A Parameterization of Heterogeneous Hydrolysis of N_2O_5 for Mass-based Aerosol Models: Improvement of Particulate Nitrate Prediction

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Abstract

Heterogeneous hydrolysis of N_2O_5 on the surface of deliquescent aerosol leads to HNO_3 formation and acts as a major sink of NOx in the atmosphere during night-time. The reaction constant of this heterogeneous hydrolysis is determined by temperature (T), relative humidity (RH), aerosol particle composition as well as the surface area concentration (S). However, these parameters were not comprehensively considered in the parameterization of 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 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 NewN2O5 significantly reduces the overestimation of $[NO_3^-]$ by ~35%. Particularly, the overestimation factor was reduced to approximately 1.4 in our case study (September 12, 17-18 and 25, 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 $[NO_3^-]$ 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 are needed 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 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 (NOx) 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 NOx is to be heterogeneously hydrolyzed N$_2$O$_5$ on surface of deliquescent aerosol (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 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$_2$O$_5$ 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 typically the values for $\gamma_{N_2O_5}$ are in an 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 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) developed a parameterization scheme (Davis08) of $\gamma_{N_2O_5}$ for aerosols containing nitrate, sulfate and ammonium. It was developed on 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$_2$O$_5$ 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 if cloud droplets are at presence, with a particle surface area concentration of 2700 µm^2/cm^3. Riemer et al. (2003) proposed a more complex scheme (P1 in the literature) with respect to the particle surface

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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 of particulate nitrate due to organic coating in the regions where both N_2O_5 and secondary

5   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), 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

10   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 northwestern Europe (Morgan et al., 2015). Recently, Chang et al. (2016)

15   improved the P1 (Riemer et al., 2003) with '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 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

20   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/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, e.g. EMEP (Simpson et al., 2012) and GEOS-Chem (Walker et al., 2012), as well as long-term modelling studies (e.g.

25   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 (**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) with the mass-based aerosol treatment according to Simpson et al., 2003. However, the P2 still showed a large difference

30   in comparison to the more-complete P1 (Riemer et al., 2003). The reasons may be the missing of complex considerations of S and $\gamma_{N_2O_5}$ in the P2.

To improve the representativeness of heterogeneous hydrolysis of N_2O_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. This NewN2O5 was validated by the state-of-the-art parameterization in

35   Chang et al. (2016). We also incorporated NewN2O5 into the 3-D fully on-line 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 Melpitz site (12.93ºE,

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 the operation forecast of pollutants as well as 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 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 several overlapping short periods, each of which included a one-day spin-up followed by a two-days 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 aerosols 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 boudary 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 EMEP model, Simpson et al., 2003) is used to represent the aerosol processes with high efficiency. The formation of secondary inorganic particulate matter is though reactions of ammonia with sulfuric acid and nitric acid, which are produced from gaseous precursors SO_2 and NOx (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), considering the kinetic viscosity, the atmospheric turbulence state, and the gravitational settling of particles. The resistances for 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 the 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, 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 × 0.0625^o (lon-lat, about 7×7 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, surface 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 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$_2$O$_5$ to nitrate avoiding the influence of transport. T1 represents the contribution of N$_2$O$_5$ on chemical formation of nitric acid; T3-T2 represents 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 2×10^{-8} mol/m^2/s.

2.2 A novel mass-based parameterization of heterogeneous hydrolysis of N$_2$O$_5$

The heterogeneous hydrolysis of N$_2$O$_5$ on the surface of deliquescent aerosol is believed to be considerable, since N$_2$O$_5$ 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 references therein).

The P2 of Riemer et al. (2003), which adapted from Chang et al. (1987), was originally incorporated in COSMO-MUSCAT to represent the heterogeneous hydrolysis of N$_2$O$_5$ (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 $k_{N_2O_5}$.

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

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 µm^2/cm^3, when RH is higher than 60%. However, this high surface area concentration can only be expected in areas suffered 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 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).

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

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

where SA_{fine} / SA_{coarse} is the specific surface area for fine/coarse mode particles in m^2/g, PM_{fine} / PM_{coarse} is the mass concentration of fine/coarse mode particles in µg/m^3. A value 11 m^2/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). S_{ref} is the reference particle surface area concentration, here, we suggest '$S_{ref} = 600$ µm²/cm³'. Since equation (2) will provide a result that is very close to a complex parameterization with a particle surface area concentration of 600 µm²/cm³ (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 $k_{N_2O_5}$, leads 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 equation (4) is considered as 1.3 times of sulfate mass concentration based on filter measurements during the HOPE-Melpitz campaign.

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

where γ_{core} is the N₂O₅ reaction probability with the core of the particle, which can be estimated by Table 1; $\gamma_{coating}$ is the N₂O₅ 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); γ_{ref} is the reference reaction probability. Here, we suggest 'γ_{ref} =0.1', since equation (2) is developed on basis of the assumption '$\gamma_{N_2O_5} = 0.1$' (Riemer et al., 2003).

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

where T is the temperature, $D_{N_2O_5}$ is the diffusion coefficient of N₂O₅ in the organic coating, $H_{N_2O_5}$ is the Henry's Law constant of N₂O₅ 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.

γ_{core} 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 N₂O₅ hydrolysis on ammonium-sulfate-nitrate particles, with respect to RH and temperature. Evans and Jacob (2005) provided the parameterizations for N₂O₅ 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

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The Weather Research and Forecasting/Chemistry model (WRF-Chem V3.5.1) is a fully on-line coupled regional air quality model. Chang et al. (2016) incorporated several parameterizations for the N_2O_5 hydrolysis into a sectional aerosol treatment (MOSAIC, Zaveri et al., 2008) in WRF-Chem. '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 section 3.1.

