Biogeosciences Discuss., 6, 10663–10706, 2009
www.biogeosciences-discuss.net/6/10663/2009/

Biogeosciences
Discussions

Exchange of reactive nitrogen compounds: concentrations and fluxes of total ammonium and total nitrate above a spruce forest canopy

V. Wolff[1], **I. Trebs**[1], **T. Foken**[2], **and F. X. Meixner**[1,3]

[1]Max Planck Institute for Chemistry, Biogeochemistry Department, P.O. Box 3060, 55020 Mainz, Germany
[2]University of Bayreuth, Department of Micrometeorology, 95440 Bayreuth, Germany
[3]University of Zimbabwe, Department of Physics, P.O. Box MP 167, Harare, Zimbabwe

Received: 4 November 2009 – Accepted: 8 November 2009 – Published: 16 November 2009

Correspondence to: V. Wolff (veronika.wolff@mpic.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Total ammonium (tot-NH_4^+) and total nitrate (tot-NO_3^-) provide a chemically conservative quantity in the measurement of exchange processes of reactive nitrogen compounds ammonia (NH_3), particulate ammonium (NH_4^+), nitric acid (HNO_3), and particulate nitrate (NO_3^-), using the aerodynamic gradient method. Total fluxes were derived from concentration differences of total ammonium (NH_3 and NH_4^+) and total nitrate (HNO_3 and NO_3^-) measured at two levels. Gaseous species and related particulate compounds were measured selectively, simultaneously and continuously above a spruce forest canopy in south-eastern Germany in summer 2007. Measurements were performed using a wet-chemical two-point gradient instrument, the GRAEGOR. Median concentrations of NH_3, HNO_3, NH_4^+, and NO_3^- were 0.57, 0.12, 0.76, and 0.48 $\mu\,\mathrm{g\,m^{-3}}$, respectively. Total ammonium and total nitrate fluxes showed large variations depending on meteorological conditions, with concentrations close to zero under humid and cool conditions and higher concentrations under dry conditions. Mean fluxes of total ammonium and total nitrate in September 2007 were directed towards the forest canopy and were $-65.77\,\mathrm{ng\,m^{-2}\,s^{-1}}$ and $-41.02\,\mathrm{ng\,m^{-2}\,s^{-1}}$ (in terms of nitrogen), respectively. Their deposition was controlled by aerodynamic resistances only, with very little influence of surface resistances. Including measurements of wet deposition and findings of former studies at the study site on occult deposition (fog water interception), the total N deposition in September 2007 was estimated to 5.86 $\mathrm{kg\,ha^{-1}}$.

1 Introduction

Reactive nitrogen (N_r) compounds, comprising inorganic reduced forms of N (e.g., ammonia (NH_3) and ammonium (NH_4^+)), inorganic oxidized forms (e.g., nitrogen oxide (NO_x), nitric acid (HNO_3), nitrate (NO_3^-) and nitrous oxide (N_2O)) as well as organic compounds (e.g., urea, amines, proteins, and nucleic acids), play important roles in atmospheric chemistry and in ecosystem functioning. Since the 1960s N_r is accumulating in the environment due to (a) widespread cultivation of crops that are able to convert atmospheric nitrogen (N_2) into N_r, (b) combustion of fossil fuels and therefore conversion of fossil N and atmospheric N_2 into N_r and (c) the Haber-Bosch process, which enables humans to produce NH_3 from N_2 for food production (Galloway et al., 2003). Increased N_r deposition rates result in several negative effects, like a decrease in productivity, degradation of ecosystems, loss of biodiversity and leaching of nutrients into the groundwater (Gruber and Galloway, 2008).

Atmospheric wet and dry deposition is a major removal pathway of N_r from the atmosphere and constitutes a major input path into ecosystems. Wet deposition encompasses the processes which transfer airborne species to the Earth's surface in aqueous form, while dry deposition is the transport of gaseous and particulate species towards the surface in the absence of precipitation. Wet deposition estimates are derived from measurements of the amount of precipitation combined with the concentration analysis of dissolved substances in the rain water. A special component of wet deposition, which might be important in specific areas, is the occult deposition through the interception of fog water. Although the hydrological input may not be important in comparison to rain, the concentration of dissolved compounds may be significantly higher, thus being an important pollutant and nutrient input (Eugster, 2008; Klemm and Wrzesinsky, 2007; Zimmermann and Zimmermann, 2002). The measurement of deposition through fog is still challenging and rarely performed (Klemm and Wrzesinsky, 2007). The relative importance of the different deposition processes for a given chemical compound depends on whether the substance is present in gaseous or particulate form, its solubility in water, the amount of precipitation in the region and the terrain and land surface cover type (Seinfeld and Pandis, 1998; Erisman et al., 2005b; Foken, 2008).

Several methods exist to estimate bulk and dry N_r deposition loads. These are throughfall methods and micrometeorological methods to determine exchange fluxes of single N_r compounds or sums of those. Throughfall, often used in forestry studies (Lovett and Lindberg, 1984; Berger et al., 2008; Hovmand and Andersen, 1995), may be regarded as the sum of wet and dry deposition and canopy exchange, as throughfall is the sum of direct precipitation, wash off of formerly dry deposited material and exchange processes within the canopy (Lovett and Lindberg, 1984). Dry deposition estimates from throughfall measurements are very controversial, particularly for those species that potentially interact with the canopy (NH_4^+ and NO_3^-) (Lovett et al., 1996; Berger et al., 2009), but they are still often used as reasonable estimates (van Breemen and van Dijk, 1988). Micrometeorological methods, like the eddy covariance method have advantages such as the capability to directly measure the dry deposition flux, spatial representativeness and high temporal resolution. They do, however, have high demands to the study site, such as horizontal homogeneity and atmospheric stationarity. Moreover, eddy covariance measurements require fast sensors for the detection of chemical species (∼10 Hz). If such instruments are not available (e.g., for HNO_3), the aerodynamic gradient method is often applied, based on the flux-gradient-similarity theory (see below). Both, the eddy covariance as well as the aerodynamic gradient method demand high logistical and financial effort as well as sophisticated measurement techniques for the chemical species of interest (cf. Thomas et al., 2009). Since these prerequisites are often not available, dry deposition is frequently modelled using the inferential method, which is based on the "big leaf multiple resistance approach" (Hertel et al., 2006; Andersen and Hovmand, 1999; Wesely and Hicks, 2000). Typically, the concentration of the chemical specie is measured at a single level above the surface and the deposition process is described by resistances, i.e., the aerodynamic resistance (R_a) derived from micrometeorological quantities, the laminar boundary layer resistance (R_b), dependent on the individual species of interest, and the surface resistance (R_c) (or its concentration analogue the canopy compensation point (C_0), for example for NH_3; Farquhar et al., 1980). The surface resistance is often described by several resistances in series and in parallel, e.g. the cuticular, stomata and soil surface resistances. While R_a and R_b can be calculated from measured micrometeorological quantities, surface related parameters like R_c or C_0 are derived using empirical parameterizations or are deduced from other studies (cf. Nemitz et al., 2004a; Trebs et al., 2006; Sutton et al., 2000). However, parameterisations of the individual resistances are mostly derived for flat homogeneous terrain and low vegetation and may not be adequate for complex sites, like highly structured, hilly, or forested sites (Hertel et al., 2006; Wesely and Hicks, 2000; Andersen and Hovmand, 1999). Additionally, parameterizations of surface related parameters are only valid for certain temperature and humidity ranges, fertilisation state and vegetation types (cf. Farquhar et al., 1980) and may not always be applied for other ecosystems. The dry deposition of particles, such as particulate NH_4^+ and NO_3^- is typically very different to the dry deposition of gaseous species (Nemitz et al., 2004a). Generally, deposition velocities depend on aerosol particle size and roughness of the underlying surface and they are about one order of magnitude smaller than those of gaseous compounds (Gallagher et al., 1997, 2002).

From all N_r compounds, NH_3 and HNO_3 and their particulate counterparts NH_4^+ and NO_3^- are regarded as in the main contributors to atmospheric N_r deposition (Andersen and Hovmand, 1999). NH_3 is emitted primarily by agricultural activities, such as volatilization from animal waste and synthetic fertilizers, but also from biomass burning, losses from soils, and fossil fuel combustion (Krupa, 2003). It is an important base constituent in the atmosphere, and neutralises acids, such as sulphuric and nitric acid (HNO_3) and hydrochloric acid, forming ammonium (NH_4^+) salts, whose major portion is present in the fine particle fraction (Finlayson-Pitts and Pitts, 1999). High concentrations of NH_3 are usually found close to sources since it is either effectively dry deposited close to its source and/or rapidly converted to NH_4^+ (Ferm, 1998). Particulate NH_4^+ is deposited less quickly and may thus be transported over larger distances. HNO_3 is produced from the oxidation of nitrogen oxides (NO_x), which are emitted primarily by anthropogenic activities, such as fossil fuel burning. Natural sources are biogenic emissions of nitric oxide (NO) from soils and lightning. The polar and very water soluble HNO_3 is removed quickly from the atmosphere, either by dry and wet deposition or by gas-to-particle conversion. This leads to comparatively short atmospheric lifetimes of about 1 day (Huebert and Robert, 1985). Particulate NO_3^- is formed by the reaction of HNO_3 with atmospheric base compounds, such as NH_3 and also crustal material such as sodium and calcium, and is found in different size ranges of particles, in the accommodation and in the coarse mode (Seinfeld and Pandis, 1998). Particulate NH_4^+ and NO_3^- form the majority of the long-range transported N_r in the atmosphere (Hertel et al., 2006).

NH_3, HNO_3 and NH_4NO_3 form a thermodynamic equilibrium between the gaseous species (NH_3, HNO_3) and particulate NH_4NO_3 (in solid or in aqueous form), which is a function of temperature (T) and relative humidity (RH) (Mozurkewich, 1993; Stelson and Seinfeld, 1982):

$$NH_{3(\text{gaseous})} + HNO_{3(\text{gaseous})} \xleftrightarrow{T,\text{RH}} NH_4NO_{3(\text{solid/aqueous})} \tag{R1}$$

Additionally, the equilibrium of React. (R1) depends on the chemical composition of aerosol particles, especially on concentrations of those ions that are competing with NO_3^- for the NH_4^+, such as SO_4^{2-} and Cl^- (Wexler and Seinfeld, 1990).

The application of the flux-gradient-similarity theory (see below) presumes that vertical fluxes of the measured compounds are constant with height within the atmospheric surface layer (Dyer and Hicks, 1970), which implies that they are considered chemically non-reactive tracers (e.g., Trebs et al., 2006). Phase changes due to shifts of the thermodynamic equilibrium between gaseous and particulate species (as a result of fluctuations in T and RH) may, however, induce a chemical flux divergence of NH_3, HNO_3, NH_4^+ and/or NO_3^-. Without correcting for these effects, dry deposition estimates derived from gradient measurements may substantially under- or overestimate the actual turbulent flux (Nemitz and Sutton, 2004; Nemitz et al., 2004a). The sum of both phases, total ammonium (tot-NH_4^+) and total nitrate (tot-NO_3^-), are, however, conservative quantities in this respect (Kramm and Dlugi, 1994; Brost et al., 1988). While, for the quantification of the N_r input in an ecosystem like in this study, the partitioning among gas and particulate phase is of minor importance, measurements of exchange fluxes of individual compounds (NH_3, HNO_3, NH_4^+ and NO_3^-) are a prerequisite for investigating near-surface mechanistic processes required for atmospheric chemistry and transport models.

In this paper we will present measurements of concentrations of ammonia (NH_3), nitric acid (HNO_3), particulate ammonium (NH_4^+) and nitrate (NO_3^-), and their sums total ammonium (tot-NH_4^+) and total nitrate (tot-NO_3^-) above a spruce forest canopy in southeast Germany in summer 2007. We focus on flux determinations of the conservative quantities (tot-NH_4^+ and tot-NO_3^-), thereby avoiding the potential impact of gas-particle interactions and chemical flux divergences. Using measurements of wet deposition and estimations on occult deposition, we estimate a total N_r deposition rate for September 2007. In a subsequent paper, we will investigate chemical gas-particle conversion processes and the corresponding potential influence on fluxes of individual N_r compounds.

