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# Gas-particle interactions above a Dutch heathland: I. Surface exchange fluxes of NH<sub>3</sub>, SO<sub>2</sub>, HNO<sub>3</sub> and HCl

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## Abstract

A field measurement campaign was carried out over a Dutch heathland to investigate the effect of gas-to-particle conversion and ammonium aerosol evaporation on surface/atmosphere fluxes of ammonia and related species. Continuous micrometeorological measurements of the surface exchange of  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{HNO}_3$  and  $\text{HCl}$  were made and are analyzed here with regard to average fluxes, deposition velocities ( $V_d$ ), canopy resistances ( $R_c$ ) and canopy compensation point for  $\text{NH}_3$ . Gradients of  $\text{SO}_2$ ,  $\text{HNO}_3$  and  $\text{HCl}$  were measured with a novel wet-denuder system with online anion chromatography. Measurements of  $\text{HNO}_3$  and  $\text{HCl}$  indicate an  $R_c$  of 100 to 200  $\text{s m}^{-1}$  during warm daytime periods, probably at least partly due to non-zero acid partial pressures above  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  on the leaf surfaces. Although it is likely that this observation is exacerbated by the effect of the evaporation of airborne  $\text{NH}_4^+$  on the gradient measurements, the findings nevertheless add to the growing evidence that  $\text{HNO}_3$  and  $\text{HCl}$  are not always deposited at the maximum rate. Ammonia ( $\text{NH}_3$ ) fluxes show mainly deposition, with some periods of significant daytime emission. The net exchange could be reproduced both with an  $R_c$  model (deposition fluxes only) using resistance parameterizations from former measurements, as well as with the canopy compensation point model, using parameterizations derived from the measurements. The apoplastic ratio of ammonium and hydrogen concentration ( $\Gamma_s = [\text{NH}_4^+]/[\text{H}^+]$ ) of 1200 estimated from the measurements is large for semi-natural vegetation, but smaller than indicated by previous measurements at this site.

## 1. Introduction

The correct quantification of inputs of atmospheric pollutants such as oxidized nitrogen ( $\text{NO}_y$ ), reduced nitrogen ( $\text{NH}_x$ ) and sulphur compounds is an important prerequisite for the assessment of the impact of anthropogenic activities on natural and semi-natural ecosystems. The deposition of sulphur dioxide ( $\text{SO}_2$ ), sulphate aerosols ( $\text{SO}_4^{2-}$ ), nitric

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acid (HNO<sub>3</sub>) and hydrochloric acid (HCl) have a direct acidifying effect, but even the deposition of the normally alkaline ammonia gas (NH<sub>3</sub>) and neutral ammonium aerosol (NH<sub>4</sub><sup>+</sup>) can cause acidification, depending on their fate within soil, water and plants (e.g. Binkley and Richter, 1987; Sutton and Fowler, 1993a). The additional eutrophying effect of the nitrogen (N) compounds (NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup> and HNO<sub>3</sub>) may also be detrimental for many nitrogen limited ecosystems (e.g. Fangmeier et al., 1994).

Particularly in the Netherlands, with high concentrations of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> arising from large livestock densities, inputs of atmospheric nitrogen have been held responsible for the poor state of heathland ecosystems (e.g. Bobbink et al., 1998): the additional N supply favours more nitrophyllous grass species which out-compete heather species characteristic of more oligotrophic conditions. It has also been suggested that atmospheric N deposition may raise the NH<sub>4</sub><sup>+</sup> concentration in the intercellular liquid in contact with the ambient air. This results in a high NH<sub>3</sub> emission potential (compensation point) of the heathland that partly limits the uptake of further NH<sub>3</sub> through stomata (Sutton et al., 1995a). However, large quantities of NH<sub>3</sub> and other reactive N can still be deposited to the leaf cuticles and may subsequently be washed off the leaves and taken up by the roots.

Measuring the deposition of reactive N is complicated through the dynamics of the chemical gas/aerosol equilibria of NH<sub>3</sub> and atmospheric acids with their associated NH<sub>4</sub><sup>+</sup> salts. Given the much faster exchange rate of gaseous species (NH<sub>3</sub>, HNO<sub>3</sub>, HCl and SO<sub>2</sub>) if compared with their particulate counterparts (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) (e.g. Duyzer, 1994), the phase partitioning between gas and aerosol can have a significant effect on local budgets and atmospheric transport distances. In addition, the formation (gas-to-particle conversion, gtpc) or evaporation of NH<sub>4</sub><sup>+</sup> aerosols (together gas-particle interconversion, gpic) can be fast enough to affect the micrometeorological techniques by which the surface exchange fluxes are estimated (Brost et al., 1988; Van Oss et al., 1998).

From 1995 to 1997 the “EXAMINE” project (“EXchange of AMmonia IN Europe”) formed a first pan-European initiative to quantify the surface-exchange fluxes of NH<sub>3</sub>

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over a wide range of ecosystems and climates (Sutton et al., 1996). As part of EX-AMINE, integrated international field campaigns were carried out to quantify exchange fluxes above a cereal crop in Germany (“Bellheim experiment”, Meixner et al., 1996) and an oilseed rape field in southern Scotland (“North Berwick experiment”, Sutton et al., 2000). During the latter campaign, surface exchange fluxes of HNO<sub>3</sub>, HCl, SO<sub>2</sub> and aerosols were measured alongside the NH<sub>3</sub> exchange to study the effect of gas-particle interactions at a clean, maritime Scottish location (Nemitz et al., 2000b). It was found that, above the canopy, low acid concentrations led to a potential for evaporation of NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl. Due to low aerosol concentrations in general, however, time-scales for the evaporation were estimated to be too slow for flux measurements and net exchange budgets to be affected by the process. This would be expected to be generally the case in clean environments. By contrast, within the canopy, the joint effect of daytime emission of NH<sub>3</sub> and HCl (the latter from unidentified sites in the canopy), gave rise to an occasional exceedance of the dissociation constant of NH<sub>4</sub>Cl. Together with long residence-times within the canopy this may have provided a mechanism for aerosol production (Nemitz et al., 2000b).

A further integrated field campaign as part of EXAMINE was designed to study the surface-atmosphere exchange of NH<sub>3</sub> and to quantify the effects of gas-particle-interconversion in a more polluted environment than at North Berwick. These measurements took place at Elspeetsche Veld, a Dutch heathland three kilometres south of the village of Elspeet near Appeldoorn, from 21 May to 13 June 1996, while measurements of the NH<sub>3</sub> surface exchange continued until the end of July (Hansen et al., 1999). At this location continental air masses, together with the high NH<sub>3</sub> concentrations typical for the Netherlands, were expected (a) to make gas-particle interactions more significant than at North Berwick and (b) to lead to concentrations well above the detection limit of the instruments. Elspeetsche Veld is a well studied field site, at which surface exchange fluxes were measured during several periods between 1989 and 1992 (Erisman and Duyzer, 1991; Bobbink et al., 1992; Erisman and Wyers, 1993; Erisman et al., 1994), although partly with less accurate instrumentation than available

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for this study. Previous measurements showed the NH<sub>3</sub> surface exchange at Elspeet to be bi-directional with deposition at night-time and emission fluxes of up to 550 ng m<sup>-2</sup> s<sup>-1</sup> during the day (Erisman and Wyers, 1993). Hence Elspeetsche Veld offered the prospect to study the effect of gpic during both strong emission and deposition of

5 NH<sub>3</sub>.

The present paper outlines the measurements and reports the concentrations of gaseous NH<sub>3</sub>, HNO<sub>3</sub>, HCl, HNO<sub>2</sub> and SO<sub>2</sub> measured with mainly denuder-based gradient systems. Surface exchange fluxes are quantified using the aerodynamic gradient technique assuming effects of gpic to be negligible. Furthermore, the NH<sub>3</sub> exchange is modelled using both an existing  $R_c$  resistance parameterization, obtained during a former campaign at the same site, and the canopy compensation point model of Sutton and Fowler (1993b) with parameterizations derived from the measurements presented here.

In order to simplify the analysis, the flux calculations are made here assuming the effects of gpic are negligible. However, parallel assessment of the aerosol-gas phase equilibrium at different heights in comparison with four other measurement sites suggests that there is significant potential for interaction with the dry deposition process Nemitz (1998). These interactions and their implications are therefore considered further in two companion papers: Firstly, Nemitz et al. (2004b) report parallel eddy-covariance (EC) measurements of particle number fluxes as well as NH<sub>4</sub><sup>+</sup> aerosol fluxes by aerodynamic gradient method (AGM) from the Elspeet site, and apply these to assess the evidence of chemical interactions. Secondly, Nemitz and Sutton (2004) present a new numerical model developed to quantify the effects of gpic on the measured vertical gradients of NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> and on the size spectra of NH<sub>4</sub><sup>+</sup> containing aerosols.

## 2. Methods

### 2.1. Field site description and synoptic meteorological situation.

The vegetation of the Elspeetsche Veld (52°12' N, 5°45' E) is Genisto-Callunetum, a dry inland heath dominated by *Calluna vulgaris* (L.) (Erisman and Wyers, 1993). The canopy was 9–10 year old canopy, with a height of 0.3–0.4 m, with patches of shorter rejuvenated heather (0.1–0.2 m), mainly in the SE wind sector. The measuring instruments were situated in the north-east part of the heathland, providing a uniform fetch of >200 m up to 1000 m in the wind sector 145° to 300° from N which covered the predominant SE and W wind directions (Fig. 1). Local NH<sub>3</sub> sources included several small farms located in the SW at distances of at least 3 km, and one farm as close as 1 km at WNW (Fig. 1).

The synoptic meteorology during the experiment can be divided into two periods: from 21 to 28 May the weather was dominated by the formation of an anticyclonic system with the centre over the British Isles. This period was characterized by light drizzle and moderate air temperatures (1 m height above the zero plane, *d*) reaching from 7–11°C at night to 14–16°C during daytime. Winds veered from SW on 21 to NNW on 25 May, while the surface windspeed at 1 m above *d* decreased from typically 4 m s<sup>-1</sup> down to 1 m s<sup>-1</sup>. On 26 May the wind increased again with the wind direction remaining unsteady between SW and N for the rest of this first period.

On 28 May a frontal system passed through, which was followed by a long warm period, dominated by a persistent high-pressure area stretching from Eastern Europe to the Iberian Peninsula. Until 4 June the overcast sky resulted in daytime temperatures of 15–27°C, whereas after 4 June temperatures increased from day to day reaching their maximum of above 34°C on 7 June (cf. Figs. 3 and 8 below). During clear nights temperatures dropped as low as 3°C, leading to significant dewfall during 5–11 June. At the same time the wind speed was more variable and showed a clear diurnal pattern with daytime values of 2–4 m s<sup>-1</sup> and often dropped as low as 0.5 m s<sup>-1</sup> during night. In the centre of the high pressure area, wind direction was unsteady, dominated by

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westerly winds but ranging from N through W to S.

