Aerosol fluxes and particle growth above managed grassland

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Abstract

Particle deposition velocities (11–3000 nm diameter) measured above grassland by eddy covariance during the EU GRAMINA experiment in June 2000 averaged 0.24 and 0.03 mm s\(^{-1}\) to long (0.75 m) and short (0.07 m) grass, respectively. After fertilisation with 108 kg N ha\(^{-1}\) as calcium ammonium nitrate, sustained apparent upward fluxes of particles were observed. Analysis of concentrations and fluxes of potential precursor gases, including NH\(_3\), HNO\(_3\), HCl and selected VOCs, shows that condensation of HNO\(_3\) and NH\(_3\) on the surface of existing particles is responsible for this effect. A novel approach is developed to derive particle growth rates at the field scale, from a combination of measurements of vertical fluxes and particle size-distributions. For the first 9 days after fertilisation, growth rates of 11 nm particles of 3.5 nm hr\(^{-1}\) and 0.89 nm hr\(^{-1}\) were derived for day and night-time conditions, respectively. This implies total NH\(_4\)NO\(_3\) production rates of 1.1 and 0.44 µg m\(^{-3}\) h\(^{-1}\), respectively. The effect translates into a small error in measured ammonia fluxes (0.06% day, 0.56% night) and a larger error in NH\(_4^+\) and NO\(_3^-\) aerosol fluxes of 3.6% and 10%, respectively. By converting rapidly exchanged NH\(_3\) and HNO\(_3\) into slowly depositing NH\(_4\)NO\(_3\), the reaction modifies the total N budget, though this effect is small (<1% for the 10 days following fertilization), as NH\(_3\) emission dominates the net flux. It is estimated that 3.8% of the fertilizer N was volatilised as NH\(_3\), of which 0.05% re-condensed to form NH\(_4\)NO\(_3\) particles within the lowest 2 m of the surface layer. This surface induced process would at least scale up to a global NH\(_4\)NO\(_3\) formation of ca. 0.21 kt N yr\(^{-1}\) from NH\(_4\)NO\(_3\) fertilisers and potentially 45 kt N yr\(^{-1}\) from NH\(_3\) emissions in general.

1 Introduction

Aerosols make an important contribution to the Earth’s radiation budget (IPCC, 2007). An important constituent of aerosols in this respect are hygroscopic compounds formed from anthropogenic precursors, such as ammonium sulphates ((NH\(_4\))\(_2\)SO\(_4\), NH\(_4\)HSO\(_4\)),
ammonium nitrate (NH$_4$NO$_3$) and ammonium chloride (NH$_4$Cl), which are formed by the neutralization of atmospheric ammonia (NH$_3$) by sulphuric acid (H$_2$SO$_4$), nitric acid (HNO$_3$) and hydrochloric acid (HCl), respectively. Adams et al. (2001) estimated present-day forcing potentials of sulphates and nitrates to be of the order of $-0.95$ and $-0.19$ W m$^{-2}$, respectively. In Europe sulphur (S) emissions have been reduced dramatically, by 61% over the period 1990 to 1998 (Vestreng and Støren, 2000), with the UK figure being 57% (NEGTAP, 2001) and the German figure 84% (Umweltbundesamt, 2001). Similar trends are expected for other industrialised countries.

However, as with Germany, a decrease in sulphur emissions is not always mirrored by a decline in aerosol sulphate concentrations, which have been limited by NH$_3$ emissions (Umweltbundesamt, 2001). European emissions of oxidized nitrogen (NO$_x$) have declined very little and global NO$_x$ emissions are expected to increase. As a net result, for 2100 Adams et al. (2001) projected global sulphate forcing to decline to $-0.85$ W m$^{-2}$, while an increasing amount of the NH$_3$ will be neutralized by NO$_x$, increasing the nitrate forcing to $-1.28$ W m$^{-2}$. This prognosis is further supported by measurements that indicate that nitrates already dominate the light-scattering in the Netherlands, which are characterized by continental nitrate rich air masses and large NH$_3$ emissions from high livestock densities (ten Brink et al., 1996).

In addition to the climate effect, the incorporation of relatively fast depositing reactive gaseous pollutants into small particles, that are deposited relatively inefficiently, increases the atmospheric lifetime and thus the transport distance of these acidifying and eutrophying pollutants. This obviously has important consequences for both local and national budgets but and trans-boundary air pollutant transport (Sutton et al., 2007).

A third important effect of changes in the gas/aerosol partitioning concerns the applicability of methods to measure surface/atmosphere exchange fluxes. Micrometeorological flux measurement techniques are formulated for chemically inert tracers and have to be modified if a compound experiences sources or sinks within the atmosphere (e.g. Kramm et al., 1991). Under these conditions, the flux of a reactive tracer may
change considerably with height and the vertical transport derived for a measurement height deviate from the true exchange at the surface. Unexpected observations have been made in a number of studies. Since NH$_3$ exchange with vegetation is potentially bi-directional (e.g. Sutton et al., 1995, 2007), its a priori estimation is often uncertain. HNO$_3$ and HCl, however, are expected to deposit at the maximum deposition velocity permitted by turbulence ($V_{\text{max}}$), while particles deposit slowly to vegetation, at rates of typically <1 up to 5 mm s$^{-1}$. Departures from these rates have been observed and attributed to gas-to-particle conversion or the evaporation of NH$_4^+$ aerosols (Huebert et al., 1988; Nemitz et al., 1996, 2002, 2004; van Oss et al., 1998).

The potential for formation of NH$_4$NO$_3$ and NH$_4$Cl is most likely to be found near strong sources of either NH$_3$ or the acids. Ammonia originates particularly from agricultural point sources such as cattle, pig and poultry units. A large fraction also originates from diffuse surface sources, such as the spreading of manure, organic or mineral fertilizers. These may either cause direct evaporation or raise the nutrient status of the crop or grassland resulting in a raised emission potential, or stomatal compensation point (e.g. Farquhar et al., 1980).

In May/June 2000 a major European integrated experiment, with 12 participating institutes, was organized to investigate NH$_3$ exchange processes with managed agricultural grassland as part of the EU GRAMINAE project. The strategy of GRAMINAE has been described elsewhere, together with the set-up and overall results of this particular experiment (Sutton et al., 2001, 2008a, b). During the campaign, the experimental grassland was cut, fertilised with 108 kg N ha$^{-1}$ as calcium ammonium nitrate and the course of grass regrowth followed.

As part of this experiment, particle number flux measurements were made by eddy-covariance above long grassland (before the cut), above short grassland (between cut and fertilization) and above the fertilized grassland, to study the behaviour of the aerosol and its interaction with the ammonia exchange. In addition to the observation of slow mean aerosol deposition fluxes to the unfertilized grassland, consistent diurnal patterns of apparent emissions were observed during the first 10 days following fertil-
ization. The particle counter used for these measurements had a lower cut-off of 11 nm and an upper cut-off of effectively 3 µm. The observation of upward fluxes of particles could either be caused by the formation of new particles, which grow quickly to a size of >11 nm, or by the condensation of vapours on the surface of existing particles, resulting in the growth of some particles across the 11 nm threshold.

In this paper we represent the particle flux measurements and interpret the results in the context of simultaneous measurements of (i) fluxes of NH₃, HNO₃, and selected biogenic volatile organic compounds (BVOCs); (ii) concentrations of gaseous SO₂, HNO₃ and HCl, as well as aerosol NH₄⁺, NO₃⁻, Cl⁻ and SO₄²⁻; (iii) particle size spectra and (iv) meteorological parameters. A novel technique is developed to derive aerosol growth rates at the field scale from a combination of the particle number fluxes and aerosol size distributions. The overall objectives of this paper are:

(a) to quantify particle deposition rates to (unfertilised) grassland;
(b) to identify the potential and mechanism of the particle production or growth following fertilisation;
(c) to quantify particle growth rates;
(d) to quantify the effect on the measurement of fluxes of NH₃ and total nitrogen;
(e) to indicate the importance of surface ammonia emissions from fertilizer application for particle production globally.

