

Interactive comment on “Further improvement of wet process treatments in GEOS-Chem v12.6.0: Impact on global distributions of aerosol precursors and aerosols” by Gan Luo et al.

Gan Luo et al.

gluo@albany.edu

Received and published: 24 April 2020

We thank the referee for the detailed reviews and constructive comments that help to improve the manuscript. Below we respond to the comments in detail. (Referee's comments are in *Italic*).

Interactive comment on “Further improvement of wet process treatments in GEOSChem v12.6.0: Impact on global distributions of aerosol precursors and aerosols” The authors aim to improve the wet processes simulation of aerosols and aerosol precursors in GEOS-Chem v12.6.0 by further revising their previous work Luo et al. (2019), including updates to aqueous-phase chemistry and wet scavenging of

C1

aerosols and aerosol precursors in and below different types of cloud and during different types of precipitation, as well as dry deposition to different wet surface. The authors evaluate their updated wet process simulations using surface and aircraft measurements of aerosols and aerosol precursors concentrations from the US, Europe, Asia and Arctic, as well as AToM-1 and AToM-2 campaigns. This work is interesting and this topic is important for regional and global modeling of aerosol and aerosol precursors.

Thanks for the positive comment about the importance of this work.

However, major revision is recommended before being suitable for publication. While this work represents an admirable set of updates that are ostensibly improvements, the main drawback is that there is no systematic exploration of the impacts of any of the updates included in this paper. All changes are updated simultaneously, and then the model is evaluated in a rather generic fashion, without for example seeking out spatiotemporal subsets of data that would be most useful for isolating the impacts of any of the processes studied here. Notably, neither wet deposition measurements nor precipitation measurements are considered in the model evaluation. While the overall simulation updates are indeed an improvement, the paper leaves a bit to be desired in terms of explanations and scientific analysis. I believe addressing these requires more targeted use of the observations, additional simulation that examine the impact of subsets of the model updates tested individually, and evaluation of these to potentially refine some of the assumptions made during the model development. The work needs extensive proofreading throughout (every paragraph contains several grammatical errors; it goes beyond what I'm willing to edit myself), and several of the references are inappropriate. Further comments are described below.

Thanks for the constructive comments. The manuscript has been revised following the suggestions.

Major comments: 1. As this work focus on improving the wet processes (mainly wet scavenging) simulation of aerosols and aerosol precursors, validation by mea-

C2

measurements of wet deposition of aerosols and aerosol precursors is quite necessary given the availability of a bunch of wet deposition measurements over the US (<http://nadp.slh.wisc.edu/ntn/>), Europe (<https://projects.nilu.no/ccc/emepdata.html>) and China (<https://www.nature.com/articles/s41597-019-0061-2>) and also from EANET network (<https://www.eanet.asia/about/site-information/>). Please at least validate your simulated wet deposition of sulfate + SO₂, nitrate + HNO₃, ammonium + ammonia using available measurements. Precipitation itself should also be evaluated.

We added comparison of simulated wet deposition of sulfate+SO₂, nitrate+HNO₃, ammonium+NH₃ with available measurements. Associated discussions are in section 3.1.

2. Although the authors claim that they have surface measurement-based validation for Asia, the number of the Asian sites is very limited and none of these sites is in China or India, where there are high emissions of aerosols and aerosol precursors and a large amount of precipitation. So robust validations in China and India are necessary if the authors claim that their updates also improve aerosol and aerosol precursor simulation for Asia.

We clarified in the revised paper that wet process updates improve aerosol and aerosol precursor simulation over Asia remote regions.

3. The number of AMoN/EANET sites in Figure 7 seems to be much fewer than the total number of AMoN/EANET sites. Please give a brief description of all the measurements (IMPROVE, CSN, CASTNET, AMoM, EMEP, EANET, AToM-1 and AToM-2), number of valid sites, and data filtering you are using.

The criterion of observations used for model validation is that valid data are available for every month in 2011. For EANET observations, due to too much missing data, the criterion is loosen to monthly mean data available for each month during a 3-year period (2010-2012). Seto et al. (2007) pointed out that EANET observations at urban sites are much higher than those at remote sites. Since the number of the Asian sites

C3

is very limited, to make the validation more appropriate, only remote and rural sites are used for model validation. A brief description on these has been added at section 3.1.

