

Response to Editor:

Dear ACP Editor Prof. Herman Russchenberg,

We would like to thank the two referees for their very helpful comments, which have been fully taken into account upon manuscript revision. The ambiguous reference to Riemer et al. (2003) is clarified and the typos in formula (2) and (3) have been corrected. We revised the introduction and title to emphasize differences between our mass-based parameterization (NewN2O5) and the sectional-based parametrization (Chang et al. 2016, see the last comment from the Referee#02). In addition, we performed a new simulation with WRF-Chem (MOSAIC, a sectional aerosol treatment), in order to validate our NewN2O5 with the state-of-the-art sectional-based parameterization (Chang et al., 2016). This evaluating closure further confirmed a good performance of NewN2O5.

Please find more details in the point-by-point response to all the comments and the marked-up manuscript version, as shown below.

Best Regards,

Ying Chen

Response to comments of referee #1

General Comments:

Chen et al. have studied a new parameterization of heterogeneous hydrolysis of N_2O_5 within a 3D model over Germany. Clear improvement of using this parameterization with respect to original parameterizations is shown by comparing against measurements. Sensitivity tests have been performed to study the effect of NH_3 emission, reaction constant and organic coating. The paper is well structured and easy for reading. It is recommended for publishing with minor revisions.

The measurement data used to evaluate the model performance are based on 24h filter sampler, but it is interesting to know the detailed temporal evolution at least in the model and have some discussion on the uncertainties related to NO_x and N_2O_5 prediction. This new parameterization of heterogeneous hydrolysis of N_2O_5 established from many previous laboratory experiments improves the prediction, but large gaps still exist between the model results and the measurement at all stations. Among the reasons given in section 3.1, how about the kN_2O_5 calculating with overestimated nitrate and what about its impact on the simulation?

Response:

Many thanks to the reviewer for the comments and suggestions.

This is a good suggestion. NO_x is also an important precursor of nitrate. However, in this study, the overprediction of nitrate was not stem from NO_x , which was in line with the measured concentration level. The detailed temporal evolutions of NO_x and N_2O_5 were added in the supplementary information Text S1, as shown below.

“S1. Temporal evolutions of NO_x and N_2O_5

The concentration of gaseous precursor (NO_x) was observed under the frame of HOPE-Melpitz campaign with 1h temporal resolution. As shown in Fig. S3 (newly added), the modelled NO_x concentration was in line with the measurement, with a factor of 0.9 for both Old N_2O_5 and New N_2O_5 cases. Therefore, the high overestimation of particulate nitrate should not be resulted from the uncertainty of NO_x .

The N_2O_5 concentration was accumulated during nighttime in NewN2O5 case, and was totally dissociated into NO_2 and NO_3 during daytime (Fig. S3b). However, the N_2O_5 could not accumulate during nighttime in OldN2O5 case, due to its highly overestimated reaction constant.”

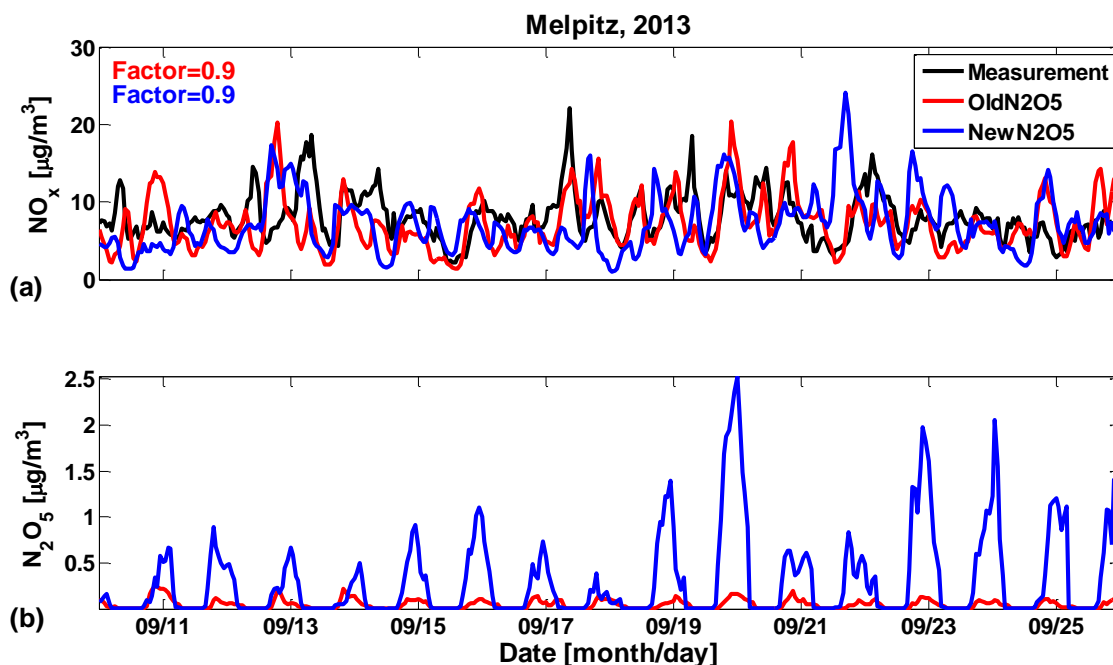


Figure S3 (newly added). Time series of NO_x (a) and N_2O_5 (b) at Melpitz.

In addition, one sentence has been added in the manuscript (section 3.2) to summarize the above information, as shown below.

“The modelled NO_x 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).”

As reviewer mentioned, large gaps still exists between the model results and the measurements at all stations. However, this should not be stem from NewN2O5 scheme. Since, NewN2O5 may provide a $k_{N_2O_5}$ in the range of 0.36-1.2 times of the realistic one, as discussed in the newly added section 3.1. There must be some other reasons that are responsible for the remained large gaps. In addition to the reasons given in section 3.2 (revised version), the underprediction of coating organic matter budget in the model may also be a possible reason

(Chang et al., 2016). A sentence has been added in section 3.2 to include this information, as shown below.

“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)” has been **added**.

And the impact of overestimated nitrate was excluded when calculate $k_{N_2O_5}$ in NewN2O5 scheme. In order to state this more clearly, we rephrased the description in section 2.2, as shown below.

~~“Note that the nitrate mass concentration in (4) is considered as 1.3 times of sulfate mass concentration, based on the filter measurements during HOPE-Melpitz campaign. This is aimed to calculate the contribution of the surface area concentration by nitrate in the model, meanwhile, avoiding errors with positive feedback between $k_{N_2O_5}$ and the modelled particulate nitrate mass concentration.”~~ **changed to**

“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.”

Specific Comments:

(1) P6, line 27, “is considered as 1.3 times of sulfate mass concentration”, does this mean sulfate is not explicitly simulated in the model? What can be the “positive feedback” on line 29?

Response:

Thanks for the comment. The sulfate is simulated in the model. Here, we considered the nitrate as 1.3 times of sulfate mass concentration when calculate $k_{N_2O_5}$, is aiming to avoid the positive feedback mechanism in nitrate simulation, as described in General Comments. The corresponding statement has also been rephrased, as shown in General Comments.

(2) Table 1, SSA abbreviation is not introduced.

Response:

The introduction of sea salt aerosol (SSA) abbreviation has been added in Table 1.

(3) P8, line 5: RH and wind speed have relatively important bias with respect to the measurement on 15-17 and 20-23 during the night. It should be discussed their relative impact on simulation results.

Response:

Thanks for the comment. The discussion about the impact of RH and wind speed bias during the night on the particulate nitrate simulation has been added in the first paragraph of section 3, as shown below.

“Although model simulations slightly underestimated RH during the nighttime 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).”

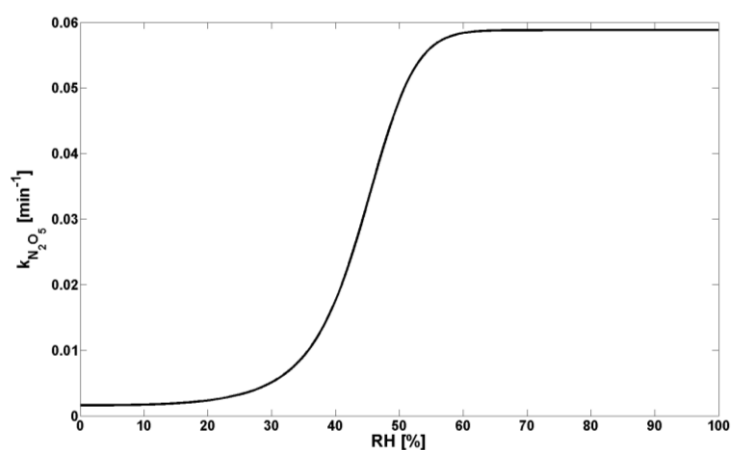


Figure R1. Rate constant for the heterogeneous hydrolysis of N_2O_5 with relation to RH. Modified from Figure 1 of Riemer et al. (2003), or calculated from the equation (2) with $a=17$.

(4) P8, line 20, Are the factors calculated based on average concentration during the campaign?

Response:

Yes, as reviewer understood, the factors are calculated based on the average concentration during the campaign.

(5) P8, line 22, is the 20-30% overestimation due to NH₃ overestimation a conclusion from previous study?

Response:

Thanks for the comment. Yes, as reported in previous studies that a 50% ammonia emission reduction leads to a 16-50% reduction (Backes et al., 2016) or a maximum of 30% reduction (Renner and Wolke, 2010) of particulate nitrate concentration. These are in line with our result, and the corresponding sentence in section 3.1 has been modified to include this information. As shown below:

~~“Similar results were reported in Renner and Wolke (2010).”~~ changed to

“This is in line with the previous studies (Renner and Wolke, 2010; Backes et al., 2016).”

(6) P8, line 29, please quantify “significant”.

Response:

Thanks for the comment. The corresponding sentence has been modified, as shown below.

~~“This indicated a significant decrease in the reaction constant of heterogeneous hydrolysis of N₂O₅ by the new scheme.”~~ changed to

“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 N₂O₅ by NewN₂O₅”

(7) P8, line 36, what does it mean “higher temporal resolution”.

Response:

Thanks for the comment. It means the filter measurements at Melpitz were operated every day, instead of the every third day at other UBA stations (Neuglobsow, Schmücke and Zingst). In

order to state this more clearly, the corresponding statement has been modified, as shown below.

“and the comparison with Melpitz measurements (Fig. 3d), which ~~have a higher temporal resolution~~” changed to

“and the comparison with Melpitz measurements (Fig. 3d), which were sampled on filter every day and off-line analyzed”

(8) Figure 3, the shade cannot be clearly seen.

Response:

Thanks for the comment. The shading colors have been deepened. As shown below.

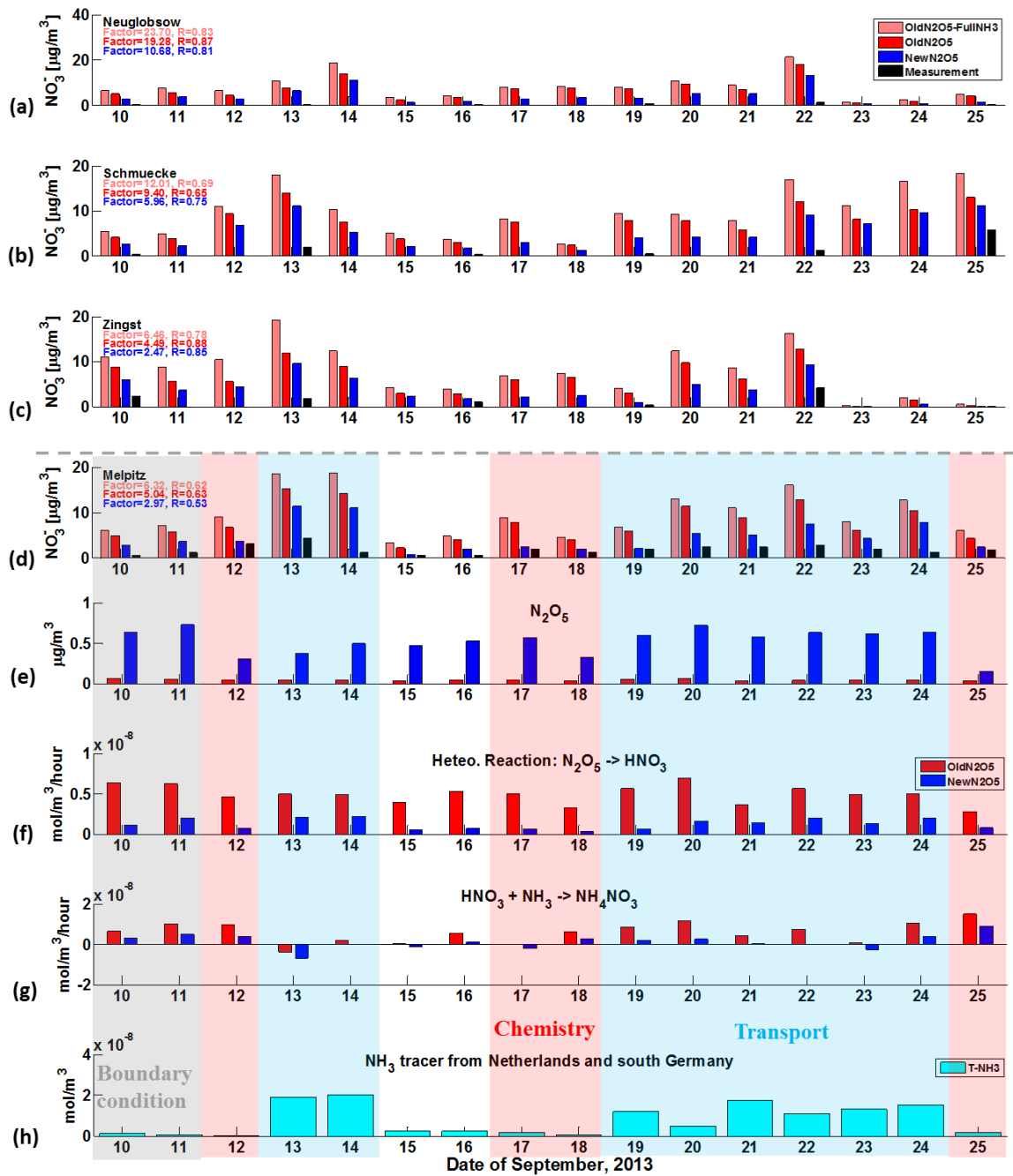


Figure 3. Comparison of particulate nitrate mass concentration between filter measurements and modelled results: (a) Neuglobsow; (b) Schmuecke; (c) Zingst; (d) Melpitz. Modelled concentrations at Melpitz: (e) N_2O_5 ; (f) marker species T1 for chemical reaction R1; (g) marker species for chemical formation 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).

