

Replies to Interactive comment on Ozone Impacts of Gas-Aerosol Uptake in Global Chemistry Transport Models by Scarlet Stadtler et al.

1 Anonymous Referee #1

Received and published: 17 July 2017

1.1 General comments

The manuscript "Ozone Impacts of Gas-Aerosol Uptake in Global Chemistry Transport Models" by Stadtler et al. deals with the importance of heterogeneous chemical uptake of several inorganic compounds for the tropospheric chemical budget of ozone. To investigate the relevance of the uptake, parameterised reaction rates producing a loss term to the budget of N_2O_5 , NO_3 , NO_2 , O_3 , HNO_3 and HO_2 are implemented in two chemistry models, i.e. the EMEP chemical transport model and the ECHAM-HAMMOZ CCM. The analysis of the results is based on sensitivity tests, each neglecting one of the reactions. The dominating heterogeneous reaction for the tropospheric O_3 burden is the (well known) heterogeneous uptake of N_2O_5 , whereas the other reactions show a minor relevance. Given the large temporal variability of the ozone measurements at the given stations, even the heterogeneous N_2O_5 uptake is hardly significant, whereas for the other reactions a statistical significance cannot be stated. For some reactions the two models even give results of the opposite sign. The paper is well written and the study is reasonable and should be published in ACP after addressing the comments below. However, as the main finding is the importance of the N_2O_5 uptake, which is well known since more than 20 years, the new findings from this manuscript are relatively limited.

Reply: We thank the referee for the positive and constructive comments. Concerning the last point, we agree that the importance of N_2O_5 has been established for many years, but we believe that our paper is novel in using very up-to-date chemical transport models (CTMs) which we show can reproduce well daily variations at sites around the world, and with a demonstration of a fair ability to capture aerosol surface area compared to satellite data. In addition, we also illustrate in detail how seasonal patterns are affected by this reaction. We also believe we are the first to systematically compare the impacts of the different reactions in a harmonized way across two model systems. We have now added also a comparison to previous models studies and also new sensitivity tests on the impact of different assumptions for γ . Details can be found in the new Discussion Section 5.4.

Before giving the main replies below, we should point out that for the revised manuscript we re-ran all results with an updated version of the EMEP model. This was done following some

bug-fixes in the rv4.15 version originally used, including in the deposition of N_2O_5 and radiation schemes. These changes have not affected basic model performance very much, but especially the deposition change affects N_2O_5 levels, and the impact of the noN2O5 scenarios. Indeed, the impacts in the EMEP system now resemble much more those of ECHAM-HAMMOZ. We have added a small Appendix to explain these changes, and modified the manuscript to reflect the updated results.

1.2 Major comments

1) The neglect of direct nitrate formation in HAMMOZ might not only lead to a shift between chloride release and nitrate formation, but might affect also the size distribution and therefore the surface area of the aerosol. To which degree does the SAD change in the EMEP simulations in case of the neglect of N_2O_5 or HNO_3 uptake? Can you quantify the total loss of these compounds in the EMEP simulations versus the HAMMOZ runs?

Reply: As shown in Figure 5 SAD hardly changes in EMEP simulations with the neglect of N_2O_5 reactions, and a similar pattern is seen for HNO_3 reactions (not shown).

Unfortunately the models do not track the various loss terms so we cannot compare the total losses in EMEP versus ECHAM-HAMMOZ. We agree that this would be very valuable information, but it would require re-writing the model code and re-running all simulations.

2) To which degree do you think that reactive nitrogen chemistry as in Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China: Yafang Cheng, Guangjie Zheng, Chao Wei, Qing Mu, Bo Zheng, Zhibin Wang, Meng Gao, Qiang Zhang, Kebin He, Gregory Carmichael, Ulrich Pschl, Hang Su Science Advances, 21 Dec. 2016; DOI: 10.1126/sciadv.1601530 is relevant on the global scale in your simulations?