2 Methods and theory

2.1 Site description and overview of measurements

The measurements were made above a 12 ha experimental agricultural grassland of the Agricultural Research Station Völkenrode near Braunschweig, Germany (52°18′ N, 34°5′ E).
10°26′ E; 79 m a.s.l.) during the period 21 May to 16 June 2000. The field was cut on 29 May (06:00–10:00 GMT) and fertilized on 5 June (06:00–07:00 GMT) with 108 kg N ha⁻¹ of calcium ammonium nitrate. The grass was mechanically turned in the morning of 30 May and lifted 31 May (06:00–10:00 GMT). Canopy height before the cut was ≈ 0.75 m and after the cut 0.07 m. The comprehensive set of instrumentation deployed has been summarized elsewhere (Sutton et al., 2008a; Nemitz et al., 2008a). We here focus on the description of those measurements related to the study of the gas/particle interaction.

Particle fluxes were made with an eddy-correlation system including a TSI condensation particle counter (TSI CPC 3760), with a sample flow rate of 1 l min⁻¹ and a size-range of 11 nm up to 3 µm, similar to the setups used by Dorsey et al. (2002) and Nemitz et al. (2002). A sonic anemometer (Model HS, Gill Instruments, UK) was mounted at a height of 2.02 m. A stainless steel inlet (1/8″ OD) led from just below the anemometer to the condensation particle counter, housed in a box at the foot of the measurement mast. The pulse output of the CPC was recorded on a PC based logging system at 10 Hz, and fluxes were calculated according to standard eddy-covariance protocols (Dorsey et al., 2002). In addition, size-segregated particle fluxes over the range 0.1 to 0.4 µm were measured at two different heights using optical particle counters, as presented elsewhere (Dorsey, 2002; Gallagher et al., 2002). In addition, ammonia fluxes were measured by a total of four automated and continuous gradient systems (Milford et al., 2008) and four relaxed eddy accumulation systems (Hensen et al., 2008). Concentrations and gradients of gaseous HNO₃, HCl, SO₂ and aerosol NH₄⁺, NO₃⁻, Cl⁻ and SO₄²⁻ were measured above the grassland with a continuous sampling system combining wet annular denuders and steam jet aerosol collectors with online conductivity analysis for NH₄⁺ and anion chromatography. The system (SJAC/WAD) was a forerunner of the GRAEGOR instrument described by Thomas et al. (2008), and differed from the GRAEGOR in that it used peristaltic pumps rather than syringe pumps to control the liquid flows. In brief, the system consists of two sampling boxes (SB, at 0.7 m and 2.0 m) and a common detector box (DB). In each SB the gas phase is stripped from
a 15 lpm air sample through a continuously flushed wet annual rotating denuder, while
the water soluble aerosol components are collected by passing the sample through
steam and collecting the solution in a cyclone. The four channels (gas phase and
aerosol phase at two heights) are alternately analysed online in the DB for anions by
ion chromatography and for $\text{NH}_4^+$ with a selective ion membrane/conductivity detector.
Continuous addition of an internal $\text{Br}^-$ standard ensures high precision between mea-
measurements. Fluxes were calculated according to the aerodynamic gradient technique
as described by Milford et al. (2008) and Thomas et al. (2008). The instrument was
operated without a size-segregating cut-off inlet.

In addition, a combination of a tandem differential mobility analyzer (DMPS; Williams,
1999) and an Aerodynamic Particle Sizer (APS 3320, TSI, Minnesota, USA) was de-
dployed to measure the particle size distribution over the range 3 nm to 20 $\mu$m at a
10-min resolution. Additional information on the size distribution of the major ions was
provided by MOUDI runs (Micro orifice uniform deposit impactor; MSP Corp., Min-
nesota, USA) runs, integrated over typically 3 days. In order to investigate the effect
of the chemical interactions and deposition on concentrations of $\text{NH}_3$ and acid gases,
the background concentration of $\text{NH}_3$, $\text{HNO}_3$ and $\text{HCl}$ were measured with an autom-
ated rotating wet batch denuder (RBD), providing 40-min batch samples in every
hour (Keuken et al., 1988). This denuder was placed on the roof of a disused, 47 m tall
building of the Physikalisch Technische Bundesanstalt (PTB), about 1 km ENE of the
field site (see map in Sutton et al., 2008a). Daily concentrations of gases ($\text{NH}_3$, $\text{HNO}_3$,
$\text{HCl}$, $\text{HNO}_2$ and $\text{SO}_2$) and aerosol components ($\text{NH}_4^+$, $\text{NO}_3^-$, $\text{Cl}^-$) were also measured
250 m north of the grassland site, above wheat, using a KAPS (Kananaskis Air Pollu-
tant Sampler) combination of 3-stage annular denuders and filter pack (PTFE, nylon)
(e.g. Dämmgen, 2007). Throughflow was adjusted so that the cut-off point of KAPS is
approx. 3 $\mu$m, and 24-h samples were taken between 0 and 24 h CET. Details of the
experimental set-up, the sampling properties and quality parameters are described in
Zimmerling et al. (1997). These samplers had shown to be reliable even under extreme
weather conditions and yielded good results in sampler intercomparisons (e.g. Wiebe
et al., 1990). Although the sampling height of 1.2 m was insufficient for concentrations to be fully unaffected by the atmosphere/surface exchange, these concentrations were not affected by the fertiliser application at the grassland site. Analysis was by liquid ion chromatography (IC) at FAL, Braunschweig for the KAPS samplers and at CEH Lancaster for the samples of MOUDI and RBD.

2.2 Concentration and flux measurements of selected biogenic volatile organic compounds (BVOCs)

The rationale behind the BVOC flux measurements was twofold: firstly, BVOCs potentially provide an alternative biogenically controlled precursor gas for particle formation and, secondly, high emissions of leaf alcohols from grass cutting have been reported in the literature (Kirstine et al., 1998; Karl et al., 2001). VOCs were collected onto Tenax TA (200 mg) and Carbotrap (100 mg) packed in steel tubes (6.1 mm OD, 90 mm length, Perkin Elmer). In the relaxed eddy accumulation (REA) approach (e.g. Desjardins, 1977), fast switching valves are used to sample air from up- and down-moving eddies conditionally onto two separate collection tubes. The valves were controlled by the switching logic of the CEH/UMIST REA system for atmospheric NH$_3$ (Nemitz et al., 2001; Hensen et al., 2008), logging an ultrasonic anemometer (Solent R1012; Gill Instruments, Lymington, UK) at a rate of 20.83 Hz. The sample tubes were tied directly onto the cage of the anemometer, operated at a height of 2.1 m, to minimize flux losses, and mass flow controllers ensured a flow rate of 0.5 l min$^{-1}$, resulting in a total sample volume of approximately 15 l per channel. Field blanks were taken by exposing a third tube at the same height, without flow. After sampling, tubes were sealed with Swagelok© end caps and Teflon ferrules and stored at 4°C, under which conditions the analytes are stable for at least one week.

For gas chromatography – flame ionization detection (GC-FID) analysis, tubes were desorbed using a Perkin-Elmer ATD-400 thermal desorption unit connected to a Hewlett Packard (HP) 5860 series II GC-FID. Separation of the compounds was achieved
through the use of an Ultra-2 cross linked 5% phenyl methyl silicone column. The detection limit for the monoterpenes is about 0.05 ng for the column, corresponding to 40 ppt in air for a 1 l sample, with a level of analytical precision of better than +5%.

For gas chromatography – mass spectrometry (GC-MS) analysis, a Perkin-Elmer ATD-400 thermal desorption unit is connected via a heated transfer line held at 200°C to a HP 5890 GC and a HP 5970 mass selective detector. Desorption, prefocussing and separation of the analytes is achieved using the same column and conditions as with the FID system. This system allows positive identification of a wide range of VOC on the basis of peak retention times, mass spectra contained in the library of the National Bureau of Standards and generated from authentic standards. Monoterpenes were quantified by preparing liquid standards by dilution of the pure compounds in methanol. Diluted standards (1–5 μl) were directly injected onto sampling tubes and the methanol removed by passage of ~0.3 l He. Chromatographic data were handled with a VG Minichrom or HP system.