2 Experimental

2.1 Weidenbrunnen research site

The experiment was conducted in summer/autumn 2007 (25 August–03 October) within the framework of the project EGER (ExchanGE processes in mountainous Regions) at the research site "Weidenbrunnen" (50°08′ N, 11°52′ E; 774 m a.s.l.), a Norway spruce forest site located in a mountainous region in south east Germany (Fichtelgebirge). The surrounding mountainous area extends approx. 1000 km^2 and is covered mainly with forest, but also some agricultural land, meadows and lakes. Continuous air quality measurements indicate that the site is characterized as a rural site of Central Europe (Klemm and Lange, 1999). It is located in the transition zone from maritime to continental climates with annual average temperatures of 5.0°C (1971–2000; Foken, 2003) and average annual precipitation sum of 1162.5 mm (1971–2000; Foken, 2003). The study site is maintained for more than 10 years by the University of Bayreuth and a variety of studies have been conducted there (Falge et al., 2005; Held and Klemm, 2006; Klemm et al., 2006; Rebmann et al., 2005; Thomas and Foken, 2007; Wichura et al., 2004). The stand age of the Norway spruce (Picea abies) was approx. 54 years (according to Alsheimer, 1997), the mean canopy height was estimated to be

23 m (Staudt, 2007), and the single sided leaf area index during the measurement campaign was approximately 5.3. Measurements were performed on a 31 m walk-up tower. For the Weidenbrunnen site, Thomas and Foken (2007) determined the roughness parameters displacement height (d) and roughness length (z_0) as 14 m and 2 m, respectively.

2.2 Aerodynamic gradient method

The aerodynamic gradient method (AGM) is based on the gradient-flux similarity and derives fluxes from measured vertical concentration differences and micrometeorological exchange parameters (Ammann, 1998; Foken, 2008). The flux, F, is calculated as the product of a turbulent diffusion transfer coefficient, expressing mechanically and thermally induced turbulence, and the vertical concentration difference, ΔC.

$$F = -\underbrace{\frac{u_* \cdot \kappa}{\ln\left(\frac{z_2}{z_1}\right) + \Psi_H\left(\frac{z_2}{L}\right) - \Psi_H\left(\frac{z_1}{L}\right)}}_{v_{\text{tr}}} \cdot \Delta C\,, \tag{1}$$

where u_* is the friction velocity (m s^{-1}), κ the von Kármán constant (0.4), Ψ_H the integrated stability correction function for sensible heat (considered equal to that of trace compounds), and z/L is height z over the Obukhov length L, a measure of atmospheric stability. The first term in the product on the right hand site of the equation is often referred to as the transfer velocity, v_{tr} (m s^{-1}). It represents the inverse resistance of the turbulent transport between the two heights z_1 and z_2 (Ammann, 1998). Note here, that we use all measurement heights z_1, z_2, and z, as aerodynamic heights above the zero plane displacement height, d. Equation (1) is strictly valid only for "smooth" surfaces (e.g. pastures, meadows). However, when using this relationship close to a canopy to infer fluxes from measured vertical concentration gradients, corresponding fluxes have been found to be underestimated (Thom et al., 1975; Garratt, 1978; Hogstrom et al., 1989). Nevertheless, the flux-gradient relationship was found to hold above forest canopies, introducing a so-called enhancement factor into the left hand term of the right hand side of Eq. (1) (e.g., Simpson et al., 1998). However, as we have made use of directly measured u_*, measured by an eddy covariance system (at 31 m height), it is not necessary to consider roughness sublayer enhancement factors in our evaluations (Garratt, 1992).

An underlying assumption of the AGM is that the flux to or away from the reference surface (e.g., canopy top) is identical to the vertical flux measured at a reference level in some distance above the surface (see above). This assumption may not hold due to chemical reactions occurring within the air layer between the surface and the reference height (Fowler and Duyzer, 1989; Meixner, 1993). For the determination of total ammonium and total nitrate this is not of relevance, but does affect flux determination of individual gaseous and/or particulate compounds (NH_3, HNO_3, NH_4^+, NO_3^-) as phase changes may lead to flux divergence (e.g., Nemitz et al., 2004a; Brost et al., 1988; Huebert et al., 1988). However, as long as the characteristic time scale of chemical transformation is large in comparison to the turbulent timescale, fluxes of compounds that underlie rapid chemical transformation may be determined with sufficient accuracy (De Arellano and Duynkerke, 1992; Nemitz et al., 2004b). Photochemical reactions involving NH_3 and HNO_3 are slow compared to turbulence; however, timescales of phase changes within the NH_3-HNO_3-NH_4NO_3 triad (see React. R1), may be comparable to characteristic times of turbulent transport (Trebs et al., 2006). The turbulent timescales are estimated according to Mayer (2008). The timescales to achieve thermodynamic equilibrium between gas and aerosol phase of the NH_3-HNO_3-NH_4NO_3 triad can be approximated as a function of the aerosol particle surface available for the equilibrium reaction (Wexler and Seinfeld, 1990, 1992).

2.3 The GRadient of AErosol and Gases Online Registrator (GRAEGOR)

The GRAEGOR is a wet chemical instrument for semi-continuous two-point gradient measurements of water-soluble reactive trace gas species (NH_3, HNO_3, HONO, HCl, and SO_2) and their related particulate compounds (NH_4^+, NO_3^-, Cl^-, SO_4^{2-}) (Thomas et al., 2009). GRAEGOR collects the gas and particulate samples simultaneously at two heights (for EGER: 24.4 m and 30.9 m) using horizontally aligned wet-annular rotating denuders and steam-jet aerosol collectors (SJAC), respectively. Air is simultaneously drawn through GRAEGOR's sample boxes, passing first the wet-annular rotating denuders, where water-soluble gases diffuse from a laminar air stream into the sample liquid. In both SJACs, the sample air (now containing only the aerosol particles) is then mixed with water vapour from double-deionized water and the supersaturation causes particles to grow rapidly (within 0.1 s) into droplets of at least 2 μm diameter. These droplets, containing the dissolved particulate species are then collected in a cyclone (cf. Slanina et al., 2001). The airflow through the two sample boxes is ~14 L min^{-1} (at STP=0°C and 1013.25 hPa) per box and is kept constant through a critical orifice downstream of the SJAC. The inlets of the sample boxes, directly connected to the wet-annular rotating denuders, consisted of PFA (perflouroalkoxy) Teflon tubing (I.D.=0.8cm, length=20cm), ended upstream in a home-made PFA Teflon rain protection, and were covered by a PFA gauze. Liquid samples (from both denuders and SJACs) are analyzed online using ion chromatography for anions and by flow injection analysis for NH_4^+. GRAEGOR provides one half-hourly averaged gas and particulate concentrations for each height for each species within each hour (cf. Thomas et al., 2009). The analytical performance of the instrument is continuously checked using an internal bromide standard that is added to each sample. Calibrations of the ion chromatograph using Merck certiPUR® standard solutions were performed twice, 6–7 September and 26 September. The FIA detector was calibrated weekly. The limit of detection (LOD) for the individual species was determined from in-field blanks once a week (for details see Wolff et al., 2009). The errors of the air concentrations of NH_3, HNO_3, particulate NH_4^+, and particulate NO_3^- were calculated according to Trebs et al. (2004) and Thomas et al. (2009) using Gaussian error propagation. The precision of the measured concentration differences ($\sigma_{\Delta C}/C$) was investigated by extended side-by-side measurements in the beginning and at the end of the experiment (Wolff et al., 2009).

2.4 Supporting measurements

Vertical profiles of meteorological parameters, such as ambient temperature (T), relative humidity (RH), and wind speed were measured at the tower (31 m high) at three heights above the canopy (at z=24.4, 26.6, and 30.9 m (T, RH, using psychrometers (fine-wire thermocouples, custom build)) and z=24.3, 26.2 and, 31.2 m (wind speed, 3 cup anemometer (A100ML, Vector Instruments, UK))). On top of the tower (z=32 m), an eddy covariance system (Gill R2 sonic anemometer in combination with a LI-COR-7000) measured three-dimensional wind speed, wind direction, friction velocity, stability, latent, sensible heat and CO_2 fluxes. Atmospheric visibility using a present weather detector (PWD 11, Vaisala), global irradiance (pyranometer CM14, Kipp & Zonen B.V.) and wind direction (potentiometric wind vane, Vector Instruments) were also measured on top of the tower at 32 m height. Aerosol number size distributions were measured at 28 m height at the tower using a SMPS (Scanning Mobility Particle Sizer, Grimm).

At a nearby clearing (distance to tower ~250m), a wet-only rainwater collector (NSA 181/KHS Eigenbrodt, 2007) was operated. During the field study, samples were collected event-based and stored cool until analysis (Bayerische Landesamt für Umwelt, Augsburg, ion chromatography). In September a total of six rain samples were analysed for chloride, nitrite, nitrate, phosphate, sulphate, sodium, ammonium, potassium, magnesium, and calcium.

3 Results

3.1 Meteorological conditions

Meteorological quantities, such as RH, T, wind speed ($\mathrm{m\,s^{-1}}$), wind direction (°), rain (mm), visibility (m) and global radiation ($\mathrm{W\,m^{-2}}$) for the month of September in 2007 are summarized in Fig. 1. Two episodes with several consecutive sunny days are in contrast to prevailing humid, foggy conditions with frequent rain and reduced visibility. During fog and rain, the temperature amplitude was reduced and temperatures ranged between below 5 and 15°C, while RH almost always remained above 70–80%. During the sunny episodes (12–17 September and 19–24 September) temperatures show a diel variation with increasing temperatures from day to day (up to more than 20°C). During these days, RH dropped to below 70% during daytime. The wind speed was generally quite high with a median of $2.8\,\mathrm{m\,s^{-1}}$, ranging between 2 and $4\,\mathrm{m\,s^{-1}}$ (inter quartile range). During the first half of September (foggy conditions), the wind blew frequently from northerly directions, turning towards south westerly directions afterwards.

3.2 Detection limits, precision and mean concentrations

To facilitate comparison between the concentrations and fluxes of the different nitrogen containing compounds all numbers are given in terms of nitrogen[1]. In this paper we focus on the measurements made in September 2007. Until the 26 September we measured concentrations at two levels, and after that concentration measurements at one level are available (side-by-side measurements, see Wolff et al., 2009). Determined LOD values (3σ-definition) were $0.017\,\mu\mathrm{g m^{3}}$ for NH_3 and particulate NH_4^+, and $0.029\,\mu\,\mathrm{g\,m^{-3}}$ for HNO_3 and particulate NO_3^-, respectively (see Wolff et al., 2009). Less than 1% of the total NH_3 concentrations were below the detection limit, less than 2% of the total particulate NH_4^+ concentrations, but 30% of the HNO_3 concentrations and 8% of the particulate NO_3^- concentrations were below corresponding detection limits. Below LOD concentrations were predominantly measured during rainy periods. For tot-NH_4^+ and for tot-NO_3^- the precision was found to be 5.3% and 4.8%, respectively. The median error of the concentration difference ($\sigma_{\Delta C}/\Delta C$) was found to be 52.1% and

---

[1] All concentrations and fluxes are given in $\mu\,\mathrm{g\,m^{-3}}$ in terms of N. To convert these to $\mu\,\mathrm{g\,m^{-3}}$ they must be multiplied with the ratio of the molar masses, i.e. for NH_3:1.216, for NH_4^+ (and tot-NH_4^+):1.288, for HNO_3:4.499 and NO_3^- (and tot-NO_3^-):4.427.

