

Gas-particle interactions above a Dutch heathland: II. Concentrations and surface exchange fluxes of atmospheric particles

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Abstract. Size-dependent particle number fluxes measured by eddy-covariance (EC) and continuous fluxes of ammonium (NH_4^+) measured with the aerodynamic gradient method (AGM) are reported for a Dutch heathland. Day-time deposition velocities (V_d) by EC with peak values of 5 to 10 mm s^{-1} increased with particle diameter (d_p) over the range $0.1\text{--}0.5 \mu\text{m}$, and are faster than predicted by current models. With a mean V_d of 2.0 mm s^{-1} (daytime: 2.7; nighttime 0.8 mm s^{-1}) NH_4^+ fluxes by AGM are overall in agreement with former measurements and NH_4^+ -N dry deposition amounts to 20% of the dry input of NH_3 -N over the measurement period. These surface exchange fluxes are analyzed together with simultaneous gas-phase flux measurements for indications of gas-particle interactions. On warm afternoons the apparent fluxes of acids and aerosol above the heathland showed several coinciding anomalies, all of which are consistent with NH_4^+ evaporation during deposition: (i) canopy resistances for HNO_3 and HCl of up to 100 s m^{-1} , (ii) simultaneous particle emission of small particles ($D_p < 0.18 \mu\text{m}$) and deposition of larger particles ($D_p > 0.18 \mu\text{m}$), (iii) NH_4^+ deposition faster than derived from size-distributions and size-segregated EC particle fluxes. These observations coincide with the observations of (i) surface concentration products of NH_3 and HNO_3 well below the thermodynamic equilibrium value and (ii) Damköhler numbers that indicate chemical conversion to be sufficiently fast to modify exchange fluxes. The measurements imply a removal rate of volatile NH_4^+ of $3\text{--}30 \times 10^{-6} \text{ s}^{-1}$ averaged over the 1 km boundary-layer, while NH_3 deposition is underestimated by typically $20 \text{ ng m}^{-2} \text{ s}^{-1}$ (28%) and flux reversal may occur.

1 Introduction

1.1 Background

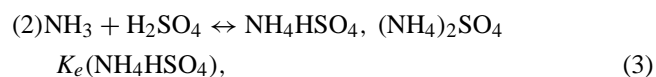
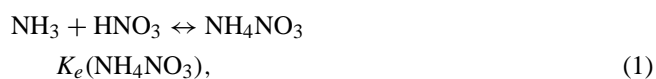
The deposition of atmospheric aerosol particles can considerably contribute to the atmospheric inputs of pollutants such as nitrogen and sulphate compounds (Hanson and Lindberg, 1991; Wyers and Duyzer, 1997; Dammgén and Zimmerling, 2002; Sanz et al., 2002), in particular in dry and remote environments and over aerodynamically rough surfaces. The deposition of the aerosol components ammonium (NH_4^+), nitrate (NO_3^-), chloride (Cl^-) and sulphate (SO_4^{2-}) contributes to acidification and eutrophication of ecosystems. Since in general particles deposit more slowly than reactive gases, they often dominate long-range transport and transboundary fluxes of air pollutants. Yet, the surface/atmosphere exchange of particles has been studied in less detail than their gaseous counterparts. This is partly due to difficulties in the application of micrometeorological techniques to particles: their deposition velocity (V_d) is small, while vertical concentration gradients are weak and difficult to detect. In addition, there are no fast-response sensors for these aerosol chemical species that would enable the application of direct measurement techniques such as eddy-covariance (EC). However, the latter has been applied to infer size-dependent particle number fluxes using optical particle counters (e.g. Sievering, 1983, 1987; Gallagher et al., 1993; Gallagher et al., 1997; Nemitz et al., 2002).

Particles may be emitted by combustion processes, resuspended from soils and road surfaces and generated by frictional processes. Primary particle emissions from vegetation canopies are confined to biological aerosols such as spores and pollen. The slower deposition of particles if compared

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with gases has been derived by several theoretical approaches (Slinn, 1982; Peters and Eiden, 1992; Ruijgrok et al., 1997) and validated in wind tunnel studies (Chamberlain, 1966) as well as measurements above short vegetation (Nemitz et al., 2002). There is growing evidence, however, that deposition rates to forests may be much larger than previously assumed (Gallagher et al., 1997; Wyers and Duyzer, 1997; Garland, 2001).

As a further complication, measurements of the surface exchange of reactive compounds, both gases and aerosols, may be affected by chemical conversions (Fitzjarrald and Lenschow, 1983). For example, fluxes of nitrous oxide (NO) have to be corrected for the chemistry of the photochemical NO-NO₂-O₃ triad. Similarly, for the accurate measurement of fluxes of ammonia (NH₃), nitric acid (HNO₃), hydrochloric acid (HCl), sulphuric acid (H₂SO₄) as well as their associated aerosol species (NH₄⁺, NO₃⁻, Cl⁻, SO₄²⁻), the following reactions need to be considered:



where the K_e are the dissociation constants of the associated ammonium salts. The vapour pressure above sulphate (SO₄²⁻) aerosols is sufficiently small to consider Reaction (3) irreversible. It is therefore assumed that any sulphuric acid (H₂SO₄) produced in the atmosphere, for example by oxidation of SO₂ by OH radicals, is immediately neutralized by NH₃ (Seinfeld and Pandis, 1997). By contrast, the reactions of Eqs. (1) and (2) can lead to either gas-to-particle conversion (gtpc) or aerosol evaporation; both processes are here commonly referred to as gas-particle interconversion (gpic). Despite its similarity to the NO-O₃-NO₂ triad, gpic involving NH₃ is more difficult to model. Whereas the reaction of NO with O₃ is a homogenous gas-phase reaction with well-defined reaction rates and (photochemical) equilibrium state, the reaction mechanisms and time-scales of the (probably) inhomogeneous gpic are an issue of controversy in the literature.

1.2 Effects of gas-particle interconversion on surface exchange fluxes of gases and aerosols

The height (z) dependence of the flux (F_χ) of a tracer (χ) for which there are chemical sources or sinks in the atmosphere, may be approximated by first-order relaxation towards equilibrium (Brost et al., 1988):

$$\frac{dF_\chi}{dz} = Q_\chi = \frac{\chi - \chi_{eq}}{\tau_c} \quad (4)$$

where Q_χ is the chemical source/sink term, χ is the actual concentration and χ_{eq} is the hypothetical concentration of χ if equilibrium were attained. τ_c is the chemical relaxation time-scale for the attainment of equilibrium (Wexler and Seinfeld, 1990). Thus flux divergence is a result of deviation from thermodynamic equilibrium, which in the atmosphere may have several causes (Nemitz, 1998):

- Close to strong sources of NH₃, HNO₃ or HCl there is likely to be potential for aerosol formation.
- Surface/atmosphere exchange leads to vertical gradients of both acidic gases and ammonia. As a result thermodynamic equilibrium may be restricted to a single height or not occur at all.
- The equilibrium constant (K_e) is a function of temperature and relative humidity (Pio and Harrison, 1987; Mozurkewich, 1993) and therefore changes with height.

If equilibration is sufficiently fast (τ_c small) compared with the time-scale of turbulent diffusive transfer (τ_d), the concentration gradients, and therefore the fluxes, will be modified by the tendency to re-attain equilibrium. If gtpc affects the gradient, then micrometeorological techniques overestimate the deposition of the gases, compared with the true surface exchange flux, at the same time as they underestimate the deposition of the aerosol or even indicate apparent aerosol emission. By contrast, in the case of aerosol evaporation, measurements may derive unexpected small deposition rates or apparent emission of the gases as well as over-rapid deposition of the aerosol species.

Direct validation of the influence of the NH₃-NH₄⁺ equilibrium on surface exchange fluxes has so far proven difficult. Measurement approaches that derive the flux at a single height would be needed to detect vertical flux divergence directly. However, the implementation of eddy-covariance techniques for sticky gases such as NH₃ and HNO₃ and aerosols is difficult, while relaxed eddy accumulation techniques for NH₃ are still insufficiently precise to resolve such flux divergence (Nemitz et al., 2001). It is much harder to derive evidence for gpic from measurements of vertical gradients of concentration (rather than of fluxes). Nevertheless, from simultaneous gradient measurements of HNO₃ and NH₃, Harrison et al. (1989) concluded that gpic effects are negligible, and this work has often been cited as a justification for the applicability of aerodynamic gradient techniques to NH₃. However, Sutton et al. (1993) statistically re-analyzed the data by Harrison et al. (1989) and found some indication for interactions. Similarly, Yamulki et al. (1996) ruled out artefacts on their NH₃ flux measurements on the grounds that measured gradients did not significantly deviate from logarithmic profiles. However, even weak changes in concentration profiles that are smaller than the scatter in typical measurement data may lead to a significant height-dependence of F (cf. modelled concentration profiles by Van Oss et al., 1998; Nemitz and Sutton, 2004).

There is ample evidence that the $\text{NH}_3\text{-NH}_4^+$ equilibrium can result in anomalous fluxes: Gallagher et al. (1993, 1997a) observed upward fluxes of particles with a diameter (D_p) $< 0.25 \mu\text{m}$ above Dutch heathland and forest ecosystems, which were correlated with times of NH_3 emission, while Zhang et al. (1995) attributed apparent HNO_3 emission fluxes to dissociation of NH_4NO_3 . The opposite observation, HNO_3 deposition faster than permitted by turbulence, has been reported by Meixner et al. (1990) and can also be seen in data presented by Dollard et al. (1987), also re-analyzed by Sutton et al. (1993). In addition, the potential effect of gpic on measurements of NH_3 exchange fluxes has been estimated by comparison of chemical time-scales, obtained from measurements of the aerosol size distribution, with diffusive time-scales (Kins et al., 1996; Seidl et al., 1996; Nemitz et al., 2000).