In order to validate the mass-based NewN2O5 with the sectional-based Ch&Davis, we performed WRF-Chem simulation 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, respectively. We followed the physics relating configuration according to Chen et al. (2016a), which well reproduced meteorological conditions during the HOPE-Melpitz campaign. 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). 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) with 39 vertical layers were set up for the simulated case, with a resolution of 54 km, 18 km and 6 km respectively.

In Ch&Davis the aerosol liquid water is considered when calculating particle surface area for each size bin. Details of the sectional-based method for estimating S in Ch&Davis scheme are given by Chang et al. (2016). In NewN2O5 scheme, the first six bins (with diameter in the range of 40nm – 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 with COSMO-MUSCAT. In order to be consistent with COSMO-MUSCAT, the organic coating effect is considered for fine particles in NewN2O5, since the maximum effective particle diameter of Anttila06 scheme is 2 µm (Anttila et al., 2006). In order to quantify the uncertainty stem 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 section 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, www.umweltbundesamt.de) were used to validate the modelled results. The observations at the TROPOS research station Melpitz represent the regional background of 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 ~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, 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°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 & 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-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 meteorological parameters in this study for N_2O_5 heterogeneous hydrolysis during night-time, were in a good agreement with the measurement. Although model simulations slightly underestimated RH during the night-time of September 17 and 22 (Fig. 2b), modelled RH was still higher than 80% where $k_{N_2O_5}$ 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 NewN2O5 case (Fig. 3d), especially during September 20-24 when 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 $k_{N_2O_5}$ 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 'Davis + coat' (Daivs08 + Anttila06) approach produced a best agreement of $\gamma_{N_2O_5}$ 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), the Ch&Davis still showed a relatively good linear relationship with the observed $\gamma_{N_2O_5}$, 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), the 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 ~7% contribution from total OC mass based on filter measurements at Melpitz. Therefore, not much SOA was available for coating effect, different to the OC-high case (contributed about 50-80% to total mass, Figure 9 in Chang et al., 2016) in the CalNex-2010 campaign. The coating effect exerted a negligible influence at Melpitz, this point will be discussed in detail in section 3.4. We validated NewN2O5 scheme by comparing $k_{N_2O_5}$ instead of $\gamma_{N_2O_5}$, because NewN2O5 scheme was developed on basis of a parameterization to directly calculate $k_{N_2O_5}$ proposed by Chang et al. (1987) and Riemer et al (2003).

As shown in Fig. 4, the $k_{N_2O_5}$ showed a good linear relationship (R=0.91) between NewN2O5 and Ch&Davis, much better than using the OldN2O5 (Fig. 4). Mass-based NewN2O5 estimated lower $k_{N_2O_5}$ than the sectional-based Ch&Davis by a factor of ~8. However, Ch&Davis may overestimate the $\gamma_{N_2O_5}$ 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 $k_{N_2O_5}$ by a factor of 3-10 according to the equation (1). Therefore, NewN2O5 may provide a $k_{N_2O_5}$ in the range of 0.36-1.2 times of the realistic one.

Two important uncertainties are needed to be kept in mind in this validation. First, the estimation of S is very challenging, due to the uncertainties of particle number/mass size distribution, partitioning processes, secondary formation and etc. In addition, the hygroscopic growth of particle 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 30% difference of $k_{N_2O_5}$ between NewN2O5 and Ch&Davis is stem from the different treatments of S. As shown in Fig. 4, the factor between NewN2O5 and Ch&Davis reduced from ~8.3 to ~5.9, with a slightly increase of R, when we adopted the sectional-based S (same as Ch&Davis) in NewN2O5. Second, the 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, the SSA, BC and dust should exert a sensible influence in an OC-low case, and should also be considered in a parameterization, as we did in NewN2O5. This can be also 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 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 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 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 NOx was in line with the observed concentration level at Melpitz, and should not be the reason of the overprediction of particulate nitrate (see details in Supplement Text S1 and Fig. S3). Nevertheless, the overestimation of NH$_3$ emission might contribute about 20-30% of the particulate nitrate overprediction, compared between OldN2O5-FullNH3 and OldN2O5 cases. This is in line with the 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 all consumed by the heterogeneous reaction at Melpitz in OldN2O5 case, but not in the NewN2O5 case (Fig. 3e). It is due to a significant decrease (by averagely more than a factor of 20, see Fig. 4) in the reaction constant of heterogeneous hydrolysis of N_2O_5 by NewN2O5. However, there must be other reasons that might explain the remained overestimations in the simulated particulate nitrate mass concentrations. One possible reason can be the underprediction of 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, e.g. deposition process, long-range transport, 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 off-line. 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. S4, 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 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_2O_5 by NewN2O5. During September 15-16 (without 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 night-time 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, $[NO_3^-]$ was lower than 4 $\mu g/m^3$ and 3 $\mu g/m^3$ in OldN2O5 and NewN2O5 cases, respectively. Moderate $[NO_3^-]$ was found over central Europe (Melpitz and the surrounding region), about 6-8 $\mu g/m^3$ and 4-5.5 $\mu g/m^3$ in the OldN2O5 and NewN2O5 cases, respectively. The highest $[NO_3^-]$ occurs over the region of the Netherlands and near-by regions, about 9-12 $\mu g/m^3$ and 6-8 $\mu g/m^3$ in 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, about 8-10 $\mu g/m^3$ and 5-6.5 $\mu g/m^3$ in the OldN2O5 and NewN2O5 cases, respectively. In general, the $[NO_3^-]$ was reduced by ~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$$^-$] (reduced by about 3-4.5 μg/m^3) was found, followed by the near Melpitz region (reduced by about 2-3 μg/m^3, Fig. 5c). This is caused by a significant reduction (by more than a factor of 20, see Fig. 4) of $k_{N_2O_5}$, which is resulted from the consideration of particle mass concentration's influence on S and comprehensive treatments for $\gamma_{N_2O_5}$. Therefore, the regions with high [NO$_3$$^-$] during night-time indicates a considerable nitrate formation from the heterogeneous hydrolysis of N$_2$O$_5$, where [NO$_3$$^-$] was reduced by about 3-4.5 μg/m^3 (~35%, see Fig. 5) in the new scheme. However, this heterogeneous hydrolysis was negligible over the regions where [NO$_3$$^-$] was low during night-time, and did not have relevant contribution on the formation of particulate nitrate. Hence, the improvement of particulate nitrate prediction by NewN2O5 was more significant over the high-[NO$_3$$^-$] regions than the low-[NO$_3$$^-$] regions.