Reply: It is actually very hard to answer this question. The strong uptake and impact of NO_2 in aerosol water systems as explored by Cheng et al. is not included in either of our models. However, Cheng et al. were concerned with extreme aerosol pollution events with concentrations exceeding $(100 \mu \text{g m}^{-3})$. These cannot be modeled at present in global scale models because of the dilution effect of the coarse grid resolution, and such extreme pollution events are likely to only have a local importance. Finally, it is not certain that the mechanism suggested by Cheng et al., is sufficient to explain some other extreme smog events (Guo et al. 2017 doi:10.1038/s41598-017-11704-0). As well as considerable scientific uncertainties in gas-aerosol interactions in such extreme conditions, proper implementation of these type of effects would depend on very good estimates of all emissions (including base-cations), air-liquid interactions, activity coefficients, pH, etc.; factors which are beyond the capabilities of current global atmospheric chemistry models.

We have added some extra words on these problems in a new Discussion Section, 5.4.

3) The interaction of the individual uptake reactions might lead to a masking of the direct effects of the reactions by chemical interactions. Why did you not choose to analyse individual reactions, but always the sum of reactions neglecting only one of them. Would a method such as a Factor Separation Method (see Stein, U. and P. Alpert, 1993: Factor Separation in Numerical Simulations. *J. Atmos. Sci.*, 50, 21072115, [https://doi.org/10.1175/1520-0469\(1993\)050;2107:FSINS;2.0.CO;2](https://doi.org/10.1175/1520-0469(1993)050;2107:FSINS;2.0.CO;2)) not be more suitable to address your scientific question (given the extra computation time is available).

Reply: Our procedure is to start with the reference run which provides the best estimate of the photochemical system we can make with our models, and to then eliminate each reaction one by one. Thus, each change is a simple perturbation due to that individual reaction, which we believe gives both a fair and simple comparison across the reactions. For n factors, the Factor Separation Method of Stein and Alpert requires 2^n simulations. Thus, our 6 reactions would have required 64 simulations, which would have been prohibitive for ECHAM-HAMMOZ at least. Further, the changes we calculate are generally very small for most reactions, so a linear (perturbation) analysis should be both clearer and accurate.

4) To which degree might your results depend on the selected year. Would you expect substantial inter-annual variability based on the variability in both the aerosol surface and the constituents?

Reply: New tests have been conducted with the EMEP model for 2011, and in Tables 1 and 2 below we compare the percentage changes of this year to those of 2012. It can be seen that the results are remarkably similar, across all compounds and reaction tests. This suggests that the strong day-to-day variability in atmospheric and pollution conditions, and impacts of these reactions, average out to a large extent and annual results are rather robust.

5) How sensitive are your results to the selected values for the individual compounds? Are the values important or is the uptake anyhow mostly determined by the available aerosol surface and the availability of the constituents?

Reply: This is a complicated question, since these reactions also change the composition of NO_y in the atmosphere, the lifetime of NO_2 and hence the photooxidation processes leading to O_3 . In order to address this, we have run the EMEP model with four new configurations:

1. $\gamma = 0.01$ for N_2O_5 , a value lower than our typical values, and at the low end of estimates (manuscript Sect. 3.1)
2. $\gamma = 0.1$ for N_2O_5 , equivalent to values used by e.g. Dentener and Crutzen (1993), which is substantially higher than our values
3. $\gamma = 1.0 \times 10^{-3}$ for NO_2 , at the top end of estimates (Sect. 3.3)

Table 1: Impacts of gas-aerosol reactions on regional average mixing ratios of O₃ and key NO_y compounds: EMEP model, year 2011.

