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A parameterization of the heterogeneous hydrolysis of N_2O_5 for mass-based aerosol models: improvement of particulate nitrate prediction

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Abstract. The heterogeneous hydrolysis of N_2O_5 on the surface of deliquescent aerosol leads to HNO_3 formation and acts as a major sink of NO_x in the atmosphere during nighttime. The reaction constant of this heterogeneous hydrolysis is determined by temperature (T), relative humidity (RH), aerosol particle composition, and the surface area concentration (S). However, these parameters were not comprehensively considered in the parameterization of the heterogeneous hydrolysis of N_2O_5 in previous mass-based 3-D aerosol modelling studies. In this investigation, we propose a sophisticated parameterization (NewN2O5) of N_2O_5 heterogeneous hydrolysis with respect to T, RH, aerosol particle compositions, and S based on laboratory experiments. We evaluated closure between NewN2O5 and a state-of-the-art parameterization based on a sectional aerosol treatment. The comparison showed a good linear relationship ($R = 0.91$) between these two parameterizations. NewN2O5 was incorporated into a 3-D fully online coupled model, COSMO–MUSCAT, with the mass-based aerosol treatment. As a case study, we used the data from the HOPE Melpitz campaign (10–25 September 2013) to validate model performance. Here, we investigated the improvement of nitrate prediction over 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 $[NO_3^-]$ was 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 NewN2O5 significantly reduces the overestimation of $[NO_3^-]$ by ~ 35 %. Particularly, the overestimation factor was reduced to approximately 1.4 in our case study (12, 17–18 and 25 September 2013) when $[NO_3^-]$ was dominated by local chemical formations. In our case, the suppression of organic coating was negligible over western and central Europe, with an influence on $[NO_3^-]$ of less than 2 % on average and 20 % at the most significant moment. To obtain 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 organic coating effect on the reaction probability of N_2O_5 may not be as significant as expected over western and central Europe.

1 Introduction

The budget of nitrogen oxides (NO_x) is of fundamental importance for tropospheric chemistry (Ehhalt and Drummond, 1982). The removal of nitrogen from the atmosphere is largely contributed by the formation of HNO_3, which is eventually transferred to particles and deposited (Riemer et al., 2003). In the daytime, HNO_3 is mainly produced via the reaction of OH and NO_2. At night, the major sink of NO_x is heterogeneously hydrolyzed N_2O_5 on the surface of deliquescent aerosol (Jacob, 2000; Brown and Stutz, 2012; Platt et al., 1984; Brown et al., 2004). Given that NO_x is the key precursor of ozone, chemical mechanisms controlling the budget of NO_x also greatly affect ozone and thereby the atmospheric oxidizing capacity on a global scale (Dentener and Crutzen, 1993; Evans and Jacob, 2005).

The reaction probability ($\gamma_{N_2O_5}$) is used to quantify the reaction constant of N_2O_5 hydrolysis ($k_{N_2O_5}$) on the surface of deliquescent aerosol. Several techniques could be employed to measure $\gamma_{N_2O_5}$ on the surface of different aqueous solutions (Hallquist et al., 2000; Robinson et al., 1997; Hu and Abbatt, 1997; Behnke et al., 1997; Fenter et al., 1996; Van Doren et al., 1990; Mozurkewich and Calvert, 1988). It was reported that the typical values for $\gamma_{N_2O_5}$ are on the order of 10^{-2}. Organic coating of the particles may reduce this reaction probability. Anttila et al. (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) reported 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) parameterized the effect of chloride salts on $\gamma_{N_2O_5}$ as a function of RH. However, the influence of temperature was not considered in their study. Recently, Morgan et al. (2015) demonstrated that this influence of chloride may not be represented properly, and the "high" O : C regime defined in Gaston et al. (2014) was scarcely observed over north-western Europe by airborne regional measurements. 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) developed a parameterization scheme (Davis08) of $\gamma_{N_2O_5}$ for aerosols containing nitrate, sulfate, and ammonium. It was developed on the basis of numerous previous laboratory studies (Badger et al., 2006; Folkers et al., 2003; Hallquist et al., 2003; Folkers, 2002; Kane et al., 2001; Hu and Abbatt, 1997; Mozurkewich and Calvert, 1988) with respect to temperature, RH, and particle compositions.

Several studies have implemented the heterogeneous hydrolysis of N_2O_5 in global and regional chemical transport models in order to investigate its influences on atmospheric chemistry. Dentener and Crutzen (1993) assumed a constant $\gamma_{N_2O_5}$ of 0.1 in a global modelling study, which might be overestimated. Chang et al. (1987) proposed a scheme to parameterize the $k_{N_2O_5}$ for 3-D models without complex aerosol treatments. Riemer et al. (2003) reported that the scheme of Chang et al. (1987) could only be representative of heavily polluted conditions or in the presence of cloud droplets, with a particle surface area concentration of $2700 \, \mu m^2 \, cm^{-3}$. Riemer et al. (2003) proposed a more complex scheme (P1 in the literature) with respect to the particle surface area concentration (S) and $\gamma_{N_2O_5}$ of nitrate and sulfate, which were reported by Mentel et al. (1999) and Wahner et al. (1998). However, the influence of temperature and RH on $\gamma_{N_2O_5}$ was still not considered in the P1 of Riemer et al. (2003). Later, by applying Anttila06 to the P1 of Riemer et al. (2003), Riemer et al. (2009) reported an up to 90 % decrease in particulate nitrate due to organic coating in the regions where both N_2O_5 and secondary organic compounds were built up. Evans and Jacob (2005) proposed 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 (Hallquist et al., 2003; Kane et al., 2001), elemental carbon (EC; Sander et al., 2003), and organic carbon (OC; Thornton et al., 2003) and also took into account the dependence of $\gamma_{N_2O_5}$ on RH. However, $\gamma_{N_2O_5}$ of nitrate and its 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). Furthermore, as mentioned above, the reported influence of chloride on $\gamma_{N_2O_5}$ (Bertram and Thornton, 2009) may not be realistic in north-western Europe (Morgan et al., 2015). Recently, Chang et al. (2016) improved the P1 (Riemer et al., 2003) with the Davis08 + Anttila06 scheme and incorporated it into WRF-Chem with a sectional aerosol treatment (MOSAIC, Zaveri et al., 2008). They validated the improved P1 with the aircraft measurements from the CalNex 2010 campaign. Davis08 + Anttila06 showed a better result than that from the scheme according to Bertram and Thornton (2009) and significantly improved the model performance (Chang et al., 2016). However, the influences of black carbon (BC), sea salt aerosol (SSA), and dust were still missing in the parameterizations according to Chang et al. (2016). The P1 scheme (Riemer et al., 2003; Chang et al., 2016) is very helpful for models with complex aerosol treatments (modal and/or sectional aerosol approach; e.g. WRF-Chem with MOSAIC). However, it cannot be easily adopted in the computationally efficient mass-based aerosol approaches, which are commonly used in atmospheric chemistry transport or climate models, for example EMEP (Simpson et al., 2012) and GEOS-Chem (Walker et al., 2012), or long-term modelling studies (e.g. Bellouin et al., 2011; Hardiman et al., 2017). Riemer et al. (2003) also improved a simplified scheme (P2

in the literature) based on the work of Chang et al. (1987), which is easily adopted in the mass-based aerosol models and is currently used in COSMO–MUSCAT (Consortium for Small-scale Modelling and Multi-Scale Chemistry Aerosol Transport, http://projects.tropos.de/cosmo_muscat; Wolke et al., 2004, 2012) with the mass-based aerosol treatment according to Simpson et al. (2003). However, the P2 still showed a large difference in comparison to the more complete P1 (Riemer et al., 2003). The reasons may be the missing complex considerations of S and $\gamma_{N_2O_5}$ in the P2.