(9) Figure 4, why Melpitz is pointed in red?

Response:

Thanks for the comment. Melpitz is pointed in red in Figure 1, Figure 4 and Figure 5, since its results were detailed discussed in section 3.1, Figure 2 and Figure 3. This information has been added in the caption of Figure 1, as shown below.

“Neuglobsow, Schmiecke 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.”

(10) P9, line 31, please quantify “more reasonable”.

Response:

Thanks for the comment. The corresponding sentence has been modified, as shown below.

*“Therefore, the regions with high $[NO_3^-]$ during nighttime indicates considerable nitrate formation from the heterogeneous hydrolysis of N_2O_5 , which was reduced to a more reasonable value in our new scheme.” **changed to***

*“Therefore, the regions with high $[NO_3^-]$ during nighttime indicates **a** considerable nitrate formation from the heterogeneous hydrolysis of N_2O_5 , **where $[NO_3^-]$ was reduced by about 3-4.5 $\mu\text{g}/\text{m}^3$ (~35%, see Fig. 5) in the new scheme.”***

Reference:

- 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.
- 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](https://doi.org/10.1002/2015JD024737), 2016.
- 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](https://doi.org/10.5194/acp-8-5295-2008), 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 photochemical conditions, *Journal of Geophysical Research: Atmospheres*, 108, n/a-n/a, [10.1029/2002JD002436](https://doi.org/10.1029/2002JD002436), 2003.

Response to comments of referee #2

General Comments:

This paper describes a new parametrization for the N_2O_5 hydrolysis which is dependent on T, RH and aerosol composition. The development of such a parameterization for N_2O_5 hydrolysis for a model framework that does not explicitly track aerosol surface area could be of interest to the community. However, the paper presented here has several serious shortcomings and errors, detailed below, so that I cannot recommend it for publication.

Response:

Thanks to the reviewer for the comments and suggestions. Yes, as emphasized by the reviewer, this work proposed a parameterization for N_2O_5 hydrolysis for the computationally efficient mass-based aerosol models. This work can be very useful for some regional models (e.g. COSMO-MUSCAT with aerosol treatment based on Simpson et al., 2003), and also for some global models (e.g. HadGEM3-ES, Bellouin et al. 2011; Hardiman et al., 2017). In order to emphasize this, we modified the title, as shown below.

*“A Parameterization of Heterogeneous Hydrolysis of N_2O_5 for 3-D Atmospheric Modelling: Improvement of Particulate Nitrate Prediction” **changed to***

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

The manuscript has been modified accordingly. Please find the detailed point-to-point modifications and corrections in the following.

Major concerns:

(1.1) The paper completely misrepresents the parameterization from Riemer et al. (2003): It is stated by the authors that the particle surface area in Riemer et al. (2003) was set to a constant value of $600 \mu m^2 cm^{-3}$. However, this constant value was used only for box model runs. In all other simulations (KAMM/DRAIS and EURAD) a constant value was not used, instead the mass, the number and thus the particle surface area were calculated with the modal aerosol

model MADE and were highly variable. In Figures 8a and 11a of Riemer et al. (2003), examples of these variable horizontal distributions of the aerosol surface area density are depicted. It is clearly stated in Riemer et al. (2003) that even the corrected formula of Chang et al. (1987) shows a big difference in comparison to the more-complete parameterization that takes into account the dependence on aerosol surface area concentration (Sec. 4.2 in Riemer et al., 2003).

Response:

We apologize for the misleading introduction of the parameterization from Riemer et al. (2003), who proposed two parameterizations (P1 and P2) as shown in Table R1 and Fig. R1. The reviewer was right, the particle surface area (S) was comprehensively considered in P1, but was not considered in P2. P2 was only used in the box model (Figure 2 of Riemer et al., 2003) and 1-D simulations (Figure 5 of Riemer et al., 2003). Riemer et al. (2003) suggested to use 'a=17' instead of 'a=5' (suggested by Chang et al., 1987) for a better approximation of the more realistic P1. This produces a result that is very close to the P1 with 'S=600 $\mu\text{m}^2 \text{cm}^{-3}$ ' when RH>60%, as shown in Fig. R1. Here, we only adopted and improved the P2. However, we mistakenly named P2 as 'Riemer03' with a constant 'S=600 $\mu\text{m}^2 \text{cm}^{-3}$ ', which is inappropriate for introducing parameterizations from Riemer et al. (2003). We changed the 'Riemer03 scheme' to 'Original scheme of COSMO-MUSCAT' or 'OldN2O5', and corrected the corresponding context throughout the manuscript, as shown later.

The sophisticated P1 is more suitable for models with complex aerosol treatment, e.g. KAMM/DRAIS and EURAD with the modal aerosol module (Riemer et al. 2003) or WRF-Chem with a sectional aerosol module MOSAIC (Chang et al., 2016). However, the simulation of particle surface area is still a challenging task even in the models with complex aerosol treatment. As mentioned in Chang et al. (2016), the aerosol liquid water need to be considered when estimating its particle surface area. However, the aerosol thermodynamic models may not accurately capture aerosol liquid water at low RH.

Nevertheless, P2 is very suitable for the computationally efficient mass-based aerosol models (as described in the reply of General Comments), where P1 is difficult to be adopted. Therefore, P2 is used in the current version of COSMO-MUSCAT. Unfortunately, as pointed out by the reviewer, even the corrected formula of Chang et al. (1987) (P2 with 'a=17') shows a big difference in comparison to the more-complete parameterization (P1) that takes into account the dependence on aerosol surface area concentration. This shows the

importance of our work: to propose/improve a parametrization for the N_2O_5 hydrolysis that is suitable for the computationally efficient mass-based aerosol modules, without a big compromise of accuracy.

Table R1. Parameterizations (P1 and P2) from Riemer et al. (2003).

$$k_{N_2O_5} = \frac{1}{4} \cdot c_{N_2O_5} \cdot S \cdot \gamma_{N_2O_5}, \quad (\text{P1})$$

Where $k_{N_2O_5}$ is the reaction constant, $c_{N_2O_5}$ is the mean molecular velocity of N_2O_5 , $\gamma_{N_2O_5}$ is the reaction probability, and S is the aerosol surface area density

$$k_{N_2O_5} = \frac{1}{600 \exp\left(-\left(\frac{RH}{28}\right)^{2.8}\right) + a}. \quad (\text{P2})$$

where RH is the relative humidity in % and $k_{N_2O_5}$ results in min^{-1} .

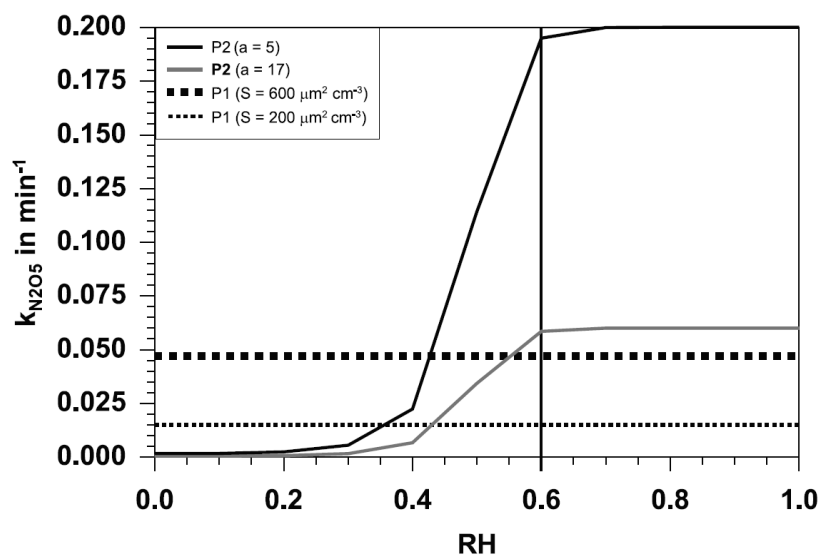


Figure R1. Rate constants for the heterogeneous hydrolysis of N_2O_5 when different parameterizations are used. Source: Figure 1 of Riemer et al. (2003)

We changed the description of parameterizations in Riemer et al. (2003), as shown below.

In the ‘Introduction’ part:

“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. ~~However, the parameterizations may not properly represent this process.~~ Dentener and Crutzen (1993) investigated the importance of the heterogeneous hydrolysis of N_2O_5 on a global scale, ~~but by assuming~~ a constant value $\gamma_{N_2O_5} = 0.1$, 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 $2700 \mu m^2/cm^3$. ~~Riemer et al. (2003) developed a scheme (Riemer03) based on the Chang scheme and applied it in box, 1-D~~ Riemer et al. (2003) proposed a more complex scheme (P1 in the literature) with respect to the particle surface area concentration (S) and 3-D models, with the published $\gamma_{N_2O_5}$ of nitrate and sulfate values from, which were reported by Mentel et al. (1999) and Wahner et al. (1998). However, the influence of temperature and ~~particle compositions~~ 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) found that organic coatings could decrease particulate nitrate concentrations by up to 90% where both N_2O_5 and secondary organic compounds were built-up. Evans and Jacob (2005) developed a parameterization scheme (EJ05) that has an extensive description of aerosol composition to improve the GEOS-CHEM simulations. EJ05 included $\gamma_{N_2O_5}$ of dust (Bauer et al., 2004), sea salt (Sander et al., 2003), sulfate (Kane et al., 2001; Hallquist et al., 2003), elemental carbon (EC, Sander et al., 2003) and organic carbon (OC, Thornton et al., 2003), also took into account the dependence of $\gamma_{N_2O_5}$ on RH. However, $\gamma_{N_2O_5}$ of nitrate and ~~the-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 realized-realistic in northwestern Europe (Morgan et al., 2015). Recently, Chang et al. (2016) 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 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 can not 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. 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; Wolke et al., 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 of complex considerations of S and $\gamma_{N_2O_5}$ in the P2.~~

~~Aiming to~~ 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) of $\gamma_{N_2O_5}$ with respect to temperature, RH, and particle composition and particle surface area. The influence of surface area concentration on $k_{N_2O_5}$ is also comprehensively considered. This NewN2O5 was validated by the state-of-the-art parameterization in Chang et al. (2016). This new scheme was We also incorporated NewN2O5 into the 3-D fully on-line coupled model COSMO-MUSCAT (Consortium for Small-scale Modelling and Multi-Scale Chemistry Aerosol Transport, http://projects.tropos.de/cosmo_muscat, Wolke et al., 2004; Wolke et al., 2012), in order to investigate the impact of heterogeneous hydrolysis of N_2O_5 on the improvement of particulate nitrate prediction”

In the ‘Data & Methods’ part:

“~~Riemer03~~The P2 of Riemer et al. (2003), which adapted from Chang et al. (1987), was originally ~~incorporated~~adopted in COSMO-MUSCAT to represent the heterogeneous hydrolysis of N_2O_5 (OldN2O5).”

“This produced a ~~$k_{N_2O_5}$~~ value, which represents the particle surface area concentration of about $600 \mu m^2/cm^3$ ($RH > 60\%$) and treats ~~$\gamma_{N_2O_5}$~~ based on the measurements of Mentel et al. (1999) as a homogeneously internal mixture of nitrate and sulfate (Riemer et al., 2003).

In Riemer03, ~~$\gamma_{N_2O_5}$~~ was considered as independent of temperature, RH and detailed particle compositions (only nitrate and sulfate were considered). Furthermore, S was set to a constant value ($600 \mu m^2/cm^3$) without sufficient consideration of the influence of particle surface area concentration. Thus, some uncertainties were found, applying this scheme in 3-D chemical transport. However, the complex considerations of S and $\gamma_{N_2O_5}$ is still missing in the OldN2O5.

In this study, we proposed a sophisticated parameterization ~~based on Riemer03~~ to improve the OldN2O5 for mass-based aerosol models, with ~~the~~ full consideration of temperature, RH, aerosol particle compositions and S.”

The ‘Riemer03’ in the ‘Results & Discussion’ and ‘Conclusion’ parts of the original manuscript were revised to ‘OldN2O5’ accordingly. Please find the detailed corrections in the revised manuscript with track changes.

(1.2) The comparison with the so-called Riemer03 parametrization and an assumption of a reaction probability of 0.1 (Dentener and Crutzen, 1993) is not very helpful because numerous papers (e.g. Davis et al. (2008)) show that 0.1 is seen as an upper limit of gamma.

Response:

Thanks for the comment. In this work, we compared NewN2O5 with the P2 (‘a=17’, Riemer et al., 2003) which is currently used in COSMO-MUSCAT. In the original manuscript, we called

it a comparison with an assumption of ' $\gamma_{\text{N2O5}}=0.1$ ', since P2 is developed on basis of ' $\gamma_{\text{N2O5}}=0.1$ ', as described in Riemer et al (2003):

“The parameterization P2 is based on the assumption that the relative humidity is an indicator for the aerosol surface area density and that $\gamma_{\text{N2O5}}= 0.1$.” from page 5-3 of Riemer et al (2003).

However, we agree with the reviewer that this interpretation is misleading and confusing. Therefore, we renamed this comparison to ‘the comparison with the original parameterization of COSMO-MUSCAT’, and modified corresponding texts throughout the manuscript, as shown later. And the Figure S2 (in the original manuscript) is replaced by a more interesting comparison with Chang et al. (2016). This was added in the section 3.1 of the revised manuscript, as described below.

Chang et al. (2016) also used Davis et al. (2008) and Anttila et al. (2006) to estimate the γ_{N2O5} . Their study adopted P1 (Riemer et al., 2003) into WRF-Chem with a sectional aerosol treatment (MOSAIC). Their results were validated by the aircraft measurements (γ_{ss} , estimated reaction probability in steady state) in the CalNex-2010 campaign, and showed a reasonable result (Fig. 4). In order to validate the performance of our mass-based parameterization (NewN2O5), we performed the simulation with WRF-Chem (MOSAIC) during the HOPE-Melpitz campaign. The WRF-Chem results with 8 aerosol size bins (40 nm to 10 μm) were carried out for off-line estimations (see a new method section 2.3) of $k_{\text{sectional}}$ (reaction constant according to Chang et al. 2016, y-axis in Fig. S2) and mass-based k_{NewN2O5} (according to our parameterization, x-axis in Fig. S2). The comparison between $k_{\text{sectional}}$ and k_{NewN2O5} shows a good agreement ($R=0.91$), although k_{NewN2O5} may be lower by a factor of ~ 8 (Fig. S2) than $k_{\text{sectional}}$. The possible reasons for this difference and the uncertainties are discussed in the section 3.1 of the revised manuscript, as shown later. This comparison further approves a reasonable performance of our mass-based NewN2O5 parameterization.