## 2.2. Instrumentation

Concentration gradients of  $\text{NH}_3$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{HCl}$  and  $\text{SO}_2$  were principally measured by a range of continuous and automated wet-chemistry analyzers. Annular denuder inlets were used as a state-of-the-art method to discriminate between the gas and the aerosol phase with minimal interference. The rotating denuders consist of two concentric glass cylinders, that form a 1.3 mm wide annulus, through which a laminar air stream of about  $28 \text{ l min}^{-1}$  is drawn. Adsorption is provided by a  $\text{NaHSO}_4$  solution for  $\text{NH}_3$  and a  $\text{K}_2\text{CO}_3$  solution for  $\text{NH}_3$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{HCl}$  and  $\text{SO}_2$ . This solution is pumped through the denuder inlets in a counter flow and the solution from the different heights is fed sequentially to a conductivity cell for  $\text{NH}_4^+$  analysis (AMANDA, ECN, Petten, Wyers et al., 1993) and to a Dionex anion chromatography (IC) system for the analysis of the other species (ECN, Petten) (Jongejan et al., 1997; Slanina et al., 2001). Previously, the denuder/IC system (DENIC) had only been used for concentration measurements of  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HNO}_2$  and  $\text{SO}_2$  (Oms et al., 1996), but at Elspeet it was used for the first time in the field to obtain 2-point concentration gradients. The prototype employed here proved to be sensitive to the high ambient temperatures of  $>34^\circ\text{C}$  temporarily observed at Elspeet, which led to occasional gaps in the data.

In addition, a 3-point gradient system of automated rotating batch denuders ("RBD", ECN, Petten) (Keuken et al., 1988) was used as a backup system. In these systems the collection solution, containing formic acid and  $\text{NaOH}$ , remained in the denuder tube for a 40-min sampling period, after which it was automatically pumped into test tubes for subsequent laboratory analysis. While all samples were analyzed for  $\text{NH}_4^+$  on an Ammonia Flow Injection Analyzer (AMFIA, ECN, Petten, NL), financial restrictions meant that only a limited number of the batch denuder samples (7 days) could be analyzed for anions ( $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) by anion chromatography using a DIONEX system. Further to these denuder systems, concentration gradients of the same species were also measured during 14 2-h runs using up to ten  $\emptyset$  90-mm filter-packs (Sutton, 1990),

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containing a 1  $\mu\text{m}$  PTFE particle pre-filter, a NaF impregnated filter for HCl and  $\text{HNO}_3$  capture as well as a  $\text{H}_3\text{PO}_4$  impregnated filter for  $\text{NH}_3$  (Harrison and Kitto, 1990).

Accompanying the main measurements, a passive wind-vane sampling system for the cost-efficient measurement of long-term  $\text{NH}_3$  fluxes was compared with the  $\text{NH}_3$  fluxes derived from the AMANDA  $\text{NH}_3$  gradient system for an extended period (23 May to 1 August). These results are reported elsewhere (Hansen et al., 1999). The main meteorological parameters and gas concentrations measured at Elspeet are listed in Table 1, together with the instrumentation and a reference to the techniques applied.

### 2.3. Micrometeorological theory

In the absence of fast response sensors for reactive and highly water-soluble gases such as  $\text{NH}_3$  and  $\text{HNO}_3$ , (which would be necessary to measure fluxes by eddy-covariance), vertical concentration gradients were measured and the aerodynamic gradient technique was applied. According to Fick's law, the flux ( $F_\chi$ ) of a tracer ( $\chi$ ) is related to the vertical gradient of  $\chi$  through the flux-gradient relationship for heat and inert tracers ( $K_H$ ):

$$F_\chi = -K_H \left( \frac{z-d}{L} \right) \frac{\partial \chi}{\partial z} \quad (1)$$

$K_H$  is a function of the height ( $z$ ) above  $d$  and atmospheric stability, parameterized as the Monin-Obukhov length ( $L$ ), which is derived in this study from the sensible heat flux ( $H$ ) and the friction velocity ( $u_*$ ) measured by eddy-covariance using an ultrasonic anemometer (Garrat, 1992). In praxis,  $F_\chi$  can be calculated from the logarithmic concentration profile as (Garland, 1977; Sutton et al., 1992; Flechard and Fowler, 1998):

$$F_\chi = -u_* \kappa \frac{\partial \chi}{\partial \{ \ln(z-d) - \Psi_H [(z-d)/L] \}} \quad (2)$$

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where  $\kappa$  is the von Kármán constant (0.41).  $\Psi_H$  is the integrated stability correction function for heat and inert tracers, given as (Thom, 1975):

$$\Psi_H(\zeta) = -5.2 [(z-d)/L] \quad (3)$$

for stable conditions ( $L > 0$ ) and

$$\Psi_H(\zeta) = 2 \ln \left( \frac{1 + [1 - 16 ((z-d)/L)]^2}{2} \right) \quad (4)$$

for unstable conditions ( $L < 0$ ).

## 2.4. Existing parameterizations of NH<sub>3</sub> surface/atmosphere exchange

### 2.4.1. The canopy resistance ( $R_c$ ) modelling approach

A common way of parameterizing and predicting pollutant exchange with ecosystems is the resistance analogue. The flux is the result of a difference between the air concentration ( $\chi_a$ ) and the surface concentration ( $\chi_0$ ), as well as of the total atmospheric resistance ( $R_t$ ).

$$F_t = -\frac{\chi_a - \chi_0}{R_t} \quad (5)$$

Two atmospheric resistances always contribute to  $R_t$ : the aerodynamic resistance ( $R_a$ ) describes the transport through the turbulent part of the atmosphere, and the sublayer resistance ( $R_b$ ) describes the influence of the quasi laminar sub-layer. Both resistances can be parameterized using micrometeorological parameters, and here the formulations of Garland (1977) are used. For many tracers the canopy acts as an efficient sink and therefore the surface concentration ( $\chi_0$ ) is assumed to be zero. In this case, the reciprocal resistance may be equated with the deposition velocity ( $V_d = 1/R_t$ ). In

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general, the exchange rate is limited by a further resistance at the surface itself, the canopy resistance ( $R_c$ ):

$$F_c = -\frac{\chi_a}{R_t} = -\frac{\chi_a}{R_a + R_b + R_c} = -V_d \chi_a \quad (6)$$

The maximum value of the deposition velocity ( $V_{\max}$ ) is obtained where  $R_c = 0$  as

$$V_{\max} = (R_a + R_b)^{-1} \quad (7)$$

Earlier measurements at Elspeetsche Veld were used to derive parameterizations of  $R_c$  for SO<sub>2</sub> and NH<sub>3</sub> (Erisman et al., 1994; Jakobsen et al., 1997). The deposition of NH<sub>3</sub> to vegetation takes place via two main parallel pathways: exchange through the leaf stomata (described by the stomatal resistance,  $R_s$ ) and adsorption to the leaf cuticles (described by the cuticular resistance,  $R_w$ ) (Sutton and Fowler, 1993b). In the canopy resistance approach,  $R_c$  is calculated as the reciprocal sum of  $R_s$  and  $R_w$  (Fowler, 1978; Erisman et al., 1994):

$$R_c = \left( R_s^{-1} (\text{NH}_3) + R_w^{-1} \right)^{-1} \quad (8)$$

$R_w$  can be considered as consisting of two parallel resistances for the deposition to leaves during high humidity ( $R_h$  or  $R_{\text{ext}}$ ) and after rain ( $R_{\text{rain}}$ ), respectively. Given the very infrequent rain events at Elspeet during the sampling period,  $R_w$  for NH<sub>3</sub> may be identified with  $R_{\text{ext}}$  as given by (Jakobsen et al., 1997):

$$R_w = 19257 \exp(-0.094 h) + 5 \quad (9)$$

where  $R_w$  is given in s m<sup>-1</sup> and  $h$  is relative humidity in %. Erisman et al. (1994) furthermore suggested that  $R_s$  (SO<sub>2</sub>) at Elspeet be modelled according to Wesely (1989), using a minimum value of  $R_{s,\text{min}} = 250$  s m<sup>-1</sup> for SO<sub>2</sub>, which needs to be corrected for differences in molecular diffusivities ( $D_\chi$ ):

$$R_s (\text{NH}_3) = 250 \frac{D_{\text{SO}_2}}{D_{\text{NH}_3}} \left( \frac{200}{St + 0.1} \right)^2 \frac{400}{T(40 - T)} \quad (10)$$

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where  $St$  is the global radiation in  $\text{W m}^{-2}$  and  $T$  is the surface temperature in  $^{\circ}\text{C}$ .

It has been pointed out that parameterizations obtained for Dutch conditions (NH<sub>3</sub>/SO<sub>2</sub> ratios, temperature, humidity) may not be transferable to other countries (Erisman and Wyers, 1993). Indeed, problems have been encountered when these parameterizations were applied to less polluted environments such as a Scottish moorland site (Flechar and Fowler, 1998). By contrast, Eqs. (8)–(10) should be re-applicable to Elspeet, apart from possible effects of changes in the pollution climate or vegetation status over the previous 5 years.

### 2.4.2. The canopy compensation point ( $\chi_c$ ) modelling approach

Clearly, the  $R_c$  approach adopted by Jakobsen et al. (1997) can only describe deposition and fails where NH<sub>3</sub> exchange is bi-directional, as in the case of agricultural high nitrogen ecosystems (Farquhar et al., 1980; Sutton et al., 1995b; Meixner et al., 1996). Periods of NH<sub>3</sub> emission were also observed during earlier measurements at Elspeet (Erisman and Wyers, 1993; Sutton et al., 1995b). Above such vegetation, emission is usually observed during warm daytime periods when high temperatures lead to elevated NH<sub>3</sub> concentrations in the substomatal cavities above the NH<sub>4</sub><sup>+</sup> dissolved in the apoplastic fluid, which is commonly referred to as the “stomatal compensation point” ( $\chi_s$ ) (Farquhar et al., 1980). The value of  $\chi_s$  may be calculated from the ratio  $\Gamma_s = [\text{NH}_4^+]/[\text{H}^+]$  of the apoplastic concentration of ammonium and hydrogen ions ( $[\text{H}^+] = 10^{-\text{pH}}$ ) as (Nemitz et al., 2000a):

$$\chi_s = \frac{161\,500}{T} \exp\left(-\frac{10\,380}{T}\right) \frac{[\text{NH}_4^+]}{[\text{H}^+]} = \frac{161\,500}{T} \exp\left(-\frac{10\,380}{T}\right) \Gamma_s \quad (11)$$

where all concentrations are given in  $\text{mol l}^{-1}$  at 1 atm and  $T$  is the temperature of the canopy in Kelvin. By contrast, during night, when stomata are closed, deposition to leaf surfaces (described by  $R_w$ ) is the dominating pathway. The two competing processes of bi-directional stomatal exchange and cuticular adsorption are implemented in a single