Brost et al. (1988) were the first to model the effect of the $\text{NH}_3\text{-HNO}_3\text{-NH}_4\text{NO}_3$ equilibrium on surface exchange fluxes of NH_3 and successfully reproduced anomalous observations of HNO_3 emission and fast NO_3^- deposition by Huebert et al. (1988) as the effect of NH_4NO_3 evaporation. Kramm and Dlugi (1994) proposed an alternative model, which they coupled with an inferential resistance model for the estimation of surface exchange fluxes from single point concentration data. For the application of such models to UK measurement data suggesting upward fluxes of NH_4^+ aerosol, Nemitz et al. (1996) incorporated of the $\text{NH}_3\text{-HCl-NH}_4\text{Cl}$ triad as well as of the effect of vertical gradients of T and relative humidity (h) on the values of the dissociation constants. Wyers and Duyzer (1997) observed NO_3^- aerosol deposition faster than permitted by turbulence above the Dutch forest Speulderbos. Van Oss et al. (1998) successfully simulated this observation and at the same time demonstrated that NH_3 emission fluxes obtained at Speulderbos may not originate from the foliage but could at least partly be explained by the evaporation of NH_4NO_3 close to or within the canopy. The same explanation was used by Neftel et al. (1997) who reported apparent HNO_3 emission gradients. Nemitz et al. (2000) reported emissions of both NH_3 and HCl for an oilseed rape canopy at a coastal Scottish location. Although air concentrations above the canopy were below the equilibrium value, there was potential for NH_4Cl formation within the canopy. The effect of gpic within forest canopies was modelled by Faust (1996) who also examined its influence on the aerosol size distributions of NH_4^+ , NO_3^- and SO_4^{2-} aerosol.

1.3 The Elspeet experiment

A field campaign at the Dutch heathland of Elspeet was designed to measure gas and particle fluxes and to study the effects of gas-to-particle conversion and evaporation of the volatile NH_4^+ compounds (NH_4NO_3 and NH_4Cl). This experiment, conducted between 21 May to 13 June 1996, formed part of the European 'EXAMINE' project ('Ex-

change of Ammonia with European Ecosystems') Sutton et al., 1996). This paper reports the flux measurements of particles made in this experiment and examines the whole dataset (including gas fluxes) for indications of gpic. The measurements reported here include size-segregated particle number flux measurements over the range of 0.1 to 0.5 μm diameter by eddy-covariance (EC) and fluxes of NH_4^+ derived from continuous automated gradient measurements using the aerodynamic gradient method (AGM). The results of simultaneous gas-phase measurements (NH_3 , HNO_3 , HCl , SO_2) are reported elsewhere (Nemitz et al., 2004), while the effects of gpic were modelled quantitatively by Nemitz and Sutton (2004).

2 Methods

2.1 Aerosol instrumentation

Particle number fluxes were measured with an EC system comprising of an optical particle counter (ASASP-x, PMS, Boulder, Colorado, US) and an ultrasonic anemometer (Solent Research Anemometer 1012, Gill Instrument, Lymington, UK), a combination similar to that used in previous studies (Sievering, 1983; Katen and Hubbe, 1985; Sievering, 1987; Duan et al., 1988; Gallagher et al., 1993; Gallagher et al., 1997; Nemitz et al., 2002). The ASASP-x was placed at $z=1.3 \text{ m}$, drawing a sample at a rate of 3 ml s^{-1} through a short narrow bore copper tube from the downwind edge of the ultrasonic anemometer cage at a height of 2.65 m. Tests revealed that this setup had a 95% response time of $< 0.3 \text{ s}$, sufficient for eddy-covariance flux measurements even over short vegetation. The 32 size channels of the ASASP-x, covering the size range 0.1 to $3 \mu\text{m}$, were logged at 10 Hz on a data acquisition system developed at UMIST and stored on a computer together with the raw turbulence data (Gallagher et al., 1997). In this way a nearly continuous dataset covering 21 days was obtained.

The concentrations of NH_4^+ , NO_3^- , Cl^- and SO_4^{2-} were continuously monitored at two heights (0.64 and 3.44 m) using a Steam Jet Aerosol Collector (SJAC; ECN, Petten, NL)(Khlystov et al., 1995). Gases were stripped from an air stream of 30 l min^{-1} in a horizontal wet denuder. This denuder consists of two rotating concentric glass cylinders that form a 1.5 mm annulus. A suitable collection solution (NaHSO_4 for NH_4^+ and K_2CO_3 for the anions) is continuously pumped through the denuder using two independent peristaltic pumps: while the solution is pumped out of the denuder at a constant rate, the refilling pump is controlled by an optical measurement to maintain a constant liquid level in the denuder. Within the SJAC after the denuder, the airstream (free of soluble gases) is mixed with steam, allowing hygroscopic aerosol particles to grow to a size large enough to be impacted in a cyclone. At Elspeet two independent two-point gradient systems were used: in one setup the collection

Table 1. Summary of the aerosol measurements at Elspeet.

| Flux technique ^{a)} | Parameter (number of measurement heights) | Methodology | Averaging time | Manufacturer/ (method reference) |
|------------------------------|---|---|-------------------------|---|
| | Aerosol size spectra NH ₄ ⁺ , Na ⁺ , Mg ₂ ⁺ , K ⁺ , Ca ₂ ⁺ , SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻ | Berner low pressure cascade impactor | 12 h | Hauke GmbH, Gmunden, A |
| | aerosol number size spectra (0.01–15 μm) | scanning mobility particle sizer/aerodynamic particle sizer | 1 h | SMPS 3934 & APS 3210, TSI GmbH, Aachen, D |
| AGM | aerosol NH ₄ ⁺ , NO ₃ ⁻ , Cl ⁻ , SO ₄ ²⁻ (2) | Steam Jet Aerosol Collector (SJAC) | 30 min cycle (2 inlets) | (Khlystov et al., 1995) |
| AGM | NH ₄ ⁺ , SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻ (≤10) | filter-packs | 1–3 h | (Harrison and Kitto, 1990) |
| EC | aerosol number fluxes 0.1–3 μm (2) | optical particle counter | 20 min | ASASP-x, PMS, Boulder, Colorado, USA |

^{a)} AGM: aerodynamic gradient method; EC: eddy-covariance technique.

solution was analyzed for NH₄⁺ in a membrane conductivity cell (Khlystov et al., 1995), while in the second setup the cyclone was connected to an anion-chromatograph (IC), similar to the one described for the gas sampling system of Oms et al. (1996).

These aerosol measurements were complemented by filter-pack profile runs of a duration of 1 to 3 h using up to 10 filter-packs (Harrison and Kitto, 1990) and 12-h runs with a 6-stage Berner impactor (Hauke GmbH, Gmunden, Austria) for the size-resolved sampling of NH₄⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, NO₃⁻, Cl⁻ and SO₄²⁻. In addition, hourly values of the number particle distribution over the size range from 10 nm to 15 μm were continuously recorded using a combination of a Scanning Mobility Particle Sizer (SMPS 3934) and an Aerodynamic Particle Sizer (APS 3310, both TSI Instruments GmbH, Aachen, Germany). A list of the aerosol measurements carried out at Elspeet is shown in Table 1, while the measurements of gases and micrometeorological parameters have been summarized by Nemitz et al. (2004).

2.2 Micrometeorological theory

2.2.1 The eddy-covariance technique

Eddy-covariance particle number fluxes (F_N) were calculated from the fluctuations of the particle number concentrations (χ_N) of the ASASP-x and the vertical wind component (w) from the ultrasonic anemometer sampled at 10 Hz:

$$F_N = \overline{w'\chi'_N} = \overline{w\chi_N} - \overline{w}\overline{\chi_N}. \quad (5)$$

Data conditioning included (i) correction for time-lags, (ii) rotational corrections in two dimensions (Tanner and

Thurtell, 1969), (iii) linear detrending and (iv) windowing of the individual time-series. Fontan et al. (1997) presented a spectral analysis model to filter EC data for particle fluxes for low frequencies that may contaminate the flux. Power spectral and co-spectral densities, calculated using a Fast Fourier Transform (FFT) algorithm (Press et al., 1989), showed a considerable contribution of white noise in the high frequency range, which is a sign of poor counting statistics and an intrinsic problem of optical particle counters (OPCs) (Katen and Hubbe, 1985; Duan et al., 1988; Nemitz et al., 2002). Statistical noise is uncorrelated with w and does not affect the flux (Neumann and den Hartog, 1985), but it nevertheless results in high scatter of the (co-)spectral density function. Therefore the spectral analysis model by Fontan et al. (1997) proved to be unsuitable for the ASASP-x data. Nevertheless, the results of Lamaud et al. (1994) and Fontan et al. (1997) were adapted to filter out potential contamination of low frequencies: during two independent studies these authors found that frequencies below 0.01 Hz did not contribute to turbulent transport, but contaminated the measurements. Consequently, frequencies <0.01 Hz were omitted in the calculation of the fluxes.

To fulfil the counting requirements for statistically significant deposition velocities (Fairall, 1984), the 32 size channels had to be allocated to a smaller number of groups that were chosen to match the cut-off diameters of the cascade impactor stages (Table 2). Fluxes proved reliable for $D_p < 0.50 \mu\text{m}$, but small number concentrations led to poor counting statistics of larger particles.

Table 2. Grouping of the ASASP-x size classes in comparison with the cut-off diameters of the Berner cascade impactor. Group numbers in brackets represent size ranges, for which fluxes generally had to be discarded due to low number concentrations.

| Impactor stage no. | Diameter ($D_{p,50}$) [μm] | ASASP-x group number | ASASP-x size channels | ASASP-x diameter range covered D_p [μm] |
|--------------------|---|----------------------|-----------------------|--|
| 0 (base filter) | <0.25 | 1 | 1–2 | 0.10–0.12 |
| | | 2 | 3–5 | 0.13–0.15 |
| | | 3 | 6–8 | 0.15–0.18 |
| | | 4 | 9–11 | 0.18–0.24 |
| 1 | 0.25–0.5 | 5 | 12–17 | 0.24–0.50 |
| 2 | 0.5–1.0 | (6) | 18–22 | 0.50–1.0 |
| 3 | 1.0–2.0 | (7) | 23–27 | 1.0–2.0 |
| 4 | 2.0–4.0 | | | |
| 5 | 4.0–8.0 | | | |

2.2.2 The aerodynamic gradient method

Above a homogeneous surface the flux (F_χ) of an inert tracer (χ) is constant up to a height of roughly $1/100\times$ fetch (the upwind distance to the next surface inhomogeneity). Within this constant-flux layer the flux (F_χ) of a constituent (χ) may be derived from the averaged vertical concentration profile ($d\chi/dz$) (Monteith and Unsworth, 1990):

$$F_\chi = -K_H \left(\frac{z-d}{L} \right) \frac{d\chi}{dz}, \quad (6)$$

where K_H , the eddy-diffusivity for heat and inert tracers, is a function of the height (z) above the zero-plane displacement (d), which was 0.54 m for the heathland site, and the atmospheric stability, parameterized through the Monin-Obukhov length (L). The application of the aerodynamic gradient method (AGM), which is described in more detail in a companion paper (Nemitz et al., 2004), is particularly useful for chemical species for which fast response sensors are not available.