Although Chang et al. (2016) reported that ‘Davis+coat’ provided the best results compared with observations, here, we validated our NewN2O5 with the ‘Davis’ (without OC coating) according to Chang et al. (2016), namely Ch&Davis in the revised manuscript, due to the following reasons:

(1) HOPE-Melpitz campaign is an OC-low (less than 7%) case, there is hence not so much organic carbon (OC) available for coating. Therefore, validating with a non-coating parameterization (Ch&Davis) would be more reasonable. Furthermore, the OC coating effect will only make a difference less than 1% at Melpitz during our case.

(2) The treatments of OC coating are different between Chang et al. (2016) and NewN2O5, although we both used Anttila et al. (2006) scheme. In Chang et al. (2016), total OC (Primary OC + SOA) was treated as OC coating. However, our NewN2O5 only treat SOA for coating, which should be more reasonable and is consistent with the original literature Riemer et al. (2009).

(3) Chang et al. (2016) used the WRF-Chem (V3.3.1) with CBMZ-MOSAIC scheme, which does not consider the formation of SOA, as described by the MOSAIC developer (Zaveri et al., 2008). However, in this study, we would like to adopt NewN2O5 scheme into COSMO-MUSCAT, which treat SOA formation based on SORGAM (Schell et al., 2001; Li et al., 2013).

(4) The equation (11) written in the Chang et al. (2016) is not identical with its citation (Riemer et al., 2009), which described the OC coating effect according to Anttila et al. (2006). As shown following:

$$\gamma_{\text{coat}} = \frac{4RTH_{\text{org}}D_{\text{org}}R_{\text{c}}}{c_{\text{N}_2\text{O}_5}} \cdot \ell \cdot R_{\text{p}} \quad , \quad (\text{Eq. 11 in Chang et al. 2016})$$

$$\gamma_{i,\text{coat}} = \frac{4RTH_{\text{org}}D_{\text{org}}R_{\text{c},i}}{c_{\text{N}_2\text{O}_5}\ell_i R_{\text{p},i}} \quad , \quad (\text{Eq. 6 in Riemer et al. 2009, also Eq. 11 in Anttila et al. 2006})$$

We believe that it is just a typo in the paper, and the model simulations were correctly calculated in Chang et al. (2016). However, to make sure that our validation is completely reliable and to avoid unnecessary confusion, we would prefer to validate our results with the ‘Davis’ (without OC coating) according to Chang et al. (2016), namely Ch&Davis in the revised manuscript.

A new section 3.1 was added in the revised manuscript to validate the mass-based NewN2O5 parameterization with the more sophisticated sectional-based approach according to Chang et al., (2016), as shown below.

“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’ (Davis08 + 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 very 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 grow 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.”

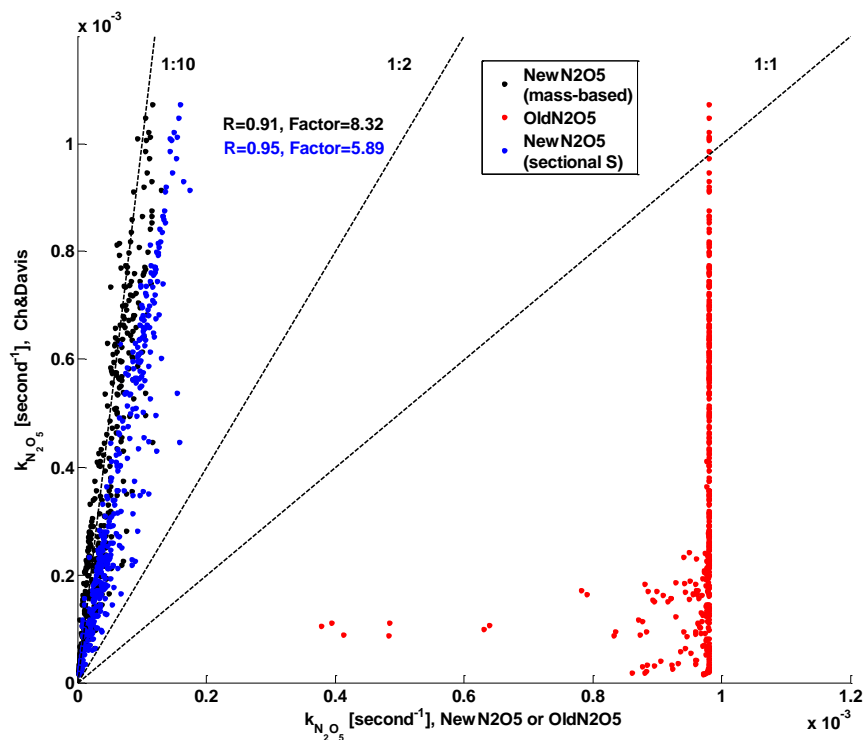


Figure 4 (newly added). Comparison between the sectional-based Ch&Davis (‘Davis’ of Chang et al., 2016) and mass-based NewN2O5 (mass-based, black), NewN2O5 (with a sectional-based particle surface area, blue) and OldN2O5 (red). The results are offline calculated on basis of WRF-Chem simulation with a sectional aerosol treatment (MOSAIC).

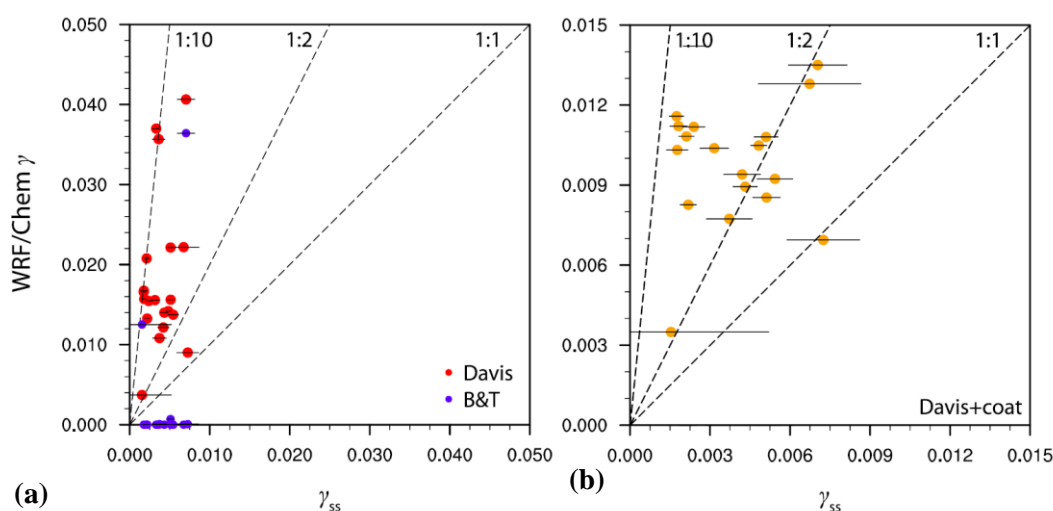


Figure S2 (newly added). Modelled γ (Chang et al., 2016) versus calculated γ_{ss} (reaction probability in steady state) using aircraft observations from the 31 May flight of CalNex 2010 campaign. (a) Davis (Davis et al., 2008, namely Ch&Davis) and B&T (Bertram and Thornton, 2009) parameterization; (b) Davis+coat (Anttila06).

Source: Figure 10 of Chang et al. (2016).

A new section 2.3 was added in the revised version (as shown below), to describe the WRF-Chem simulations that we used for evaluating closure between NewN2O5 and Chang et al. (2016). The incorporation of mass-based NewN2O5 to the sectional aerosol module in WRF-Chem is also described.

“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 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.”

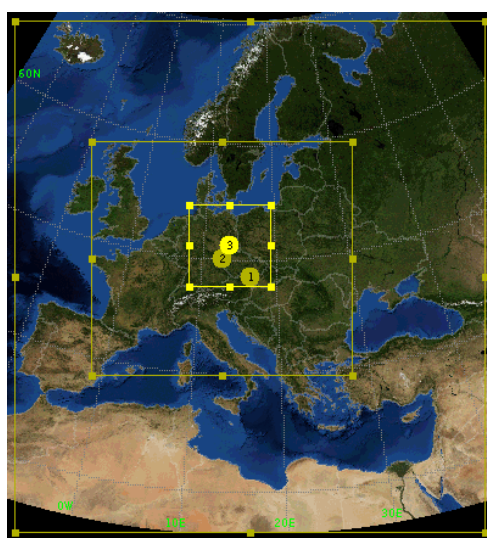


Figure S1 (newly added). Domain setting of WRF-Chem simulation.

(2) Chang et al. (1987) calculated the rate constant by the following equation: Eq. 17, Chang et al. (1987). Whereas in this paper: Eq. 2 and 3, this study is written. It is not clear whether this is an error in the paper, or also in the parameterization itself. It is not clear which formulation was the basis for the presented simulations. The authors need to check this because using the equation written in the paper gives values that are orders of magnitude different.

Response:

Thanks a lot for pointing out the typo in Eq. 2 and 3. We have double checked that in the model, the equation is identical with the Eq. 17 in Chang et al. (1987). The calculated $k_{N_2O_5}$ is given in Fig. R2, which is identical with the Figure 1 in Riemer et al. (2003) (see also Fig. R1). We apologize for the mistake, and corrected the equations, as shown below.

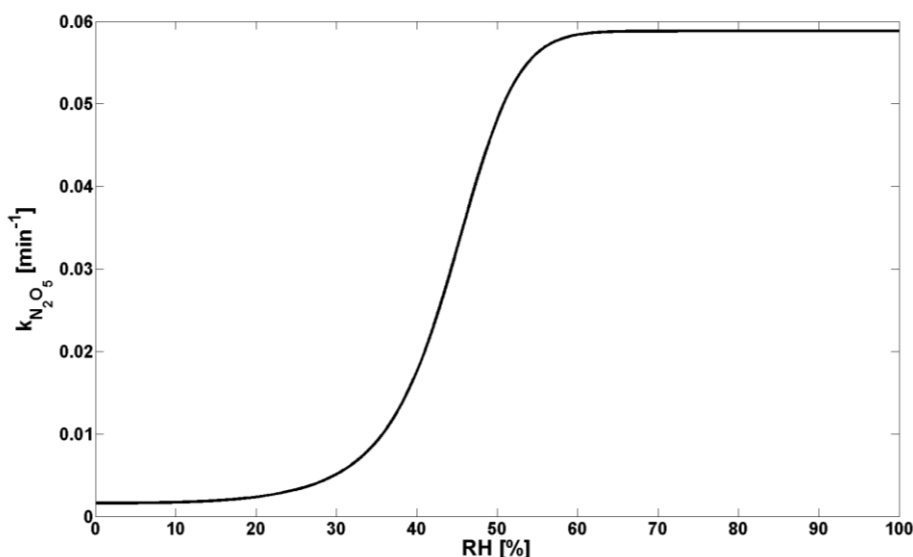


Figure R2. Rate constant for the heterogeneous hydrolysis of N_2O_5 with relation to RH. Modified from Figure 1 of Riemer et al. (2003), or calculated from the equation (2) with $a=17$.

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

changed to

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

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

changed to

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

(3) In equation 5, there is no explanation as to why the expression for gammaN2O5 is divided by a factor of 0.1. This leaves me with the impression that the factors are introduced to yield the best fit with the nitrate observations, which limits the general applicability of the parameterization to other domains and conditions. Similarly, there is a division by 600 in equation 4 which is also not explained. Furthermore, the units of fs are unclear. Based on the units stated in the text below equation 4, fs appears to have units of m⁻¹, but the factor should be unitless.

Response:

Thanks for the comment. In this study, we would like to propose a mass-based parameterization (NewN2O5) based on the P2 (Riemer et al., 2003). This NewN2O5 is the best approximation of P1 (Riemer et al., 2003), which is with respect to reaction probability (γ) and particle surface area concentration (S). Therefore, we introduced two factors (f_s and f_{γ_{N2O5}}) to adjust the kN2O5 according to P2. The f_{γ_{N2O5}} is calculated as Eq. 5, which is used to adjust the impact of γ. The f_s is calculated as Eq. 4, which is used to adjust the impact of particle surface area (S).

As described in Riemer et al. (2003), P2 is developed on basis of the assumption ‘γN2O5 = 0.1’, and ‘a=17’ will provide a result that is very close to the more-complete P1 with ‘S~ = 600 μm² cm⁻³’, when RH is higher than 60% (see Fig. R1). Therefore, when we calculate the correction factors in NewN2O5, we divide γN2O5 by 0.1 and divide particle surface area (S) by 600 μm² cm⁻³.

The original text is given: “The parameterization P2 is based on the assumption that the relative humidity is an indicator for the aerosol surface area density and that γN2O5 = 0.1. In

addition, the values of kN_2O_5 as they follow from P1 for different aerosol surface area densities ($S = 200 \mu\text{m}^2 \text{cm}^{-3}$ and $S = 600 \mu\text{m}^2 \text{cm}^{-3}$) are given in Figure 1. Although the aerosol surface area density is far from being constant in the real atmosphere, we included the curves based on P1 for comparison. P1 will be identical to P2 at high relative humidity ($RH > 60\%$), if the surface area density is about $2700 \mu\text{m}^2 \text{cm}^{-3}$. However, such surface area densities can only be expected in highly polluted areas or if cloud droplets are present. Therefore P2 overestimates kN_2O_5 under cloud free and unpolluted conditions. If we use $a = 17$ instead of $a = 5$ in P2, it is a much better approximation for P1, as can be seen from Figure 1 (see also Fig. R1 of this response)” page 5-3 from Riemer et al. (2003).

However, we agree with the reviewer that the descriptions of Eq. 4 and Eq. 5 are not clear enough. We modified the descriptions and equations, and the f_s is unitless, as shown below.