3.4 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. Riemer et al., (2009) reported that organic coating could decrease [NO$_3$$^-$] by up to 90% where both N$_2$O$_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$_2$O$_5$ and secondary organic compounds, the meteorological conditions (e.g. RH and temperature) may also exert a sensible influence on organic coating effect. In this study, we introduced a parameterization (NewN2O5) for heterogeneous hydrolysis of N$_2$O$_5$ 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 SOA coating effect.

At night-time, much higher N$_2$O$_5$ concentrations occurred and the heterogeneous hydrolysis is more important than that during daytime (Jacob, 2000). As shown in Fig. 6a and Fig. 6b, the influence 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$$^-$] only by about 2-4 μg/m^3 (less than 10-20%) over the black-polygon marked and near-by regions (Fig. S5). Meanwhile, for night-time averages during the campaign, the organic coating could only reduce [NO$_3$$^-$] by less than 0.1 μg/m^3 or 2% over the whole domain (Fig. 6). This is because appropriate meteorological conditions, as described following, are needed in NewN2O5 for a significant organic coating. In addition to the simultaneous build-up of SOA and N$_2$O$_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$_2$O$_5$ 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 the regions with high RH and low temperature, 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$$^-$]) could be found over the Netherlands and near-by regions (black polygon). Over this area, these five conditions were fulfilled to some extent: (1) temperature was 13.5-14.5 °C; (2) RH was higher than 75%; (3) SOA concentration was ~1.6 μg/m^3; (4) N$_2$O$_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. 6a and Fig. 6b). 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. 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 (OldN2O5). A sophisticated mass-based parameterization of heterogeneous hydrolysis of N_2O_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 relationship (R=0.91) and indicated that NewN2O5 could estimate the reaction probability of N_2O_5 in a reasonable range, within about 0.36-1.2 times of 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 a good agreement between OldN2O5 and NewN2O5 cases. 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 lacking of 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_2O_5 were considered in NewN2O5. The reaction constant was averagely 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, 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).

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. 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_2O_5, SOA and NH_3 must be present at the same location, appropriate meteorological conditions (relatively high RH and low temperature) are also indispensable for the organic coating to exert a sensible impact. This is because 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 into account in the parameterization of the heterogeneous hydrolysis of N_2O_5. A sophisticated parameterization is proposed for the mass-based aerosol models. It 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 significant as expected over Europe.

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.

Bellouin, N., Rae, J., Jones, A., Johnson, C., Haywood, J., and Boucher, O.: Aerosol forcing in the Climate Model Intercomparison Project (CMIP5) simulations by HadGEM2-ES and the role of ammonium nitrate, Journal of Geophysical Research: Atmospheres, 116, n/a-n/a, 10.1029/2011JD016074, 2011.

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.

Chang, W. L., Brown, S. S., Stutz, J., Middlebrook, A. M., Bahreini, R., Wagner, N. L., Dubé, W. P., Pollack, I. B., Ryerson, T. B., and Riemer, N.: Evaluating N2O5 heterogeneous hydrolysis parameterizations for CalNex 2010, Journal of Geophysical Research: Atmospheres, 121, 5051-5070,

10.1002/2015JD024737, 2016.

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.

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.

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: 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.

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, 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, 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 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.

Gong, S. L.: A parameterization of sea-salt aerosol source function for sub- and super-micron particles, Global Biogeochemical Cycles, 17, 10.1029/2003GB002079, 2003.

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.

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.

Hardiman, S. C., Butchart, N., O'Connor, F. M., and Rumbold, S. T.: The Met Office HadGEM3-ES chemistry–climate model: evaluation of stratospheric dynamics and its impact on ozone, Geosci. Model Dev., 10, 1209-1232, 10.5194/gmd-10-1209-2017, 2017.

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.

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.

Li, Y. P., Elbern, H., Lu, K. D., Friese, E., Kiendler-Scharr, A., Mentel, T. F., Wang, X. S., Wahner, A., and Zhang, Y. H.: Updated aerosol module and its application to simulate secondary organic aerosols during IMPACT campaign May 2008, Atmos. Chem. Phys., 13, 6289-6304, 10.5194/acp-13-6289-2013, 2013.

