A Parameterization of Heterogeneous Hydrolysis of N_2O_5 for 3-D Atmospheric Modelling: Improvement of Particulate Nitrate Prediction

5   Ying Chen[1,2], Ralf Wolke[1], Liang Ran[3], Wolfram Birmili[1,4], Gerald Spindler[1], Wolfram Schröder[1], Hang Su[2,5], Yafang Cheng[2,5], Ina Tegen[1] and Alfred Wiedensohler[1]

[1]Leibniz-Institute for Tropospheric Research (TROPOS), Leipzig, 04318, Germany
[2]Multiphase Chemistry Department, Max Planck Institute for Chemistry, Mainz, 55128, Germany
[3]Key Laboratory of Middle Atmosphere and Global Environment Observation, Institute of Atmospheric Physics,
10 Chinese Academy of Sciences, Beijing, 100029, China
[4]German Environment Agency, Dessau-Roßlau, 06844, Germany
[5]Institute for Environmental and Climate Research, Jinan University, Guangzhou, China

Correspondence to: Y. Chen (chen@tropos.de) and R. Wolke (wolke@tropos.de)

Abstract

Heterogeneous hydrolysis of N_2O_5 on the surface of deliquescent aerosol particles leads to HNO_3 formation and acts as a major sink of NOx in the atmosphere during nighttime. The reaction constant of this heterogeneous hydrolysis is determined by temperature (T), relative humidity (RH), aerosol particle composition as well as the
20 surface area concentration (S). However, its parameterization in previous 3-D modelling studies did not comprehensively consider these parameters. In this investigation, we propose a sophisticated parameterization of the heterogeneous hydrolysis of N_2O_5 with respect to T, RH, aerosol particle compositions and S, based on laboratory experiments. This new parameterization was incorporated into a 3-D fully online coupled model: COSMO-MUSCAT. As case study, we used the data from the HOPE-Melpitz campaign (10-25 September 2013).
25 Here, we investigated the improvement of nitrate prediction over the western and central Europe. The modelled particulate nitrate mass concentrations ($[NO_3^-]$) were validated by filter measurements over Germany (Neuglobsow, Schmücke, Zingst, and Melpitz). The modelled $[NO_3^-]$ were significantly overestimated for this period by a factor of 5-19, with the corrected NH_3 emissions (reduced by 50%) and the original parameterization of N_2O_5 heterogeneous hydrolysis. The proposed new parameterization significantly reduces the overestimation
30 of $[NO_3^-]$ by ~35%. Particularly, the overestimation factor was reduced to approximately 1.4 within our case study period (September 12, 17-18 and 25, 2013), when $[NO_3^-]$ was dominated by local chemical formations. Furthermore, the organic coating effect on a suppression of the N_2O_5 reaction probability may have been also significantly overestimated in previous modelling studies, due to a strong overestimation of the N_2O_5 reaction probability on coatings. Based on the original parameterization, previous studies reported a decrease of modelled
35 $[NO_3^-]$ up to 90%, where both secondary organic aerosol (SOA) and N_2O_5 were built-up over western and central Europe. For this case study, the suppression of organic coating was negligible over western and central Europe, with influence on $[NO_3^-]$ less than 2% on average and 20% at the most significant moment. As for a significant impact of the organic coating effect, N_2O_5, SOA and NH_3 need to be present when RH is high and T is low. However, those conditions were rarely fulfilled simultaneously over western and central Europe. Hence, the
40 organic coating effect on reaction probability of N_2O_5 over Europe may not be as important as expected in previous studies.

1 Introduction

The budget of nitrogen oxides (NOx) is of fundamental importance for tropospheric chemistry (Ehhalt and Drummond, 1982). The most important removal path of nitrogen from the atmosphere is the formation of HNO_3, which is transferred to particles or deposited eventually (Riemer et al., 2003). HNO_3 is mainly produced via the

5   reaction of NO_2 and OH at daytime. At nighttime, the heterogeneous hydrolysis of N_2O_5 on the surface of deliquescent aerosol particles forming HNO_3 is a major sink of NOx (Jacob, 2000; Brown and Stutz, 2012; Platt et al., 1984; Brown et al., 2004). Given that NOx is the key precursor of ozone, chemical mechanisms controlling the budget of NOx also have an important impact on ozone and oxidizing capacity of the atmosphere on a global scale (Dentener and Crutzen, 1993; Evans and Jacob, 2005).

10   The reaction constant of the hydrolysis of N_2O_5 ($k_{N_2O_5}$) on the surface of deliquescent aerosol particles can be quantified by the reaction probability ($\gamma_{N_2O_5}$). It has been measured for surfaces of different aqueous solutions by several techniques (Mozurkewich and Calvert, 1988; Van Doren et al., 1990; Fenter et al., 1996; Robinson et al., 1997; Behnke et al., 1997; Hu and Abbatt, 1997; Hallquist et al., 2000). They reported that typical values for $\gamma_{N_2O_5}$ are in the order of 10^{-2}. Organic coating of the particles may reduce this reaction probability. Anttila et al.

15   (2006) proposed a parameterization (Anttila06) that described the organic coating suppression effect on $\gamma_{N_2O_5}$. Based on laboratory experiments and Anttila06, Gaston et al. (2014) proposed that the suppression of $\gamma_{N_2O_5}$ by organic coating is dependent on a range of factors including the O:C ratio, the organic particle mass fraction and the relative humidity (RH). Bertram and Thornton (2009) developed a parameterization to describe the influence of chloride salts on $\gamma_{N_2O_5}$ as a function of RH. However, the influence of temperature was not considered.

20   Recently, Morgan et al. (2015) reported that the influence of chloride may not be represented properly, and the "high" O:C regime defined in Gaston et al. (2014) was scarcely observed over northwestern Europe by airborne regional measurement. Several laboratory studies reported that $\gamma_{N_2O_5}$ substantially varies with temperature, RH, and particle composition (Mentel et al., 1999; Kane et al., 2001; Hallquist et al., 2003; Chang et al., 2011; Brown and Stutz, 2012; Gaston et al., 2014). Davis et al. (2008) derived a parameterization (Davis08) of $\gamma_{N_2O_5}$ on the

25   surface of particles containing ammonium, sulfate and nitrate. It was developed based on numerous previous laboratory studies (Mozurkewich and Calvert, 1988; Hu and Abbatt, 1997; Folkers, 2002; Kane et al., 2001; Folkers et al., 2003; Hallquist et al., 2003; Badger et al., 2006), with respect to temperature, RH and particle compositions.

Several studies have implemented the heterogeneous hydrolysis of N_2O_5 in global and regional chemical

30   transport models, in order to investigate its influences on atmospheric chemistry. However, the parameterizations may not properly represent this process. Dentener and Crutzen (1993) investigated the importance of the heterogeneous hydrolysis of N_2O_5 on a global scale, but assumed a constant value $\gamma_{N_2O_5}$ =0.1, which might be overestimated. Riemer et al. (2003) reported that the scheme of Chang et al. (1987) could only be representative of heavily polluted conditions or if cloud droplets are at presence, with a particle surface area concentration of

35   2700 $\mu m^2/cm^3$. Riemer et al. (2003) developed a scheme (Riemer03) based on the Chang scheme and applied it

in box, 1-D and 3-D models, with the published $\gamma_{N_2O_5}$ values from Mentel et al. (1999) and Wahner et al. (1998). However, the influence of temperature and particle compositions on $\gamma_{N_2O_5}$ was still not considered in Riemer et al. (2003). Later, by applying Anttila06 to Riemer03, Riemer et al. (2009) found that organic coatings could decrease particulate nitrate concentrations by up to 90% where both N_2O_5 and secondary organic compounds were built-up. Evans and Jacob (2005) developed a parameterization scheme (EJ05) that has an extensive description of aerosol composition to improve the GEOS-CHEM simulations. EJ05 included $\gamma_{N_2O_5}$ of dust (Bauer et al., 2004), sea salt (Sander et al., 2003), sulfate (Kane et al., 2001; Hallquist et al., 2003), elemental carbon (EC, Sander et al., 2003) and organic carbon (OC, Thornton et al., 2003), also took into account the dependence on RH. However, $\gamma_{N_2O_5}$ of nitrate and the dependence on temperature were not carefully considered in EJ05. Archer-Nicholls et al. (2014) incorporated Bertram and Thornton (2009) into WRF-Chem. Lowe et al. (2015) further took the organic coating effect into account by applying Anttila06 to Bertram and Thornton (2009). However, $\gamma_{N_2O_5}$ with respect to EC, OC and dust was lacking in Bertram and Thornton (2009). As mentioned above, the reported influence of chloride on $\gamma_{N_2O_5}$ (Bertram and Thornton, 2009) may not be realized in northwestern Europe (Morgan et al., 2015).

Aiming to improve the representativeness of heterogeneous hydrolysis of N_2O_5 in 3-D models, we propose a new parameterization of $\gamma_{N_2O_5}$ with respect to temperature, RH, and particle composition. The influence of surface area concentration on $k_{N_2O_5}$ is also comprehensively considered. This new scheme was incorporated into the 3-D fully on-line coupled model COSMO-MUSCAT (**Co**nsortium for **S**mall-scale **Mo**delling and **Mu**lti-**S**cale **C**hemistry **A**erosol **T**ransport, http://projects.tropos.de/cosmo_muscat, Wolke et al., 2004; Wolke et al., 2012), in order to investigate the impact of heterogeneous hydrolysis of N_2O_5 on the particulate nitrate prediction. The measurements of the HOPE campaign (HD(CP)[2] Observational Prototype Experiment, Macke et al., 2016) at Melpitz site (12.93°E, 51.53°N, 86 m a.s.l., a regional background observatory of central Europe) and other three stations of the German federal environmental agency (UBA) over Germany were used to validate the simulation results.

2 Data & Methods

2.1 The model system COSMO-MUSCAT

The online-coupled chemical transport model COSMO-MUSCAT is qualified for process studies as well as the operation forecast of pollutants in local and regional areas (Heinold et al., 2011; Hinneburg et al., 2009; Stern et al., 2008; Renner and Wolke, 2010). Two nested domains with 50 vertical layers were used for this model study. The outer domain covers the whole Europe, with a spatial grid resolution of 14×14 km. The inner domain (N2) covers Germany, the Netherlands and near-by regions, with a spatial grid resolution of 7×7 km (Fig. 1). The simulation period was divided into overlapping short-term cycles. Each of these cycles consisted of a one-day spin-up for the meteorology followed by a two-day coupled run of meteorology and chemistry transport. The main features of the model system are described below. More details are given in Wolke et al. (2004, 2012) and Baldauf et al. (2011).