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

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

changed to:

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

where γ_{core} is the N_2O_5 reaction probability with the core of the particle, which can be estimated by Table 1; γ_{coating} is the N_2O_5 reaction probability with the secondary organic coating shell of the particle, which can be estimated by the formula (6) according to Anttila et al. (2006) and Riemer et al. (2009); γ_{ref} is the reference reaction probability. Here, we suggest ‘ $\gamma_{\text{ref}} = 0.1$ ’, since Eq. 2 is developed on basis of the assumption ‘ $\gamma_{N_2O_5} = 0.1$ ’ (Riemer et al., 2003).

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

~~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 $\mu g/m^3$. A value 11 m^2/g was used for SA_{fine} , considering recently reported values of 11.9 m^2/g and 10.2 m^2/g from laboratory studies (Okuda, 2013) and measurements in Japanese urban regions (Hatoya et al., 2016). A value of 1.2 m^2/g was used for SA_{coarse} (Okuda, 2013).~~

changed to:

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

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 $\mu g/m^3$. A value 11 m^2/g was used for SA_{fine} , considering recently reported values of 11.9 m^2/g and 10.2 m^2/g from laboratory studies (Okuda, 2013) and measurements in Japanese urban regions (Hatoya et al., 2016). A value of 1.2 m^2/g was used for SA_{coarse} (Okuda, 2013). S_{ref} is the reference particle surface area concentration, here, we suggest ' $S_{ref} = 600 \mu m^2 cm^{-3}$ '. Since Eq. 2 will provide a result that is very close to a complex parameterization with $600 \mu m^2 cm^{-3}$ particle surface area concentration (Riemer et al., 2003), when ' $a=17$ ' and ' $RH>60\%$ '.

(4) The reference to Chang et al. (2016) is missing. They also combined the Davis et al. (2008) parametrization with the coating parameterization of Riemer et al. (2009). Chang, W. L., S.S. Brown, J. Stutz, A.M. Middlebrook, R. Bahreini, N.L. Wagner, W.P. Dubé I.B. Pollack, T. B. Ryerson, and N. Riemer (2016), Evaluating N_2O_5 heterogeneous hydrolysis parameterizations for CalNex 2010, J. Geophys. Res. Atmos., 121, 5051–5070, doi:10.1002/2015JD024737.

Response:

Thanks for the very helpful latest study. This literature (Chang et al., 2016) has been added in the references. The differences of focuses, different applications and the comparison between our New N_2O_5 and Chang et al. (2016) have been discussed in detail, as shown above.

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A Parameterization of Heterogeneous Hydrolysis of N_2O_5 for ~~3-D Atmospheric Modelling~~ 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 particles 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 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 did not comprehensively consider these parameters. In this investigation, we propose a sophisticated parameterization (NewN2O5) of ~~N_2O_5 the~~ heterogeneous hydrolysis ~~of N_2O_5~~ 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. This NewN2O5 new parameterization 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 ($[\text{NO}_3^-]$) were validated by filter measurements over Germany (Neuglobsow, Schmücke, Zingst, and Melpitz). The modelled $[\text{NO}_3^-]$ 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 proposed new parameterization significantly reduces the overestimation of $[\text{NO}_3^-]$ by ~35%. Particularly, the overestimation factor was reduced to approximately 1.4 ~~within in~~ our case study period (September 12, 17-18 and 25, 2013), when $[\text{NO}_3^-]$ was dominated by local chemical formations. ~~Furthermore, the organic coating effect on a suppression of the N_2O_5 reaction probability may have been also significantly overestimated in previous modelling studies, due to a strong overestimation of the N_2O_5 reaction probability on coatings. Based on the original parameterization, previous studies reported a decrease of modelled $[\text{NO}_3^-]$ up to 90%, where both secondary organic aerosol (SOA) and N_2O_5 were built up over western and central Europe. For this case study. In our case,~~ the suppression of organic coating was negligible over western and central Europe, with an influence on $[\text{NO}_3^-]$ less than 2% on

average and 20% at the most significant moment. ~~As for~~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 ~~over Europe~~ may not be as important-significant as expected ~~in previous studies~~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 most important removal path of nitrogen from the atmosphere is the formation of HNO_3 , which is transferred to particles or deposited eventually (Riemer et al., 2003). HNO_3 is mainly produced via the reaction of NO_2 and OH at daytime. At nighttime, the heterogeneous hydrolysis of N_2O_5 on the surface of deliquescent aerosol particles forming HNO_3 is a major sink of NOx (Jacob, 2000; Brown and Stutz, 2012; Platt et al., 1984; Brown et al., 2004). Given that NOx is the key precursor of ozone, chemical mechanisms controlling the budget of NOx also have an important impact on ozone and oxidizing capacity of the atmosphere on a global scale (Dentener and Crutzen, 1993; Evans and Jacob, 2005).

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

(2006) proposed a parameterization (Anttila06) that described the organic coating suppression effect on $\gamma_{N_2O_5}$.

Based on laboratory experiments and Anttila06, Gaston et al. (2014) ~~proposed-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) developed a parameterization to describe the influence of chloride salts on $\gamma_{N_2O_5}$ as a function of RH. However, the influence of temperature was not

considered in their study. Recently, Morgan et al. (2015) ~~reported-demonstrated~~ that ~~the-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) derived a parameterization (Davis08) of $\gamma_{N_2O_5}$ on the surface of particles containing ammonium,

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

Several studies have implemented the heterogeneous hydrolysis of N_2O_5 in global and regional chemical transport models, in order to investigate its influences on atmospheric chemistry. ~~However, the parameterizations may not properly represent this process.~~ Dentener and Crutzen (1993) investigated the importance of the heterogeneous hydrolysis of N_2O_5 on a global scale, ~~but by assuming~~ a constant value $\gamma_{N_2O_5} = 0.1$, 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 $2700 \mu m^2/cm^3$. ~~Riemer et al. (2003) developed a scheme (Riemer03) based on the Chang scheme and applied it in box, 1-D~~ Riemer et al. (2003) proposed a more complex scheme (P1 in the literature) ~~with respect to the particle surface area concentration (S) and 3-D models, with the published $\gamma_{N_2O_5}$ of nitrate and sulfate values from, which were reported by~~ Mentel et al. (1999) and Wahner et al. (1998). However, the influence of temperature and ~~particle compositions~~ 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) found that organic coatings could decrease particulate nitrate concentrations by up to 90% where both N_2O_5 and secondary organic compounds were built-up. Evans and Jacob (2005) developed a parameterization scheme (EJ05) that has an extensive description of aerosol composition to improve the GEOS-CHEM simulations. EJ05 included $\gamma_{N_2O_5}$ of dust (Bauer et al., 2004), sea salt (Sander et al., 2003), sulfate (Kane et al., 2001; Hallquist et al., 2003), elemental carbon (EC, Sander et al., 2003) and organic carbon (OC, Thornton et al., 2003), also took into account the dependence of $\gamma_{N_2O_5}$ on RH. However, $\gamma_{N_2O_5}$ of nitrate and ~~the 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 ~~realized-realistic~~ in northwestern Europe (Morgan et al., 2015). Recently, Chang et al. (2016) 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 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 can not 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. 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; Wolke et al., 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 of complex considerations of S and $\gamma_{N_2O_5}$ in the P2.

5 ~~Aiming 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) ~~of $\gamma_{N_2O_5}$~~ with respect to temperature, RH, ~~and~~ particle composition and particle surface area. ~~The influence of surface area concentration on $k_{N_2O_5}$ is also comprehensively considered. This NewN2O5 was validated by the state-of-the-art parameterization in Chang et al. (2016). This new scheme was~~We also incorporated NewN2O5 into the 3-D fully on-line coupled
10 model COSMO-MUSCAT ~~(Consortium for Small scale Modelling and Multi Scale Chemistry Aerosol Transport, http://projects.tropos.de/cosmo_muscat, Wolke et al., 2004; Wolke et al., 2012)~~, in order to investigate the impact of heterogeneous hydrolysis of N_2O_5 on the improvement of particulate nitrate prediction. The measurements of the HOPE campaign (HD(CP)² Observational Prototype Experiment, Macke et al., 2016) at Melpitz site (12.93°E, 51.53°N, 86 m a.s.l., a regional background observatory of central Europe) and other
15 three stations of the German federal environmental agency (UBA) over Germany were used to validate the simulation results.

2 Data & Methods

2.1 The model system COSMO-MUSCAT

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

An adequate modelling of dynamics requires an online coupling between the chemical transport model MUSCAT and the meteorological model COSMO. Here, the compressible non-hydrostatic flow in a moist
30 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 based on 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. Aerosol particles, clouds and tracers gases are considered as optically active constituents, modifying the radiative fluxes by absorption,
35 scattering and emission. The meteorological forcing of COSMO is performed by reanalysis data of the German Weather Service DWD, which are derived from the global meteorological model GME (Majewski et al., 2002).

MUSCAT describes the transport, chemical and removal processes. The chemical mechanism RACM-MIM2 (Karl et al., 2006; Stockwell et al., 1997) with 87 species and more than 200 reactions is applied to represent the gaseous chemistry. A simplified mass based approach (similar to EMEP model, Simpson et al., 2003) is used to represent the aerosol processes with high efficiency. The formation of secondary inorganic particulate matter is performed by reactions between ammonia and sulfuric or nitric acid, which are produced from the gas phase precursors SO₂ and NO_x (Hinneburg et al., 2009). The applied particle/gas partitioning depends on temperature and humidity. As in ISORROPIA (Nenes et al., 1998), the equilibrium is shifted towards the gas phase for dry and warm conditions. The implementation of this partitioning scheme is comparable to Galperin and Sofiev (1998) by using the equilibrium approach of Mozurkewich (1993). 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 described by Seinfeld and Pandis (2006), considering the atmospheric turbulence state, the kinetic viscosity, and the gravitational settling of particles. The aerodynamic and quasi-laminar layer resistances are taken from COSMO by analogy with the deposition of water vapour. The wet deposition is parameterized in dependence on the size resolved scavenging and collection efficiency (Simpson et al., 2003).

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, SO₂, NH₃ 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° × 0.0625° (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 NH₃ was reduced by 50%, since over 90% of NH₃ emissions in Europe are contributed by agricultural sources (Hertel et al., 2011; Erisman et al., 2008; Reidy et al., 2008) and agriculture emissions of NH₃ are overestimated by ~50% or even more (Sintermann et al., 2012; Backes et al., 2016). Also, Chen et al. (2016b) adopted the same NH₃ emission inventory in the WRF-Chem model and reported that total NH₃ was overestimated by a factor 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). Sea salt emissions are parameterized depending on salinity and wind speed (Long et al., 2011). Biogenic emissions depends on land-use and meteorology by the approach of Steinbrecher et al. (2009) and for “soil NO” by Williams et al. (1992) and Stohl et al. (1996). Saarikoski et al. (2007) scheme was applied to estimate the biomass burning emissions.

The chemical inactive tracers (T1, T2 and T3) were added into RACM-MIM2 to investigate the chemical fluxes of the selected reactions. T1, T2 and T3 (representing R1, R2 and R3 respectively) were reset to zero every hour in the simulation in order to quantify the chemical fluxes from N₂O₅ to nitrate avoiding the influence of transport. T1 represents the contribution of N₂O₅ on chemical formation of nitric acid; T3-T2 represents local chemical net formation of particulate nitrate.





Furthermore, in order to investigate the influence of transport from the NH₃ 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/m²/s.

2.2 A novel mass-based parameterization of heterogeneous hydrolysis of N₂O₅

5 The reaction of N₂O₅ with water vapour is very slow, therefore a considerable loss of N₂O₅ is assumed to occur on the surface of deliquescent aerosol particles (Platt et al., 1984), as shown in R1. Many laboratory experiments have shown that $\gamma_{\text{N}_2\text{O}_5}$ depends principally on particle composition and water content (and so atmospheric RH). Reducing the RH, or adding organics or nitrate to the solutions, suppresses $\gamma_{\text{N}_2\text{O}_5}$ by an order of magnitude (Chang et al., 2011 and references therein).

10 ~~Rierner03~~The P2 of Rierner et al. (2003), which adapted from Chang et al. (1987), was originally ~~incorporated~~adopted in COSMO-MUSCAT to represent the heterogeneous hydrolysis of N₂O₅. ~~(OldN2O5).~~ Reaction R1 is implemented into chemical transport models as a first-order loss (Rierner et al., 2003). The reaction constant ($k_{\text{N}_2\text{O}_5}$) is defined as:

$$k_{\text{N}_2\text{O}_5} = \frac{1}{4} \cdot v_{\text{N}_2\text{O}_5} \cdot S \cdot \gamma_{\text{N}_2\text{O}_5} \quad (1)$$

15 where $v_{\text{N}_2\text{O}_5}$ is the mean molecular velocity of N₂O₅, and S is the surface area concentration of aerosol particles.

Based on the first-order reaction constant, Chang et al. (1987) ~~assumed $\gamma_{\text{N}_2\text{O}_5} = 0.1$ and~~ proposed the following scheme to represent $k_{\text{N}_2\text{O}_5}$.

$$k_{\text{N}_2\text{O}_5} = \frac{1}{600 \exp\left(-\left(\frac{\text{RH}}{28}\right)^{2.8} + a\right)} \quad (2)$$

$$k_{\text{N}_2\text{O}_5} = \frac{1}{600 \exp\left(-\left(\frac{\text{RH}}{28}\right)^{2.8}\right) + a} \quad (2)$$

20 RH is the relative humidity in %, which was used as an indicator for the influence of hygroscopic growth on S, $k_{\text{N}_2\text{O}_5}$ results in min⁻¹, and ‘a=5’ was originally adopted in Chang et al. (1987). According to Rierner et al. (2003), ‘a=5’ represents the surface area concentration of 2700 μm²/cm³, when RH is higher than 60%. However, this high surface area concentration can only be expected in highly polluted areas or if cloud droplets are present.

Therefore, we adopted ‘a=17’ in this study as suggested by Rierner et al. (20072003). ~~This produced a $k_{\text{N}_2\text{O}_5}$~~

value, which represents the particle surface area concentration of about $600 \mu\text{m}^2/\text{cm}^3$ (RH>60%) and treats $\gamma_{N_2O_5}$ based on the measurements of Mentel et al. (1999) as a homogeneously internal mixture of nitrate and sulfate (Riemer et al., 2003).