Seto, S., Sato, M., Tatano, T., Kusakari, T. and Hara, H., Spatial distribution and source identification of wet deposition at remote EANET sites in Japan. Atmos. Environ. 41, 9386–9396, 2007.

4. Quantitative evaluation for simulated vertical profiles of aerosol and aerosol precursors using AToM-1 and AToM-2 aircraft measurements is necessary to support your conclusions about improvements using your updated wet processes.

Normalized mean biases (NMB) and correlation coefficient (r) have been used to quantitative evaluation for simulated vertical profiles of aerosol and aerosol precursors with AToM-1 and AToM-2 aircraft measurements.

5. Section 2.6: How are wet surfaces defined in GEOS-Chem? Are these based on land-type or some other classification? Are they altered by precipitation? Overall this strikes me as a level of details beyond what this model can actually resolve.

GEOS-Chem determined wet surfaces based on land use type from the Olson 2001 land map (Olson, 1992). They are not altered by precipitation. This has been clarified in the text.

Olson, J, World Ecosystems (WE1.4): Digital raster data on a 10 minute geographic 1080 x 2160 grid, in Global Ecosystems Database, version 1.0, Disc A, edited by NOAA Natl. Geophys. Data Center, Boulder, Colorado, 1992.

6. Fig 1: a. It seems evident that the updates in both L2019 and WETrev degraded the model performance for SO₂ and SO₄ in the US, especially for SO₂. This needs to be mentioned, explicitly, and discussed.

Accepted.

b. Why is the modeled SO₄ seasonality incorrect in comparison to EANET?

C4

It is caused by the overestimation of January SO₄ at Primorskaya, Russia (43.63°N, 132.24°E) whose value is high up to 12 μg m⁻³, 2.5 times higher than observation at this site. This overestimation is associated with aqueous phase chemistry over there.

c. Fig 1: Are model values for entire region or only sites at which observations are available?

Model values were sampled at sites where observations are available.

d. Other factors mentioned in previous studies that may possibly impact overestimated HNO₃ and nitrate concentrations are the constant hourly emissions of NH₃. Has that been addressed here?

The present version of GEOS-Chem considers diurnal, seasonal, and interannual variability of ammonia emission.

e. The authors seem to gloss over the impacts on NH₃. First, the initial model performance compared to the observed NH₃ concentrations is surprisingly good, given uncertainties in NH₃ emissions. Second, there does seem to be significant difference between WETrev and the other simulations, in comparison to the observations. In many months it would appear the bias compared to the measurements has increased by up to a factor of 2. None of the simulations correctly replicate the spring time NH₃ maximum, most notably in Europe.

The unreasonable seasonal variation of ammonia in the Europe is caused by the updated emission treatment in GC12.6. GC12.6 replaced old EMEP emissions and seasonal scaling factors with CEDS global emissions. After switching back to EMEP emissions, seasonal variation of ammonia was captured by the model. We rerun the cases with EMEP emissions and updated the results in the revised manuscript.

7. Figs 7 - 8: It is hard to get much out of the comparison to observations in these figures. Those are better represented by the previous figures, or require zoomed subplot of the US, Europe and E Asia. What would be more useful in Figs 7 - 8 would be to

C5

see the base case model (GC12) and the differences between this model and WETrev, as absolute and relative differences.

The two figures were provided to show the impacts of WETrev on a global scale. One can derive globally averaged absolute and relative differences from values given on top of each panel. Interested readers can use the enlarge function for pdf figures to zoom into specific regions. There will be too many figures if we provide zoomed subplots and plots for both absolute and relative differences.

Minor comments: 1. Page 1, line 25-28: "we compared model simulation . . . successfully improved by considering the updated wet processes." Please give quantitative metrics to support this conclusion.

Quantitative metrics have been added.

2. Pag1, line 20: So results for the decrease in NMB of these species in the US are from L2019? If so, probably shouldn't be presented in the abstract as results from the current study.

The decrease in NMB of these species is mainly caused by the updated ICCW and empirical washout. Excluding the results in the US sounds strange here.

3. Page 3, line 26 and page 12, line16: I don't think the web site wiki is a suitable citation Please refer the peer reviewed literature upon which such material is based.

As shown in the web site wiki, H* of SO₂, H₂O₂, and NH₃ for dry deposition was originally in $\text{drydep}_{mod.F.We}$ were not able to locate the peer reviewed literature on this.