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model by (Sutton and Fowler, 1993b). Central to the prediction of the net exchange flux is the canopy compensation point ( $\chi_c$ ), the average concentration at the canopy height:

$$\chi_c = \frac{\chi_s R_s^{-1} + \chi_a (R_a(z) + R_b)^{-1}}{(R_a(z) + R_b)^{-1} + R_s^{-1} + R_w^{-1}} \quad (12)$$

from which  $F_t$  may be calculated from  $\chi_c$  as

$$F_t = \frac{\chi_c - \chi_a}{R_a(z) + R_b} \quad (13)$$

For dry daytime periods,  $R_s(\text{NH}_3)$  may be derived from the stomatal resistance of water vapour transfer ( $R_s(\text{H}_2\text{O})$ ):

$$R_s(\text{NH}_3) = \frac{D_{\text{H}_2\text{O}}}{D_{\text{NH}_3}} R_s(\text{H}_2\text{O}) = - \frac{D_{\text{H}_2\text{O}}}{D_{\text{NH}_3}} \frac{e_w(z'_0) - e_{\text{sat}}(T(z'_0))}{E} \quad (14)$$

Water vapour pressure ( $e_w$ ) and temperature ( $T$ ) at the mean canopy height ( $z'_0$ ) can be calculated from the water vapour flux ( $E$ ) and sensible heat flux ( $H$ ), respectively (e.g. Nemitz, 1998). The water vapour flux ( $E$ ) in  $\text{g H}_2\text{O m}^{-2} \text{s}^{-1}$  was derived here from gradient measurements of the water vapour pressure with a Bowen ratio system (Campbell Scientific, Shepshed, UK).  $e_{\text{sat}}(T(z'_0))$  is the saturated water vapour pressure at the mean  $T$  of the canopy ( $T(z'_0)$ ).

In the Netherlands, the  $\chi_c$ -model has been successfully applied to NH<sub>3</sub> measurements over both forest and pasture (Sutton et al., 1995b; Plantaz et al., 1996; Wyers and Erisman, 1998), but this model has not yet been applied to Dutch heathland. However, from former measurements at Elspeet (Erisman and Wyers, 1993) an approximate compensation point may be estimated: for example, at 11:00 GMT on 14 September 1991 the flux switched from emission to deposition at an air concentrations ( $\chi_a$ ) of about  $11 \mu\text{g m}^{-3}$  and a temperature ( $T$ ) of 23°C, which corresponds to an emission potential ( $\Gamma_s$ ) of 2500.

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### 3. Measurement results

#### 3.1. Concentrations

Ammonia concentrations were measured quasi-continuously by both the AMANDA system and RBD with additional support through several filter-pack runs, a comparison of which is shown in Fig. 2. Bearing in mind that the chemical analysis of the AMANDA concentrations was carried out online in the field, whereas batch denuder samples and filter extracts were analyzed in the lab by AMFIA, the agreement is reasonable. Compared with the other two methods, the filter-packs tended to underestimate the concentrations slightly. To assess the performance of the DENIC system, tested for the first time in the field, the SO<sub>2</sub> concentration was compared with a gas analyzer (Fig. 2b). Unfortunately, the gas analyzer proved to be noisy with a day-to-day zero drift of up to 2 μg m<sup>-3</sup>. Considering this, the agreement is good, although the DENIC system underestimated the concentration on average by 12% compared with the gas analyzer. The concentrations of HNO<sub>3</sub> and HCl measured with the RBD systems were compared with the online IC system (data not shown) and linear regression analysis gave the relationships  $\chi_{\text{HNO}_3}(\text{RBD}) = 1.04 \chi_{\text{HNO}_3}(\text{DENIC}) + 0.59$  ( $R^2 = 0.79$ ) and  $\chi_{\text{HCl}}(\text{RBD}) = 1.32 \chi_{\text{HCl}}(\text{DENIC}) + 0.22$  ( $R^2 = 0.55$ ), where concentrations are in μg m<sup>-3</sup>.

From the gradient data, concentrations were interpolated to a height of  $z - d = 1$  m, and higher resolution data were block-averaged over 30 min. A summary of averages and standard deviations is given in Table 2.

#### 3.2. Surface – atmosphere exchange fluxes

In this and the following sections the surface exchange fluxes of NH<sub>3</sub> and acidic gases are analyzed assuming the gradients to be unaffected by chemical reactions. The validity of this assumption is discussed elsewhere (Nemitz et al., 2004b). The complete time-series of the NH<sub>3</sub> biosphere/atmosphere exchange flux is presented in Fig. 3, to-

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gether with time-series of temperature ( $T$ ) and relative humidity ( $h$ ). According to  $T$  and  $h$  measurements the measurement period may be divided into four distinct measurement periods. The flux shows mainly deposition with the occasional appearance of daytime emissions (e.g. 4, 5 and 10 June 1996), mainly during period (3). The emissions on 4 and 5 June were associated with some of the highest canopy temperatures encountered so far in the growing season. Although the temperature increased even further during the subsequent two days the emission was not sustained. Possible reasons are discussed in Sect. 5.2 below.

During the intensive phase of the campaign presented here, the exchange flux ranged from  $-580$  to  $+240$   $\text{ng m}^{-2} \text{s}^{-1}$ , with an arithmetic mean of  $-55.1$   $\text{ng m}^{-2} \text{s}^{-1}$ , a median of  $-34.8$   $\text{ng m}^{-2} \text{s}^{-1}$  and a standard deviation of  $78.3$   $\text{ng m}^{-2} \text{s}^{-1}$ . By contrast, a considerably larger average of  $-109$   $\text{ng m}^{-2} \text{s}^{-1}$  was reported for the whole measurement period (Hansen et al., 1999). Despite stable stratification and reduced wind speeds at night, the deposition tended to be largest in the second half of the night, indicating a smaller  $R_c$  and higher  $\text{NH}_3$  concentrations during night-time than during the day. This was also reflected in the averaged diurnal cycle of the deposition velocity for  $\text{NH}_3$  (Fig. 4a), showing deposition at a rate close to  $V_{\text{max}}$  at night-time, as well as substantial deviation from  $V_{\text{max}}$  during the day.

The surface uptake resistance and/or the emission potential of the surface increased at 06:00 GMT and were largest around midday (09:00–16:00 GMT). The agreement in the fluxes measured with the AMANDA and RBD gradient is mostly impressive, although some periods of disagreement can be identified. By contrast, the FP gradients derive at times very different fluxes (e.g. 6–8 June).

A typical example of the surface exchange fluxes of  $\text{HNO}_3$  and  $\text{HCl}$  is shown in Fig. 5, together with the comparison of  $V_d$  with  $V_{\text{max}}$  and  $R_c$ . During this period (3–4 June), both  $\text{HNO}_3$  and  $\text{HCl}$  were found to be continuously deposited, but during daytime  $V_d$  calculated with the AGM for both gases was significantly less than permitted by turbulence. As  $R_c$  is calculated from the reciprocal  $V_d$  (Eq. 7), which is very large and uncertain during calm periods, values of  $R_c$  are only reliable during reasonably windy periods

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(i.e.  $u_* > 0.1 \text{ m s}^{-1}$ ; e.g. 4 June 04:00–20:00 GMT), where they show maximum values around midday of  $>200$  and  $100 \text{ s m}^{-1}$  for HNO<sub>3</sub> and HCl, respectively. From the averaged diurnal cycles of  $V_d(\text{HNO}_3)$  and  $V_d(\text{HCl})$  (Fig. 4c, d) it may be seen that this is a general phenomenon for the whole period. Statistics of the deposition parameters  $V_d$ ,  $V_{\text{max}}$ ,  $R_c$  and  $\chi(z_0')$  are summarized in Table 3, separated for day and night-time as well as dry and wet periods as detected by the simple wetness grid sensor. The theoretical values of  $V_{\text{max}}$  are generally much smaller during night than during the day due to stable and calm conditions. Similarly, variability in  $V_d$  reflects not only changes in the uptake properties of the vegetation, but also changes in atmospheric turbulence. Thus,  $R_c$  and  $\chi(z_0')$  are generally more meaningful parameters for the description of the surface properties. Averaged values of  $R_c$ , however, should be treated with caution since negative values of  $R_c$  can be caused by two contrary conditions: over-fast deposition ( $V_d > V_{\text{max}}$ ) and emission. For NH<sub>3</sub>, considerably larger values of  $R_c$  were derived for dry than for wet conditions.

For NH<sub>3</sub>,  $\chi(z_0')$  may be identified with the canopy compensation point ( $\chi_c$ ). This was largest during dry daytime conditions ( $4.8 \mu\text{g m}^{-3}$ ) and much smaller during wet daytime conditions ( $0.6 \mu\text{g m}^{-3}$ ). During wet conditions, a large fraction of stomatal emission would be recaptured by the leaf cuticle, which would provide efficient sinks. Wet canopies also coincide with cooler conditions and lower radiation, suppressing the stomatal emissions. The acidic gases were measured with prototype instrumentation at a lower time-resolution and at fewer heights than NH<sub>3</sub> and some more scatter in the data is therefore expected. On average, deposition velocities amount to only half of their theoretical maximum value. This is reflected by non-zero values of both  $R_c$  and  $\chi(z_0')$ .



## 4. Resistance modelling of the NH<sub>3</sub> vegetation/atmosphere exchange

The NH<sub>3</sub> flux was modelled with two different resistance models, using (a) the  $R_c$  model with parameterizations according to Eqs. (8) to (10), and (b) the  $\chi_c$ -model according to Eqs. (11) to (13). In the following the parameterizations of the resistances  $R_w$  and  $R_s$  and  $\Gamma_s$  are derived for use in the  $\chi_c$ -model.

### 4.1. Stomatal resistance

During stomatal opening, the mostly dry conditions allowed  $R_s(\text{NH}_3)$  to be calculated from  $R_s(\text{H}_2\text{O})$ , derived from the measured evapotranspiration (Eq. 12).  $R_s(\text{H}_2\text{O})$  was likely to be inaccurate either if turbulence was too low for  $R_a$  and  $R_b$  to be calculated accurately, or if evaporation of leaf-water layers contributed to  $E$ . Periods were therefore excluded if  $R_a + R_b > 200 \text{ s m}^{-1}$  or  $h(z'_0) > 85\%$ , and here  $R_{s,\text{NH}_3}$  was parameterized as a function of photosynthetically active radiation (PAR). In addition,  $R_s(\text{NH}_3)$  was generally set to a night-time value of  $4000 \text{ s m}^{-1}$  (Van Hove et al., 1989) for  $\text{PAR} < 20 \text{ W m}^{-2}$ . By fitting a curve of the shape suggested by Sutton and Fowler (1993b) to  $R_s$ , the following overall parameterization was obtained:

$$R_s(\text{NH}_3) = \begin{cases} \frac{D_{\text{H}_2\text{O}}}{D_{\text{NH}_3}} R_s(\text{H}_2\text{O}) & , R_a + R_b < 200 \text{ s m}^{-1} \text{ and } h(z'_0) < 85\% \\ 4000 & , \text{PAR} < 20 \text{ W m}^{-2} \\ 100 \left(1 + \frac{25}{2 \times \text{PAR}}\right) & , \text{PAR} \geq 20 \text{ W m}^{-2} \end{cases} \quad (15)$$

For the temperatures encountered in this study, this parameterization agrees closely with the formulation by Erisman et al. (1994) of Eq. (10), suggesting that the stomatal conductance measured here is similar to the earlier measurements at this site.