2.2.3 Deposition velocities

The rate at which a tracer is deposited to the surface may be expressed by the height-dependent deposition velocity ($V_d(z)$), which is the negative ratio of its flux (F_χ) and the concentration (χ) at height z . $V_d(z)$ may also be identified with the reciprocal total resistance for deposition (R_t):

$$V_d(z) = -\frac{F_\chi}{\chi(z)} = \frac{1}{R_t(z)}. \quad (7)$$

As discussed in more detail elsewhere (Nemitz et al., 2004), for gases R_t is composed of the aerodynamic resistance (R_a), the laminar boundary-layer resistance (R_b) as well as the canopy resistance (R_c), which itself may be composed of a network of parallel and serial resistances. R_a describes the turbulent transport between a height (z) and the mean height

of momentum exchange, the roughness length (z_0), and for gases R_b describes the diffusion through the quasi-laminar sub-layer. For a gas that is perfectly adsorbed by the canopy ($R_c=0$), the maximum deposition velocity (V_{\max}) is given by

$$V_{\max} = (R_a + R_b)^{-1}. \quad (8)$$

For particles the interaction with the canopy is complex (Peters and Eiden, 1992), and therefore the effect of the canopy is usually parameterized using the value of V_d at z_0 ($V_{ds}=V_d(z_0)$) rather than R_b and R_c . This may be calculated from V_d and R_a as:

$$V_{ds} = \left(V_d^{-1} - R_a(z-d) \right)^{-1}. \quad (9)$$

2.3 Time-scale analysis of gas-particle interactions

Whether equilibration is sufficiently fast to modify the vertical flux, depends on the Damköhler ratio (D_r) of diffusive time-scale (τ_d) to chemical time-scale (τ_c); gpic is often considered important for $D_r > 0.1$ (Foken et al., 1995). For neutral conditions, τ_d is given by Brost et al. (1988):

$$\tau_d = \frac{\kappa(z-d)}{1.75u_*} \quad (10)$$

where κ is the von Kármán constant (0.41) and u_* is the friction velocity. For a size-distributed aerosol τ_c may be estimated from measurements of the mass contained in discrete size bins (m_i) as (Wexler and Seinfeld, 1990, 1992):

$$\tau_c^{-1} = 3\bar{D} \sum_i \frac{m_i}{\left(1 + \frac{\lambda}{\alpha R_{p,i}}\right) R_{p,i}^2 \rho_{p,i}} \quad (11)$$

where \bar{D} is the geometric mean of the diffusivities of the relevant gases (e.g. NH_3 and HNO_3), λ is the mean free-path length in air ($0.065 \mu\text{m}$), α is the accommodation coefficient ($0.01 < \alpha < 1$) and $R_{p,i}$ and $\rho_{p,i}$ are radius and density of the particles in size range i . A critical value of u_* ($u_{*,\text{crit}}$) below

Table 3. Summary of the aerosol concentrations measured at Elspeet.

| chemical species (instrument) | μ_A [$\mu\text{g m}^{-3}$] | μ_A [$\mu\text{eq m}^{-3}$] | σ_A [$\mu\text{g m}^{-3}$] | μ_M [$\mu\text{g m}^{-3}$] | σ_G [$\mu\text{g m}^{-3}$] | χ_{\min} [$\mu\text{g m}^{-3}$] | χ_{\max} [$\mu\text{g m}^{-3}$] | coverage [days] | meas t [min] | N [#] |
|----------------------------------|-------------------------------------|--------------------------------------|--|-------------------------------------|--|---|---|--------------------|-------------------|------------|
| NH_4^+ -N (SJAC) | 3.08 | 0.22 | 2.83 | 2.22 | 2.58 | 0.00 | 14.73 | 22 | 30 | 700 |
| SO_4^{2-} -S (SJAC) | 1.55 | 0.097 | 1.42 | 1.11 | 0.75 | 0.21 | 9.63 | 22 | 30 | 227 |
| NO_3^- -N (SJAC) | 1.15 | 0.082 | 1.31 | 0.72 | 0.62 | 0.04 | 8.36 | 22 | 30 | 158 |
| Cl^- | 0.54 | 0.015 | 0.42 | 0.39 | 2.09 | 0.10 | 2.10 | 22 | 30 | 701 |

μ_A : arithmetic mean; σ_A : arithmetic standard deviation; μ_M : median; σ_G : geometric standard deviation; χ_{\min} , χ_{\max} : minimum and maximum concentration; meas. t : measurement time; N : number of observations.

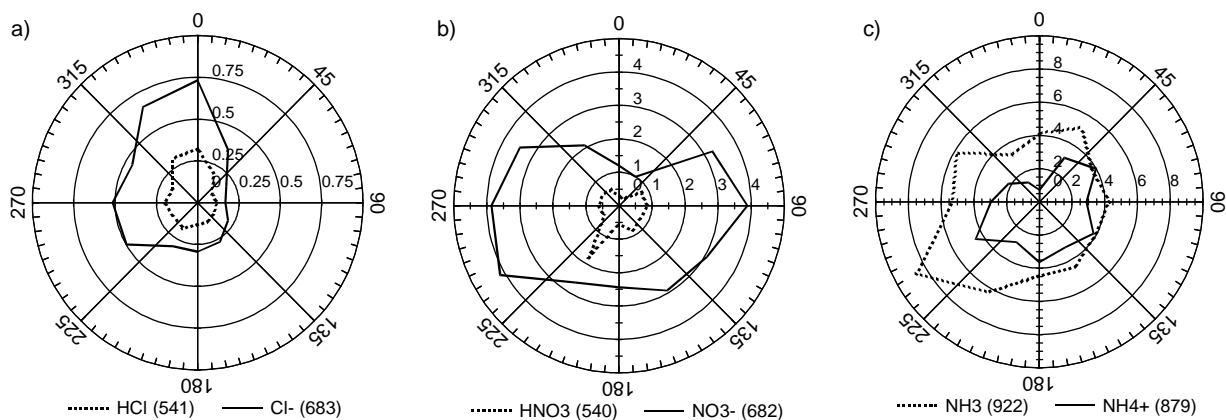


Fig. 1. Wind-sector dependencies of median concentration ($\mu\text{g m}^{-3}$ as Cl and N) of (a) HCl and Cl^- aerosol, (b) HNO_3 and NO_3^- aerosol, as well as (c) NH_3 and NH_4^+ measured at Elspeet, with the number of observation provided in parentheses.

which gpic may be expected to affect gradients can be calculated by solving the inequality $\tau_d > 0.1 \times \tau_c$ for u_* (Nemitz et al., 2000).

3 Results

3.1 Comparison of associated gas and aerosol concentrations

Statistics of the aerosol concentrations are summarized in Table 3. On an equivalent basis, NH_4^+ was on average balanced by the sum of SO_4^{2-} , NO_3^- and Cl^- , indicating that (a) other cations such as Na^+ were of secondary importance, (b) that the SO_4^{2-} was fully neutralized and (c) that NH_4NO_3 is ubiquitous in the Netherlands: on average, NH_4^+ was evenly distributed between SO_4^{2-} and NO_3^- .

The wind sector dependency of the concentration of selected associated gas and aerosol species, calculated for 30° wind sectors, is presented in Fig. 1. Each wind sector distribution represents between 500 and 1000 half-hourly data points. The various chemical species show distinct wind sector dependencies reflecting differences in their origin. A high similarity was found for the wind sector dependency of HCl and Cl^- concentrations (Fig. 1a). Both concentrations were

very low, showing elevated concentrations in the more maritime wind sectors W to N. The concentration of HNO_3 gas was much lower than of NO_3^- aerosol (Fig. 1b) and despite an otherwise high similarity, HNO_3 showed a peak in SSW, which also coincided with the maximum in the SO_2 concentration (not shown), while the distribution of SO_4^{2-} was similar to that of NO_3^- . NH_4^+ and NH_3 also showed very similar wind dependencies (Fig. 1c), but an elevated NH_3 concentration at WNW was not reflected in the NH_4^+ .

3.2 Eddy-covariance particle number flux measurements

Despite the poor counting statistics reflected in noisy power-spectra the diurnal cycles of the surface values of the particle deposition velocities (V_{ds}) of the five smallest size-classes (Table 2) show a clear structure. Two distinct patterns can be observed, which are exemplified in Fig. 2: on some days all size classes showed deposition throughout the day, and an increase of V_{ds} with particle size (Fig. 2a), which is in agreement with other measurements and model predictions for this size range ($D_p > 0.1 \mu\text{m}$) (Gallagher et al., 1997). Many days, however, included periods, during which smaller particles ($D_p < 0.18 \mu\text{m}$) showed some emission, while larger particles were continuously deposited. This emission was usually restricted to the afternoon ($\sim 13:00$ – $18:00$ GMT; see Fig. 6d),

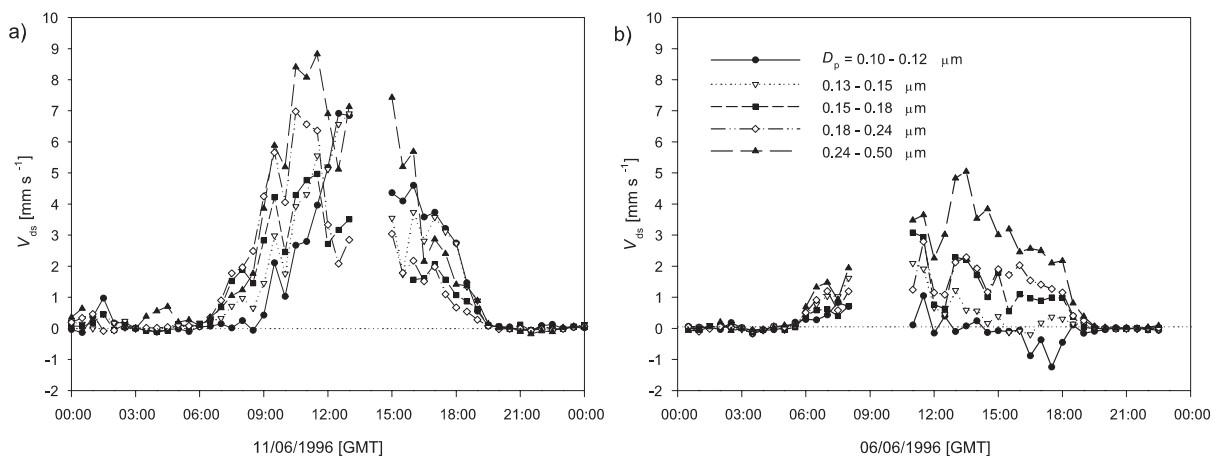


Fig. 2. Example daily courses of the deposition velocity of five size classes of particles as measured by eddy-covariance with the ASASP-x. In case (a) particles of all sizes are continuously deposited, at a rate that increases with particle size, whereas (b) on 6 June apparent emission of small particles was observed in the afternoon.

but occasionally it occurred for most of the day (Fig. 2b; see also Figs. 6d and 7d).