Region	Run	Unit	O ₃	NO _x	NO _y	HNO ₃	PAN	N ₂ O ₅	NO ₃
NA	Base	Conc*:	39.85	0.80	1.79	0.20	0.54	4.50	4.09
NA	noN2O5pm	%:	6	10	4	-11	9	202	70
NA	noHO2pm	%:	0	-1	0	1	1	-2	-11
NA	noHNO3pm	%:	0	0	-3	23	0	0	0
NA	noNO2pm	%:	0	2	1	0	0	4	2
NA	noNO3pm	%:	0	0	0	0	0	1	4
NA	noO3pm	%:	0	0	0	0	0	0	0
EUR	Base	Conc*:	40.15	0.99	2.40	0.25	0.50	6.98	5.90
EUR	noN2O5pm	%:	7	17	3	-16	11	316	86
EUR	noHO2pm	%:	1	-3	0	1	4	-4	-14
EUR	noHNO3pm	%:	1	0	-6	59	0	0	3
EUR	noNO2pm	%:	0	5	1	-1	-1	6	4
EUR	noNO3pm	%:	0	0	0	0	0	2	10
EUR	noO3pm	%:	0	0	0	0	0	0	2
EA	Base	Conc*:	42.65	2.17	4.50	0.54	0.79	10.88	4.62
EA	noN2O5pm	%:	8	15	5	-19	13	316	127
EA	noHO2pm	%:	2	-4	0	2	7	0	-8
EA	noHNO3pm	%:	0	0	-2	16	0	0	0
EA	noNO2pm	%:	-1	29	9	-11	-7	12	3
EA	noNO3pm	%:	0	0	0	0	0	1	3
EA	noO3pm	%:	0	0	0	0	0	0	0
SA	Base	Conc*:	47.12	1.09	2.83	0.40	0.29	8.78	11.27
SA	noN2O5pm	%:	7	12	1	-4	15	175	73
SA	noHO2pm	%:	1	-3	0	1	5	-5	-12
SA	noHNO3pm	%:	1	0	-8	63	0	1	4
SA	noNO2pm	%:	1	4	1	0	1	9	5
SA	noNO3pm	%:	1	0	0	0	1	5	10
SA	noO3pm	%:	0	0	0	0	0	0	0

Notes: Base-case concentrations from the surface-level of the model are given in ppt for NO₃ and N₂O₅, otherwise ppb (Conc* flags this difference in units). Results for the sensitivity tests are given as (test-base)/base in %. The first column refers to the region over which the annual mean is spatially averaged, and the second column refers to the corresponding run. Regions are defined as follows: NA (15° N55° N; 60° W125° W), EU (25° N65° N; 10° W-50° E), EA (15° N50° N; 95° E160° E), and SA (5° N35° N; 50° E95° E).

Table 2: Impacts of gas-aerosol reactions on regional average mixing ratios of O₃ and key NO_y compounds: EMEP model, year 2012.

Region	Run	Unit	O ₃	NO _x	NO _y	HNO ₃	PAN	N ₂ O ₅	NO ₃
NA	Base	Conc*:	40.33	0.82	1.81	0.21	0.55	5.08	4.54
NA	noN2O5pm	%:	5	9	4	-10	8	160	59
NA	noHO2pm	%:	0	-1	0	1	1	-2	-10
NA	noHNO3pm	%:	0	0	-2	18	0	0	0
NA	noNO2pm	%:	0	2	1	-1	0	4	2
NA	noNO3pm	%:	0	0	0	0	0	1	3
NA	noO3pm	%:	0	0	0	0	0	0	0
EUR	Base	Conc*:	40.89	1.01	2.43	0.25	0.54	7.73	6.48
EUR	noN2O5pm	%:	7	16	3	-16	10	280	72
EUR	noHO2pm	%:	1	-3	0	1	4	-4	-14
EUR	noHNO3pm	%:	1	0	-6	58	0	0	3
EUR	noNO2pm	%:	0	5	1	-1	-1	6	4
EUR	noNO3pm	%:	0	0	0	0	0	2	10
EUR	noO3pm	%:	0	0	0	0	0	0	2
EA	Base	Conc*:	43.96	2.23	4.63	0.54	0.89	12.59	5.52
EA	noN2O5pm	%:	8	14	4	-19	13	278	106
EA	noHO2pm	%:	2	-4	0	2	7	0	-7
EA	noHNO3pm	%:	0	0	-2	13	0	0	0
EA	noNO2pm	%:	-1	30	9	-11	-8	13	4
EA	noNO3pm	%:	0	0	0	0	0	1	3
EA	noO3pm	%:	0	0	0	0	0	0	0
SA	Base	Conc*:	47.33	1.12	2.90	0.42	0.33	10.37	12.04
SA	noN2O5pm	%:	6	11	1	-4	15	139	63
SA	noHO2pm	%:	1	-3	0	1	5	-5	-12
SA	noHNO3pm	%:	1	0	-8	61	0	1	4
SA	noNO2pm	%:	1	4	1	0	1	10	5
SA	noNO3pm	%:	1	0	0	0	1	5	11
SA	noO3pm	%:	0	0	0	0	0	0	0

Notes: Base-case concentrations from the surface-level of the model are given in ppt for NO₃ and N₂O₅, otherwise ppb (Conc* flags this difference in units). Results for the sensitivity tests are given as (test-base)/base in %. The first column refers to the region over which the annual mean is spatially averaged, and the second column refers to the corresponding run. Regions are defined as follows: NA (15° N55° N; 60° W125° W), EU (25° N65° N; 10° W-50° E), EA (15° N50° N; 95° E160° E), and SA (5° N35° N; 50° E95° E).