4. Page 6, line 16-17: "we assume that total amount . . . aerosol thermodynamics (SNVC) is 25 % of sulfate". Why do you use 25% here? You should have some rational for this 25% although it is assumed.

It is based on the work of Guo et al. (2018) cited in the text which suggested ammonium-sulfate aerosol molar ratio is $1.47 \pm 0.43 (\approx 1.5)$.

C6

5. Page, line 22-30: You are encouraged to validate your rainwater pH using precipitation pH measurements over the US, Europe and Asia.

We will investigate this in our future work.

6. Page 6, line 2: I'm curious how this problem is formulated and how the updated solution method using Newton's method is applied. These are the sorts of details that should be described explicitly here, at the level at which they are reproducible from reading the text. Citation of unpublished preliminary work from a conference presentation (Moch 2019) is not an adequate reference nor explanation.

More detailed description on this has been added.

7. Page 6, line 17: What is the basis for picking 25% here? No explanation or reference has been provided.

The assumption of 25 % is based on the work of Guo et al. (2018) cited in the text. More robust calculation of SNVC need to be investigated in future works.

8. Section 2: It's not clear how this particular model distinguishes / defines the processes of rainout vs washout could this be clarified?

Rainout is the removal due to formation of precipitation in cloud, while washout is the removal due to falling precipitation from upper layers. This has been clarified in the text.

9. Page 7, line 22-27: I can understand that you take the ice surface as an aqueous layer when temperature higher than 263K in the mixed cloud, and this means aqueous chemistry can happen at the surface layer of the ice cloud. But I don't understand why it is reasonable to assume aqueous phase cloud fraction equals grid mean cloud fraction: $f_{aq}=f_c$. This formula means you assume the aqueous chemistry happen in the ice cloud the way as it does in an aqueous cloud, not just at the pre-melt layer of the ice cloud, most of which is ice-phase. The ice-phase cloud water in one grid is 3 dimensional and I can accept the assumption that the aqueous chemistry can happen

C7

at the surface pre-melt layer, but it doesn't make sense that the aqueous chemistry can happen in an ice-phase cloud the way in aqueous-phase cloud. Also, does this assumption of aqueous layer of ice also increase the wet scavenging of HNO₃ in the same grid cell?

Yes, it is right. Due to uncertainty of the thickness of aqueous layer of ice, we decide to only use equation 9 to calculate aqueous phase cloud fraction. The assumption of aqueous layer of ice does not increase the wet scavenging of HNO₃ in the same grid cell.

10. Page 8, line 14 – 18: It's not clear to me this is double counting. It seems one process describes the absorption and the other the oxidation, with both steps being necessary. Am I missing something here? If so, could the authors explain the model treatment of these processes in more detail? Schematics could be helpful.

In GC12, rainout of SO₂ is limited by the aqueous phase oxidation of SO₂ by H₂O₂ rather than the absorption by cloud water (Chin et al., 1996). However, the conversion of SO₂ to sulfate in cloud has been accounted for in the aqueous phase chemistry. In this work, rainout of SO₂ is limited by the absorption by cloud water. More explanation of the processes has been added in the revised text.

11. Page 8, line 25-30: "the rationale . . . as water soluble aerosols . . . The composition . . . for cloud activation calculation." Please include some appropriate references here.

Added. Abdul-Razzak, H., and Ghan, S. J., A parameterization of aerosol activation: 2. Multiple aerosol types, J. Geophys. Res., 105(D5), 6837– 6844, doi:10.1029/1999JD901161, 2000.

12. Page 9, line 1-3: "However, in the actual atmosphere, . . . coated with SNA". Please also include some appropriate references here.

Added. Fassi-Fihri, A., Suhre, K., and Rosset, R.: Internal and external mixing in

C8

atmospheric aerosols by coagulation: impact on the optical and hygroscopic properties of the sulphate-soot system, *Atmos. Environ.*, 10, 1393–1402, 1997.