Typical values of V_{ds} at Elspeet ranged from 1 to 9 mm s^{-1} during the day and $<0.5 \text{ mm s}^{-1}$ at night. Parameterizations of V_{ds} are commonly normalized by u_* , and Fig. 3 shows the averaged plots of measured V_{ds}/u_* as a function of the stability parameter (L^{-1}). The data included in this figure were filtered for sufficient fetch ($>200 \text{ m}$), but not for statistical validity as described by Fairall (1984). Since counting requirements increase with decreasing V_{ds} , this filtering procedure tended to eliminate the small values of V_{ds} and biased the night-time average V_{ds} towards unrealistically large values. Since each data point in Fig. 3 already represents an average of at least twenty 20-min values, statistical variation due to poor counting statistics is largely eliminated. Following similarity theory considerations, Wesley et al. (1985) suggested a generic response curve of V_{ds}/u_* as a function of stability, the parameter of which were here chosen to provide a good fit to the measured values for $L^{-1} > -0.07 \text{ m}^{-1}$ (Fig. 3):

$$\frac{V_{ds}}{u_*} = \begin{cases} a_1 \left(1 + (-a_2 L^{-1})^{\frac{2}{3}} \right), & L \leq 0 \\ a_1, & L > 0 \end{cases} \quad (12)$$

with $a_1=0.001$; $a_2[\text{m}]=960D_p[\mu\text{m}]-88$

For highly unstable conditions ($L^{-1} < -0.07 \text{ m}^{-1}$), the measured curves of the three smallest size classes fall increasingly below the predicted lines, indicating frequent occurrence of apparent emission fluxes. For comparison, Wesley et al. (1985) derived parameters of $a_1=0.002$ and $a_2=300$.

3.3 Deposition velocities of NH_4^+

Values of $\chi_{\text{NH}_4^+}$ (1 m) and V_d (1 m) as derived from the gradients measured with the SJAC and filter-packs are presented

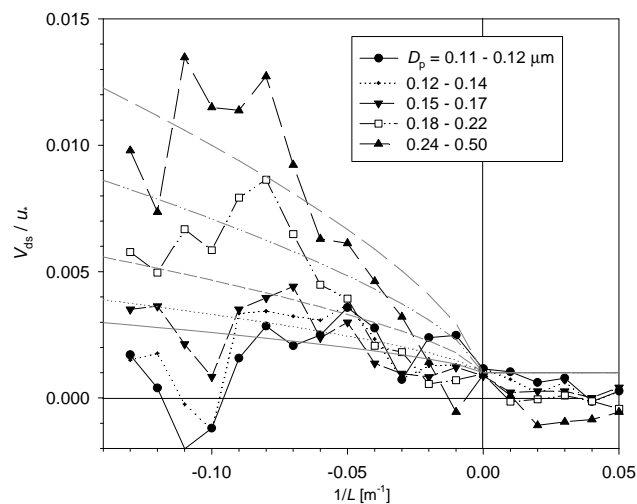


Fig. 3. Normalized values of the measured deposition velocity (V_{ds}/u_*) as a function of the stability parameter (L^{-1}) for five ranges of particle diameter (D_p). Theoretically predicted curves according to Eq. (12) are also shown (grey lines).

in Fig. 4. The SJAC detected somewhat higher concentrations than the filter-packs. This might be explained by the possibility for evaporation of collected NH_4^+ in the filter-packs. However, the filter pack NH_4^+ shows better agreement with the sum of SJAC SO_4^{2-} , NO_3^- and Cl^- than the SJAC NH_4^+ , suggesting that the SJAC overestimates NH_4^+ at times. This overestimate would be reflected in slightly overestimated fluxes, but it does not affect values of V_d .

The 30-min values of V_d derived from the SJAC gradients show considerable scatter, but the 3-h running mean reveals a consistent pattern with very small V_d during the night and values of 10 mm s^{-1} or above during the day. Bearing in mind that NH_4^+ evaporation from low-pressure

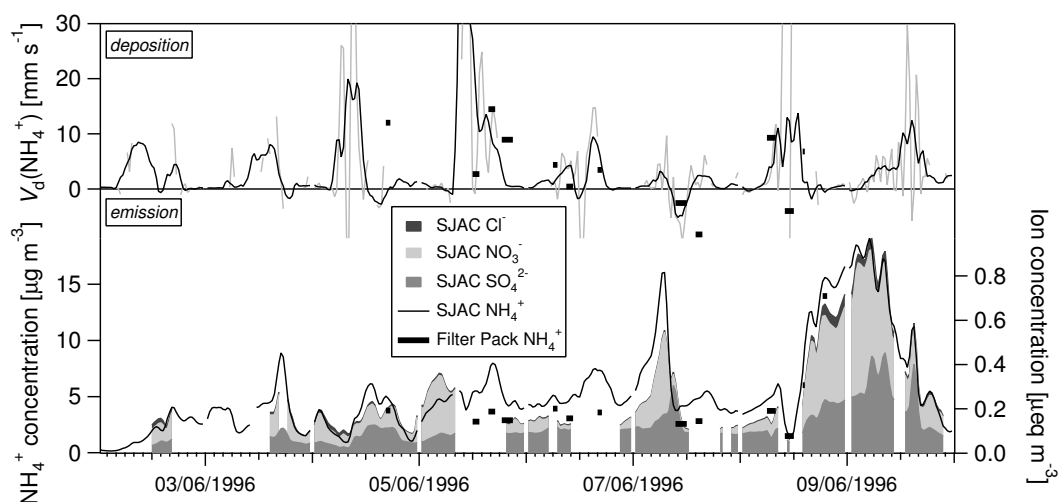


Fig. 4. Example time series of NH_4^+ concentrations and deposition velocities (V_d) derived by gradient method from the SJAC and filter-pack data. For the SJAC both 30-min measurement data (thin grey) and a 3-h running mean (bold black) are shown. Also shown are the equivalent concentrations of the main anions associated with NH_4^+ (SO_4^{2-} , NO_3^- and Cl^-).

Table 4. Chemical time-scales (τ_c) calculated for the Berner impactor runs from the mass distribution of the total hydrophilic aerosol. Also shown are critical values of u_{*c} , below which the effect of gpic on flux measurements is expected to become important.

| Run no. | Start date/time [GMT] | Duration [h] | $\alpha = 0.1$ | | $\alpha = 1$ | |
|---------|-----------------------|--------------|----------------|------------------------------------|----------------|------------------------------------|
| | | | τ_c [min] | $u_{*crit.}$ [m s^{-1}] | τ_c [min] | $u_{*crit.}$ [m s^{-1}] |
| 1 | 21.05.96 08:00 | 12:00 | 3.95 | 0.025 | 0.75 | 0.130 |
| 2 | 21.05.96 20:00 | 12:00 | 3.97 | 0.025 | 0.84 | 0.117 |
| 9 | 29.05.96 08:00 | 12:00 | 4.87 | 0.020 | 0.99 | 0.099 |
| 10 | 29.05.96 20:00 | 12:00 | 14.40 | 0.007 | 3.19 | 0.031 |
| 11 | 30.05.96 08:05 | 12:00 | 5.56 | 0.018 | 1.12 | 0.087 |
| 12 | 31.05.96 08:00 | 12:00 | 8.19 | 0.012 | 1.67 | 0.058 |
| 13 | 01.06.96 08:00 | 12:00 | 8.66 | 0.011 | 1.75 | 0.056 |
| 14 | 04.06.96 08:00 | 12:00 | 4.71 | 0.021 | 0.92 | 0.106 |
| 15 | 04.06.96 20:00 | 12:00 | 4.81 | 0.020 | 1.05 | 0.093 |
| 16 | 05.06.96 11:00 | 09:00 | 6.30 | 0.015 | 1.23 | 0.080 |
| 17 | 05.06.96 20:00 | 12:00 | 5.74 | 0.017 | 1.10 | 0.089 |
| 18 | 06.06.96 08:00 | 12:00 | 9.28 | 0.011 | 1.75 | 0.056 |
| 19 | 06.06.96 20:00 | 12:00 | 3.08 | 0.032 | 0.60 | 0.163 |
| 20 | 07.06.96 08:00 | 12:00 | 11.40 | 0.009 | 2.23 | 0.044 |
| 21 | 07.06.96 20:00 | 12:00 | 6.16 | 0.016 | 1.27 | 0.077 |
| 22 | 10.06.96 20:00 | 12:00 | 3.94 | 0.025 | 0.80 | 0.122 |
| 23 | 11.06.96 08:00 | 12:00 | 3.22 | 0.030 | 0.64 | 0.153 |

impactors can be considerable, the impactor measurements indicated that the bulk of the NH_4^+ was contained in particles of $D_p < 0.5 \mu\text{m}$, with an average mass median diameter (MMD) of about $0.29 \mu\text{m}$. The V_d of NH_4^+ should therefore be comparable to those derived from the EC measurements above. By contrast, on several days considerably larger V_d values were derived from the AGM than from the EC measurements.

