Author's response to the discussion paper:

Nucleation modeling of the Antarctic stratospheric CN layer and derivation of sulfuric acid profiles

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We thank the reviewers for carefully reading our manuscript and for providing numerous helpful comments. The reviewer comments are given below in black font with our replies in blue font. Text that was changed in the manuscript is shown in red font.

Note that the simulations were not changed for this revision. Most changes concerned the writing style and additional information and sensitivity tests were added at some places.

Answers to Referee # 1

Version 2 of this paper is significantly improved in regards to the scientific significance and quality of the SAWNUC model results presented; however, it still needs improvement in some of the analysis methods and discussion of the results, and in the presentation quality and writing.

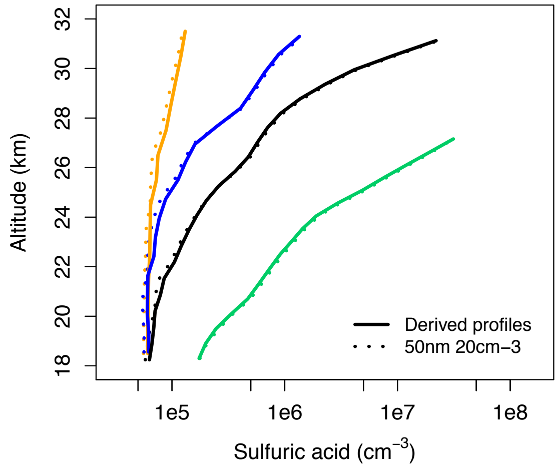
The main issues raised by both Reviewer 1 and 2 on Version 1 of the paper are well addressed, where major changes have been made to provide a more focused paper on Antarctic CN layer formation, while providing valuable results that include derived sulfuric acid profiles in the Antarctic stratosphere (no measurements available). Some of my concerns that should be addressed going forward include the 1) impacts from preexisting particles, 2) temperature effects and sensitivity simulations, 3) trajectories of subsiding air parcels, methods, and sensitivity simulations, 4) zero sulfuric acid conditions for coagulation assessment, 5) initial preexisting particle size sensitivity simulations, 6) fixed ionization rate with altitude, 7) comparison against mid-latitude sulfuric acid concentrations, and 8) main conclusions and writing style. Please see the annotated PDF copy of my edits, suggestions, and final questions. Thank you.

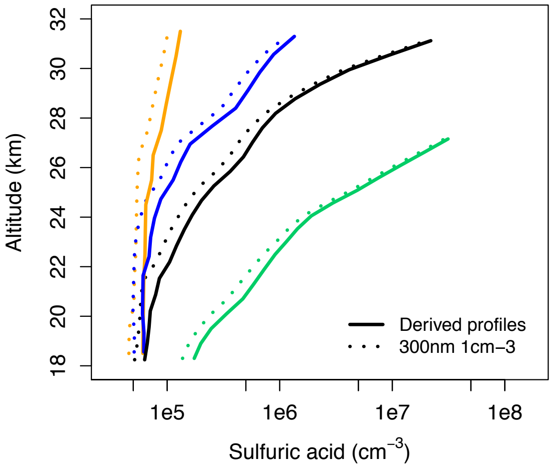
Thank you for carefully reading our manuscript again, pointing out the unclear sections, and making suggestions for improvements. Our detailed answers are given below. We first answer the larger points in combined answers and then answer to the remaining individual points.

Preexisting particle size

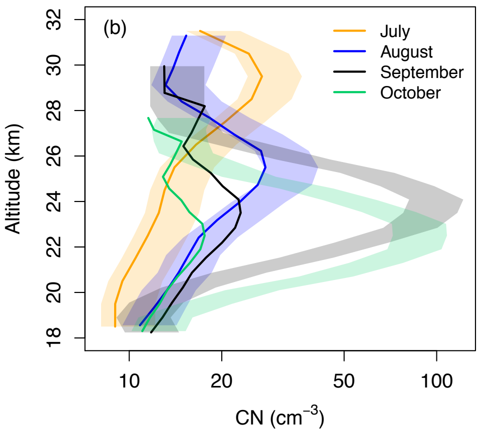
4.19-21 This is a difficult argument to sell, as the pre-existing particles would of course be a mixture of sizes. We actually do have measurements of the size distribution of pre-existing particles from OPC measurements (down to a optically detectable size of 300 nm in diameter) during the time just before new CN formation above McMurdo (see Deshler or Hofmann papers), but you are correct that we don't know the size distribution of the smaller "pre-existing CN" that are below the optical detection limits (< 300 nm diameter). Thus it is understandable you must make an arbitrary size of pre-existing CN at 10 cm-3 at 100 nm, but why not slightly increase the sensitivity test concentration at 50 nm since we could assume more particles at the lower size, while also maybe a test at a larger size but lower concentration, say 300 nm and 1 cm-3 (this has been observed in the stratosphere)?
7.29-30 When lowering the size from 100 nm to 50 nm, should you still assume the 10 cm-3 concentration, or should you increase it somewhat (e.g., 20 cm-3). What about a test at a much larger pre-existing particles, say 300 nm at 1 cm-3, which we have OPC measurements that confirm their existence in the stratosphere?

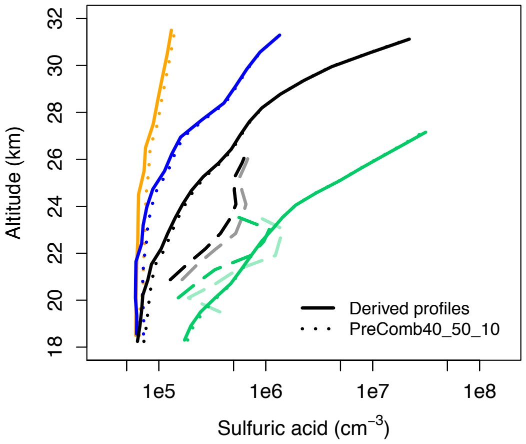
We performed the suggested sensitivity tests only for the nucleation threshold profiles as this changes the initial number of CN and then CN reproduction doesn’t work any more:





However, we can make a more sophisticated test. Here we redo the simulations but instead of assuming all preexisting particles to be 100 nm, we now assume that 10% are 300 nm, 50% are 100 nm, and 40% of the preexisting particles are 50 nm in size.





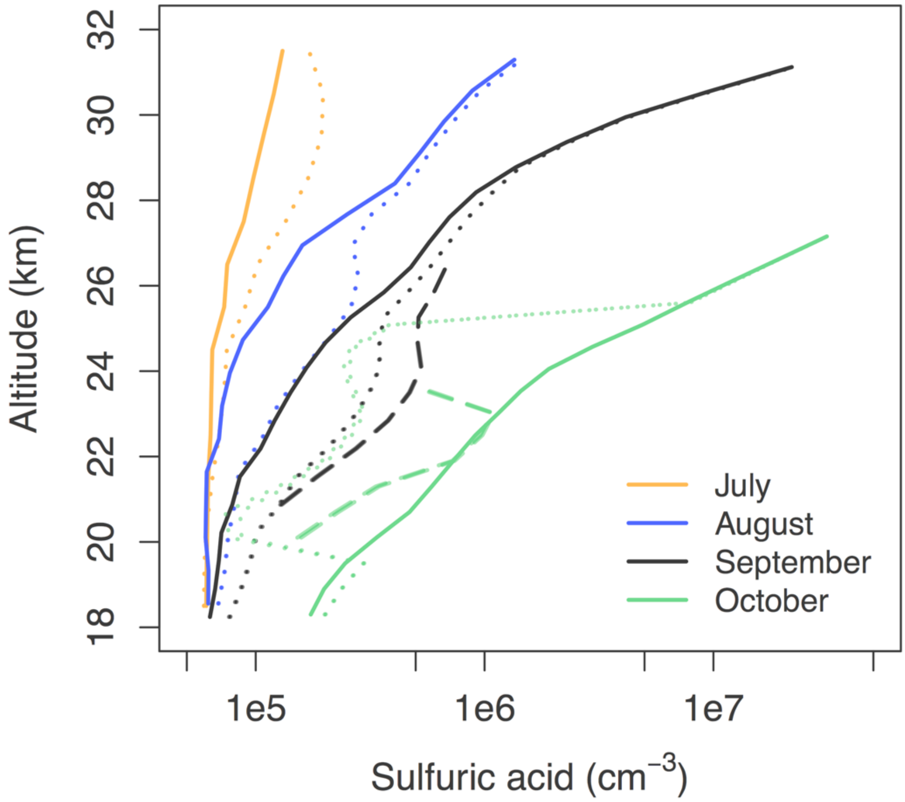
Here we see that this reduces the simulated CN and increases the derived sulfuric acid profiles. However, the amount of this effect depends on the exact size distribution which is still unknown. We added this sensitivity test to the supplementary information.

[in 2.2][…] but we also perform sensitivity studies assuming different sizes in Sect. 3.3.
[in 3.3] If we assume the initial preexisting particles to be a distribution of different sizes (e.g. 40% of 50 nm, 50% of 100 nm, and 10% of 300 nm particles), the coagulation efficiency increases and leads to less simulated CN and higher derived sulfuric acid profiles (Fig S1).

Zero sulfuric acid condition

4.30-31 This seems like an unphysical situation of zero sulfuric acid. See additional detailed comment below regarding coagulation condition.
5.15-16 I have somewhat a problem with this condition of zero sulfuric acid being present. You must qualify the limitations of this condition, such that your coagulation results are only representative of zero sulfuric acid condition (unphysical).
5.19 at zero sulfuric acid condition (unphysical) with no competitive effects.
6.32-7.3 Yes, this relates to my previous comments on the zero sulfuric acid condition, which is rather unphysical. At the least, this should be discussed prior to these results for clarity. Then, these statements can be made in a more clear and concise writing style.