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., Barthlott, C., Beekmans, C., Behrendt, A., Bohn, B., Brueck, M., 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.,

Trömel, S., Wehner, B., Wieser, A., Wulfmeyer, V., and Xie, X.: The HD(CP)2 Observational Prototype Experiment (HOPE) – an overview, Atmos. Chem. Phys., 17, 4887-4914, 10.5194/acp-17-4887-2017, 2017.

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.

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.

Neumann, D., Matthias, V., Bieser, J., Aulinger, A., and Quante, M.: A comparison of sea salt emission parameterizations in northwestern Europe using a chemistry transport model setup, Atmos. Chem. Phys., 16, 9905-9933, 10.5194/acp-16-9905-2016, 2016.

Okuda, T.: Measurement of the specific surface area and particle size distribution of atmospheric aerosol 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.

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 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 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 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

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 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, 3577-3589, 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 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.

Simpson, D., Benedictow, A., Berge, H., Bergström, R., Emberson, L. D., Fagerli, H., Flechard, C. R., Hayman, G. D., Gauss, M., Jonson, J. E., Jenkin, M. E., Nyíri, A., Richter, C., Semeena, V. S., Tsyro, S., Tuovinen, J. P., Valdebenito, Á., and Wind, P.: The EMEP MSC-W chemical transport model – technical description, Atmos. Chem. Phys., 12, 7825-7865, 10.5194/acp-12-7825-2012, 2012.

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.

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.

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.

Walker, J. M., Philip, S., Martin, R. V., and Seinfeld, J. H.: Simulation of nitrate, sulfate, and ammonium aerosols over the United States, Atmos. Chem. Phys., 12, 11213-11227, 10.5194/acp-12-11213-2012, 2012.

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.

Zaveri, R. A., and Peters, L. K.: A new lumped structure photochemical mechanism for large-scale applications, J. Geophys. Res., 104, 30387-30415, 1999.

Zaveri, R. A., Easter, R. C., Fast, J. D., and Peters, L. K.: Model for Simulating Aerosol Interactions and Chemistry (MOSAIC), Journal of Geophysical Research: Atmospheres, 113, 10.1029/2007JD008782, 2008.

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	$\gamma_{ASN} = \gamma^*_{AB} \cdot x_{AB} + \gamma^*_{aq/d,AS} \cdot x_{AS} + \gamma^*_{AN} \cdot x_{AN}$ $\gamma^*_{AB} = \min(\gamma_{AB}, 0.08585)$, $\quad \gamma_{AB} = \dfrac{1}{1+e^{-\lambda_{AB}}}$ $\gamma^*_{aq,AS} = \min(\gamma_{aq,AS}, 0.053)$, $\gamma_{aq,AS} = \dfrac{1}{1+e^{-\lambda_{aq,AS}}}$ $\gamma^*_{d,AS} = \min(\gamma_{d,AS}, 0.0124)$, $\gamma_{d,AS} = \dfrac{1}{1+e^{-\lambda_{d,AS}}}$ $\gamma^*_{AN} = \min(\gamma_{AN}, 0.0154)$, $\quad \gamma_{AN} = \dfrac{1}{1+e^{-\lambda_{AN}}}$ $\lambda_{AB} = \beta_{10} + \beta_{11} \cdot RH + \beta_{12} \cdot T_{291}$ $\lambda_{aq,AS} = (\beta_{10} + \beta_{20}) + \beta_{11} \cdot RH + (\beta_{12} + \beta_{22}) \cdot T_{291}$ $\lambda_{d,AS} = \beta_{d0} + \beta_{d1} \cdot RH + \beta_{d2} \cdot T_{293}$ $\lambda_{d,AN} = \beta_{30} + \beta_{31} \cdot RH$	$x_{AB} = 1 - (x_{AS} + x_{AN})$ $x_{AS} = \max(0, \min(1 - x_{AN}, \dfrac{[A]}{[N]+[S]} - 1))$ $x_{AN} = \dfrac{[N]}{[N]+[S]}$ $\beta_{10} = -4.10612$ $\beta_{11} = 0.02386$ $\beta_{12} = -0.23771$ $\beta_{20} = -0.80570$ $\beta_{22} = 0.10225$ $\beta_{30} = -8.10774$ $\beta_{31} = 0.04902$ $\beta_{d0} = -6.13376$ $\beta_{d1} = 0.03592$ $\beta_{d2} = -0.19688$ $T_{291} = \max(T - 291, 0)$ $T_{293} = \max(T - 293, 0)$	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 OC)	$\gamma_{OC} = RH \times 5.2 \times 10^{-4}$ $\quad RH < 57\%$ $\gamma_{OC} = 0.03$ $\quad RH \geq 57\%$		Evans and Jacob (2005) Thornton et al. (2003)
Sea Salt Aerosol (SSA)	$\gamma_{SSA} = 0.005$ $\quad RH < 62\%$ $\gamma_{SSA} = 0.03$ $\quad RH \geq 62\%$		Evans and Jacob (2005) Sander et al. (2003)
Dust	$\gamma_{Dust} = 0.01$		Evans and Jacob (2005) Bauer et al. (2004)
Black Carbon (BC)	$\gamma_{BC} = 0.005$		Sander et al. (2003)

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% [*]