An adequate modelling of dynamics requires an online coupling between the chemical transport model MUSCAT and the meteorological model COSMO. Here, the compressible non-hydrostatic flow in a moist atmosphere is described by the primitive hydro-thermodynamic equations (Steppeler et al., 2003; Doms et al., 2011a). The vertical diffusion is parameterized by a level 2.5 closure scheme based on a prognostic equation for

5 turbulent kinetic energy (Doms et al., 2011b). Moist convection is parameterized according to Tiedtke (1989). A two-stream formulation (Ritter and Geleyn, 1992) is applied for radiative transfer. Aerosol particles, clouds and tracers gases are considered as optically active constituents, modifying the radiative fluxes by absorption, scattering and emission. The meteorological forcing of COSMO is performed by reanalysis data of the German Weather Service DWD, which are derived from the global meteorological model GME (Majewski et al., 2002).

10 MUSCAT describes the transport, chemical and removal processes. The chemical mechanism RACM-MIM2 (Karl et al., 2006; Stockwell et al., 1997) with 87 species and more than 200 reactions is applied to represent the gaseous chemistry. A simplified mass based approach (similar to EMEP model, Simpson et al., 2003) is used to represent the aerosol processes. The formation of secondary inorganic particulate matter is performed by reactions between ammonia and sulfuric or nitric acid, which are produced from the gas phase precursors SO_2

15 and NOx (Hinneburg et al., 2009). The applied particle/gas partitioning depends on temperature and humidity. As in ISORROPIA (Nenes et al., 1998), the equilibrium is shifted towards the gas phase for dry and warm conditions. The implementation of this partitioning scheme is comparable to Galperin and Sofiev (1998) by using the equilibrium approach of Mozurkewich (1993). SORGAM (Schell et al., 2001) is coupled with the mass-based aerosol approach to predict the formation of secondary organic aerosol (SOA). Dry deposition is

20 modelled by using the resistance approach described by Seinfeld and Pandis (2006), considering the atmospheric turbulence state, the kinetic viscosity, and the gravitational settling of particles. The aerodynamic and quasi-laminar layer resistances are taken from COSMO by analogy with the deposition of water vapour. The wet deposition is parameterized in dependence on the size resolved scavenging and collection efficiency (Simpson et al., 2003).

25 The European anthropogenic emission inventory and the temporal resolved emission factors are provided by TNO for the AQMEII project (Pouliot et al., 2012; Wolke et al., 2012). The inventory includes the gaseous pollutants (CO, NOx, SO_2, NH_3 methane and non-methane volatile organic compounds) and primary emitted particulate matters ($PM_{2.5}$, $PM_{2.5-10}$, organic carbon-OC and elemental carbon-EC) with a spatial resolution of $0.125^o \times 0.0625^o$ (lon-lat, about 7×7 km). Note that EC and BC are usually interchangeable in modelling studies

30 (Vignati et al., 2010; Chen et al., 2016a; Nordmann et al., 2014). The emission of NH_3 was reduced by 50%, since over 90% of NH_3 emissions in Europe are contributed by agricultural sources (Hertel et al., 2011; Erisman et al., 2008; Reidy et al., 2008) and agriculture emissions of NH_3 are overestimated by ~50% or even more (Sintermann et al., 2012; Backes et al., 2016). Also, Chen et al. (2016b) adopted the same NH_3 emission inventory in the WRF-Chem model and reported that total NH_3 was overestimated by a factory of ~2 at Melpitz

35 during the campaign period. The modelled dust emissions depend on surface wind friction velocities, surface roughness, soil particle size distribution, and soil moisture (Heinold et al., 2011). Sea salt emissions are parameterized depending on salinity and wind speed (Long et al., 2011). Biogenic emissions depends on land-use and meteorology by the approach of Steinbrecher et al. (2009) and for "soil NO" by Williams et al. (1992) and Stohl et al. (1996). Saarikoski et al. (2007) scheme was applied to estimate the biomass burning emissions.

The chemical inactive tracers (T1, T2 and T3) were added into RACM-MIM2 to investigate the chemical fluxes of the selected reactions. T1, T2 and T3 (representing R1, R2 and R3 respectively) were reset to zero every hour in the simulation in order to quantify the chemical fluxes from N_2O_5 to nitrate avoiding the influence of transport. T1 represents the contribution of N_2O_5 on chemical formation of nitric acid; T3-T2 represents local chemical net formation of particulate nitrate.

$$N_2O_5 + H_2O \overset{\text{(aerosol)}}{\rightarrow} 2HNO_3 + T1 \tag{R1}$$

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 + T2 \tag{R2}$$

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 + T3 \tag{R3}$$

Furthermore, in order to investigate the influence of transport from the NH_3 source regions (the Netherlands and southern Germany) on particulate nitrate, the marker tracer (T-NH3) was emitted into the first layer of regions with high ammonia emissions (white bars in Fig. 1) with an emission rate of 2×10^{-8} mol/m^2/s.

2.2 A novel parameterization of heterogeneous hydrolysis of N_2O_5

The reaction of N_2O_5 with water vapour is very slow, therefore a considerable loss of N_2O_5 is assumed to occur on the surface of deliquescent aerosol particles (Platt et al., 1984), as shown in R1. Many laboratory experiments have shown that $\gamma_{N_2O_5}$ depends principally on particle composition and water content (and so atmospheric RH). Reducing the RH, or adding organics or nitrate to the solutions, suppresses $\gamma_{N_2O_5}$ by an order of magnitude (Chang et al., 2011 and references therein).

Riemer03, which adapted from Chang et al. (1987), was originally adopted in COSMO-MUSCAT to represent the heterogeneous hydrolysis of N_2O_5. Reaction R1 is implemented into chemical transport models as a first-order loss (Riemer et al., 2003). The reaction constant ($k_{N_2O_5}$) is defined as:

$$k_{N_2O_5} = \frac{1}{4} \cdot v_{N_2O_5} \cdot S \cdot \gamma_{N_2O_5} \tag{1}$$

where $v_{N_2O_5}$ is the mean molecular velocity of N_2O_5, and S is the surface area concentration of aerosol particles.

Based on the first-order reaction constant, Chang et al. (1987) assumed $\gamma_{N_2O_5} = 0.1$ and proposed the following scheme to represent $k_{N_2O_5}$.

$$k_{N_2O_5} = \frac{1}{600 \exp(-(\frac{RH}{28})^{2.8} + a)} \tag{2}$$

RH is the relative humidity in %, which was used as an indicator for the influence of hygroscopic growth on S, $k_{N_2O_5}$ results in min^{-1}, and 'a=5' was originally adopted in Chang et al. (1987). According to Riemer et al.

(2003), 'a=5' represents the surface area concentration of 2700 μm²/cm³, when RH is higher than 60%. However, this high surface area concentration can only be expected in highly polluted areas or if cloud droplets are present. Therefore, we adopted 'a=17' in this study as suggested by Riemer et al. (2007). This produced a $k_{N_2O_5}$ value, which represents the particle surface area concentration of about 600 μm²/cm³ (RH>60%) and treats $\gamma_{N_2O_5}$ based on the measurements of Mentel et al. (1999) as a homogeneously internal mixture of nitrate and sulfate (Riemer et al., 2003).

In Riemer03, $\gamma_{N_2O_5}$ was considered as independent of temperature, RH and detailed particle compositions (only nitrate and sulfate were considered). Furthermore, S was set to a constant value (600 μm²/cm³) without sufficient consideration of the influence of particle surface area concentration. Thus, some uncertainties were found, applying this scheme in 3-D chemical transport models. In this study, we proposed a sophisticated parameterization based on Riemer03 with the full consideration of temperature, RH, aerosol particle compositions and S.

As shown in equation (1), $k_{N_2O_5}$ is linearly related to S and $\gamma_{N_2O_5}$. We adapted equation (2) with factors f_s and $f_{\gamma_{N_2O_5}}$, which represent the impact of S and $\gamma_{N_2O_5}$ respectively, as shown in equation (3). f_s can be estimated from the particle mass concentration, according to equation (4). $f_{\gamma_{N_2O_5}}$ can be estimated from the core-shell model of aerosol particles considering the secondary organic coating effect according to Anttila et al. (2006) and Riemer et al. (2009), as given in equation (5). The influence of O:C ratio on the organic coating effect (Gaston et al., 2014) was not considered here, since the O:C ratio information is not available in COSMO-MUSCAT. Also the "high" O:C regime defined in Gaston et al. (2014) may not represent the northwestern Europe case compared with airborne measurements (Morgan et al., 2015).

$$k_{N_2O_5} = \frac{1}{600\exp(-(\frac{RH}{28})^{2.8} + 17)} \cdot f_s \cdot f_{\gamma_{N_2O_5}} \tag{3}$$

$$f_s = (SA_{fine} \cdot PM_{fine} + SA_{coarse} \cdot PM_{coarse}) / 600 \tag{4}$$

where SA_{fine} / SA_{coarse} is the specific surface area for fine/coarse mode particles in m²/g, PM_{fine} / PM_{coarse} is the mass concentration of fine/coarse mode particles in μg/m³. A value 11 m²/g was used for SA_{fine}, considering recently reported values of 11.9 m²/g and 10.2 m²/g from laboratory studies (Okuda, 2013) and measurements in Japanese urban regions (Hatoya et al., 2016). A value of 1.2 m²/g was used for SA_{coarse} (Okuda, 2013). Note that the nitrate mass concentration in (4) is considered as 1.3 times of sulfate mass concentration, based on the filter measurements during HOPE-Melpitz campaign. This is aimed to calculate the contribution of the surface area concentration by nitrate in the model, meanwhile, avoiding errors with positive feedback between $k_{N_2O_5}$ and the modelled particulate nitrate mass concentration.

$$f_{\gamma_{N_2O_5}} = (\gamma_{core}^{-1} + \gamma_{coating}^{-1})^{-1} / 0.1 \tag{5}$$

where γ_{core} is the N_2O_5 reaction probability with the core of the particle, which can be estimated by Table 1; $\gamma_{coating}$ is the N_2O_5 reaction probability with the secondary organic coating shell of the particle, which can be estimated by the formula (6) according to Anttila et al. (2006) and Riemer et al. (2009).

$$\gamma_{coating} = \frac{4RTH_{N_2O_5} D_{N_2O_5} R_{core}}{v_{N_2O_5} l_{shell} R_{particle}} \tag{6}$$

where R is the universal gas constant, T is the temperature, $H_{N_2O_5}$ is the Henry's Law constant of N_2O_5 for the organic coating, and $D_{N_2O_5}$ is the diffusion coefficient of N_2O_5 in the organic coating, R_{core} is the radius of the core, $R_{particle}$ is the radius of the particle, and l_{shell} is the thickness of the organic coating shell.