We understand that it seems a little strange to make this unphysical assumption of zero sulfuric acid. To test if this unphysical state influences the results, we did a sensitivity test, were we derived all sulfuric acid and CN profiles with a minimum sulfuric acid concentration of 1e4 cm-3 instead of 0 cm-3. The changes in the CN profiles of Figure 2+3 are so small that they can not be seen with the eye. And also the sulfuric acid profiles of Figure 4 hardly change; see here an overlay of both versions with half transparency:



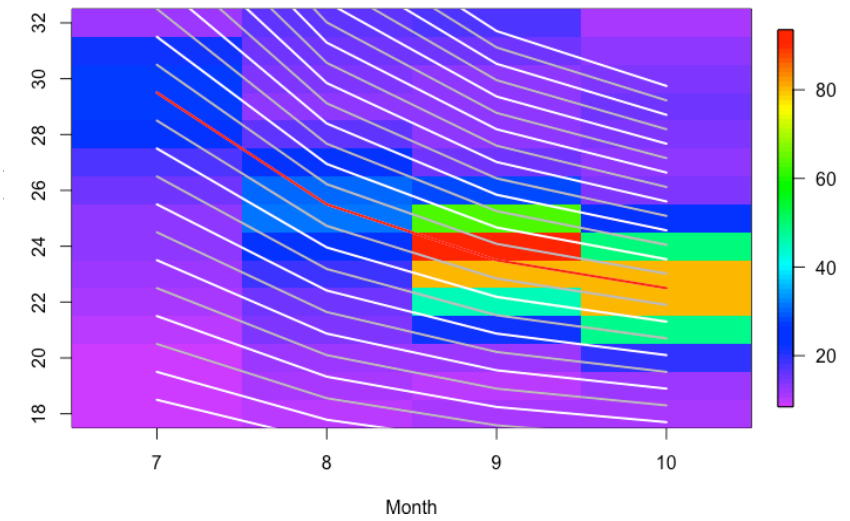
Although zero sulfuric acid is an unphysical state, the choice of this model idealization does not change the results. But for the process analysis and interpretation the zero sulfuric acid assumption is a ”clean” condition as it switches off all processes that need gaseous sulfuric acid with only coagulation and air volume change remaining. Therefore we prefer to keep the idealized zero sulfuric acid assumption in the text but we add a sentence about this 1e4 sensitivity test and the validity of the assumption.
Also due to this test, we have to remove statement that the too high CN in September at 28 km could be explained by the zero sulfuric acid assumption.

Note, that even though the idealized assumption of zero gaseous sulfuric acid is unphysical, it helps us to fully isolate and understand the processes that occur. All results of this study hardly change if we assume a minimum sulfuric acid concentration of 10^4 cm^{-3} instead of zero sulfuric acid. Although the 10^4 cm^{-3} sulfuric acid would be more realistic, we preferred the idealized choice of zero sulfuric acid to be able to completely decouple the processes. ~~Note, however, that we assume no sulfuric acid. If there were some sulfuric acid present, it would condense on the existing CN, increase their size and coagulation efficiency, which would result in lower CN concentrations.~~

Placing trajectories

5.12-13 Exactly how do you "place" them around the CN maximum trajectory, and what do these trajectories represent physically? I am a little confused as to how these trajectories actually represent different geographical locations of parcels descending outside of the CN layer in the vortex. Couldn't these trajectories have been better estimated (or at least compared to) using HYSPLIT parcel trajectory model? I suppose your method may be a rough estimation, but at the very least you should qualify this approximation of parcel trajectories in other regions of the polar vortex based only on CN layer measurements and parcel descent from Campbell and Deshler (2014).

Unfortunately, we were not really successful using HYSPLIT trajectories. We agree that the trajectories as assumed here only represent a rough estimate. We did this by taking the CN maximum trajectory and increasing the descent with altitude so that the trajectories fit the CN profiles and the simulation results make sense (see sensitivity question below). Trajectories plotted over the CN concentrations (color):



For the July altitudes we start at 18.5 km and then go up in steps of 1 km. For the following months the values are determined by using the following estimates:

$$August = July - 4.0 \cdot \frac{July - X}{29.0 - X}$$

$$September = August - 2.0 \cdot \frac{August - X}{25.5 - X}$$

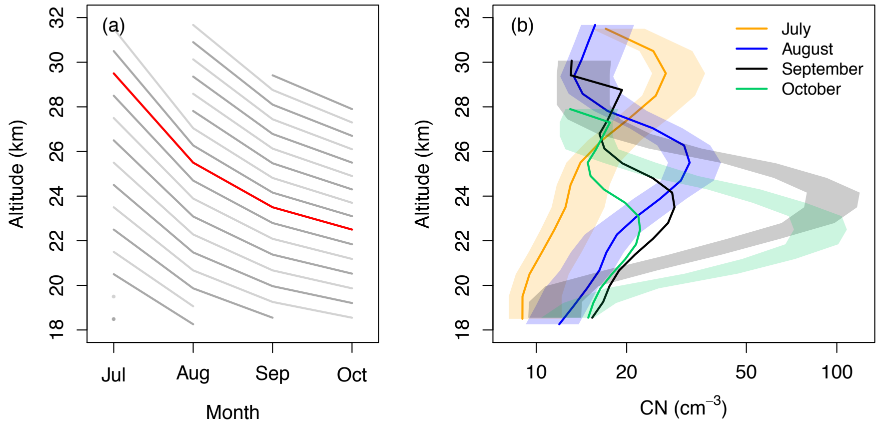
$$October = September - 1.0 \cdot \frac{September - X}{23.5 - X}$$

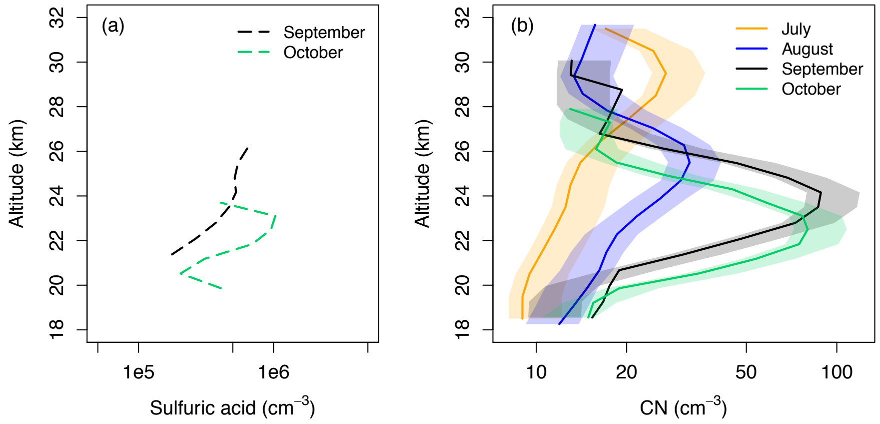
with X = 15 above the CN maximum trajectory and X = 12 below it. We added this description to the supplementary material. This is only a rough estimate and we added some caveats about this procedure to the text:

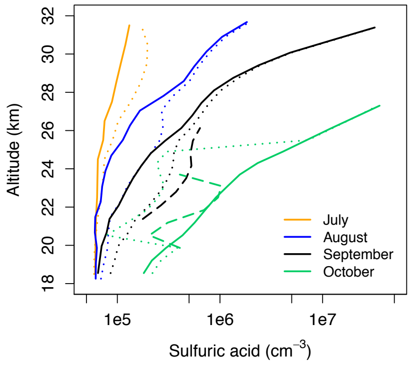
[in 3.1] Campbell and Deshler (2014) suggested air subsidence inside the polar vortex as the explanation for the subsidence of the CN maximum from July to October. We follow their suggestion and assume that the CN maximum of each month resides in a single subsiding air parcel, and place the other air parcel trajectories around this CN maximum trajectory (Fig. 2a). Note, that the CN maximum subsidence trajectory is an average over 24 years of measurements and that therefore our air parcel trajectories represent idealized descents. The pathways outside the CN layer are just rough estimates. However, our trajectories seem reasonable as Hardiman et al. (2013) find residual vertical velocities of about 0.6 mm/s (≈ 1.5 km per month) at 80 °S and 70 hPa that increase with height in their analysis of the Brewer-Dobson circulation in CMIP5 simulations.

7.22 As particle subsidence is an important process, why is there no sensitivity study addressing this?

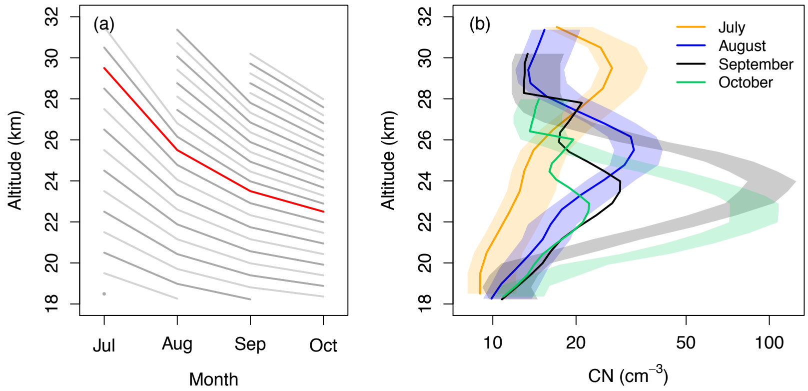
Actually, if we change this factor X in the equations for the trajectories, either nothing interesting happens or the results become inconsistent, indicating that the choice of X is outside of a reasonable range.
Here are Figures 2-4 with X = 12:

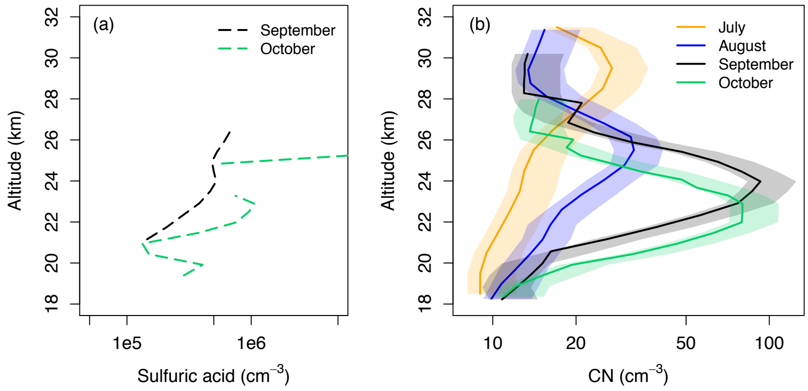


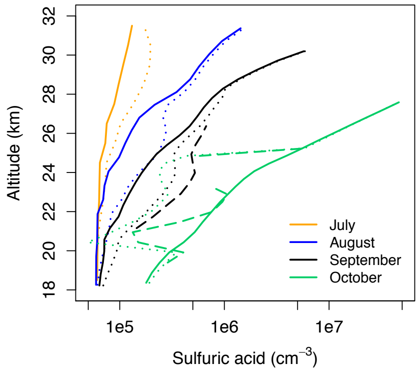




And here are Figures 2-4 with X = 18:







At least here in the last case the structure of the October CN layer profile makes no sense and should be wrong. On the other hand, the sulfuric acid concentrations in September in the CN layer hardly change in both tests. In general, everything that is close to the CN layer maximum should not change so much as there the surrounding trajectories should not be completely different from the maximum trajectory; but this is where most of the "action" happens; so the important messages stay the same. Also, the nucleation profiles are independent from the trajectories and do not change.
However, we added a little sensitivity test to the supplementary material concerning the descent from July to August and the simulation length in October:

[Text added in Section 3.3] Our trajectories might descend too fast from July to August as the CN profile of Campbell and Deshler (2014) is representative for June and July. Also, Campbell and Deshler (2014) note that most measurements were performed between late August and early October while our October simulations reproduce the measured CN as a monthly mean. If we run our simulations from mid June until mid October, the simulated CN in August are lower as the preexisting CN have more time to coagulate and in October less sulfuric acid is necessary to reproduce the CN layer (Fig. S2). Note, that in combination with a preexisting particle size distribution this might necessitate some nucleation already in August.