3.4 Potential for chemical interactions

3.4.1 State of gas/aerosol phase equilibrium

By comparing the measured gas concentration products (K_m) $\text{NH}_3 \times \text{HNO}_3$ and $\text{NH}_3 \times \text{HCl}$ with the theoretical concentration products in equilibrium with the particle phase (K_e), it may be investigated whether air masses are in equilibrium, or whether there is potential for gtpc or potential for aerosol evaporation. At Elspeet, measurements of vertical concentration gradients of NH_3 , HNO_3 and HCl reported by Nemitz et al. (2004) enabled comparisons of K_m and K_e to be carried out at several heights, as discussed in detail by Nemitz (1998). These show that at the average measurement height of 1 m above the canopy, there was potential for aerosol evaporation for most of the time, except for some periods with $h > 85\%$. However, for NH_4NO_3 , concentration products extrapolated to a notional height of 50 m above the heathland vegetation were close to their equilibrium value. In addition, the deposition gradient of both NH_3 and HNO_3 together with an increase in temperature resulted in $K_m \ll K_e$ close to the surface, and therefore in strong potential for aerosol evaporation. For NH_4Cl , it was found that $K_m < K_e$ at all heights. Nemitz (1998) concluded that although both NH_4^+ and Cl^- were present, these were externally mixed, i.e. contained in different particles, and could therefore not evaporate jointly.

3.4.2 Chemical time-scales

To assess whether chemical conversion above the canopy would have been fast enough to affect gradient measurements of the NH_3 flux, chemical time-scales were estimated from the particle size spectra measured with both Berner impactor

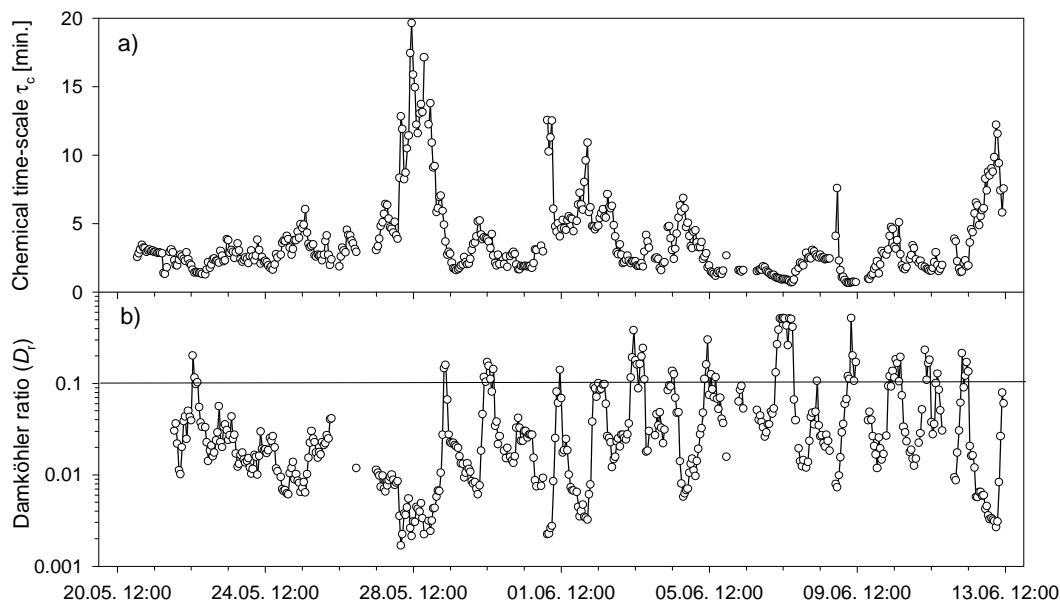


Fig. 5. (a) Chemical time-scales (τ_c) estimated from the SMPS/APS particle number size distribution, assuming the reaction to take part at the surface of half of the particles and $\alpha=1$. (b) Damköhler ratio (D_r) for a height of $z-d=3$ m. Chemical conversions may become important for $D_r > 0.1$ (e.g. Foken et al., 1995).

and the particle sizers (SMPS, APS) according to Eq. (11). Table 4 shows the values calculated for $z-d=3$ m from the total aerosol mass detected by the impactor for two plausible values of the sticking coefficient (α).

For $\alpha=1$ the critical value of u_* , below which the effect of gpic on surface exchange fluxes becomes significant (u_{*crit}), often approached or exceeded 0.1 m s^{-1} , and chemical conversions may therefore have been important. Figure 5 shows the Damköhler ratio (D_r) of turbulent transport time-scale to chemical time-scale for $z-d=3$ m, calculated from the size distribution of the total particle number as measured with the SMPS and APS systems, assuming that 50% of the particles contained NH_4NO_3 . This arbitrary particle fraction was assumed to contain NH_4^+ and to be available for the heterogeneous reaction (Wexler and Seinfeld, 1990). During the first part of the campaign D_r was small, due to high wind speeds and low aerosol loadings. Values of D_r larger than a critical value of 0.1 were observed during daytime later on in the campaign, and here this time-scale analysis predicts that chemical conversions may have altered the flux.

3.4.3 Temporal correlation between surface exchange fluxes of NH_3 , acids and aerosols

The surface/atmosphere exchange of the individual chemical species depends on too many factors (meteorological conditions, air mass, plant physiological parameters, aerosol compositions) for interactions between the phase (disequilibrium and surface fluxes to show up in statistical bulk analyses. Indication for chemical interactions may nevertheless be seen

in the temporal correlation of several unexpected measurement features on individual days. This section draws together results of the gas flux measurements (Nemitz et al., 2004), the comparison of measured vapour phase concentration products with their theoretical equilibrium values (Nemitz, 1998) and the here presented aerosol flux measurements.

In Fig. 6 the diurnal cycles of the NH_3 flux and V_d of HNO_3 , HCl and NH_4^+ as derived by the aerodynamic gradient method (AGM) are shown together with the size-resolved particle V_{ds} by EC. Between 07:00 and 08:00 GMT two changes occur: i) the NH_3 flux estimated with AGM switched from deposition to emission and ii) V_d of HCl and HNO_3 deviated increasingly from V_{max} (Fig. 6b).

An alternative estimate of $V_{ds}(\text{NH}_4^+)$ may be obtained by combining the long-term average of the NH_4^+ size distribution derived from the cascade impactor with the size-dependent particle deposition velocity derived by EC (e.g. Gallagher et al., 1993). In the afternoon $V_{ds}(\text{NH}_4^+)$ derived by AGM from the SJAC gradient showed positive divergence from this value (Fig. 6b), and at the same time the EC V_{ds} of small particles ($D_p < 0.18 \mu\text{m}$) was reduced, while emission of the two smallest size classes was found after 14:00 GMT.

Figure 7 shows a second example of the correlation between periods of a high $R_c(\text{NH}_3)$ or NH_3 emission derived by the gradient technique, fast NH_4^+ deposition by AGM and apparent particle emission of small particles by EC. Whereas NH_3 was found to deposit at V_{max} during night within the accuracy of the measurements (Fig. 7b), V_d was much smaller than V_{max} during daytime, and the measurements indicate

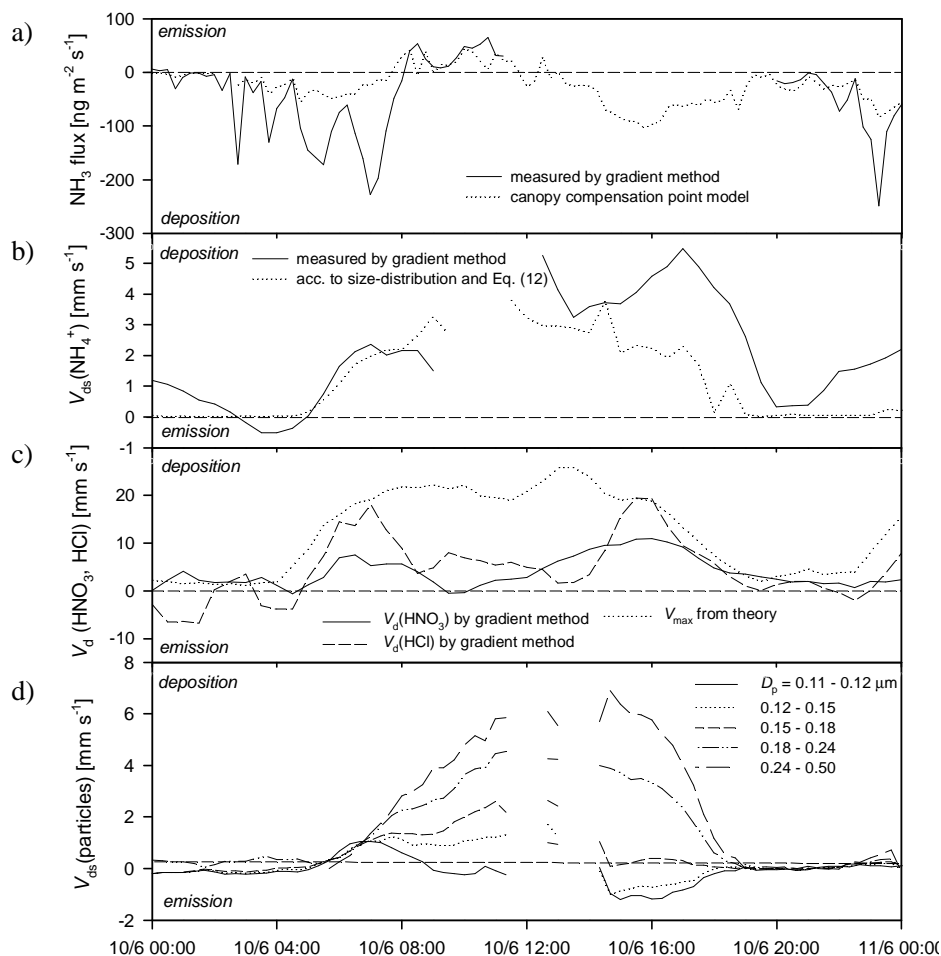


Fig. 6. Time series obtained at Elspeat on 10 June 1996. **(a)** NH_3 fluxes as measured and predicted by the canopy compensation point model (Nemitz et al., 2004). **(b)** HNO_3 and HCl deposition velocity (V_d) in comparison with their maximum value (V_{max}). **(c)** $V_{d_s}(\text{NH}_4^+)$ in comparison with the value according to the NH_4^+ size-distribution and parameterization of Eq. (12), all derived by gradient method. **(d)** Size-dependent particle V_{d_s} as obtained by EC with the ASASP-x.