γ_{core} can be estimated from previous laboratory experiments (Table 1) of inorganic and primary organic

10 compositions (Davis et al. 2008; Evans and Jacob, 2005, and references therein;). Davis et al. (2008) proposed an extended parameterization for N_2O_5 hydrolysis on ammonium-sulfate-nitrate particles, with respect to RH and temperature. Evans and Jacob (2005) provided the parameterizations for N_2O_5 hydrolysis on primary organic particles (Thornton et al., 2003), black carbon (Sander et al., 2003), sea salt (Sander et al., 2003) and dust (Bauer et al., 2004). The core of the aerosol particle was assumed to be homogeneously internally mixed. γ_{core} is a

15 mass-weighted average (Riemer et al., 2003) of each single-component parameterization (Table 1).

2.3 Observations

The filter chemical composition measurements of the HOPE-Melpitz campaign (10-25 September 2013) and at three UBA stations (Neuglobsow, Schmücke, and Zingst, www.umweltbundesamt.de) were used to validate the modelled results. The observations at the TROPOS research station Melpitz represent the regional background of

20 central Europe (Spindler et al., 2012; Spindler et al., 2010; Brüggemann and Spindler, 1999; Poulain et al., 2011; Birmili et al., 2001). During the HOPE-Melpitz campaign, high volume samplers DIGITEL DHA-80 (Walter RiemerMesstechnik, Germany), with a sampling flow of about 30 m³/h, were used to collect 24-hour daily filter samples with 10 μm cutoff inlets. Additionally, 24-hour filter sampler measurements with PM$_{10}$ inlet at 3 UBA station in Germany were collected every third day. The filter material is quartz fibre (Munktell, Grycksbo,

25 Sweden, Type MK 360), which allows the determination of particle mass, water-soluble ions (SO_4^{2-}, NO_3^{-}, NH_4^{+}, Cl^{-}, Na^{+}, K^{+}, Mg^{2+} and Ca^{2+}), OC and EC from one filter. The filters were pre-heated before sampling for at least 24 hours at 105 ℃ to minimize the blank values of OC. More details about filter measurement are given in (Spindler et al., 2013). Near-ground meteorological parameters (e.g. temperature, relative humidity, wind speed, wind direction) were simultaneously measured at Melpitz. More details about the HOPE campaign are given in

30 Macke et al. (2016).

3. Results & Discussion

The model performance was examined by comparing simulated meteorological fields with the Melpitz near-ground measurements (Fig. 2). Generally, the meteorological conditions during the HOPE-Melpitz campaign were well captured by the model, with correlation coefficients (R) of 0.87, 0.85, 0.73, and 0.85 for temperature,
5   RH, 10-meter wind speed and wind direction, respectively. The factors between modelled results and the meteorological measurements were ~1, except for an overestimation of wind speed with a factor of 1.44, possibly due to the vertical resolution of the model. Nevertheless, the temperature and RH, which are the most important parameters in this study for N_2O_5 heterogeneous hydrolysis during nighttime, were in a good agreement with the measurement.

10   **3.1 Improvement of the particulate nitrate prediction**

In previous evaluation studies (Im et al., 2015; Wolke et al., 2012), the COSMO-MUSCAT model predicted particulate nitrate mass concentrations ($[NO_3^-]$) in a fair agreement with the measurements, with an overestimation in the range of 50% on long-term average. This is comparable with other models (Im et al., 2015). However, short periods with strong overestimations of $[NO_3^-]$ were also observed in these previous
15   studies. This seems to be the case for the HOPE-Melpitz campaign simulation, where COSMO-MUSCAT highly overpredicted $[NO_3^-]$ over Germany in this study (Fig. 3) as well as WRF-Chem in a previous study (Chen et al, 2016b). In order to evaluate the improvement of our new N_2O_5 scheme and quantify the influence of NH_3 emission overestimation on the particulate nitrate prediction, three sensitivity simulations were conducted (Table 2).

20   In this HOPE-Melpitz campaign case, the particulate nitrate mass concentrations were overestimated by factors of 23.7, 12, 6.5 and 6.3 for Neuglobsow, Schmücke, Zingst, and Melpitz, respectively (Fig. 3). The overestimation of NH_3 emission might contribute about 20-30% of the particulate nitrate overprediction, compared between Riemer03-FullNH3 and Riemer03 cases. Similar results were reported in Renner and Wolke et al. (2010). However, even with a 50% reduction of NH_3 emissions, the particulate nitrate was still highly
25   overestimated over Germany with factors of about 19, 9, 4.5 and 5 for these four stations, respectively. Our new N_2O_5 parameterization scheme would further moderate the overprediction by another ~35% (Fig. 3). Correspondingly, the overestimation factors of particulate nitrate were reduced to about 10.7, 6, 2.5 and 3 for the four stations, respectively. The N_2O_5 was almost all consumed by the reaction at Melpitz in Riemer03 case, but not the NewN2O5 case (Fig. 3e). This indicated a significant decrease in the reaction constant of heterogeneous
30   hydrolysis of N_2O_5 by the new scheme. However, there must be other reasons that might explain the remained overestimations in the simulated particulate nitrate mass concentrations. Possible reasons should be investigated in future studies, e.g., deposition process, long-range transport, formation of nitrogen-containing OC, neutralization process.

The improvement of particulate nitrate prediction with the new scheme can be more clearly shown associated
35   with the tracers (T1 in Fig. 3f; T3-T2 in Fig. 3g, and T-NH3 in Fig. 3h) and the comparison with Melpitz measurements (Fig. 3d), which have a higher temporal resolution. The overestimation of $[NO_3^-]$ in September 10-11 (grey shaded period in Fig. 3) stemmed from the uncertainty of boundary conditions in the model. As shown in Fig. S1, an air mass with high $[NO_3^-]$ was transported from the southwestern boundary area to Melpitz.

The [NO$_3^-$] at Melpitz was dominated by the transport from the Netherlands and southern Germany on September 13-14 and 19-24 (blue shaded period in Fig. 3), as indicated by the high T-NH3 concentration (Fig. 3h) and the negligible local chemical formations (Fig. 3g). In contrast, the local chemical formations dominated the [NO$_3^-$] in September 12, 17-18 and 25 (red shaded period in Fig. 3). During the red shaded period, T-NH3

5 was almost zero (Fig. 3h) and the modelled wind speed was less than 4 m/s in average (Fig. 2c). A much stronger reduction on the overestimation of particulate nitrate occurred during the red shaded period (a factor of ~1.4 in average), which was dominated by the local chemical formations. This further confirmed the improvement of heterogeneous hydrolysis of N$_2$O$_5$ by the new scheme. During September 15-16 (without shaded period in Fig. 3), the contributions from both transport and local chemical formations of particulate nitrate were

10 very limited (Fig. 3f-h), resulting in very low [NO$_3^-$].

3.2 Comparison between NewN2O5 and Riemer03

The NewN2O5 case improved the particulate nitrate overestimation problem compared with Riemer03. Meanwhile, the spatial distribution pattern of [NO$_3^-$] was similar between these two cases (Fig. 4). Here, we focus on the nighttime period of the HOPE-Melpitz campaign, since the N$_2$O$_5$ heterogeneous reaction is much

15 more significant during the night than in the daytime. The lowest [NO$_3^-$] was found over Poland and ocean regions during nighttime, [NO$_3^-$] was lower than 4 μg/m^3 and 3 μg/m^3 in Riemer03 and NewN2O5 cases, respectively. Moderate [NO$_3^-$] was found over central Europe (Melpitz and the surrounding region), about 6-8 μg/m^3 and 4-5.5 μg/m^3 in the Riemer03 and NewN2O5 cases, respectively. The highest [NO$_3^-$] occurs over the region of the Netherlands and near-by regions, about 9-12 μg/m^3 and 6-8 μg/m^3 in Riemer03 and NewN2O5

20 cases, respectively, due to the high agriculture emission of NH$_3$ in this region. There was also a remarkably high amount of particulate nitrate over southern Germany, about 8-10 μg/m^3 and 5-6.5 μg/m^3 in the Riemer03 and NewN2O5 cases, respectively. In general, the [NO$_3^-$] was reduced by ~35% over the entire N2 domain (Fig. 4). The most significant reduction of [NO$_3^-$] is found over the Netherlands and southern Germany where the highest [NO$_3^-$] (reduced by about 3-4.5 μg/m^3) was found, followed by the near Melpitz region (reduced by about 2-3

25 μg/m^3, Fig. 4c). This is caused by a significant reduction of $k_{N_2O_5}$ by decreasing the surface area concentration of aerosol particle (S) and reaction probability of N$_2$O$_5$ ($\gamma_{N_2O_5}$), in the new scheme compared to Riemer03, which assumed a constant value of 600 μm^2/cm^3 and 0.1 for these two parameters, respectively. As shown in Fig. S2, the S and $\gamma_{N_2O_5}$ at Melpitz were in average reduced to ~14% and ~23% of the Riemer03 case, respectively. Correspondingly, the $k_{N_2O_5}$ was reduced by a factor of more than 10. Therefore, the regions with high [NO$_3^-$]

30 during nighttime indicates considerable nitrate formation from the heterogeneous hydrolysis of N$_2$O$_5$, which was reduced to a more reasonable value in our new scheme. However, this heterogeneous hydrolysis was slow over the regions where [NO$_3^-$] was low during nighttime, and did not have relevant contribution on the formation of particulate nitrate. Therefore, the improvement of particulate nitrate prediction by the new scheme was more significant over the high-[NO$_3^-$] regions than the low-[NO$_3^-$] regions.

35 **3.3 Influence of organic coating on the N$_2$O$_5$ heterogeneous hydrolysis**

The secondary organic coating on particle surface may significantly decrease the reaction probability of N$_2$O$_5$ and influence the particulate nitrate concentration. As shown by Riemer et al. (2009), which coupled Anttila06 to

Riemer03, organic coating could decrease [NO_3^-] by up to 90% where both N_2O_5 and secondary organic compounds were built-up. The highest reduction over Europe was found over the Netherlands followed by western Germany (both covered by the domain N2) in their study. However as discussed above, Riemer03 may overestimate nitrate formation from the heterogeneous hydrolysis of N_2O_5, because of simplifying S and $\gamma_{N_2O_5}$.

5   In this study, we introduced a more sophisticated parameterization for heterogeneous hydrolysis of N_2O_5. The influence of the organic coating suppression effect on particulate nitrate prediction would be re-evaluated, based on our new scheme.