In Riemer03, $\gamma_{N_2O_5}$ was considered as independent of temperature, RH and detailed particle compositions (only nitrate and sulfate were considered). Furthermore, S was set to a constant value ($600 \mu\text{m}^2/\text{cm}^3$) without sufficient consideration of the influence of particle surface area concentration. Thus, some uncertainties were found, applying this scheme in 3-D chemical transport models. However, the complex considerations of S and $\gamma_{N_2O_5}$ are still missing in the OldN2O5. In this study, we proposed a sophisticated parameterization based on Riemer03 to improve the OldN2O5 for mass-based aerosol models, with the full consideration of temperature, RH, aerosol particle compositions and S.

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

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

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

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

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

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 $\mu\text{g}/\text{m}^3$. A value $11 \text{ m}^2/\text{g}$ was used for SA_{fine} , considering recently reported values of $11.9 \text{ m}^2/\text{g}$ and $10.2 \text{ m}^2/\text{g}$ from laboratory studies (Okuda, 2013) and measurements in Japanese urban regions (Hatoya et al., 2016). A value of $1.2 \text{ m}^2/\text{g}$ was used for SA_{coarse} (Okuda, 2013). S_{ref} is the reference particle surface area concentration, here, we suggest ' $S_{ref} = 600 \mu\text{m}^2/\text{cm}^3$ '. Since equation (2) will provide a result that is very close to a complex parameterization with a particle surface area concentration of 600

$\mu\text{m}^2/\text{cm}^3$ (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 $k_{N_2O_5}$, 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. Note that the nitrate mass concentration in (4) is considered as 1.3 times of sulfate mass concentration, based on the filter measurements during HOPE Melpitz campaign. This is aimed to calculate the contribution of the surface area concentration by nitrate in the model, meanwhile, avoiding errors with positive feedback between $k_{N_2O_5}$ and the modelled particulate nitrate mass concentration.

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

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

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 the formula (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 equation (2) is developed on basis of the assumption ' $\gamma_{N_2O_5} = 0.1$ ' (Riemer et al., 2003).

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

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

γ_{core} can be estimated from previous laboratory experiments (Table 1) of inorganic and primary organic compositions (Davis et al. 2008; Evans and Jacob, 2005, and references therein;). Davis et al. (2008) proposed an extended parameterization for N_2O_5 hydrolysis on ammonium-sulfate-nitrate particles, with respect to RH and temperature. Evans and Jacob (2005) provided the parameterizations for N_2O_5 hydrolysis on primary organic particles (Thornton et al., 2003), black carbon (Sander et al., 2003), sea salt (Sander et al., 2003) and dust (Bauer et al., 2004). γ_{core} can be derived by a mass-weighted average (Riemer et al., 2003) of each single-component

parameterization (Table 1). The core of the aerosol particle was assumed to be homogeneously internally mixed. γ_{core} is 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 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.

2.43 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 about 30 m^3/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. temperature, relative humidity, wind speed, wind direction) were simultaneously measured at Melpitz. More details about the HOPE campaign are given in Macke et al. (2016).

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 nighttime, were in a good agreement with the measurement. Although model simulations slightly underestimated RH during the nighttime of September 17 and 22 (Fig. 2b), modelled RH was still higher than 80% where $k_{\text{N}_2\text{O}_5}$ 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 $k_{\text{N}_2\text{O}_5}$ 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’ (Davis08 + Anttila06) approach produced a best agreement of $\gamma_{\text{N}_2\text{O}_5}$ 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 $\gamma_{\text{N}_2\text{O}_5}$, 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 $\sim 7\%$ 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 grow 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.

3.2.1 Improvement of the particulate nitrate prediction

In previous evaluation studies (Im et al., 2015; Wolke et al., 2012), the COSMO-MUSCAT model predicted particulate nitrate mass concentrations ($[NO_3^-]$) in a fair agreement with the measurements, with an overestimation in the range of 50% on long-term average. This is comparable with other models (Im et al., 2015). However, short periods with strong overestimations of $[NO_3^-]$ were also observed in these previous studies. This seems to be the case for the HOPE-Melpitz campaign simulation, where COSMO-MUSCAT highly overpredicted $[NO_3^-]$ over Germany in this study (Fig. 3) as well as WRF-Chem in a previous study (Chen et al, 2016b). In order to evaluate the improvement of ~~our new~~ N_2O_5 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 of the overprediction of particulate nitrate (see details in Supplement Text S1 and Fig. S3). Nevertheless, the overestimation of NH₃ emission might contribute about 20-30% of the particulate nitrate overprediction, compared between ~~Riemer03OldN2O5~~-FullNH3 and ~~OldN2O5Riemer03~~ cases. ~~Similar results were reported in~~ This is in line with the previous studies (Renner and Wolke, et al., 2010; Backes et al., 2016). However, even with a 50% reduction of NH₃ 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. ~~Our new N₂O₅ parameterization~~ 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 N₂O₅ was almost all consumed by the heterogeneous reaction at Melpitz in ~~Riemer03 OldN2O5~~ case, but not in the NewN2O5 case (Fig. 3e). ~~This indicated~~ 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 N₂O₅ by NewN2O5the new scheme. 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 ~~the new scheme~~ 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, which have a higher temporal resolution. The overestimation of [NO₃] in September 10-11 (grey shaded period in Fig. 3) stemmed from the uncertainty of boundary conditions in the model. As shown in Fig. ~~S1S3S4~~, an air mass with high [NO₃] was transported from the southwestern boundary area to Melpitz. The [NO₃] 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 [NO₃] 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 N₂O₅ by ~~the new scheme~~ 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 [NO₃].

3.3.2 Comparison between NewN2O5 and ~~OldN2O5Riemer03~~

The NewN2O5 case improved the particulate nitrate overestimation problem compared with ~~OldN2O5Riemer03~~. Meanwhile, the spatial distribution pattern of [NO₃] was similar between these two cases (Fig. 45). Here, we focus on the nighttime period of the HOPE-Melpitz campaign, since the N₂O₅ heterogeneous reaction is much

more significant during the night than in the daytime. The lowest $[\text{NO}_3^-]$ was found over Poland and ocean regions during nighttime, $[\text{NO}_3^-]$ was lower than $4 \mu\text{g}/\text{m}^3$ and $3 \mu\text{g}/\text{m}^3$ in OldN2O5 Riemer03 and NewN2O5 cases, respectively. Moderate $[\text{NO}_3^-]$ was found over central Europe (Melpitz and the surrounding region), about $6-8 \mu\text{g}/\text{m}^3$ and $4-5.5 \mu\text{g}/\text{m}^3$ in the OldN2O5 Riemer03 and NewN2O5 cases, respectively. The highest $[\text{NO}_3^-]$ occurs over the region of the Netherlands and near-by regions, about $9-12 \mu\text{g}/\text{m}^3$ and $6-8 \mu\text{g}/\text{m}^3$ in OldN2O5 Riemer03 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 $8-10 \mu\text{g}/\text{m}^3$ and $5-6.5 \mu\text{g}/\text{m}^3$ in the OldN2O5 Riemer03 and NewN2O5 cases, respectively. In general, the $[\text{NO}_3^-]$ was reduced by $\sim 35\%$ over the entire N2 domain (Fig. 45). The most significant reduction of $[\text{NO}_3^-]$ is found over the Netherlands and southern Germany where the highest $[\text{NO}_3^-]$ (reduced by about $3-4.5 \mu\text{g}/\text{m}^3$) was found, followed by the near Melpitz region (reduced by about $2-3 \mu\text{g}/\text{m}^3$, Fig. 4e5c). This is caused by a significant reduction (by more than a factor of 20, see Fig. 4) of $k_{\text{N}_2\text{O}_5}$, which is resulted from the consideration of particle mass concentration's influence on S and comprehensive treatments for $\gamma_{\text{N}_2\text{O}_5}$ by decreasing the surface area concentration of aerosol particle (S) and reaction probability of N_2O_5 ($\gamma_{\text{N}_2\text{O}_5}$), in the new scheme compared to Riemer03, which assumed a constant value of $600 \mu\text{m}^2/\text{cm}^3$ and 0.1 for these two parameters, respectively. As shown in Fig. S2, the S and $\gamma_{\text{N}_2\text{O}_5}$ at Melpitz were in average reduced to $\sim 14\%$ and $\sim 23\%$ of the Riemer03 case, respectively. Correspondingly, the $k_{\text{N}_2\text{O}_5}$ was reduced by a factor of more than 10. Therefore, the regions with high $[\text{NO}_3^-]$ during nighttime indicates a considerable nitrate formation from the heterogeneous hydrolysis of N_2O_5 , which where $[\text{NO}_3^-]$ was reduced by about $3-4.5 \mu\text{g}/\text{m}^3$ ($\sim 35\%$, see Fig. 5) to a more reasonable value in our the new scheme. However, this heterogeneous hydrolysis was slow-negligible over the regions where $[\text{NO}_3^-]$ was low during nighttime, and did not have relevant contribution on the formation of particulate nitrate. ThereforeHence, the improvement of particulate nitrate prediction by the new schemeNewN2O5 was more significant over the high- $[\text{NO}_3^-]$ regions than the low- $[\text{NO}_3^-]$ regions.

3.43 Influence of organic coating on the N_2O_5 heterogeneous hydrolysis

The secondary organic coating on particle surface may significantly decrease the reaction probability of N_2O_5 and influence the particulate nitrate concentration. As shown by Riemer et al. (2009), which coupled Anttila06 to Riemer03, Riemer et al., (2009) reported that organic coating could decrease $[\text{NO}_3^-]$ by up to 90% where both N_2O_5 and secondary organic compounds were built-up. The highest reduction over Europe was found over the Netherlands followed by western Germany (both covered by the domain N2) in their study. However as discussed above, Riemer03 may overestimate nitrate formation from the heterogeneous hydrolysis of N_2O_5 , because of simplifying S and $\gamma_{\text{N}_2\text{O}_5}$. In addition to N_2O_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 more sophisticated parameterization (NewN2O5) for heterogeneous hydrolysis of N_2O_5 , considering meteorological conditions. The influence of the organic coating suppression effect on particulate nitrate prediction would be was investigated byre-evaluated, based on our new scheme a comparison between NewN2O5 with and without SOA coating effect.

~~The At nighttime, results were analysed, since~~ much higher N_2O_5 concentrations occurred and ~~theirs~~ heterogeneous hydrolysis is more important than ~~that~~ during daytime (Jacob, 2000). As shown in Fig. ~~5a-6a~~ and Fig. ~~5b6b~~, 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 $\mu g/m^3$ (less than 10-20%) over the black-polygon marked and near-by regions (Fig. ~~S3S4S5~~). Meanwhile, for nighttime averages during the campaign, the organic coating could only reduce $[NO_3^-]$ by less than 0.1 $\mu g/m^3$ or 2% over the whole domain (Fig. ~~56~~). This is because ~~much stricter conditions appropriate meteorological conditions~~, as described following, are needed in NewN2O5 for a significant organic coating ~~effect compared with Riemer03~~. In addition to the simultaneous build-up of SOA and N_2O_5 (Riemer et al., 2009), high NH_3 concentrations and $\gamma_{N_2O_5}$ are also indispensable conditions for a significant organic coating effect. High NH_3 concentrations are necessary for neutralizing the HNO_3 , which came from the heterogeneous hydrolysis of N_2O_5 during the night. High $\gamma_{N_2O_5}$ causes a significant reduction of $\gamma_{N_2O_5}$ by organic coating (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. ~~56~~, 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 $\sim 1.6 \mu g/m^3$; (4) N_2O_5 concentration was about 0.4-0.6 $\mu g/m^3$; (5) NH_3 concentration was about 4-6 $\mu g/m^3$ (Fig. 1). There was almost no influence of organic coating over the other regions (Fig. ~~5a-6a~~ and Fig. ~~5b6b~~). 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 (~~OldN2O5Riemer03~~). 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 Riemer03~~ and NewN2O5 cases. ~~OldN2O5 case Riemer03~~ overestimated particulate nitrate by a factor of 19, 9, 4.5 and 5 for Neuglobsow, Schmöcke, Zingst, and Melpitz, respectively. This may be caused by ~~an overestimation of the particle surface area concentration and the reaction probability of N_2O_5 ($\gamma_{N_2O_5}$), by assuming constant values of $600 \mu m^2/cm^3$ and 0.1, respectively~~ 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 ~~10-20~~ 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. ~~In contrast to previous studies (e.g., Riemer et al. 2009),~~ ~~Our~~ results showed a negligible (less than 2% or $0.1 \mu g/m^3$) influence of coating on particulate nitrate over the Netherlands and Germany. ~~This is because~~ 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. ~~In addition, 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. in this investigation and 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 ~~important-significant~~ as expected over Europe.