NH_3 emission from 08:00–13:00 GMT (Fig. 7a). During the same period, high NH_4^+ V_{d_s} by AGM (Fig. 7c) and substantial emission of particles up to a size of $0.18 \mu\text{m}$ by EC were observed (Fig. 7d).

On first sight the high values of $V_{d_s}(\text{NH}_4^+)$ by AGM seem to be in contradiction to the observation of reduced V_{d_s} and even emission of small particles by EC. Each of these observations can be used to infer a first-order correction for the NH_3 flux:

1. From the combination of the SJAC NH_4^+ concentrations, the average size-distribution from the impactor and $V_{d_s}(D_p)$ according to Eq. (12), an “expected” NH_4^+ surface exchange flux and $V_{d_s}(\text{NH}_4^+)$ can be derived (Figs. 6b and 7c). This may be compared with the measured NH_4^+ flux to estimate the amount of NH_4^+ , which would have had to evaporate and contribute to the NH_3 flux at the measurement height. Application of this cor-

rection predicts larger NH_3 deposition (or reduced NH_3 emission) at the surface that at the measurement height.

2. A second correction may be estimated from comparison of measured size-dependent particle number V_{d_s} by EC and Eq. (12). From the particle volume and the density of NH_4NO_3 , the difference in the number fluxes may be related to a difference in the NH_4^+ flux, which can subsequently be converted into the additional NH_3 emission, necessary to evoke the slow particle deposition or emission observed by EC. This correction leads to increased NH_3 emission (or reduced NH_3 deposition) at the surface compared with the measurements.

Naturally, these two “corrections” have opposite effects on the NH_3 flux as exemplified in Fig. 7a. However, size-dependent modelling of the effect of gpic on EC measurements of aerosol fluxes (Nemitz and Sutton, 2004) revealed that, contrary to intuition, apparent emission of small

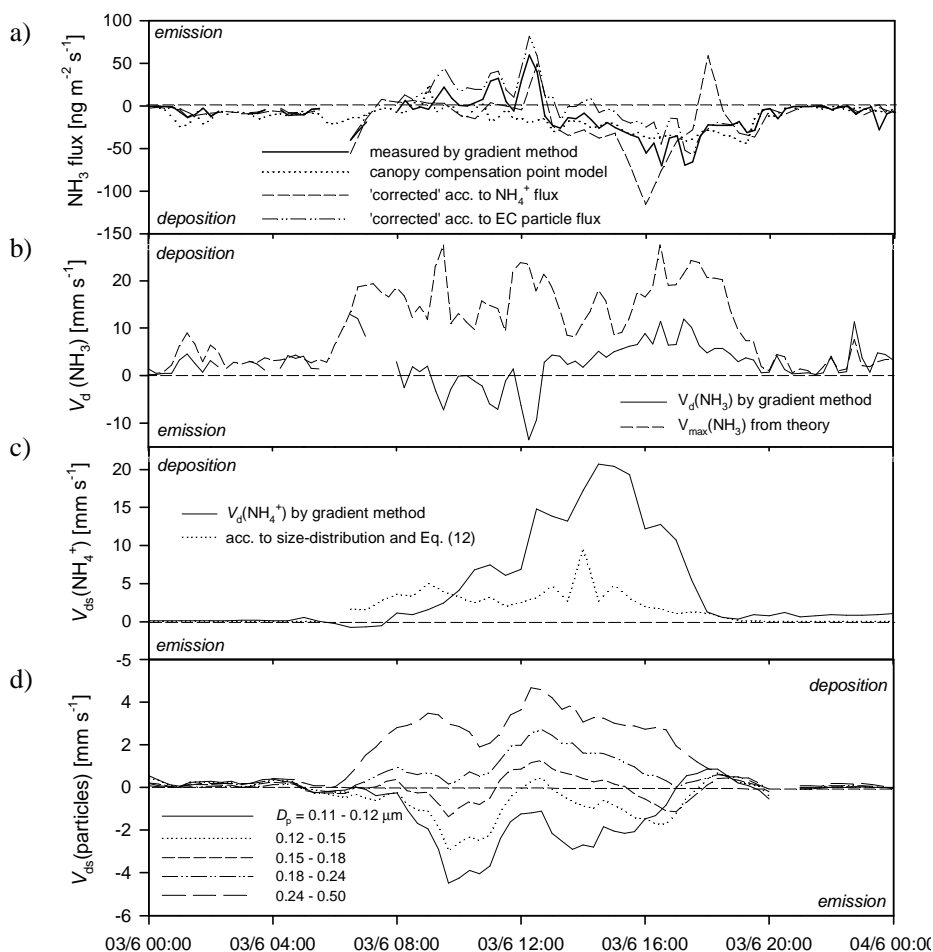


Fig. 7. Time series obtained at Elspeet on 3 June 1996. **(a)** NH₃ flux as measured and modelled by the canopy compensation point model (Nemitz et al., 2004). **(b)** NH₃ deposition velocity (V_d) compared with V_{max} . **(c)** $V_{ds}(\text{NH}_4^+)$ obtained with the SJAC, all by gradient method. **(d)** Particle deposition velocities as obtained by EC with the ASASP-x. Also shown in (a) are the fluxes of NH₃ which would be necessary to produce i) the fast apparent NH₄⁺ deposition (dashed line) and ii) the observed particle number emission of small particles (dashed-dotted line).

particles of certain sizes may also result from aerosol evaporation. Particles that evaporate during deposition contribute to a larger number concentration of particles of a smaller size class close to the surface, leading to apparent emission gradients in this smaller size class. This reconciles the anomalous EC measurements and the over-fast NH₄⁺ deposition. Thus the first “correction” is likely to be more appropriate, and at daytime the uncorrected gradient measurements overestimate the NH₃ emission flux (or underestimated the deposition flux) by about 20 ng m⁻² s⁻¹ (or on average 28%). This is also supported by the fact that for this day a canopy compensation point resistance model predicts smaller emission (larger deposition) than indicated by the uncorrected gradient measurements (Fig. 7a)(Nemitz et al., 2004).

4 Discussion

4.1 Gas-aerosol conversions during advection

At Elspeetsche Veld the wind sector dependency of the median HCl concentration followed that of Cl⁻ aerosol very closely (Fig. 1a), and the impactor measurements showed that at maritime wind directions, the coarse mode NO₃⁻ can be as large as the Cl⁻ equivalent concentration (not shown). Both observations indicate that, by the time the maritime air reached the site, a considerable fraction of the sea salt chloride had been substituted by NO₃⁻, and that this process presented the main HCl source at this site. The correlations between HNO₃ and NO₃⁻ as well as NH₃ and NH₄⁺ emphasize the role of HNO₃ and NH₃ as precursor gases of NH₄NO₃ aerosol (Fig. 1b and c). Whereas both NH₃ and NH₄⁺ show the highest concentrations in the SW, where several farms are located at a distance of at least 5 km, the closest farm

Table 5. Summary of average aerosol dry deposition fluxes to the heathland at Elspeet during the 3-week measurement period in comparison with gaseous ammonia and nitric acid (Nemitz et al., 2004). Values in parenthesis are % of the total measured dry N input (sum of $\text{NH}_3 + \text{HNO}_3 + \text{NH}_4^+ + \text{NO}_3^-$). Daytime is defined according to non-zero solar radiation as 05:00 to 20:00 GMT.

| Species | Average | | Daytime | | Nighttime | |
|-----------------------------|-----------------------------------|-------------------------------------|-----------------------------------|-------------------------------------|-----------------------------------|-------------------------------------|
| | $\text{ng m}^{-2} \text{ s}^{-1}$ | $\text{kg ha}^{-1} \text{ yr}^{-1}$ | $\text{Ng m}^{-2} \text{ s}^{-1}$ | $\text{kg ha}^{-1} \text{ yr}^{-1}$ | $\text{ng m}^{-2} \text{ s}^{-1}$ | $\text{kg ha}^{-1} \text{ yr}^{-1}$ |
| $\text{NH}_3\text{-N}$ | 43 (75) | 14 | 41 (66) | 13 | 45 (90) | 14 |
| $\text{HNO}_3\text{-N}$ | 3.2 (6) | 1.0 | 5.5 (9) | 1.7 | 0.77 (2) | 0.24 |
| $\text{NH}_4^+\text{-N}$ | 8.6 (15) | 2.7 | 12 (19) | 3.9 | 3.1 (6) | 0.97 |
| $\text{NO}_3^-\text{-N}$ | 2.3 (4) | 0.74 | 3.9 (6) | 1.2 | 0.91 (2) | 0.29 |
| $\text{SO}_4^{2-}\text{-S}$ | 9.1 | 2.9 | 15 | 4.9 | 3.3 | 1.0 |

(1.5 km) in the NW may have contributed to the NH_3 , but not significantly to the NH_4^+ concentration (Fig. 1c). The transport time was possibly too fast for gas-particle-conversion to be effective. The concentration of HNO_3 showed a peak in the SW, where the SO_2 concentration was also largest (not shown). This correlation suggests photochemical production of HNO_3 from NO_x , which, like SO_2 , originates from industrial and combustion sources.