To improve the representativeness of the heterogeneous hydrolysis of N$_2$O$_5$ in 3-D models with mass-based aerosol treatment, we propose a new parameterization (NewN2O5) with respect to temperature, RH, particle composition, and particle surface area. NewN2O5 was validated by the state-of-the-art parameterization in Chang et al. (2016). We also incorporated NewN2O5 into the 3-D fully online coupled model COSMO–MUSCAT in order to investigate the improvement of particulate nitrate prediction. The measurements of the HOPE campaign (HD(CP)^2 Observational Prototype Experiment; Macke et al., 2017) at the Melpitz site (12.93° E, 51.53° N; 86 m a.s.l.; a regional background observatory of central Europe) and three other stations of the German federal environmental agency (UBA) over Germany were used to validate the simulation results.

2 Data and methods

2.1 The model system COSMO–MUSCAT

The online coupled chemical transport model COSMO–MUSCAT is qualified for the operation forecast of pollutants and process studies in regional and local areas (Heinold et al., 2011; Renner and Wolke, 2010; Hinneburg et al., 2009; Stern et al., 2008). Two nested domains with 50 vertical layers were used for this model study. The outer domain covers the whole of Europe, with a spatial grid resolution of 14 km × 14 km. The inner domain (N2) covers Germany, the Netherlands, and nearby regions, with a spatial grid resolution of 7 km × 7 km (Fig. 1). The simulation period was divided into several overlapping short periods, each of which included a 1-day spin-up followed by a 2-day run with meteorology and chemistry coupled. 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-thermodynamical equations (Steppeler et al., 2003; Doms et al., 2011a). The vertical diffusion is parameterized by a level 2.5 closure scheme, which adopts a prognostic equation for 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.

Radiative fluxes could be modified by aerosol clouds and tracer gases via absorption, scattering, and emission. The reanalysis data of the German Weather Service DWD derived from the global meteorological model GME (Majewski et al., 2002) were used for initial and boundary conditions. MUSCAT describes the transport, chemical, and removal processes. The gaseous chemistry is represented by RACM-MIM2, which consists of 87 species and more than 200 reactions (Karl et al., 2006; Stockwell et al., 1997). A simplified mass-based approach (similar to the EMEP model; Simpson et al., 2003) is used to represent the aerosol processes with high efficiency. The formation of secondary inorganic particulate matter is through reactions of ammonia with sulfuric acid and nitric acid, which are produced from gaseous precursors SO$_2$ and NO$_x$ (Hinneburg et al., 2009). The applied particle–gas partitioning depends on temperature and humidity. As in ISORROPIA, under dry and warm conditions the equilibrium shifts toward the gas phase (Nenes et al., 1998). By using the equilibrium approach of Mozurkewich (1993), the partitioning scheme was comparable to Galperin and Sofiev (1998). The extended SORGAM (Schell et al., 2001; Li et al., 2013) is coupled with the mass-based aerosol approach to predict the formation of secondary organic aerosol (SOA). Dry deposition is modelled by using the resistance approach following Seinfeld and Pandis (2006) and considering the kinetic viscosity, the atmospheric turbulence state, and the gravitational settling of particles. The resistances for the aerodynamic and quasi-laminar layer are taken from COSMO and analogous to the deposition of water vapour. The parameterization of the wet deposition is dependent upon size-resolved collection efficiency and scavenging (Simpson et al., 2003).

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, NO$_x$, SO$_2$, NH$_3$ methane, and non-methane volatile organic compounds) and primary emitted particulate matter (PM$_{2.5}$, PM$_{2.5-10}$, organic carbon OC, and elemental carbon EC) with a spatial resolution of 0.125° × 0.0625° (longitude–latitude, about 7 km × 7 km). Note that EC and BC are usually interchangeable in modelling studies (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 during the campaign period. The modelled dust emissions depend on surface wind friction velocities, sur-
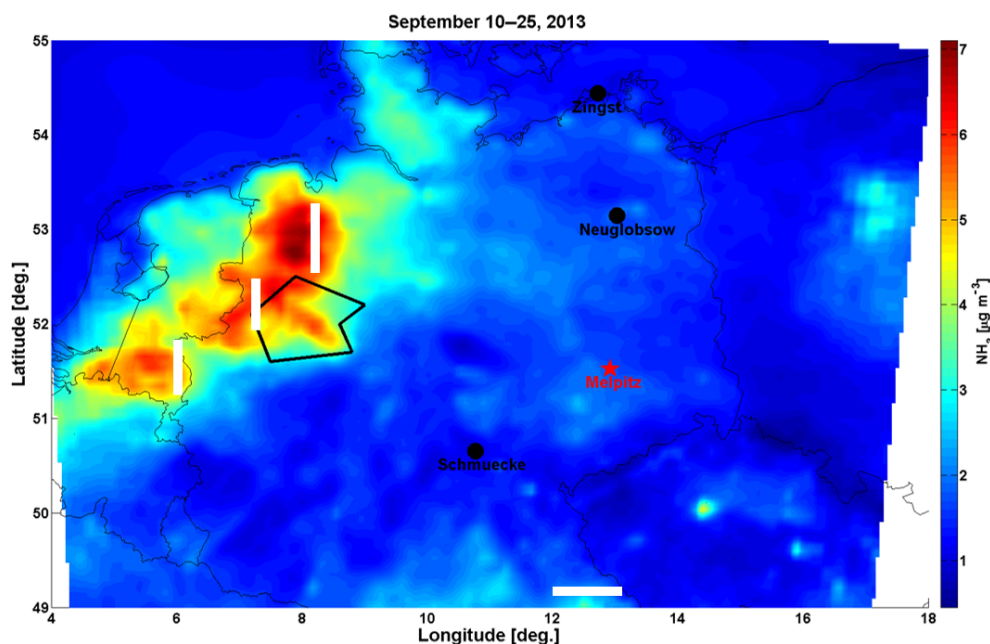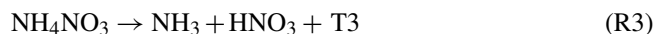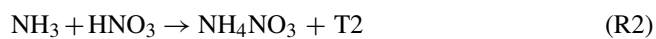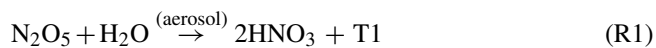
Figure 1. Results (domain N2) of the NewN2O5 case of averaged NH_3 mass concentration during 10–25 September 2013. The added emissions of marker tracer (T-NH3) from NH_3 source regions (the Netherlands and southern Germany) are marked by the white bars. The locations of the considered measurement stations are also marked: Neuglobsow, Schmücke, and Zingst are marked by black dots; Melpitz is marked with a red star and its results are discussed in Figs. 2 and 3. The region with the most significant organic coating effect is highlighted by the black polygon and will be analysed together with Fig. 6.

face roughness, soil particle size distribution, and soil moisture (Heinold et al., 2011). Emissions of sea salt depend on salinity and wind speed (Long et al., 2011). Biogenic emissions depend on land use and meteorology in the approach of Steinbrecher et al. (2009) and for "soil NO" in Williams et al. (1992) and Stohl et al. (1996). The 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 to the chemical formation of nitric acid; T3 and T2 represent the local chemical net formation of particulate nitrate.