Individual remaining comments

1.11 Your simulations rather confirm recent analysis... (Antarctic CN layer formation already shown to be due to BHN in numerous works)
New text: Our simulations confirm recent analysis that the development of the CN layer can be explained with neutral sulfuric acid-water nucleation and we show that outside the CN layer the measured CN concentrations are well reproduced just considering coagulation and the subsidence of the air parcels.

1.25-26 OK with this improved definition of CN, but may also want to say "... that are large enough to be measured by a CN-counter operating at a given supersaturation, ..."
Done

3.26 why now? Is this an update you make in this work, or is this just awkwardly worded?
Yes this is an update of the original SAWNUC model that we also used in Kürten et al. (2015). We reworded the sentence to make this point clearer. We removed the second part of the sentence (the updated dimer stabilities) as we only use them in the sensitivity test but not for the main simulations.
As in Kürten et al. (2015), coagulation rates between neutral clusters are calculated including van der Waals forces according to Chan and Mozurkewich (2001).

3.28 to allow for changes in ambient conditions
Done

3.30-31 This is an awkward sentence, as it seems you describing how this was simulated in the previous version 1 of the manuscript. Just explain more clearly what was done in this version.
The surface area loss term was used in other previous studies with SAWNUC so we think that it is important to report that it is done differently in this study. We suggest to change the text to:
We do not use SAWNUC's procedure to represent losses to preexisting particles by a single surface area loss term, but instead we now fully simulate preexisting particles as initial particle concentrations.

4.11-13 Is this a separate paragraph? If so, it is only one sentence and would not be considered a new paragraph.
Done. This part is now included in the previous paragraph.

4.15 MLS: need to spell acronyms out and provide adequate references
[…] based on Microwave Limb Sounder (Waters et al., 2006) and hygrometer (Vömel et al., 1995) measurements in Fig. 7a in Campbell and Deshler (2014).

4.27 Which altitudes? Please explicitly state.

For this reference case, we do not simulate the region above 31 km in September and above 27 km in October […]

4.28 This is a little strange as SAWNUC does simulate evaporation, as is stated in the previous section.

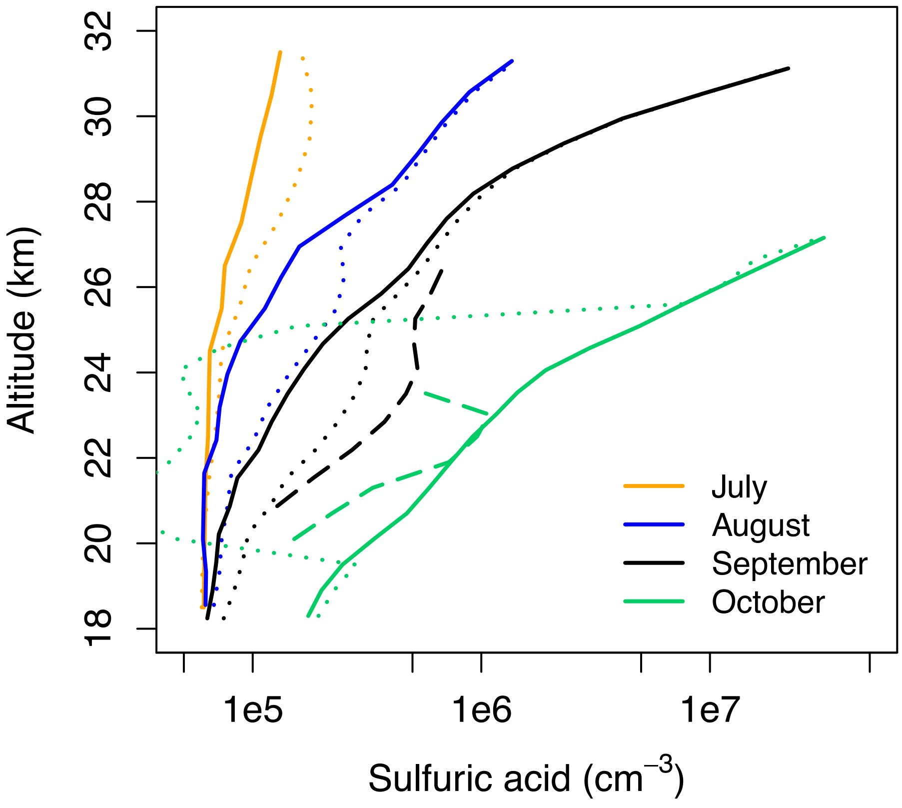
Yes it does, and because the preexisting CN evaporate there, the interpretation gets more complicated. At lower temperatures evaporation is only relevant for nucleation of new particles. The existing CN are stable. At these higher temperatures, however, the existing background CN evaporate. And then the derived sulfuric acid concentration also needs to keep the existing CN larger than the cutoff threshold.

[…] as high temperatures lead to evaporation of the initial background CN and complicate the interpretation.

5.3 Why is this "about" 1 CN per cm3 per month? If you are inverting SAWNUC, shouldn't the threshold profile be derived when "exactly" nucleation creates 1 CN per cm3 per month?

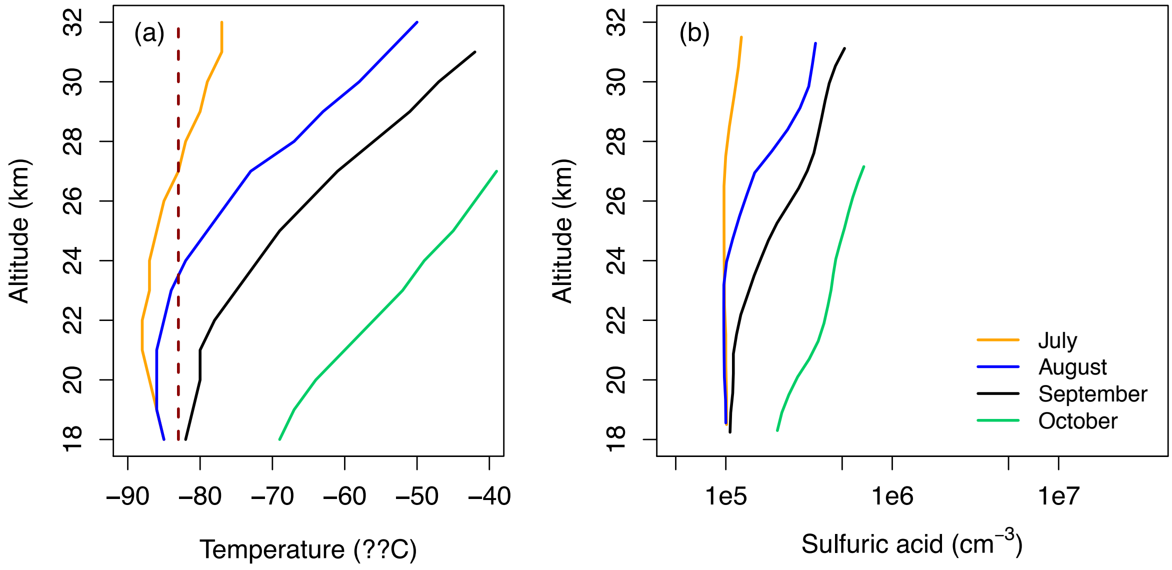
It is about 1 CN per cm3 as we want the monthly mean CN to increase by 10 %. Starting with 10 CN at the beginning of the month that then coagulate, the monthly mean CN is slightly below 10 CN. Therefore, a 10 % increase leads to slightly less than 1 CN per month -> "about".

We redid the simulation with the criteria of exactly 1 CN per month and cm3 and the nucleation threshold profiles look essentially the same. The upper limit profiles are more influenced as there, when we also use the criteria of 10% or 1 CN per month, the 10 % increase requires nucleation of up to 9 CN (10% of 90 in September in the CN layer):



So both criteria could work. We decide to keep the 10 % criteria, as then the derived profiles lead to noticeable change in CN concentration.

5.6-7 If this is true, then why in Figure 1b, when temperature remains fixed at 190 K from 24.5 to 27 km in July, and 22 to 23.5 km in August, the H2SO4 profiles still increase with increasing altitude? Since temperature is constant in these altitude ranges for July and August, what other process must contribute to the H2SO4 increase? Air volume change?
Actually, it is the changing water concentration. In July, starting at 25 km and going higher we assume a water vapor mixing ratio of 6 ppm. As the air density decreases with height, the water vapor concentration decreases, which requires slightly higher sulfuric acid concentrations for nucleation.
See here the profiles derived for a fixed water vapor concentration:



However, also the water vapor concentration has a small influence on the derived profiles as can be seen e.g. in July below 27 km where the temperature is fixed to 190 K but the derived profile still varies slightly.

5.9-11 Be explicit, and state that these are based on the monthly average profiles of Figure 1c in Campbell and Deshler (2014).
The monthly average CN profiles presented in Fig. 1c in Campbell and Deshler (2014) are our basis for the air parcel subsidence trajectories.

5.23 Explain briefly how this occurs (e.g., air volume compression).
Therefore, the only two effects on CN concentration are a decrease due to coagulation and an increase when the ambient conditions change between the months. The latter results from an air volume expansion by temperature increase and an air volume compression by pressure increase which is mostly dominated by the pressure effect and consequently results in a net CN concentration increase.

5.31-34 Overall, this is very poorly phrased paragraph, which needs to be written in a more clear and concise manner. It is rather a simple concept that can be written actively in one sentence.
Using the same method as before, we now derive the amount of sulfuric acid needed to match the simulated and measured CN. This sulfuric acid causes nucleation of new particles, growth of these new particles to CN size, and growth of existing CN.