### 4.2. Cuticular resistance

$R_w$  was parameterized from periods selected for large  $R_s$  ( $> 1000 \text{ s m}^{-1}$ ) and excluding conditions of large  $R_a + R_b$  ( $> 500 \text{ s m}^{-1}$ ). During these periods,  $R_w$  can be approxi-

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mated by the excess resistance of  $R_t$  compared with  $R_a + R_b$  (e.g. Sutton et al., 1995b):

$$R_w \approx -\frac{\chi_a}{F_\chi} - (R_a + R_b) \quad (16)$$

The dependence of  $R_w$  on  $h(z_0')$  and  $VPD(z_0')$  is shown in Fig. 6, together with parameterizations, derived from the data by least-square optimization:

$$R_w [\text{s m}^{-1}] = 11.4 + 178.7 \times (1 - \exp(-0.546 \times VPD [\text{kPa}])) \quad (17)$$

$$R_w [\text{s m}^{-1}] = 956.24 \times \exp(-0.0382 h [\%]) \quad (18)$$

and according to Eq. (9) for comparison. Equation (18) is numerically equivalent to the form of  $R_w$  applied by Sutton et al. (1995b) of  $R_w = a \exp((100-h)/b)$ , where  $a = 21.0 \text{ s m}^{-1}$  and  $b = 26.2$ . During the present study  $R_w$  was larger and showed a weaker response to  $h$  than had previously been derived (Eq. 9) by Jackobsen et al. (1997).

#### 4.3. Emission and the stomatal compensation point

Ammonia emission from plant foliage can be the result either of a stomatal compensation point or desorption from leaf surfaces. Two observations suggest that stomatal exchange was probably the main reason for the emission observed: (i) emission occurred during long dry periods of up to 8 h (Fig. 3), while cuticular desorption is usually confined to the short periods of water layer evaporation (e.g. Sutton et al., 1998), and (ii) a high value of  $\Gamma_s$  was estimated from former measurements at Elspeet. However, the greatly reduced  $V_d$  for  $\text{HNO}_3$  and  $\text{HCl}$  might also indicate that the sustained dissociation of previously deposited  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  salts provided sustained non-zero gas-phase concentration at the leaf surfaces, which could have led to the observation of prolonged emission at low concentrations and high leaf temperatures. Dynamic models, which have been described elsewhere, would be required to simulate cuticular desorption (Sutton et al., 1998; Flechard et al., 1999). For the application of the

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$\chi_c$ -model, the emission is therefore assumed in the present analysis to originate from leaf stomata.

Neglecting cuticular desorption, the emission potential of the foliage ( $\Gamma_s$  may be estimated from  $\chi_a$ , observed during zero net fluxes: if stomatal exchange is dominant, as in the case for dry conditions ( $R_w$  large), a zero flux implies that  $\chi_a = \chi_c = \chi_s$  (Eq. 13). Therefore, at low  $h$ ,  $\chi_s$  may be estimated from those values of  $\chi_a$  at which the net flux changes from deposition to emission or vice versa (Spindler et al., 2001). Figure 7 shows these events as a function of  $T$ , together with the  $T$ -response curve of  $\chi_s$  according to Eq. (11) for two values of  $\Gamma_s$ . A value of  $\Gamma_s = 1200$  leads to a reasonable fit for  $h < 50\%$ , but for higher  $h$ , a distinct population of sign changes of the flux occur at larger air concentrations, which are better described by  $\Gamma_s = 2000$ . This is probably caused by a contribution of cuticular desorption to the emission, which is most pronounced during the transition from a wet to a dry canopy.

#### 4.4. Model results

The flux modelled with the  $\chi_c$ -model and a value of  $\Gamma_s = 1200$  is compared with the measured flux in Fig. 3. The model reproduces night-time deposition well, especially for the first half of the campaign, while emission is overestimated for the warm days 6 and 7 June. Daytime and night-time averages of the fluxes modelled with both the present parameterizations as well as the  $R_c$  model and the former parameterizations of Eqs. (8) to (10) are compared with the measurements in Fig. 8. Table 4 shows measured and modelled day- and night-time fluxes for four distinct periods. The  $R_c$  model tends to overestimate daytime deposition, except for Period 3. By contrast, the canopy compensation point model underestimates net deposition during the wetter and cooler night-time conditions (Periods 2 and 4). This suggests that the  $R_w$  response to  $h$  may give rise to lower resistances during the day than at night, as found by Wyers and Erisman (1998), possibly due to the increased humidity around open stomata. During daytime the  $\chi_c$ -model performs slightly better than the  $R_c$ -approach and predicts net

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emission on two days.

## 5. Discussion

### 5.1. Comparison of concentrations and fluxes and performance of the denuder/IC system

5 Bearing in mind the independent analysis techniques, the  $\text{NH}_3$  concentration inter-comparison between AMANDA, RBDs and filter-packs showed good agreement (Fig. 2a; Table 2), comparable to that found during other comparisons (Harrison and Kitto, 1990). Whereas the AMANDA denuders were continuously flushed, some “outliers” in the batch denuder data may be the result of carry-over after episodes of high concentrations. Also, while the amount of collection solution was kept constant in the continuous denuders, strong variations in  $T$  and  $h$  led to evaporation of up to 80% of the collection solution from the RBDs, possibly resulting in periods of reduced capture efficiency. Despite problems with a noisy baseline of the  $\text{SO}_2$  gas analyzer, the general functionality of the continuous denuder/IC combination (DENIC) was validated by the  $\text{SO}_2$  inter-comparison (Fig. 2b). However, the HCl concentration detected by the RBDs was on average 25% larger than by the DENIC, which may reflect  $\text{Cl}^-$  contamination of the RBD samples during transport and storage.

20 The AMANDA gradient system with online analysis is widely recognized to be a reference system for  $\text{NH}_3$  flux measurements. By contrast, the much simpler RBDs are potentially affected by errors due to storage and operational checks in the field are virtually impossible. In this light, the agreement in the fluxes measured with AMANDA and RBD gradients is unexpectedly impressive, despite divergence on individual days.

### 5.2. Quantification and modelling of the $\text{NH}_3$ net exchange

25 From measurements at Elspeet carried out over the period 1990–1992, Erisman et al. (1994) estimated an average annual net throughfall flux of  $\text{NH}_x$  (which is less than to-

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tal NH<sub>x</sub> deposition due to canopy exchange processes) to be 52 ng N m<sup>-2</sup> s<sup>-1</sup> (16.5 kg N ha<sup>-1</sup> yr<sup>-1</sup>), with a substantial contribution of NH<sub>3</sub> dry deposition (41 ng N m<sup>-2</sup> s<sup>-1</sup> = 13.0 kg N ha<sup>-1</sup> yr<sup>-1</sup>). This latter value agrees remarkably well with the averaged dry deposition of 45 ng N m<sup>-2</sup> s<sup>-1</sup> found during the intensive 3-week period of this study. However, the average dry deposition flux during the whole inter-comparison period detected by AMANDA and passive flux samplers was much larger, at 89 and 105 ng N m<sup>2</sup> s<sup>-1</sup>, respectively (Hansen et al., 1999). While the passive flux samplers may therefore on average overestimate deposition slightly, the AMANDA values were filtered for  $u > 1 \text{ m s}^{-1}$ , which removed small night-time fluxes and may have biased the overall average and could thus explain a small part of the discrepancy. However, the same filtering procedure applied to the intensive period raised the net deposition estimate only slightly (by 9%) to 49 ng N m<sup>-2</sup> s<sup>-1</sup>. Another possible explanation could be the typically wetter and more turbulent conditions over the extended period (not quantified), while air concentrations were similar.

Using parameterizations of  $R_s$ ,  $R_w$  and  $\chi_s$  derived from the field data, the  $\chi_c$ -model of Sutton and Fowler (1993b) reproduces the measured net exchange flux of the first two weeks of the campaign well (Fig. 3), while during 4–8 June daytime emission is overestimated compared with measurements. This predicted large emission flux is a consequence of the high canopy temperatures (up to 40°C), together with the high emission potential ( $\Gamma_s = 1200$ ), which was found from estimates of the stomatal compensation point (Fig. 7), but which is also necessary to obtain the observed emission on 3, 5 and 10 June.

The measurements during the very warm period 4 to 8 June show considerable day-to-day variability, while similar values in  $\chi_a$ ,  $T(z_0')$ ,  $h$  and  $S_t$  led to similar emissions predicted by the  $\chi_c$  model for 5 to 8 June. Concentrations were somewhat larger during 6 and 7 June (11  $\mu\text{g m}^{-3}$ ) as compared with 3 and 5 June (6  $\mu\text{g m}^{-3}$ ), but the difference is insufficient to have suppressed emissions during 6 and 7 June efficiently. Equation (11) implies that  $\chi_s$  doubles every 5 or 6°C, and the temperature effect should have more than compensated for the differences in air concentration. Since daytime

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$R_s$  was inferred from the rate of measured evapotranspiration, the effects of drought closure would be accounted for in the NH<sub>3</sub> modelling and can therefore be ruled out as the reason for the overestimation.

It is possible that apoplastic [NH<sub>4</sub><sup>+</sup>] concentrations (e.g. Husted et al., 2000) were reduced during hot periods, for example due to temperature sensitive biochemical production/assimilation processes or as a result of the emission. An alternative explanation may lie in the determination of the leaf temperature that determines  $\chi_s$ . Unpublished measurements over an agricultural grassland have shown that the micrometeorologically derived value of  $T(z_0')$  may be considerably larger than the actual temperature of growing leaves (Integrated GRAMINAE Experiment, Pierre Cellier, pers. commun.). The most likely cause is the contribution to  $T(z_0')$  by dry litter material and senescent leaves which heat up more effectively than transpiring vegetation. Finally, there is convincing evidence that the flux measurements were affected by the evaporation of NH<sub>4</sub><sup>+</sup> aerosol both in the air, but also on the leaf surfaces (see Sect. 5.5). This effect would have led to an overestimate of  $\Gamma_s$  in Fig. 7. Aerosol evaporation would have been larger during the warmer second and third week of the campaign and could explain at least a part of the poorer agreement between measured and modelled NH<sub>3</sub> flux found for this period (Nemitz et al., 2004b).