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

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

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

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 $2 \times 10^{-8} \, mol \, m^{-2} \, s^{-1}$.

2.2 A novel mass-based parameterization of the heterogeneous hydrolysis of N_2O_5

The heterogeneous hydrolysis of N_2O_5 on the surface of deliquescent aerosol is believed to be considerable, since N_2O_5 reacts quite slowly with water vapour (Platt et al., 1984). 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 the references therein).

The P2 of Riemer et al. (2003), which was adapted from Chang et al. (1987), was originally incorporated in COSMO–MUSCAT to represent the heterogeneous hydrolysis of N_2O_5 (OldN2O5). 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 S is the surface area concentration of aerosol particles and $v_{N_2O_5}$ is the mean molecular velocity of N_2O_5. Based on the first-order reaction constant, Chang et al. (1987) proposed the following scheme to represent $k_{N_2O_5}$.

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

RH is the relative humidity in percent, 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 $2700 \, \mu m^2 \, cm^{-3}$ when RH is higher than 60 %. However, this high surface area concentration can only be expected in areas suffering from severe pollution or where cloud droplets exist. Therefore, we adopted $a = 17$ in this study as suggested by Riemer et al. (2003). However, the complex considerations of S and $\gamma_{N_2O_5}$ are still missing in the OldN2O5. In this study, we propose a sophisticated parameterization to improve the OldN2O5 for mass-based aerosol models, with a full consideration of temperature, RH, aerosol particle compositions, and S.

As shown in Eq. (1), $k_{N_2O_5}$ is linearly related to S and $\gamma_{N_2O_5}$. We adapted Eq. (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 Eq. (3); f_s can be estimated from the particle mass concentration according to Eq. (4) and $f_{\gamma_{N_2O_5}}$ 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 Eq. (5). The influence of the 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 north-western European case compared with airborne measurements (Morgan et al., 2015).

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

$$f_s = (SA_{fine} \cdot PM_{fine} + SA_{coarse} \cdot PM_{coarse}) / S_{ref} \quad (4)$$

SA_{fine} and SA_{coarse} represent the specific surface area for fine- and coarse-mode particles in $m^2 \, g^{-1}$, and PM_{fine} and PM_{coarse} represent the mass concentration of fine- and coarse-mode particles in $\mu g \, m^{-3}$. A value $11 \, m^2 \, g^{-1}$ was used for SA_{fine}, considering recently reported values of 11.9 and $10.2 \, m^2 \, g^{-1}$ from laboratory studies (Okuda, 2013) and measurements in Japanese urban regions (Hatoya et al., 2016). A value of $1.2 \, m^2 \, g^{-1}$ was used for SA_{coarse} (Okuda, 2013). S_{ref} is the reference particle surface area concentration; here, we suggest $S_{ref} = 600 \, \mu m^2 \, cm^{-3}$. Equation (2) will provide a result that is very close to a complex parameterization with a particle surface area concentration of $600 \, \mu m^2 \, cm^{-3}$ (Riemer et al., 2003) when $a = 17$ and RH > 60 %. Note that a small initial overestimation of particulate nitrate may result in a significant overprediction of nitrate through the integration in models due to a feedback in this scheme. That is, higher nitrate concentrations result in a larger f_s and promise a higher $k_{N_2O_5}$, leading to a higher production of nitrate. In order to avoid the uncertainty of this feedback mechanism and to calculate a reasonable $k_{N_2O_5}$ in this case study, the nitrate mass concentration in Eq. (4) is

considered as 1.3 times the sulfate mass concentration based on filter measurements during the HOPE Melpitz campaign.

$$f_{\gamma_{N_2O_5}} = \left(\gamma_{core}^{-1} + \gamma_{coating}^{-1}\right)^{-1} / \gamma_{ref}, \quad (5)$$

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 Eq. (6) according to Anttila et al. (2006) and Riemer et al. (2009); γ_{ref} is the reference reaction probability. Here, we suggest $\gamma_{ref} = 0.1$, since Eq. (2) is developed on the basis of the assumption $\gamma_{N_2O_5} = 0.1$ (Riemer et al., 2003).

$$\gamma_{coating} = \frac{4RT H_{N_2O_5} D_{N_2O_5} R_{core}}{v_{N_2O_5} l_{shell} R_{particle}}, \quad (6)$$

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

The γ_{core} values can be estimated from previous laboratory experiments (Table 1) of inorganic and primary organic compositions (Davis et al., 2008; Evans and Jacob, 2005, and references therein;). Davis et al. (2008) developed a 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); γ_{core} can be derived by a mass-weighted average (Riemer et al., 2003) of each single-component parameterization (Table 1).

2.3 Estimation of reaction probabilities with a sectional aerosol model

The Weather Research and Forecasting–Chemistry model (WRF-Chem V3.5.1) is a fully online coupled regional air quality model. Chang et al. (2016) incorporated several parameterizations for N_2O_5 hydrolysis into a sectional aerosol treatment (MOSAIC; Zaveri et al., 2008) in WRF-Chem. The "Davis" approach from Chang et al. (2016), hereinafter referred to as Ch&Davis, was chosen to be compared with NewN2O5. The reasons for this choice will be discussed in detail in Sect. 3.1.

In order to validate the mass-based NewN2O5 with the sectional-based Ch&Davis, we performed WRF-Chem simulations during the HOPE Melpitz campaign. The same WRF-Chem results were adopted for offline estimating $k_{N_2O_5}$ according to NewN2O5 and Ch&Davis. We followed the physics-relating configuration according to Chen et al. (2016a), which reproduced meteorological conditions

Table 1. Representation of the reaction probability of aerosol particle core (γ_{core}) for N_2O_5 hydrolysis.

