Response to comments of referee #1

General Comments:

Chen et al. have studied a new parameterization of heterogeneous hydrolysis of N2O5 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 NH3 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 NOx and N2O5 prediction. This new parameterization of heterogeneous hydrolysis of N2O5 established from many previous laboratory experiments improves the prediction, but large gaps still exists between the model results and the measurement at all stations. Among the reasons given in section 3.1, how about the kN2O5 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. NOx is also an important precursor of nitrate. However, in this study, the overprediction of nitrate was not stem from NOx, which was in line with the measured concentration level. The detailed temporal evolutions of NOx and N_2O_5 were added in the supplementary information Text S1, as shown below.

"S1. Temporal evolutions of NOx and N_2O_5

The concentration of gaseous precursor (NOx) was observed under the frame of HOPE-Melpitz campaign with 1h temporal resolution. As shown in Fig. S3 (newly added), the modelled NOx 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 NOx.

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."

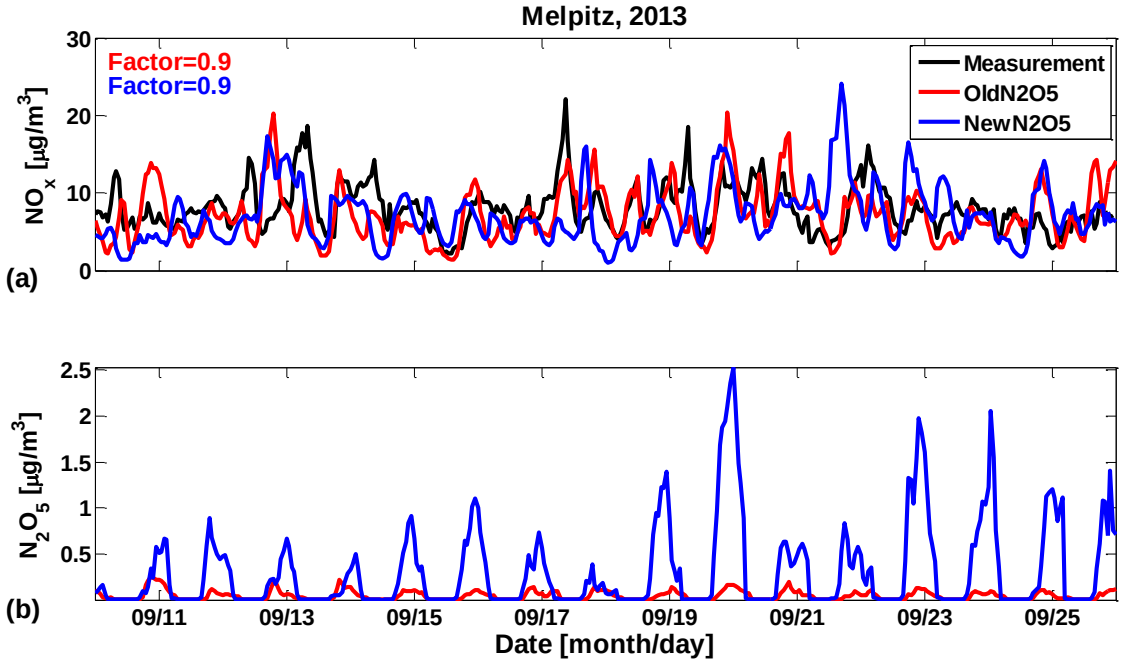

Figure S3 (newly added). *Time series of NOx (a) and N_2O_5 (b) at Melpitz.*

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

"The modelled NOx was in line with the observed concentration level at Melpitz, and should not be the reason of the overprediction of particulate nitrate (see details in Supplement Text S1 and Fig. S3)."

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 kN2O5 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)."*

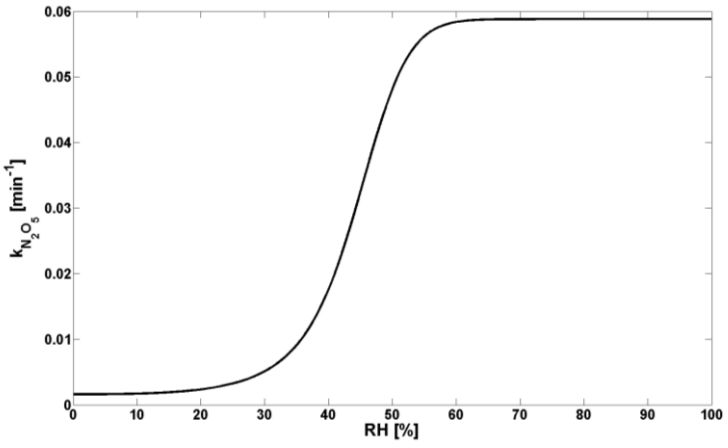

Figure R1. *Rate constant for the heterogeneous hydrolysis of* N_2O_5 *with relation to RH. Modified from Figure 1 of Riemer et al. (2003), or calculated from the equation (2) with a=17.*

(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 Wolker, 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 N_2O_5 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 N_2O_5 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.