There is a clear trend in the comparative magnitudes of modelled and measured fluxes during the period 4 to 7 June: the model predicts emissions during 5 to 7 June, related to the canopy temperature, while the measurements indicate emissions on 4 and 5 June, which were not sustained during 6 and 7 June. This could be explained by the evaporation of previously deposited NH<sub>4</sub><sup>+</sup> salts on the leaf surfaces, which might have been completely volatilised by the end of 5 June. Emission events appear to occur at the firsts warm days after rain events (cf. also 10 June). Brief emission events have previously observed when leaf water layers evaporate in the morning and these may be reproduced by dynamic models (Flechard et al., 1999). By contrast, sustained emission events covering two days, such as 4 and 5 June have so far been attributed to stomatal emission.

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For the first two weeks of the campaign the average deposition predicted by the  $\chi_c$ -model agreed within 10% with the measured average, while the overestimated daytime emission during 4–7 June led to a 23% underestimation in net deposition ( $-42.7 \text{ ng m}^{-2} \text{ s}^{-1}$ ) for the whole period. In contrast, the  $R_c$  parameterization of Erisman et al. (1994) and Jakobsen et al. (1997) underestimated the deposition during the first two weeks, but led to a more accurate estimate over the whole period, although some features of the exchange pattern, such as net emission on 2 days, were not reproduced (Fig. 3).

When the first measurements of NH<sub>3</sub> exchange over natural and semi-natural surfaces were made, it was expected that NH<sub>3</sub> would be deposited at rates approaching  $V_{\text{max}}$  (e.g. Sutton et al., 1993; Duyzer, 1994). The observation of large  $R_c$  values and even emission from unfertilized canopies took researchers by surprise (Sutton et al., 1992; Erisman and Wyers, 1993). In particular, NH<sub>3</sub> emission from heathland at ambient concentrations of up to  $5 \mu\text{g m}^{-3}$  has been taken as an indication, that the input of atmospheric N can lift the N status of natural and semi-natural plant communities, thereby raising their  $\Gamma_s$  (Sutton et al., 1992; Sutton and Fowler, 1993b; Sutton et al., 1995a). The value of  $\Gamma_s = 1200$  used in the model is smaller than derived from former measurements at Elspeetsche Veld, but much larger than found for other semi-natural surfaces in cleaner environments. For example, Flechard and Fowler (1998) derived  $\Gamma_s = 132$  for a Scottish moorland and a  $\Gamma_s$  between 50 and 130 may be inferred from NH<sub>3</sub> flux measurements at a Scottish upland site, dominated by *Trichophorum cespitosum* and *Calluna vulgaris* (Milford et al., 2001). Similarly, Rattray and Sievering (2001) derived compensation points for alpine tundra vegetation in the Rocky Mountains of Colorado, which would be consistent with  $\Gamma_s = 16$ . A value of  $\Gamma_s \approx 500$  was derived from laboratory measurements of the NH<sub>3</sub> exchange fluxes with commercially grown *Calluna vulgaris* plants (Schjoerring et al., 1998), and  $\Gamma_s$  values as low as 20 were found from gas fumigation experiments and direct bioassay analysis of *Luzula sylvatica* (woodrush) (Hill et al., 2001).

The increase in  $\Gamma_s$  due to long term atmospheric N deposition effectively restricts the uptake of further atmospheric NH<sub>3</sub> by stomata. The NH<sub>3</sub> deposition that a low-N

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semi-natural surface would receive from the air concentrations found at Elspeet may be simulated in a scenario using the present parameterizations of  $R_w$  and  $R_s$  together with a value of  $\Gamma_s = 132$ . For such a canopy the  $\chi_c$ -model predicts an average increase of the deposition flux of  $-8.0 \text{ ng m}^{-2} \text{ s}^{-1}$  (i.e. an additional input of  $2.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ).

Hence the present NH<sub>3</sub> dry deposition to this site may have been suppressed by this amount as a feedback response to the high inputs of N over past decades. In terms of the within-canopy fluxes, the largest differences apply to the stomatal component flux: the model for present day conditions predicts a net stomatal emission of  $+8.9 \text{ ng m}^{-2} \text{ s}^{-1}$  (equivalent to  $+2.3 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ), while that for a pristine heathland predicts a net stomatal uptake of  $-2.8 \text{ ng m}^{-2} \text{ s}^{-1}$  (equivalent to  $-0.7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ). However, the component modelled cuticular fluxes dominate the net flux, with values of  $-41.2 \text{ ng m}^{-2} \text{ s}^{-1}$  under present conditions, and  $-45.5 \text{ ng m}^{-2} \text{ s}^{-1}$  for the pristine heathland model estimate.

### 5.3. Biosphere-atmosphere exchange of SO<sub>2</sub> and NH<sub>3</sub>-SO<sub>2</sub> co-deposition.

The average annual sulphur loading at Elspeet had previously been estimated as  $50.7 \text{ ng S m}^{-2} \text{ s}^{-1}$  ( $16.0 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ) from throughfall measurements to which SO<sub>2</sub> dry deposition contributed with  $35.5 \text{ ng S m}^{-2} \text{ s}^{-1}$  ( $11.2 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ) (Erisman et al., 1994). At  $18.4 \text{ ng S m}^{-2} \text{ s}^{-1}$  the average deposition flux measured with the DENIC was considerably lower, which is consistent with the lower average air concentrations during this study ( $3.4$  compared with  $6 \mu\text{g m}^{-3}$ ). Although the figures reported by (Erisman et al., 1994) must be considered more reliable for yearly averages, Dutch SO<sub>2</sub> concentrations have indeed declined continuously since 1979 (e.g. Erisman and Bleeker, 1997).

It can be shown theoretically that NH<sub>3</sub> deposition fluxes to leaf cuticles are larger, if they are accompanied by SO<sub>2</sub> deposition and vice versa (co-deposition) (Flechard et al., 1999). This is due the neutralization reaction within leaf water layers. However, field investigations into this effect are difficult to interpret (Erisman and Wyers, 1993;



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Sutton et al., 1993). Flechard (1998) found that  $R_w(\text{NH}_3)$  at a clean Scottish moorland site was smaller the more  $\text{SO}_2$  compared with  $\text{NH}_3$  had been deposited to the canopy during the 24 h preceding the measurements. Nemitz et al. (2001) compiled various  $R_w$  parameterisations derived for a range of ecosystems and found a significant positive correlation with the annual average  $\text{NH}_3/\text{SO}_2$  concentration ratio across these sites.

The cuticular resistance ( $R_w$ ) for  $\text{NH}_3$  derived in this study is larger than had been found at Elspeet during 1990–1992 (Fig. 6). This increase of  $R_w$  would therefore be consistent with a decrease in  $\text{SO}_2$  deposition at this site. It should be noted, however, that the  $R_w$  parameterization derived here may have been biased by the unrepresentatively warm conditions found during the intensive period of this study. This caveat is supported by the higher  $\text{NH}_3$  deposition found during the extended period of this study, which could be caused by smaller values of  $R_w$ , but also by more turbulent conditions (not compared).

#### 5.4. Biosphere-atmosphere exchange of $\text{HNO}_3$ and HCl

Due to their reactivity and high water-solubility,  $\text{HNO}_3$  and HCl are generally thought to be perfectly absorbed by plant canopies ( $R_c = 0$ ;  $V_d = V_{\text{max}}$ ). This hypothesis has been supported by a number of measurements (Huebert and Robert, 1985; Dollard et al., 1987; Meyers et al., 1989; Muller et al., 1993), during which no significant deviation of  $V_d$  from  $V_{\text{max}}$  was observed. A re-evaluation of the  $\text{HNO}_3$   $V_d$  measured by Dollard et al. (1987) and Harrison et al. (1989), however, revealed a correlation with the  $R_c$  of  $\text{NH}_3$ , which may reflect effects of gas-to-particle conversion (Sutton et al., 1993).

At Elspeet both  $\text{HNO}_3$  and HCl were found to be continuously deposited. The diurnal variation in  $V_d$  of these gases closely followed that of  $\text{NH}_3$  and showed values close to  $V_{\text{max}}$  at night, but considerable divergence from  $V_{\text{max}}$  between 06:00 and 20:00 GMT (Figs. 4 and 5). This could either be due to a measurement artefact caused by airborne gas-particle interconversion or may reflect a real surface uptake resistance of the sometimes extremely warm dry canopy.

The concept of perfect adsorption of  $\text{HNO}_3$  and HCl has repeatedly been challenged:

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Huebert et al. (1988) observed HNO<sub>3</sub> emission, which, although it could be explained by airborne NH<sub>4</sub><sup>+</sup> evaporation (Brost et al., 1988), might nevertheless have represented real surface emission. In addition, Neftel et al. (1996) reported emission gradients of HNO<sub>3</sub> above semi-natural grassland, which they explained by volatilization of NH<sub>4</sub>NO<sub>3</sub> from warm leaf surfaces, while Zhang et al. (1995) made similar observations above a Dutch heathland. Strong evidence for HCl emission from an oilseed rape canopy, probably due to HNO<sub>3</sub> reaction with sea salt deposited to the leaf cuticle, was reported by Nemitz et al. (2000b). And, finally, in fumigation experiments with 10 ppb HNO<sub>3</sub>, Cadle et al. (1991) observed that the resistance for HNO<sub>3</sub> deposition to the cuticle increased by factor of 15 within 16 h after the leaf surfaces had been washed.

There is therefore ample evidence for a non-zero canopy resistance and even emission of HNO<sub>3</sub> and HCl in certain situations. Considering the small vapour pressure over HNO<sub>3</sub> and HCl solutions (Clegg and Brimblecombe, 1986; Brimblecombe and Clegg, 1990), apoplastic concentrations of NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> are unlikely to be sufficient to cause a significant compensation point. By contrast, it is quite plausible that a non-zero gas-phase concentration in equilibrium with NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> particles on (warm) leaf cuticles may have been responsible for the observations. These particles could either have been previously dry-deposited or may have formed on the cuticle as a result of evaporation of rain, dew or microscopic water layers. Such a cuticular concentration ( $\chi_d$ ) of HNO<sub>3</sub> and HCl would obviously increase with increasing  $T$  and decreasing  $h$ .

### 5.5. Gas-particle interconversion

The same conditions that favour re-evaporation of HNO<sub>3</sub> and HCl from leaf cuticles would also result in the volatilization of airborne NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl. This can lead to a positive flux divergence of HNO<sub>3</sub> and HCl, consistent with the observation of  $V_d < V_{\max}$  (Brost et al., 1988). That evaporation of NH<sub>4</sub><sup>+</sup> exercised an important effect on flux measurements at Elspeet is supported by several independent observations. These issues are discussed in detail in the companion paper by Nemitz et al. (2004b) and these include (i) large apparent deposition rates of NH<sub>4</sub><sup>+</sup> aerosol, (ii) partial gas pres-

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sure products below the value in equilibrium with the aerosol phase, especially near the canopy (Nemitz, 1998), (iii) apparent emission of very fine particles. The quantification of the effect of NH<sub>4</sub><sup>+</sup> evaporation on HNO<sub>3</sub> fluxes through numerical modelling in the companion paper of Nemitz and Sutton shows that the flux at the upper measurement height may underestimate the surface deposition by typically 5.5%. This figure was inferred for an example day with high HNO<sub>3</sub> concentrations and the divergence from thermodynamic equilibrium may have been underestimated. Hence, airborne NH<sub>4</sub><sup>+</sup> evaporation could contribute significantly to the observation of  $V_d < V_{max}$  for HNO<sub>3</sub> and HCl but is very unlikely to be sufficient to account for all the deviation.