Particle type	Parameterization	Parameters	References and remarks
Core of particle	$\gamma_{core} = \sum_i \gamma_i \cdot \text{ratio}_i$	$\text{ratio}_i = \frac{[m_i]}{[m_{core}]}$ $[m_{core}] = \sum_i [m_i]$ i: the following particle types $i = [\text{ASN, OC, SSA, dust, BC}]$	γ : reaction probability m: mass [mass]: mass concentration
ASN: (A) Ammonium (S) Sulfate (N) Nitrate	$\gamma_{ASN} = \gamma_{AB}^* \cdot x_{AB} + \gamma_{aq/d,AS}^* \cdot x_{AS} + \gamma_{AN}^* \cdot x_{AN}$ $\gamma_{AB}^* = \min(\gamma_{AB}, 0.08585),\ \gamma_{AB} = \frac{1}{1+e^{-\lambda_{AB}}}$ $\gamma_{aq,AS}^* = \min(\gamma_{aq,AS}, 0.053),$ $\gamma_{aq,AS} = \frac{1}{1+e^{-\lambda_{aq,AS}}}$ $\gamma_{d,AS}^* = \min(\gamma_{d,AS}, 0.0124),\ \gamma_{d,AS} = \frac{1}{1+e^{-\lambda_{d,AS}}}$ $\gamma_{AN}^* = \min(\gamma_{AN}, 0.0154),\ \gamma_{AN} = \frac{1}{1+e^{-\lambda_{AN}}}$ $\lambda_{AB} = \beta_{10} + \beta_{11} \cdot RH + \beta_{12} \cdot T_{291}$ $\lambda_{aq,AS} = (\beta_{10} + \beta_{20}) + \beta_{11} \cdot RH + (\beta_{12} + \beta_{22}) \cdot T_{291}$ $\lambda_{d,AS} = \beta_{d0} + \beta_{d1} \cdot RH + \beta_{d2} \cdot T_{293}$ $\lambda_{d,AN} = \beta_{30} + \beta_{31} \cdot RH$	$x_{AB} = 1 - (x_{AS} + x_{AN})$ $x_{AS} = \max\left(0, \min\left(1 - x_{AN}, \frac{[A]}{[N]+[S]} - 1\right)\right)$ $x_{AN} = \frac{[N]}{[N]+[S]}$ $\beta_{10} = -4.10612$ $\beta_{11} = 0.02386$ $\beta_{12} = -0.23771$ $\beta_{20} = -0.80570$ $\beta_{22} = 0.10225$ $\beta_{30} = -8.10774$ $\beta_{31} = 0.04902$ $\beta_{d0} = -6.13376$ $\beta_{d1} = 0.03592$ $\beta_{d2} = -0.19688$ $T_{291} = \max(T - 291, 0)$ $T_{293} = \max(T - 293, 0)$	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 solid phase (Martine et al., 2003)
Organic carbon (Primary OC)	$\gamma_{OC} = RH \times 5.2 \times 10^{-4}$ RH < 57% $\gamma_{OC} = 0.03$ RH $\geq$ 57%		Evans and Jacob (2005) Thornton et al. (2003)
Sea salt aerosol (SSA)	$\gamma_{SSA} = 0.005$ RH < 62% $\gamma_{SSA} = 0.03$ 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 (BC)	$\gamma_{BC} = 0.005$		Sander et al. (2003)

during the HOPE Melpitz campaign well. The sea salt emission (Gong, 2003) was reduced by a factor of 20 in WRF-Chem, considering that Gong (2003) may highly overestimate sea salt emission (Neumann et al., 2016), and thus leads to an overestimation of sea salt by a factor of 20 during the HOPE campaign at Melpitz (Chen et al., 2016b). The configuration of chemical and aerosol treatments followed Chang et al. (2016). The CBMZ (Zaveri and Peter, 1999) mechanism was used to describe gas-phase reactions. MOSAIC (Zaveri et al., 2008) with eight size bins was chosen to represent aerosol properties. Three nested domains (Fig. S1 in the Supplement) with 39 vertical layers were set up for the

simulated case, with a resolution of 54, 18, and 6 km, respectively.

In Ch&Davis aerosol liquid water is considered when calculating the particle surface area for each size bin. Details of the sectional-based method for estimating S in the Ch&Davis scheme are given by Chang et al. (2016). In the NewN2O5 scheme, the first six bins (with diameter in the range of 40 nm–2.5 μm) are counted as fine mode, and the last two bins (2.5–10 μm) are counted as coarse mode. This definition is identical to COSMO–MUSCAT. In order to be consistent with COSMO–MUSCAT, the organic coating effect is considered for fine particles in NewN2O5, since the max-

imum effective particle diameter of the Anttila06 scheme is 2 µm (Anttila et al., 2006). In order to quantify the uncertainty stemming from the different S treatments between NewN2O5 (mass based) and Ch&Davis (sectional based), an estimation result according to an adapted NewN2O5 (with sectional-based S) will also be discussed in Sect. 3.1.

2.4 Observations

The filter chemical composition measurements of the HOPE Melpitz campaign (10–25 September 2013) and at three UBA stations (Neuglobsow, Schmücke, and Zingst; http://www.umweltbundesamt.de) were used to validate the modelled results. The observations at the TROPOS research station at Melpitz represent the regional background of central Europe (Spindler et al., 2010, 2012; Brüggemann and Spindler, 1999; Poulain et al., 2011; Birmili et al., 2001). During the HOPE Melpitz campaign, high-volume samplers (DIGITEL DHA-80; Walter Riemer Messtechnik, Germany) with a sampling flow of $\sim 30\,\mathrm{m^3\,h^{-1}}$ were used to collect 24 h daily filter samples with 10 µm cut-off inlets. Additionally, 24 h filter sampler measurements with a PM$_{10}$ inlet at three UBA stations in Germany were collected every third day. The filter material is quartz fibre (Munktell, Grycksbo, Sweden; type MK 360), which allows for 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 preheated before sampling for at least 24 h at 105 °C 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. relative humidity, temperature, wind speed, wind direction) were simultaneously measured at Melpitz. More details about the HOPE campaign are given in Macke et al. (2017).

3 Results and discussion

The COSMO–MUSCAT 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, RH, 10 m 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 meteorological parameters in this study for N$_2$O$_5$ heterogeneous hydrolysis during nighttime, were in good agreement with the measurement. Although model simulations slightly underestimated RH during the night-time of 17 and 22 September (Fig. 2b), modelled RH was still higher than 80 % where $k_{\mathrm{N_2O_5}}$ is insensitive to

RH as shown in Table 1 and Riemer et al. (2003). Therefore, this bias of RH will not lead to a significant uncertainty in nitrate simulation. However, the overestimation of wind speed may favour the transport of ammonia from western Europe (e.g. the Netherlands). This could be a possible reason for the nitrate overprediction in the NewN2O5 case (Fig. 3d), especially during 20–24 September when a western wind was constantly dominant (Fig. 2d).

3.1 Evaluating closure for mass-based NewN2O5 and a sectional approach

In order to confirm that the mass-based NewN2O5 estimates $k_{\mathrm{N_2O_5}}$ with a reliable accuracy, we evaluated closure between NewN2O5 and a sectional-based state-of-the-art parameterization (Chang et al., 2016) based on the WRF-Chem (MOSAIC) results. Chang et al. (2016) reported that the Davis + coat (Daivs08 + Anttila06) approach produced the best agreement of $\gamma_{\mathrm{N_2O_5}}$ with aircraft observations during the CalNex 2010 campaign, with overestimation by a factor mostly within in a range of 2–8 (Fig. S2b). Without considering OC coating effect (Davis08 only), Ch&Davis still showed a relatively good linear relationship with the observed $\gamma_{\mathrm{N_2O_5}}$, which was, however, overestimated with a higher factor ranging about 3–10 (Fig. S2a). Considering the different treatments of OC coating between NewN2O5 (SOA coating only) and Chang et al. (2016) (Davis + coat, primary OC, and SOA), NewN2O5 was validated using the Ch&Davis scheme. This would not significantly influence the comparison results, since the HOPE Melpitz campaign was an OC-low case, with only a $\sim 7\,\%$ contribution from total OC mass based on filter measurements at Melpitz. Therefore, not much SOA was available for the coating effect in contrast to the OC-high case (contributed about 50–80 % to total mass; Fig. 9 in Chang et al., 2016) in the CalNex 2010 campaign. The coating effect exerted a negligible influence at Melpitz, and this point will be discussed in detail in Sect. 3.4. We validated the NewN2O5 scheme by comparing $k_{\mathrm{N_2O_5}}$ instead of $\gamma_{\mathrm{N_2O_5}}$ because NewN2O5 scheme was developed on the basis of a parameterization to directly calculate $k_{\mathrm{N_2O_5}}$ as proposed by Chang et al. (1987) and Riemer et al (2003).