6.3 expected result as the derived sulfuric acid profiles are indeed dependent on the measured CN profiles.
[…] and as expected […]

6.3-5 Again, writing style needs improvement.
Moved between introduction of Fig. 3a and 3b and changed to:
Sulfuric acid is needed in September at 21-26 km to form the CN layer and in October at 20-24 km to prevent the CN layer from decreasing too fast by coagulation.

6.13-15 I can only assume that you are talking about profiles in your simulation of observed CN (dotted). Please be more explicit to be clear for the reader.
In July, August, and September, the upper limit profiles (dotted) show the sulfuric acid that is necessary for nucleation and growth to CN size and leads to additional 10% CN within one month.

6.16-19 I understand what you are saying here, essentially analyzing where the October CN layer derived sulfuric acid profile (dashed) is actually equal to or less than the nucleation threshold profile (solid), however, the way it is written here needs much improvement. The idea theoretically makes sense, as in September the nucleation rate of the CN layer is maximized, while the nucleation rates slows down later in October, as discussed in Campbell and Deshler (2014), and Campbell et al. (2014).
6.20 Again, this is awkwardly worded. You should start by saying "The sulfuric acid profile based on the CN layer region in September
6.22-24 Does this fall in line with what you are discussing in the paragraph above for October? If so, then it is redundant, and these paragraphs should be restructured and re-written.
We did some restructuring and reformulation and added the line types in brackets to make this clearer.
In September, the sulfuric acid profile that forms the CN layer (dashed) has higher concentrations than both the nucleation profile (solid) and the upper limit profile (dotted). This means that new particles are nucleating and that more than the 10% additional CN of the upper limit case have to form. However, as the nucleation rate is very sensitive to changes in sulfuric acid, the derived CN layer sulfuric acid concentrations are not much higher than the upper limit concentrations.
In October in the area of the CN layer however, the upper limit profile (dotted) and the CN layer formation profile (dashed) are both lower than the nucleation profile (solid), showing that no new particles have to nucleate. Instead, small particles that still exist from the nucleation event in September can grow above the CN counting threshold, which requires less sulfuric acid than nucleation and growth of new CN. Therefore, the history of the nucleation event in September allows for a CN increase without new particle formation in October.

6.26 Again, this is very awkward and should not precede the results. If anything, you should make this statement after you show the uncertainty for October.
Removed

6.27-29 These statements need to be re-written, as they are not clear. You should start with the statement Campbell and Deshler (2014) note that most CN measurements are made...." and go from there with a more focused argument.
[moved to 3.3] Also, Campbell and Deshler (2014) note that most measurements were performed between late August and early October while our October simulations reproduce the measured CN as a monthly mean.

7.6 outside of the CN layer?
No, also for the upper limit profiles (for no nucleation and growth to CN size) inside the CN layer.

7.8 This is another example of a poor writing style to open a paragraph, and is not acceptable for scientific journals in my opinion. Better example: "Figure 5 shows the impacts of ion-induced nucleation on the derived sulfuric acid profiles by removing all ion from the simulations, and then comparing the derived profiles to those that included ions."
Done

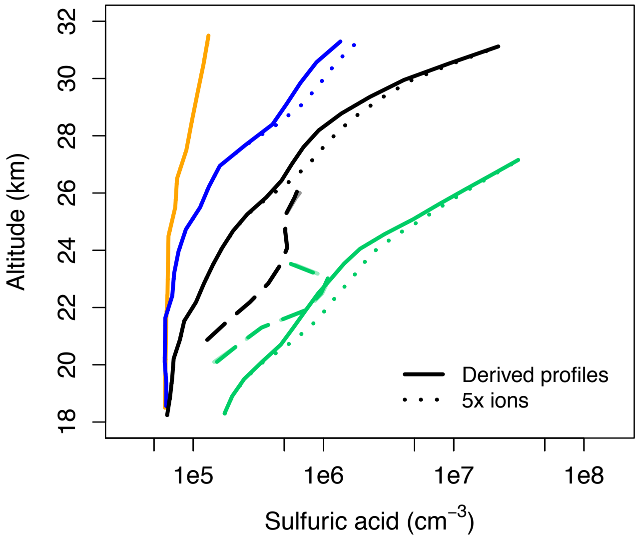
7.17 This is awkward, because it seems you imply there are a larger background pre-existing CN in the CN layer, where this is not true, but rather that there are simply more new CN formed in this region.
No, what we mean is that in the nucleation profiles we assume a background CN concentration of 10 cm-3. But during the actual formation of the CN layer there are more CN present from the background CN.
For the nucleation threshold profiles with 10 cm^{-3} background CN, ion-induced nucleation starts to occur at sulfuric acid concentrations of ~$4 \cdot 10^5$ cm^{-3}. During the formation of the CN layer, however, there are more preexisting CN present which reduce the nucleation efficiency and therefore ion-induced nucleation only starts to occur at sulfuric acid concentrations of ~$6 \cdot 10^5$ cm^{-3}.

7.18-21 This again is poorly written, is cumbersome, and needs to be changed to be appropriate for a scientific journal. I encourage the authors to write, re-write, and have a detailed proof-read here and in other sections of the paper before final submission.
As the derived sulfuric acid concentrations are below that limit in September, the CN layer formation is not influenced significantly by ion-induced nucleation. In October, the CN layer is located mostly in the area of ion-induced nucleation, but as there is no nucleation of new particles, the derived sulfuric acid hardly changes by ion-induced nucleation.

8.11-16 Please rewrite this and be more explicit with your analysis and discussion. It would be more worthwhile to state the range (or maximum) of sulfuric acid profile uncertainty due to assuming a fixed temperature profile of 190 K in those altitude regions of July and August.
A 5 K temperature increase significantly increases the sulfuric acid profiles by a factor of 2 in the coldest regions and up to a factor of 15 in the warmest regions. Fortunately, the temperature measurement uncertainty is only 0.5 K (Campbell and Deshler, 2014). However, this temperature sensitivity shows that our sulfuric acid profiles in July and August at low altitudes are up to a factor of 2 too high as there we had to increase the temperature to SAWNUC’s lower temperature limit of 190 K (maximum increase of 5 K, see Fig. 1a).

8.18 Is there really no need to mention the impacts of holding the ion pair concentration fixed with altitude? Wouldn't there be more uncertainty at higher altitudes (lower vs. upper stratosphere)?

The zero ions case in Figure 5 represents already an extreme sensitivity test concerning ions. Even in this extreme case, the derived profiles only change in the high sulfuric acid areas. Additionally, even in a sensitivity test with ion concentrations increased by a factor of 5 (in the solar forcing for CMIP6 (Matthes et al., 2016) we see a factor of less than 0.2 in the ion pair production rate per gram and second going from 20km to 30km) the derived profiles do not change much:



We added this sensitivity test to the supplementary material.

8.32-33 I don't see how you can come to this conclusion from the previous two statements. While the no nucleation condition makes sense in comparison of Antarctic July and the Arctic stratosphere, as you mention there is a significant temperature difference between the Antarctic and Arctic stratosphere. Why are there different trends in sulfuric acid profiles above about 26 km for July Antarctic and over the Arctic? Please revise and be more clear.

We decided to remove this comparison to make the paper more focused. However, here is our answer to your question:

It is important that the profiles are not comparable but only compatible to each other. One of them is an upper limit while the other one is an actual concentration profile. So different trends are possible.

Krieger and Arnold (1994) presented inferred sulfuric acid concentrations for the Arctic stratosphere in January 1992. Their concentrations are mostly below or slightly above our Antarctic July nucleation threshold profile, which was derived for temperatures colder than in the Arctic. As our profile represents only an upper limit for no nucleation but their profile are derived concentrations, our derived Antarctic July nucleation threshold profile is compatible/in agreement with the inferred Arctic January concentrations of Krieger and Arnold (1994) as no nucleation should occur there.

9.6 I don't understand this argument. Why?

9.7 Awkwardly worded.

9.7-9 Again, I do not see how previous comparisons with mid-latitude profiles can lead up to this conclusion. Please revise.

In July and August our nucleation threshold profiles lie within the mid-latitude values. However, as nucleation does not occur, these profiles represent upper limits and Antarctic winter sulfuric acid concentrations are lower than average mid-latitude concentrations. In September our derived sulfuric acid concentrations in the CN layer are higher than average mid-latitude concentrations. This comparison supports the formation explanation of the CN layer with low sulfuric acid during Antarctic winter followed by an area of high sulfuric acid after sunrise.

9.19 It is a concise summary, which needs to be improved for writing style. Also however, I think noting the range in stratospheric sulfuric acid concentrations in each month would be a nice way to provide important results to the scientific community.

Sulfuric acid concentrations in September during the CN layer formation range from $1 \cdot 10^5$ cm^{-3} at 21 km to $6 \cdot 10^5$ cm^{-3} at 26 km […]

The upper limits start at 18 km at concentrations below 10^5 cm^{-3} and increase to about 10^5 cm^{-3} in July, 10^6 cm^{-3} in August, and 10^7 cm^{-3} in September at 32 km, while in October they start at $2 \cdot 10^5$ cm^{-3} at 18 km and increase above 10^7 cm^{-3} at 27 km.

9.25 Please continue to revise using previous writing suggestions to improve the quality of this manuscript.

Done

Antarctic CN concentrations outside the CN layer can be explained by coagulation if air volume compression due to air parcel subsidence is considered. Neutral sulfuric acid-water nucleation forms the CN layer in September, while in October growth of small particles maintains the layer. Ion-induced nucleation does not occur at significant levels as sulfuric acid concentrations are too low and charged clusters recombine too fast. Our results complement […]

[+ additional smaller revisions in the rest of the summary]

Fig. 6 Missing panel labels, a, b, c, and d.

Done

Fig. 7 Add minor tick marks on y-axis.

Done

Answers to Referee # 2

This paper has improved considerably and now represents a useful contribution to the literature, and to what can be derived from condensation nuclei measurements. There are just a few minor points the authors should attend to in preparing their final copy.

Thank you for carefully reading our manuscript again, pointing out the unclear sections, and making suggestions for improvements. Please find our detailed answers below.

2.34-35. What was preformed 2-3 times a year during winter? Please rewrite to clarify.
More recently, Campbell and Deshler (2014) presented a long-term record of stratospheric balloon-borne CN measurements that were performed 2-3 times a year during winter from 1986 until 2010 above McMurdo Station, Antarctica (78°S).