## 6. Conclusions

Simultaneous measurements of the gradients of NH<sub>3</sub>, HNO<sub>3</sub>, HCl, and SO<sub>2</sub>, were analyzed to infer surface exchange fluxes, net inputs and deposition velocities to a heathland site. The NH<sub>3</sub> fluxes were reproduced using an existing  $R_c$  parameterization, as well as a canopy compensation point ( $\chi_c$ ) model, with parameters derived from the field measurements. The same dataset has been applied elsewhere to investigate gas-aerosol phase equilibrium at this heathland and its potential interaction with dry deposition processes (Nemitz, 1998; Nemitz et al., 2004b).

Ammonia exchange was found to be bi-directional with mainly deposition and occasional emission events during the day. The  $\chi_c$ -model reproduced the bi-directional net NH<sub>3</sub> exchange flux reasonably well, although on some warm and sunny days daytime emission is overestimated. In the absence of direct measurements of the apoplastic ammonium/hydronium ratio ( $\Gamma_s = [\text{NH}_4^+]/[\text{H}^+]$ ), it cannot be decided whether  $\Gamma_s$  was biochemically suppressed during these warm days, whether the micrometeorologically derived average canopy temperature was unrepresentative for the temperature of growing leaves or whether  $\Gamma_s$  was derived too large for these days. While the extended nature of the measured NH<sub>3</sub> emissions suggest stomatal emission as the cause, a contribution to the emission from evaporation of NH<sub>4</sub><sup>+</sup> salts on leaf surfaces cannot be

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Although the  $R_c$  parameterization is methodically not able to account for periods of emission, it could still reproduce the measured flux fairly well, owing to often strong deposition caused by high  $\text{NH}_3$  air concentrations and the relatively small percentage of emission events ( $< 15\%$  of the time). The value of  $\Gamma_s = 1200$  estimated here is an order of magnitude larger than those reported for other heathland and moorland ecosystems, which is likely due to a feedback from the high N deposition in the Netherlands on the  $\Gamma_s$  value. This maybe overestimated if  $\text{NH}_4^+$  volatilisation contributed to the emission events. However,  $\Gamma_s$  is still smaller than inferred from former measurements at the same site in 1991/92.

Direct measurements of the  $\text{SO}_2$  dry deposition and higher cuticular resistance for  $\text{NH}_3$ , compared with measurements carried out in 1992, indicate a reduction of  $\text{SO}_2$  inputs over the past few years. The averaged diurnal cycle of the deposition velocities of  $\text{HNO}_3$  and  $\text{HCl}$  as derived by the unmodified aerodynamic gradient technique, using a new continuous denuder-based gradient system with online analysis by ion chromatography, show surface uptake resistances ( $R_c$ ) of up to  $100\text{--}200 \text{ s m}^{-1}$  during the day. Flux divergence due to the evaporation of airborne  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  containing aerosol probably accounts for a fraction of the difference between  $V_d$  and  $V_{\text{max}}$ . However, the largest part of the discrepancy almost certainly reflects a non-zero  $R_c$ , possibly due to the acid gas partial pressure in equilibrium with  $\text{NH}_4^+$  salts on leaf surfaces. This confirms the occurrence of a non-zero  $R_c$  for  $\text{HNO}_3$  and  $\text{HCl}$  suggested in previous studies.

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**Table 1.** Key parameters measured during the Elspeet campaign.

Approach applied <sup>a)</sup>	Parameter (number of measurement heights)	Methodology	Averaging time	Manufacturer / (method reference)
<b>(1) Gases:</b>				
AGM	NH <sub>3</sub> (3)	continuous AMANDA denuders with 3 inlets	6 min cycle (3 inlets)	ECN, Petten, NL (Wyers et al., 1993)
AGM	NH <sub>3</sub> (4)	passive denuders (flux samplers)	5 days	(Hansen et al., 1999)
AGM	HNO <sub>3</sub> , HCl, HNO <sub>2</sub> , NH <sub>3</sub> (3)	automatic rotating batch denuder (RBD)	1 h cycle (40 min sampling)	ECN, Petten, NL (Keuken et al., 1988)
AGM	HNO <sub>3</sub> , HCl, HNO <sub>2</sub> , SO <sub>2</sub> (2)	continuous denuder / online anion chromatography (DENIC)	30 min (2 inlets)	ECN, Petten, NL (Oms et al., 1996)
AGM	NH <sub>3</sub> (≤10)	filter-packs	1-3 h	(Harrison and Kitto, 1990)
AGM	SO <sub>2</sub> (3)	pulsed chemiluminescence analyzer	15 min cycle (2 inlets)	Thermo Environ. Inst., model 43s, Franklin, Mass., USA
<b>(2) Micro-met. measurements</b>				
	mean humidity and temperature (1)	thermistor and capacitance probe.	15 min	Rotronic Instr., Horley, Surrey, UK; Vaisala Ltd. Cambridge, UK
	net radiation, photo-synthetically active radiation, wetness, precipitation	Bowen ratio system, wetness sensor, tipping bucket	15 min	Bowen ratio system, Campbell Scientific, Shepshed, UK
EC	instantaneous windspeed and temperature fluctuations (3)	ultrasonic anemometers	15 min	Solent Research 1012, Gill Instruments, Lymington, UK
EC	instantaneous water vapour fluctuations (1)	Krypton hygrometer (KH <sub>2</sub> O)	15 min	Campbell Scientific, Shepshed, UK
AGM	horizontal mean windspeed (6)	cup anemometers	15 min	Vector Instruments, Clywd, UK
AGM	temperature and humidity gradients (2)	fine thermocouples and dewpoint meter	15 min	Bowen ratio system, Campbell Scientific, Shepshed, UK

<sup>a)</sup> Key for flux measurement techniques: AGM - aerodynamic gradient method; EC - eddy covariance technique.

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**Table 2.** Summary of measured gas concentrations at Elspeet during the intensive measurement phase.

chemical species (instrument)	$\mu_A$ ( $\mu\text{g m}^{-3}$ )	$\mu_A$ ( $\mu\text{eq m}^{-3}$ )	$\sigma_A$ ( $\mu\text{g m}^{-3}$ )	$\mu_M$ ( $\mu\text{g m}^{-3}$ )	$\sigma_G$	$\chi_{\text{min.}}$ ( $\mu\text{g m}^{-3}$ )	$\chi_{\text{max.}}$ ( $\mu\text{g m}^{-3}$ )	coverage (days)	meas. <i>t</i> (min)	<i>N</i> (#)
NH <sub>3</sub> -N (AMANDA) <sup>1)</sup>	5.19 (6.07)	0.37 (0.43)	4.08 (4.46)	4.33 (5.05)	1.97 (1.72)	0.12 (0.40)	59.0 (59.0)	23 (15)	15 (15)	1881 (1157)
NH <sub>3</sub> -N (RBD)	6.75	0.48	5.09	5.00	1.81	0.19	47.9	15	60	305
SO <sub>2</sub> -S DENIC	1.69	0.11	1.45	1.33	1.44	0.16	8.69	21	30	284
SO <sub>2</sub> -S (gas analyzer)	1.86	0.12	1.74	1.21	1.47	0.00	16.6	21	30	508
HNO <sub>3</sub> -N (DENIC)	0.34	0.024	0.53	0.14	0.90	0.01	2.83	21	30	124
HONO-N (DENIC)	0.18	0.013	0.20	0.11	0.86	0.01	1.45	21	30	167
HCl-Cl (DENIC)	0.29	0.008	0.34	0.17	2.29	0.03	4.17	21	30	544

$\mu_A$ : arithmetic mean;  $\sigma_A$ : arithmetic standard deviation;  $\mu_M$ : median;  $\sigma_G$ : geometric standard deviation;  $\chi_{\text{min.}}$ ,  $\chi_{\text{max.}}$ : minimum and maximum concentration; meas. *t*: measurement time; *N*: number of observations. <sup>1)</sup> Values in brackets are for the same period as the rotating batch denuders (RBDs) to enable direct comparison of the results. Values are ½ h averages, except for RBD (40 min).

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**Table 3.** Summary of deposition velocities and canopy resistances of gases at Elspeet for dry and wet conditions, as defined by the wetness sensor (day (04:00–19:00)/night-time (19:00–04:00)).

			NH <sub>3</sub>	SO <sub>2</sub>	HNO <sub>3</sub>	HCl
$V_d$ [mm s <sup>-1</sup> ]	dry	min.	-27.7 / -3.3	-32.6 / -26.0	-30.1 / -11.9	-21.9 / -6.2
		max.	31.1 / 40.2	49.6 / 28.7	42.4 / 26.2	66.9 / 32.5
		$\mu_A$	6.0 / 6.9	9.3 / 4.8	10.9 / 3.4	13.3 / 2.5
		$\mu_M$	7.2 / 4.8	8.4 / 2.8	11.5 / 2.2	11.7 / 1.7
	wet	min.	-7.0 / -2.5	-28.4 / -31.2	-33.3 / -13.1	-22.0 / -14.1
		max.	49.9 / 48.5	51.2 / 35.0	34.5 / 21.2	15.9 / 9.9
		$\mu_A$	18.2 / 16.3	8.7 / 8.3	3.5 / 5.0	0.6 / 1.5
		$\mu_M$	18.0 / 15.7	9.6 / 7.9	3.4 / 6.1	1.3 / 1.7
$V_{max}$ [mm s <sup>-1</sup> ]	dry	min.	3.4 / 0.9	3.5 / 1.2	3.5 / 1.2	4.0 / 1.3
		max.	44.9 / 29.8	31.0 / 24.5	31.0 / 24.5	35.2 / 27.5
		$\mu_A$	25.8 / 8.0	19.5 / 6.5	19.5 / 6.5	21.9 / 7.2
		$\mu_M$	19.5 / 5.9	19.9 / 4.6	19.9 / 4.6	22.3 / 5.1
	wet	min.	4.0 / 1.9	5.8 / 3.7	5.8 / 3.7	6.2 / 3.9
		max.	42.7 / 29.8	29.7 / 23.3	29.7 / 23.3	33.4 / 26.0
		$\mu_A$	22.5 / 16.9	17.9 / 14.0	17.9 / 14.0	20.0 / 15.5
		$\mu_M$	23.1 / 19.5	18.2 / 16.3	18.2 / 16.3	20.5 / 18.2
$R_c$ [s m <sup>-1</sup> ]	dry	$\mu_M$	58 / 65	32.0 / 31.6	15.0 / 94.5	12.9 / 153
	wet	$\mu_M$	9.6 / 8.5	-10.8 / -13.9	21.2 / 38.6	46.7 / 183
$\chi(z_0)$ [ $\mu\text{g m}^{-3}$ ]	dry	min.	<0 / <0	<0 / <0	<0 / <0	<0 / <0
		max.	18.7 / 15.2	21.1 / 11.2	5.3 / 7.3	1.7 / 3.4
		$\mu_A$	4.9 / 1.3	0.82 / 0.28	0.44 / 0.73	0.04 / 0.26
		$\mu_M$	4.8 / 1.9	1.45 / 0.34	0.42 / 0.34	0.10 / 0.10
	wet	min.	<0 / <0	<0 / <0	<0 / <0	<0 / 0.03
		max.	10.3 / 10.8	16.9 / 6.8	4.9 / 4.5	1.9 / 1.4
		$\mu_A$	0.59 / 1.1	0.19 / 0.60	0.51 / 0.28	0.21 / 0.21
		$\mu_M$	0.75 / 0.70	0.27 / 0.04	0.17 / 0.12	0.15 / 0.11

min.: minimum value; max.: maximum value;  $\mu_A$ : arithmetic mean;  $\mu_M$ : median

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**Table 4.** Summary of the measured and modelled NH<sub>3</sub> fluxes (in ng m<sup>-2</sup> s<sup>-1</sup>), divided into day and night as well as 4 meteorologically distinct periods. Bold figures indicate values that deviate from the measured fluxes by more than 25%. Night-time is taken as 7:00–20:00 GMT.