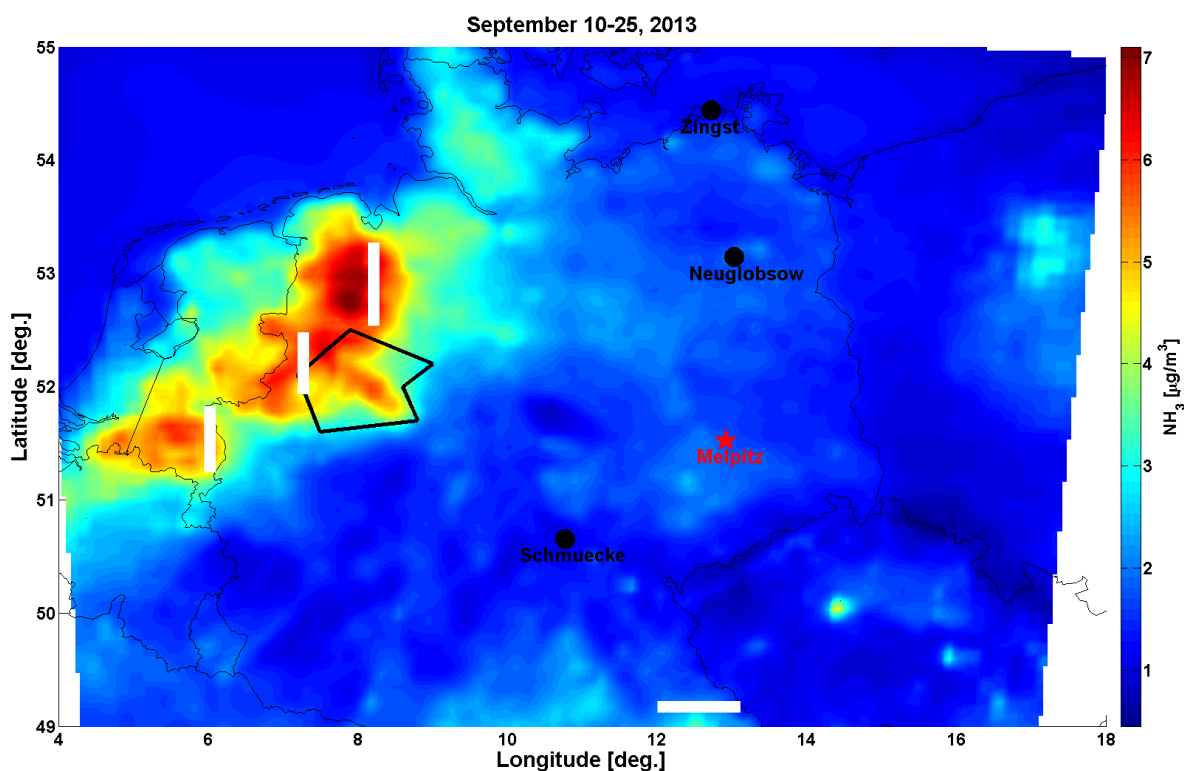[*] Suggested by Sintermann et al. (2012), Backes et al. (2016) and Chen et al. (2016b)