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

Particle Type	Parameterization	Parameters	References and Remarks
Core of particle	$\gamma_{core} = \sum_i \gamma_i \cdot ratio_i$	$ratio_i = \frac{[m_i]}{[m_{core}]}$	γ : reaction probability m : mass $[mass]$: mass concentration
		$[m_{core}] = \sum_i [m_i]$	
		i : the following particle types $i = [ASN, OC, SSA, Dust, BC]$	
ASN: (A) Ammonium (S) Sulfate (N) Nitrate	$\gamma_{ASN} = \gamma_{AB}^* \cdot x_{AB} + \gamma_{aq/d,AS}^* \cdot x_{AS} + \gamma_{AN}^* \cdot x_{AN}$ $\gamma_{AB}^* = \min(\gamma_{AB}, 0.08585)$, $\gamma_{AB} = \frac{1}{1 + e^{-\lambda_{AB}}}$ $\gamma_{aq,AS}^* = \min(\gamma_{aq,AS}, 0.053)$, $\gamma_{aq,AS} = \frac{1}{1 + e^{-\lambda_{aq,AS}}}$ $\gamma_{d,AS}^* = \min(\gamma_{d,AS}, 0.0124)$, $\gamma_{d,AS} = \frac{1}{1 + e^{-\lambda_{d,AS}}}$ $\gamma_{AN}^* = \min(\gamma_{AN}, 0.0154)$, $\gamma_{AN} = \frac{1}{1 + e^{-\lambda_{AN}}}$ $\lambda_{AB} = \beta_{10} + \beta_{11} \cdot RH + \beta_{12} \cdot T_{291}$ $\lambda_{aq,AS} = (\beta_{10} + \beta_{20}) + \beta_{11} \cdot RH + (\beta_{12} + \beta_{22}) \cdot T_{291}$ $\lambda_{d,AS} = \beta_{d0} + \beta_{d1} \cdot RH + \beta_{d2} \cdot T_{293}$ $\lambda_{d,AN} = \beta_{30} + \beta_{31} \cdot RH$	$x_{AB} = 1 - (x_{AS} + x_{AN})$ $x_{AS} = \max(0, \min(1 - x_{AN}, \frac{[A]}{[N] + [S]} - 1))$ $x_{AN} = \frac{[N]}{[N] + [S]}$ $\beta_{10} = -4.10612$ $\beta_{11} = 0.02386$ $\beta_{12} = -0.23771$ $\beta_{20} = -0.80570$ $\beta_{22} = 0.10225$ $\beta_{30} = -8.10774$ $\beta_{31} = 0.04902$ $\beta_{d0} = -6.13376$ $\beta_{d1} = 0.03592$ $\beta_{d2} = -0.19688$ $T_{291} = \max(T - 291, 0)$ $T_{293} = \max(T - 293, 0)$	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)

Table 2. Sensitivity simulation cases

Case	N ₂ O ₅ parameterization	NH ₃ emission
<u>OldN2O5Riemer03</u> -FullNH3	<u>P2 of</u> Riemer et al. (2003)	100%
<u>Riemer03OldN2O5</u>	<u>P2 of</u> Riemer et al. (2003)	50% *
NewN2O5	New scheme (this study)	50% *

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

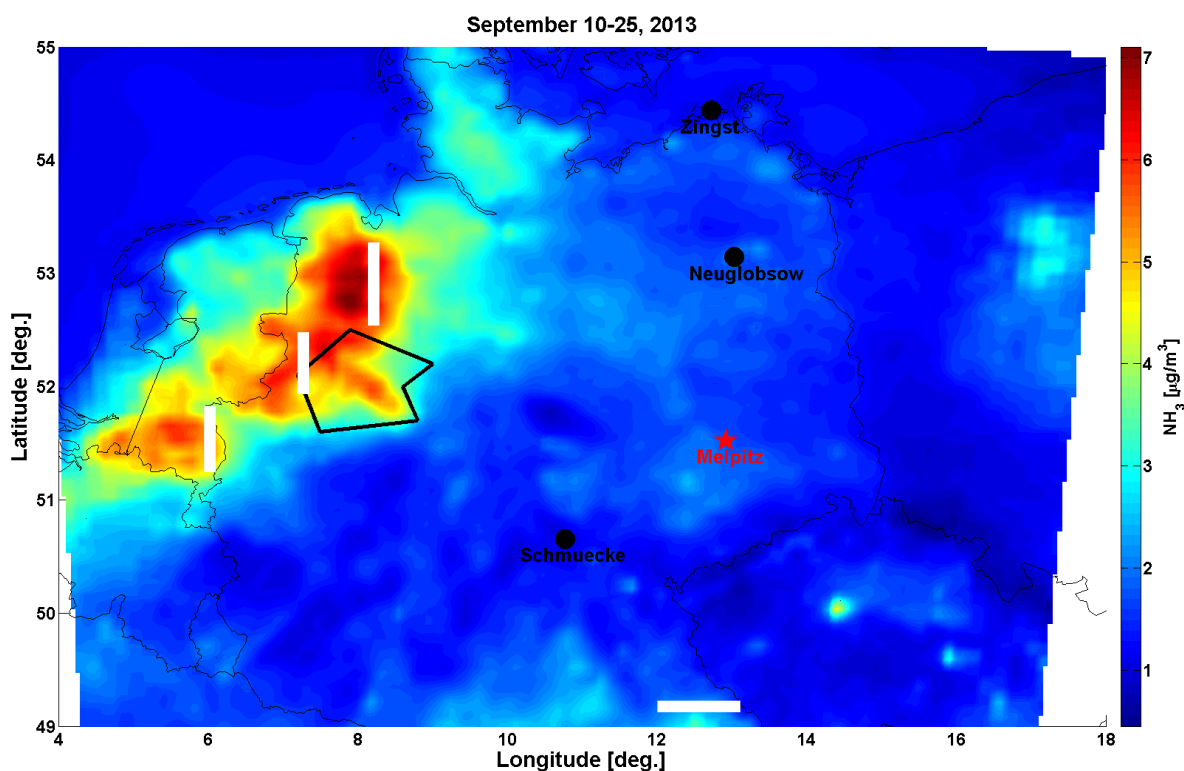


Figure 1. Results (domain N2) of NewN2O5 case of averaged NH₃ mass concentration during 10-25 September 2013. The added emissions of marker tracer (T-NH₃) from NH₃ source regions (the Netherlands and south Germany) are marked by the white bars. The locations of the considered measurement stations are 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. 56.

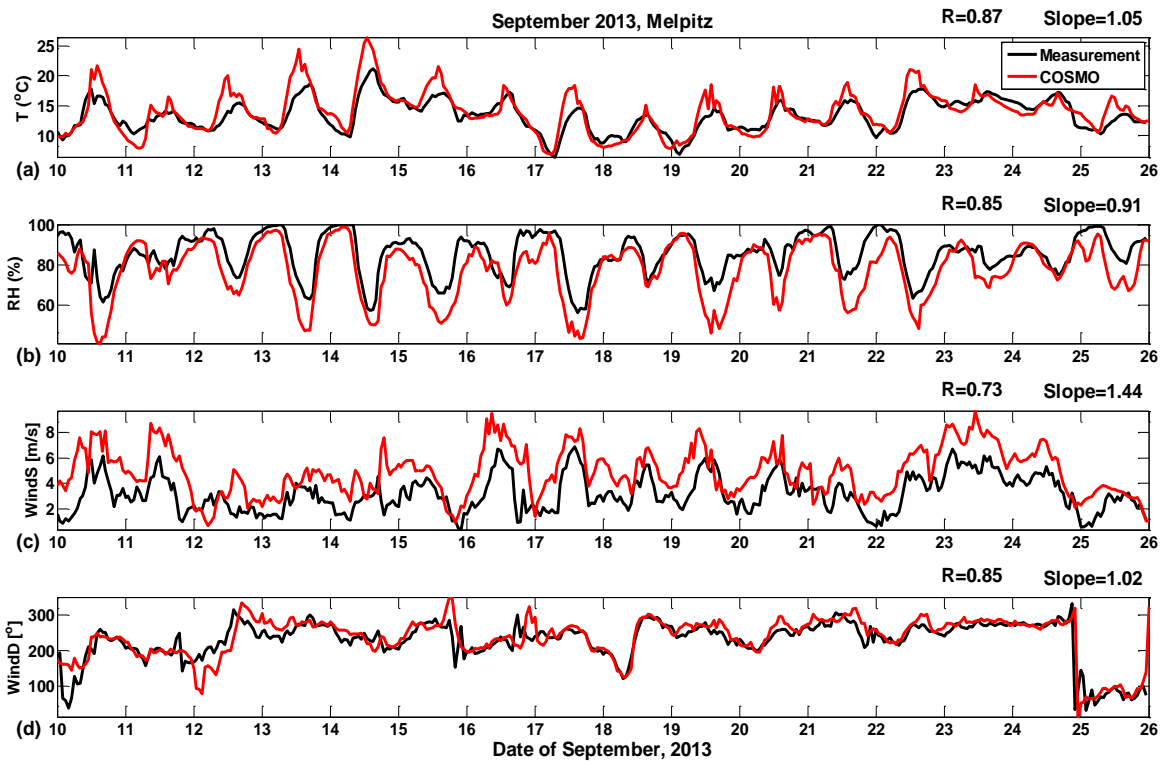


Figure 2. Comparison between modelled and measured meteorological conditions. (a) Temperature (T); (b) relative humidity (RH); (c) wind speed; (d) wind direction.

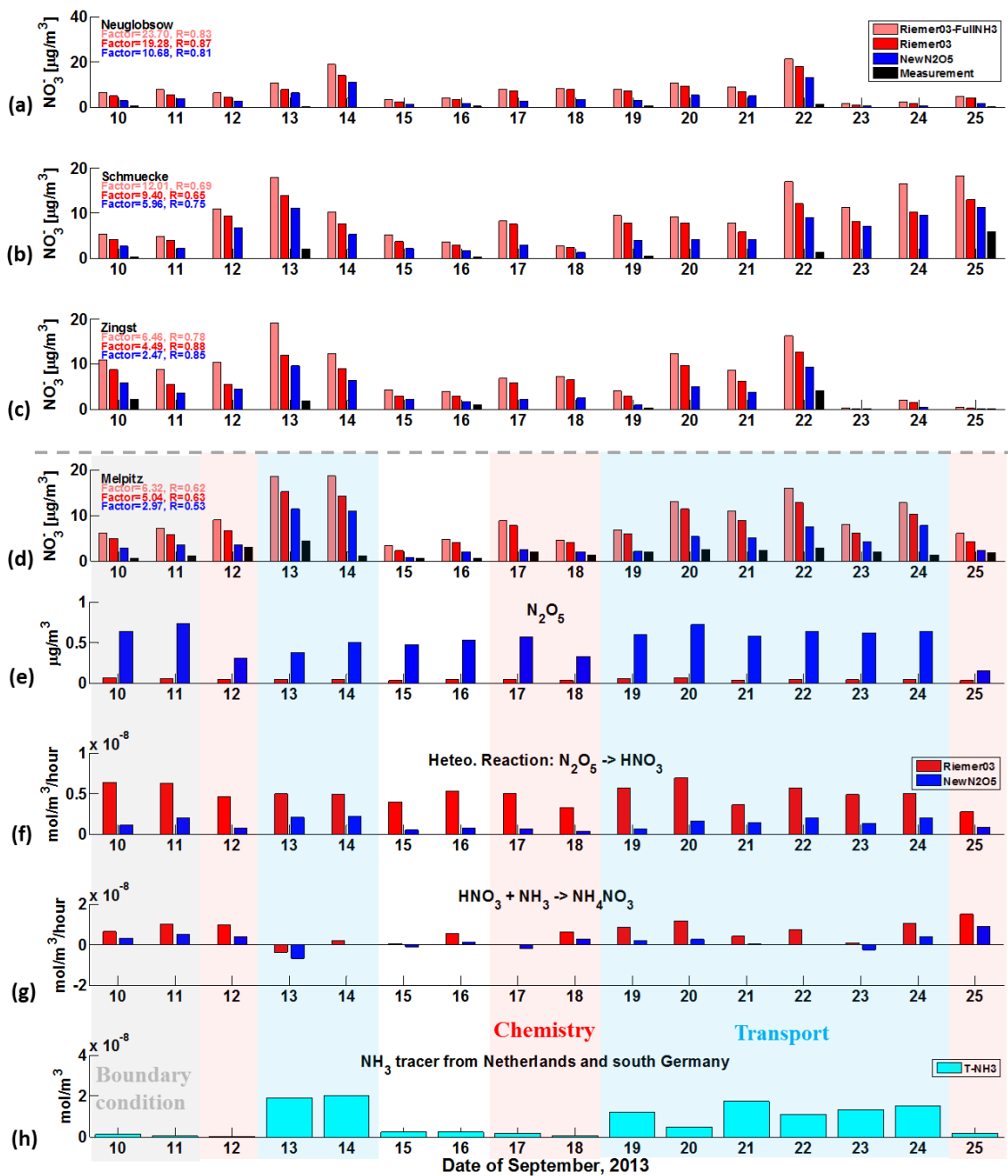


Figure 3. Comparison of particulate nitrate mass concentration between filter measurements and modelled results: (a) Neuglobsow; (b) Schmuecke; (c) Zingst; (d) Melpitz. Modelled concentrations at Melpitz: (e) N_2O_5 ; (f) marker species T1 for chemical reaction R1; (g) marker species for chemical formation of particulate nitrate (T3-T2); (h) the NH_3 -marker tracer (T-NH3) for transport from the Netherlands and south Germany. The light red colour bars indicate the results of Riemer03-FullNH3 case; the red colour bars indicate the results of Riemer03 case; and the blue colour bars indicate the results of NewN2O5 case. The shaded periods indicate the dominating processes for high concentrations of particulate nitrate: chemical formation (red), transport (blue), and boundary conditions (grey).

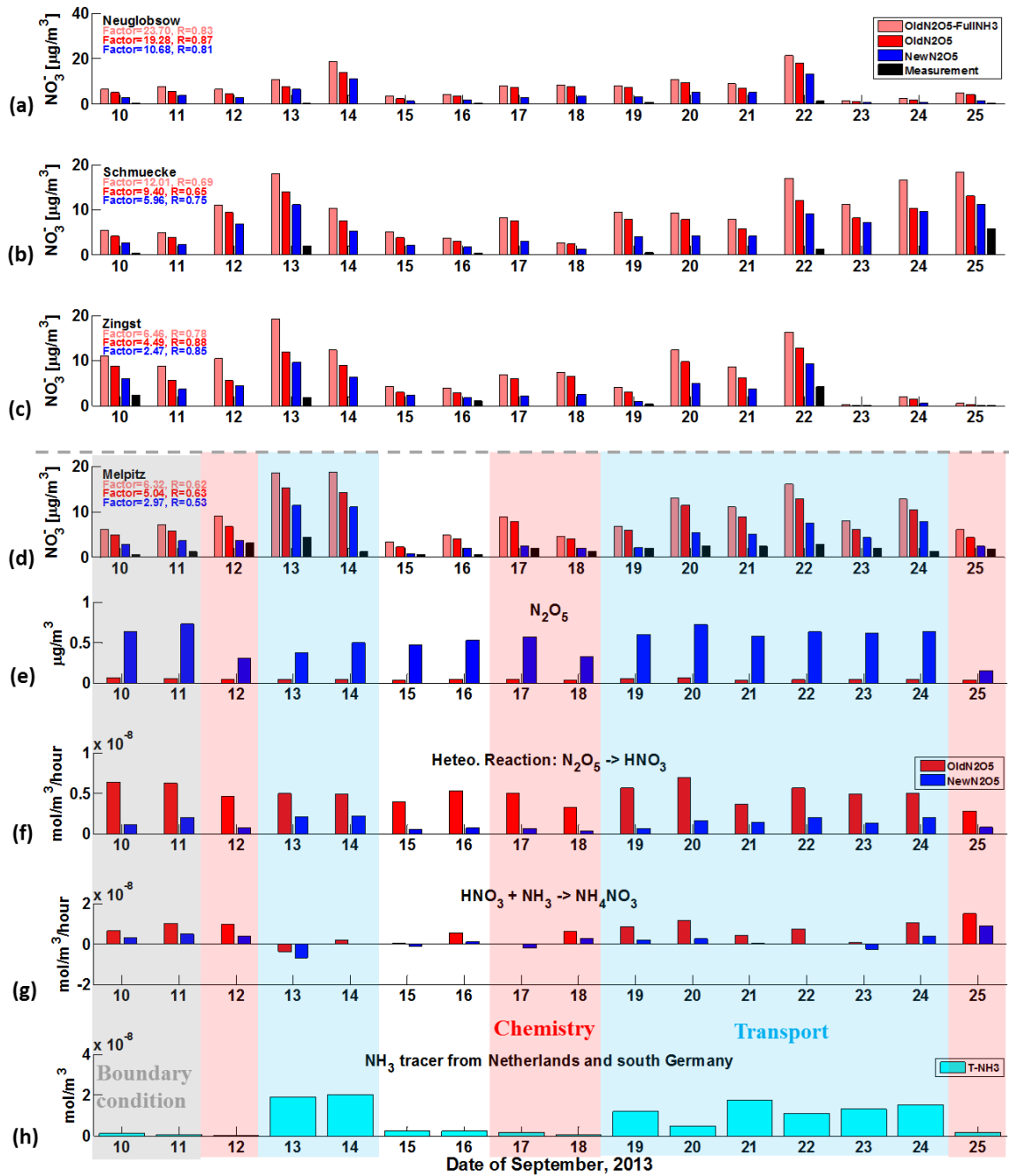


Figure 3. Comparison of particulate nitrate mass concentration between filter measurements and modelled results: (a) Neuglobsow; (b) Schmuecke; (c) Zingst; (d) Melpitz. Modelled concentrations at Melpitz: (e) N_2O_5 ; (f) marker species T1 for chemical reaction R1; (g) marker species for chemical formation 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 [Riemer03OldN2O5-FullNH3](#) case; the red colour bars indicate the results of [Riemer03-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).