37.9%. Measured concentration differences larger than the precision were considered to be significant and subsequently used for flux calculations, while those below the precision were determined to be insignificantly different from zero. For tot-NH_4^+, 55% of the 443 total measured concentration differences were found to be significant, for tot-NO_3^-, 77% of the 373 total concentration differences were significant. From the error of the concentration difference, the flux error is derived in combination with an estimated error of v_{tr} of around 10% (see Wolff et al., 2009). For the period 1–30 September 2007 the concentration data coverage was around 75%. Data gaps are due to in-field blank determination, calibration, instrument failure, bad or noisy chromatograms; poor de-ionized water quality as well as air and liquid flow instability (cf. Wolff et al., 2009). Statistical distributions of NH_3 and particulate NH_4^+ concentrations as well as of HNO_3 and particulate NO_3^- concentrations are presented in Table 1. NH_3 concentrations ranged between 0.25 and 1.00 $\mu g\,m^{-3}$ (inter quartile range), with the median (0.57 $\mu g m^{-3}$) being only slightly smaller than the one of particulate NH_4^+ of 0.76 $\mu g\,m^{-3}$ (inter quartile range between 0.32 and 1.39 $\mu g m^{-3}$). HNO_3 varied between 0.05 and 0.28 $\mu g\,m^{-3}$ (median: 0.12 $\mu g\,m^{-3}$), while the particulate counterpart, NO_3^- was three to six times larger, varying between 0.18 and 0.80 $\mu g\,m^{-3}$ (inter quartile range; median: 0.48 $\mu g\,m^{-3}$). Concentrations varied with meteorological conditions and were generally higher during periods with higher temperatures and lower RH and reached their minimum in rainy periods. During the sunny and drier days (Fig. 1, white bars) the overall data coverage and the percentage of significant concentration differences were higher. High RHs, rain and fog droplets may cause problems with losses in the inlet lines (Wolff et al., 2009). Thus, our investigation of dry deposition and exchange processes of tot-NH_4^+ and tot-NO_3^- will focus on the two sunny and dry episodes.

3.3 Diel variations

The diel variations of gaseous NH_3 and HNO_3 and their particulate counterparts NH_4^+ and NO_3^- are determined by production and loss (e.g., chemical production, dry deposition and phase partitioning), as well as horizontal and vertical transport within the planetary boundary layer. NH_3 and particulate NH_4^+ share the same concentration range during the study and reveal a regular pattern of higher particle concentrations at night and higher gas phase concentrations during daytime, especially during the drier and sunnier episodes (cf. Fig. 2a, especially 22–25 September). HNO_3 and particulate NO_3^- concentrations are very different, with particle concentrations of up to four times higher than gas phase concentrations (note different scales of the *y*-axes in Fig. 2b). Generally, HNO_3 and particulate NO_3^- concentrations also follow the pattern of high nighttime particle concentrations and high daytime gas phase concentrations. In the time series of tot-NH_4^+ and tot-NO_3^- (Fig. 2c) the effect of gas-particle interactions is removed. Their concentrations, however, still vary with time, reflecting meteorological conditions, with low values during rainy and foggy conditions and higher concentrations during the sunnier episodes (cf. Fig. 1). This difference between fair weather conditions and rainy/foggy episodes is more pronounced for tot-NO_3^-, reflecting to some extent the fact that production is linked with photochemical processes (oxidation of NO_2 with OH to HNO_3). Tot-NH_4^+ shows a regular pattern of higher concentrations towards the afternoons, while in the time series of tot-NO_3^- such a pattern can not be identified.

3.4 Timescale analysis

The diel variations of NH_3, HNO_3, NH_4^+ and NO_3^- were most likely influenced by changes of T and RH (see Figs. 1 and 2) and subsequent changes of the thermodynamic equilibrium (React. R1) between gaseous and particulate phase. To estimate the effect of the system striving towards equilibrium on the determination of exchange fluxes, we performed a timescale analysis for the time of available aerosol particle size distribution measurements (Wexler and Seinfeld, 1990, 1992). The Damköhler ratio (Fig. 3), the ratio of characteristic turbulent timescales to equilibration timescales ($Da=\tau_{turb}/\tau_{equi}$), is a measure of the degree to which chemical conversion may affect the determination of exchange fluxes by micrometeorological methods (Foken et al., 1995). Assuming that all surfaces of the particles take part in the equilibrium reaction (black line in Fig. 3), Da often approaches and exceeds unity (10^0), especially during nighttime. For a smaller fraction of the aerosol particle surface taking part (e.g., 10% red line in Fig. 3), turbulent transport would be fast enough to exclude the influence of chemical divergence affecting the concentration gradients, at least during daytime ($Da<0.1$). Consequently, for flux measurements of individual N_r compounds of the NH_3-HNO_3-NH_4NO_3 triad, the gas-particle partitioning processes need to be considered. In this paper, focusing on the total dry deposition of ammonium and nitrate, we confine ourselves to the derivation of fluxes of the conservative sums of gaseous and particulate phase, tot-NH_4^+ and tot-NO_3^-. As stated above, chemical divergences and single compound fluxes will be investigated in a subsequent publication.

3.5 Fluxes and deposition velocities

Due to the high roughness of the forest, the transfer velocity was quite large with $0.45\pm0.25\,\mathrm{m\,s^{-1}}$. Maximum transfer velocities of $0.70\pm0.18\,\mathrm{m\,s^{-1}}$ were found at noon, while during nighttime minimum values were $0.25\pm0.22\,\mathrm{m\,s^{-1}}$. From the measured concentrations at two levels above the forest canopy, we calculated the fluxes for total ammonium and total nitrate. In September, concentration measurements at two levels were available until the morning of the 26th. Fluxes varied significantly according to the prevailing meteorological conditions (see Fig. 4). Fluxes of tot-NH_4^+ were generally smaller during fog and humid conditions and showed emission events from wet or drying surfaces and large deposition fluxes during the sunny days. Fluxes of tot-NO_3^- were always directed downward, but were significantly larger during the sunny episodes, while being almost zero under cooler and foggy conditions. Maximum daytime deposition fluxes of tot-NH_4^+ ranged between -200 and $-500\,\mathrm{ng\,m^{-2}\,s^{-1}}$. Deposition fluxes of tot-NO_3^- were about half of those of tot-NH_4^+, with the midday maximum ranging between -100 and $-260\,\mathrm{ng\,m^{-2}\,s^{-1}}$. Median flux errors for tot-NH_4^+ and tot-NO_3^- fluxes were 50% and 44%, respectively (see Wolff et al., 2009). Median deposition velocities[2] (or normalised fluxes; v_d=flux/concentration) calculated for the geometric mean of the measurement heights (13.3 m above displacement height) were 3.4 cm s^{-1} for tot-NH_4^+ and 4.2 cm s^{-1} for tot-NO_3^-. Especially during the sunny episodes, both v_d, of tot-NH_4^+ and tot-NO_3^-, follow closely the inverse of the aerodynamic resistance ($1/R_a$), which provides a measure of the maximum possible v_d. The median diel variations of v_d with inter quartile ranges for tot-NH_4^+ and tot-NO_3^- in September 2007 are shown in Fig. 5. Nighttime median v_d values are in the range of 0.6 to 1.4 cm s^{-1} for tot-NH_4^+ and 0.7 and 2.4 cm s^{-1} for tot-NO_3^-. At around 08:00 h v_d increases rapidly to maxima of around 10–12 cm s^{-1} for tot-NH_4^+ and to 8–12 cm s^{-1} for tot-NO_3^-. The diel course of v_d is skewed somewhat towards the early afternoon; the maximum is reached at around 14:00 LT (tot-NH_4^+) and 15:00 LT (tot-NO_3^-). Afterwards, v_d drops again, reaching the lower nighttime values at around 18:00h/19:00 LT. Median v_d values for both, tot-NH_4^+ and tot-NO_3^-, remain below the aerodynamically maximum possible value, indicated as $1/R_a$.

3.6 Total N deposition in September 2007

Major constituents of dry N_r deposition are particulate NH_4^+ and NO_3^- and gaseous compounds NH_3, HNO_3 and to a minor extent also nitrogen dioxide (NO_2), nitrous acid (HONO), peroxyacetyl nitrate (PAN), and nitric oxide (NO) (Andersen and Hovmand, 1999). Surface-atmosphere exchange fluxes of NO and NO_2 measured by eddy covariance at our site were found to be one order of magnitude lower than the fluxes of tot-NH_4^+ and tot-NO_3^- (Tsokankunku et al., 2009). The daytime NO flux was directed downward to the forest canopy with –5 to –7 ng m^{-2} s^{-2} (in terms of N, inter quartile

---

[2] Note here that the use of the term "deposition velocity" may be a controversial issue for species that feature bi-directional exchange such as NH_3 and thus also tot-NH_4^+. However, the use of a normalised flux, termed as "deposition velocity", may be useful for comparison with the aerodynamic upper limit of transport, the inverse of the aerodynamic resistance.

range) and the daytime NO_2 flux was directed upward with about 14 to 28 $ng\,m^{-2}\,s^{-2}$ (inter quartile range). The directions of NO and NO_2 fluxes are in contrast to what would be expected for low vegetation (Delany and Lenschow, 1987), however they are mainly due to chemically induced flux divergence (Meixner, 1993). Concentrations of HONO were in the order of 0.03 to 0.09 $\mu g\,m^{-3}$ (inter quartile range), and concentrations of PAN were not measured at the site. Hence, the high importance of tot-NH_4^+ and tot-NO_3^- in N_r deposition generally recognized (Erisman and Draaijers, 2003; Erisman et al., 2003, 2005a, 2007; Andersen and Hovmand, 1999; Asman et al., 1998; Galloway et al., 2008; Sutton et al., 2007) is confirmed by our study. Median diel tot-NH_4^+ and tot-NO_3^- dry deposition fluxes for September 2007 are presented in Fig. 6. Fluxes were larger during daytime, median tot-NH_4^+ fluxes reached $-197\,ng\,m^{-2}\,s^{-1}$, while median tot-NO_3^- fluxes reached $-134\,ng\,m^{-2}\,s^{-1}$. Median nighttime values were around zero to $-40\,ng\,m^{-2}\,s^{-1}$ for tot-NH_4^+ and -7 to $-20\,ng\,m^{-2}\,s^{-1}$ for tot-NO_3^-. The dry deposition for the whole month of September was estimated from the median diel deposition (tot-NH_4^+:5.68 $mg\,m^{-2}\,d^{-1}$ and tot-NO_3^-:3.54 $mg\,m^{-2}\,d^{-1}$) multiplied by the number of days in September (30). This method was used because we do not have uninterrupted flux measurements, especially under foggy and rainy conditions, when the instrument worked less reliable (see above and Wolff et al., 2009). Flux values derived from non-significant concentration differences were also included in the calculation, as these were usually close to zero and had thus a significant influence on the median. Estimated dry deposition of tot-NH_4^+ and tot-NO_3^- were 1.70 $kg\,ha^{-1}$ and 1.06 $kg\,ha^{-1}$, respectively. If we excluded the insignificant flux values, the deposition for the month of September would be overestimated by 38% in the case of tot-NH_4^+ and by 28% in the case of tot-NO_3^-.

Wet deposition was calculated from analysed samples taken at the nearby clearing from six rain events in September 2007 (cf. Fig. 1). In most of the rain samples NH_4^+ was dominating over NO_3^- (Fig. 7), with concentrations being about one third larger. In the rain storm after the six days of sun (19–25 September), NO_3^- concentrations were higher, which was also the case in the end of September. In September 2007 wet NH_4^+ deposition was 0.88 kg ha^{-1} and NO_3^- to 0.67 kg ha^{-1}, their sum yielding 1.55 kg ha^{-1}.

In both, wet and dry deposition, NH_4^+ dominated over NO_3^-, NO_3^- deposition being roughly two thirds of the NH_4^+ deposition. The dry deposition was almost twice the amount of the wet deposition. The total N deposition due to dry and wet deposition of tot-NH_4^+ and tot-NO_3^- yielded 4.31 kg ha^{-1} (with 64% due to dry deposition and 36% due to wet deposition) in September 2007.