2.3 Chemical reactions, equilibrium constants and time scales

Ammonia reacts reversibly with nitric acid and hydrochloric acid to form the associated ammonium salts:

\[ \text{NH}_3 + \text{HNO}_3 \leftrightarrow \text{NH}_4 \text{NO}_3 \]  
\[ \text{NH}_3 + \text{HCl} \leftrightarrow \text{NH}_4 \text{Cl} \]

The dissociation constants (\(K_{\text{NH}_4\text{NO}_3}\) and \(K_{\text{NH}_4\text{Cl}}\)) describe the equilibrium vapour concentration products (\(K_e\)), which are expected to form if enough time is provided for aerosol and gas phase to equilibriate. Mozurkewich (1993) and Pio and Harrison (1987) provided expressions for \(K_e\) as a function of temperature (\(T\)) and relative humidity (\(h\)) for pure \(\text{NH}_4\text{NO}_3\) and \(\text{NH}_4\text{Cl}\), respectively. The vapour concentration in equilibrium with mixed aqueous solutions, including deliquescent aerosols, is lowered compared with pure solutions, especially by the presence of sulphates (e.g. Stelson and Seinfeld,
1982), while for ultrafine particles partial pressures may be elevated by the Kelvin effect. The effective vapour concentrations in equilibrium with an externally mixed aerosol consisting of different types and sizes is impossible to predict exactly. $K_e$ is a good approximation for humidities below the relative humidity of deliquescence (about 80% for (NH$_4$)$_2$SO$_4$ and 60% for NH$_4$NO$_3$). Whether equilibrium is attained depends on the comparative time-scales of attainment of equilibrium ($\tau_c$) and the processes perturbing equilibrium, including turbulent diffusive transport ($\tau_t$). Conversely, the Damköhler ratio ($D_r = \tau_t/\tau_c$) is also a measure of the degree to which chemical conversions may affect surface/atmosphere exchange fluxes (Foken et al., 1995). Expressions for $\tau_c$ and $\tau_t$ can be found elsewhere (e.g. Wexler and Seinfeld, 1990, 1991), as summarized by Nemitz et al. (2000).

2.4 A novel method for the calculation of growth rates from particle flux measurements at the field scale

Particle growth implies that some particles will grow across the lower cut-off of the particle counter ($d_p=11$ nm or $r=5.5$ nm) as they deposit. Therefore the concentration of particles $>11$ nm may increase towards the ground at the same time as the total number of particles decreases due to deposition, resulting in an apparent upward flux of particles $>11$ nm.

The equation of mass conservation of a tracer ($\chi$) is given by (e.g. Fowler and Duyzer, 1989):

$$\frac{\partial F_\chi}{\partial z} = -\frac{\partial \chi}{\partial t} + \bar{u} \frac{\partial \chi}{\partial x} + \bar{w} \frac{\partial \chi}{\partial z} + Q_\chi,$$

(3)

where $F_\chi$ is the vertical flux of the tracer, $t$ is time, $u$ and $w$ are the wind components along the stream-wise and vertical co-ordinates ($x$ and $z$), and $Q_\chi$ represents in situ production/ destruction of the tracer. The right-hand-side (r.h.s.) terms represent storage, horizontal and vertical advection as well as production/ destruction, usually attributed to chemical effects of emissions. Assuming stationary and homogeneous
conditions, the first three terms vanish. If we consider particle number \( N \) as the tracer, the production term may be written as \( Q_N = \frac{dN}{dt} \). Despite the similarity to the first r.h.s. term of Eq. (3), this represents production rather than changes in concentration due to storage. For particle number fluxes measured within a certain size bin (for the CPC in the radius bin \( 5.5 \text{ nm} < r < 1.5 \text{ µm} \)), flux divergence is related to effects that change the concentration within this size bin only:

\[
\frac{dF_N(5.5 \text{ nm} < r < 1.5 \text{ µm})}{dz} = \frac{dN(5.5 \text{ nm} < r < 1.5 \text{ µm})}{dt}
\]  

These may either be direct emissions of particles in this size range, coagulation or growth/shrinkage across the lower or upper size cuts. We here assume that there are no emissions sources at the point of measurement and that coagulation is unimportant (see discussion below). Thus the change in \( N(5.5 \text{ nm} < r < 1.5 \text{ µm}) \) is only affected by the growth into the size range over the lower size-cut and growth out of the size range across the upper size cut. After application of the chain rule for forming derivatives the vertical flux divergence can be expressed as:

\[
\frac{dF_N}{dz} = \frac{dN}{dr} \bigg|_{r=5.5 \text{ nm}} \times \frac{dr}{dt} \bigg|_{r=5.5 \text{ nm}} \left( -\frac{dN}{dr} \bigg|_{r=1.5 \text{ µm}} \times \frac{dr}{dt} \bigg|_{r=1.5 \text{ µm}} \right)
\]  

Here \( F_N \) and \( N \) are particle number flux and number concentration in the radius \( r \) range \( 5.5 \text{ nm} \) to \( 1.5 \text{ µm} \), respectively. The (non-logarithmic) particle size distribution function \( (dN/dr) \) at \( r=5.5 \text{ nm} \) and \( r=1.5 \text{ µm} \) can be measured directly with appropriate instrumentation. Owing to the small number concentration of super-micron particles, the second r.h.s. term, i.e. the growth across the 1.5 µm threshold can be neglected. The growth rate \( (dr/dt) \) can be expressed as (Kulmala et al., 2001):

\[
\frac{dr}{dt} = \frac{m_v \beta_m D \chi_v}{r \rho_p}
\]  

where \( m_v \) and \( \chi_v \) are the molecular mass and effective concentration of the condensable vapour, respectively, and \( \rho_p \) is the particle density, while \( \beta_m \) is the correction factor.
for mass flux in the transition regime (Fuchs and Sutugin, 1971):

$$\beta_m = \frac{K_n + 1}{0.377 K_n + 1 + 4/3 \alpha^{-1} K_n^2 + 4/3 \alpha^{-1} K_n^4}.$$  \hspace{1cm} (7)

Here $K_n$ is the Knudsen number

$$K_n = \frac{\lambda}{r}.$$ \hspace{1cm} (8)

with $\lambda$ being the mean molecular free path in air (0.065 $\mu$m). Research suggests that the sticking coefficient ($\alpha$) for NH$_3$/HNO$_3$ is in the range 0.3 to 0.8 (Dassios and Pandis, 1999; Cruz et al., 2000; Rudolf et al., 2001); here $\alpha=0.5$ is used, which results in a value of $\beta_m=0.031$ for $r=5.5$ nm and $\beta_m=0.918$ for $r=1.5$ $\mu$m. $D$ in Eq. (6) is the binary diffusion coefficient for vapour diffusion towards a particle (Reid et al., 1987):

$$D = \frac{RT}{6\pi N_A \nu r}.$$ \hspace{1cm} (9)

Here, $R$ is the universal gas constant, $T$ is temperature in K, $N_A$ is the Avogadro constant and $\nu$ is the gas dynamic viscosity. A first estimate of the flux change with height ($dF_N/dz$) is derived from the difference between the measured flux and the flux expected in the absence of chemical reactions, parameterised using an average deposition velocity ($V_d = -F_N/\chi_N$; with $\chi_N$ the particle number concentration) of 0.14 mm s$^{-1}$ derived from measurements before fertilization (cf. Sect. 3.1 below):

$$dF_{Ni}/dz = F_N + V_d \times \chi_{Ni} \frac{z_m}{z}.$$ \hspace{1cm} (10)

With Eqs. (5) and (10), the growth rate across the size cut-offs of the particle counter can be estimated from the measured fluxes and particle size spectra. By inverting Eq. (6), the effective vapour concentration available for condensation ($\chi_v$) can be derived. The growth rate across the 11 nm threshold may be extrapolated to derive the
growth rate of all particle sizes, again using Eq. (6). The total mass transport from the gas to the particle phase \( (j_v) \) is then given by integration over all size classes \( (i) \) as:

\[
j_v = \sum_{i=1}^{n} 4\pi r_i^2 N_i g \frac{\rho_p}{m_v} \frac{dr_i}{dt}
\]

(11)

where the particle density \( (\rho_p) \) is set to that of NH\(_4\)NO\(_3\) for consistency. Assuming the mass transport to be due to the combined condensation of NH\(_3\) and HNO\(_3\), 21.25\% of \( j_v \) (in terms of mass) is due to the condensation of NH\(_3\).