4.30. … as initial particle concentrations at the beginning …
Done

5.25-30. Concerning the initial CN concentrations chosen at the beginning of each month, a few more words would help. I presume these choices are represented by the altitude regions at the beginning of each month in Fig. 2a where each trajectory begins. Thus in July all trajectories begin so this matches the observations perfectly. In August, only trajectories above about 28 km begin in that month. All lower trajectories began in July. Similarly for September, the three trajectories begun that month are indicated as those beginning above about 29 km. This correspondence could be indicated to the reader here.
We agree that this should be communicated more clearly. But instead of just writing it in the text, we make the first values dotted in the figures. We think that this is the best way to directly indicate this.
As the first value of every simulated air parcel is chosen based on the observations, the CN in July and at the top in August and September are identical with the measurements (dotted). In the following months, the CN result from our simulation (solid).

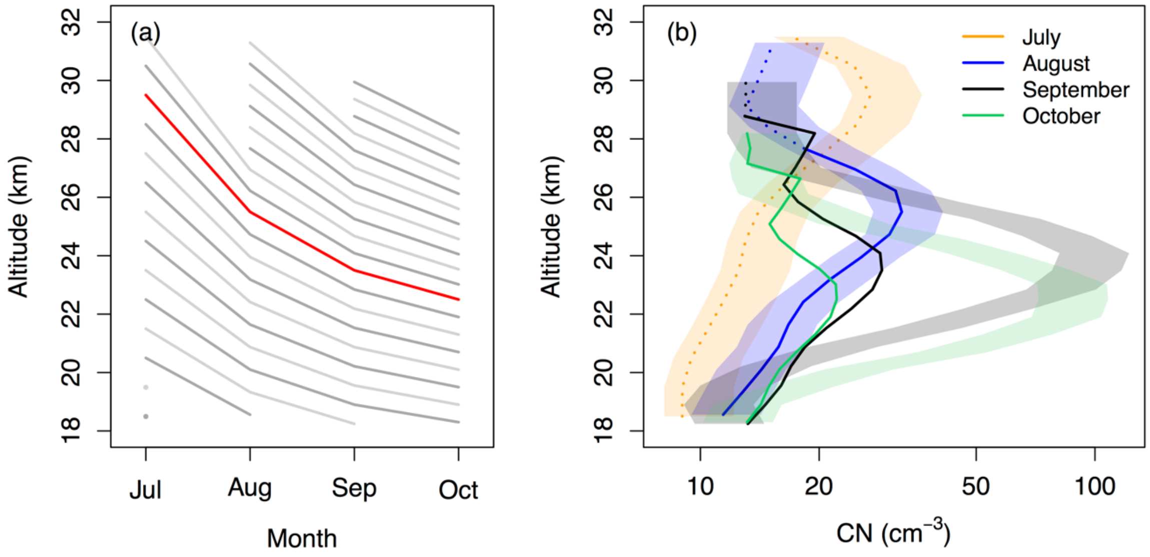


Fig 2b). It might also be worth pointing out here that the subsidence and air compression leads to increased CN concentrations throughout the profile below the CN peak

concentration which began at 30 km in July. It is also worth noting that the region of CN nucleation appears to be tied to the layer in July with the initial peak in CN concentration, as that layer subsides over winter.
We added the first point. However, the second point is a result from our choice of the trajectories. When we assume that the CN maximum of each month is one descending air parcel, we force the later CN layer nucleation to occur around the initial CN peak in July.
In August, subsidence and air compression of the July CN dominates over coagulation throughout the simulated profile and leads to higher CN concentrations. Thereby, the measured CN can be fully reproduced within the uncertainty range without nucleation of new particles being necessary.

7.19-21. This long sentence is difficult to follow, and the writing rather awkward. Rewrite using several shorter sentences to convey the idea.
In October, the CN layer is located mostly in the area where ions do change the nucleation rates, but as there is no nucleation of new particles during that time, the derived sulfuric acid hardly changes by ion-induced nucleation.

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To study the uncertainty introduced by the assumed particle size threshold of the CN measurements, we derive the sulfuric acid profiles assuming a lower CN counter threshold of 6 nm diameter, which is the CN counter's lower end according to Campbell and Deshler (2014).

7.26. "This effect …" Do the authors mean, The impact of CN threshold size …
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Reference

Matthes et al., (2016). Solar forcing for CMIP6 (v3. 1). Geoscientific Model Development Discussions, 1-82.

Nucleation modeling of the Antarctic stratospheric CN layer and derivation of sulfuric acid profiles

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Abstract. Recent analysis of long-term balloon-born measurements of Antarctic stratospheric condensation nuclei (CN) between July and October showed the formation of a volatile CN layer at 21-27 km altitude in a background of existing particles. We use the nucleation model SAWNUC to simulate these CN in subsiding air parcels and study their nucleation and coagulation characteristics. Our simulations confirm recent analysis that the development of the CN layer can be explained with neutral sulfuric acid-water nucleation and we show that outside the CN layer the measured CN concentrations are well reproduced just considering coagulation and the subsidence of the air parcels. While ion-induced nucleation is expected as the dominating formation process at higher temperatures, it does not play a significant role during the CN layer formation as the charged clusters recombine too fast. Further, we derive sulfuric acid concentrations for the CN layer formation. Our concentrations are about one order of magnitude higher than previously presented concentrations as our simulations consider that nucleated clusters have to grow to CN size and can coagulate with preexisting particles. Finally, we calculate threshold sulfuric acid profiles that show which concentration of sulfuric acid is necessary for nucleation and growth to observable size. These threshold profiles should represent upper limits of the actual sulfuric acid outside the CN layer. According to our profiles, sulfuric acid concentrations seem to be below mid-latitude average during Antarctic winter but above mid-latitude average for the CN layer formation.

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1 Introduction

Atmospheric aerosol particles are of interest due to their various influences on radiation, clouds, chemistry, and air quality. Condensation nuclei counters measure the number concentration of aerosol particles by growing them to optically detectable sizes by condensation (e.g. McMurry, 2000). Therefore, condensation nuclei (CN) are defined as all aerosol particles that are large enough to be measured by a CN-counter operating at a given supersaturation, which typically can measure particles with diameters larger than ~10 nm. New particle formation to supply the particles for the stratosphere mostly occurs in the tropical tropopause layer (Brock et al., 1995; Thomason and Peter, 2006; Weigel et al., 2011). The particles are then distributed in the lower stratosphere and constitute the stratospheric aerosol layer (Junge et al., 1961). The particles are sulfuric acid-water droplets (Arnold et al., 1998; Deshler, 2008; Junge et al., 1961) and if they are completely volatile, they are assumed to be formed by ion-induced or neutral homogeneous nucleation of sulfuric acid and water (binary nucleation). Binary nucleation occurs at low temperatures and high sulfuric acid concentrations. In the stratosphere the lowest temperatures are found in the polar vortex of the winter hemisphere. In the Antarctic polar vortex a background CN concentration of ~10 cm^{-3} is found (Campbell and Deshler, 2014). Volatility measurements indicate that more than half of them have a nonvolatile core which could be meteoric material (Campbell and Deshler, 2014; Curtius et al., 2005). Sulfuric acid is expected to condense on these CN (Borrmann et al., 2010; Murphy et al., 1998, 2013) and the formation rate of gaseous sulfuric acid should be very small during polar night. Therefore, nucleation is not expected to occur in the polar vortex.

Contrary to this expectation, Rosen and Hofmann (1983) first observed an increase of volatile CN at 25-30 km altitude during winter at Laramie, Wyoming (41°N). They assumed the CN to be freshly nucleated sulfuric acid-water particles with the polar stratosphere as the source region. Above McMurdo Station, Antarctica (78°S), Hofmann and Rosen (1985) also observed an increased CN concentration between 20 and 25 km after sunrise (CN layer). To check if the occurrence of this CN layer was an annual polar phenomenon, further measurements were performed that also observed the formation of a CN layer after sunrise (e.g. Hofmann (1990) at Kiruna, Sweden (68°N)). Therefore, sulfuric acid production by sunlight after the end of the polar night was suggested as the nucleation source.

Based on these observations, modeling studies began to investigate the formation of the CN layer. Hamill et al. (1990) calculated nucleation rates indicating that binary nucleation could occur in the polar winter stratosphere if sulfuric acid concentrations were high enough. Zhao et al. (1995) developed a one-dimensional (altitude) aerosol model that showed that the transformation of OCS to SO_2 and further oxidation of SO_2 to sulfuric acid are too slow to reproduce the observed CN increase. They could only reproduce the formation of the CN layer when they added downward transport of SO_2 from the mesosphere inside the polar vortex. Mills et al. (1999) and Mills et al. (2005) presented modeling with a two dimensional (altitude and latitude) aerosol model that was able to reproduce the formation of the CN layer when including production of mesospheric SO_2 by photolysis of sulfuric acid and SO_3 (see also Vaida et al., 2003).

In summary, and contrary to the initial expectation, nucleation seems to occur in the polar stratosphere. During polar winter, more SO_2 is transported downward inside the polar vortex without being oxidized by photochemical reactions. After sunrise, this SO_2 is oxidized to sulfuric acid which initiates nucleation and forms the volatile CN layer despite the presence of nonvolatile background CN.

More recently, Campbell and Deshler (2014) presented a long-term record of stratospheric balloon-borne CN measurements that were performed 2-3 times a year during winter from 1986 until 2010 above McMurdo Station, Antarctica (78°S). 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 the CN layer at 21-27 km, with concentrations increasing to 100 cm^{-3} from August until October during sunrise and warming. Campbell and Deshler (2014) also presented volatility measurements of the CN showing that in general more than half of the CN have a nonvolatile core except in the CN layers where they observe significant and rapid formation of new particles that are completely volatile. Additionally, Campbell et al.

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(2014) used a 3-dimensional chemistry climate model (English et al., 2011; Hurrell et al., 2013) to reveal the global extent of the CN layer.

Campbell and Deshler (2014) describe a method where they derive an Antarctic sulfuric acid profile from the measured CN by inverting the neutral binary nucleation equation. They used the difference between the CN before sunrise and two weeks after sunrise averaged over all years to derive a nucleation rate for all altitudes from which they derived the corresponding sulfuric acid. This profile is useful e.g. for evaluating global models (Campbell et al., 2014) as no Antarctic sulfuric acid measurements exist. However, Campbell and Deshler (2014) and Campbell et al. (2014) also note that their derived profile might be an underestimation as their method does not consider the particles smaller than their experimental CN detection threshold particle size, losses to preexisting particles, and ion-induced nucleation.