The nighttime results were analysed, since much higher N_2O_5 concentrations occur and its heterogeneous hydrolysis is more important than during daytime (Jacob, 2000). As shown in Fig. 5a and Fig. 5b, the influence

10   of the organic coating effect was negligible over the domain N2 including the Netherlands and Germany. Even at 24 September 23:00 CET when changes were most significant, the organic coating reduced [NO_3^-] only by about 2-4 μg/m^3 (less than 10-20%) over the black-polygon marked and near-by regions (Fig. S3). Meanwhile, for nighttime averages during the campaign, the organic coating could only reduce [NO_3^-] by less than 0.1 μg/m^3 or 2% over the whole domain (Fig. 5). This is because much stricter conditions, as described following, are needed

15   in NewN2O5 for a significant organic coating effect compared with Riemer03. In addition to the simultaneous build-up of SOA and N_2O_5 (Riemer et al., 2009), high NH_3 concentrations and $\gamma_{N_2O_5}$ are also indispensable conditions for a significant organic coating effect. High NH_3 concentrations are necessary for neutralizing the HNO_3, which came from the heterogeneous hydrolysis of N_2O_5 during the night. High $\gamma_{N_2O_5}$ causes a significant reduction of $\gamma_{N_2O_5}$ by organic coating. Therefore, a large impact should be expected in the regions with high RH

20   and low temperature. As show in Fig. 5, the most significant organic coating effect (still less than 2% influence on [NO_3^-]) could be found over the Netherlands and near-by regions (black polygon). Over this area, these five conditions were fulfilled to some extent: (1) temperature was 13.5-14.5 °C; (2) RH was higher than 75%; (3) SOA concentration was ~1.6 μg/m^3; (4) N_2O_5 concentration was about 0.4-0.6 μg/m^3; (5) NH_3 concentration was about 4-6 μg/m^3 (Fig. 1). There was almost no influence of organic coating over the other regions (Fig. 5a and

25   Fig. 5b). These five conditions (not very high temperature; relatively high RH; built-up of SOA, N_2O_5 and NH_3) could not be simultaneously fulfilled over the western and central Europe, therefore the organic coating effect was not very significant.

4 Conclusions

Generally, the COSMO-MUSCAT model predicted particulate nitrate in a reasonable range in long-term average.

30   The results were comparable with other models in previous studies. However during the HOPE-Melpitz campaign (10-25 September 2013), particulate nitrate was significantly overestimated by the COSMO-MUSCAT model over Germany, despite a good performance of meteorological simulation. This can be partly (~35%) attributed to the parameterization of heterogeneous hydrolysis of N_2O_5 (Riemer03). A sophisticated parameterization of heterogeneous hydrolysis of N_2O_5 (NewN2O5) was proposed in this study, aiming at

35   improving the particulate nitrate prediction in atmospheric modelling.

In order to quantify the improvement of the nitrate prediction by using NewN2O5, sensitivity studies were performed based on more realistic NH_3 emissions, which are reduced by 50%. This correction was based on previous studies that showed NH_3 emissions were overestimated by a factor of ~2. The overestimation of NH_3 emissions led to about 20-30% overprediction of particulate nitrate over Germany. The horizontal distribution

5 patterns of particulate nitrate were in a good agreement between Riemer03 and NewN2O5 cases. Riemer03 overestimated particulate nitrate by a factor of 19, 9, 4.5 and 5 for Neuglobsow, Schmücke, Zingst, and Melpitz, respectively. This may be caused by an overestimation of the particle surface area concentration and the reaction probability of N_2O_5 ($\gamma_{N_2O_5}$), by assuming constant values of 600 $\mu m^2/cm^3$ and 0.1, respectively. Based on many previous laboratory experiments, the influences of temperature, RH, aerosol particle compositions and surface

10 area concentration on the heterogeneous reaction constant of N_2O_5 were considered in NewN2O5. The reaction constant was reduced by a factor of more than 10 in NewN2O5. Correspondingly, the overestimation of particulate nitrate was reduced by ~35% for the whole period. Particularly, the NewN2O5 significantly improved particulate nitrate prediction, with a factor of ~1.4 compared with the filter measurements, when particulate nitrate was dominated by the local chemical formations at Melpitz (September 12, 17-18 and 25).

15 In this study, we additionally investigated how the decrease of $\gamma_{N_2O_5}$ due to organic coating (Anttila et al., 2006) influences the particulate nitrate prediction over western and central Europe. Based on NewN2O5, the simulation results with and without organic coating were analyzed. In contrast to previous studies (e.g., Riemer et al. 2009), our results showed a negligible (less than 2% or 0.1 $\mu g/m^3$) influence of coating on particulate nitrate over the Netherlands and Germany. This is because considerable amounts of N_2O_5, SOA and NH_3 must be present at the

20 same location for the organic coating to exert an impact. In addition, low RH and high temperature would lead to a low $\gamma_{N_2O_5}$ value, and thereby no significant organic coating suppression on $\gamma_{N_2O_5}$ would be observed. These conditions were rarely fulfilled simultaneously over western and central Europe; hence, the influence of the organic coating effect on particulate nitrate prediction was negligible in this study.

This study suggests that temperature, RH, particle compositions and surface area concentration should be taken

25 into account in the parameterization of the heterogeneous hydrolysis of N_2O_5. A sophisticated parameterization is proposed in this investigation and should be included in model simulations to improve the representativeness of the N_2O_5 hydrolysis of in the ambient atmosphere. The results also implicate that the organic coating effect on suppressing the heterogeneous hydrolysis of N_2O_5 may not be as important as expected over Europe.

30 **Acknowledgements:** The HOPE campaign was funded by the German Research Ministry under the project number 01LK1212 C. We would like to thanks TNO (the Netherlands) and the AQMEII project (http://aqmeii.jrc.ec.europa.eu/aqmeii2.htm) provide the European anthropogenic emission inventory, and German federal environmental agency (UBA) provide the filter measurements of particle compositions. Furthermore, the JSC Jülich and the DWD Offenbach supported the work by providing computing time and

35 meteorological data. We also would like to thanks Prof. Dr. Ulrich Pöschl, Prof. Dr. Hartmut Herrmann and Dr. Andreas Tilgner for the discussion and help.

References:

Anttila, T., Kiendler-Scharr, A., Tillmann, R., and Mentel, T. F.: On the Reactive Uptake of Gaseous Compounds by Organic-Coated Aqueous Aerosols: Theoretical Analysis and Application to the Heterogeneous Hydrolysis of N2O5, The Journal of Physical Chemistry A, 110, 10435-10443, 10.1021/jp062403c, 2006.

Archer-Nicholls, S., Lowe, D., Utembe, S., Allan, J., Zaveri, R. A., Fast, J. D., Hodnebrog, Ø., Denier van der Gon, H., and McFiggans, G.: Gaseous chemistry and aerosol mechanism developments for version 3.5.1 of the online regional model, WRF-Chem, Geosci. Model Dev., 7, 2557-2579, 10.5194/gmd-7-2557-2014, 2014.

Backes, A. M., Aulinger, A., Bieser, J., Matthias, V., and Quante, M.: Ammonia emissions in Europe, part II: How ammonia emission abatement strategies affect secondary aerosols, Atmospheric Environment, 126, 153-161, http://dx.doi.org/10.1016/j.atmosenv.2015.11.039, 2016.

Badger, C. L., Griffiths, P. T., George, I., Abbatt, J. P. D., and Cox, R. A.: Reactive Uptake of N2O5 by Aerosol Particles Containing Mixtures of Humic Acid and Ammonium Sulfate, The Journal of Physical Chemistry A, 110, 6986-6994, 10.1021/jp0562678, 2006.

Baldauf, M., Seifert, A., Förstner, J., Majewski, D., Raschendorfer, M., and Reinhardt, T.: Operational Convective-Scale Numerical Weather Prediction with the COSMO Model: Description and Sensitivities, Monthly Weather Review, 139, 3887-3905, 10.1175/mwr-d-10-05013.1, 2011.

Bauer, S. E., Balkanski, Y., Schulz, M., Hauglustaine, D. A., and Dentener, F.: Global modeling of heterogeneous chemistry on mineral aerosol surfaces: Influence on tropospheric ozone chemistry and comparison to observations, Journal of Geophysical Research: Atmospheres, 109, n/a-n/a, 10.1029/2003JD003868, 2004.

Behnke, W., George, C., Scheer, V., and Zetzsch, C.: Production and decay of ClNO2 from the reaction of gaseous N2O5 with NaCl solution: Bulk and aerosol experiments, Journal of Geophysical Research: Atmospheres, 102, 3795-3804, 10.1029/96JD03057, 1997.

Bertram, T. H., and Thornton, J. A.: Toward a general parameterization of N2O5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmos. Chem. Phys., 9, 8351-8363, 10.5194/acp-9-8351-2009, 2009.

Birmili, W., Wiedensohler, A., Heintzenberg, J., and Lehmann, K.: Atmospheric particle number size distribution in central Europe: Statistical relations to air masses and meteorology, Journal of Geophysical Research, 106, 32005-32018, DOI: 10.1029/2000JD000220, 2001.

Brown, S. S., Dibb, J. E., Stark, H., Aldener, M., Vozella, M., Whitlow, S., Williams, E. J., Lerner, B. M., Jakoubek, R., Middlebrook, A. M., DeGouw, J. A., Warneke, C., Goldan, P. D., Kuster, W. C., Angevine, W. M., Sueper, D. T., Quinn, P. K., Bates, T. S., Meagher, J. F., Fehsenfeld, F. C., and Ravishankara, A. R.: Nighttime removal of NOx in the summer marine boundary layer, Geophysical Research Letters, 31, n/a-n/a, 10.1029/2004GL019412, 2004.

Brown, S. S., and Stutz, J.: Nighttime radical observations and chemistry, Chemical Society reviews, 41, 6405-6447, 10.1039/c2cs35181a, 2012.

Brüggemann, E., and Spindler, G.: Wet and dry deposition of sulphur at the site Melpitz in East Germany, Water Air Soil Pollut 109, 81-99, 1999.

Chang, J. S., Brost, R. A., Isaksen, I. S. A., Madronich, S., Middleton, P., Stockwell, W. R., and Walcek, C. J.: A three-dimensional Eulerian acid deposition model: Physical concepts and formulation, Journal of Geophysical Research: Atmospheres, 92, 14681-14700, 10.1029/JD092iD12p14681, 1987.

Chang, W. L., Bhave, P. V., Brown, S. S., Riemer, N., Stutz, J., and Dabdub, D.: Heterogeneous Atmospheric Chemistry, Ambient Measurements, and Model Calculations of N2O5: A Review, Aerosol Science and Technology, 45, 665-695, 10.1080/02786826.2010.551672, 2011.