As shown in Fig. 4, the $k_{\mathrm{N_2O_5}}$ showed a good linear relationship ($R = 0.91$) between NewN2O5 and Ch&Davis that is much better than using the OldN2O5 (Fig. 4). Mass-based NewN2O5 estimated lower $k_{\mathrm{N_2O_5}}$ than the sectional-based Ch&Davis by a factor of ~ 8. However, Ch&Davis may overestimate the $\gamma_{\mathrm{N_2O_5}}$ by a factor of 3–10 (Chang et al, 2016, see also Fig. S2a). Assuming that S was correctly given by the WRF-Chem sectional aerosol module, we can expect that Ch&Davis may overestimate $k_{\mathrm{N_2O_5}}$ by a factor of 3–10 according to Eq. (1). Therefore, NewN2O5 may provide a $k_{\mathrm{N_2O_5}}$ in the range of 0.36–1.2 times the realistic one.

Two important uncertainties need to be kept in mind in this validation. First, the estimation of S is very challenging due to the uncertainties of, for example, particle num-
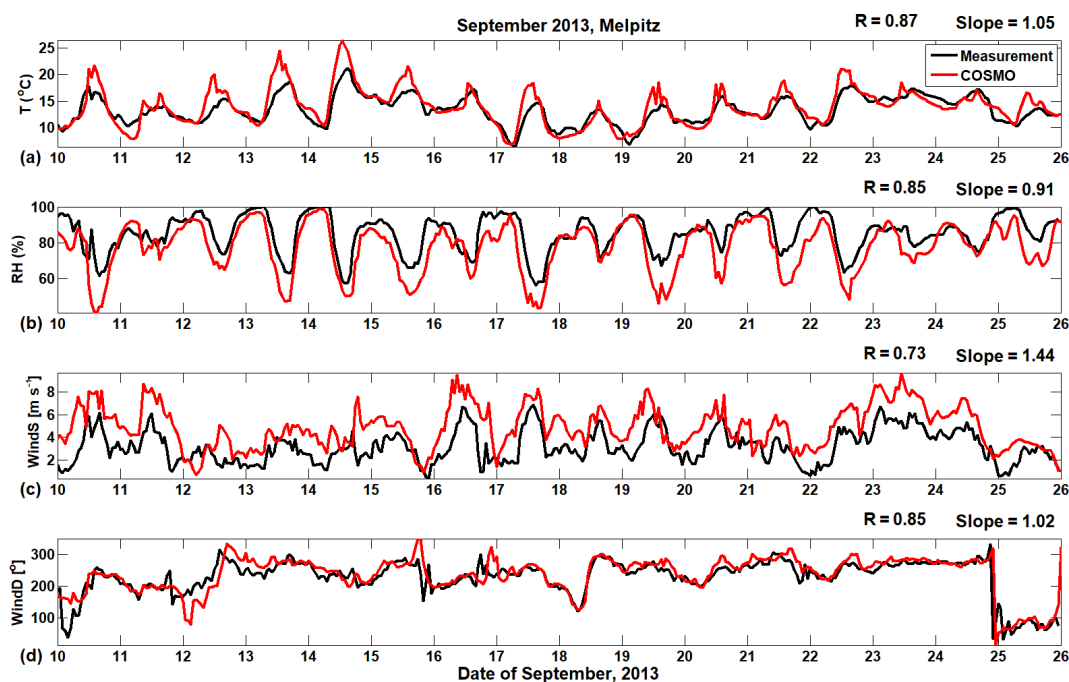
Figure 2. Comparison between modelled and measured meteorological conditions. **(a)** Temperature (T); **(b)** relative humidity (RH); **(c)** wind speed; **(d)** wind direction.

ber and mass size distribution, partitioning processes, and secondary formation. In addition, the hygroscopic growth of particles can also be an important source of the uncertainty of S due to the challenge in the estimation of particle liquid water, especially at low RH, even by a complex aerosol treatment (Chang et al., 2016). About a 30 % difference in $k_{N_2O_5}$ between NewN2O5 and Ch&Davis stems from the different treatments of S. As shown in Fig. 4, the factor between NewN2O5 and Ch&Davis was reduced from ~ 8.3 to ~ 5.9 with a slightly increase in R when we adopted the sectional-based S (same as Ch&Davis) in NewN2O5. Second, Ch&Davis was validated by aircraft measurements in an OC-high case during the CalNex 2010 campaign. Therefore, the overestimation factor of Ch&Davis may not be as high as expected in an OC-low case during the HOPE Melpitz campaign. However, SSA, BC, and dust should exert an influence in an OC-low case and should also be considered in a parameterization, as we did in NewN2O5. This can also be a reason for the difference between Ch&Davis and NewN2O5.

3.2 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 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 previous

Table 2. Sensitivity simulation cases.

Case	N$_2$O$_5$ parameterization	NH$_3$ emission
OldN2O5-FullNH3	P2 of Riemer et al. (2003)	100 %
OldN2O5	P2 of 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).

studies. This seems to be the case for the HOPE Melpitz campaign simulation, during which COSMO–MUSCAT highly overpredicted [NO$_3^-$] over Germany in this study (Fig. 3), and WRF-Chem in a previous study (Chen et al., 2016b). In order to evaluate the improvement of the NewN2O5 scheme and quantify the influence of NH$_3$ emission overestimation on the particulate nitrate prediction, three sensitivity simulations were conducted (Table 2).