We find this approach of deriving a sulfuric acid profile from the measured CN intriguing. Here we use the nucleation model SAWNUC that simulates small particles, ion-induced nucleation, coagulation, and losses to preexisting particles. We model the Antarctic CN layer based on the observations of Campbell and Deshler (2014), and derive Antarctic stratospheric sulfuric acid profiles.

2 Methods

2.1 The SAWNUC model

The SAWNUC model (Sulfuric Acid Water NUCeation model, Lovejoy et al., 2004) simulates binary sulfuric acid water neutral and ion-induced nucleation. SAWNUC uses thermodynamic stabilities that are based on experimental values and quantum chemical calculations (Lovejoy and Curtius, 2001; Froyd and Lovejoy, 2003a, b; Hanson and Lovejoy, 2006), and it explicitly simulates step-by-step addition of sulfuric acid molecules in linear size bins for cluster sizes below 2 nm. Above 2 nm particle concentrations are collected in geometric size bins. Here we simulate 30 geometric size bins with a scale factor of 1.7, ranging up to about 400 nm for neutral and negatively charged clusters. For each size bin, SAWNUC can simulate condensation and evaporation of sulfuric acid, coagulation with neutral clusters, recombination of negative clusters with positive ions, and losses to preexisting particles. SAWNUC has been previously described and used (among others) by Lovejoy et al. (2004), Ehrhart and Curtius (2013), Kürten et al. (2015), Ehrhart et al. (2016), and its parameterized version PARNUC (Kazil and Lovejoy, 2007) is used in Kirkby et al. (2011).

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For this study, we extended the SAWNUC model. As in Kürten et al. (2015), coagulation rates between neutral clusters are now calculated including van der Waals forces according to Chan and Mozurkewich (2001). We redesigned the model code to allow for changes in ambient conditions during a simulation and added the ability to perform multiple simulations within one program run. We do not use SAWNUC's procedure to represent losses to preexisting particles by a single surface area loss term, but instead we now fully simulate preexisting particles as initial particle concentrations. For this study, the basic processes simulated by SAWNUC are condensation and evaporation of sulfuric acid and coagulation for every size bin. Condensation

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and evaporation of sulfuric acid are the dominating processes for the formation of new particles while coagulation and condensation of sulfuric acid, if present, determine growth and number reduction of existing particles.

2.2 Ambient parameters

To perform a regular SAWNUC simulation for a given region of the Antarctic stratosphere, the temperature, pressure, ion pair production rate, relative humidity, and sulfuric acid concentration are required. Particle concentrations and sizes are the model output at every time step. When inverting SAWNUC, the particle concentrations are required to derive the sulfuric acid concentrations.

Temperatures above Antarctica are taken from Campbell and Deshler (2014), and those temperatures that are below 190 K (maximum 5 K below), which is SAWNUC's lower limit of the temperature range, are fixed at 190 K. This introduces some uncertainty which is estimated in our sensitivity test of a 5 K temperature increase (Sect. 3.3). Altitudes are converted to pressures according to the global modeling of Campbell et al. (2014). The ionization rate of the Antarctic stratosphere in August-September 2010 was 3e5 ion pairs per gram of air and second (Ilya Usoskin, personal communication; according to Usoskin et al., 2011) which converts to e.g. ~10 ion pairs cm^{-3} s^{-1} at 200 K and 20 hPa. The water vapor profile for July increases linearly from 3.0 to 6.0 ppm between 18 and 25 km, while remaining at a constant value of 6.0 ppm up to 32 km based on the Microwave Limb Sounder (Waters et al., 2006) and hygrometer (Vömel et al., 1995) measurements in Fig. 7a in Campbell and Deshler (2014). The water vapor mixing ratio is kept constant during the subsidence of the simulated air parcels (see below).

CN concentrations are taken from Campbell and Deshler (2014). The measured CN are then compared with the simulated CN by summing over all simulated particles with diameters above 20 nm, as Campbell and Deshler (2014) reported a detection limit of their CN counters of 6-20 nm diameter. As we do not know the exact size of the measured CN, we assume the initial preexisting CN to have a diameter of 100 nm (see below), but we also perform sensitivity studies assuming different sizes in Sect. 3.3. We simulate them as pure sulfuric acid-water particles but as temperatures are too low for significant evaporation, they could also include a nonvolatile core.

3 Results

3.1 CN simulations and sulfuric acid profiles

We start our simulations with a simplified *reference case* where we assume for all altitudes (18 - 32 km) and for every month (July - October) a constant monodisperse background CN concentration of 10 cm^{-3} with a size of 100 nm diameter. For this reference case, we do not simulate the region above 31 km in September and above 27 km in October, as high temperatures lead to evaporation of the initial background CN and complicate the interpretation. For all other altitudes and months, we simulate one month with constant ambient conditions chosen according to Sect. 2.2. We use the temperatures reported by Campbell and Deshler (2014) which are reproduced in Fig. 1a. We set the 10 CN cm^{-3} as initial particle concentrations at the

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beginning of the month and simulate the month without gaseous sulfuric acid being present. The CN concentration then reduces somewhat over time as the particles coagulate. Then, we simulate the month again and derive the gaseous sulfuric acid concentration that leads to a 10 % higher monthly mean CN concentration. This we term the "*nucleation threshold profile*" for sulfuric acid as it defines the minimum gaseous sulfuric acid that leads to nucleation and growth to observable CN size of about 1 additional CN per cm^3 and month in a background of 10 preexisting CN cm^{-3}. Note, that even though the idealized assumption of zero gaseous sulfuric acid is unphysical, it helps us to fully isolate and understand the processes that occur. All results of this study do hardly change if we assume a minimum sulfuric acid concentration of 10^4 cm^{-3} instead of zero sulfuric acid. Although the 10^4 cm^{-3} sulfuric acid would be more realistic, we preferred the idealized choice of zero sulfuric acid to be able to completely decouple the processes.

The nucleation threshold sulfuric acid profiles are shown in Fig. 1b. Their shapes are similar to the temperature profiles because temperature, sulfuric acid, and losses to preexisting particles mainly determine the nucleation rate. As the preexisting particle concentrations are the same and we target almost the same nucleation rate everywhere, the temperature determines the derived sulfuric acid concentration, and the nucleation threshold profiles consequently increase with increasing temperature. However, also the water vapor concentration has a small influence on the derived profiles as can be seen e.g. in July below 27 km where the temperature is fixed to 190 K but the derived profile still varies slightly.

We continue by studying how the measured CN of Campbell and Deshler (2014) coagulate outside the CN layer. Therefore, we drop the assumption of 10 CN cm^{-3} from the reference case and simulate the CN inside air parcels that subside in the polar vortex. The monthly average CN profiles presented in Fig. 1c in Campbell and Deshler (2014) are our basis for the air parcel subsidence trajectories. Campbell and Deshler (2014) suggested air subsidence inside the polar vortex as the explanation for the subsidence of the CN maximum from July to October. We follow their suggestion and assume that the CN maximum of each month resides in a single subsiding air parcel, and place the other air parcel trajectories around this CN maximum trajectory (Fig. 2a; description in Sect. S2). Note, that the CN maximum subsidence trajectory is an average over 24 years of measurements and therefore our air parcel trajectories represent idealized descents. The pathways outside the CN layer are just rough estimates. However, our trajectories seem reasonable as Hardiman et al. (2013) find residual vertical velocities of about 0.6 mm/s (≈ 1.5 km per month) at 80 °S and 70 hPa that increase with height in their analysis of the Brewer-Dobson circulation in CMIP5 simulations. For an air parcel simulation, we set the ambient conditions at the beginning of each month according to Sect. 2.2 and keep them constant for the whole month. We simulate and compare the values on a monthly basis as the measured input and target values (temperature and CN) are monthly averages as well. For the first month of each parcel simulation, we use the measurements of Campbell and Deshler (2014) to determine the initial CN concentration and subsequently simulate this month. As we still assume no gaseous sulfuric acid being present, coagulation is the only process taking place which reduces the CN by some amount. We choose the initial CN concentration so that the mean CN concentration in the first month matches the measurements. After the first month, we let the model run free, still assuming zero gaseous sulfuric acid. Therefore, the only two effects on CN concentration are a decrease due to coagulation and an increase when the

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ambient conditions change between the months. The latter results from an air volume expansion by temperature increase and an air volume compression by pressure increase which is mostly dominated by the pressure effect and consequently results in a net CN concentration increase.

Figure 2b shows the simulated CN without sulfuric acid being present and therefore no nucleation. The uncertainty ranges of the measured CN from Campbell and Deshler (2014) are shown for comparison (-10% to +35%). As the first value of every simulated air parcel is chosen based on the observations, the CN in July and at the top in August and September are identical with the measurements (dotted). In the following months, the CN result from our simulation (solid). In August, subsidence and air compression of the July CN dominates over coagulation throughout the simulated profile and leads to higher CN concentrations. Thereby, the measured CN can be fully reproduced within the uncertainty range without nucleation of new particles being necessary. In September and October, the modeled CN concentrations at 20-27 km are too small under a zero gaseous sulfuric acid condition, and the CN layer is not simulated.

In September, above the CN layer at ~28 km, too many CN are simulated even without any gaseous sulfuric acid being present (Fig. 2b). This is the result of an air volume compression in the subsiding air parcels from 31 km in August to 28 km in September which increases the CN concentration by ~60 %. Here, coagulation is not efficient enough to reduce the monthly mean CN to the observed value. The high October CN at ~26.5 km are then a result of the high September values. If the August CN concentration at ~31 km is reduced by about one third, the simulated CN in September and October would be within the measurement range.

It is important to understand how much sulfuric acid is necessary to form the CN layer, and thus reproduce the observations. Using the same method as before, we now derive the amount of sulfuric acid needed to match the simulated and measured CN. This sulfuric acid causes nucleation of new particles, growth of these new particles to CN size, and growth of existing CN. Figure 3a shows the sulfuric acid profiles that are necessary to form the CN layer and reproduce the observations (termed "*CN layer profiles*"). Sulfuric acid is needed in September at 21-26 km to form the CN layer and in October at 20-24 km to prevent the CN layer from decreasing too fast by coagulation. Figure 3b shows the simulated CN using the derived sulfuric acid profiles, and as expected the measured CN profiles are reproduced for all months at almost all altitudes.