Chen, Y., Cheng, Y. F., Nordmann, S., Birmili, W., Denier van der Gon, H. A. C., Ma, N., Wolke, R., Wehner, B., Sun, J., Spindler, G., Mu, Q., Pöschl, U., Su, H., and Wiedensohler, A.: Evaluation of the size segregation of elemental carbon (EC) emission in Europe: influence on the simulation of EC long-range transportation, Atmos. Chem. Phys., 16, 1823-1835, 10.5194/acp-16-1823-2016, 2016a.

Chen, Y., Cheng, Y., Ma, N., Wolke, R., Nordmann, S., Schüttauf, S., Ran, L., Wehner, B., Birmili, W., van der Gon, H. A. C. D., Mu, Q., Barthel, S., Spindler, G., Stieger, B., Müller, K., Zheng, G. J., Pöschl, U., Su,

    H., and Wiedensohler, A.: Sea salt emission, transport and influence on size-segregated nitrate simulation: a case study in northwestern Europe by WRF-Chem, Atmos. Chem. Phys., 16, 12081-12097, 10.5194/acp-16-12081-2016, 2016b.

5   Davis, J. M., Bhave, P. V., and Foley, K. M.: Parameterization of N2O5 reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate, Atmos. Chem. Phys., 8, 5295-5311, 10.5194/acp-8-5295-2008, 2008.

Dentener, F. J., and Crutzen, P. J.: Reaction of N2O5 on tropospheric aerosols: Impact on the global distributions of NO x , O3, and OH, Journal of Geophysical Research: Atmospheres, 98, 7149-7163, 10.1029/92JD02979, 1993.

10 Doms, G., Schättler, U., Thomas, S., Gassmann, A., and Baldauf, M.: A Description of the Nonhydrostatic Regional COSMO-Model In: Part I: Dynamics and Numerics, Deutscher Wetterdienst, Offenbach, Available from: http://www.cosmo-model.org, 2011a.

Doms, G., Forstner, J., Heise, E., Herzog, H.-J., Raschendorfer, M., Reinhardt, T., Ritter, B., Schrodin, R., Schulz, J. P., and Vogel, G.: A Description of the Nonhydrostatic Regional COSMO-Model In: Part II:
15   Physical Parametrizations, Deutscher Wetterdienst, Offenbach. Available from: http://www.cosmomodel.org, 2011b.

Ehhalt, D., and Drummond, J. W.: The tropospheric cycle of NOx: chemistry of the unpolluted and polluted troposphere, edited by: Georgii, W. J., Proc. NATO Adv. Study Inst.,Corfu, Greece, 28 September-10 Octtober 1981 Reidel, Dordrecht, 219-251, 1982.

20 Erisman, J. W., Bleeker, A., Hensen, A., and Vermeulen, A.: Agricultural air quality in Europe and the future perspectives, Atmospheric Environment, 42, 3209-3217, http://dx.doi.org/10.1016/j.atmosenv.2007.04.004, 2008.

Evans, M. J., and Jacob, D. J.: Impact of new laboratory studies of N2O5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH, Geophysical Research Letters, 32, n/a-n/a,
25   10.1029/2005GL022469, 2005.

Fenter, F. F., Caloz, F., and Rossi, M. J.: Heterogeneous Kinetics of N2O5 Uptake on Salt, with a Systematic Study of the Role of Surface Presentation (for N2O5 and HNO3), The Journal of Physical Chemistry, 100, 1008-1019, 10.1021/jp9503829, 1996.

Folkers, M.: Bestimmung der Reaktionswahrscheinlichkeit von N2O5 an troposphärisch relevanten Aerosolen,
30   PhD thesis, Universität zu Köln, 2002.

Folkers, M., Mentel, T. F., and Wahner, A.: Influence of an organic coating on the reactivity of aqueous aerosols probed by the heterogeneous hydrolysis of N2O5, Geophysical Research Letters, 30, n/a-n/a, 10.1029/2003GL017168, 2003.

Galperin, M. V., and Sofiev, M. A.: The long-range transport of ammonia and ammonium in the Northern
35   Hemisphere, Atmospheric Environment, 32, 373-380, http://dx.doi.org/10.1016/S1352-2310(97)00045-9, 1998.

Gaston, C. J., Thornton, J. A., and Ng, N. L.: Reactive uptake of N2O5 to internally mixed inorganic and organic particles: the role of organic carbon oxidation state and inferred organic phase separations, Atmos. Chem. Phys., 14, 5693-5707, 10.5194/acp-14-5693-2014, 2014.

40 Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses, Journal of Geophysical Research: Atmospheres, 98, 12609-12617, 10.1029/93JD00527, 1993.

Hallquist, M., Stewart, D. J., Baker, J., and Cox, R. A.: Hydrolysis of N2O5 on Submicron Sulfuric Acid Aerosols, The Journal of Physical Chemistry A, 104, 3984-3990, 10.1021/jp9939625, 2000.

45 Hallquist, M., Stewart, D. J., Stephenson, S. K., and Anthony Cox, R.: Hydrolysis of N2O5 on sub-micron sulfate aerosols, Physical Chemistry Chemical Physics, 5, 3453-3463, 10.1039/B301827J, 2003.

Hatoya, K., Okuda, T., Funato, K., and Inoue1, K.: On-line Measurement of the Surface Area Concentration of Aerosols in Yokohama, Japan, using the Diffusion Charging Method, Asian Journal of Atmospheric Environment, 10(1), 1-12, 10.5572/ajae.2016.10.1.001, 2016.

50 Heinold, B., Tegen, I. N. A., Schepanski, K., Tesche, M., Esselborn, M., Freudenthaler, V., Gross, S., Kandler, K., Knippertz, P., MÜLler, D., Schladitz, A., Toledano, C., Weinzierl, B., Ansmann, A., Althausen, D., MÜLler, T., Petzold, A., and Wiedensohler, A.: Regional modelling of Saharan dust and biomass-

burning smoke, Tellus B, 63, 781-799, 10.1111/j.1600-0889.2011.00570.x, 2011.

Hertel, O., Reis, S., Skjøth, C. A., Bleeker, A., Harrison, R., Cape, J. N., Fowler, D., Skiba, U., Simpson, D., Jickells, T., Baker, A., Kulmala, M., Gyldenkaerne, S., Sørensen, L. L., and Erisman, J. W.: Nitrogen processes in the atmosphere, in: The European Nitrogen Assessment - Sources, Effects and Policy Perspectives, edited by Sutton, M. A., Howard, C. M., Erisman, J. W., Billen, G., Grennfelt, P., van Grinsven, H., and Grizzetti, B., 177-207, Cambridge University Press, Cambridge, UK, Available from: http://www.cambridge.org/ena, 2011.

Hinneburg, D., Renner, E., and Wolke, R.: Formation of secondary inorganic aerosols by power plant emissions exhausted through cooling towers in Saxony, Environmental Science and Pollution Research, 16, 25-35, 10.1007/s11356-008-0081-5, 2009.

Hu, J. H., and Abbatt, J. P. D.: Reaction Probabilities for N2O5 Hydrolysis on Sulfuric Acid and Ammonium Sulfate Aerosols at Room Temperature, The Journal of Physical Chemistry A, 101, 871-878, 10.1021/jp9627436, 1997.

Im, U., Bianconi, R., Solazzo, E., Kioutsioukis, I., Badia, A., Balzarini, A., Baró, R., Bellasio, R., Brunner, D., Chemel, C., Curci, G., Denier van der Gon, H., Flemming, J., Forkel, R., Giordano, L., Jiménez-Guerrero, P., Hirtl, M., Hodzic, A., Honzak, L., Jorba, O., Knote, C., Makar, P. A., Manders-Groot, A., Neal, L., Pérez, J. L., Pirovano, G., Pouliot, G., San Jose, R., Savage, N., Schroder, W., Sokhi, R. S., Syrakov, D., Torian, A., Tuccella, P., Wang, K., Werhahn, J., Wolke, R., Zabkar, R., Zhang, Y., Zhang, J., Hogrefe, C., and Galmarini, S.: Evaluation of operational online-coupled regional air quality models over Europe and North America in the context of AQMEII phase 2. Part II: Particulate matter, Atmospheric Environment, 115, 421-441, http://dx.doi.org/10.1016/j.atmosenv.2014.08.072, 2015.

Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, Atmospheric Environment, 34, 2131-2159, 2000.

Kane, S. M., Caloz, F., and Leu, M.-T.: Heterogeneous Uptake of Gaseous N2O5 by (NH4)2SO4, NH4HSO4, and H2SO4 Aerosols, The Journal of Physical Chemistry A, 105, 6465-6470, 10.1021/jp010490x, 2001.

Karl, M., Dorn, H.-P., Holland, F., Koppmann, R., Poppe, D., Rupp, L., Schaub, A., and Wahner, A.: Product study of the reaction of OH radicals with isoprene in the atmosphere simulation chamber SAPHIR, J Atmos Chem, 55, 167-187, 10.1007/s10874-006-9034-x, 2006.

Long, M. S., Keene, W. C., Kieber, D. J., Erickson, D. J., and Maring, H.: A sea-state based source function for size- and composition-resolved marine aerosol production, Atmos. Chem. Phys., 11, 1203–1216, doi:10.5194/acp-11-1203-2011, 2011

Lowe, D., Archer-Nicholls, S., Morgan, W., Allan, J., Utembe, S., Ouyang, B., Aruffo, E., Le Breton, M., Zaveri, R. A., Di Carlo, P., Percival, C., Coe, H., Jones, R., and McFiggans, G.: WRF-Chem model predictions of the regional impacts of N2O5 heterogeneous processes on night-time chemistry over north-western Europe, Atmos. Chem. Phys., 15, 1385-1409, 10.5194/acp-15-1385-2015, 2015.

Macke, A., Seifert, P., Baars, H., Beekmans, C., Behrendt, A., Bohn, B., Bühl, J., Crewell, S., Damian, T., Deneke, H., Düsing, S., Foth, A., Di Girolamo, P., Hammann, E., Heinze, R., Hirsikko, A., Kalisch, J., Kalthoff, N., Kinne, S., Kohler, M., Löhnert, U., Madhavan, B. L., Maurer, V., Muppa, S. K., Schween, J., Serikov, I., Siebert, H., Simmer, C., Späth, F., Steinke, S., Träumner, K., Wehner, B., Wieser, A., Wulfmeyer, V., and Xie, X.: The HD(CP)2 Observational Prototype Experiment HOPE – An Overview, Atmos. Chem. Phys. Discuss., 2016, 1-37, 10.5194/acp-2016-990, 2016.