4. $\gamma = 0.0$ for NO_2 , since the lowest estimates are extremely low.

The model has been run for new base-cases, and for the noN2O5, noHNO3 and (except for test 4) noNO2 cases. Results for the regional averages (equivalent to manuscript Tables 4-5) are shown in Tables 3-4 below. Considering the N_2O_5 tests first, then the changes in ozone over for example North America range from 3% ($\gamma = 0.01$) to 8% ($\gamma = 0.1$), compared to our original estimate of 5% (Table 4). Changes for NO_x follow a similar pattern (e.g. 6-13% for NA, versus original 9%), but changes for N_2O_5 itself are much more significant (80% versus 354%, compared to the original 160%).

Considering the γ tests for NO_2 , then again the test results for the noN2O5 tests generally span those of the original runs, e.g. changes of 4-6% for ozone in North America versus 5% in the original run, or 113-170% for N_2O_5 versus 160% for the original case. Test (3), with the high $\gamma = 1.0 \times 10^{-3}$ for NO_2 does have significant impacts on the NO_x levels though, from e.g. 2% in the original run to 16% in test (3) for NA, or from 30% to 109% in East Asia. In these runs the impacts of noNO2 on ozone become comparable to those of noN2O5, and in South Asia the ozone changes from noNO2 actually exceed those from noN2O5.

Test (4), using zero γ actually gives results which are very similar to our default $\gamma = 1.0 \times 10^{-4}$, suggesting that this reaction only becomes important if higher values than $\times 10^{-4}$ can be justified.

Thus, we find that the exact changes in ozone and N-compounds do depend on the assumed γ values, but the relative importance of the different heterogeneous reactions generally remains. The N_2O_5 reactions are in nearly all cases the most important driver of ozone changes, but the use of a very high values for γ for NO_2 changes the picture somewhat. We can note though that use of the high 0.001 values for $\gamma(\text{NO}_2)$ leads to quite significant reductions in annual NO_2 concentrations (not shown), resulting in degraded performance of the EMEP model compared to measurements, at least across the EMEP observational network in Europe (Tørseth et al. 2012).

6) Why did you only consider O_3 uptake on dust and not on liquid aerosol particles, where it can contribute to "in-aerosol" sulphate formation by oxidation of dissolved SO_2 . Even though the solubility of O_3 is quite low, the effective uptake is determined by the reaction rate.

Reply: Regarding the sulphate oxidation in ECHAM-HAMMOZ. We don't take into account SO_2 oxidation in aerosol phase (only in cloud droplets) as a chemical process. However, the oxidation is considered so, that part of SO_2 is emitted as primary sulphate. This approximation represents the aerosol phase oxidation of SO_2 in ECHAM-HAMMOZ. Similarly, in EMEP, SO_2 oxidation to sulphate on aerosols is assumed to take in gas and cloud rather than via aerosol water. As with ECHAM, a certain percentage (5%) of S emissions are assumed to be as sulphate.

7) What is the tropospheric CH_4 lifetime in your simulations? Due to HO_2 uptake, the oxidation capacity might be reduced, but due to HONO formation and subsequent photolysis otherwise affected. Is this similar in both models? Is there a substantial impact on the oxidation capacity

Table 3: Sensitivity Study: As in Table 4 (main manuscript), but with $\gamma(\text{N}_2\text{O}_5)$ set to either 0.01 or 0.1. calculations with EMEP model, year 2012.