4 Discussion

4.1 Fluxes and deposition velocities

Concentrations levels of gaseous NH_3 and HNO_3 and particulate NH_4^+ and NO_3^-, observed in our study (Fig. 2) are comparable to previous observations at the Weidenbrunnen site (Held et al., 2002). Also the dominance of the particulate phase over the respective gas phase was observed by Held et al. (2002).

Flux values and values of v_d derived in this study are relatively large. There are indications that the exchange of reactive species at our site is not limited by any surface resistance. In summer 2001 exchange fluxes of hydrogen peroxide (H_2O_2) were determined at our site using a relaxed eddy accumulation technique (Valverde-Canossa et al., 2006). The characteristics of H_2O_2 are comparable to HNO_3, as it is produced above the canopy in the gas phase (mainly by recombination of two HO_2 radicals) with sinks in the particulate phase and efficient dry deposition to surfaces due to its high solubility and reactivity (Hall et al., 1999; Walcek, 1987). A modelling analysis indicated that H_2O_2 exchange was largely controlled by turbulent transport to and into the canopy, and also by the supply from above where chemical production occurs (Ganzeveld et al., 2006). Measured daytime v_d of H_2O_2 were 5±2cms^{-1} (Valverde-Canossa et al., 2006).

Most previous studies derived fluxes of individual N_r compounds only or derived total fluxes using the inferential method that is constrained by required parameterizations of surface related exchange parameters (see Sect. 1).We found only one study (Sievering et al., 1994) that reported directly measured tot-NO_3^- fluxes (using the AGM) and v_d above the forest. They found evidence for large deposition rates of tot-NO_3^- above a predominately spruce forest (Bayrischer Wald) in Germany (approx. 250 km SE from our site). They measured concentrations of particulate NH_4^+, NO_3^- and gaseous NH_3 and HNO_3 at two levels, using filter packs. Tot-NO_3^- concentrations were about half of our observed values, ranging between 0.34 and 0.68 μg m^{-3}. Particulate NO_3^- contributed 15–20% to the tot-NO_3^-. The found diel tot-NO_3^- flux ranged from 0.7 to 5.2 mgm^{-2}s^{-1}, which is very similar to what we found. The observed geometric median mass diameters of NO_3^- and NH_4^+ were 2.24±0.85μm and <0.9μm, respectively. For these particle diameters, Peters and Eiden (1992) modelled possible v_d 2–8 cms^{-1} for the particulate NO_3^- dry deposition at the Bayrische Wald site. Values of tot-NO_3^- v_d derived by Sievering et al. (1994) were in the range of 2–9 cms^{-1}, being approximately equal for HNO_3 and NO_3^-. Due to large uncertainties in particulate NH_4^+ measurement, they could not determine exchange fluxes and/or v_d for tot-NH_4^+. Since the particulate phase dominated our measured concentrations (see Sect. 3.2) we presume that they also dominate the deposition fluxes, at least in tot-NO_3^-. Aerosol particle fluxes and v_d depend on particle diameter, atmospheric conditions (friction velocity and stability) and surface conditions, such as roughness and canopy morphology (Erisman et al., 1997; Gallagher et al., 1997; Peters and Eiden, 1992; Fowler et al., 2009). Reported v_d range from some mms^{-1} for small particles (<1 μm) and for low wind speeds to more than 10 cms^{-1} for larger particles (>10μm) and high wind speeds. The high roughness and the large surface of the needles of the spruce forest at our site combined with the aerodynamic regime of high friction velocities (inter quartile range 0.32–0.63 m s^{-1}) partly explain the finding of large aerosol particle v_d (Fowler et al., 2009). Furthermore, the 50% theoretical particle cut-off diameters of the GRAEGOR due to inlet design and denuder airflow regime is 0.2 nm and 18 µm (Thomas et al., 2009). According to Peters and Eiden (1992) v_d for aerosol particles captured by the GRAEGOR at typical wind speeds at our site (2–4 m s^{-1}) may have varied between 0.08 and more than 10 cm s^{-1}. Measurements at the Weidenbrunnen site by Held et al. (2002) revealed consistent patterns in the size distributions of particulate NH_4^+ and NO_3^-, with the former one dominating the fine particle concentrations (mean particle diameter of 0.25 and 0.71 µm), and the latter dominating the coarse particles ranges (mean particle diameter of 0.71 and 2 µm). For particles with mean diameters of 0.25, 0.71 and 2 µm, v_d at the encountered wind speeds would theoretically range between 0.01–0.6, 0.01–1.08, and 0.06–3.5 cm s^{-1}, respectively (Peters and Eiden, 1992). According to Gallagher et al. (1997) these values would be 0.05–1, 0.03–2, and 0.11–0.8 cm s^{-1}. Thus, another possible explanation for the large v_d found in our study (Sect. 3.5 and Fig. 5), could be the presence of large (≥10 µm) NH_4^+ and NO_3^- containing particles.

Deposition velocities of NH_4^+ and NO_3^- (derived from eddy covariance measurements) larger than those of SO_4^{2-} and those derived from particle number flux measurements have been reported (Nemitz et al., 2004b; Thomas, 2007). These were explained by changes in the thermodynamic equilibrium towards the more rapidly depositing gaseous species between the measurement height and the vegetated surface (Fowler et al., 2009). The quick removal processes of NH_3 and HNO_3 just above and within the canopy together with warm surface temperatures would favour aerosol evaporation, consequently enhancing total deposition of both, particulate and gaseous phase. We observed highest v_d during daytime of the sunny episodes during our measurement period. During these times, temperature was highest at the canopy top. Although using the chemically conservative quantities of tot-NH_4^+ and tot-NO_3^-, the derived total deposition fluxes were probably influenced by this additional sink, resembling thus more v_d of gaseous species than those of particles. Assuming such a mechanism we can follow up reports which claimed the importance of particulate N species in N deposition estimates and the use of effective deposition velocity parameterisations for highly volatile aerosol compounds rather than using parameterisations regardless of the particulates' chemical composition (Erisman et al., 1995, 1997; Fowler et al., 2009).

4.2 Deposition of reactive nitrogen

Wet deposition rates of NH_4^+ and NO_3^- measured previously in summer 2001 at the Weidenbrunnen site were very similar to ours, with September sums being 0.906 kg ha^{-1} NH_4^+ and 0.835 kg ha^{-1} NO_3^- (see Klemm and Wrzesinsky, 2007). In order to determine the total nitrogen deposition at our site we also have to take into account the occult deposition through the interception of fog water. The Weidenbrunnen research site shows a high frequency of fog events throughout the year and throughout our measurement campaign (see meteorological conditions, Fig. 1). Several studies on fog meteorology and chemistry have been conducted at that site (Klemm and Wrzesinsky, 2007; Wrzesinsky and Klemm, 2000), in which the importance of the so called occult deposition was stressed. For a study between April 2001 and March 2002, most fog events were found to be associated with clouds being advected from westerly directions, intercepting with the forest vegetation of the site as it is located on a mountain range of about 1000 m a.s.l. (Klemm and Wrzesinsky, 2007). The most important ionic constituents of fog water were found to be NH_4^+, NO_3^- and SO_4^{2-}. These three ions were significantly enriched in the fog water compared to the rain water samples (ratios fog/rain concentrations 18.1, 12.7 and 11.8, respectively), which led to the conclusion that during the study of April 2001 and March 2002 the occult deposition of NH_4^+, NO_3^- and SO_4^{2-} in fog water was similar and often larger than the wet deposition, although more liquid water was deposited through rain than through fog. Accounting these findings, we estimate the occult deposition in September 2007 as equal to the wet deposition. Consequently, the total N_r deposition in September 2007 sums up to 5.86 kg ha^{-1}.

To compare our measurement results with results from other deposition studies of reactive nitrogen (N_r), we derive estimates on potential annual deposition sums. Held et al. (2002) found substantial differences in concentrations of N_r species in winter as compared to summer values at the Weidenbrunnen site, with winter values being less than half of the summer values. Concentrations of NH_3 were below the detection limit during the winter 2001 measurements. Obviously, the total N_r deposition varies throughout the year. If we would consider that six month of a year the wet, dry and occult deposition was the same as in September 2007 and that the other six month deposition for all three pathways was half of the values in September 2007, we obtain a total annual N_r (lower) deposition estimate of 52.74 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$. The total estimated N_r input based on dry and wet deposition alone yields 38.79 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$. Assuming that the differences in concentrations and deposition fluxes balance each other in the run of a year, and thus estimating the annual deposition by multiplying the September values by twelve yields 70.32 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$ (upper estimate) including fog/cloud water deposition, of which are 51.72 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$ due to dry and wet deposition. Both values exceed the critical load threshold (12.5–15 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$) for the area (Nagel et al., 2004). Figure 8 gives an overview of results from different N_r deposition studies to spruce forest ecosystems compared to our site. Some of the estimates rely on throughfall measurements; some are combinations of direct measurements and inferential modelling. The comparison between our short-term measurements based on the AGM method with the long-term monitoring data is not straight forward. Firstly, the estimation of annual deposition from measurements during one month only is very rough, especially in comparison with long-term observations. The throughfall approach is very different to a micrometeorological approach. It is an integrated, straight forward and relatively cheap approach for deposition monitoring, but drawbacks comprise spatial representativeness and the missing knowledge on canopy exchange, especially of N_r species. The canopy exchange includes both leaching and consequently efflux from the canopy as well as uptake or retention and therefore influx to the canopy. Throughfall methods may therefore easily either over- or underestimate total deposition fluxes.

Although Klemm and Wrzesinsky (2007) found similar wet deposition values in September 2001 compared to our September measurements, the annual wet deposition for April 2001 to March 2002 was much higher. 2001 was a comparatively wet year with high fog occurrence (on 233 days compared to an annual mean (1997–2007) of 200 days). The estimate we made using similar deposition rates through rain and fog/cloud water interception is, however, also valid for the annual budget. For the "Fichtelgebirge" mountains, Matzner et al. (2001) reported average throughfall fluxes of mineral N of 21 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$, pointing out that this value underestimates the actual atmospheric deposition due to the canopy uptake, which they estimate as high as 28 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$. Our two estimates of the annual $\mathrm{N_r}$ deposition flux are both larger than their throughfall flux data but the lower estimate is within the range of estimated throughfall plus canopy uptake. Zimmermann et al. (2006) measured deposition of $\mathrm{NH_4^+}$ and $\mathrm{NO_3^-}$ in the Erzgebirge in south east Germany for several years (2001–2004). He used both micrometeorological and throughfall methods and measured dry, wet, and occult deposition. The wet deposition is comparable to our results, being more important than dry deposition. Differences between the dry deposition estimate of Zimmermann et al. (2006) and our study could be due to the use of the inferential model by Zimmermann et al. (2006) and, of course, to our very rough estimation of the annual deposition on only one month measurements. The fog/cloud water deposition was not very significant in the study of Zimmermann et al. (2006), but it is pointed out that it is important for the forest at higher altitudes of the Erzgebirge (Zimmermann and Zimmermann, 2002). Throughfall fluxes were roughly two thirds of the sum of dry, wet, and occult deposition, suggesting possible canopy uptake of $\mathrm{NH_4^+}$ and $\mathrm{NO_3^-}$. Rothe et al. (2002) reported $\mathrm{N_r}$ bulk deposition fluxes of 10.7 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$ and $\mathrm{N_r}$ throughfall fluxes of 29.6 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$ to a spruce forest in south west Bavaria, Germany, about 190 km south southwest of our site. Their study includes $\mathrm{N_r}$ deposition loads of 15 European spruce stands (all determined using throughfall methods) ranging from 11.2 to 56 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$. Sievering et al. (1994) reported a range of diel deposition fluxes of tot-$\mathrm{NO_3^-}$ and annual wet deposition of total inorganic $\mathrm{N_r}$ from which we derived an annual deposition range (cf. Fig. 8). The upper end of this range would yield a similar annual deposition load like our lower estimate (based on dry and wet deposition only), not yet including dry deposited NH_4^+. Sievering et al. (1994) point out that their results indicate an exceedance of the critical N loads. Berger et al. (2009) measured throughfall fluxes in a nutrient poor spruce forest in northern Austria and found relatively small values, slightly less than deposition values estimated by Matzner et al. (2001) for our site. Berger et al. (2009) used a canopy exchange model to estimate total deposition fluxes and modelled the canopy to be a source for NO_3^- and a sink for NH_4^+. Direct deposition estimates (AGM) of different N_r species for the year 1995 at the Speuld forest in The Netherlands were reported by Erisman et al. (1996). Dry deposition rates of tot-NH_4^+ and tot-NO_3^- were 22.60 $kg ha^{-1} yr^{-1}$ and 4.67 $kg ha^{-1} yr^{-1}$, respectively. Reported wet deposition rates were 11.3 $kg ha^{-1} yr^{-1}$ for NH_4^+ and 5.2 $kg ha^{-1} yr^{-1}$ for NO_3^-. Total N deposition (the sum of dry and wet deposition) yielded 43.77 $kg ha^{-1} yr^{-1}$, which is very similar to our estimates (when looking at dry and wet deposition). Andersen and Hovmand (1999) report dry deposition estimates derived using the AGM (NH_3) and inferential modelling (HNO_3, NO_3^-, NH_4^+) for one year (July 1995–June 1996) of 9.2 $kg ha^{-1} yr^{-1}$ of tot-NH_4^+ and 2.2 $kg ha^{-1} yr^{-1}$ of tot-NO_3^- for a Norway spruce forest site in west Denmark. In Denmark the dry deposition of N_r compounds to forest ecosystems contributes with 50–67% to the total composition (Andersen and Hovmand, 1999). Thus, the total deposition would yield an annual N deposition flux of 17.1 to 22.8 $kg ha^{-1} yr^{-1}$.