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 modelled NO$_x$ was in line with the observed concentration level at Melpitz and should not be the reason for the overprediction of particulate nitrate (see details in the Supplement Sect. S1 and Fig. S3). Nevertheless, the overestimation of NH$_3$ emissions might contribute about 20–30 % of the particulate nitrate overprediction compared between the OldN2O5-FullNH3 and
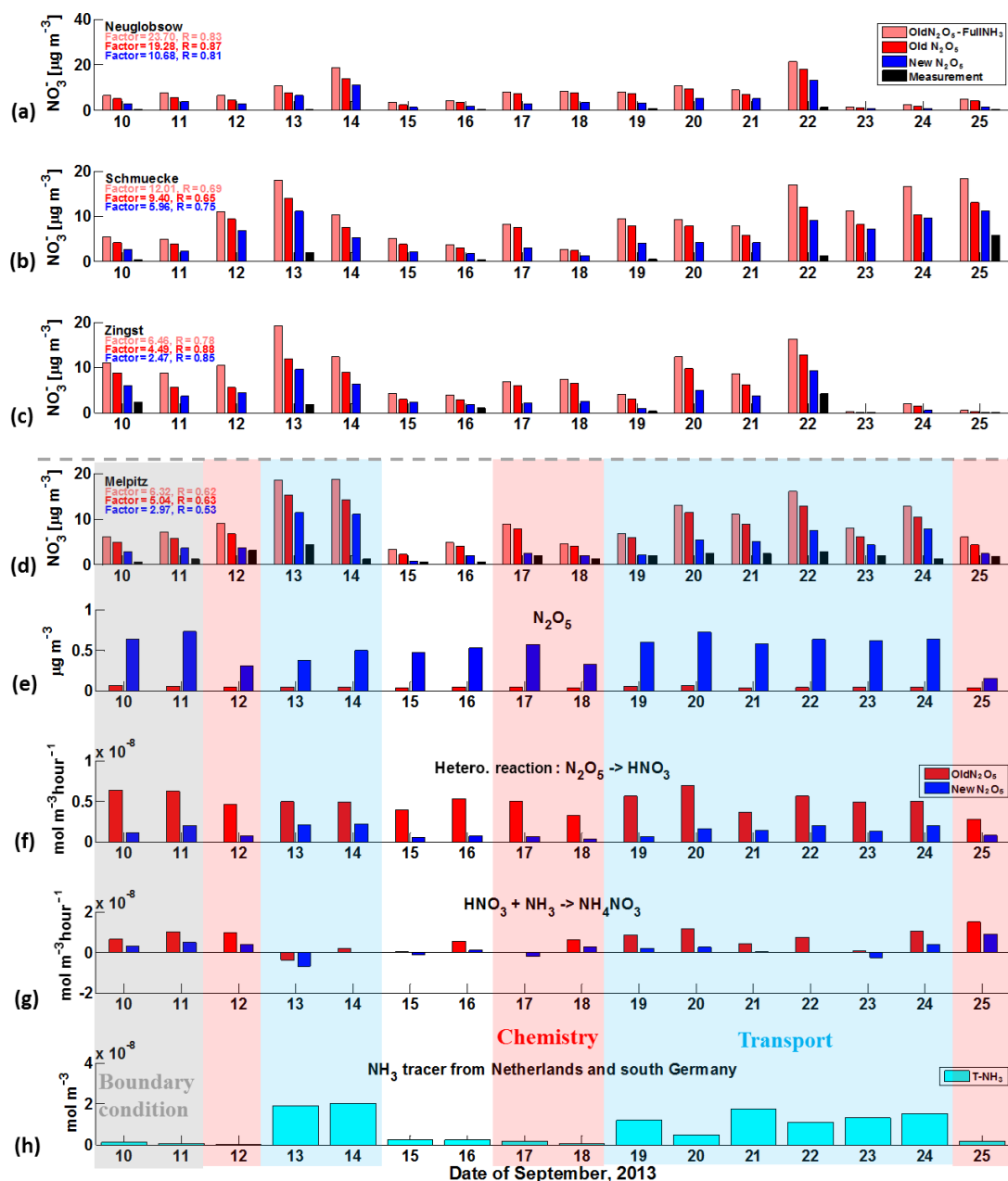
Figure 3. Comparison of particulate nitrate mass concentration between filter measurements and modelled results: **(a)** Neuglobsow; **(b)** Schmuecke; **(c)** Zingst; **(d)** Melpitz. Modelled concentrations at Melpitz: **(e)** N_2O_5; **(f)** marker species T1 for chemical reaction R1; **(g)** marker species for the chemical formation of particulate nitrate (T3-T2); **(h)** the NH_3 marker tracer (T-NH3) for transport from the Netherlands and southern Germany. The light-red colour bars indicate the results of the OldN2O5-FullNH3 case, the red colour bars indicate the results of the OldN2O5 case, and the blue colour bars indicate the results of the NewN2O5 case. The shaded periods indicate the dominating processes for high concentrations of particulate nitrate: chemical formation (red), transport (blue), and boundary conditions (grey).

OldN2O5 cases. This is in line with previous studies (Renner and Wolke, 2010; Backes et al., 2016). However, even with a 50 % reduction of NH_3 emissions, the particulate nitrate was still highly overestimated over Germany with factors of about 19, 9, 4.5, and 5 for these four stations, respectively. The NewN2O5 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 completely consumed by the heterogeneous reaction at Melpitz in the OldN2O5 case, but not in the NewN2O5 case (Fig. 3e). This is due to a significant de-
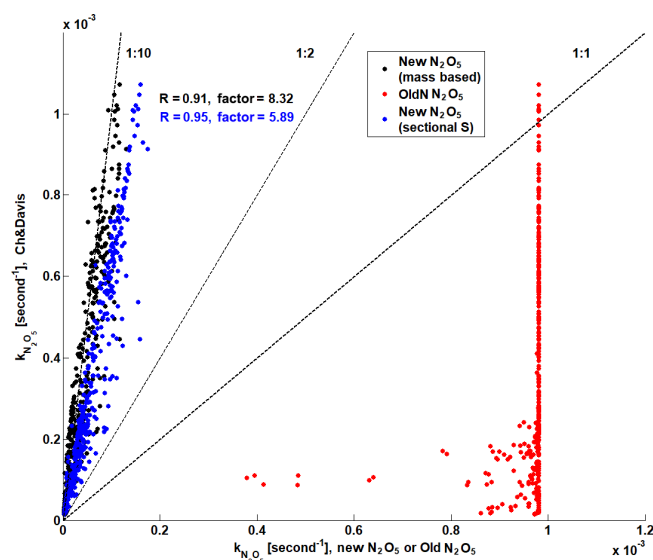
Figure 4. Comparison between the sectional-based Ch&Davis ("Davis" of Chang et al., 2016) and mass-based NewN2O5 (mass based, black), NewN2O5 (with a sectional-based particle surface area, blue), and OldN2O5 (red). The results are offline calculated on the basis of the WRF-Chem simulation with a sectional aerosol treatment (MOSAIC).

crease (by an average of more than a factor of 20, see Fig. 4) in the reaction constant of the heterogeneous hydrolysis of N_2O_5 by NewN2O5. However, there must be other reasons that might explain the remaining overestimations in the simulated particulate nitrate mass concentrations. One possible reason can be the underprediction of the coating organic matter budget in the model leading to an overestimation of $\gamma_{N_2O_5}$ (Chang et al., 2016); other possible reasons should be investigated in future studies, such as the deposition process, long-range transport, the formation of nitrogen-containing OC, and neutralization processes.

The improvement of particulate nitrate prediction with NewN2O5 can be more clearly shown associated 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 were sampled on the filter every day and analysed offline. The overestimation of $[NO_3^-]$ on 10–11 September (grey shaded period in Fig. 3) stemmed from the uncertainty of boundary conditions in the model. As shown in Fig. S4, an air mass with high $[NO_3^-]$ was transported from the south-western boundary area to Melpitz. The $[NO_3^-]$ at Melpitz was dominated by transport from the Netherlands and southern Germany on 13–14 and 19–24 September (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, local chemical formations dominated the $[NO_3^-]$ on 12, 17–18, and 25 September (red shaded period in Fig. 3). During the red shaded period, T-NH3 was almost zero (Fig. 3h)

and the modelled wind speed was less than $4\,\mathrm{m\,s^{-1}}$ on average (Fig. 2c). A much stronger reduction in the overestimation of particulate nitrate occurred during the red shaded period (a factor of ~ 1.4 on average), which was dominated by local chemical formations. This further confirmed the improvement of the heterogeneous hydrolysis of N_2O_5 by NewN2O5. During 15–16 September (without the shaded period in Fig. 3), the contributions from both transport and local chemical formations of particulate nitrate were very limited (Fig. 3f–h), resulting in a very low $[NO_3^-]$.