5

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: Neuglobsow, Schmücke and Zingst are marked by black dots; Melpitz is marked in a red star and its results will be detailed discussed in Fig. 2 and Fig. 3. The region with the most significant organic coating effect is highlighted by the black polygon, and will be analysed together with Fig. 6.
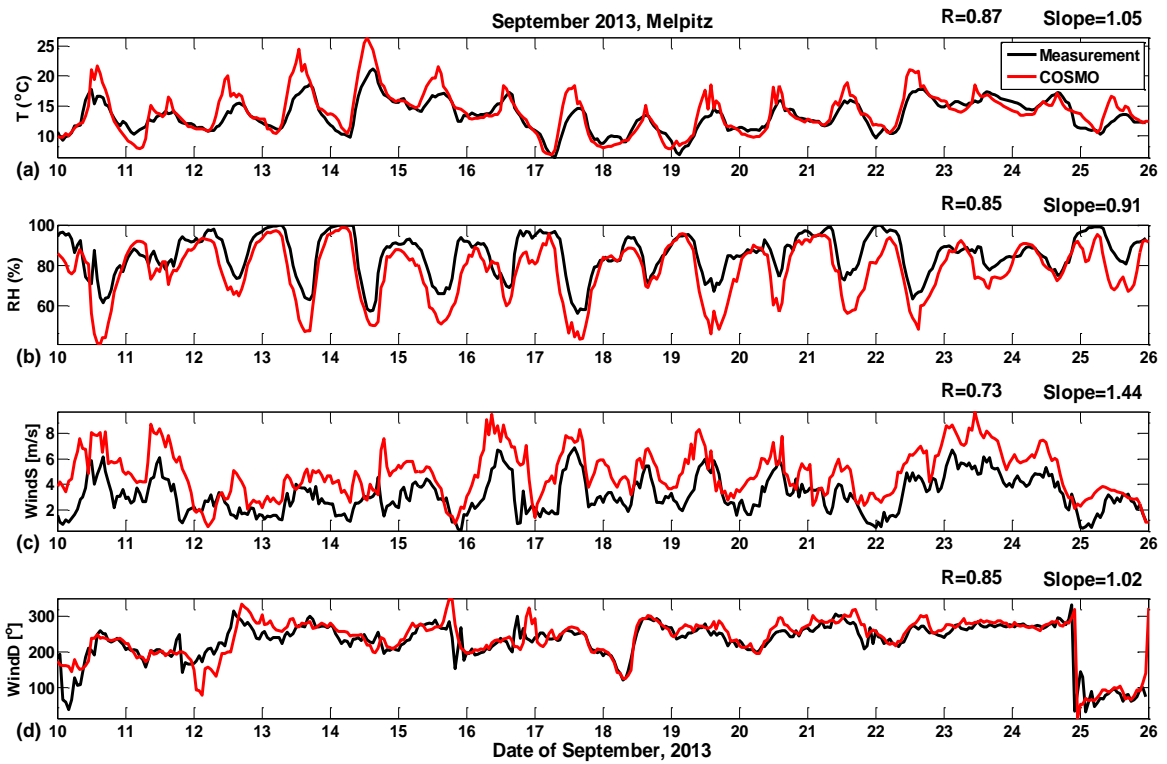
Figure 2. Comparison between modelled and measured meteorological conditions. (a) Temperature (T); (b) relative humidity (RH); (c) wind speed; (d) wind direction.
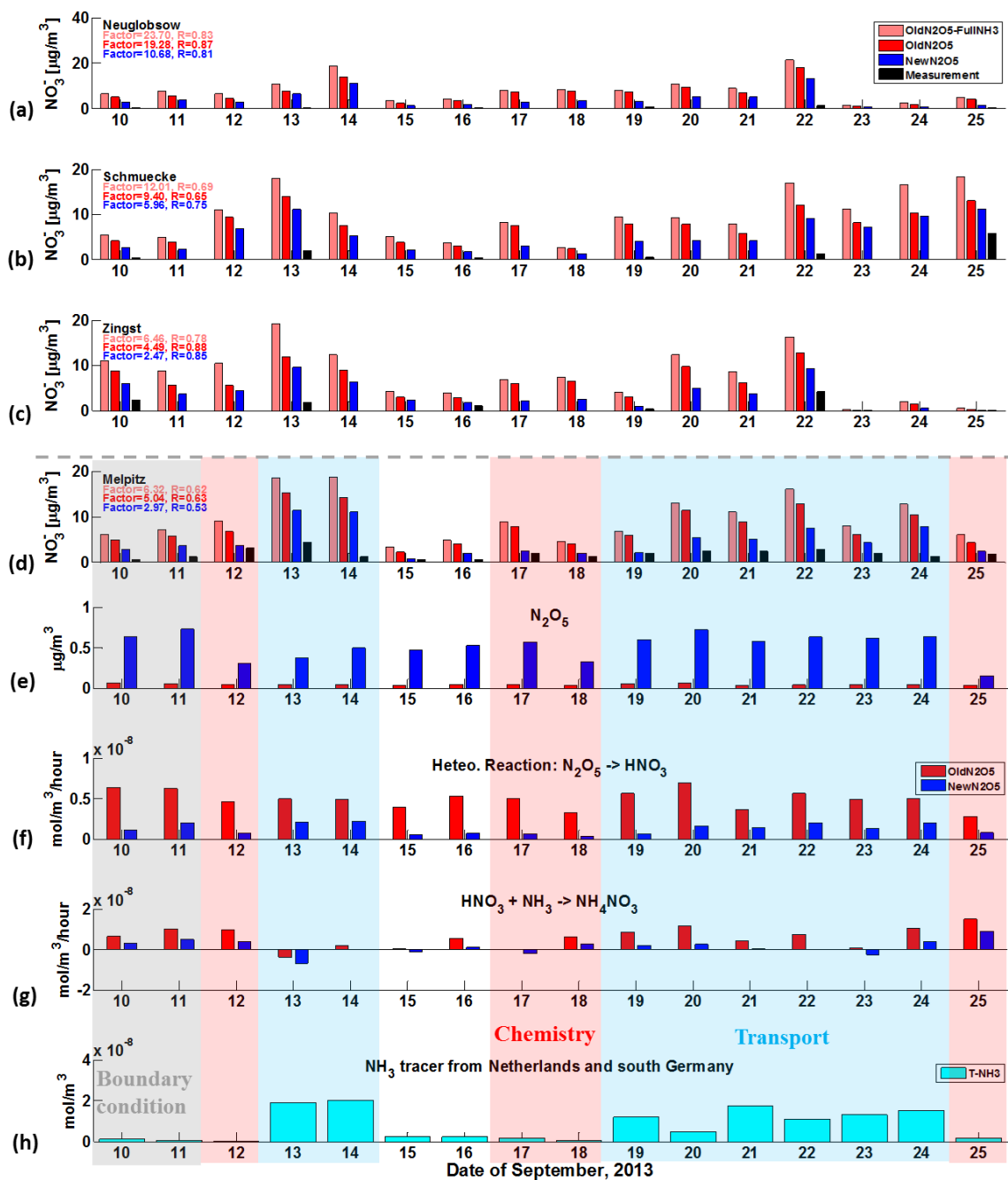
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Figure 3. Comparison of particulate nitrate mass concentration between filter measurements and modelled results: (a) Neuglobsow; (b) Schmuecke; (c) Zingst; (d) Melpitz. Modelled concentrations at Melpitz: (e) N_2O_5; (f) marker species T1 for chemical 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 OldN2O5-FullNH3 case; the red colour bars indicate the results of OldN2O5 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).
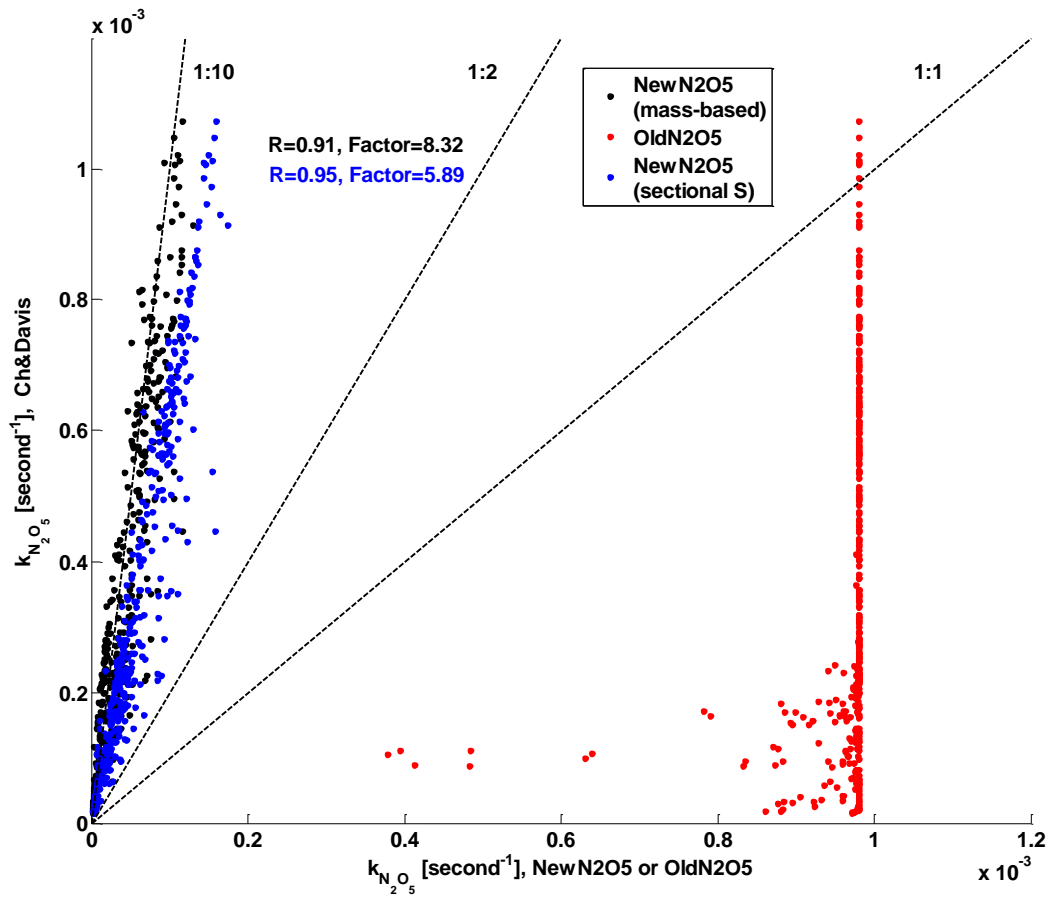
Figure 4. Comparison between the sectional-based Ch&Davis ('Davis' of Chang et al., 2016) and mass-based NewN2O5 (mass-based, black), NewN2O5 (with a sectional-based particle surface area, blue) and OldN2O5 (red). The results are offline calculated on basis of WRF-Chem simulation with a sectional aerosol treatment (MOSAIC).
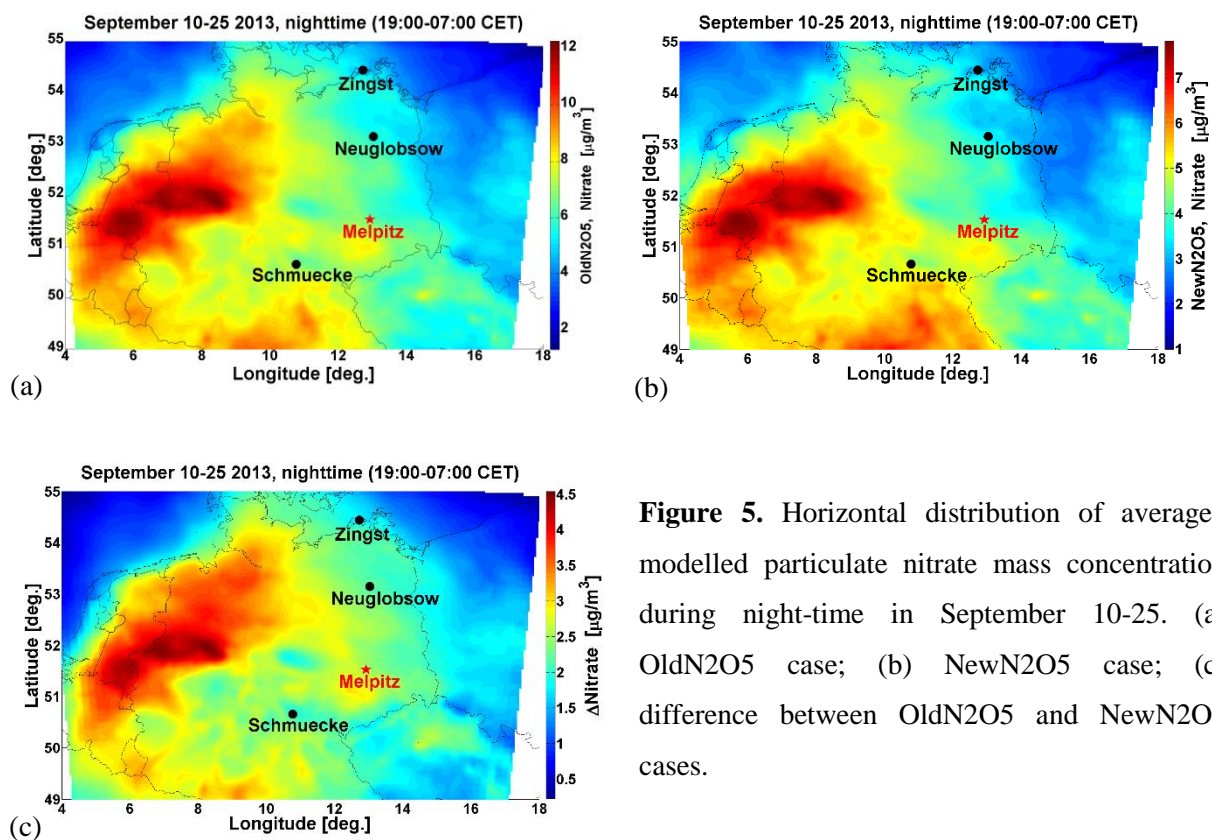
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(a)