Although we estimated the annual dry deposition to our site from one month measurements only, the comparison to long term direct measurements in The Netherlands (Erisman et al., 1996) and Denmark (Andersen and Hovmand, 1999) is remarkable good. Additionally the ratio of dry to wet deposition compares very well with these studies. Occult deposition was only measured in two studies and the importance of this deposition pathway at our site was stressed (Zimmermann et al., 2006; Klemm and Wrzesinsky, 2007). All of the studies listed in Fig. 8 were conducted above/in spruce forest. Rothe et al. (2002) and Berger et al. (2008, 2009) compared deposition loads between beech, mixed and spruce forests and found enhanced acid deposition in the spruce forests due to more efficiently scavenging of the coniferous canopies, which is also reflected in higher seepage rates of NO_3. The high surface to volume ratio of the canopy may thus also enhance dry deposition. The deposition load also largely depends on the pollution levels of the surrounding air masses, i.e. the proximity of agriculture, industry and traffic. The effect of this becomes evident when comparing the studies by Andersen and Hovmand (1999) and Erisman et al. (1996) in Denmark (west of Denmark, close to the sea, few sources nearby) and The Netherlands (surrounded by intensive agriculture), respectively.

5 Conclusions

An intensive field campaign with hourly resolved two-level measurements of ammonia (NH_3), nitric acid (HNO_3), particulate ammonium (NH_4^+) and nitrate (NO_3^-) were conducted above a spruce forest in southeast Germany. For the first time, the complete NH_3-HNO_3-NH_4NO_3 triad was measured continuously and simultaneously at two levels above a forest canopy, allowing for the calculation of surface-atmosphere exchange fluxes using the aerodynamic gradient method. However, indications for rapid phase changes in the NH_3-HNO_3-NH_4NO_3 triad required the calculation of exchange fluxes of the chemically conservative quantities tot-NH_4^+ and tot-NO_3^- (sums of gaseous and particulate compounds). In September 2007 exchange fluxes were comparatively large and median diel dry deposition velocities were $3.4\,\mathrm{cm\,s^{-1}}$ for tot-NH_4^+ and $4.2\,\mathrm{cm\,s^{-1}}$ for tot-NO_3^-. Large deposition velocities of tot-NH_4^+ and tot-NO_3^- were most likely the result of a combination of several effects, such as:

(a) high roughness of the forest canopy, large receptor surfaces (needles) of coniferous trees, and surface resistances of tot-NH_4^+ and tot-NO_3^- close to zero

(b) partly presence of particulate NO_3^- in large aerosol particles (i.e. $\geq 10\,\mu\mathrm{m}$, typically featuring large deposition velocities due to the influence of gravitational settling)

(c) potential strong chemical sink below our measurement height due to phase changes between NH_3, HNO_3 and NH_4NO_3 towards the more efficiently deposited gases

Consequently, we like to state, that the measurement of concentrations of only one single compound at one single level above forest using the inferential model to calculate fluxes (deriving R_c values) may lead to underestimation of the actual deposition load, especially in the case of aerosol particles. In our study, tot-NH_4^+ dry and wet deposition was larger than the respective tot-NO_3^- deposition. An estimated annual total nitrogen deposition load, approximated from dry, wet, and occult (fog interception) deposition is at the upper end of the range reported in literature. Thus, our site is a significant receptor region for reactive nitrogen.

Acknowledgements. The authors gratefully acknowledge financial support by the German Science foundation (DFG project EGER, ME 2100/4-1) and by the Max Planck Society. The authors wish to thank the University of Bayreuth (Micrometeorology Department) for hosting and supporting us during the EGER study. We thank the Bayerische Landesamt für Umwelt for the analysis of the rain water samples. For very valuable support in the field measurements we would like to express our gratitude to the whole EGER IOP1 crew, especially to D. Plake and J. Sintermann.

The service charges for this open access publication
have been covered by the Max Planck Society.

References

Alsheimer, M.: Charakterisierung räumlicher und zeitlicher Heterogenitäten der Transpiration unterschiedlicher montaner Fichtenbestände durch Xylemflussmessungen, Bayreuther Forum Ökologie, 1–143, 1997.

Ammann, C.: On the Applicability of Relaxed Eddy Accumulation and Common Methods for Measuring for Measuring Trace Gas Fluxes, Ph.D., Geographisches Institut, ETH, Zürich, 229 pp., 1998.

Andersen, H. V. and Hovmand, M. F.: Review of dry deposition measurements of ammonia and nitric acid to forest, Forest Ecol. Manag., 114, 5–18, 1999.

Asman, W. A. H., Sutton, M. A., and Schjorring, J. K.: Ammonia: emission, atmospheric transport and deposition, New Phytol., 139, 27–48, 1998.

Berger, T. W., Untersteiner, H., Schume, H., and Jost, G.: Throughfall fluxes in a secondary spruce (*Picea abies*), a beech (*Fagus sylvatica*) and a mixed spruce-beech stand, Forest Ecol. Manag., 255, 605–618, 2008.

Berger, T. W., Untersteiner, H., Toplitzer, M., and Neubauer, C.: Nutrient fluxes in pure and mixed stands of spruce (*Picea abies*) and beech (*Fagus sylvatica*), Plant Soil, 322, 317–342, 2009.

Brost, R. A., Delany, A. C., and Huebert, B. J.: Numerical modeling of concentrations and fluxes of HNO_3, NH_3, and NH_4NO_3 near the surface, J. Geophys. Res.-Atmos., 93, 7137–7152, 1988.

De Arellano, J. V. and Duynkerke, P. G.: Influence of chemistry on the flux-gradient relationships for the NO-O_3-NO_2 system, Bound.-Lay. Meteorol., 61, 375–387, 1992.

Delany, A. C. and Lenschow, D. H.: Measurement of NO and NO_2 soil crop level fluxes with a micrometeorological technique, Abstr. Pap. Am. Chem. Soc., 193, 174-ENVR, 1987.

Eigenbrodt: Betriebs- und Wartungsanleitung Automatischer Niederschlagssammler NSA 181/KHS, Eigenbrodt GmbH & Co. KG., 2007.

Erisman, J. W., Draaijers, G., Duyzer, J., Hofschreuder, P., Vanleeuwen, N., Romer, F., Ruijgrok, W., and Wyers, P.: Particle deposition to forests, Stud. Environ. Sci., 64, 115–126, 1995.

Erisman, J. W., Draaijers, G. P. J., Mennen, M. G., Hogenkamp, J. E. M., van Putten, E., Uiterwijk, W., Kemkers, E., Wiese, H., Duyzer, J. H., Otjes, R., and Wyers, G. P.: Towards Development of a Deposition Monitoring Network for Air Pollution of Europe, RIVM, Bilthoven, The Netherlands, 1996.

Erisman, J. W., Draaijers, G., Duyzer, J., Hofschreuder, P., VanLeeuwen, N., Romer, F., Ruijgrok, W., Wyers, P., and Gallagher, M.: Particle deposition to forests – Summary of results and application, Atmos. Environ., 31, 321–332, 1997.

Erisman, J. W. and Draaijers, G.: Deposition to forests in Europe: most important factors influencing dry deposition and models used for generalisation, Environ. Pollut., 124, 379–388, 2003.

Erisman, J. W., Grennfelt, P., and Sutton, M.: The European perspective on nitrogen emission and deposition, Environ. Int., 29, 311–325, 2003.

Erisman, J. W., Hensen, A., Mosquera, J., Sutton, M., and Fowler, D.: Deposition monitoring networks: what monitoring is required to give reasonable estimates of ammonia/ammonium?, Environ. Pollut., 135, 419–431, 2005a.

Erisman, J. W., Vermeulen, A., Hensen, A., Flechard, C., Dammgen, U., Fowler, D., Sutton, M., Grunhage, L., and Tuovinen, J. P.: Monitoring and modelling of biosphere/atmosphere exchange of gases and aerosols in Europe, Environ. Pollut., 133, 403–413, 2005b.

Erisman, J. W., Bleeker, A., Galloway, J., and Sutton, M. S.: Reduced nitrogen in ecology and the environment, Environ. Pollut., 150, 140–149, 2007.

Eugster, W.: Fog research, Erde, 139, 1–10, 2008.

Falge, E., Reth, S., Bruggemann, N., Butterbach-Bahl, K., Goldberg, V., Oltchev, A., Schaaf, S., Spindler, G., Stiller, B., Queck, R., Kostner, B., and Bernhofer, C.: Comparison of surface energy exchange models with eddy flux data in forest and grassland ecosystems of Germany, Ecol. Model., 188, 174–216, 2005.

Farquhar, G. D., Firth, P. M., Wetselaar, R., and Weir, B.: On the gaseous exchange of ammonia between leaves and the environment – Determination of the ammonia compensation point, Plant Physiol., 66, 710–714, 1980.

Ferm, M.: Atmospheric ammonia and ammonium transport in Europe and critical loads: a review, Nutr. Cycl. Agroecosyst., 51, 5–17, 1998.

Finlayson-Pitts, B. J. and Pitts, J. N.: Chemistry of the Upper and Lower Atmosphere, Academic Press, New York, 1999.

Foken, T., Dlugi, R., and Kramm, G.: On the determination of dry deposition and emission of gaseous compounds at the biosphere-atmosphere interface, Meteorol. Z., 4, 91–118, 1995.

Foken, T.: Lufthygienisch-bioklimatische Kennzeichnung des oberen Egertales (Fichtelgebirge bis Karlovy Vary), Bayreuther Forum Ökologie, 1–70, 2003.

Foken, T.: Micrometeorology, 2nd ed., Springer, Berlin, 290 pp., 2008.

Fowler, D. and Duyzer, J. H.: Micrometeorological Techniques for the Measurement of Trace Gas Exchange, in: Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere, edited by: Andreae, M. O., and Schimel, D. S., John Wiley & Sons Ltd., 189–207, 1989.