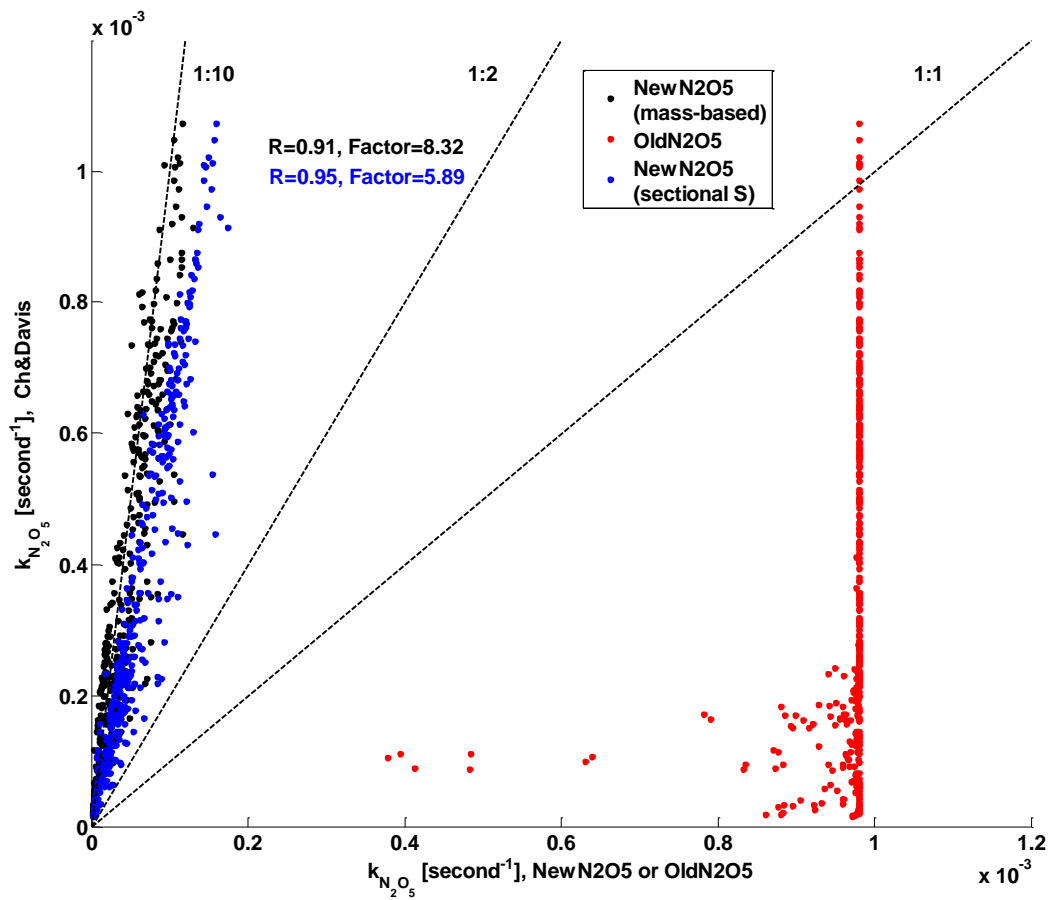


Figure 4. Comparison between the sectional-based Ch&Davis (‘Davis’ of Chang et al., 2016) and mass-based NewN2O5 (mass-based, black), NewN2O5 (with a sectional-based particle surface area, blue) and OldN2O5 (red). The results are offline calculated on basis of WRF-Chem simulation with a sectional aerosol treatment (MOSAIC).

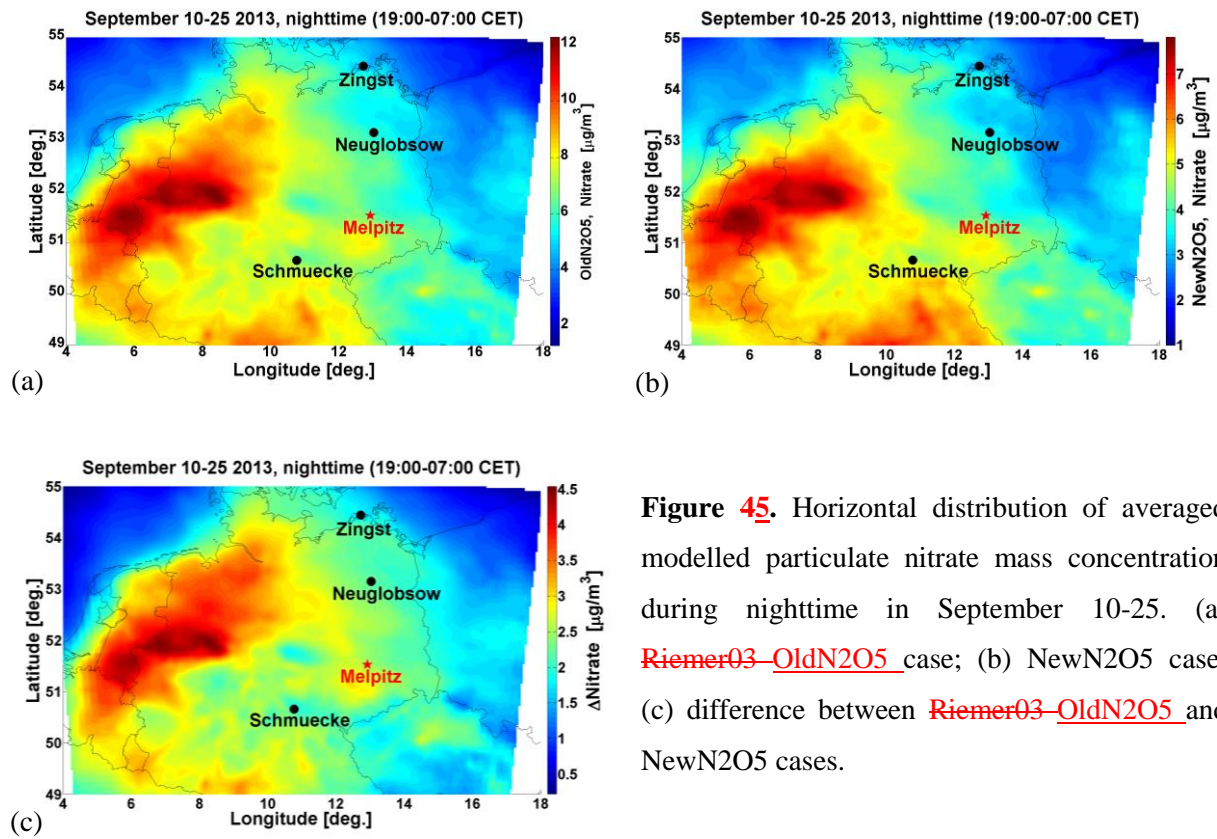


Figure 45. Horizontal distribution of averaged modelled particulate nitrate mass concentration during nighttime in September 10-25. (a) Riemer03-OldN2O5 case; (b) NewN2O5 case; (c) difference between Riemer03-OldN2O5 and NewN2O5 cases.

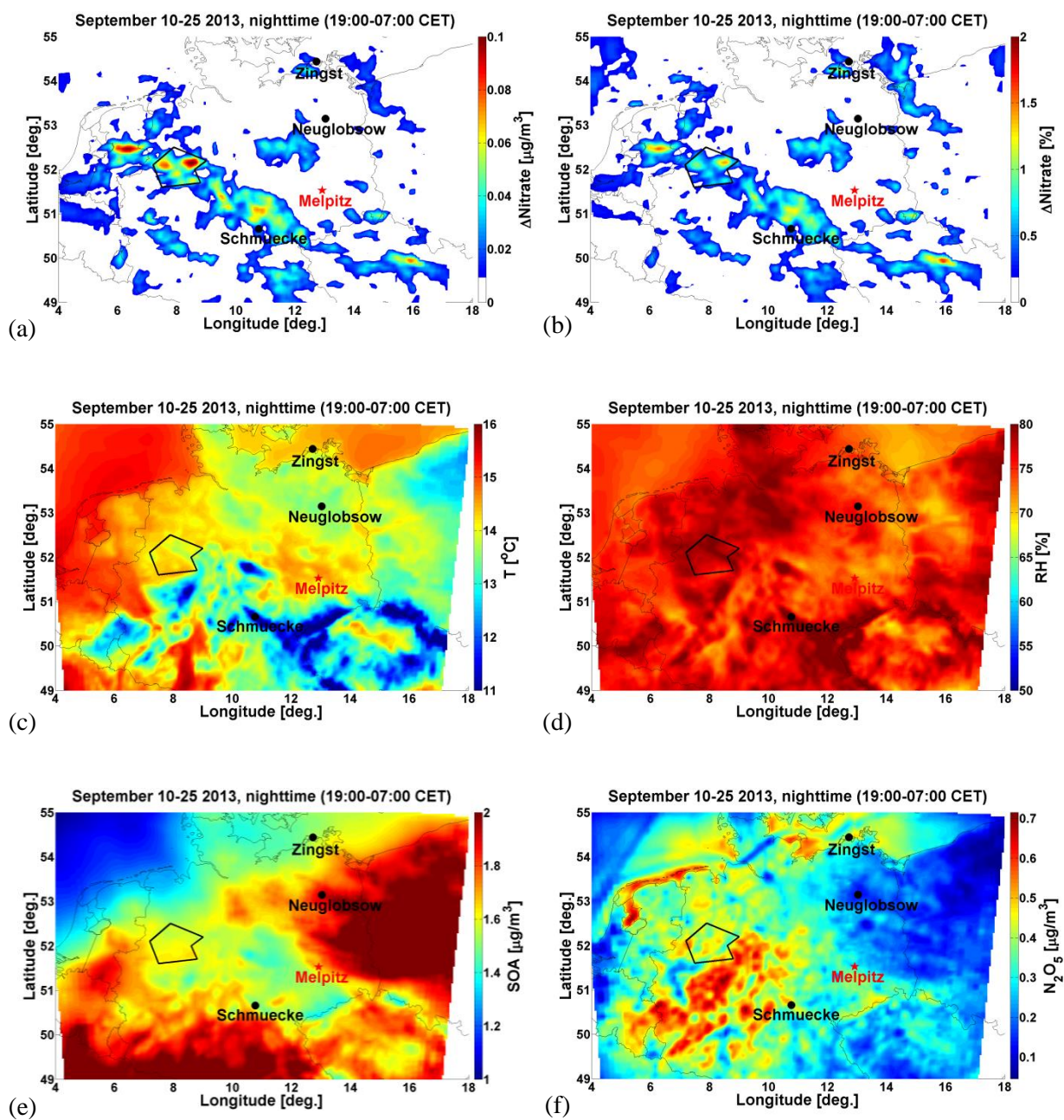


Figure 56. Horizontal distribution of averaged model results during nighttime in September 10-25, computed with the ~~new- N_2O_5 -scheme~~NewN2O5. (a) Difference of particulate nitrate mass concentration between model cases with and without considering organic coating effect; (b) difference of particulate 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.

Supplement of

**A Parameterization of Heterogeneous Hydrolysis of N_2O_5
for ~~3-D Atmospheric Modelling~~ Mass-based Aerosol
Models: Improvement of Particulate Nitrate Prediction**

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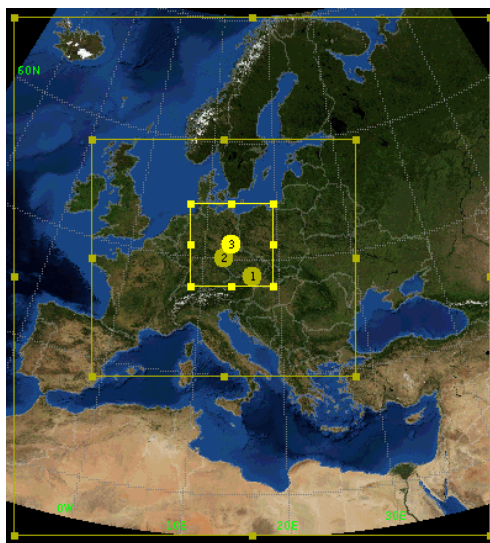


Figure S1. Domain setting of WRF-Chem simulation.