Region	Run	Unit	O ₃	NO _x	NO _y	HNO ₃	PAN	N ₂ O ₅	NO ₃
Test 1: $\gamma(\text{N}_2\text{O}_5) = 0.01$									
NA	Base	Conc*:	41.18	0.84	1.83	0.20	0.57	7.35	5.62
NA	noN2O5pm	%:	3	6	3	-7	5	80	29
NA	noHNO3pm	%:	0	0	-2	18	0	0	1
NA	noNO2pm	%:	0	2	1	-1	0	5	2
EUR	Base	Conc*:	41.89	1.06	2.46	0.24	0.56	12.75	7.88
EUR	noN2O5pm	%:	4	11	2	-12	6	131	41
EUR	noHNO3pm	%:	1	0	-6	60	0	0	3
EUR	noNO2pm	%:	0	5	1	-1	-1	7	4
EA	Base	Conc*:	45.00	2.28	4.68	0.53	0.92	16.98	7.05
EA	noN2O5pm	%:	5	12	3	-16	9	180	61
EA	noHNO3pm	%:	0	0	-2	13	0	0	1
EA	noNO2pm	%:	-1	30	9	-12	-7	16	5
SA	Base	Conc*:	48.05	1.15	2.91	0.41	0.33	11.95	13.39
SA	noN2O5pm	%:	5	9	0	-3	12	107	47
SA	noHNO3pm	%:	1	0	-8	62	0	1	4
SA	noNO2pm	%:	1	4	1	0	1	10	6
Test 2: $\gamma(\text{N}_2\text{O}_5) = 0.1$									
NA	Base	Conc*:	39.30	0.79	1.78	0.21	0.53	2.91	3.24
NA	noN2O5pm	%:	8	13	6	-14	12	354	123
NA	noHNO3pm	%:	0	0	-2	17	0	0	1
NA	noNO2pm	%:	0	2	1	0	0	3	2
EUR	Base	Conc*:	39.69	0.97	2.40	0.26	0.52	4.20	4.55
EUR	noN2O5pm	%:	10	21	5	-20	14	600	145
EUR	noHNO3pm	%:	1	0	-6	56	0	1	4
EUR	noNO2pm	%:	0	5	1	0	-1	5	4
EA	Base	Conc*:	42.83	2.15	4.58	0.56	0.86	8.25	3.95
EA	noN2O5pm	%:	11	19	6	-22	16	477	188
EA	noHNO3pm	%:	0	0	-2	13	0	0	1
EA	noNO2pm	%:	-1	30	9	-10	-8	10	3
SA	Base	Conc*:	45.80	1.06	2.87	0.43	0.31	7.18	8.57
SA	noN2O5pm	%:	10	18	2	-7	22	245	129
SA	noHNO3pm	%:	1	0	-8	60	0	1	4
SA	noNO2pm	%:	1	4	1	0	1	9	5

Notes: as in manuscript Table 4.

Table 4: Sensitivity Study: As in Table 4 (main manuscript), but with $\gamma(\text{NO}_2)$ set to either 0.001 or zero. calculations with EMEP model, year 2012.