Fowler, D., Pilegaard, K., Sutton, M. A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Fuzzi, S., Schjoerring, J. K., Granier, C., Neftel, A., Isaksen, I. S. A., Laj, P., Maione, M., Monks, P. S., Burkhardt, J., Daemmgen, U., Neirynck, J., Personne, E., Wichink-Kruit, R., Butterbach-Bahl, K., Flechard, C., Tuovinen, J. P., Coyle, M., Gerosa, G., Loubet, B., Altimir, N., Gruenhage, L., Ammann, C., Cieslik, S., Paoletti, E., Mikkelsen, T. N., Ro-Poulsen, H., Cellier, P., Cape, J. N., Horváth, L., Loreto, F., Niinemets, Ü., Palmer, P. I., Rinne, J., Misztal, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M. W., Vesala, T., Skiba, U., Brüggemann, N., Zechmeister-Boltenstern, S., Williams, J., O'Dowd, C., Facchini, M. C., de Leeuw, G., Flossman, A., Chaumerliac, N., and Erisman, J. W.: Atmospheric composition change: Ecosystems-Atmosphere interactions, Atmos. Environ., 43, 5193–5267, 2009.

Gallagher, M. W., Beswick, K. M., Duyzer, J., Westrate, H., Choularton, T. W., and Hummelshoj, P.: Measurements of aerosol fluxes to Speulder forest using a micrometeorological technique, Atmos. Environ., 31, 359–373, 1997.

Gallagher, M. W., Nemitz, E., Dorsey, J. R., Fowler, D., Sutton, M. A., Flynn, M., and Duyzer, J.: Measurements and parameterizations of small aerosol deposition velocities to grassland, arable crops, and forest: influence of surface roughness length on deposition, J. Geophys. Res.-Atmos., 107, 2002.

Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B., and Cosby, B. J.: The nitrogen cascade, Bioscience, 53, 341–356, 2003.

Galloway, J. N., Townsend, A. R., Erisman, J. W., Bekunda, M., Cai, Z. C., Freney, J. R., Martinelli, L. A., Seitzinger, S. P., and Sutton, M. A.: Transformation of the nitrogen cycle: recent trends, questions, and potential solutions, Science, 320, 889–892, 2008.

Ganzeveld, L., Valverde-Canossa, J., Moortgat, G. K., and Steinbrecher, R.: Evaluation of peroxide exchanges over a coniferous forest in a single-column chemistry-climate model, Atmos. Environ., 40, S68–S80, 2006.

Garratt, J. R.: Flux profile relations above tall vegetation, Q. J. Roy. Meteor. Soc., 104, 199–211, 1978.

Garratt, J. R.: The Atmospheric Boundary Layer, Cambridge University Press, 1992.

Gruber, N. and Galloway, J. N.: An Earth-system perspective of the global nitrogen cycle, Nature, 451, 293–296, 2008.

Hall, B., Claiborn, C., and Baldocchi, D.: Measurement and modeling of the dry deposition of peroxides, Atmos. Environ., 33, 577–589, 1999.

Held, A., Wrzesinsky, T., Mangold, A., Gerchau, J., and Klemm, O.: Atmospheric phase distribution of oxidized and reduced nitrogen at a forest ecosystem research site, Chemosphere, 48, 697–706, 2002.

Held, A. and Klemm, O.: Direct measurement of turbulent particle exchange with a twin CPC eddy covariance system, Atmos. Environ., 40, S92–S102, 2006.

Hertel, O., Skjoth, C. A., Lofstrom, P., Geels, C., Frohn, L. M., Ellermann, T., and Madsen, P. V.: Modelling nitrogen deposition on a local scale – A review of the current state of the art, Environ. Chem., 3, 317–337, 2006.

Hogstrom, U., Bergstrom, H., Smedman, A. S., Halldin, S., and Lindroth, A.: Turbulent exchange above a pine forest. 1. Fluxes and gradients, Bound.-Lay. Meteorol., 49, 197–217, 1989.

Hovmand, M. F. and Andersen, H. V.: Nine years of measurements of atmospheric nitrogen and sulphur deposition to Danish forest, Water Air Soil Poll., 85, 2205–2210, 1995.

Huebert, B. J. and Robert, C. H.: The Dry Deposition of Nitric-Acid to Grass, J. Geophys. Res.-Atmos., 90, 2085–2090, 1985.

Huebert, B. J., Luke, W. T., Delany, A. C., and Brost, R. A.: Measurements of concentrations and dry surface fluxes of atmospheric nitrates in the presence of ammonia, J. Geophys. Res.-Atmos., 93, 7127–7136, 1988.

Klemm, O. and Lange, H.: Trends of air pollution in the Fichtelgebirge mountains, Bavaria, Environ. Sci. Pollut. R., 6, 193–199, 1999.

Klemm, O., Held, A., Forkel, R., Gasche, R., Kanter, H. J., Rappengluck, B., Steinbrecher, R., Muller, K., Plewka, A., Cojocariu, C., Kreuzwieser, J., Valverde-Canossa, J., Schuster, G., Moortgat, G. K., Graus, M., and Hansel, A.: Experiments on forest/atmosphere exchange: climatology and fluxes during two summer campaigns in NE Bavaria, Atmos. Environ., 40, S3–S20, 2006.

Klemm, O. and Wrzesinsky, T.: Fog deposition fluxes of water and ions to a mountainous site in Central Europe, Tellus B, 59, 705–714, 2007.

Kramm, G. and Dlugi, R.: Modeling of the vertical fluxes of nitric-acid, ammonia, and ammonium-nitrate, J. Atmos. Chem., 18, 319–357, 1994.

Krupa, S. V.: Effects of atmospheric ammonia (NH_3) on terrestrial vegetation: a review, Environ. Pollut., 124, 179–221, 2003.

Lovett, G. M. and Lindberg, S. E.: Dry deposition and canopy exchange in a mixed oak forest as determined by analysis of throughfall, J. Appl. Ecol., 21, 1013–1027, 1984.

Lovett, G. M., Nolan, S. S., Driscoll, C. T., and Fahey, T. J.: Factors regulating throughfall flux in a new New-Hampshire forested landscape, Can. J. Forest Res., 26, 2134–2144, 1996.

Matzner, E., Alewell, C., Bittersohl, J., Lischeid, G., Kammerer, G., Manderscheid, B., Matschonat, G., Moritz, K., Tenhunen, J. D., and Totsche, K.: Biogeochemistry of a Spruce Forest Catchment of the Fichtelgebirge in Response to Changing Atmospheric Deposition, in: Ecosystem Approaches to Landscape Management in Central Europe, Ecological Studies: Analysis and Synthesis, Springer-Verlag Berlin, Berlin, 463–503, 2001.

Mayer, J. C.: Transport Processes of Reactive Trace Gases in the Atmospheric Boundary Layer, Ph.D., Faculty of Biology, Chemistry and Geosciences, University of Bayreuth, Bayreuth, 119 pp., 2008.

Mozurkewich, M.: The dissociation constant of ammonium nitrate and its dependence on temperature, relative humidity and particle size, Atmos. Environ. A-Gen., 27, 261–270, 1993.

Nagel, H. D., Becker, R., Eitner, H., Hübener, P., Kunze, F., Schlutow, A., Schütze, G., and Weigelt-Kirchner, R.: Critical Loads für Säure und eutrophierenden Stickstoff, Umweltbundesamt, 172 pp., 2004.

Nemitz, E. and Sutton, M. A.: Gas-particle interactions above a Dutch heathland: III. Modelling the influence of the NH_3-HNO_3-NH_4NO_3 equilibrium on size-segregated particle fluxes, Atmos. Chem. Phys., 4, 1025–1045, 2004, http://www.atmos-chem-phys.net/4/1025/2004/.

Nemitz, E., Sutton, M. A., Wyers, G. P., and Jongejan, P. A. C.: Gas-particle interactions above a Dutch heathland: I. Surface exchange fluxes of NH_3, SO_2, HNO_3 and HCl, Atmos. Chem. Phys., 4, 989–1005, 2004, http://www.atmos-chem-phys.net/4/989/2004/.

Nemitz, E., Sutton, M. A., Wyers, G. P., Otjes, R. P., Mennen, M. G., van Putten, E. M., and Gallagher, M. W.: Gas-particle interactions above a Dutch heathland: II. Concentrations and surface exchange fluxes of atmospheric particles, Atmos. Chem. Phys., 4, 1007–1024, 2004, http://www.atmos-chem-phys.net/4/1007/2004/.

Peters, K. and Eiden, R.: Modelling the dry deposition velocity of aerosol particles to a spruce forest, Atmos. Environ. A-Gen., 26, 2555–2564, 1992.

Rebmann, C., Gockede, M., Foken, T., Aubinet, M., Aurela, M., Berbigier, P., Bernhofer, C., Buchmann, N., Carrara, A., Cescatti, A., Ceulemans, R., Clement, R., Elbers, J. A., Granier, A., Grunwald, T., Guyon, D., Havrankova, K., Heinesch, B., Knohl, A., Laurila, T., Longdoz, B., Marcolla, B., Markkanen, T., Miglietta, F., Moncrieff, J., Montagnani, L., Moors, E., Nardino, M., Ourcival, J. M., Rambal, S., Rannik, U., Rotenberg, E., Sedlak, P., Unterhuber, G., Vesala, T., and Yakir, D.: Quality analysis applied on eddy covariance measurements at complex forest sites using footprint modelling, Theor. Appl. Climatol., 80, 121–141, 2005.

Rothe, A., Huber, C., Kreutzer, K., and Weis, W.: Deposition and soil leaching in stands of Norway spruce and European Beech: Results from the Hoglwald research in comparison with other European case studies, Plant Soil, 240, 33–45, 2002.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Wiley, New York, 1998.

Sievering, H., Enders, G., Kins, L., Kramm, G., Ruoss, K., Roider, G., Zelger, M., Anderson, L., and Dlugi, R.: Nitric-acid, particulate nitrate and ammonium profiles at the Bayerischer-Wald – Evidence for large deposition rates of total nitrate, Atmos. Environ., 28, 311–315, 1994.

Simpson, I. J., Thurtell, G. W., Neumann, H. H., Den Hartog, G., and Edwards, G. C.: The validity of similarity theory in the roughness sublayer above forests, Bound.-Lay. Meteorol., 87, 69–99, 1998.

Staudt, K. and Foken, T.: Documentation of Reference Data for the Experimental Areas of the Bayreuth Center for Ecology and Environmental Research (BayCEER) at the Waldstein Site, Dep. Micromet., University of Bayreuth, 2007.

Stelson, A. W. and Seinfeld, J. H.: Relative-humidity and temperature-dependence of the ammonium-nitrate dissociation-constant, Atmos. Environ., 16, 983–992, 1982.

Sutton, M. A., Nemitz, E., Milford, C., Fowler, D., Moreno, J., San Jose, R., Wyers, G. P., Otjes, R. P., Harrison, R., Husted, S., and Schjoerring, J. K.: Micrometeorological measurements of net ammonia fluxes over oilseed rape during two vegetation periods, Agr. Forest Meteorol., 105, 351–369, 2000.

Sutton, M. A., Nemitz, E., Erisman, J. W., Beier, C., Bahl, K. B., Cellier, P., de Vries, W., Cotrufo, F., Skiba, U., Di Marco, C., Jones, S., Laville, P., Soussana, J. F., Loubet, B., Twigg, M., Famulari, D., Whitehead, J., Gallagher, M. W., Neftel, A., Flechard, C. R., Herrmann, B., Calanca, P. L., Schjoerring, J. K., Daemmgen, U., Horvath, L., Tang, Y. S., Emmett, B. A., Tietema, A., Penuelas, J., Kesik, M., Brueggemann, N., Pilegaard, K., Vesala, T., Campbell, C. L., Olesen, J. E., Dragosits, U., Theobald, M. R., Levy, P., Mobbs, D. C., Milne, R., Viovy, N., Vuichard, N., Smith, J. U., Smith, P., Bergamaschi, P., Fowler, D., and Reis, S.: Challenges in quantifying biosphere-atmosphere exchange of nitrogen species, Environ. Pollut., 150, 125–139, 2007.