3 Results

3.1 Particle number flux measurements before and after fertilisation

The measured particle number unfiltered flux is shown in Fig. 1. Spikes are primarily due to emissions associated with the operations of agricultural machinery in the field (e.g. cutting on 29 May, turning of the cut grass 30 May and removal of the cut grass on 1 June). Otherwise, the measurement show small fluxes, dominated by deposition before the fertilisation, and a diurnal pattern of apparent emission fluxes after fertilisation, which slowly subsided.

The statistics of the concentrations and fluxes before and after fertilisation are summarised in Table 1, after management periods had been removed and data filtered for suitable wind directions. Mean air concentrations were similar during the four periods, ranging from 7190 to 8628 cm\(^{-3}\). Both emission and deposition fluxes were measured during all four periods, but were least frequent (31\%) before the cut and most frequent (60\%) during the first week after fertilization. The average apparent emission flux after fertilization was larger than the deposition fluxes to the short vegetation. The average (median) deposition velocities were 0.24 (0.24) mm s\(^{-1}\) before the cut, 0.03 (0.06) mm s\(^{-1}\) between cut and fertilization and 0.06 (0.05) mm s\(^{-1}\) 7–10 days
after fertilization, qualitatively consistent with the known dependence of deposition velocities on surface roughness (e.g. Gallagher et al., 2002).

3.2 Atmospheric concentrations, equilibrium considerations and potential for \( \text{NH}_4\text{NO}_3 \) formation

The time-series of the concentration in air of \( \text{NH}_3 \), \( \text{HNO}_3 \) and \( \text{HCl} \) at 1 m and 47 m are presented in Fig. 2, clearly showing the effect of fertilisation on the concentration of \( \text{NH}_3 \). The average \( \text{NH}_3 \) concentration at the notional canopy height (\( z_0' \)) can be estimated from the additional knowledge of the \( \text{NH}_3 \) flux (\( F_{\text{NH}_3} \); cf. Fig. 7 below – Sutton et al., 1993; Milford et al., 2008), under the simplifying assumption that the flux is unaffected by the chemical conversion:

\[
\chi_{\text{NH}_3}(z_0') = \chi_{\text{NH}_3}(1 \text{ m}) + F_{\text{NH}_3}[R_a(1 \text{ m}) + R_b].
\]  

(12)

Here \( R_a \) and \( R_b \) are the aerodynamic sub-layer resistance describing the transport through the turbulent and the quasi-laminar part of the atmosphere, respectively. This concentration is also shown in Fig. 2 for comparison. All concentrations undergo a clear diurnal cycle, with daytime maxima. Both acids are depleted over the first two days after fertiliser application on the morning of 5 June. However, this change is also reflected in the background gas measurements (Fig. 2; both by RBD and KAPS), indicating that this decrease is not due to depletion by reaction with \( \text{NH}_3 \) above the field, but reflects changes in air masses or regional chemistry.

\( \chi_{\text{NH}_3}(z_0') \) exhibits the behaviour expected for a gas concentration that is governed by equilibrium with dry or aqueous \( \text{NH}_4^+ \), with the diurnal pattern reflecting the temperature control and the long-term decrease in soil and plant \( \text{NH}_4^+ \) after fertilization (cf. Milford et al., 2001; Sutton et al., 2008b). On an equivalent basis, \( \text{NH}_4^+ \) aerosol concentrations exceeded the \( \text{NO}_3^- \) concentrations by a factor of two (Fig. 3), the rest of the \( \text{NH}_4^+ \) being neutralized by \( \text{SO}_4^{2-} \) (not shown). The measurements indicated that \( \text{NO}_3^- \) concentrations appeared to be increased at the grassland site, compared with the control site 400 m to the north. However, this observation was also made prior to fertilization.
and may at least be partially due to a larger cut-off diameter of the SJAC capturing additional coarse NO$_3^-$ compared with the KAPS.

The comparison of measured ($K_m$) with theoretical equilibrium ($K_e$) vapour concentration products of NH$_3$ with the acids shows $K_m \ll K_e$ prior to fertilizer application (Fig. 4). Since the NH$_3$ concentration above the grassland increased on 5 June, measured products $[\text{NH}_3] \times [\text{HCl}]$ increased also, but were still much smaller than $K_e$. Measured products of $[\text{NH}_3] \times [\text{HNO}_3]$ were close to their theoretical equilibrium values during 5 to 11 June with exceedances during most nights.

### 3.3 Concentrations and fluxes of VOCs

Financial constraints meant that out of the 27 hourly VOC REA runs performed only 14 could be analyzed, and only for a limited suite of oxygenated compounds and terpenoids (benzaldehyde, nonanal, $\alpha$-pinene, 1-$\beta$-pinene and d-3-carene). Grass cutting has been found to increase emissions of some BVOCs by a factor of 180 (Kirstine et al., 1998; Karl et al., 2001), but the leaf alcohols, the primary BVOCs released, are not very efficient particle precursors until they are processed to form less volatile compounds. By constrast, biogenic alkenes have been found to be efficient aerosol precursors (e.g. Hoffmann et al., 1997). The suite of VOCs was selected to provide information on the magnitude of emissions allowing the estimation of their potential for particle formation/particle growth. Averaged concentrations and fluxes after the cut and before fertilization are contrasted with the measurements after fertilization in Table 2. The flux measurements should be interpreted with caution. However, neither concentrations nor fluxes show significant changes before and after fertilization. Irrespective of fertilization, benzaldehyde showed a clear diurnal cycle with daytime maxima of 8 $\mu$g m$^{-3}$ and night-time minima of 2 $\mu$g m$^{-3}$ (not shown).
3.4 Calculation of particle growth rates

Growth rates of 11 nm, total gas-to-particle conversion mass transfer fluxes, estimated vapour concentration and the effect of vapour condensation on the NH$_3$ flux are presented in Fig. 5 and summarized in Table 3 as typical values for 12-h day and night-time periods following fertilizer application. They are compared with measurements of vapour concentrations and estimated total particle surface area.

3.5 Effects on the measurements of ammonia flux

Even if there is potential for the formation or evaporation of aerosol, the time-scale of this process may be too slow for surface exchange fluxes to be altered significantly. The chemical time-scale ($\tau_c$) (Wexler and Seinfeld, 1990) depends strongly on the surface area of the aerosol, while the turbulent time-scale ($\tau_t$) depends on the turbulence as characterised by the friction velocity ($u_*$). Chemistry is thought to alter fluxes for Damköhler numbers ($D_r = \tau_t / \tau_c$) greater than 0.1 (Foken et al., 1995). Figure 6 demonstrates that this critical ratio is exceeded regularly, but only during night, when turbulent diffusive time scales are long, and the aerosol concentration (and hence surface area) is enhanced.