Majewski, D., Liermann, D., Prohl, P., Ritter, B., Buchhold, M., Hanisch, T., Paul, G., Wergen, W., and Baumgardner, J.: The Operational Global Icosahedral–Hexagonal Gridpoint Model GME: Description and High-Resolution Tests, Monthly Weather Review, 130, 319-338, 10.1175/1520-0493(2002)130<0319:TOGIHG>2.0.CO;2, 2002.

Mentel, T., F., Sohn, M., and Wahner, A.: Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, Physical Chemistry Chemical Physics, 1, 5451-5457, 10.1039/A905338G, 1999.

Morgan, W. T., Ouyang, B., Allan, J. D., Aruffo, E., Di Carlo, P., Kennedy, O. J., Lowe, D., Flynn, M. J., Rosenberg, P. D., Williams, P. I., Jones, R., McFiggans, G. B., and Coe, H.: Influence of aerosol chemical composition on N2O5 uptake: airborne regional measurements in northwestern Europe, Atmos. Chem. Phys., 15, 973-990, 10.5194/acp-15-973-2015, 2015.

Mozurkewich, M., and Calvert, J. G.: Reaction probability of N2O5 on aqueous aerosols, Journal of Geophysical Research: Atmospheres, 93, 15889-15896, 10.1029/JD093iD12p15889, 1988.

Mozurkewich, M.: The dissociation constant of ammonium nitrate and its dependence on temperature, relative

humidity and particle size, Atmospheric Environment, 27A, 261-270, 1993.

Nenes, A., Pandis, S. N., and Pilinis, C.: ISORROPIA: A New Thermodynamic Equilibrium Model for Multiphase Multicomponent Inorganic Aerosols, Aquatic Geochemistry, 4, 123-152, 10.1023/a:1009604003981, 1998.

5 Nordmann, S., Cheng, Y. F., Carmichael, G. R., Yu, M., Denier van der Gon, H. A. C., Zhang, Q., Saide, P. E., Pöschl, U., Su, H., Birmili, W., and Wiedensohler, A.: Atmospheric black carbon and warming effects influenced by the source and absorption enhancement in central Europe, Atmos. Chem. Phys., 14, 12683-12699, 10.5194/acp-14-12683-2014, 2014.

Okuda, T.: Measurement of the specific surface area and particle size distribution of atmospheric aerosol
10   reference materials, Atmospheric Environment, 75, 1-5, http://dx.doi.org/10.1016/j.atmosenv.2013.04.033, 2013.

Platt, U. F., Winer, A. M., Biermann, H. W., Atkinson, R., and Pitts, J. N.: Measurement of nitrate radical concentrations in continental air, Environmental Science & Technology, 18, 365-369, 10.1021/es00123a015, 1984.

15 Poulain, L., Spindler, G., Birmili, W., Plass-Dülmer, C., Wiedensohler, A., and Herrmann, H.: Seasonal and diurnal variations of particulate nitrate and organic matter at the IfT research station Melpitz, Atmos. Chem. Phys., 11, 12579-12599, 2011.

Pouliot, G., Pierce, T., Denier van der Gon, H., Schaap, M., Moran, M., and Nopmongcol, U.: Comparing emission inventories and model-ready emission datasets between Europe and North America for the
20   AQMEII project, Atmospheric Environment, 53, 4-14, http://dx.doi.org/10.1016/j.atmosenv.2011.12.041, 2012.

Reidy, B., Dämmgen, U., Döhler, H., Eurich-Menden, B., van Evert, F. K., Hutchings, N. J., Luesink, H. H., Menzi, H., Misselbrook, T. H., Monteny, G. J., and Webb, J.: Comparison of models used for national agricultural ammonia emission inventories in Europe: Liquid manure systems, Atmospheric
25   Environment, 42, 3452-3464, http://dx.doi.org/10.1016/j.atmosenv.2007.04.009, 2008.

Renner, E., and Wolke, R.: Modelling the formation and atmospheric transport of secondary inorganic aerosols with special attention to regions with high ammonia emissions, Atmospheric Environment, 44, 1904-1912, http://dx.doi.org/10.1016/j.atmosenv.2010.02.018, 2010.

Riemer, N., Vogel, H., Vogel, B., Schell, B., Ackermann, I., Kessler, C., and Hass, H.: Impact of the
30   heterogeneous hydrolysis of N2O5 on chemistry and nitrate aerosol formation in the lower troposphere under photosmog conditions, Journal of Geophysical Research: Atmospheres, 108, n/a-n/a, 10.1029/2002JD002436, 2003.

Riemer, N., Vogel, H., Vogel, B., Anttila, T., Kiendler-Scharr, A., and Mentel, T. F.: Relative importance of organic coatings for the heterogeneous hydrolysis of N2O5 during summer in Europe, Journal of
35   Geophysical Research: Atmospheres, 114, 10.1029/2008JD011369, 2009.

Ritter, B., and Geleyn, J.-F.: A Comprehensive Radiation Scheme for Numerical Weather Prediction Models with Potential Applications in Climate Simulations, Monthly Weather Review, 120, 303-325, 10.1175/1520-0493(1992)120<0303:acrsfn>2.0.co;2, 1992.

Robinson, G. N., Worsnop, D. R., Jayne, J. T., Kolb, C. E., and Davidovits, P.: Heterogeneous uptake of
40   ClONO2 and N2O5 by sulfuric acid solutions, Journal of Geophysical Research: Atmospheres, 102, 3583-3601, 10.1029/96JD03457, 1997.

Saarikoski, S., Sillanpää, M., Sofiev, M., Timonen, H., Saarnio, K., Teinilä, K., Karppinen, A., Kukkonen, J., and Hillamo, R.: Chemical composition of aerosols during a major biomass burning episode over northern Europe in spring 2006: Experimental and modelling assessments, Atmospheric Environment, 41, 3577-
45   3589, http://dx.doi.org/10.1016/j.atmosenv.2006.12.053, 2007.

Sander, S. P., Friedl, R. R., Ravishankara, A. R., M., G. D., Kolb, C. E., Kurylo, M. J., Molina, M. J., Moortgat, G. K., and Finlayson-Pitts, B. J.: Chemical kinetics and photochemical data for use in atmospheric studies, evaluation number 14, JPL Publ., 02-25, 334 pp., 2003.

Schell, B., Ackermann, I. J., Hass, H., Binkowski, F. S., and Ebel, A.: Modeling the formation of secondary
50   organic aerosol within a comprehensive air quality model system, Journal of Geophysical Research: Atmospheres, 106, 28275-28293, 10.1029/2001JD000384, 2001.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley & Sons, New York, 2nd Edn., 2006.

Simpson, D., Fagerli, H., Jonson, J. E., Tsyro, S., and Wind, P.: Transboundary ACIDIFICATION, Eutrophication and Ground Level Ozone in Europe. PART I: Unified EMEP Model Description, EMEP/MSC-W: EMEP Report, Available from: http://emep.int/publ/reports/2003/emep_report_1_part1_2003.pdf, 2003.

5 Sintermann, J., Neftel, A., Ammann, C., Häni, C., Hensen, A., Loubet, B., and Flechard, C. R.: Are ammonia emissions from field-applied slurry substantially over-estimated in European emission inventories?, Biogeosciences, 9, 1611-1632, 10.5194/bg-9-1611-2012, 2012.

Spindler, G., Brüggemann, E., Gnauk, T., Grüner, A., Müller, K., and Herrmann, H.: A four-year size-segregated characterization study of particles PM10, PM2.5 and PM1 depending on air mass origin at Melpitz, Atmospheric Environment, 44, 164-173, 2010.

10 Spindler, G., Gnauk, T., Grüner, A., Iinuma, Y., Müller, K., Scheinhardt, S., and Herrmann, H.: Size-segregated characterization of PM10 at the EMEP site Melpitz (Germany) using a five-stage impactor: a six year study, J Atmos Chem, 69, 127-157, 10.1007/s10874-012-9233-6, 2012.

Spindler, G., Grüner, A., Müller, K., Schlimper, S., and Herrmann, H.: Long-term size-segregated particle (PM10, PM2.5, PM1) characterization study at Melpitz -- influence of air mass inflow, weather conditions and season, J Atmos Chem, 70, 165-195, 10.1007/s10874-013-9263-8, 2013.

Steppeler, J., Doms, G., Schättler, U., Bitzer, H. W., Gassmann, A., Damrath , U., and Gregoric, G.: Meso-gamma scale forecasts using the nonhydrostatic model LM, Meteorology and Atmospheric Physics, 82, 75-96, 10.1007/s00703-001-0592-9, 2003.

20 Stern, R., Builtjes, P., Schaap, M., Timmermans, R., Vautard, R., Hodzic, A., Memmesheimer, M., Feldmann, H., Renner, E., Wolke, R., and Kerschbaumer, A.: A model inter-comparison study focussing on episodes with elevated PM10 concentrations, Atmospheric Environment, 42, 4567-4588, http://dx.doi.org/10.1016/j.atmosenv.2008.01.068, 2008.

Steinbrecher, R., Smiatek, G., Köble, R., Seufert, G., Theloke, J., Hauff, K., Ciccioli, P., Vautard, R., and Curci, G.: Intra- and inter-annual variability of VOC emissions from natural and semi-natural vegetation in Europe and neighbouring countries, Atmospheric Environment, 43, 1380-1391, http://dx.doi.org/10.1016/j.atmosenv.2008.09.072, 2009.

Stockwell, W. R., Kirchner, F., Kuhn, M., and Seefeld, S.: A new mechanism for regional atmospheric chemistry modeling, Journal of Geophysical Research: Atmospheres, 102, 25847-25879, 10.1029/97JD00849, 1997.

Stohl, A., Williams, E., Wotawa, G., and Kromp-Kolb, H.: A European inventory of soil nitric oxide emissions and the effect of these emissions on the photochemical formation of ozone, Atmospheric Environment, 30, 3741-3755, http://dx.doi.org/10.1016/1352-2310(96)00104-5, 1996.

Thornton, J. A., Braban, C. F., and Abbatt, J. P. D.: N2O5 hydrolysis on sub-micron organic aerosols: the effect of relative humidity, particle phase, and particle size, Physical Chemistry Chemical Physics, 5, 4593-4603, 10.1039/B307498F, 2003.

Tiedtke, M.: A Comprehensive Mass Flux Scheme for Cumulus Parameterization in Large-Scale Models, Monthly Weather Review, 117, 1779-1800, 10.1175/1520-0493(1989)117<1779:acmfsf>2.0.co;2, 1989.