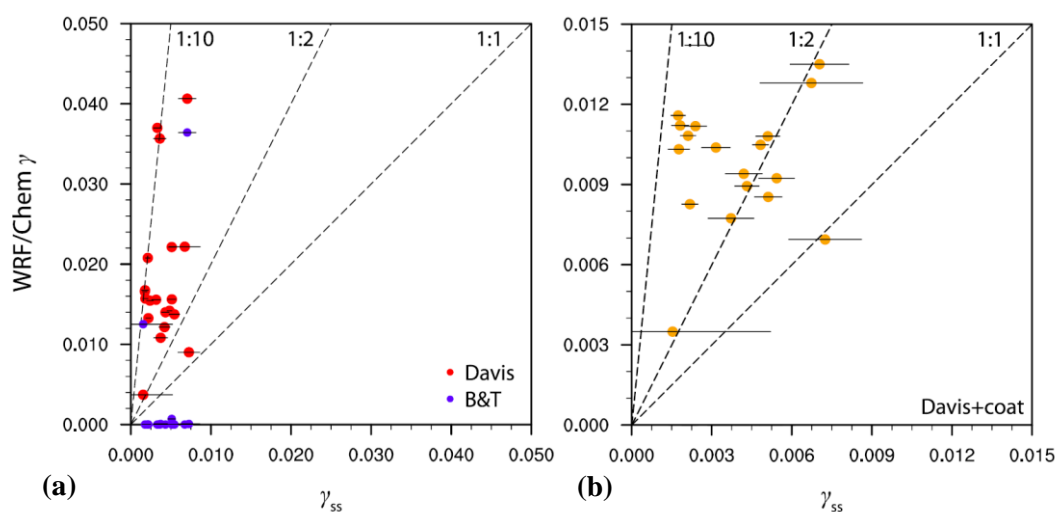


Figure S2. Modelled γ (Chang et al., 2016) versus calculated γ_{ss} (reaction probability in steady state) using aircraft observations from the 31 May flight of CalNex 2010 campaign. (a) Davis (Davis et al., 2008, namely Ch&Davis) and B&T (Bertram and Thornton, 2009) parameterization; (b) Davis+coat (Anttila06).

Source: Figure 10 of Chang et al. (2016).

S1. Temporal evolutions of NO_x and N₂O₅

The concentration of gaseous precursor (NO_x) was observed under the frame of HOPE-Melpitz campaign with 1h temporal resolution. As shown in Fig. S3 (newly added), the modelled NO_x concentration was in line with the measurement, with a factor of 0.9 for both OldN2O5 and NewN2O5 cases. Therefore, the high overestimation of particulate nitrate should not be resulted from the uncertainty of NO_x.

The N₂O₅ concentration was accumulated during nighttime in NewN2O5 case, and was totally dissociated into NO₂ and NO₃ during daytime (Fig. S3b). However, the N₂O₅ could not accumulate during nighttime in OldN2O5 case, due to its highly overestimated reaction constant.

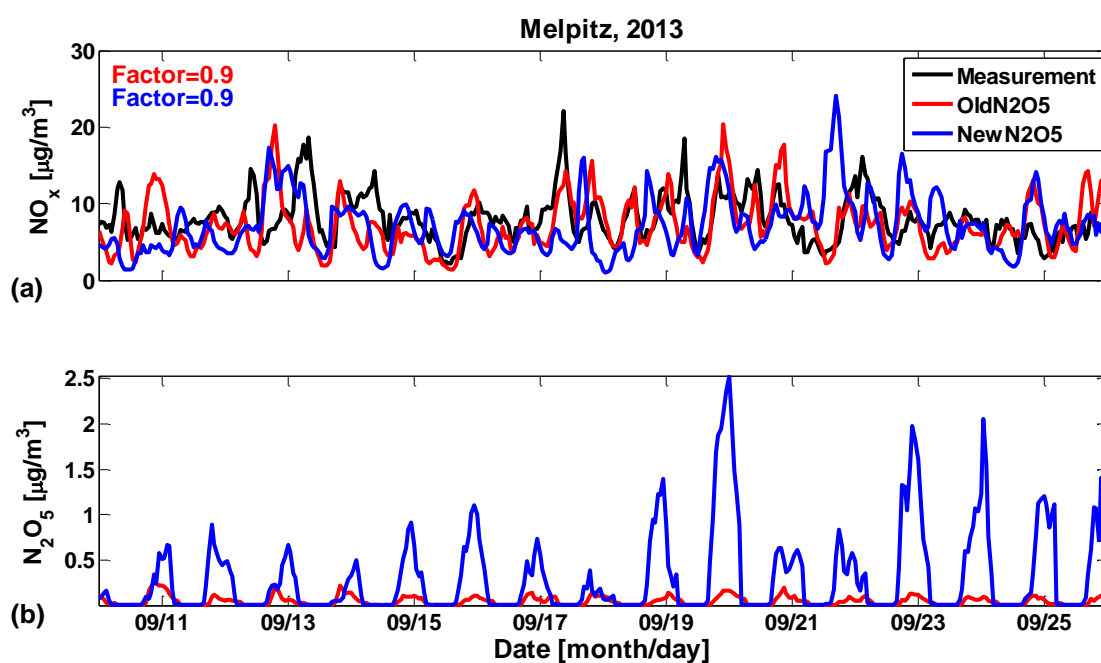


Figure S3. Time series of NO_x (a) and N₂O₅ (b) at Melpitz.

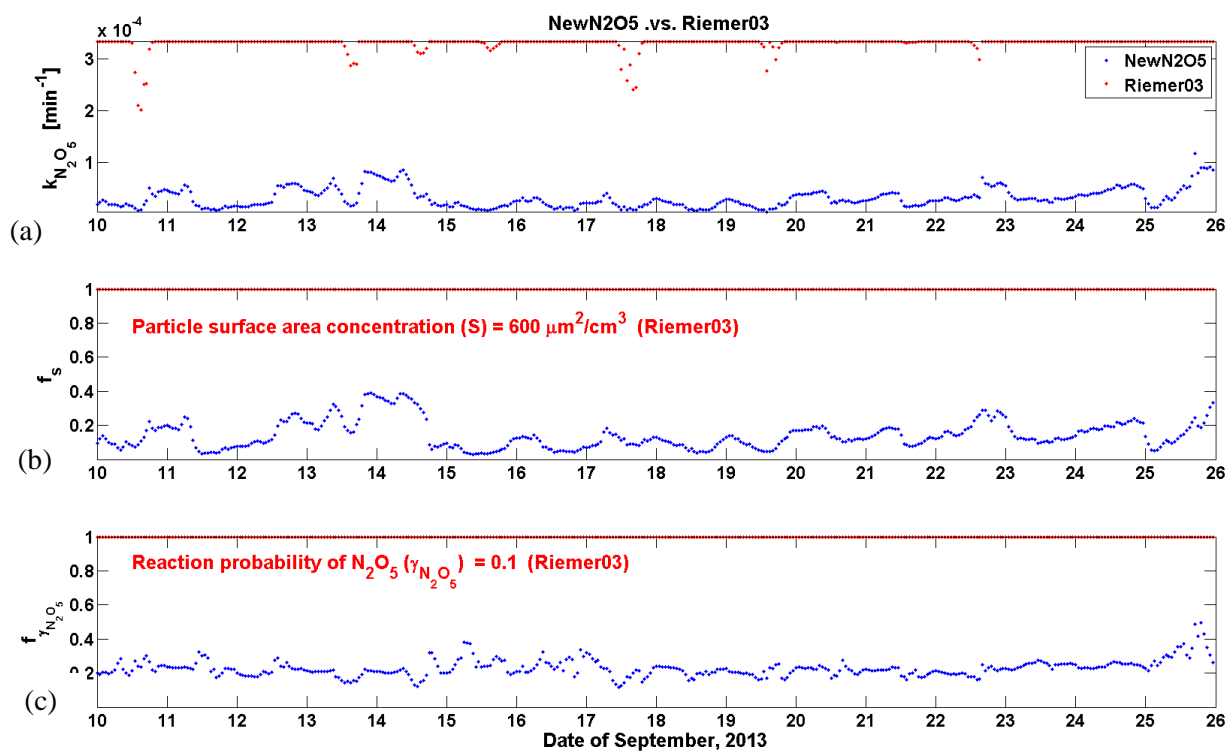


Figure S2. Comparison of modelled results at Melpitz between Riemer03 (red) and NewN2O5 (blue) cases. (a) Heterogeneous reaction constant of N_2O_5 ; (b) factor of particle surface area concentration; (c) factor of reaction probability of N_2O_5 .

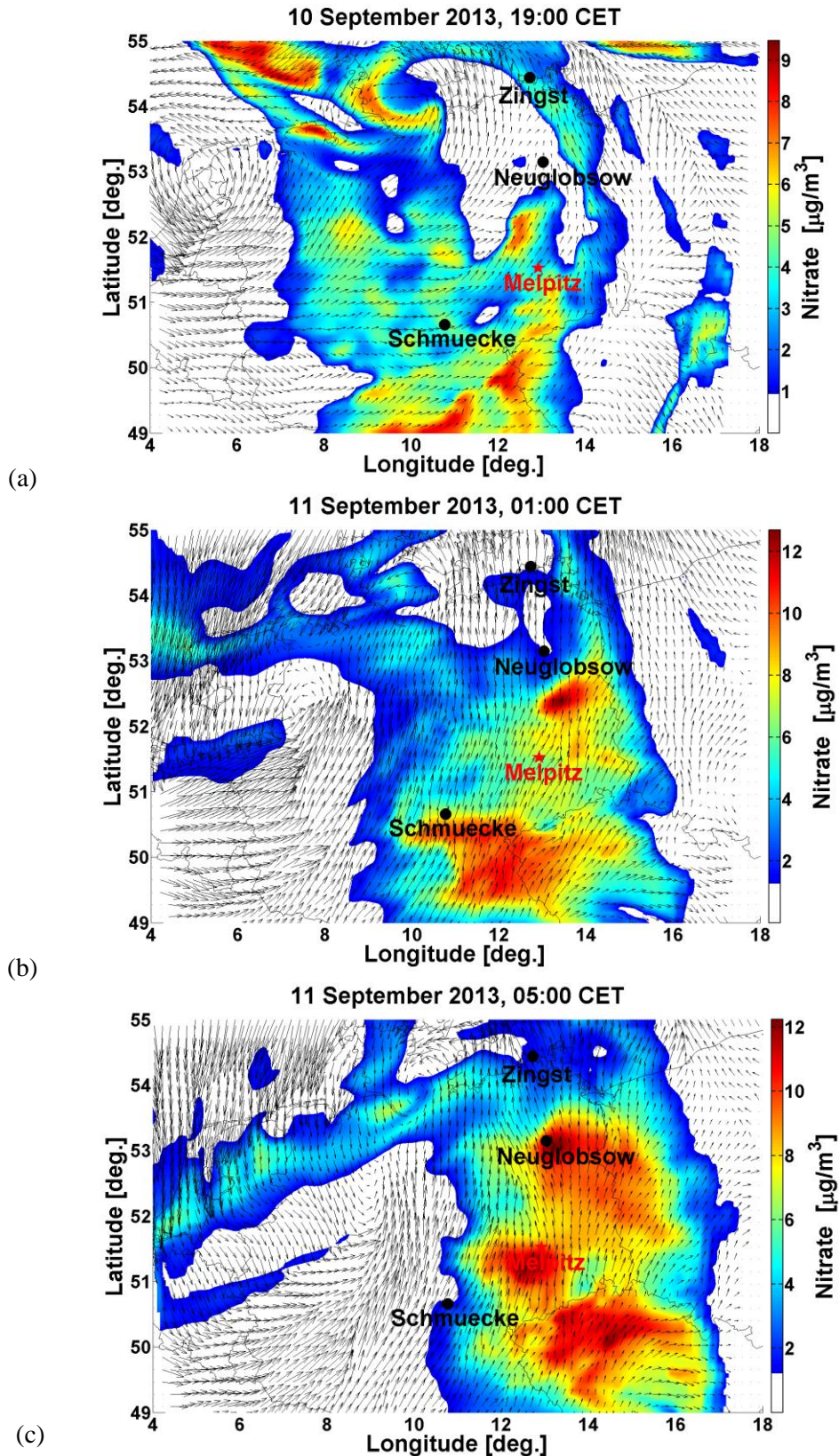


Figure S1S3S4. Spatial distribution of particulate nitrate mass concentration and wind pattern, modelled results of NewN2O5 case. (a) 2013-09-10, 19:00 CET; (b) 2013-09-11, 01:00 CET; (c) 2013-09-11, 05:00 CET.

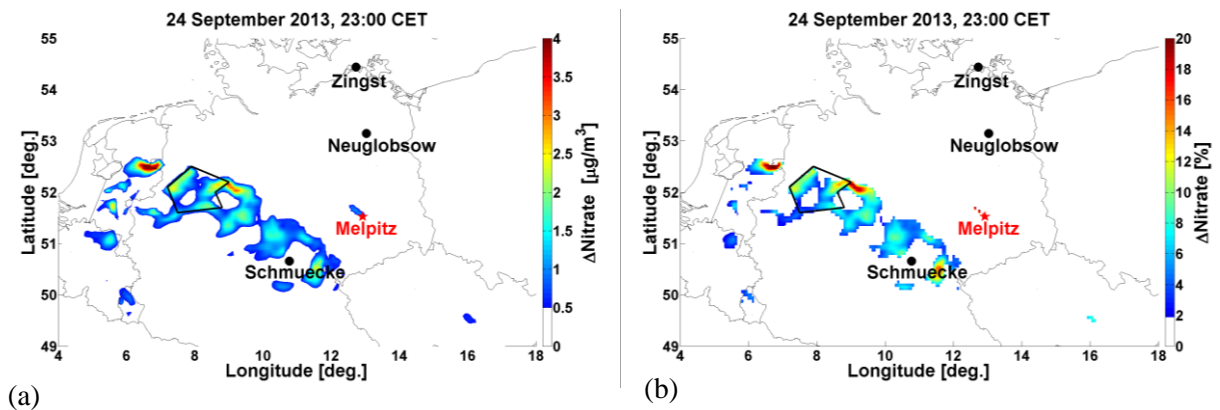


Figure S3S4S5. Horizontal distribution of modelled results at 24 September 23:00 CET, based on [new N₂O₅-schemeNewN2O5](#). (a) Difference of particulate nitrate mass concentration between with and without organic coating effect; (b) difference of particulate nitrate mass concentration in percentage between with and without organic coating effect, where with differences less than 2% or 0.5 $\mu\text{g}/\text{m}^3$ are indicated by white colour.

References:

[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.](#)