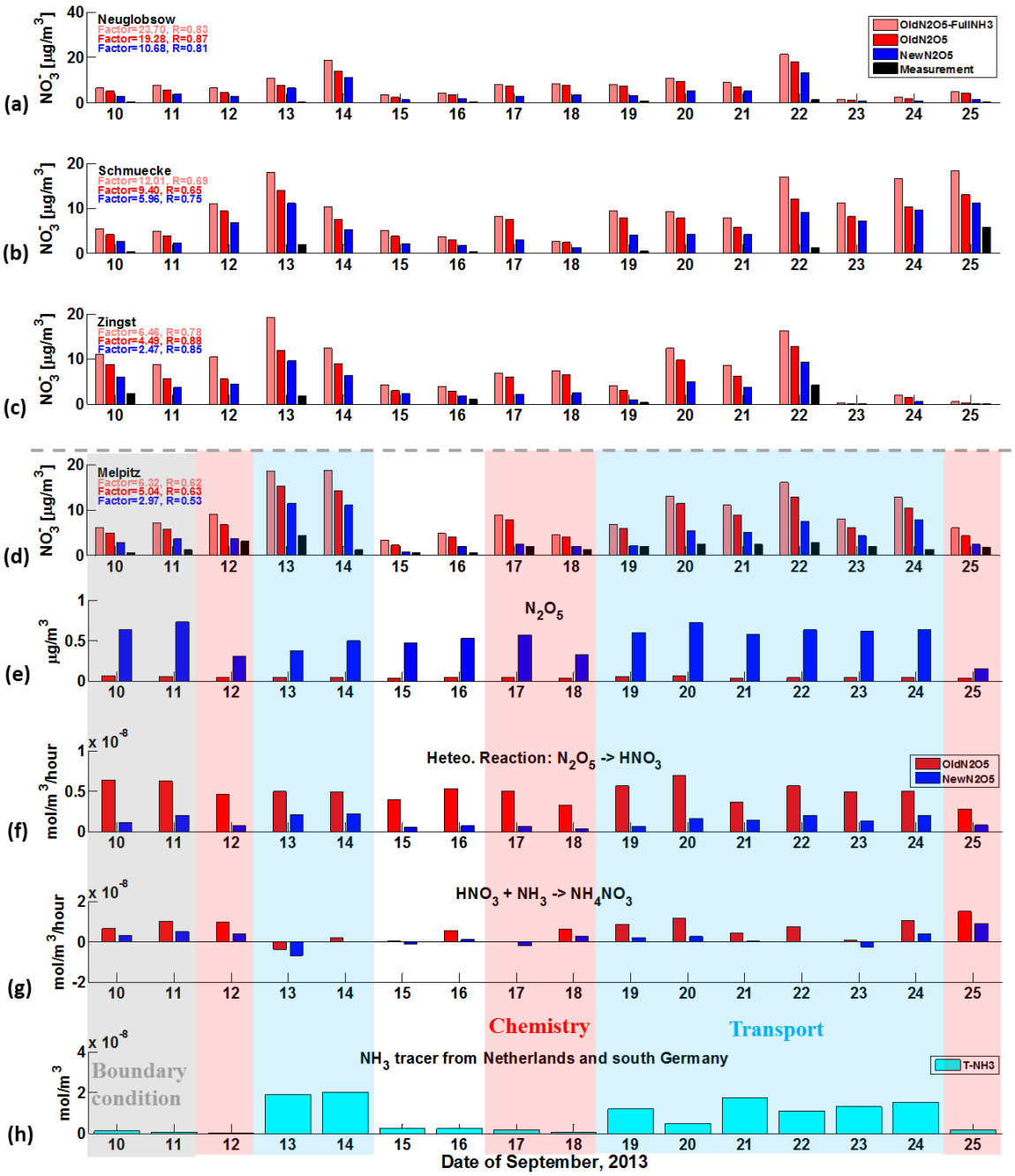

Figure 3. *Comparison of particulate nitrate mass concentration between filter measurements and modelled results: (a) Neuglobsow; (b) Schmuecke; (c) Zingst; (d) Melpitz. Modelled concentrations at Melpitz: (e) N_2O_5; (f) marker species T1 for chemical reaction R1; (g) marker species for chemical formation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

(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 $\mu g/m^3$ (~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, 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, 2008.

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

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