	Period 1 21-29/05		Period 2 29/05-03/06		Period 3 04-07/06		Period 4 08-14/06		Mean	
	day	night	day	night	day	night	day	night	day	night
measured flux	-50.2	-67.4	-16.6	-53.7	-36.6	-72.8	-63.4	-106.6	-39.5	-72.3
modelled flux ( $\chi_c$ - model)	-42.6	-53.3	<b>-29.8</b>	<b>-37.5</b>	<b>-10.1</b>	-62.3	-52.7	<b>-60.9</b>	-34.7	<b>-51.9</b>
modelled flux ( $R_c$ - model)	<b>-67.0</b>	-66.8	<b>-43.8</b>	-43.7	-37.6	-76.4	<b>-93.7</b>	<b>-74.1</b>	<b>-59.8</b>	-63.4
$T(z_0)$ [°C]	15.0	12.2	21.5	15.8	29.9	22.3	23.1	16.0	20.8	15.8
$h$ (1 m) [%]	66.4	74.1	54.3	82.2	46.1	83.2	64.2	93.2	59.4	81.1

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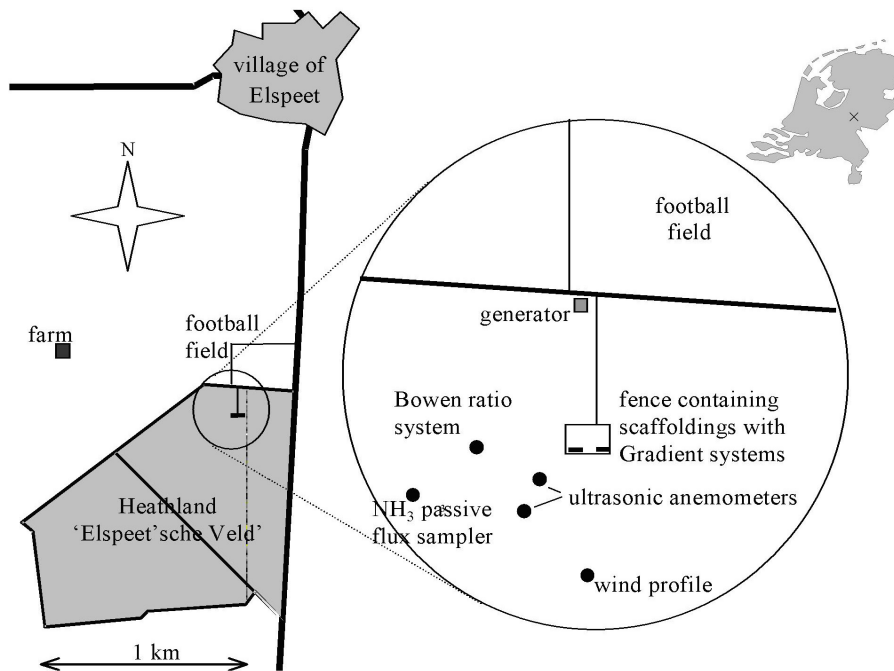
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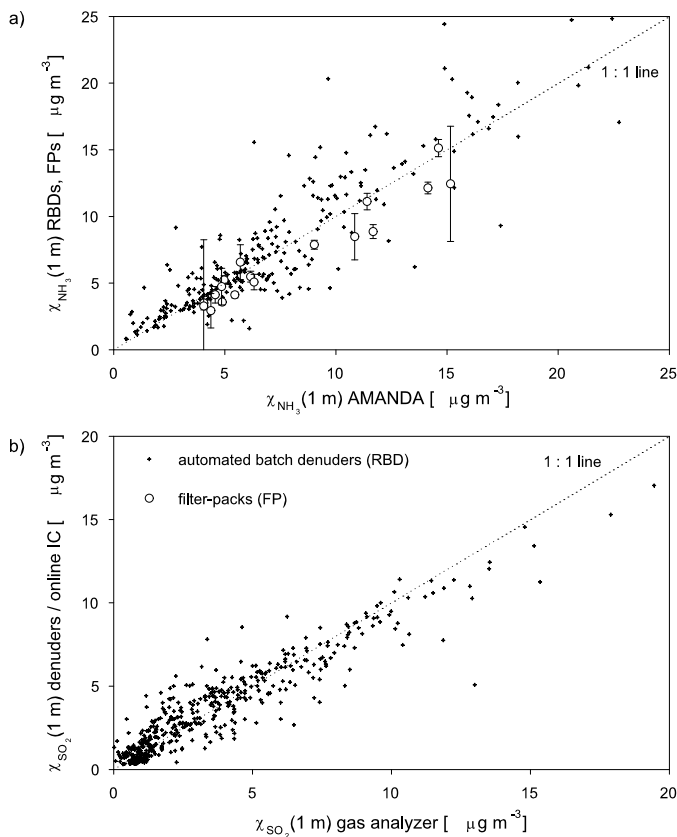


**Fig. 1.** Map of the Elspeet field site with instruments and the location within the Netherlands (inset).

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**Fig. 2.** Comparison of **(a)**  $\text{NH}_3$  concentration measured with rotating batch denuders (RBD) and filter-packs (FP) against AMANDA reference system and **(b)**  $\text{SO}_2$  concentration measured by the denuder system with online anion IC (DENIC) against a gas analyzer. Error bars show standard errors. Linear regression analysis yields:  $\chi_{\text{NH}_3}(\text{RBD}) = 1.03 \chi_{\text{NH}_3}(\text{AMANDA}) + 0.34$  ( $R^2 = 0.85$ ),  $\chi_{\text{NH}_3}(\text{FP}) = 0.89 \chi_{\text{NH}_3}(\text{AMANDA}) - 0.13$  ( $R^2 = 0.93$ ) and  $\chi_{\text{SO}_2}(\text{DENIC}) = 0.85 \chi_{\text{SO}_2}(\text{gas analyzer}) + 0.54$  ( $R^2 = 0.88$ ).

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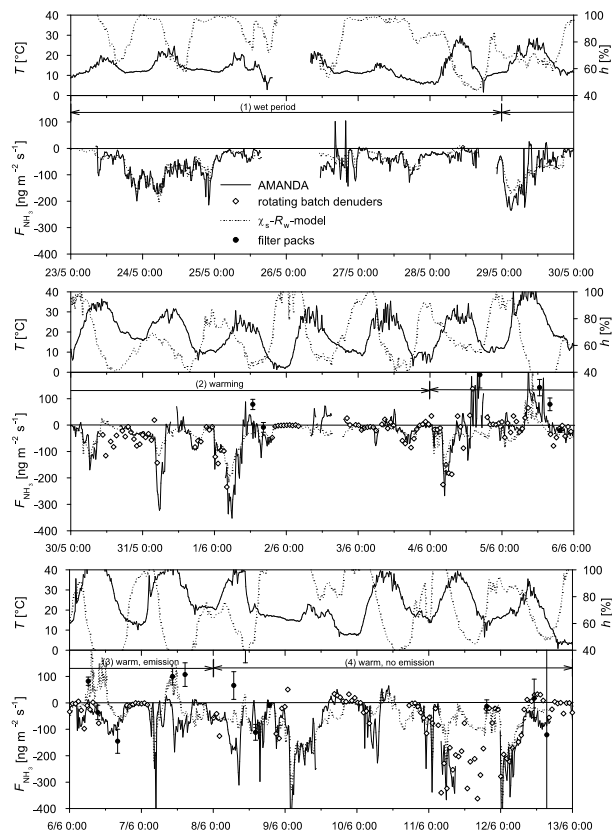
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**Fig. 3.** The  $\text{NH}_3$  flux at Elspeet measured with the AMANDA system, rotating batch denuders and filter-packs. Error bars are standard errors for 5–10 measurement heights. Also shown is the flux modelled with the  $\chi_c$ -model calculating  $R_s$  and  $R_w$  according to Eqs. (15) and (17), respectively, with  $\Gamma_s = 1200$ . The temperature at the canopy height ( $T(z_0')$ ) is shown as a solid line and the relative humidity at 1 m ( $h$ ) as a dotted line.