13. Page 9, line 29-30: “While most of . . . smaller than 500 nm.” Please include some appropriate references here.

Added. Sahu, L. K., Y. Kondo, N. Moteki, N. Takegawa, Y. Zhao, M. J. Cubison, J. L. Jimenez, S. Vay, G. S. Diskin, A. Wisthaler, T. Mikoviny, L. G. Huey, A. J. Weinheimer, D. J. Knapp, Emission characteristics of black carbon in anthropogenic and biomass burning plumes over California during ARCTAS–CARB 2008, *J. Geophys. Res.*, 117, D16302, doi:10.1029/2011JD017401, 2012.

Zender, C. S., Bian, H., and Newman, D., Mineral Dust Entrainment and Deposition (DEAD) model: Description and 1990s dust climatology, *J. Geophys. Res.*, 108, 4416, doi:10.1029/2002JD002775, D14, 2003.

14. Page 10, line 4 – 8: How was this treated in the original model?

GC12 assumed rainout efficiency of water-soluble aerosols by cold cloud is 100 %. This is clarified in the revised text.

15. Page 13, line 15-17: “One possible reason is . . . at urban sites . . . remote regions.” Please include some appropriate references here.

We didn’t find related reference. There were 288 EPA’s Air Quality System sites with valid data in each month of 2011. 69 of these sites were with the mark of ‘Not in a city’. More information can be found at <https://www.epa.gov/outdoor-air-quality-data>.

16. Page 13, line 29: Is there a scientific explanation why one would revert this change, in terms of understanding of heterogeneous chemistry? Or are the authors alternatively suggesting that these parameters be adjusted so that the model estimates better fit the data?

Uptake coefficients for heterogeneous chemistry on sulfate in the work of Holmes et

C9

al. (2019) are 10 times smaller than those used in GC12.5 which lead to less nitric acid production in GC12.6 than that in GC12.5. Due to large uncertainties of uptake coefficients for heterogeneous chemistry, further investigations are needed. Yes, at this point, we are suggesting that these parameters be adjusted so that the model estimates better fit the data.

17. Page 14: line 1-2: “The aqueous concentration of ammonia is much lower than nitric acid, . . . small impact on the simulation of ammonia.” How does this conclusion come? Isn’t it because the increasing ammonia wet deposition is compensated by less reaction with decreased HNO₃ in the air?

This is a good point and we agree it is because the increasing ammonia wet deposition is compensated by less reaction with decreased HNO₃ in the air. We have modified the sentence to reflect this.

18. Page 14, line 27-28: “The underestimate is likely . . . wildfire . . . US.” Please include some appropriate references here.

Added. Mao, Y. H., Li, Q. B., Henze, D. K., Jiang, Z., Jones, D. B. A., Kopacz, M., He, C., Qi, L., Gao, M., Hao, W.-M., and Liou, K.-N.: Estimates of black carbon emissions in the western United States using the GEOS-Chem adjoint model, *Atmos. Chem. Phys.*, 15, 7685–7702, <https://doi.org/10.5194/acp-15-7685-2015>, 2015.

19. Page 15, line 30-31: “Most of BC at Arctic . . . anthropogenic emissions,” Please include some appropriate references here.

Added. Xu, J.-W., Martin, R. V., Morrow, A., Sharma, S., Huang, L., Leaitch, W. R., Burkart, J., Schulz, H., Zanutta, M., Willis, M. D., Henze, D. K., Lee, C. J., Herber, A. B., and Abbatt, J. P. D.: Source attribution of Arctic black carbon constrained by aircraft and surface measurements, *Atmos. Chem. Phys.*, 17, 11971–11989, <https://doi.org/10.5194/acp-17-11971-2017>, 2017.

20. Page 16, line 7-11: Please provide figures for the tracks of ATom-1 and ATom-2.

C10

And why do you filter out tracks over land? Could you provide profile comparison over land?

The flight tracks of ATom-1 and ATom-2 are shown in Fig. 1, while vertical profiles over land are shown in Fig. 2. These figures have been provided in supplementary materials. ATom observations over the land, whose values vary greatly, only account for 28 % of total measurements. To make the comparison more appropriate, we filtered out the flight tracks over the land.

21. For the whole section 3.3, please give quantitative metrics (e. g. NMB and R) to show how your updated wet scavenge schemes work in reproducing the observed profiles of these chemical species. Figure 5 (a) shows WETrev underestimate HNO3 throughout the whole layers except for high bias at upper layer (nearby 200 hpa). Figure 6 shows that L2019 and WETrev largely underestimate HNO3 at lower troposphere (>800 hpa).

Added as suggested.