4.2 Biosphere-atmosphere exchange of aerosols

4.2.1 Measured apparent particle deposition velocities

Counting statistics were too poor for a rigorous spectral analysis of the aerosol (co-) spectra to be carried out, but nevertheless the particle number fluxes measured by EC with the ASASP-x OPC show regular patterns. Deposition velocities for fine particles ($0.1 \mu\text{m} < D_p < 0.5 \mu\text{m}$) range from $< 0.5 \text{ mm s}^{-1}$ at night to nearly 10 mm s^{-1} during daytime, and on various days V_{ds} increased with particle size within the measured size range (Figs. 2a, 6d). The magnitude of V_{ds} is larger than derived from theoretical considerations (e.g. Slinn, 1982), wind tunnel studies (e.g. Chamberlain, 1966) and also somewhat larger than recent micrometeorological measurements of deposition velocities to short vegetation. For the size range considered here, Nemitz et al. (2002) derived maximum daytime deposition velocities of 2 to 2.5 mm s^{-1} to Scottish moorland vegetation, with an overall average $< 1 \text{ mm s}^{-1}$. Gallagher et al. (2002) reported an average V_{ds} of 1.1 and 0.9 mm s^{-1} to tall and short grass, respectively ($0.1 < D_p < 0.2 \mu\text{m}$), while for $0.52 \mu\text{m}$ particles, Vong et al. (2004) derived average deposition velocities of 3, 2 and 5 mm s^{-1} during neutral, stable and unstable conditions, respectively. It is possible that the morphology of heather is comparably efficient in collecting aerosols, but the somewhat large average V_d found at Elspeet were probably a consequence of the strong increase in V_d during unstable conditions, which often occurred during the warm measurement period. This increase is qualitatively consistent with former observations (Wesely et al., 1985; Vong et al., 2004).

Interestingly, in neutral conditions ($1/L=0$ in Fig. 3), V_d appeared to be insensitive to particle diameter over the size-range of the measurements.

At Elspeet, during some daytime periods, especially in the afternoon, apparent particle emission was observed at the measurement height for the smallest size classes ($D_p < 0.18 \mu\text{m}$), while larger particles were continuously deposited (Figs. 2b, 6d, 7d). As a result V_{ds} normalized by u_* (Fig. 3) shows significant negative divergence from the expected functional relationship on the stability parameter for $L^{-1} < -0.07 \text{ m}^{-1}$ ($-14 \text{ m} < L < 0 \text{ m}$). Apparent emission fluxes therefore coincided with unstable conditions, which are mainly found during warm daytime periods. However, a parameterization of the form suggested by Wesley et al. (1985) may still be estimated from periods during which mostly deposition was observed (Eq. 12).

The deposition velocities of NH_4^+ as inferred from the SJAC gradient measurements (Fig. 4) show similarly small values at night, but large values in excess of 10 mm s^{-1} during some daytime conditions. These appear to be inconsistent with the small size of NH_4^+ aerosol and the V_d simultaneously derived from the EC measurements. The average deposition velocity of 2.0 mm s^{-1} (daytime: 2.7; nighttime: 0.8 mm s^{-1}) agrees well with the value of 1.8 mm s^{-1} previously observed for NH_4^+ deposition above heathland (Duyzer, 1994). By contrast, much larger NH_4^+ deposition velocities have been found over forest, with averages ranging from 11 to 23 mm s^{-1} (Wyers and Duyzer, 1997; Rattray and Sievering, 2001).

4.2.2 Dry deposition inputs

Dry deposition estimates for the measurement period of N and S are summarized in Table 5, based on the assumption that the deposition rate of the anions equals that of NH_4^+ . Without the contribution of NO_2 and PAN, the total N dry deposition measured during this period would be equivalent to a yearly total of $18.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, with a contribution of NH_4^+ and NO_3^- aerosol of 19% overall and of 25% during the day. Nitric acid, the concentration of which (as N) was 6.6%

of the $\text{NH}_3\text{-N}$ concentration at this site (cf. Fig. 1), makes only a minor (6%) contribution to the overall dry deposition. This is in contrast to sites with a less alkaline pollution climate, where HNO_3 may dominate N dry deposition (e.g. Ratnayake and Sievering, 2001). These dry deposition values may be compared with former bulk deposition measurements, which derived additional annual deposition of $11.8 \text{ kg NH}_4^+\text{-N ha}^{-1} \text{ yr}^{-1}$ and $5.3 \text{ kg NO}_3^-\text{-N ha}^{-1} \text{ yr}^{-1}$ (Erisman et al., 1994). Thus, NH_x deposition is dominated by NH_3 dry deposition, while the NO_3^- deposition is dominated by wet deposition.

4.2.3 Apparent particle emission – a measurement artefact?

Flux measurements derived from parameters that change with T and h need to be corrected for sensible and latent heat fluxes (Webb et al., 1980). Such a parameter is the particle radius, which is determined by water uptake in equilibrium with ambient humidity (Fairall, 1984; Kowalski, 2001). Unlike some other optical particle counters, the ASASP-x is thought to dry out the particles and thus measures the dry particle size, which is a conserved parameter (Gallagher et al., 1997).

Sample inlet imperfections are a common error source for particle sampling, especially for super-micron and nanometre particles, but it is unlikely that they should systematically affect measurements at certain times of the day. Finally, electrophoretic effects are also an unlikely cause: apparent particle emission was observed during cloudless skies, when the magnetic potential of the atmosphere is small. Fontan et al. (1997) attributed observations of particle emission to low-frequency contamination of the power-spectra and found that any emission events were removed by high-pass filtering. As mentioned before, poor sampling statistics hampered a general spectral analysis. However, high-pass filtering as recommended by Fontan et al. was applied and had very little effect on the particle fluxes. The aerosol sampler by Fontan et al. measured the flux of the bulk aerosol with a size mainly between 0.05 and $0.5 \mu\text{m}$, and therefore apparent emission (or growth) of the particles in a certain size-class might have been masked by the deposition of others. The observation of negative particle deposition velocities by the ASASP-x EC measurements is therefore almost certainly not the result of a physical measurement artefact.

4.3 The effect of gas-to-particle conversion on flux measurements at Elspeet

Semi-natural surfaces have been shown to occasionally emit NH_3 and provide a non-zero surface uptake resistance for HNO_3/HCl (e.g. Huebert et al., 1988; Erisman and Wyers, 1993; Neftel et al., 1996; Sutton et al., 1998; Nemitz et al., 2000). In general, however, concentrations, and therefore K_m decline towards the ground, while K_e is increased above warm vegetation. As a result, the ratio K_m/K_e is greatly low-

ered near the ground, as observed at Elspeet. In the presence of NH_4NO_3 and NH_4Cl , aerosol evaporation leads to the observation of apparent fast deposition of NH_4^+ , NO_3^- and Cl^- , apparent slow deposition or even emission of HNO_3 and HCl , as well as an underestimation of the NH_3 surface deposition by aerodynamic gradient methods. Moreover, the modelling of the height-dependent size-distribution of NH_4NO_3 aerosol as modified by the $\text{HNO}_3\text{-NH}_3\text{-NH}_4\text{NO}_3$ equilibrium by Nemitz and Sutton (2004) demonstrates that bi-directional particle number fluxes may result from this interaction, with small particles (typically $D_p < 0.15\text{--}0.2 \mu\text{m}$) showing apparent emission. This is conditional on two factors: the measurements must be carried out below the theoretical height at which equilibrium would be attained and NH_4^+ must be contained in a large fraction of the particles. The absolute error of NH_4^+ evaporation on the fluxes depends on the chemical time-scale, governed by the aerosol concentration, and the absolute divergence from equilibrium. By contrast, the relative effect is dominated by the magnitude of the fluxes and is usually larger for slowly depositing NH_4^+ aerosol than for acid gases and NH_3 , which are usually exchanged at a higher rate.

Three existing datasets, two of which were obtained above semi-natural vegetation in the Netherlands, provide evidence that NH_4^+ evaporation can indeed have a significant effect on surface exchange fluxes, and also allow the effect to be quantified:

1. *Boulder Atmospheric Observatory, Colorado*. From gradient measurements carried out in the vicinity of local NH_3 sources, Huebert et al. (1988) derived higher values of V_d for NO_3^- than they found for SO_4^{2-} aerosol and sometimes even than for HNO_3 , which occasionally showed apparent emission gradients. Brost et al. (1988) qualitatively modelled the phenomena and concluded that NH_4NO_3 evaporation was a likely explanation for the anomalies.
2. *Dutch heathland “Leende Heide”*. At Leende Heide bi-directional aerosol fluxes were found to be related to the observation of NH_3 emission (Gallagher et al., 1993), while Zhang et al. (1995) observed apparent HNO_3 emission. These authors derived a first order correction for the NH_3 flux of about $50\text{--}200 \text{ ng m}^{-2} \text{ s}^{-1}$ at daytime, which often represented about 5–20% of the flux, but even caused flux reversal when the NH_3 flux was small. However, this correction was based on the assumption that at the surface HNO_3 deposits at V_{max} , and may be an overestimate (cf. Nemitz et al., 2004).
3. *Dutch forest “Speulderbos”*. Wyers and Duyzer (1997) observed NO_3^- deposition fluxes faster than permitted by turbulence ($V_d > R_a^{-1}$) to the coniferous forest “Speulderbos”, NL, while SO_4^{2-} showed smaller gradients. Single runs of this dataset were assessed using a numerical model, and the modified concentration

gradients showed a better fit to the measurements than log-linear profiles (Van Oss et al., 1998). In the light of the new investigations into the effect of NH_4^+ evaporation on size-segregated particle number fluxes presented by Nemitz and Sutton (2004), these results are also consistent with the simultaneous observation of apparent emission of small particles ($0.10 < D_p < 0.18 \mu\text{m}$) reported by Gallagher et al. (1997). Unfortunately, gradients of HNO_3 and HCl were not measured at Speulderbos. The modelling by van Oss et al. (1998) indicated differences between fluxes of NH_3 derived under the constant flux assumption and “corrected” for chemical reactions of 20 to $250 \text{ ng m}^{-2} \text{ s}^{-1}$. These authors pointed out that the NH_3 emissions occasionally observed at Speulderbos (Duyzer et al., 1992; Wyers and Erisman, 1998) may partly have been an artefact caused by this NH_4^+ evaporation. If all NH_3 emission were due to this effect the overestimation of the flux would frequently have to be as high as $100 \text{ ng m}^{-2} \text{ s}^{-1}$. It should be noted, however, that both cuticular desorption and stomatal emission are likely to account for some of the observed NH_3 emission (Wyers and Erisman, 1998).

