laminar boundary-layer. This assumption was also made by Kramm and Dlugi (1994), but becomes doubtful considering that in Run 8 the dis-equilibrium was largest near the ground.

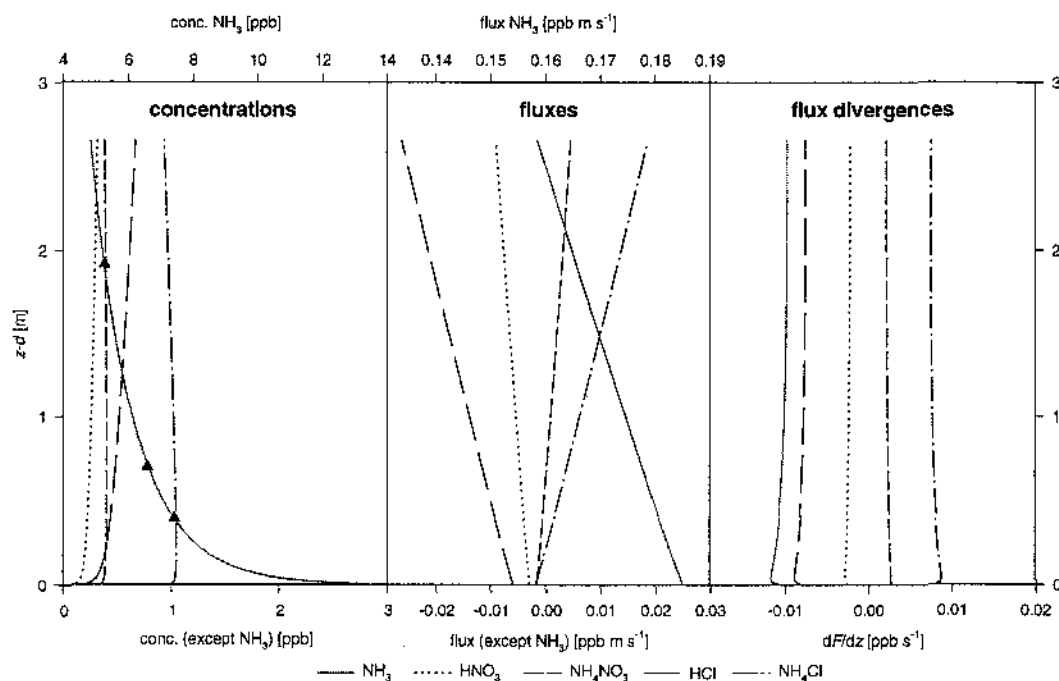


Figure 4. Model application to data from Halvergate, Run 5, showing aerosol evaporation close to the surface, including the reaction with HCl. The flux divergence is largest near the ground.

The numerical model can quantitatively simulate GPC for both aerosol production/growth and evaporation. However, not enough runs are available to enable a full model assessment. The profiles of  $\text{Cl}^-$  and  $\text{NO}_3^-$  showed too much scatter to be useful. These uncertainties give room for interpretation which was used to fit the models. Moreover, the values for the reaction rate coefficients have been chosen so as to fit the model results to the data.

For further model assessments it would be desirable to acquire more data of increased accuracy for the aerosol speciation (i.e.  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{Cl}$ ). Recent developments of automated sampling techniques for all species under consideration (e.g. Wyers *et al.*, 1993; Khlystov *et al.*, 1995) should provide statistically valid input data. Temperature and relative humidity gradients have to be measured exactly in order to account for changes in  $k_p$  with height. The measurement of aerosol

size spectra at different heights could also provide a means to detect aerosol production and growth due to GPC.

More work is necessary to predict the kinetics of the equilibria from independent measurements, since the chemical time-scales are largely unknown. For example, the equilibrium products and reaction rate coefficients might be expected to change with aerosol size and composition. Furthermore, it has to be examined whether reactions within the quasi laminar sub-layer significantly contribute to the net effect of GPC. Quantification of these processes will allow improved correction procedures for gradient methods to be formulated providing more reliable estimates of the net effect of GPC.

## Conclusions

The present analysis shows that gas-to-particle conversion (GPC) may have a substantial effect on the interpretation of flux-gradient measurements of  $\text{NH}_3$ . Examples of the measurements shown here are consistent with the occurrence of both aerosol evaporation and aerosol formation or growth. Aerosol evaporation at ground level may occur as a consequence of gaseous depletion due to dry deposition or positive relative humidity gradients, while aerosol formation or growth may result from  $\text{NH}_3$  emission or negative relative humidity gradients. These processes may lead to both under- and over-estimation of  $\text{NH}_3$  (as well as  $\text{HNO}_3$ ,  $\text{HCl}$ ) fluxes measured using classical gradient theory, and may be accounted for using the analysis presented here. GPC can also directly alter the rate of atmosphere/surface exchange, e.g. by transforming slowly depositing aerosol into fast depositing gaseous species and vice versa. Further development of the analysis will consider the need to treat reactions with acid sulphates, GPC processes within the viscous sub-layer and examine the reaction kinetics in more detail. This will be used to develop more general correction procedures as well as to assess the impacts of GPC on net fluxes with ecosystems.

## Acknowledgements

The  $\text{HNO}_3$  and  $\text{HCl}$  data were kindly provided by the University of Birmingham. The authors also gratefully acknowledge financial support through the UK Department of Environment (PECD 1/3/28) and the C.E.C. EXAMINE project (EV5V-CT94-0426).

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