For a complete interpretation of the processes in the CN layer we combine our nucleation threshold profiles and CN layer profiles in Figure 4 (solid and dashed). Additionally, we derive the sulfuric acid concentrations that lead to a CN increase in our simulation of the observed CN (Fig. 3b) and include them in Figure 4 (dotted). We use the same method as for our nucleation threshold profiles (deriving the amount of sulfuric acid that leads to a 10 % CN increase), but now with the simulated CN as background. Note that outside of the CN layer, these profiles represent only *upper limits* for the gaseous sulfuric acid in the atmosphere as neither the observations nor our simulations indicate nucleation in these areas.

In July, August, and September, the upper limit profiles (dotted) show the sulfuric acid that is necessary for nucleation and growth to CN size and leads to additional 10% CN within one month. The concentrations are higher than our nucleation

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threshold profiles (solid) because we have a higher concentration of preexisting CN compared to the 10 cm^{-3} in the reference case. Therefore, more small clusters are lost by coagulation with large CN. Here nucleation is in competition with losses to preexisting particles (Ehrhart and Curtius, 2013). In September, the sulfuric acid profile that forms the CN layer (dashed) has higher concentrations than both the nucleation profile (solid) and the upper limit profile (dotted). This means that new particles are nucleating and that more than the 10% additional CN of the upper limit case have to form. However, as the nucleation rate is very sensitive to changes in sulfuric acid, the derived CN layer sulfuric acid concentrations are not much higher than the upper limit concentrations.

In October in the area of the CN layer however, the upper limit profile (dotted) and the CN layer formation profile (dashed) are both lower than the nucleation profile (solid), showing that no new particles have to nucleate. Instead, small particles that still exist from the nucleation event in September can grow above the CN counting threshold, which requires less sulfuric acid than nucleation and growth of new CN. Therefore, the history of the nucleation event in September allows for a CN increase without new particle formation in October.

In the following sensitivity studies we show and discuss only the nucleation threshold and the CN layer profiles to avoid overloaded figures, but the conclusions for the upper limit profiles are analogous to the other profiles.

3.2 Ion-induced nucleation

Figure 5 shows the impacts of ion-induced nucleation on the derived sulfuric acid profiles by removing all ions from the simulations, and then comparing the derived profiles to those that included ions. In areas with low sulfuric acid concentrations, removing the ions has nearly no effect on the derived profiles, however, in areas with higher sulfuric acid concentrations the derived profiles increase by almost an order of magnitude. At low sulfuric acid concentrations, the small clusters are not growing fast enough by condensation. Negatively charged clusters recombine too early with positively charged ions and therefore are too small to overcome the nucleation barrier of neutral nucleation. At higher sulfuric acid concentrations, ion-induced nucleation occurs as expected. The charged clusters grow larger than the critical size before they recombine and increase the nucleation rate. Thus to create the same amount of CN without ions, more sulfuric acid is required than if ions are present.

For the nucleation threshold profiles with 10 cm^{-3} background CN, ion-induced nucleation starts to occur at sulfuric acid concentrations of ~4·10^5 cm^{-3}. During the formation of the CN layer, however, there are more preexisting CN present that reduce the nucleation efficiency and therefore ion-induced nucleation only starts to occur at sulfuric acid concentrations of ~6·10^5 cm^{-3}. As the derived sulfuric acid concentrations are below that limit in September, the CN layer formation is not influenced significantly by ion-induced nucleation. In October, the CN layer is located mostly in the area where ions do change the nucleation rates, but as there is no nucleation of new particles during that time, the derived sulfuric acid hardly changes by ion-induced nucleation.

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3.3 Sensitivity studies

To study the uncertainty introduced by the assumed particle size threshold of the CN measurements, we derive the sulfuric acid profiles assuming a lower CN counter threshold of 6 nm diameter, which is the CN counter's lower end according to Campbell and Deshler (2014). The lower threshold leads to lower sulfuric acid concentrations as the nucleated CN do not have to grow as large by sulfuric acid condensation to be counted (Fig. 6a). The impact of CN threshold size decreases with increasing sulfuric acid as at higher concentrations, the clusters grow quickly once they are nucleated. In October, however, there is more sulfuric acid needed in the CN layer as less small clusters exist that can grow across the cutoff size and therefore some nucleation of new CN is needed.

Lowering the size of the initial preexisting particles from 100 nm to 50 nm diameter reduces their coagulation efficiency and they present a smaller loss during nucleation. Therefore, the modelled sulfuric acid concentrations are lower (Fig. 6b). For the same reason there is no sulfuric acid needed in October in the CN layer. If we assume the initial preexisting particles to be a distribution of different sizes (e.g. 40% of 50 nm, 50% of 100 nm, and 10% of 300 nm particles), the coagulation efficiency increases and leads to less simulated CN and higher derived sulfuric acid profiles (Fig. S1).

We study model uncertainties according to Lovejoy et al. (2004) by adding 0.5 kcal to all changes in Gibbs free energy of negatively charged clusters. This only increases the profiles in regions where ion-induced nucleation dominates (see Sect. 3.2 and Fig. 5). A reduction of all coagulation and condensation rates by 20% increases all profiles a little but leads to a poorer CN simulation in comparison with the observations. The updated neutral sulfuric acid dimer thermodynamic stabilities presented by Kürten et al. (2015), which have a higher relative humidity dependence of the equilibrium constant, lead to higher dimer evaporation rates. Therefore they increase our profiles at low relative humidities (high temperatures), but only if neutral binary nucleation dominates. A combination of these influences is shown in Fig. 6c. The increase of the September CN layer profile at 24-26 km is mainly due to the updated dimer thermodynamic stabilities. The October CN layer profile mostly decreases as coagulation is less efficient which requires less growth of additional small particles. At the lowest altitude no nucleation is needed in September but therefore nucleation of additional CN is necessary in October.

As the derived sulfuric acid profiles are mainly determined by temperature we also test the effect of a 5 K temperature increase (Fig. 6d). We removed the responses at the highest September and October values as there the temperature was too high so that evaporating particles complicate the situation. A 5 K temperature increase significantly increases the sulfuric acid profiles by a factor of 2 in the coldest regions and up to a factor of 15 in the warmest regions. Fortunately, the temperature measurement uncertainty is only 0.5 K (Campbell and Deshler, 2014). However, this temperature sensitivity shows that our sulfuric acid profiles in July and August at low altitudes are up to a factor of 2 too high as there we had to increase the temperature to SAWNUC's lower temperature limit of 190 K (maximum increase of 5 K, see Fig. 1a).

Our trajectories might descend too fast from July to August as the CN profile of Campbell and Deshler (2014) is representative for June and July. Also, Campbell and Deshler (2014) note that most measurements were performed between late August and early October while our October simulations reproduce the measured CN as a monthly mean. If we run our simulations from

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Gelöscht: cutoff

Gelöscht: This effect

Gelöscht: so that sometimes

Gelöscht: However, the simulated CN concentrations are a little higher (not shown here) so that the observed CN can be better reproduced with an initial particle diameter of 100 nm.

Gelöscht: only

Gelöscht: there

Gelöscht: In general, higher temperatures

Gelöscht: increase

[3] verschoben

Gelöscht: .

[3] nach oben: Fortunately, the temperature measurement uncertainty is only 0.5 K (Campbell and Deshler, 2014).

Gelöscht: has to be considered when interpreting the

Gelöscht: profiles

Gelöscht: was below

Gelöscht: range

Gelöscht: below

mid June until mid October, the simulated CN in August are lower as the preexisting CN have more time to coagulate and in October less sulfuric acid is necessary to reproduce the CN layer (Fig. S2). Note, that in combination with a preexisting particle size distribution this might necessitate some nucleation already in August.

Additional sensitivity studies (Fig. S3) imply that the exact amount of ions or water molecules (e.g. 5 ppm everywhere) has only a small influence on the derived profiles because the ion concentrations are high enough so that they are not a limiting factor, and the few parts per million stratospheric water vapor uncertainty is too small to influence the profiles significantly. Also, a formation of 35 % more CN in the layer (CN measurement uncertainty) needs only little additional sulfuric acid (not shown).

3.4 Comparison with mid-latitude sulfuric acid and the derived profile of Campbell and Deshler (2014)

In Figure 7 we compare our derived September CN layer sulfuric acid profile with the profile derived by Campbell and Deshler (2014). Campbell and Deshler (2014) derived sulfuric acid concentrations for 15 to 33 km (dark red, dashed). Our derived sulfuric acid (black, dashed) is only shown between 21 and 26 km as we need no nucleation above and below the CN layer to reproduce the observations. Our concentrations are about one order of magnitude higher. This is because our CN have to form in a background of preexisting particles and they have to grow to observable size. As our sensitivity tests show, both of these effects require more sulfuric acid. In the nucleation threshold profile with a cutoff of 6 nm and a background of 10 CN cm^{-3} (black, dotted) these two effects are less pronounced, and therefore, this profile compares better with the derived profile of Campbell and Deshler (2014).

We cannot compare our derived sulfuric acid profiles with Antarctic in situ or remote sensing measurements as such data do not exist to our knowledge. However, northern mid-latitude balloon-borne measurements mainly from September and October have been published (Arnold et al., 1981; Reiner and Arnold, 1997; Schlager and Arnold, 1987; Viggiano and Arnold, 1981) and summarized by Mills et al. (2005). Note, that due to the different tropopause heights (43°N vs. 78°S) our derived profiles might need to be shifted upwards for comparison. In July and August our nucleation threshold profiles lie within the mid-latitude values. However, as nucleation does not occur, these profiles represent upper limits and Antarctic winter sulfuric acid concentrations are lower than average mid-latitude concentrations. In September our derived sulfuric acid concentrations in the CN layer are higher than average mid-latitude concentrations. This comparison supports the formation explanation of the CN layer with low sulfuric acid during Antarctic winter followed by an area of high sulfuric acid after sunrise.

We did not derive sulfuric acid profiles above Wyoming according to Campbell and Deshler (2014) Fig. 1a+b, as these CN are assumed to have nucleated in the polar region. However, as temperature mainly controls the nucleation rate, the nucleation threshold sulfuric acid profiles at temperatures representative of the stratosphere above Wyoming are used for comparison. In Autumn, temperatures above Wyoming lie between -60°C at 17 km and -40°C at 34 km (Campbell and Deshler, 2014, Fig. 1b). The same temperature range is found over Antarctica in September between 27 km and 33 km (Campbell and Deshler, 2014, Fig. 1d). If we compare our September nucleation threshold profile (black, solid) between 27 km and 33 km with the mid-latitude values, we see that at all mid-latitude altitudes the concentrations are just below our nucleation threshold values.

