

Interactive comment on “Derivation of Antarctic stratospheric sulfuric acid profiles and nucleation modeling of the polar stratospheric CN layer” by Steffen Münch and Joachim Curtius

Anonymous Referee #2

Received and published: 29 August 2016

This paper follows some work by Campbell and Deshler [2014] to derive a sulfuric acid mixing ratio profile from observations of temperature and rate of nucleation of new particles, assuming binary homogeneous nucleation. The present work employs a microphysical box model (SAWNUC) to derive the sulfuric acid mixing ratio necessary to reproduce the CN observations of Campbell and Deshler [2014]. This is a useful exercise and should lead to a publishable paper. Unfortunately the present paper needs a lot of work to bring it to scientific maturity and there are some major issues that need to be clarified.

The primary issue is the authors' seeming assumption that underlying the presence of any stratospheric sulfuric acid particle concentration is a necessary sulfuric acid

C1

concentration. Yes there was a sulfuric acid profile at one time, but once the sulfuric acid condenses its concentration decreases to vanishing amounts. Because there are CN particles existent during polar winter does not mean that they were nucleated then and there. Stratospheric CN are ubiquitous in concentrations near 10 cm^{-3} . Thus as the polar vortex forms the CN particles present at the beginning will persist in the vortex, their sedimentation quite negligible. The observations of Campbell and Deshler [2014] bear this out for much of the CN profiles they present. Here, however, the authors derive a sulfuric acid mixing ratio profile in times of the year and altitude regions where no new particle formation is observed. They then speculate on what could be causing the oxidation of SO_2 to obtain the sulfuric acid. Isn't this speculation on possibly an imaginary profile?

I understand when sulfuric acid particles are present there will be a residual sulfuric acid concentration; however, given that the vapor pressure of 75% by weight sulfuric acid is exceedingly low, this concentration will be quite small. Is this what is calculated by SAWNUC in the absence of new particle formation? The authors need to make clear at the outset how the observations of new particle formation are used in deriving the sulfuric acid profiles and how such profiles are obtained in the absence of new particle formation. In the latter case can there be anything more than an upper limit?

The other major issue is the writing is not up to the standards expected for a scientific paper. The writing is imprecise, many details are missing, while irrelevant comments creep in. The authors should consider having some English help prior to the next submission and not keep the reader working out what is intended to be said.

Here are more specific details.

1.13. Reproduces what observations? Be specific here. Reproduces the new particles that are observed or ...?

1.14 As will be mentioned further, below, it is not clear how a sulfuric acid profile is obtained in July. At most this should be an upper limit.

C2

1.16 “the observed magnitude of CN...” What does this mean? Was nucleation of new particles observed at higher temperatures?

1.18-19. The authors have not convinced me of the need to include a sulfuric acid production rate, which is then one further step removed from the observations. Thus I see no need to go further and try and explain a winter-time production mechanism, when it has not been established that one is required.

1.20. Why is there no comparison with the sulfuric acid profile derived by Campbell and Deshler [2014]?

1.23-26. This is a terrible first sentence. In fact it is not even a sentence. The clause set off with commas is a complete sentence and should stand on its own. But it is still a poor first sentence. In fact the definition of condensation nuclei (CN) is not correct. Condensation nuclei are observed by forcing small particles to grow to optically detectable sizes using a condensing fluid and a supersaturation chamber. There are a number of references available on the technique and perhaps one should be included. The size ranges vary somewhat, but typically the CN concentration is used to define the total aerosol concentration larger than some nominal size, say 10 nm. CN measurements also include particles > 300 nm, but their concentration is inconsequential compared to the total aerosol population.

1.27. Not all CN are formed by nucleation. It appears a significant fraction of CN are non-volatile suggesting that this fraction of CN particles appears due to the condensation of sulfuric acid on pre-existing solid cores [Borrmann et al., 2010; Campbell and Deshler, 2014].

2.12. Where does the h₂so₄ in the mesosphere come from to be available for photolysis?

2.15 “performed continuously for 24 years” What does this mean every month, every day? I understood the observations are only available for a few months each year.

C3

2.17-20. Very awkward sentence. Try. They present monthly averaged CN concentration and temperature profiles which capture the unperturbed CN, with concentrations around 10-20 cm⁻³ in June/July as well as the development of a layer of particles at 20-25 km, with concentrations increasing to 100 cm⁻³ from August until October during sunrise and warming.

2.26-28. Campbell et al. [2014] did not invert the nucleation equation, they ran a three dimensional chemistry model which produces its own h₂so₄.

2.30. Who are they?

3.30. Delete the sentence, “This section describes the derivation of the Antarctic stratospheric sulfuric acid profiles” and add the information to section title, e.g. Deriving the Antarctic stratospheric sulfuric acid profiles.

4.14. “3e5 ion pairs per gram of air and second” Awkward. Use standard SI units and symbols to describe a rate.

4.16-18. There should be some references for the water vapor profile and the diabatic descent rate?