(b)

(c)

Figure 5. Horizontal distribution of averaged modelled particulate nitrate mass concentration during night-time in September 10-25. (a) OldN2O5 case; (b) NewN2O5 case; (c) difference between OldN2O5 and NewN2O5 cases.
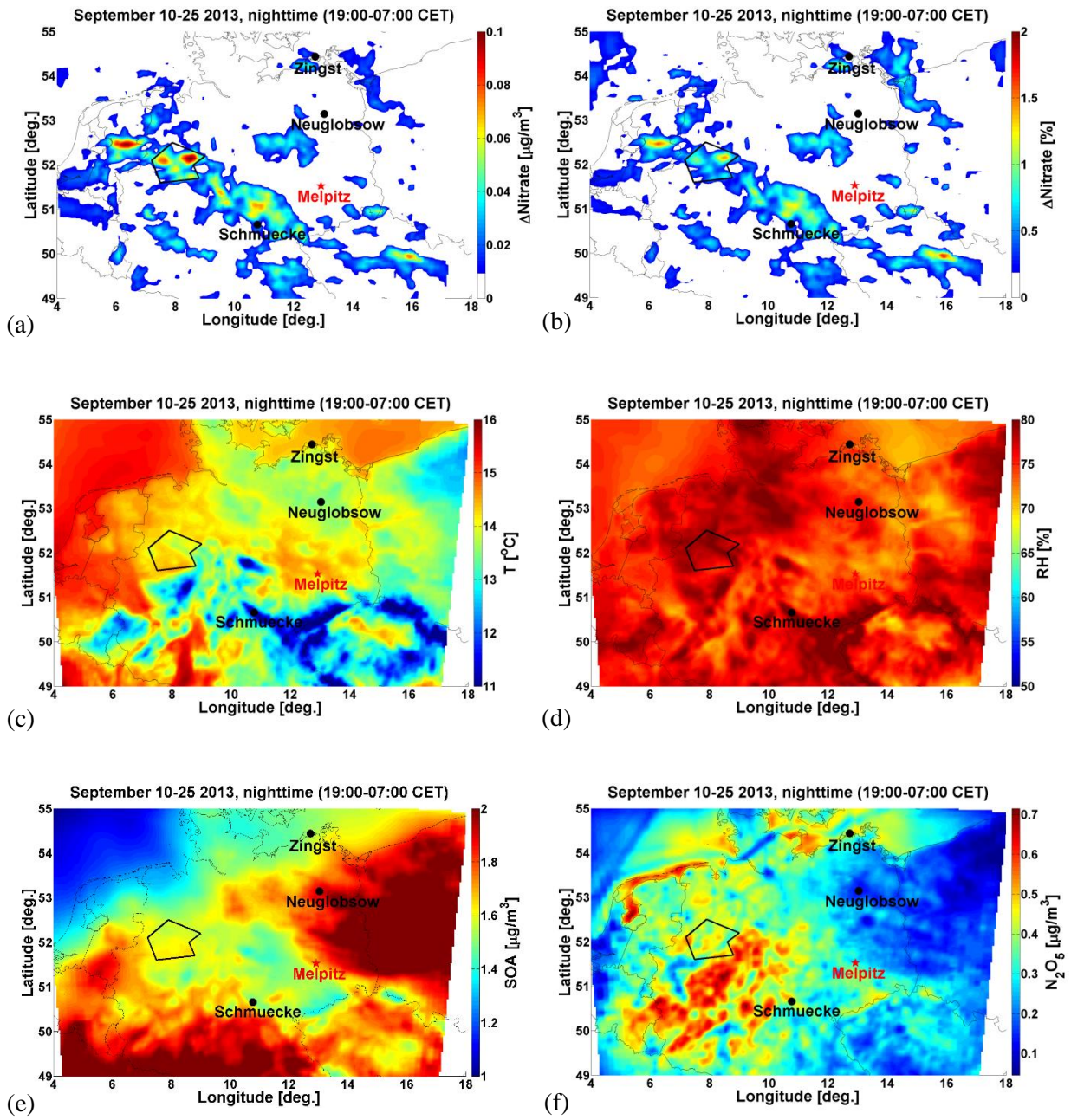
Figure 6. Horizontal distribution of averaged model results during night-time in September 10-25, computed with the NewN2O5. (a) Difference of particulate nitrate mass concentration between model cases with and without considering organic coating effect; (b) difference of particulate nitrate mass concentration 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.