According to this time-scale analysis, major effects on the NH$_3$ flux would be unlikely, at least during daytime. However, the observations presented here indicate that particle growth was considerable, also during daytime. From the growth rate of 11 nm particles, the driving force for the condensation, the effective vapour concentration ($\chi_v$) was estimated using Eq. (6). And the total mass transfer from the gas to the aerosol phase ($J_{NH_4NO_3}$) was derived by integration over the measured particle spectrum, using Eq. (11). From this mass transfer the error on the NH$_3$ flux may be estimated. These parameters are also shown in Table 3, where they are also compared with the actual measured concentrations of NH$_3$ and HNO$_3$, while Fig. 7 shows the time-series of the measured uncorrected and corrected NH$_3$ flux. The error on the NH$_3$ flux measurement is small, on average 12.2 ng m$^{-2}$ s$^{-1}$ (1.5%) during day and 12.4 ng m$^{-2}$ s$^{-1}$ (6.6%) during night.
4 Discussion

4.1 Deposition rates to unfertilised grassland

Dry deposition rates of particles to vegetation have recently been reviewed by Pryor et al. (2008) and Petroff et al. (2008). At Braunschweig, particle number size distributions were dominated by particles in the size range 10 to 200 nm (Fig. 8) and thus the total particle number flux measurements were also dominated by the Aitken mode.

The mean $V_d$ of 0.03 mm s$^{-1}$ to cut ($h_c=0.07$ m), 0.06 mm s$^{-1}$ to partly regrown ($h_c=0.12$ m) and 0.26 mm s$^{-1}$ to tall ($h_c=0.75$ m) grassland measured at the Braunschweig field site appears to be at the low end of measurements reported in the literature, but only few studies have measured total number fluxes over short vegetation: Nemitz et al. (2002) reported a mean deposition velocity of 0.3 mm s$^{-1}$ to Scottish moorland vegetation ($h_c=0.06$ m), measured with a similar setup; the difference is only partly explained by higher wind speeds during the UK measurements with an average $u_*$ of 0.25 m s$^{-1}$ compared with 0.18 m s$^{-1}$ during the present study. Lamaud et al. (1994) measured average $V_d$ of 0.7 mm s$^{-1}$ to semi arid savannah, using an instrument that measured total particle flux, but weighted by surface area. Thus, their measurement is biased towards larger particle than the measurements made here.

Other studies above short vegetation have focused on accumulation mode particles (0.1–0.5 µm) that can be sized with optical techniques (Nemitz et al., 2002; Vong et al., 2004) or mass fluxes, also dominated by the accumulation mode (Wesely et al., 1985): Vong et al. (2004) derived particle deposition velocities to grassland ($0.75 \text{ m}<h_c<1 \text{ m}$) as a function of particle size and stability. Values of $V_d$ for the smallest size ($d_p=0.34 \mu m$) ranged from 2 during stable to 6 mm s$^{-1}$ during unstable conditions, while values of $V_d$ for larger particles ($d_p=0.84 \mu m$) increased from 2 to 7 mm s$^{-1}$. At the Scottish moorland site, $V_d$ of accumulation mode particles ranged from 0.3 mm s$^{-1}$ ($d_p=0.1 \mu m$), over 2 mm s$^{-1}$ (0.5 µm) to >10 mm s$^{-1}$ (3 µm). Simi-
larly, Wesely et al. (1985) derived an average \( V_d \) of 2.2 mm s\(^{-1}\) for \( \text{SO}_4^{2-} \) deposition to grassland, with a likely mass median diameter of 0.4 \( \mu m \).

Dorsey (2002) and Gallagher et al. (2002) also presented measurements of size-segregated particle fluxes made at the Braunschweig field site, deriving average \( V_d \) for particles with 0.1 \( \mu m < d_p < 0.2 \mu m \) of 0.87 mm s\(^{-1}\) for the cut and 1.13 \( \mu m \) s\(^{-1}\) for the long grass. It is thus likely that the relative low deposition rates of total particle flux is strongly biased by inefficient deposition of particles <0.1 \( \mu m \). While the deposition rates presented here are therefore representative for primary organic aerosol which represents much of the Aitken mode, they are probably underestimations for the average deposition of secondary aerosol constituents, which occupies the accumulation mode (e.g. Allan et al., 2003).

4.2 Assessment of alternative mechanism causing apparent particle emission fluxes following fertilisation

The analysis presented so far has implied that the particle emission fluxes were due to combined \( \text{NH}_3 \) and \( \text{HNO}_3 \) condensation. We here consider alternative mechanisms.

Biogenic VOC emissions of leaf alcohols and breakdown products, but also of effective precursor gases such as alkenes, have been reported to increase dramatically immediately after grass cutting (Kirstine et al., 1998; Karl et al., 2001). Although some particle emissions were observed at the GRAMINAE experiment after grass cutting, these can be related to agricultural activities on the field (e.g. turning), while persistent apparent particle emissions occurred only after fertilization. The limited number of measurements of BVOC concentrations and, though less certain, their fluxes do not indicate that fertilization had an influence on VOCs. Non-zero water vapour fluxes can also cause artifacts for size-dependent particle flux measurements (Kowalski, 2001), but this effect would also have been similar before and after fertilization.

The only major change induced by the fertilization was a greatly increased emission of \( \text{NH}_3 \) (Fig. 7), resulting in enhanced concentrations both at the canopy height (\( z_0' \))
and the average measurement height of 1 m (Fig. 2), indicating that the change in NH$_3$ is almost certainly the cause for the observed apparent particle emissions. Having established the role of NH$_3$ as a precursor, the particle emission fluxes may still be linked to one of three processes: (i) ternary nucleation of the H$_2$O–H$_2$SO$_4$–NH$_3$ system, followed by growth across the 11 nm threshold, (ii) formation of new NH$_4$NO$_3$ or NH$_4$Cl particles, followed by growth across the 11 nm threshold and (iii) particle growth due to the combined condensation of NH$_3$ and HNO$_3$ or NH$_3$ and HCl on the surface of existing particles. It is highly improbable, however, that particle nucleation played a role in the observed apparent emission fluxes, for several reasons:

1. Binary nucleation of volatile compounds such as NH$_4$NO$_3$ and NH$_4$Cl is inefficient under ambient conditions (e.g. Korhonen et al., 1997).

2. Ternary nucleation of the H$_2$O–H$_2$SO$_4$–NH$_3$ system can be important, where H$_2$SO$_4$ concentrations are large and competing condensational sinks are small (due to low aerosol loading). However, only small NH$_3$ concentrations in the ng m$^{-3}$ range, virtually always present in agricultural areas, are necessary to promote ternary nucleation of the H$_2$O–H$_2$SO$_4$–NH$_3$ system significantly, while the nucleation rate is insensitive to further increases in NH$_3$ concentrations beyond 100 ppt ($\sim$76 ng m$^{-3}$) (e.g. Napari et al., 2002). Therefore, the enhanced NH$_3$ emission after fertilization would not have greatly changed the efficiency of this particle production mechanism.

3. Although individual nucleation events were observed at the measurement site (Sutton et al., 2008a), there was no difference in the average size distribution of the DMPS measurements before and after fertilisation, and average size distributions did not show a clear nucleation mode (Fig. 8). This suggests that the observed nucleation events were regional in nature and independent of local NH$_3$ emissions.

4. To estimate whether growth of newly nucleated particles, at a diameter of typically 2 nm, would have been sufficiently quick to be detected by the CPC, Eq. (6) can be
used to simulate the growth of 2 nm particles at different vapour concentrations. The results (Fig. 9) demonstrate that it takes almost an hour for a 2 nm particle to become detectable, even at $\chi_v=50 \mu g m^{-3}$. For comparison, at typical wind speeds of 4 m s$^{-1}$ and an extent of the grassland of between 150 and 500 m, depending on wind direction, the residence time above the field is of the order of 1 to 5 min.

In summary, it is highly unlikely that particle nucleation was involved in causing the observed upward fluxes. Instead, the observation of emission fluxes was almost certainly due to condensation particle growth of particles across the 11 nm cut-off size of the CPC.