4.19-24. 100 nm is at the upper limit of possible pre-existing particles. What concentrations are used for these particles? Since the surface area is chosen based on reasonable sources why is the particle size important? What does it mean that the surface area was converted ... according to the ideal gas equation? Do you mean the surface area density was adjusted to different temperatures and pressures assuming a constant mixing ratio?

4.28-31. Is there really a trajectory of an air parcel here, or do the authors just mean variations in the various parameters required by the SAWNUC model? The language is confusing. If the latter then I think the more appropriate words would be box model simulation rather than air parcel trajectory. If the former then where does the air parcel start, what altitude, location, dimensions? What does it mean to “connect” to the

C4

monthly maximum of the measured CN? Do the authors mean the trajectory which reproduces the monthly maximum CN concentration? The next sentence is equally awkward, "It is assumed that this maximum of the particle concentration resides in a single air parcel that descends inside the polar vortex." The maximum of the particle concentration doesn't reside in the air parcel until the nucleation has occurred. What the authors are trying to suggest, as far as I can understand, is the optimum trajectory to reproduce the observed maximum in CN concentration. The phrase "maximum trajectory" does not convey this idea and I would recommend changing this language to something more representative of what is being simulated. Something like optimum trajectory to reproduce the observed maximum in CN concentration. This maximum in CN concentration is height dependent. Is this height dependence consistent with the diabatic descent in the model?

5.1. I believe the authors mean the sulfuric acid concentrations were varied on a monthly basis? Search implies that these concentrations exist on some data base or?

5.4-6. Awkward and unnecessary detail. The authors are merely iterating the model until they achieve a match with the measured CN by varying the sulfuric acid concentrations. If so say this. It is not the sulfuric acid concentration that corresponds to the monthly CN concentrations, it is the simulated CN concentrations based on the sulfuric acid concentrations. The writing here and elsewhere is awkward and requires the reader to do a lot of guessing as to what is meant.

5.14-18, Fig. 1b. The model is initialized with a CN concentration of zero. Is this realistic? There will be some residual particles, CN, persisting in the air as the polar vortex forms. It seems more plausible to assume these residual particles appear as the background of about 10 cm-3 shown in Campbell and Deshler [2014] outside of the CN layers than to assume a concentration of zero. If the model is allowed to initialize to 110% of the June/July CN maximum, then there would not be any further new particle formation in the June/July period. So no additional sulfuric acid is required. This point

C5

needs to be clarified.

5.18-19. Since the model is already at 110% of the CN maximum, why is further searching required? Is sulfuric acid required to maintain the pre-existing particles? Are these particles losing sulfuric acid? I understood these particles change size due to fluctuations in water based on temperature but not on the loss of sulfuric acid.

It is not clear how the subsequently derived sulfuric acid profile for June/July is obtained. How does it differ from the sulfuric acid profile that is required to build up the CN from zero to 110% of June/July values? How does the work here then take advantage of the measurements which show a maximum of CN near 30 km above a possible background of around 10 cm-3? If there is no new particle formation in June July then the speculation on the source of a sulfuric acid profile is misplaced.

5.26. Please show the mean CN values on Fig. 1 a. It would also be instructive to include on both panels the observations which are being reproduced.

5.27-28. If there is a decrease from June/July – August as could be argued from Campbell and Deshler [2014] since the CN maximum concentration does not change in their Fig. 1, then it appears again that no new particles are formed so only an upper limit can be placed on the sulfuric acid concentration.

5.32. How is this month long time interval different than the previous ones? Why is the sulfuric acid concentration now strongly increased? In Campbell and Deshler [2014] there is almost no change in CN concentration between September and October in the CN layer, arguing again for little information on a sulfuric acid profile.

5.10-6.4 and Fig. 1a). Is all of this necessary to understand what is done, and do the authors really want to explain the subtleties of Fig. 1a? In the end more realistic time steps are used and profiles created. I don't really think the reader is benefitting any from the previous discussion and it raises many questions such as listed above.

6.17-24. This paragraph is confusing by suggesting that the sulfuric acid is dependent

C6

on other processes in the model rather than just the amount needed to create the CN maximums. Here the authors claim that the sulfuric acid is dependent on sunlight, which we know it is, but I didn't think this was considered by the SAWNUC model.

6.21. What is meant by, "the chemical lifetime of SO₂ by OH"?

6.23. Since the authors are now dealing with monthly averages, how can they make this claim, "Starting in September, the sulfuric acid amount increases first slowly and then strongly from September to October"? Monthly averages cannot supply this information.

Fig. 1b. What is the explanation for the fast rise in CN near the beginning of September, while the sulfuric acid only increases at the end of September? What is causing the CN formation if not the sulfuric acid? There is a disconnect here.

6.26. "To complement the profiles" What profiles? So far the authors have been calculating the conditions required to reproduce the maximum in observed CN concentrations. This would then only be a sulfuric acid concentration at one altitude in one month. Perhaps the authors intend to say they will now create profiles. If so the title of this section is misleading.

7.3 "in September" is redundant and should be deleted.