Thom, A. S., Stewart, J. B., Oliver, H. R., and Gash, J. H. C.: Comparison of aerodynamic and energy budget estimates of fluxes over a pine forest, Q. J. Roy. Meteor. Soc., 101, 93–105, 1975.

Thomas, C. and Foken, T.: Flux contribution of coherent structures and its implications for the exchange of energy and matter in a tall spruce canopy, Bound.-Lay. Meteorol., 123, 317–337, 2007.

Thomas, R.: Measurement of Speciated Aerosol Fluxes, Ph.D., Faculty of Engineering and Physical Science, University of Manchester, Manchester, 296 pp., 2007.

Thomas, R. M., Trebs, I., Otjes, R., Jongejan, P. A. C., Brink, H. T., Phillips, G., Kortner, M., Meixner, F. X., and Nemitz, E.: An automated analyzer to measure surface-atmosphere exchange fluxes of water soluble inorganic aerosol compounds and reactive trace gases, Environ. Sci. Technol., 43, 1412–1418, doi:10.1021/es8019403, 2009.

Trebs, I., Meixner, F. X., Slanina, J., Otjes, R., Jongejan, P., and Andreae, M. O.: Real-time measurements of ammonia, acidic trace gases and water-soluble inorganic aerosol species at a rural site in the Amazon Basin, Atmos. Chem. Phys., 4, 967–987, 2004, http://www.atmos-chem-phys.net/4/967/2004/.

Trebs, I., Lara, L. L., Zeri, L. M. M., Gatti, L. V., Artaxo, P., Dlugi, R., Slanina, J., Andreae, M. O., and Meixner, F. X.: Dry and wet deposition of inorganic nitrogen compounds to a tropical pasture site (Rondônia, Brazil), Atmos. Chem. Phys., 6, 447–469, 2006, http://www.atmos-chem-phys.net/6/447/2006/.

Tsokankunku, A., Zhu, Z., Meixner, F. X., Foken, T., and Andreae, M. O.: Eddy covariance fluxes of the NO-NO_2-O_3 triad above a spruce forest canopy in south-eastern Germany, EGU General Assembly, Vienna, 19–24 Apr 2009, 2009.

Valverde-Canossa, J., Ganzeveld, L., Rappengluck, B., Steinbrecher, R., Klemm, O., Schuster, G., and Moortgat, G. K.: First measurements of H_2O_2 and organic peroxides surface fluxes by the relaxed eddy-accumulation technique, Atmos. Environ., 40, S55–S67, 2006.

van Breemen, N. and van Dijk, H. F. G.: Ecosystem effects of atmospheric deposition of nitrogen in The Netherlands, Environ. Pollut., 54, 249–274, 1988.

Walcek, C. J.: A Theoretical estimate of O_3 and H_2O_2 dry deposition over the Northeast United-States, Atmos. Environ., 21, 2649–2659, 1987.

Wesely, M. L. and Hicks, B. B.: A review of the current status of knowledge on dry deposition, Atmos. Environ., 34, 2261–2282, 2000.

Wexler, A. S. and Seinfeld, J. H.: The distribution of ammonium-salts among a size and composition dispersed aerosol, Atmos. Environ. A-Gen., 24, 1231–1246, 1990.

Wexler, A. S. and Seinfeld, J. H.: Analysis of aerosol ammonium-nitrate – Departures from equilibrium during scaqs, Atmos. Environ. A-Gen., 26, 579–591, 1992.

Wichura, B., Ruppert, J., Delany, A. C., Buchmann, N., and Foken, T.: Structure of Carbon Dioxide Exchange Processes above a Spruce Forest, in: Biogeochemistry of Forested Catchments in a Changing Environment: An German Case Study, Ecological Studies: Analysis and Synthesis, Springer-Verlag, Berlin, 161–176, 2004.

Wolff, V., Trebs, I., Ammann, C., and Meixner, F. X.: Aerodynamic gradient measurements of the NH_3-HNO_3-NH_4NO_3 triad using a wet chemical instrument: an analysis of precision requirements and flux errors, Atmos. Meas. Tech. Discuss., 2, 2423–2482, 2009, http://www.atmos-meas-tech-discuss.net/2/2423/2009/.

Wrzesinsky, T. and Klemm, O.: Summertime fog chemistry at a mountainous site in central Europe, Atmos. Environ., 34, 1487–1496, 2000.

Zimmermann, F., Plessow, K., Queck, R., Bernhofer, C., and Matschullat, J.: Atmospheric N- and S-fluxes to a spruce forest – Comparison of inferential modelling and the throughfall method, Atmos. Environ., 40, 4782–4796, 2006.

Zimmermann, L. and Zimmermann, F.: Fog deposition to Norway spruce stands at high-elevation sites in the eastern Erzgebirge (Germany), J. Hydrol., 256, 166–175, 2002.

Table 1. Statistical distribution of concentrations of NH_3, NH_4^+, HNO_3, and NO_3^-, in $\mu g\,m^{-3}$ (in terms of N) measured from 31 August to 25 September 2007 at 30.9 m a.g.l. at the Weidenbrunnen site.

	NH_3 $\mu g\,m^{-3}$	NH_4^+ $\mu g\,m^{-3}$	HNO_3 $\mu g\,m^{-3}$	NO_3^- $\mu g\,m^{-3}$	Tot-NH_4^+ $\mu g\,m^{-3}$	Tot-NO_3^- $\mu g\,m^{-3}$
min	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
mean	0.67	0.94	0.19	0.65	1.73	0.84
max	2.39	4.95	0.97	4.23	5.42	4.59
25%	0.25	0.32	0.05	0.18	0.88	0.29
median	0.57	0.76	0.12	0.48	1.63	0.70
75%	1.00	1.39	0.28	0.80	2.37	1.08

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
|◀
▶|
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

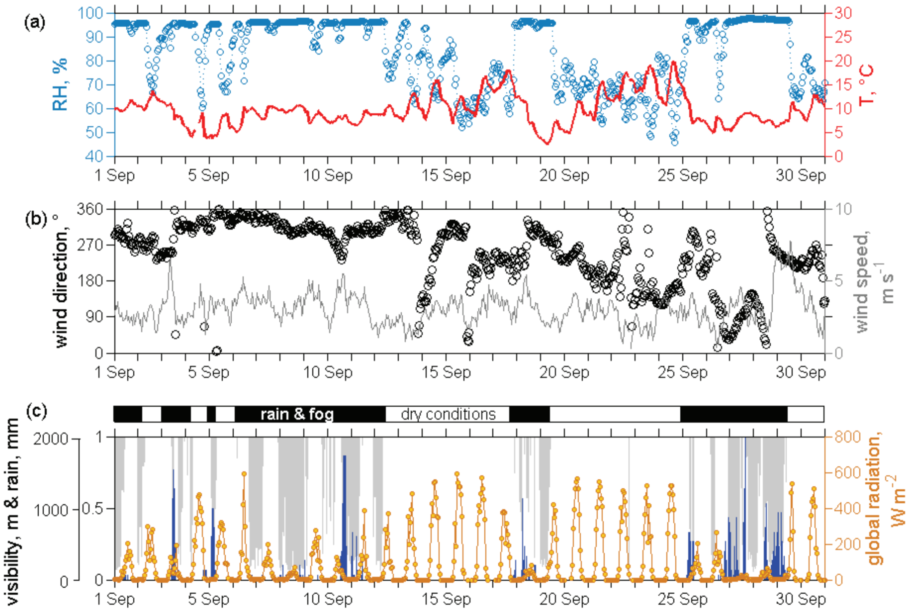

Fig. 1. **(a)** *T* (red line) and RH (blue circles), **(b)** wind speed (black line) and wind direction (black circles) and **(c)** rain (blue bars), visibility (grey shaded areas) and global radiation (yellow line) during EGER experiment (September 2007). Times and dates refer to Central European Time (major ticks indicate midnight).

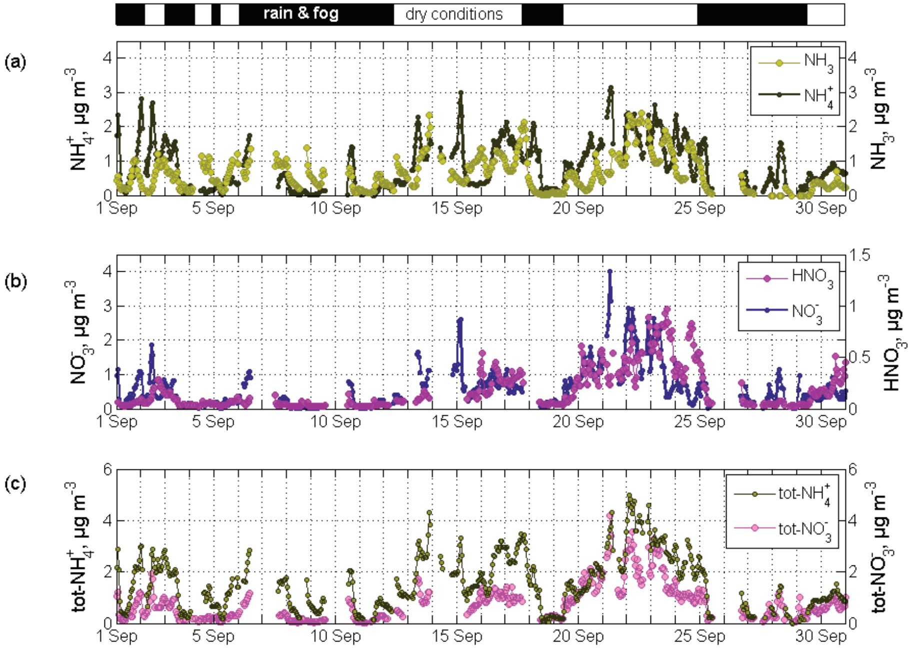

Fig. 2. Diel variations of **(a)** NH_3 and particulate NH_4^+ and **(b)** HNO_3 and particulate NO_3^-, and **(c)** tot-NH_4^+ and tot-NO_3^-, in μ g m^{-3} (in terms of N) measured in September 2007 at 30.9 m a.g.l. at the Weidenbrunnen site. Indicated by the black and white bar are episodes of rain and fog and dry periods, respectively (cf. Fig. 1).

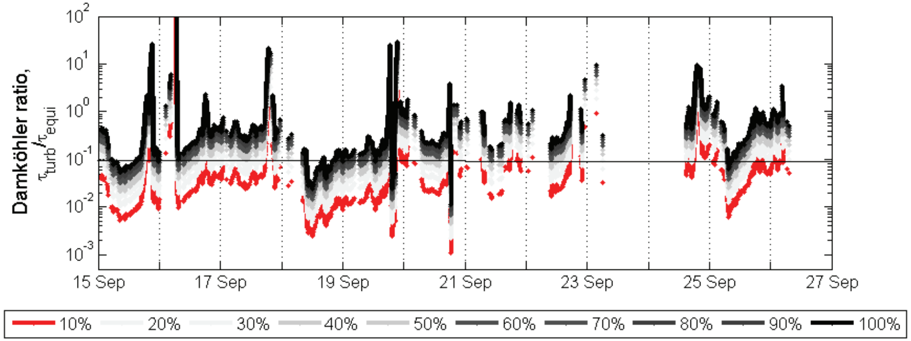

Fig. 3. Characteristic timescale analysis: Damköhler ratio ($\tau_{\mathrm{turb}}/\tau_{\mathrm{equi}}$) during the EGER campaign (15–27 September 2007). Damköhler ratios for different fractions of the particle surface available for the equilibrium reaction are presented (red line: 10% and black line: 100% of the aerosol surface takes part in the equilibrium reaction).