4.3 Proposed mechanism leading to apparent particle emission fluxes

After fertilization, close agreement was found between measured concentration products of $[\text{NH}_3] \times [\text{HNO}_3]$ at 1 m and those predicted to be in equilibrium with $\text{NH}_4\text{NO}_3$. For $\text{NH}_4\text{Cl}$ $K_m \ll K_e$ was always observed, eliminating HCl and supporting HNO$_3$ as a potential associated precursor. According to the process understanding emerging from the Braunschweig experiment work, direct NH$_3$ evaporation of fertilizer pellets would have dominated the measured emissions (Fig. 7) directly after fertilizer application, until there was a significant amount of precipitation (Sutton et al., 2008b). Precipitation of 2.6 mm was recorded for the evening of 5 June and 1.3 mm during the late morning of the 7th. From 6 or 7 June NH$_3$ emission was probably dominated by the enhanced $\text{NH}_4^+$ concentration in soil solution and leaf litter, evident in the measurements, and the gradually increasing emission potential of the plants (Riedo et al., 2002; Sutton et al., 2008b). Small night-time emissions suggest that non-stomatal emissions, such as soil emissions, still contributed to the flux even 5 days after fertilization. Leaf-litter on the soil surface represents and additional NH$_3$ source which would have been re-captured in the tall canopy, but is able to escape the canopy after the cut (David et al., 2008; Sutton et al., 2008b).
Because of their solubility in water, the acid gases HNO$_3$ and HCl are conventionally expected to deposit at the maximum rate permitted by turbulence ($V_{\text{max}}$). A reduction in the deposition velocity of acid gases indicates sources or non-zero equilibrium concentrations at or near the ground. Nemitz et al. (2004) showed that reduced HNO$_3$ deposition at a Dutch heathland was consistent with evaporation of airborne NH$_4$NO$_3$ due to small precursor gas concentration products near the ground. Nemitz et al. (2000) reported emissions of HCl and Neftel et al. (1996) reported upward gradients of HNO$_3$, both of which they explained by leaf surface chemistry.

Although not without uncertainty, the HNO$_3$ gradient measurements at Braunschweig showed reduced deposition rates ($V_d < V_{\text{max}}$) during the afternoons of some of the days after fertilisation (e.g. 9 June) (Fig. 10). The reduced deposition rates of HNO$_3$ suggest that at least some of the HNO$_3$ is also surface-derived, with fertiliser pellets and high soil NO$_3^-$ concentrations resulting in a non-zero gas-phase concentration at the ground, at least during warm afternoons. HNO$_3$ concentrations exhibited a clear diurnal cycle with the maximum concentrations during the day (Figs. 2 and 9), which would be consistent with either its production from NO$_x$, or the cycle in the equilibrium constant of NH$_4$NO$_3$ (Fig. 4).

In general, $K_m$ and $K_e$ change with height, in response to gradients of vapour concentrations, $T$ and $h$: the increase of NH$_3$ and $h$ towards the ground increase $K_m$ relative to $K_e$, while the decrease in HNO$_3$ and increase of $T$ would have the opposite effect. Unexpected particle fluxes have been attributed to the formation or evaporation of NH$_4^+$ before: van Oss et al. (1998) simulated over-rapid deposition of NO$_3^-$ aerosol to forest to aerosol evaporation. Nemitz et al. (2004) reported fast deposition of NH$_4^+$ by gradient technique to a Dutch heathland, while eddy-correlation particle fluxes appeared to detect deposition of particles $>0.2 \, \mu m$ at the same time as emission of smaller particles. In a modelling study, Nemitz and Sutton (2004) demonstrated that both observations are consistent with the evaporation of NH$_4$NO$_3$ during the deposition process, caused by the depletion of NH$_3$ and HNO$_3$ close to the ground.
In summary, the following picture emerges: a combination of NH$_4^+$ enriched soil, litter and leaf solutions combined with initial losses directly from the fertilizer pellets leads to emission of NH$_3$ which partly re-condenses on the surface of atmospheric aerosol particles above the ground, where, at least during the day, temperatures are lower. This condensation of NH$_3$ is likely to be associated with simultaneous condensation of HNO$_3$, which may be partly derived from the atmosphere or from fertilizer volatilization. It is likely that atmospheric HNO$_3$ was the main source during night, when the potential for HNO$_3$ emission from the ground was lower. This condensation results in the particles growing during the deposition process (Fig. 11), causing a deposition gradient in the total particle number, but an apparent increase of particles with $r>5.5$ nm, which is detected as an apparent particle emission flux.

4.4 Time-scales of particle growth

Particle nucleation and growth due to condensation are ubiquitous across the world, with the exception of the tropics, with typical growth rates in the region of 1–20 nm hr$^{-1}$ (Kulmala et al., 2004; Holmes, 2007) and can be attributed to a range of precursors. For example, Verheggen et al. (2000) derived growth rates due to H$_2$SO$_4$ condensation of 3 to 7 nm hr$^{-1}$ from size-distribution measurements. Growth rates of 2 to 11 nm hr$^{-1}$ were observed following nucleation events during the BIOFOR campaigns above Finnish forests, attributed to the condensation of BVOCs, while faster growth rates of 15 to 180 nm hr$^{-1}$ have been derived in the maritime environment during PARFORCE, possibly due to the uptake of biogenic methylated iodine species (Dal Maso et al., 2002). Growth rates linked to the emission of agricultural precursors do not appear to have been presented in the literature. A likely reason is that, until now, most growth rates have been derived by analysis of the time-evolution of size-distributions, typically following nucleation events or emission plumes – an approach, which requires these processes to occur at the regional scale. By contrast, agricultural activity such as fertilisation happens at the field scale. Here we have developed and applied a new
approach to derive growth rates at the field scale, through a combination of measurements of particle flux and aerosol size distribution.

The growth rates derived in this study for combined \( \text{NH}_3 - \text{HNO}_3 \) uptake (Table 3) are in the range of these previous studies, with 11 nm particles growing at about 3.52 nm hr\(^{-1}\) during the day and 0.89 nm hr\(^{-1}\) at night, with maxima of 20 to 30 nm hr\(^{-1}\) (Fig. 5), which coincided with the maxima of the \( \text{NH}_3 \) flux. It should be noted that other particle dynamic processes, in particular coagulation, are not considered in the approach presented here (Eq. 5). Since no particular nucleation mode was observed during this study, this process is not considered to be important here. This is in contrast to studies were growth rates are derived from the evolution of size-distributions following nucleation events. At the Braunschweig field site, size-distributions were similar before and after fertilization (Fig. 8) and thus coagulation would also have affected fluxes similarly. Furthermore, there is no reason to believe that coagulation would have acted differently above and below the measurement height. Thus, in the interpretation of CPC flux measurements, coagulation is not normally considered.

The approach developed here, to derive growth rates at the field scale from the combined measurement of particle flux and size distribution is sufficiently sensitive to detect growth rates of a few nm hr\(^{-1}\). The main uncertainty relates to the estimate of the dry deposition flux at the surface and thus to the variability in the dry deposition rate, which is here assumed to be constant with time (0.06 mm s\(^{-1}\)). Under the conditions encountered here, an increase of \( V_d \) to 1 mm s\(^{-1}\) translates into an increase in the estimated growth rate by about 3 nm hr\(^{-1}\).

The time-scale analysis (Fig. 6) indicates that chemistry should only be relevant during night-time conditions, while apparent emission fluxes were also observed during daytime. This highlights the limitations of the time-scale analysis based on Damköhler ratios. The analysis here is based on the above-canopy turbulent time-scale. Although chemistry may not be efficient well above the canopy, in the region for which the turbulence time-scale \( \tau_t \) was estimated, obviously a region exists where \( \tau_t \) becomes comparable to \( \tau_c \). Indeed, radon tracer measurements showed that the time-scale for diffusion
out of the grass canopy is long (Nemitz et al., 2008b). Thus all relevant time-scales need to be considered when assessing the overall potential for chemistry to modify fluxes between the point of emission and measurement.

4.5 Implications for flux measurements and local budgets of nitrogen

There are three ways in which gas-particle conversion affects fluxes and local budgets, which are assessed in this section.