Section 2.2.3 and Fig. 2. This section and figure raise again my main question about this work. How is a sulfuric acid profile derived if there is no new particle formation? The CN layers in the CN profiles shown by Campbell and Deshler [2014] are limited in altitude to a fraction of the 18-40 km to be investigated here. Thus, for example in September above 27 km there is no evidence of new particle formation. So can anything more than an upper limit be placed on the sulfuric acid profile? Yet Fig. 2 shows the September sulfuric acid profile to continue to increase above 27 km. How are profiles created to 40 km when there are no observations above 35 km?

7.10-15. Here again the authors are discussing results suggesting that the sulfuric

C7

acid profile is derived from sources outside the matching of the SAWNUC model with observations of CN.

7.17 "the shapes of both profiles are very similar" The authors discuss the temperature profile as if it were shown in Fig. 2, but it is not. Thus the readers cannot follow this point. The temperature profile should be included in Fig. 2.

7.19-21. I don't understand. Do the authors mean there is a narrow sulfuric acid concentration range leading to the nucleation of particles in the 10-100 cm⁻³ range? There is no reason particles cannot exist at these concentration levels if they are already there. The nucleation rate is not in a small window. The nucleation rate is determined by the concentration and the temperature. The small window is determined by both temperature and sulfuric acid concentration. Far too many or too few CN for what? I thought the particle concentrations were used to derive the sulfuric acid profile given the temperature, so if there are more or less CN this just affects the sulfuric acid concentration.

7.22. "20 or 50 particles present" Are these particles already existing or nucleated particles? I assume the authors mean an observation of 20 – 50 new particles has a small influence on the derived sulfuric acid.

7.25-26. This is confusing. If the CN layer were not observed then there would be no attempt to derive the sulfuric acid profile. Above and below the CN layer there is not enough information to derive the sulfuric acid profile, only upper bounds, determined by the temperature, can be placed on it.

7.30. This statement is not correct CN instruments measure all particles above some nominal size, typically about 10 nm. In addition I believe Campbell and Deshler report observations explicitly of particles > 150 nm using a second instrument, and no enhancements of these particles were observed in the CN layers.

7.27-29. These statements should give the authors pause to consider if there is an

C8

error somewhere rather than trying to explain these high sulfur amounts.

7.30-32. This argument is incorrect. The water vapor concentration is low throughout the stratosphere. The particles are not composed of water but a sulfuric acid water mixture and the temperature determines how much water is retained by the highly acidic particle. The water vapor concentration has nothing to do with it, only temperature. There are plenty of water molecules.

7.32. "To compensate there high . . ." For the reasons above I don't understand this argument. Isn't the nucleation of particles dependent on the gathering of critical clusters of the acid not the water?

8.5-7. Why is this assumption made? Campbell and Deshler, Fig. 5 show directly that the non-volatile fraction above 25 km is similar to that below 20 km, about 60%. It is not at all clear how the authors derive a sulfuric acid profile when there is no obvious nucleation. Again there can only be an upper bound.

Fig. 3. Why isn't the profile derived by Campbell and Deshler [2014] included in this figure?

8.33 "However, in the areas of higher temperatures the CN are almost exclusively produced by ion-induced nucleation." This assumes that CN are nucleated, but there is really no evidence for this, thus it is questionable whether any CN are nucleated in these areas. Sentence should be rewritten to reflect that, if particles nucleated they would require ion-induced nucleation, but in fact there is no evidence that such particles are nucleated.

10.29-30. What is over/under estimated? Why is it clearly related to the months? I believe the authors mean the size cutoff measurement uncertainty.

11.7-8. This seems somewhat obvious as all the nucleation occurs in August, September. When there is no new particle formation this approach can only provide an upper bound on the sulfuric acid.

C9

11.15-16. Sulfuric acid evaporating from freshly forming particles? How does this occur? My understanding is that the vapor pressure of sulfuric acid is very low, thus it condenses readily and then stays condensed. Same question about pre-existing particles. At the temperatures used in the modeling I would not believe that the pre-existing particles would do much more than adjust their water content to the temperature changes.

11.14-18. If I understand correctly the production rate is simulated by continually adding the necessary H_2SO_4 molecules to simulate the observations without specifying where the molecules come from e.g. SO_2 , or particles. Thus all this discussion about the possible sources is speculation without basis and should be eliminated.

11.22-25. I am again confused as to why there is production of H_2SO_4 in June July when the CN particle concentration is not changing from the model initialization. Much of the rest of this paragraph is again speculation and should be strictly limited.

12.1-4. This is all redundant.

Overall the paper would not suffer if section 3.3 and figure 6 were removed.

12.13-15. It is not clear why SAWNUC is predicting a sulfuric acid mixing ratio at this time in this region.

Borrmann, S., Kunkel, D., Weigel, R., Minikin, A., Deshler, T., Wilson, J. C., Curtius, J., Volk, C. M., Homan, C. D., Ulanovsky, A., Ravagnani, F., Viciani, S., Shur, G. N., Belyaev, G. V., Law, K. S., and Cairo, F.: Aerosols in the tropical and subtropical UT/LS: in-situ measurements of submicron particle abundance and volatility, *Atmos. Chem. Phys.*, 10, 5573-5592, doi:10.5194/acp-10-5573-2010, 2010.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2016-583, 2016.

C10