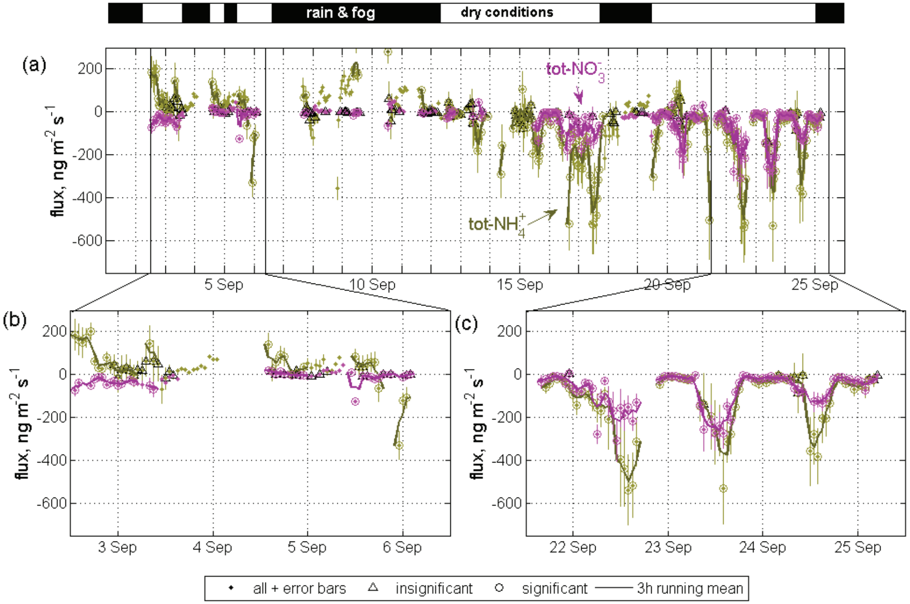

Fig. 4. Time series of tot-NH_4^+ and tot-NO_3^- fluxes in ng m^{-2} s^{-1} (in terms of N) calculated using the AGM at the Weidenbrunnen site. In **(a)** an overview about the entire flux data set is given, (**b** and **c**) show contrasting episodes: **(b)** fluxes under cooler and foggy conditions and **(c)** fluxes during warmer and sunny conditions. Shown are all flux data in green and magenta dots, separated as insignificant flux values (black triangles) and as significant flux values (from conditions without rain, RH<95%, and high visibility, green and magenta circles). Additionally, a 3 h running mean through the significant flux values is shown.

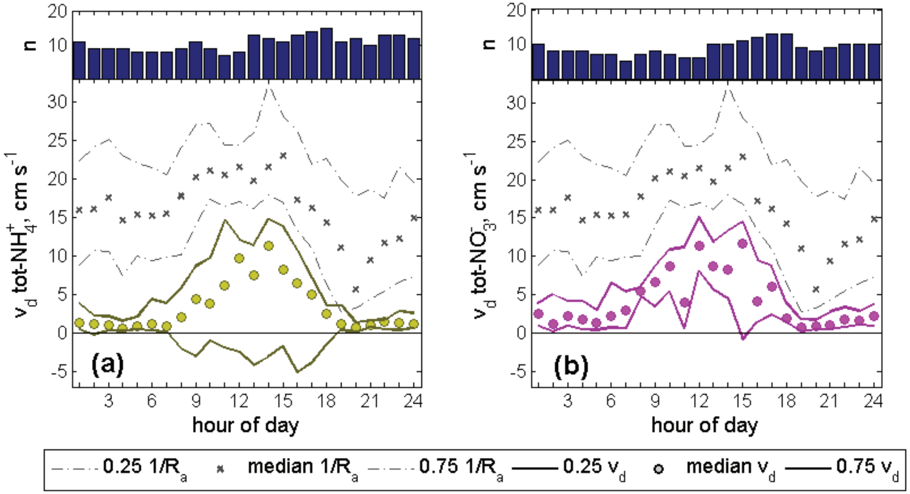

Fig. 5. Median diel variation of the v_d for tot-NH_4^+ (left panel) and tot-NO_3^- (right panel) with inter quartile ranges, in cms^{-1}, September 2007 at the Weidenbrunnen site. Only data from favourable conditions (no rain, RH<95%, high visibility) are considered. Values of $1/R_a$ (including inter-quartile ranges) are shown as a proxy for the maximum possible v_d. The number of data points used for every hour to calculate medians and inter quartile ranges (0.25 and 0.75) are given on top of each graph (blue bars).

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀| |▶

◀ ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

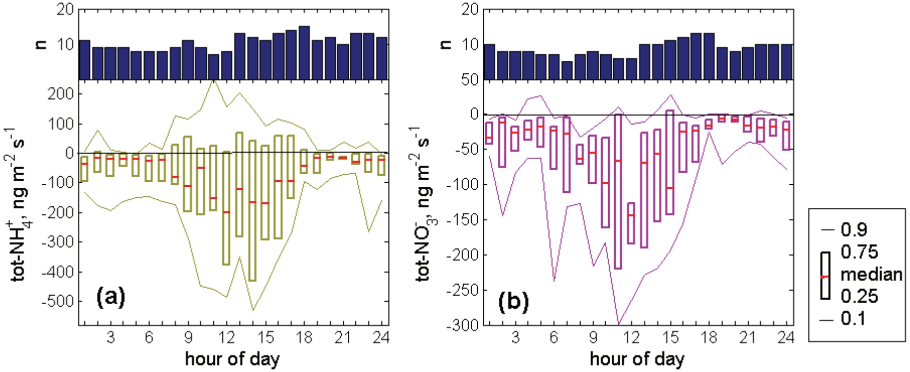

Fig. 6. Median diel variation of **(a)** tot-NH$_4^+$ flux and **(b)** tot-NO$_3^-$ flux, ng m^{-2} s^{-1} (in terms of N), from 1 to 30 September 2007 at the Weidenbrunnen site. Only flux data measured under favourable conditions (no rain, RH<95%, high visibility) were used. Shown are the medians and inter quartile ranges (0.25 and 0.75), and the 0.1 and 0.9 percentiles. The number of data points used for every hour to calculate medians and percentiles are given on top of each graph (blue bars).

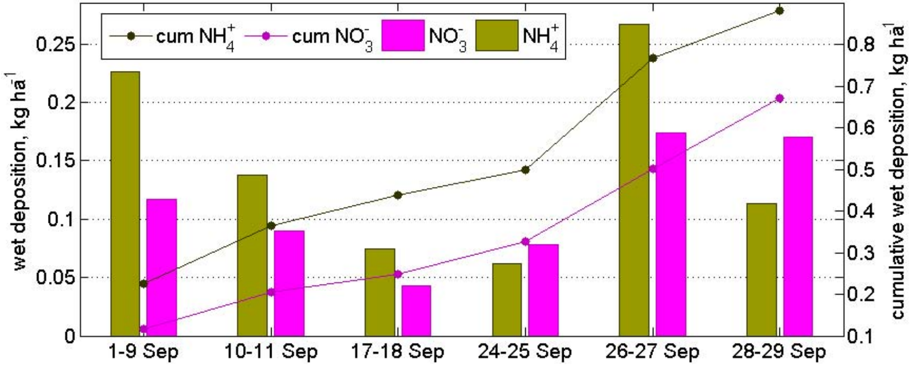

Fig. 7. Wet deposition of NH_4^+ and NO_3^- in September 2007 at the Weidenbrunnen site. Indicated are wet deposition amounts per event (in kg ha^{-1} in terms of N, left scale) and cumulative (cum) values for the entire month September 2007 (right scale).

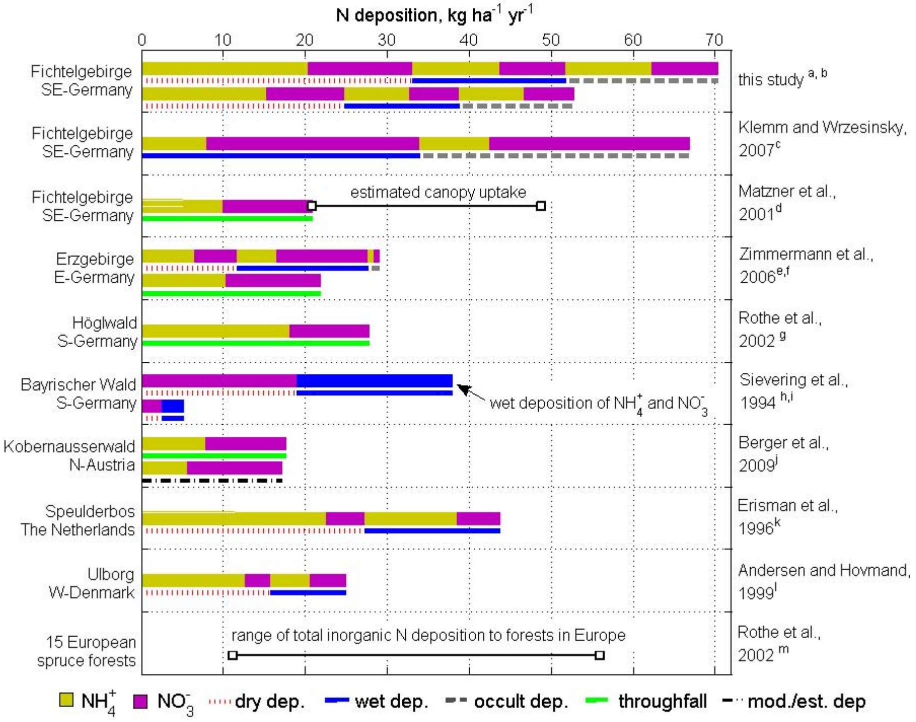
N deposition, kg ha^{-1} yr^{-1}
0
10
20
30
40
50
60
70
Fichtelgebirge SE-Germany
this study [a, b]
Fichtelgebirge SE-Germany
Klemm and Wrzesinsky, 2007[c]
Fichtelgebirge SE-Germany
estimated canopy uptake
Matzner et al., 2001[d]
Erzgebirge E-Germany
Zimmermann et al., 2006[e,f]
Höglwald S-Germany
Rothe et al., 2002 [g]
Bayrischer Wald S-Germany
wet deposition of NH_4^+ and NO_3^-
Sievering et al., 1994 [h,i]
Kobernausserwald N-Austria
Berger et al., 2009[j]
Speulderbos The Netherlands
Erisman et al., 1996[k]
Ulborg W-Denmark
Andersen and Hovmand, 1999[l]
15 European spruce forests
range of total inorganic N deposition to forests in Europe
Rothe et al., 2002 [m]
NH_4^+
NO_3^-
dry dep.
wet dep.
occult dep.
throughfall
mod./est. dep

Fig. 8.

Fig. 8. Annual N_r deposition loads for spruce forests (in kg ha^{-1} yr^{-1} in terms of N), separated in NH_4^+ (green) and NO_3^- (magenta) as well as in different deposition pathways (dry (red), wet (blue), occult (grey)) and measurement methods (direct (AGM, inferential model), throughfall (light green)). On the left hand site the locations of the studies are given and on the right hand site the references.
Annotations:

- [a] estimated as 12 times the measured fluxes during September 2007
- [b] estimated as 6 times the measured fluxes during September 2007 and as 6 times half of the measured fluxes during September 2007
- [c] direct fog water flux and wet deposition measurements (2001–2002)
- [d] throughfall measurements and estimated maximum canopy uptake (1988–1996)
- [e] concentration measurements and inferential modelling (2001–2004)
- [f] throughfall measurements from 2001 to 2004
- [g] throughfall measurements from 1994 to 1997
- [h] upper range of the annual deposition estimated from diel deposition estimates bases on deposition measurements of tot-NO_3^- using the AGM as well as wet deposition
- [i] lower range of the annual deposition estimated from diel deposition estimates bases on deposition measurements of tot-NO_3^- using the AGM as well as wet deposition
- [j] throughfall fluxes measured during 2003–2004 and modelled total deposition fluxes, using a canopy exchange model
- [k] partly measured, partly inferentially modelled with site-specific parameterizations, 1995
- [l] partly measured, partly inferentially modelled with site-specific parameterizations, 1995–1996
- [m] range of inorganic N throughfall input for 15 European spruce forests