1. *Error for flux measurement.* As the vertical gradient is modified by the chemistry, the aerodynamic gradient technique (AGM) may need to be modified to derive the correct flux. Similarly, the flux measured by micrometeorological techniques that operate at a single measurement height ($z_m$), such as EC and REA, differs from the true surface exchange.

2. *Error for inferential estimates and deposition modelling.* Deposition and emission are often derived from the air concentration in an inferential approach, using resistance models of a range of complexity. This approach does not usually consider chemical conversion within the resistance analogue. In addition, changes in the gas/particle partitioning modify air concentrations compared with the simulation of an atmospheric transport model that ignores chemical reactions. For example, the NH$_3$ air concentration is lowered by transfer to the particle phase, further stimulating stomatal emission, which is governed by the difference between stomatal compensation point and atmospheric concentration.

3. *Modification of the local N budget.* A fraction of the emitted NH$_3$ is converted into slowly depositing NH$_4$NO$_3$ aerosol, *increasing* the potential for deposition. Similarly, fast depositing HNO$_3$ is converted into slowly depositing NH$_4$NO$_3$ aerosol, *decreasing* this deposition. The net effect of gas-to-particle conversion on the local N budget will depend on the relative magnitudes of the different compounds involved.
The average NH$_4$NO$_3$ production rate below the measurement height of the CPC fluxes was estimated to be 1.11 and 0.44 µg m$^{-3}$ h$^{-1}$ for day- and night-time, respectively. If it is assumed (a) that production above this measurement height is negligible as ammonia concentrations decline with increasing height and (b) that the particle production would have lasted for 14 days after fertilization, then this would equate to a production rate of 5.2 g NH$_4$NO$_3$ ha$^{-1}$ or 0.0017% of the fertilizer N applied. By comparison, 3.2% of the fertilizer N were estimated to be emitted as NH$_3$, either by direct volatilisation or, later on, by raising the stomatal compensation point within the first 10 days of fertilisation (Milford et al., 2008), i.e. around 0.05% of the emitted ammonia was converted to ammonium aerosol within the first 2 m above the ground.

Table 4 compares three estimates of the fluxes of the different reactive nitrogen species. The first one is based on the measurements above the field itself. The second estimate summarises the best estimate of the true surface exchange, correcting for the chemical interaction, similar to the correction presented in Fig. 7. The final estimate represents the fluxes that would be expected with an inferential modeling approach, if atmospheric concentrations were not influenced by the chemistry above the field. This is based on the concentrations measured at the background field. The NH$_3$ emission from the field would be expected to be somewhat suppressed in this scenario as the NH$_3$ concentration above the field would be slightly larger, but the exact NH$_3$ emission under these modified conditions is difficult to estimate. Because at this site the total N flux is very much dominated by NH$_3$, and the relative effect on the NH$_3$ flux is small, the difference for the total N flux is small above this particular field. However, the average relative effect on the other forms of N is significant (2.4% for HNO$_3$, 3.6% for NH$_4^+$ and 10% for NO$_3^-$), suggesting that in other circumstances these interactions could have larger relative effects on local nitrogen budgets.

4.6 Implication for global budgets and climate forcing

From fertiliser consumption statistics it is estimated that 4.5 Mt of NH$_4$NO$_3$–N are used in Europe every year and 12.3 Mt globally (Matthews, 1994). Extrapolation of our mea-
surements to the globe implies global NH₄NO₃–N formation/emissions following fertil-
izer application of 0.21 kt. Again this estimate is based on the assumption that NH₄NO₃
formation is confined to the bottom 2 m, above which precursor gas concentrations are
estimated to be sufficiently diluted for continued aerosol formation, which is possibly an
underestimate. Volatilisation of NH₄NO₃ fertiliser contributes only 0.46% to the global
NH₃ emissions (Bouwman et al., 1997), with the main part of the emissions arising from
animal wastes and organic fertilizers; and hence the overall NH₄NO₃–N formation fol-
lowing NH₃ emissions could easily be as large as 45 kt NH₄NO₃–N. This reaction will
depend on background concentrations of HNO₃, competition with reaction with sulphur
and meteorology. It should also be noted that, unlike with ammonium sulphates, any
NH₄NO₃ formed has the potential to re-evaporate if the gas phase concentrations of
NH₃ and HNO₃ drop below the equilibrium values. For comparison, the global ammo-
nium sulphate formation is estimated to be in the order of 57 Mt S yr⁻¹ (IPCC, 2001).

5 Conclusions

Average deposition velocities to (unfertilised) cut, partially regrown and tall grassland
were 0.03, 0.06 and 0.24 mm s⁻¹, respectively. This is at the lower end of values re-
ported for short vegetation, but consistent with the number flux being dominated by
Aitken mode particles. The values are therefore applicable, e.g. to derive deposition of
combustion derived primary aerosol. Analysis of sustained apparent emission fluxes
after fertilisation, in relation to potential pre-cursor gases shows that these are con-
sistent with condensation of NH₃ and HNO₃ and associated growth across the 11 nm
diameter cut-off of the particle counter used for the flux measurements.

We have here developed a novel technique to derive particle growth rates from
flux measurements using instruments with well-defined cut-off diameters, together with
measurements of the size-distribution. Former estimates of growth rates have usually
relied on the presence of a clear nucleation mode, whose size evolution could easily
be monitored. By contrast our new approach is universally applicable to derive particle
growth rates over homogeneous surfaces at the field scale and could, for example, be used to derive aerosol growth rates due to biogenic secondary organic aerosol formation in natural environments, where bi-directional particle number fluxes are observed, even if this growth happens over a limited area.

Above the fertilized field growth rates of 11 nm particles of 3.5 nm hr\(^{-1}\) during the day and 0.89 nm hr\(^{-1}\) at night are similar to those reported in the literature for the uptake of organic vapours and H\(_2\)SO\(_4\), and illustrate the efficiency of the NH\(_3\)–HNO\(_3\) system as an aerosol precursor. While the chemical interactions significantly change the local flux of gaseous HNO\(_3\) and NH\(_4\)NO\(_3\) aerosol, the effect on the total nitrogen flux is small, as this is dominated by the large NH\(_3\) emission during this period for which the relative effect is small.

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Table 1. Summary of the statistics of the concentrations and fluxes measured with the CPC system before the cut and after fertilisation (based on 30-min flux values).

|                        | Period (1): before cut | Period (2): after cut, before fertilisation | Period (3): directly after fertilisation | Period (4): 7–10 days after fertilisation |
|------------------------|------------------------|---------------------------------------------|------------------------------------------|------------------------------------------|
|                         | $X_N$ [#/cm$^3$] | $N_F$ [#/cm$^2$ s$^{-1}$] | $V_d$ [mm s$^{-1}$] | $X_N$ [#/cm$^3$] | $N_F$ [#/cm$^2$ s$^{-1}$] | $V_d$ [mm s$^{-1}$] | $X_N$ [#/cm$^3$] | $N_F$ [#/cm$^2$ s$^{-1}$] | $V_d$ [mm s$^{-1}$] |
| Min                    | 2903                  | -4080                        | -5.39                     | 3004                  | -3950                        | -11.7                     | 1800                  | -5790                        | -10.8                     |
| Max                    | 23840                 | 5700                         | 4.34                      | 16526                 | 5820                         | 6.69                      | 23230                 | 9020                         | 9.26                      |
| 5‰-ile                | 4303                  | -1340                        | -0.98                     | 3831                  | -1110                        | -1.70                     | 3776                  | -1090                        | -3.17                     |
| 95‰-ile               | 12930                 | 718                          | 1.74                      | 13850                 | 1220                         | 1.56                      | 17510                 | 2570                         | 1.11                      |
| Mean                   | 7190                  | -181                         | 0.24                      | 7611                  | -17                          | 0.03                      | 8628                  | 323                          | -0.46                     |
| Median                 | 6486                  | -151                         | 0.24                      | 7057                  | -45                          | 0.06                      | 7689                  | 85                           | -0.13                     |
| Standard dev. Frequency of emission [%] | 2665                  | 710                          | 0.95                      | 2920                  | 857                          | 1.37                      | 4146                  | 1220                         | 1.48                      |
| N                      | 714                   | 701                          | 701                       | 636                   | 580                          | 580                       | 612                   | 598                          | 598                       |