4.3.1 Strong evidence for NH_4^+ evaporation at Elspeet

At Elspeet four independent observations suggest that during the day volatile NH_4^+ salts evaporated and modified the gradients of gaseous NH_3 , HNO_3 and HCl as well as NH_4^+ aerosol, and this study therefore provides more conclusive evidence than previous measurements:

1. For HNO_3 and HCl , V_d derived by the gradient method was significantly smaller than V_{max} (Figs. 6 and 7), which is in agreement with the release of these acidic gases from aerosol near the surface (Nemitz et al., 2004).
2. Large apparent values of V_d were inferred from NH_4^+ gradients during some periods, as it would have been the case if NH_4^+ had evaporated during deposition (Figs. 4, 6b and 7c).
3. K_m was usually smaller than $K_{e,\text{pure}}$ providing potential for aerosol volatilization. The extrapolation of gradients of the gas concentrations as well as T and h to a notional height of 50 m indicates that concentrations well above the surface were more likely to be in thermodynamic equilibrium than near the ground. Although the correct value of K_e is uncertain, this indicates that the deposition process led to $K_m \ll K_e$ near the surface (Nemitz, 1998).
4. The EC flux measurements of small particles ($D_p < 0.18 \mu\text{m}$) cover periods of reduced V_{ds} or even apparent emission. Intuitively this observation may be attributed to condensation and particle growth.

The modelling exercise of Nemitz and Sutton (2004) shows that, if $K_m < K_e$ near the surface, particle evaporation may lead to an increased number of small particles at lower heights and apparent emission fluxes, although all particles are physically deposited. Together with (3) the observation of bi-directional size-dependent particle fluxes is therefore consistent with NH_4^+ evaporation.

The above phenomena were temporally correlated as demonstrated in Figs. 6 and 7 and this provides additional evidence that the anomalies in the flux measurements at Elspeet were caused by NH_4^+ evaporation. The modification of surface exchange fluxes by NH_4^+ evaporation is consistent with the time-scale analysis (Table 4 and Fig. 5). Chemical time-scales estimated from the aerosol surface area are mainly in the range of 1 – 8 min and therefore in general shorter than found at a clean Scottish site (Nemitz et al., 2000), but comparable with the values reported for sites in Eastern Germany (Kins et al., 1996; Seidl et al., 1996). As a result, at Elspeet gpic was often expected to be sufficiently fast to cause significant flux divergence for $u_* < 0.12 \text{ m s}^{-1}$, a situation which arose frequently between 29 May and 12 June 1996. As pointed out by Nemitz et al. (2000), this kind of analysis only compares the chemical time-scale with the turbulent diffusive time-scale above the canopy, while diffusive transport within the canopy is much slower providing ample time for chemical conversion to occur.

4.3.2 Magnitude of the effect of gpic on flux measurements and the atmospheric lifetime of reduced nitrogen

A first-order correction of the NH_3 flux may be obtained from the comparison of the NH_4^+ flux derived from gradient measurements with expected values (Fig. 7a). During some warm daytime periods the aerodynamic gradient technique underestimates the NH_3 deposition flux by as much as $20 \text{ ng m}^{-2} \text{ s}^{-1}$ ($16 \text{ ng N m}^{-2} \text{ s}^{-1}$). Considering the average daytime NH_3 -N flux of $41 \text{ ng N m}^{-2} \text{ s}^{-1}$ this is a considerable effect on the NH_3 flux, but it constitutes an even larger relative error for the fluxes of NH_4^+ and HNO_3 . This error estimate is in general agreement with the modelling, which, for an example day with high HNO_3 concentrations, indicates average errors of 28% and 8.5% for the fluxes of NH_3 and HNO_3 , respectively. By contrast, Zhang et al. (1995) derived corrections of up to $100 \text{ ng m}^{-2} \text{ s}^{-1}$ from upward gradients of HNO_3 , which they also attributed to NH_4NO_3 evaporation. Consequently, surface exchange fluxes of NH_3 , but also of NH_4^+ and the acids, measured under these conditions, need to be calculated using modified gradient-techniques, which account for the chemical conversions (Brost et al., 1988; Kramm and Dlugi, 1994; Nemitz et al., 1996; Van Oss et al., 1998; Nemitz and Sutton, 2004). Given the current uncertainties in K_e and the chemical time-scale (or sticking

coefficient), this cannot yet be done on a systematic basis and here more investigations are urgently needed.

The flux modification through gpic would propagate to the parameterisations derived from the uncorrected NH_3 fluxes (Nemitz et al., 2004). In particular, evaporation of volatile NH_4^+ salts, either airborne and on leaf surfaces, may provide a second NH_3 emission source in addition to stomatal emission or inhibit deposition to the canopy. This would result in an overestimation of the non-dimensional stomatal compensation point (Γ) during daytime and of the cuticular resistance (R_w) during night.

This study demonstrates that size-segregated particle flux measurements are modified, not only by water vapour fluxes (Kowalski, 2001), but also by condensational particle growth and aerosol evaporation. Both effects need to be considered when interpreting measurement derived estimates of $V_d(D_p)$, especially for fine particles. Areas with high concentrations of volatile aerosol components or strong emissions of biogenic aerosol precursor gases should be avoided for studies deriving deposition velocities from eddy-covariance measurements. By contrast, flux measurements provide a powerful tool for estimating particle growth or evaporation rates within the uncertainties of the flux measurements themselves.

It should be noted that most of the effects of NH_4NO_3 evaporation are not always observed at Elspeet, but are confined to warm and dry conditions. Although the error of aerosol evaporation on the HNO_3 flux is substantial, it is therefore not sufficient to explain the divergence of V_d from V_{max} on all days in full. Here an additional surface uptake resistance, caused by a non-zero vapour pressure above deposited salts on leaf surfaces, could provide a further explanation. Aerosol evaporation may also have contributed to the very large NH_3 emission fluxes of up to $550 \text{ ng m}^{-2} \text{ s}^{-1}$, which had been previously observed at Elspeet (Erisman and Wyers, 1993; Sutton et al., 1995), but not repeated during the campaign presented (Nemitz et al., 2004).

The measurements presented here suggest evaporation rates of about $10\text{--}100 \mu\text{g NH}_4\text{NO}_3 \text{ m}^{-3} \text{ h}^{-1}$ in the surface layer. Assuming (i) a typical daytime boundary layer height of 1000 m, (ii) chemical conversions to be confined to the lowest 50 m and (iii) an average NH_4NO_3 concentration of $5 \mu\text{g m}^{-3}$, this conversion rate equates to an average removal rate of 3×10^{-6} to $3 \times 10^{-5} \text{ s}^{-1}$ for the boundary layer (or an atmospheric residence time of 9 to 90 h), somewhat lower than the values of $1 \times 10^{-4} \text{ s}^{-1}$ and $4 \times 10^{-5} \text{ s}^{-1}$ proposed by Erisman et al. (1988) for day and night-time conditions, respectively. For comparison, atmospheric life-times due to removal by dry deposition (τ_{V_d}) may be approximated by the ratio of boundary-layer height and V_d (Moeller and Schieferdecker, 1985; Sutton, 1990). Typical daytime values of τ_{V_d} at Elspeet would be 100 h for NH_4^+ and 15 h for NH_3 . Therefore the evaporation of volatile NH_4^+ over semi-natural surfaces will significantly reduce its overall lifetime in the tropo-

sphere, as well as lower the lifetime of total NH_x by increasing the fraction which can be dry deposited as NH_3 . Flechard and Fowler (1998) suggested that the effective mixing height for NH_3 may be reduced compared with the boundary-layer height as NH_3 is derived from surface sources and decreases away from the surface. This effect would reduce the absolute values but not the ratio of the residence times.

From the relatively short chemical lifetime of volatile NH_4^+ above warm semi-natural vegetation, it is likely that after long travel in dry remote locations NH_4^+ aerosol will be transported mainly as $(\text{NH}_4)_2\text{SO}_4$, while a large fraction of the NO_3^- will eventually be present as NaNO_3 . Thus the transport distance of NH_4^+ should be sensitive and positively correlated to SO_4^{2-} concentrations, while the transport distance of NO_3^- should be larger in humid maritime climates.

5 Conclusions

Aerosol number flux measurements of fine particles ($0.1 < D_p < 0.5 \mu\text{m}$) by eddy-covariance (EC) showed surface deposition velocities (V_{ds}) of $< 0.5 \text{ mm s}^{-1}$ during night, but values of up to 10 mm s^{-1} during the day, faster than those found during other recent studies over short vegetation, probably due to the observed strong increase in unstable conditions. A V_{ds} parameterization is presented for these particles as a function of particle size, turbulence and atmospheric stability. Average values of $V_{ds}(\text{NH}_4^+)$ derived by a gradient technique (overall 2.0 mm s^{-1} ; daytime: 2.7; night-time 0.8 mm s^{-1}) are similar to previous measurements. Using the uncorrected fluxes, NH_4^+ and NO_3^- deposition contribute 19% to the total N dry deposition measured.

The EC technique also inferred emission of particles $< 0.18 \mu\text{m}$ on several afternoons, while $V_{ds}(\text{NH}_4^+)$ significantly exceed the EC values during these days. These phenomena are correlated with reduced deposition rates of atmospheric acids and NH_3 reported in a companion paper, strongly suggesting that surface exchange fluxes were affected by volatilization of NH_4NO_3 aerosol. This is consistent with the estimate of short chemical time-scales ($< 4 \text{ min}$) for many daytime periods and with the observation of surface gas phase concentration well below the dissociation constant of pure NH_4NO_3 .

It is estimated that aerosol evaporation leads to a substantial overestimation of the NH_3 flux of $20 \text{ ng m}^{-2} \text{ s}^{-1}$ during the day and an equivalent value for HNO_3 . This cannot completely explain the departure of V_d from V_{max} found for the acids, which would imply the presence of a non-zero surface uptake resistance for HNO_3 and HCl .

It is concluded that NH_4^+ evaporation may lead to a significant underestimation of NH_3 deposition to semi-natural vegetation during daytime by current measurements and models where this process is not adequately treated. This is particularly true if measurements are carried out in areas where large aerosol concentrations lead to short chemical time-scales and

where large concentration of volatile NH_4NO_3 and NH_4Cl are present. These conditions are fulfilled above semi-natural vegetation in the vicinity of high NH_3 emission densities, common in the Netherlands and other areas with high livestock densities. At large NH_3 concentrations the underestimation during daytime may be as high as $100 \text{ ng m}^{-2} \text{ s}^{-1}$, although a value of $20 \text{ ng m}^{-2} \text{ s}^{-1}$ as estimated for Elspeet is probably more representative.

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