Region	Run	Unit	O ₃	NO _x	NO _y	HNO ₃	PAN	N ₂ O ₅	NO ₃
Test 3: $\gamma(\text{NO}_2) = 0.001$									
Region	Run	Unit	O3	NOx	OXN	HNO3	PAN	N2O5	NO3
TEST3									
NA	Base	Conc*:	39.16	0.72	1.73	0.21	0.54	3.88	3.85
NA	noN2O5pm	%:	4	6	3	-6	6	113	45
NA	noHNO3pm	%:	0	0	-2	17	0	0	1
NA	noNO2pm	%:	3	16	5	-4	2	36	21
EUR	Base	Conc*:	39.66	0.83	2.31	0.26	0.54	5.33	4.88
EUR	noN2O5pm	%:	5	9	2	-9	9	191	59
EUR	noHNO3pm	%:	1	0	-7	57	0	0	2
EUR	noNO2pm	%:	3	28	6	-4	-1	53	38
EA	Base	Conc*:	42.95	1.39	4.12	0.64	0.94	7.05	4.45
EA	noN2O5pm	%:	5	5	2	-5	9	127	62
EA	noHNO3pm	%:	0	0	-2	11	0	0	0
EA	noNO2pm	%:	1	109	22	-25	-13	102	28
SA	Base	Conc*:	44.70	0.89	2.73	0.42	0.30	5.31	7.98
SA	noN2O5pm	%:	3	5	1	-2	7	58	31
SA	noHNO3pm	%:	1	0	-8	60	0	0	4
SA	noNO2pm	%:	7	32	7	-2	11	114	59
Test 4: $\gamma(\text{NO}_2) = 0.0$									
NA	Base	Conc*:	40.50	0.84	1.82	0.20	0.55	5.27	4.63
NA	noN2O5pm	%:	6	9	5	-11	9	170	62
NA	noHNO3pm	%:	0	0	-2	18	0	0	0
EUR	Base	Conc*:	41.03	1.06	2.46	0.25	0.54	8.17	6.73
EUR	noN2O5pm	%:	7	17	4	-18	11	304	75
EUR	noHNO3pm	%:	1	0	-6	58	0	0	3
EA	Base	Conc*:	43.59	2.90	5.04	0.48	0.82	14.23	5.72
EA	noN2O5pm	%:	8	21	7	-26	11	336	120
EA	noHNO3pm	%:	0	0	-2	15	0	0	0
SA	Base	Conc*:	47.67	1.17	2.93	0.41	0.33	11.37	12.67
SA	noN2O5pm	%:	7	12	1	-5	16	160	70
SA	noHNO3pm	%:	1	0	-8	62	0	1	4

Notes: as in manuscript Table 4.

	REF	noN2O5	noHNO3	noHO2	noNO2	noNO3	noO3
τ_{CH_4}	8.4	8.1	7.7	8.3	8.3	8.3	8.4
$[\text{OH}]$	1.02	1.05	1.10	1.03	1.03	1.02	1.02

Table 5: CH_4 lifetime and air volume weighted global annual mean tropospheric OH concentration in $10^6 \text{ molec cm}^{-3}$ from ECHAM-HAMMOZ.

which is not that obvious in the well buffered compound O_3 ?

Reply: Table 5 shows CH_4 lifetimes and mean OH concentrations for each run done with ECHAM-HAMMOZ. As can be seen the CH_4 lifetime is 8.4 years in the reference run and gets shortened by more than a month turning off N_2O_5 , HNO_3 reactions. The impact of HNO_3 reaction has strong effect in ECHAM-HAMMOZ, as discussed in the manuscript. Activation of HO_2 reaction prolongs methane lifetime by 22 days. This means that HO_2 loss has a net effect reducing the oxidative capacity. NO_2 reactions have a comparable effect, but less strong effect (just 4 days). Changes in methane lifetime are mirrored in annual mean OH concentrations, which are lowest when methane lifetime is largest. The EMEP model does not diagnose CH_4 lifetimes, so we cannot readily provide equivalent information. (For information, calculations made some years ago suggest however a lifetime of about 9 years for the EMEP model; M. Gauss, Pers. Comm., 2017). Given that changes in CH_4 are somewhat beyond the near-ground focus on ozone and short-lived gases of our other results, and we cannot compare the models, we think it better not to bring this issue up in the manuscript.

1.3 Technical comments

1) Fig. 6 to 8: The grey shaded area is very difficult to see. Please think about a better visualisation of the observations.

Reply: Plots with lines instead of shading for the observations are hard to read, but we will change the colour of the shading to improve visibility.

2) page 7, last line: citation is missing/wrong (ibid)

Reply: Changed

3) page 13, line 7 (wrong line number): citation is missing/wrong (ibid) "transport model, GEOS-Chem (ibid),....."

Reply: Changed

Extra references

Dentener, F. J. and Crutzen, P. J.: Reaction of N_2O_5 on tropospheric aerosols: Impact on the global distributions of NO_x , O_3 , and OH, *Journal of Geophysical Research: Atmospheres* (1984–2012), 98, 7149–7163, 1993.

Tørseth, K., Aas, W., Breivik, K., Fjæraa, A. M., Fiebig, M., Hjellbrekke, A. G., Lund Myhre, C., Solberg, S., and Yttri, K. E.: Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972–2009, *Atmos. Chem. Phys.*, 12, 5447–5481, doi:10.5194/acp-12-5447-2012, URL <http://www.atmos-chem-phys.net/12/5447/2012/>, 2012.