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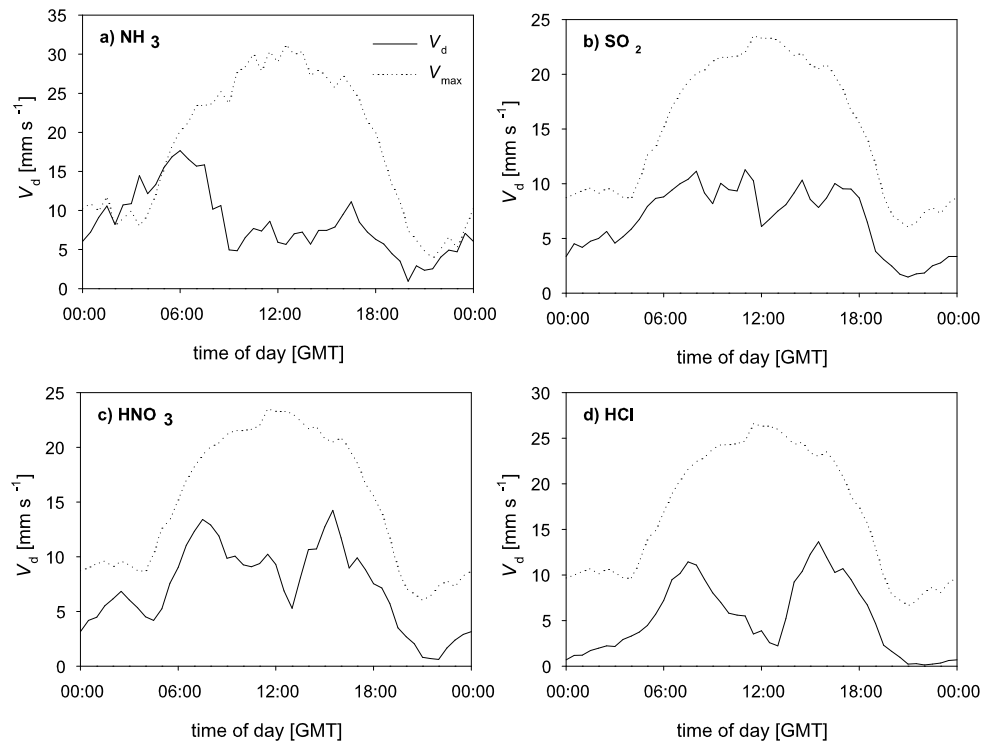
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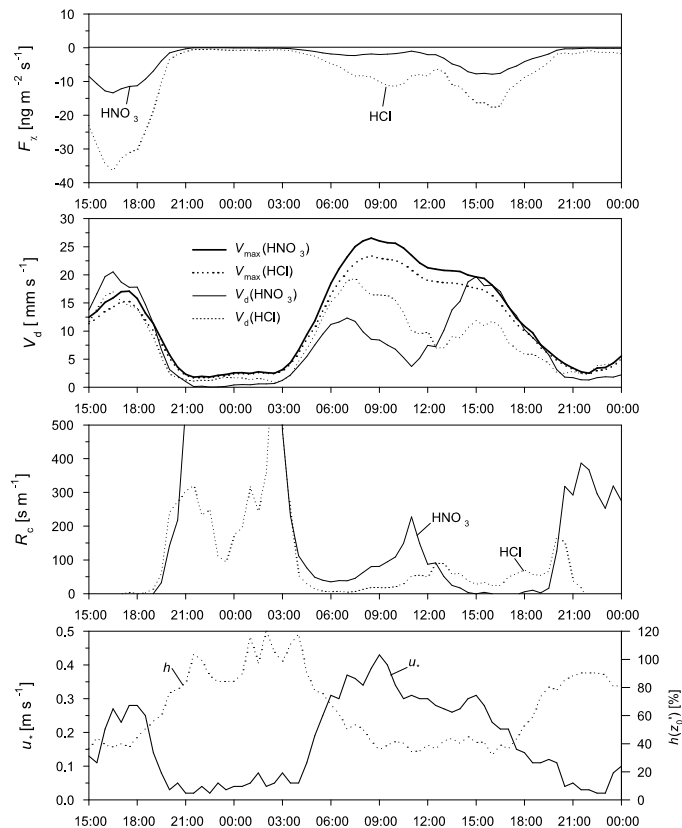


**Fig. 4.** Averaged diurnal cycles of the deposition velocities ( $V_d$ ) as calculated from the AMANDA and DENIC gradients in comparison with  $V_{\text{max}}$ .

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**Fig. 5.** Example diurnal cycle for 3–4 June 1996 of the (a) fluxes, (b) deposition velocities of  $\text{HNO}_3$  and  $\text{HCl}$  in comparison with their maximum values and (c)  $R_c$   $\text{HNO}_3$  and  $\text{HCl}$ , (d) friction velocity ( $u_*$ ) and relative humidity ( $h$ ). Data represent 2.5 h running means of 30 min values, except for  $u_*$  and  $h$  (block-averaged for 30 min).

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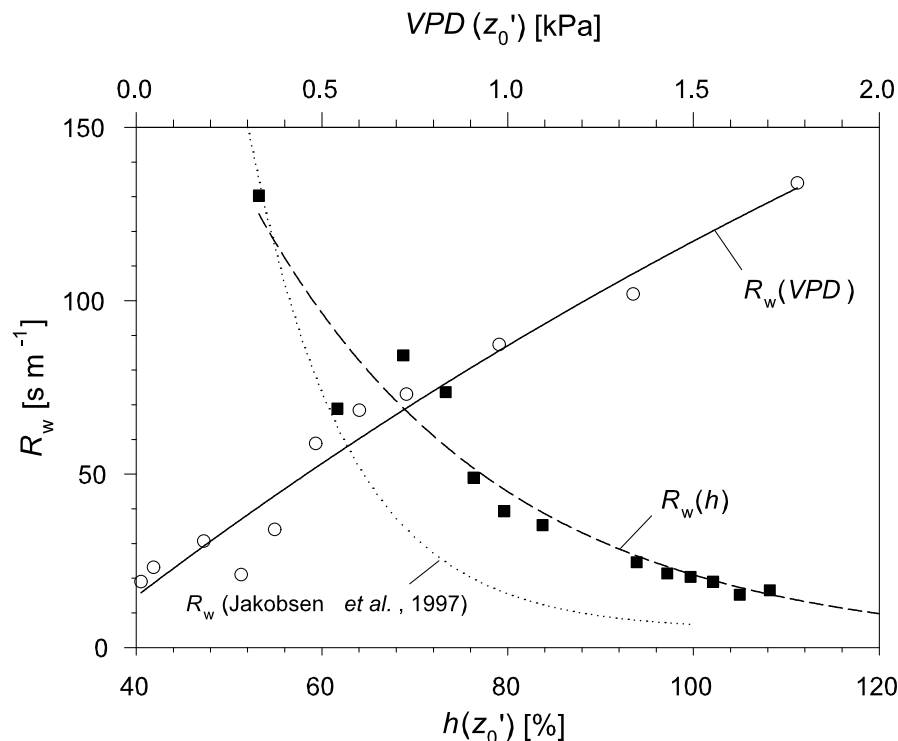
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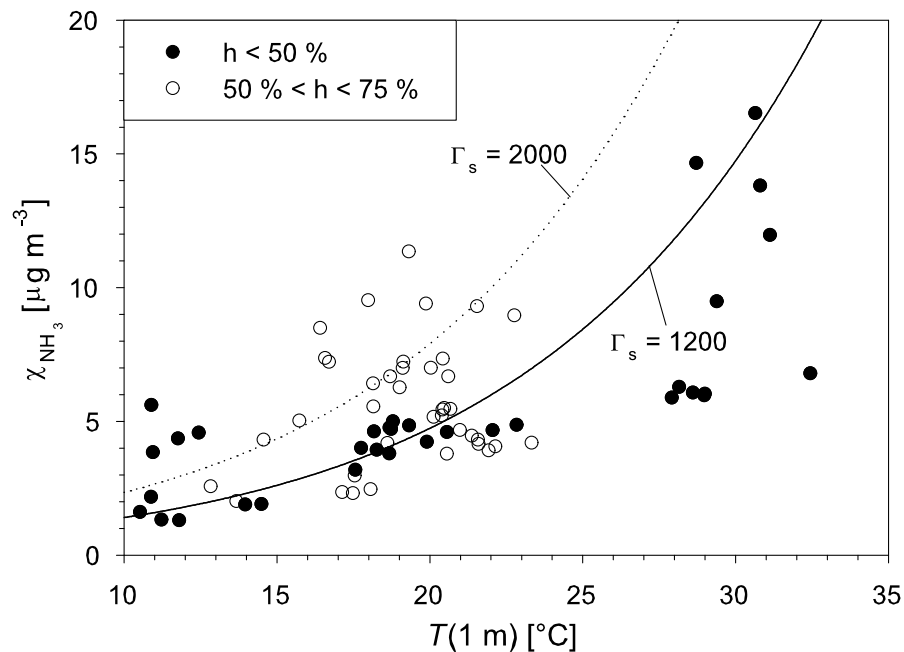


**Fig. 6.** The dependency of  $R_w$  for  $\text{NH}_3$  on the surface values of relative humidity ( $h(z_0')$ ) and vapour pressure deficit ( $\text{VPD}(z_0')$ ). The full squares and open circles represent block-averaged values for 50 sequential 30-min values of  $R_w$  values, sorted for  $h$  and  $\text{VPD}$ , respectively. The dashed and the solid lines show the parameterizations of Eqs. (17) and (18), respectively, derived as fits to the measurements. The dotted line represents the parameterization of  $R_w$  (or  $R_{\text{ext}}$ ) by Jakobsen et al. (1997), Eq. (9), for comparison.

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**Fig. 7.** The stomatal compensation point ( $\chi_s$ ) estimated from the  $\text{NH}_3$  air concentration during individual events at which the flux changed sign as a function of temperature ( $T$ ) for two ranges of relative humidities ( $h$ ). Also shown are the  $T$  response curves calculated for two values of the apoplastic  $[\text{NH}_4^+]/[\text{H}^+]$  ratio ( $\Gamma_s$ ) according to Eq. (11).

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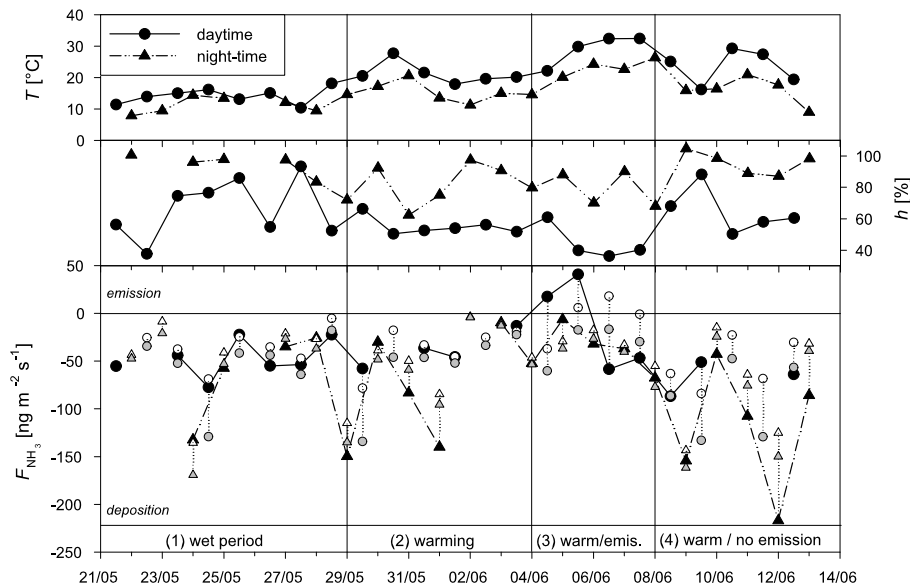
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**Fig. 8.** Daytime (circles) and night-time averages (triangles) of the  $\text{NH}_3$  exchange flux modelled with (i) the  $\chi_c$ -model (open symbols) and (ii)  $R_c$ -parameterization (grey symbols) according to Eqs. (8) to (10) in comparison with the measured values (black symbols).

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