Note: $X_N$, $N_F$, and $V_d$ are the concentrations, fluxes, and deposition velocities, respectively.
Table 2. Summary of the concentrations and fluxes of selected VOCs (averages of 9 1-hr runs between cutting and fertilization and 5 1-hr runs after fertilization).

|                  | Concentration [ng m\(^{-3}\)] | Flux [ng m\(^{-2}\) s\(^{-1}\)] |
|------------------|---------------------------------|----------------------------------|
|                  | before                          | after fertilization              | Before                        | after fertilization |
| Benzaldehyde     | 5400 (±220)                    | 5700 (±430)                      | −140 (±69)                    | −250 (±61)          |
| Nonanal          | 590 (±22)                      | 650 (±73)                        | 14 (±8.0)                     | 7.6 (±16)           |
| α-Pinene         | 84 (±9.8)                      | 47 (±4.6)                        | 1.9 (±0.6)                    | 1.4 (±1.1)          |
| 1-β-Pinene       | 75 (±2.6)                      | 97 (±26)                         | −0.33 (±1.0)                  | 14 (±16)            |
| d-3-Carene       | 290 (±7.4)                     | 300 (±28)                        | −4.3 (±3.6)                   | 8.6 (±8.4)          |
Table 3. Summary of typical particle growth parameters for various 12-h periods.

| Period      | Day/ Night | \(F_N\) | \(A_p\) | \(dr/dt|_{dp=11nm}\) | \(J_{\text{NH}_4\text{NO}_3}\) | \(\Delta F_{\text{NH}_3}\) | \(F_{\text{NH}_3}\) |
|-------------|------------|---------|---------|----------------|-----------------|-----------------|----------------|
| 5 June      | Day        | 1789    | 293     | 2.18           | 0.95            | 0.112           | 597            |
| 5–6 June    | Night      | 178     | 320     | 1.42           | 0.34            | 0.040           | 1262           |
| 6 June      | Day        | 1102    | 115     | 5.73           | 0.79            | 0.094           | 887            |
| 6–7 June    | Night      | 54      | 266     | 0.50           | 0.17            | 0.020           | 1001           |
| 7 June      | Day        | 900     | 245     | 2.75           | 1.14            | 0.135           | 443            |
| 7–8 June    | Night      | 230     | 297     | 1.23           | 0.47            | 0.055           | 1311           |
| 8 June      | Day        | 1388    | 253     | 17.24          | 5.33            | 0.629           | 549            |
| 8–9 June    | Night      | 293     | 245     | 0.55           | 0.26            | 0.031           | 193            |
| 9 June      | Day        | 285     | 240     | 1.09           | 0.67            | 0.079           | 378            |
| 9–10 June   | Night      | 149     | 401     | 0.71           | 0.46            | 0.054           | 862            |
| 10 June     | Day        | 212     | 298     | 1.92           | 0.86            | 0.102           | 495            |
| 10–11 June  | Night      | –30     | 556     | –0.02          | –0.08           | –0.009          | 160            |
| 11 June     | Day        | 99      | 294     | 2.13           | 0.54            | 0.064           | 175            |
| 11–12 June  | Night      | 114     | 327     | 3.13           | 2.01            | 0.237           | 168            |
| 12 June     | Day        | –116    | 194     | –0.77          | –0.15           | –0.018          | 202            |
| 12–13 June  | Night      | –6      | 320     | 0.59           | 0.43            | 0.051           | 98             |
| 13 June     | Day        | 39      | 240     | –0.57          | –0.14           | –0.016          | 118            |
| 13–14 June  | Night      | –129    | 333     | –0.12          | –0.10           | –0.012          | 99             |
| Average     | Day        | 633     | 241     | 3.52           | 1.11            | 0.131           | 427            |
| Average     | Night      | 95      | 341     | 0.89           | 0.44            | 0.052           | 573            |

\(F_N\): measured particle number flux; \(A_p\): aerosol surface area per unit volume of air; \(dr/dt|_{dp=11nm}\): growth rate of 11 nm particles; \(J_{\text{NH}_4\text{NO}_3}\): estimated \(\text{NH}_4\text{NO}_3\) production rate; \(\Delta F_{\text{NH}_3}\): error on the \(\text{NH}_3\) flux measurement due to gas-particle reactions; \(F_{\text{NH}_3}\): measured \(\text{NH}_3\) flux.
### Table 4. Effects of gas-to-particle conversion on flux measurements and budget estimates of reactive nitrogen (excluding NO$_x$). Fluxes are in kg N ha$^{-1}$ for the period 5 to 15 June 2000; negative values represent deposition fluxes.

| Component      | Measurements, and parameterisations not corrected for chemistry | Corrected best estimate for surface | No chemistry scenario |
|----------------|---------------------------------------------------------------|------------------------------------|-----------------------|
| NH$_3$ gas     | 3.22                                                          | 3.22                               | <3.23$^{(a)}$         |
| HNO$_3$ gas    | −0.043                                                        | −0.042                             | −0.033$^{(b)}$        |
| NH$_4^+$ aerosol| −0.028                                                        | −0.029                             | −0.027$^{(b)}$        |
| NO$_3^-$ aerosol| −0.010                                                        | −0.011                             | −0.007$^{(b)}$        |
| Net N flux     | 3.14                                                          | 3.14                               | <3.20                 |

$^{(a)}$ Emission would be reduced due to larger air concentration (cf. text).

$^{(b)}$ Estimated from KAPS filter/denuder measurements over adjacent field.
Fig. 1. Time-series of the particle number concentration and fluxes of particles (condensation nuclei, CN) measured with the CPC flux system (11 nm to \( \approx 3 \mu m \)).
Fig. 2. Evolution of the gas concentrations of NH$_3$, HCl and HNO$_3$ 1 m and 47 m above the grassland, compared with the NH$_3$ concentration extrapolated to the canopy (NH$_3$(z$_0^\prime$)). See text for details. The fertilizer was applied on 5 June 08:00 to 10:00 GMT. Also indicated are the periods of the MOUDI impacter runs (B to D). The concentrations of NH$_3$ are based on the best estimate $\chi_{NH_3}$ and $F_{NH_3}$ provided by Milford et al. (2008).
Fig. 3. Time-series of \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) aerosol concentration measured above and upwind of the grassland in both mass concentration and equivalent concentration.
Fig. 4. Comparison of measured concentration products at 1 m height of (a) NH$_3$ with HNO$_3$ and (b) NH$_3$ with HCl, compared with concentration products in equilibrium with pure NH$_4$NO$_3$ and NH$_4$Cl aerosol, respectively.
Fig. 5. Time-series of the growth rate of 11 nm particles ($dr/dt$) as derived from CPC flux measurements and DMPS measurements, using Eqs. (5), (6) and (7).
Fig. 6. Time-series of the aerosol surface area and the Damköhler ratio ($D_r = \tau_t / \tau_c$). The dashed line represents the critical value of $D_r$, above which chemistry is expected to alter the vertical gradients.
Fig. 7. Time-series of the measured NH$_3$ flux and the NH$_3$ flux at the surface, corrected for the fraction of NH$_3$ converted to NH$_4^+$ (based on the best flux estimate provided by Milford et al., 2008).
Fig. 8. Averaged particle size-distributions during the three management periods.
Fig. 9. Time-evolution of the size of particles, with an initial radius ($r$) of 1 nm, for a range of vapour concentrations ($\chi_v$).
Fig. 10. Concentration, flux and deposition velocity ($V_d$) of HNO$_3$ measured with the SJAC/WAD gradient system, in relation to the maximum deposition velocity ($V_{\text{max}}$).
Fig. 11. Schematic of the proposed processes of emission, gas-particle conversion and deposition at the fertilised grassland site.