Van Doren, J. M., Watson, L. R., Davidovits, P., Worsnop, D. R., Zahniser, M. S., and Kolb, C. E.: Temperature dependence of the uptake coefficients of nitric acid, hydrochloric acid and nitrogen oxide (N2O5) by water droplets, The Journal of Physical Chemistry, 94, 3265-3269, 10.1021/j100371a009, 1990.

Vignati, E., Karl, M., Krol, M., Wilson, J., Stier, P., and Cavalli, F.: Sources of uncertainties in modelling black carbon at the global scale, Atmos. Chem. Phys., 10, 2595-2611, doi:10.5194/acp-10-2595-2010, 2010.

Wahner, A., Mentel, T. F., Sohn, M., and Stier, J.: Heterogeneous reaction of N2O5 on sodium nitrate aerosol, Journal of Geophysical Research: Atmospheres, 103, 31103-31112, 10.1029/1998JD100022, 1998.

Williams, E. J., Guenther, A., and Fehsenfeldi, F. C.: An inventory of nitric oxide emissions from soils in the United States, Journal of Geophysical Research: Atmospheres, 97, 7511-7519, 10.1029/92JD00412, 1992.

Wolke, R., Knoth, O., Hellmuth, O., Schröder, W., and Renner, E.: The parallel model system LM-MUSCAT for chemistry-transport simulations: Coupling scheme, parallelization and application, G.R. Joubert, W.E. Nagel, F.J. Peters, and W.V. Walter, Eds., Parallel Computing: Software Technology, Algorithms, Architectures, and Applications, Elsevier, Amsterdam, The Netherlands, 363-370, 10.1016/S0927-5452(04)80048-0, 2004.

Wolke, R., Schröder, W., Schrödner, R., and Renner, E.: Influence of grid resolution and meteorological forcing on simulated European air quality: A sensitivity study with the modeling system COSMO–MUSCAT, Atmospheric Environment, 53, 110-130, http://dx.doi.org/10.1016/j.atmosenv.2012.02.085, 2012.

Table 1. Representation of reaction probability of aerosol particle core (γ_{core}) for N$_2$O$_5$ hydrolysis.

Particle Type	Parameterization	Parameters	References and Remarks
Core of particle	$\gamma_{core} = \sum_i \gamma_i \cdot ratio_i$	$ratio_i = \dfrac{[m_i]}{[m_{core}]}$ $[m_{core}] = \sum_i [m_i]$ i: the following particle types i = [ASN, OC, SSA, Dust, BC]	γ : reaction probability m: mass [mass]: mass concentration
ASN: (A) Ammounium (S) Sulfate (N) Nitrate	$\gamma_{ASN} = \gamma^*_{AB} \cdot x_{AB} + \gamma^*_{aq/d,AS} \cdot x_{AS} + \gamma^*_{AN} \cdot x_{AN}$ $\gamma^*_{AB} = \min(\gamma_{AB}, 0.08585)$, $\quad \gamma_{AB} = \dfrac{1}{1+e^{-\lambda_{AB}}}$ $\gamma^*_{aq,AS} = \min(\gamma_{aq,AS}, 0.053)$, $\quad \gamma_{aq,AS} = \dfrac{1}{1+e^{-\lambda_{aq,AS}}}$ $\gamma^*_{d,AS} = \min(\gamma_{d,AS}, 0.0124)$, $\quad \gamma_{d,AS} = \dfrac{1}{1+e^{-\lambda_{d,AS}}}$ $\gamma^*_{AN} = \min(\gamma_{AN}, 0.0154)$, $\quad \gamma_{AN} = \dfrac{1}{1+e^{-\lambda_{AN}}}$ $\lambda_{AB} = \beta_{10} + \beta_{11} \cdot RH + \beta_{12} \cdot T_{291}$ $\lambda_{aq,AS} = (\beta_{10} + \beta_{20}) + \beta_{11} \cdot RH + (\beta_{12} + \beta_{22}) \cdot T_{291}$ $\lambda_{d,AS} = \beta_{d0} + \beta_{d1} \cdot RH + \beta_{d2} \cdot T_{293}$ $\lambda_{d,AN} = \beta_{30} + \beta_{31} \cdot RH$	$x_{AB} = 1 - (x_{AS} + x_{AN})$ $x_{AS} = \max(0, \min(1 - x_{AN}, \frac{[A]}{[N]+[S]} - 1))$ $x_{AN} = \dfrac{[N]}{[N]+[S]}$ $\beta_{10} = $ -4.10612 $\beta_{11} = 0.02386$ $\beta_{12} = $ -0.23771 $\beta_{20} = $ -0.80570 $\beta_{22} = 0.10225$ $\beta_{30} = $ -8.10774 $\beta_{31} = 0.04902$ $\beta_{d0} = $ -6.13376 $\beta_{d1} = 0.03592$ $\beta_{d2} = $ -0.19688 $T_{291} = \max(T - 291, 0)$ $T_{293} = \max(T - 293, 0)$	Davis et al. (2008) *AB: ammonium bisulfate* *AS: ammonium sulfate* *AN: ammonium nitrate* *A: NH$_4^+$* *S: SO$_4^{2-}$* *N: NO$_3^-$* *Unit of RH: %* *Unit of T: K* *aq: aqueous phase* *d: dry phase (crystallized)* *AS crystallizes when RH<32.8% and forms a sold phase (Martine et al., 2003)*
Organic Carbon (Primary)	$\gamma_{OC} = RH \times 5.2 \times 10^{-4}$ $RH < 57\%$ $\gamma_{OC} = 0.03$ $\quad RH \geq 57\%$		*Evans and Jacob (2005)* *Thornton et al. (2003)*
Sea Salt Aerosol	$\gamma_{SSA} = 0.005$ $RH < 62\%$ $\gamma_{SSA} = 0.03$ $\quad RH \geq 62\%$		*Evans and Jacob (2005)* *Sander et al. (2003)*
Dust	$\gamma_{Dust} = 0.01$		*Evans and Jacob (2005)* *Bauer et al. (2004)*
Black Carbon	$\gamma_{BC} = 0.005$		*Sander et al. (2003)*

Table 2. Sensitivity simulation cases

Case	N_2O_5 parameterization	NH_3 emission
Riemer03-FullNH3	Riemer et al. (2003)	100%
Riemer03	Riemer et al. (2003)	50% [*]
NewN2O5	New scheme (this study)	50% [*]