3.3 Comparison between NewN2O5 and OldN2O5

The NewN2O5 case improved the particulate nitrate overestimation problem compared with OldN2O5. Meanwhile, the spatial distribution pattern of $[NO_3^-]$ was similar between these two cases (Fig. 5). Here, we focus on the nighttime period of the HOPE Melpitz campaign, since the N_2O_5 heterogeneous reaction is much more significant during the night than in the daytime. The lowest $[NO_3^-]$ was found over Poland and ocean regions during night-time, and $[NO_3^-]$ was lower than 4 and $3\,\mu\mathrm{g\,m^{-3}}$ in the OldN2O5 and NewN2O5 cases, respectively. Moderate $[NO_3^-]$ was found over central Europe (Melpitz and the surrounding region) at about 6–8 and 4–5.5 $\mu\mathrm{g\,m^{-3}}$ in the OldN2O5 and NewN2O5 cases, respectively. The highest $[NO_3^-]$ occurs over the region of the Netherlands and nearby regions at about 9–12 and 6–8 $\mu\mathrm{g\,m^{-3}}$ in the OldN2O5 and NewN2O5 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 of about 8–10 and 5–6.5 $\mu\mathrm{g\,m^{-3}}$ in the OldN2O5 and NewN2O5 cases, respectively. In general, the $[NO_3^-]$ was reduced by $\sim 35\,\%$ over the entire N2 domain (Fig. 5). 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 $\mu\mathrm{g\,m^{-3}}$) was found, followed by the region near Melpitz (reduced by about 2–3 $\mu\mathrm{g\,m^{-3}}$; Fig. 5c). This is caused by a significant reduction (by more than a factor of 20; see Fig. 4) of $k_{N_2O_5}$, which results from the consideration of particle mass concentration influence on S and comprehensive treatments for $\gamma_{N_2O_5}$. Therefore, the regions with high $[NO_3^-]$ during night-time indicate considerable nitrate formation from the heterogeneous hydrolysis of N_2O_5, during which $[NO_3^-]$ was reduced by about 3–4.5 $\mu\mathrm{g\,m^{-3}}$ ($\sim 35\,\%$; see Fig. 5) in the new scheme. However, this heterogeneous hydrolysis was negligible over the regions where $[NO_3^-]$ was low during night-time and did not have a relevant contribution to the formation of particulate nitrate. Hence, the improvement of particulate nitrate prediction by NewN2O5 was more significant over the high-$[NO_3^-]$ regions than the low-$[NO_3^-]$ regions.
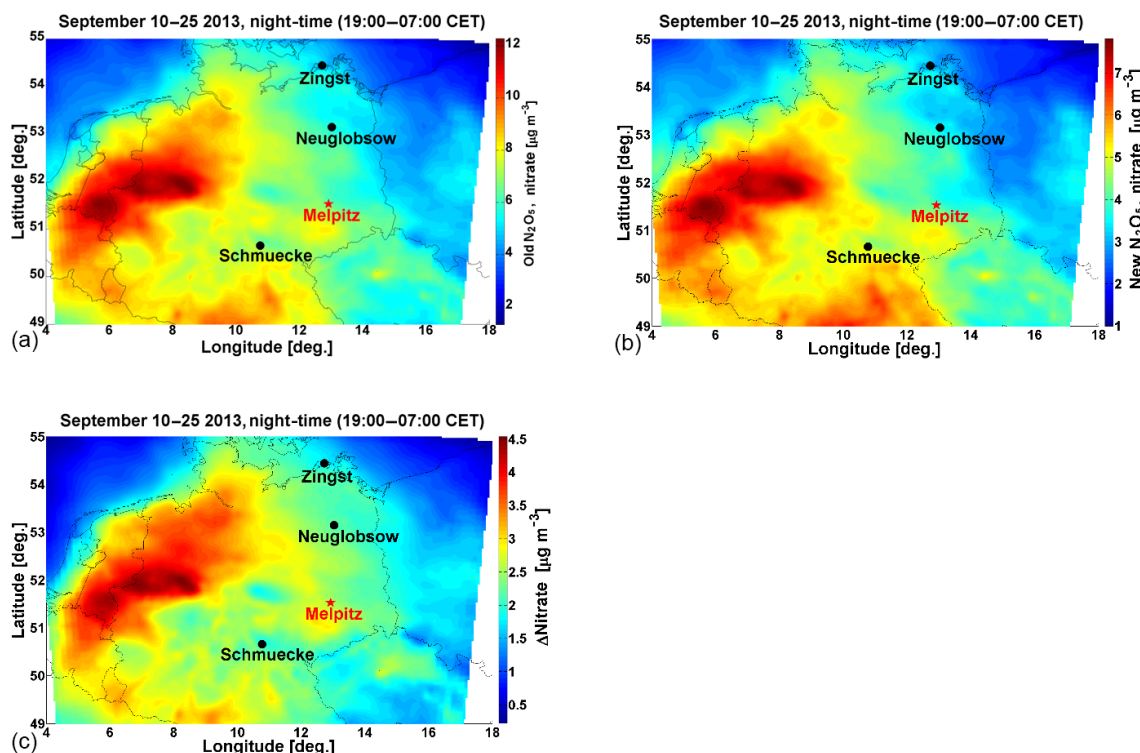
Figure 5. Horizontal distribution of averaged modelled particulate nitrate mass concentration during night-time on 10–25 September. **(a)** OldN2O5 case; **(b)** NewN2O5 case; **(c)** difference between OldN2O5 and NewN2O5 cases.

3.4 Influence of organic coating on N_2O_5 heterogeneous hydrolysis

The secondary organic coating on particle surfaces may significantly decrease the reaction probability of N_2O_5 and influence the particulate nitrate concentration. Riemer et al. (2009) reported that organic coating could decrease $[NO_3^-]$ by up to 90 % when 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. In addition to N_2O_5 and secondary organic compounds, the meteorological conditions (e.g. RH and temperature) may also exert an influence on the organic coating effect. In this study, we introduced a parameterization (NewN2O5) for the heterogeneous hydrolysis of N_2O_5 considering meteorological conditions. The influence of the organic coating suppression effect on particulate nitrate prediction was investigated by a comparison between NewN2O5 with and without the SOA coating effect.