22. Page 17, line 6: With regards to “in this work,” it seems that a bulk of the improvements are from the updates in L2019, more so than the present work.

We modified it as: the updated wet process treatments in this work and L2019 can improve the agreements of simulated and observed vertical profiles of nitric acid and aerosols.

23. Page 18 line 25 - page 19 line 6: please try to quantitatively and appropriately show how your updates improve the simulation. Like your 5th conclusion on page 19 line 5-6: “The updated wet surface . . . SO2 at Arctic sites”, I am not so sure whether your conclusion is fully supported by figure 3 or not.

Accepted. Quantitative metrics have been added. For 5th conclusion, we found NMB of SO₂ is increased from -23 % to 32 % at Nord and decreased from 27 % to 2(5) The updated wet surface uptake during dry deposition changes the performance of

C11

simulated SO₂ at Arctic sites. NMB of SO₂ is increased from -23 % to 32 % at Nord and decreased from 27 % to 22 % at Zeppelin.

Interactive comment on Geosci. Model Dev. Discuss., <https://doi.org/10.5194/gmd-2020-11>, 2020.

C12

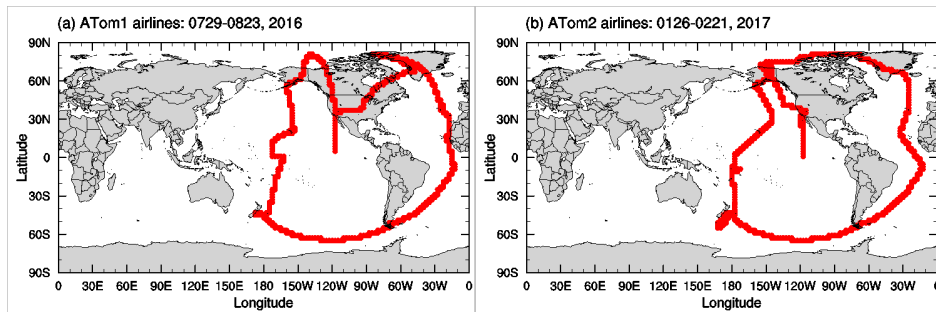


Fig. 1. The flight tracks of (a) ATom-1 and (b) ATom-2.

C13

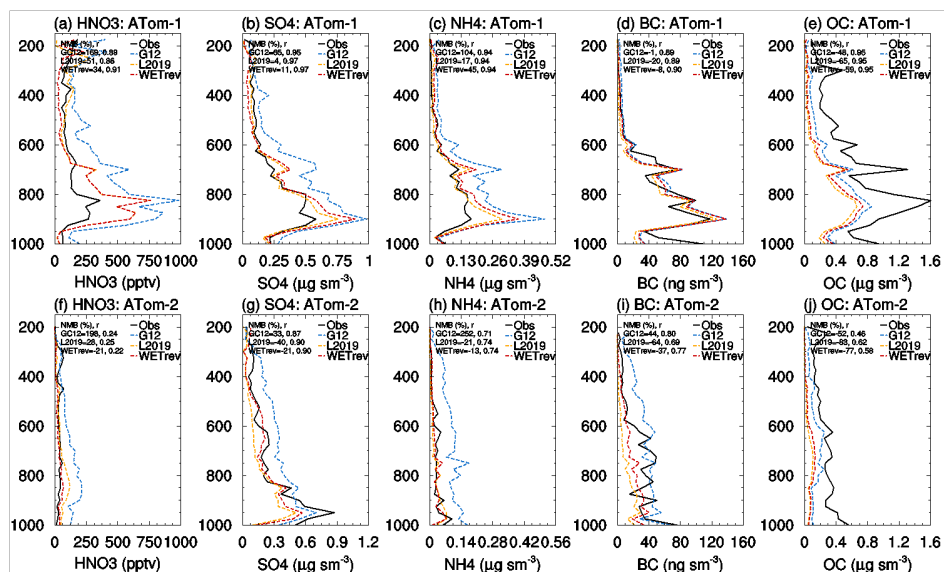


Fig. 2. Vertical profiles of nitric acid, sulfate, ammonium, black carbon, and organic carbon from ATom aircraft observations (black, ATom-1: a-e; ATom-2: f-j) and GEOS-Chem simulations by GC12 (blue), L2019

C14