[*] Suggested by Sintermann et al. (2012), Backes et al. (2016) and Chen et al. (2016b)
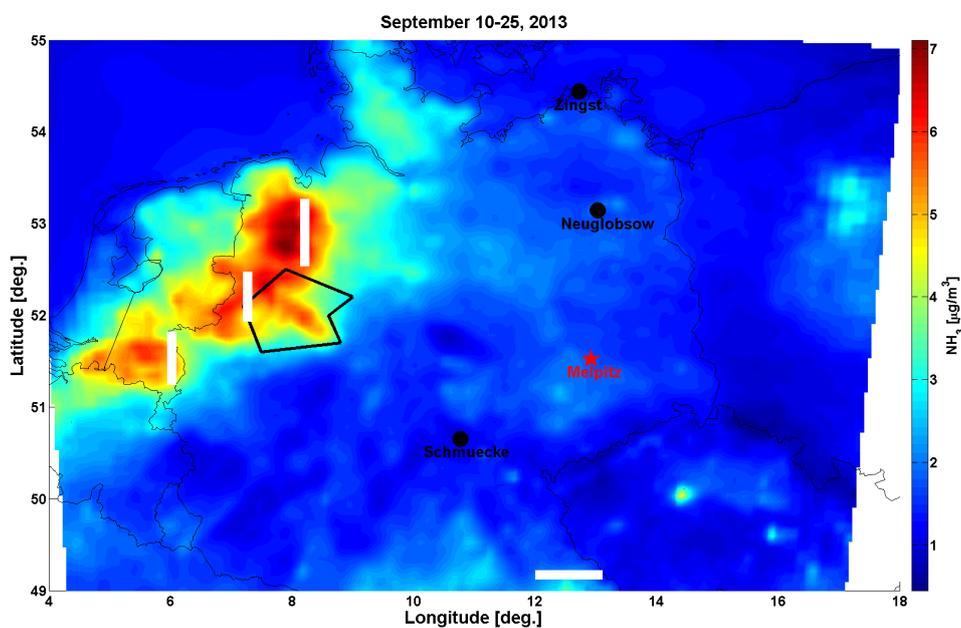
Figure 1. Results (domain N2) of NewN2O5 case of averaged NH_3 mass concentration during 10-25 September 2013. The added emissions of marker tracer (T-NH3) from NH_3 source regions (the Netherlands and south Germany) are marked by the white bars. The locations of the considered measurement stations are also marked. The region with the most significant organic coating effect is highlighted by the black polygon, and will be analysed together with Fig. 5.
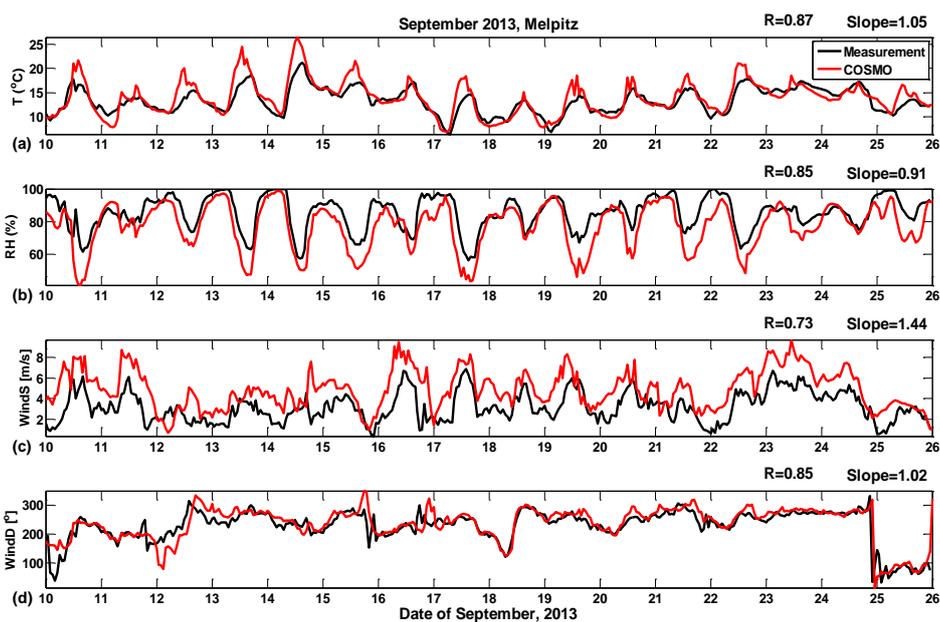
Figure 2. Comparison between modelled and measured meteorological conditions. (a) Temperature (T); (b) relative humidity (RH); (c) wind speed; (d) wind direction.
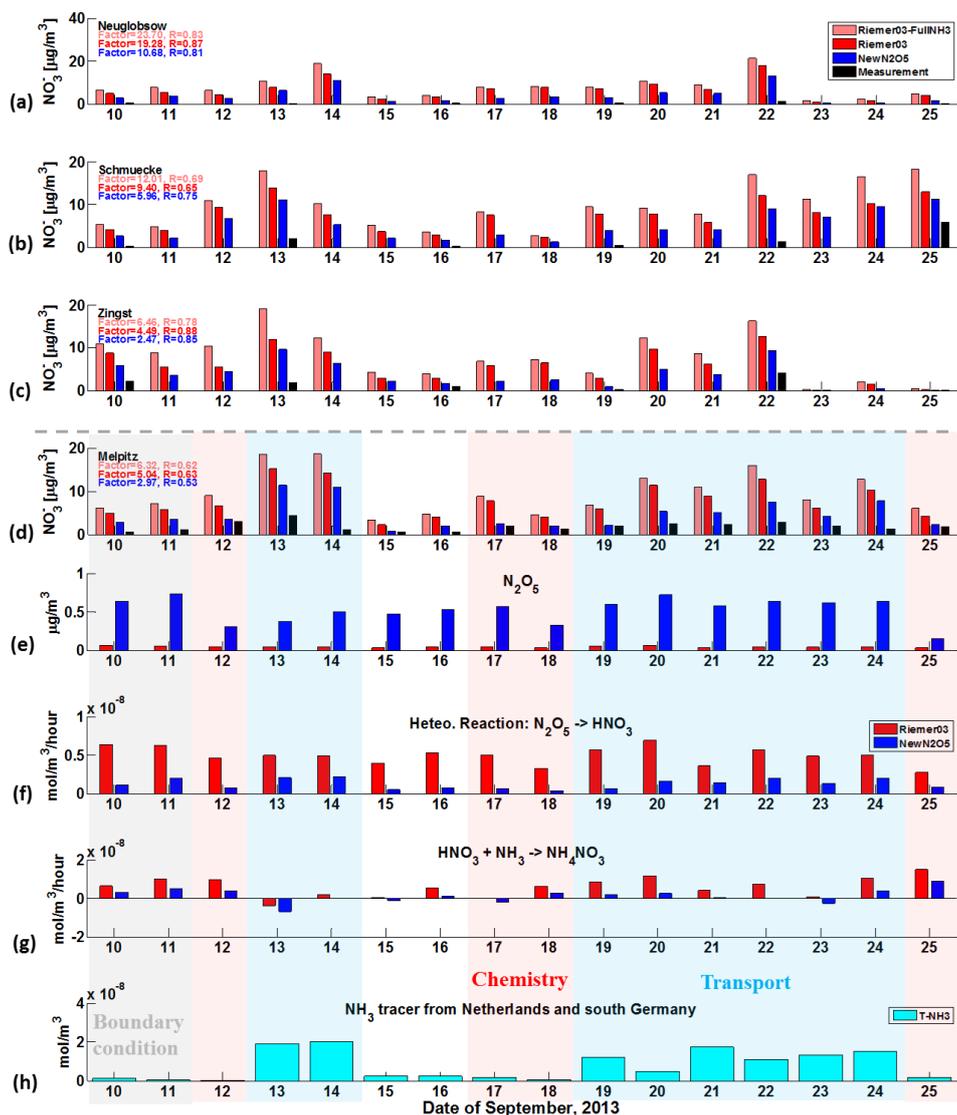
Figure 3. Comparison of particulate nitrate mass concentration between filter measurements and modelled results: (a) Neuglobsow; (b) Schmuecke; (c) Zingst; (d) Melpitz. Modelled concentrations at Melpitz: (e) N_2O_5; (f) marker species T1 for chemical reaction R1; (g) marker species for chemical formation of particulate nitrate (T3-T2); (h) the NH_3 marker tracer (T-NH3) for transport from the Netherlands and south Germany. The light-red colour bars indicate the results of Riemer03-FullNH3 case; the red colour bars indicate the results of Riemer03 case; and the blue colour bars indicate the results of NewN2O5 case. The shaded periods indicate the dominating processes for high concentrations of particulate nitrate: chemical formation (red), transport (blue), and boundary conditions (grey).
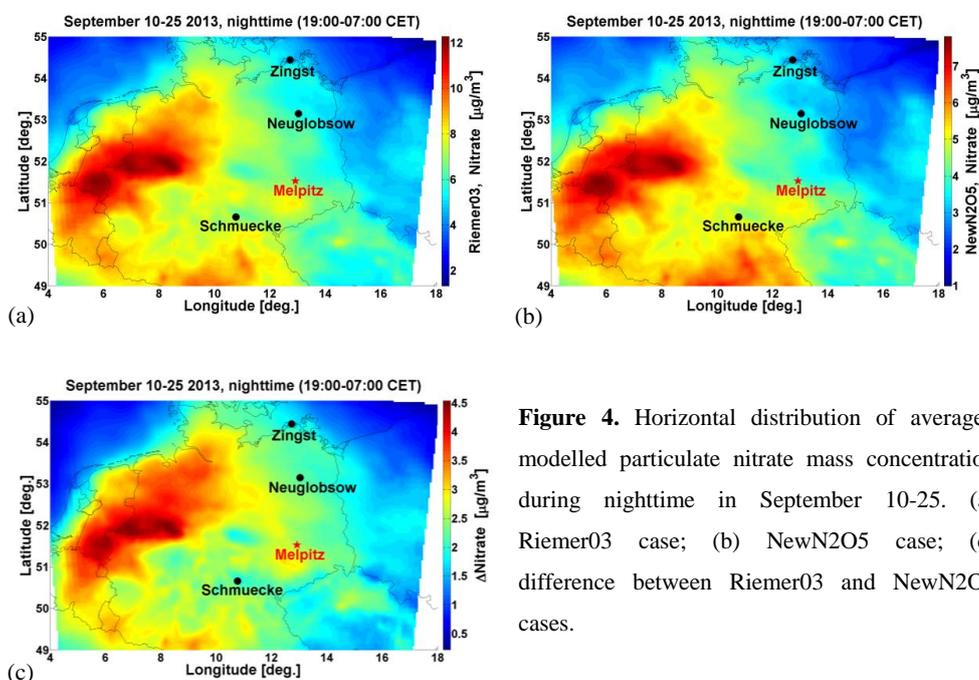
Figure 4. Horizontal distribution of averaged modelled particulate nitrate mass concentration during nighttime in September 10-25. (a) Riemer03 case; (b) NewN2O5 case; (c) difference between Riemer03 and NewN2O5 cases.
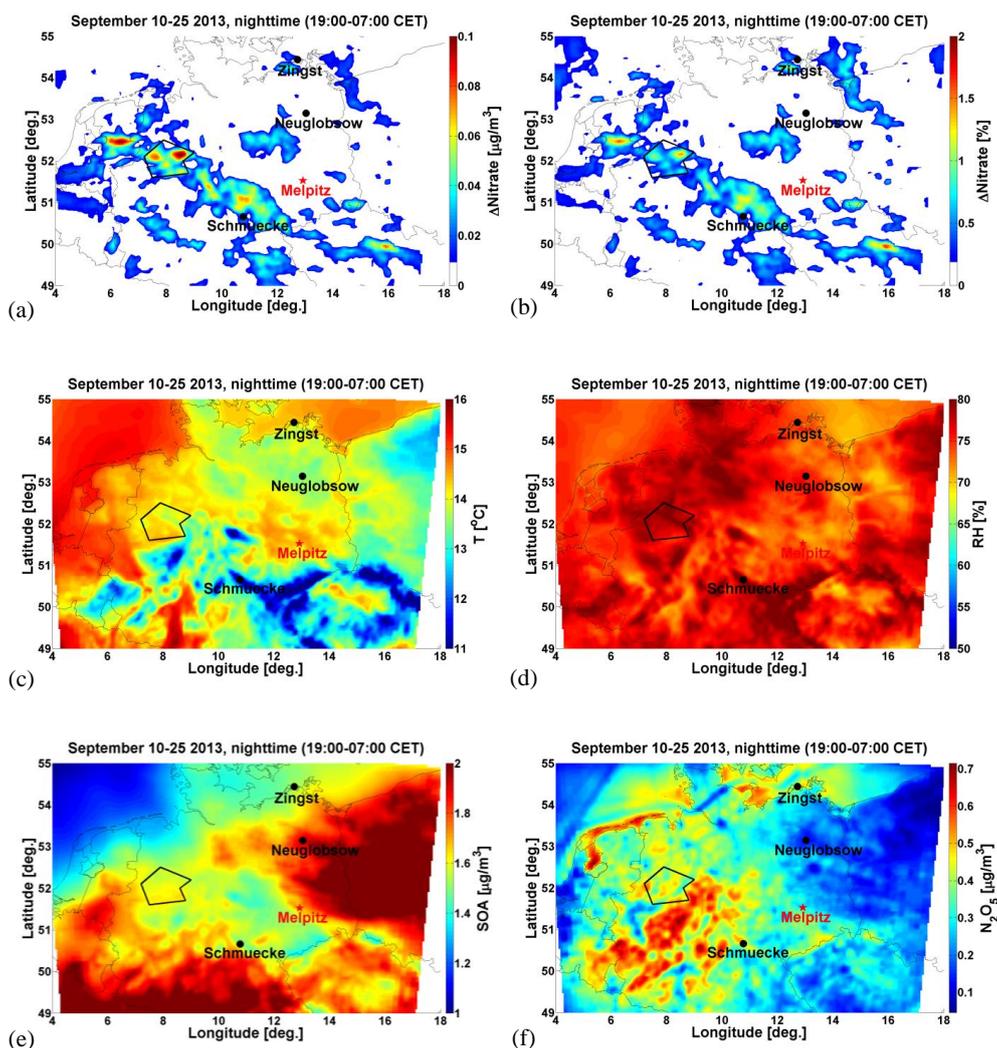
Figure 5. Horizontal distribution of averaged model results during nighttime in September 10-25, computed with the new N_2O_5 scheme. (a) Difference of particulate nitrate mass concentration between model cases with and without considering organic coating effect; (b) difference of particulate nitrate mass concentration in percent between model cases with and without considering organic coating effect; (c) temperature; (d) RH; (e) SOA mass concentration; (f) N_2O_5 mass concentration. The region with the most significant organic coating effect is highlighted by the black polygon.