At night-time, much higher N_2O_5 concentrations occurred and heterogeneous hydrolysis is more important than during daytime (Jacob, 2000). As shown in Fig. 6a and b, the influence of the organic coating effect was negligible over the domain N2 including the Netherlands and Germany. Even on 24 September at 23:00 CET when changes were most significant, organic coating reduced $[NO_3^-]$ only by about

2–4 μg m^{-3} (less than 10–20 %) over the black-polygon-marked and nearby regions (Fig. S5). Meanwhile, for night-time averages during the campaign, organic coating could only reduce $[NO_3^-]$ by less than 0.1 μg m^{-3} or 2 % over the whole domain (Fig. 6). This is because appropriate meteorological conditions, as described in the following, are needed in NewN2O5 for a significant organic coating. 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 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 (Chang et al., 2016; Riemer et al., 2009). Therefore, a large impact should be expected in regions with high RH and low temperature and hence a high $\gamma_{N_2O_5}$. As show in Fig. 6, the most significant organic coating effect (still less than 2 % influence on $[NO_3^-]$) could be found over the Netherlands and nearby 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}; and (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. 6a and b). These five conditions (not very high temperature; relatively high RH; build-up of SOA, N_2O_5, and NH_3) could
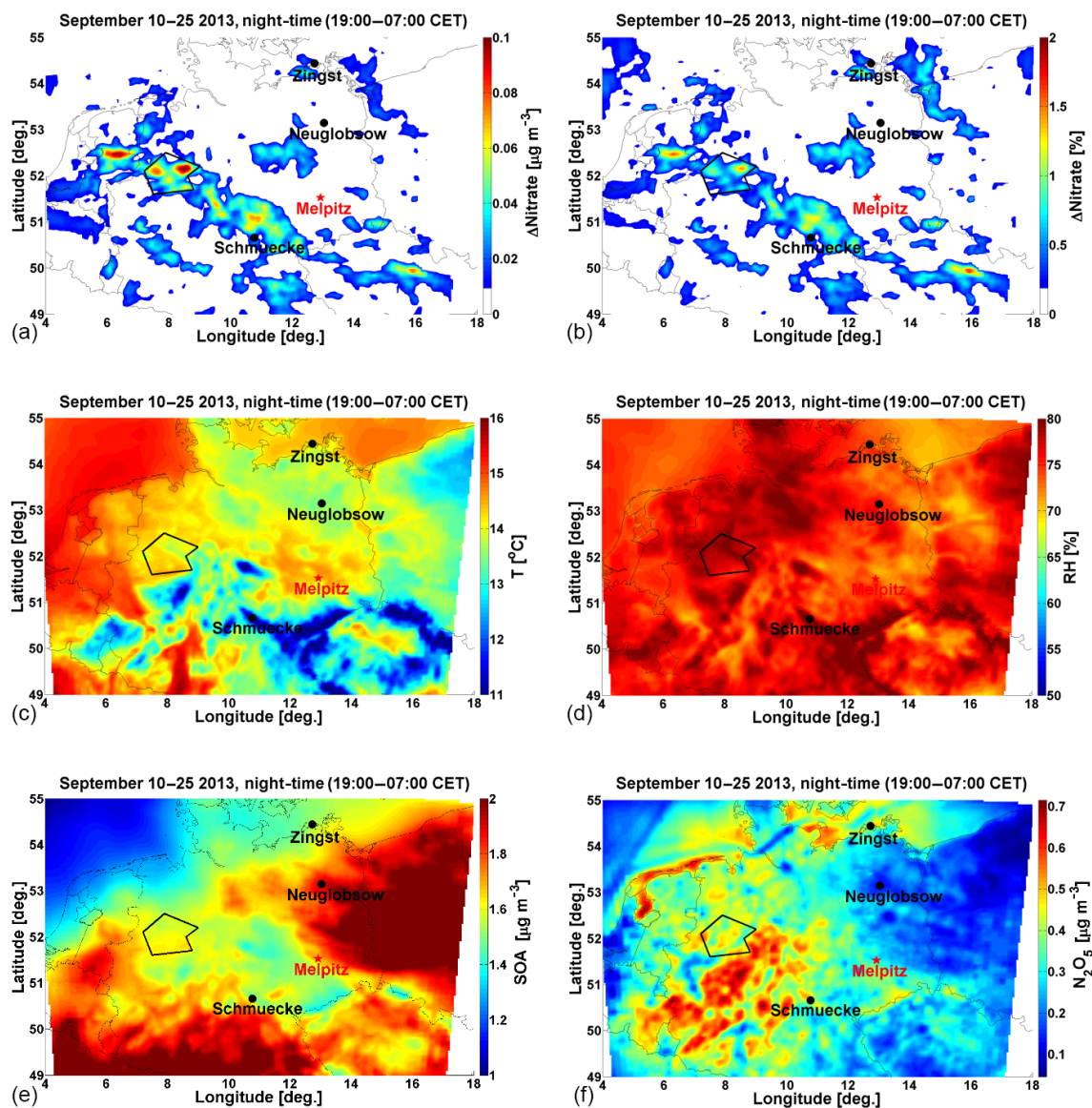
Figure 6. Horizontal distribution of averaged model results during night-time on 10–25 September computed with NewN2O5. **(a)** Difference in particulate nitrate mass concentration between model cases with and without considering the organic coating effect; **(b)** difference in particulate nitrate mass concentration in percent between model cases with and without considering the organic coating effect; **(c)** temperature; **(d)** RH; **(e)** SOA mass concentration; **(f)** N$_2$O$_5$ mass concentration. The region with the most significant organic coating effect is highlighted by the black polygon.

not be simultaneously fulfilled over western and central Europe, and therefore the organic coating effect was not very significant.

4   Conclusions

Generally, the COSMO–MUSCAT model predicted particulate nitrate in a reasonable range on long-term average. 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 the heterogeneous hydrolysis of N$_2$O$_5$ (OldN2O5). A sophisticated mass-based parameterization of the heterogeneous hydrolysis of N$_2$O$_5$ (NewN2O5) was proposed in this study, aiming at improving the particulate nitrate prediction in atmospheric modelling. This mass-based NewN2O5 was validated with a state-of-the-art parameterization (Chang et al., 2016), which is based on a sectional aerosol treatment. The validation results showed a good linear relation-

ship ($R = 0.91$) and indicated that NewN2O5 could estimate the reaction probability of N$_2$O$_5$ in a reasonable range, within about 0.36–1.2 times the realistic one.

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 patterns of particulate nitrate were in good agreement between the OldN2O5 and NewN2O5 cases. The OldN2O5 case 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 a lacking consideration of particle surface area (S) and complex treatments of $\gamma_{N_2O_5}$. Based on many previous laboratory experiments, the influences of temperature, RH, aerosol particle compositions, and surface area concentration on the heterogeneous reaction constant of N$_2$O$_5$ were considered in NewN2O5. The reaction constant was on average reduced by a factor of more than 20 in NewN2O5. Correspondingly, the overestimation of particulate nitrate was reduced by ~ 35 % for the whole period. Particularly, NewN2O5 significantly improved particulate nitrate prediction, with a factor of ~ 1.4 compared with the filter measurements, when particulate nitrate was dominated by local chemical formations at Melpitz (12, 17–18, and 25 September).

In this study, we additionally investigated how the decrease in $\gamma_{N_2O_5}$ 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 analysed. Our results showed a negligible (less than 2 % or 0.1 µg m^{-3}) influence of coating on particulate nitrate over the Netherlands and Germany. Since, in addition to the considerable amounts of N$_2$O$_5$, SOA, and NH$_3$ that must be present at the same location, appropriate meteorological conditions (relatively high RH and low temperature) are also indispensable for organic coating to exert an impact. This is because low RH and high temperature would lead to a low $\gamma_{N_2O_5}$ value, and therefore 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 into account in the parameterization of the heterogeneous hydrolysis of N$_2$O$_5$. A sophisticated parameterization is proposed for the mass-based aerosol models. It should be included in model simulations to improve the representativeness of N$_2$O$_5$ hydrolysis in the ambient atmosphere. The results also indicate that the organic coating effect on suppressing the heterogeneous hydrolysis of N$_2$O$_5$ may not be as significant as expected over Europe.

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