Gelöscht: not shown here) showed

Gelöscht: . The

Gelöscht: .

Gelöscht: requires

Gelöscht: our

Gelöscht: for

Gelöscht: which has

Gelöscht: . Therefore

Gelöscht: Krieger and Arnold (1994) presented inferred sulfuric acid concentrations for the Arctic stratosphere in January 1992. Their concentrations are mostly below or only a little above our July nucleation threshold profile which should represent an upper limit for temperatures colder than in the Arctic. Therefore, our derived Antarctic July nucleation threshold profile is compatible with the inferred Arctic January concentrations of Krieger and Arnold (1994) as no nucleation should occur there.

Gelöscht: can not

Gelöscht: does

Gelöscht: Due

Gelöscht: As our

Gelöscht: ,

Gelöscht: should be comparable to or even below the

Gelöscht: profile is comparable to or a little above the

Gelöscht: increased

Gelöscht: is

Gelöscht: determining

Gelöscht: we can use our

Gelöscht: the temperature

Gelöscht: lies

Gelöscht: end

This suggests that nucleation usually does not occur in the mid-latitude stratosphere in this altitude range. Sometimes at the highest sulfuric acid levels, however, ion-induced nucleation may become efficient.

4 Summary and Conclusions

Analysis of over 20 years (1986 - 2010) of balloon-born stratospheric CN measurements above McMurdo Station, Antarctica, between July and October reveal the formation of a layer of mainly volatile CN at 21-27 km altitude in a background of preexisting particles (Campbell and Deshler, 2014). Here, we use the nucleation box model SAWNUC to simulate these CN in subsiding air parcels and study the nucleation processes.

The observed CN of Campbell and Deshler (2014) are reproduced by simulating subsiding air parcels with volume compression, coagulation, nucleation and growth processes. Antarctic CN concentrations outside the CN layer can be explained by coagulation if air volume compression due to air parcel subsidence is considered. Neutral sulfuric acid-water nucleation forms the CN layer in September, while in October growth of small particles maintains the layer. Ion-induced nucleation does not occur at significant levels as sulfuric acid concentrations are too low and charged clusters recombine too fast. Our results complement Campbell and Deshler (2014) who showed that the CN decrease above Laramie, Wyoming, can be explained by coagulation and that almost all CN inside the CN layer are volatile and therefore can be explained by binary nucleation.

Sulfuric acid concentrations in September during the CN layer formation range from $1 \cdot 10^5$ cm^{-3} at 21 km to $6 \cdot 10^5$ cm^{-3} at 26 km which is about one order of magnitude higher than the concentrations derived by Campbell and Deshler (2014). Our sensitivity tests show that more sulfuric acid is needed in our simulations because nucleated clusters have to grow to the CN-counter's threshold size for detection and can coagulate with preexisting particles. Therefore, we can confirm Campbell and Deshler (2014) who suggested that their profiles might be an underestimation due to these effects.

Finally, we derived gaseous sulfuric acid profiles that show which concentration would be necessary for nucleation and growth to CN size to occur, which should represent upper limits of the actual sulfuric acid outside of the CN layer where neither the observations nor our simulations indicate nucleation to occur. The upper limits start at 18 km at concentrations below 10^5 cm^{-3} and increase to about 10^5 cm^{-3} in July, 10^6 cm^{-3} in August, and 10^7 cm^{-3} in September at 32 km, while in October they start at $2 \cdot 10^5$ cm^{-3} at 18 km and increase above 10^7 cm^{-3} at 27 km. According to these upper limits, sulfuric acid concentrations seem to be below mid-latitude average during Antarctic winter but above mid-latitude average during the CN layer formation while mid-latitude sulfuric acid concentrations in general seem to be too low for nucleation to occur. This is also in agreement with Campbell and Deshler (2014) and other seminal references contained within, who suggest that the mid-latitude CN layer originally formed in the polar region.

If stratospheric sulfuric acid increases above our upper limits, e.g., because of volcanic eruptions or geoengineering, nucleation could occur. In the mid-latitudes and in some relatively warm areas above Antarctica, this nucleation would be dominated by

Gelöscht: usually no

Gelöscht: occurs

Gelöscht: latitudes.

Gelöscht: , however,

Gelöscht: might be close to the limit for

Gelöscht: becoming

Gelöscht: Longtime averages

Gelöscht: We

Gelöscht: We can reproduce the

Gelöscht: and

Gelöscht: . We only need the presence of gaseous sulfuric acid in September for the formation of the CN layer and in October for maintaining it. We show that

Gelöscht: This complements

Gelöscht: . Campbell

Gelöscht: Deshler (2014) reported that more than half of the CN outside the CN layer contain a nonvolatile core but

Gelöscht: could

Gelöscht: produced

Gelöscht: . Our simulations are compatible with these findings as we only need binary nucleation to produce the CN layer. All other CN in our simulation could potentially also contain a nonvolatile core

Gelöscht: In agreement with Campbell and Deshler (2014) we find that the development of the CN layer can be explained by neutral sulfuric acid-water nucleation. The sulfuric

Gelöscht: are too low and the negative clusters recombine too fast for ion-induced nucleation to occur at significant levels. However, nucleation would be dominated by ion-induced nucleation if it occurred at slightly higher temperatures. ... [7]

Gelöscht: . Our concentrations are

Gelöscht: an

Gelöscht: this

Gelöscht: because

Gelöscht: consider that

Gelöscht: . Outside of the CN layer, these values

Gelöscht: as

Gelöscht: in these areas

Gelöscht: . Mid

Gelöscht: e.g.

Gelöscht: However, if the

Gelöscht: would increase

ion-induced nucleation and therefore would require less sulfuric acid than predicted by neutral binary nucleation theory. Note, however, that our upper limits would increase if there were more preexisting particles present.

In conclusion, our study supports the explanation of the CN layer as presented by Campbell and Deshler (2014). We can reproduce the CN that decrease over time by coagulation in a low sulfuric acid environment during Antarctic winter. In September between 21 and 26 km we can reproduce the observed CN layer only if we assume a higher sulfuric acid concentration that produces volatile CN mainly by neutral binary nucleation.

Gelöscht: These CN could contain a nonvolatile core.

Acknowledgements

We thank Edward R. Lovejoy, Karl D. Froyd, Jan Kazil, and Sebastian Ehrhart for providing the SAWNUC code and Andreas Engel for useful discussion. We thank the two anonymous reviewers for numerous helpful comments.

Gelöscht: also

Gelöscht: their help to improve the manuscript

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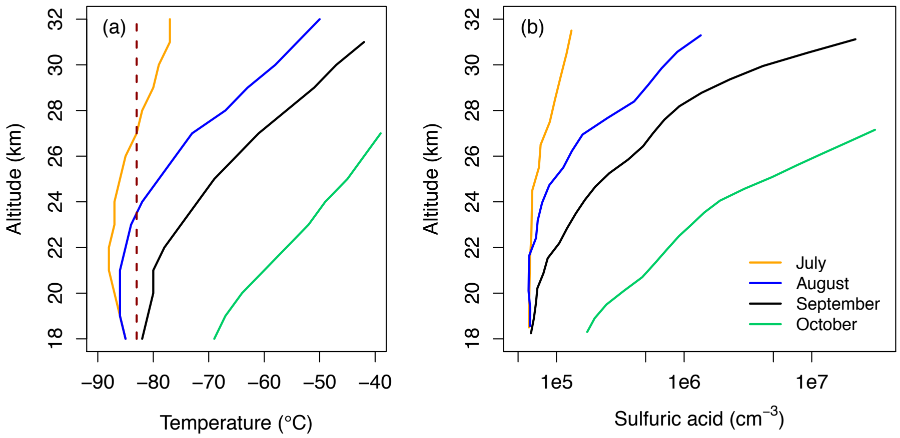


5 **Figure 1: Temperatures (a) during Antarctic winter above McMurdo, Antarctica (78°S), as presented in Campbell and Deshler (2014). The dashed line shows the lower temperature limit for which the SAWNUC model is valid and at which lower temperatures were kept fixed. In (b), corresponding sulfuric acid profiles are shown that lead to a 10 % CN increase by nucleation and growth to observable size during one month. For these *nucleation threshold profiles*, we assume a monodisperse CN background of 10 cm^{-3} with 100 nm diameter at all altitudes (18-32 km) for every month (July-October).**

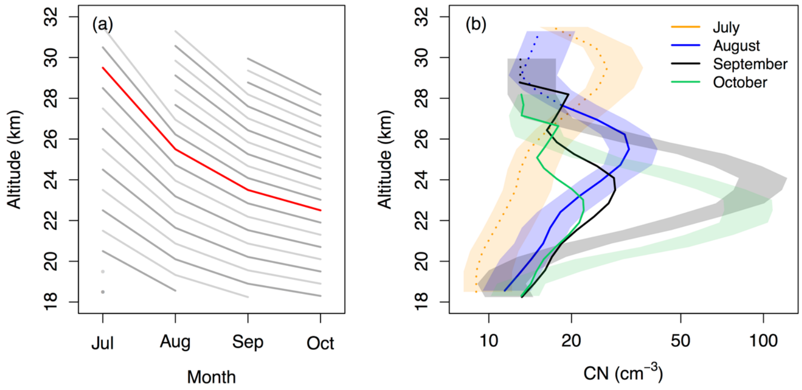
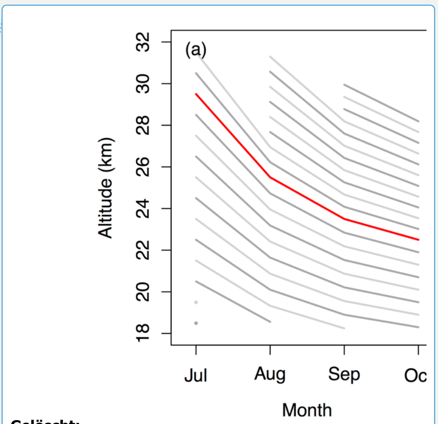


Figure 2: Air parcel subsidence trajectories (a) and simulated CN (monthly mean) without gaseous sulfuric acid being present (b). The uncertainty ranges of the measured CN presented in Campbell and Deshler (2014) are shown as shaded areas in (b) for comparison. The trajectories of the simulated air parcels were placed around the subsidence of the measured CN maximum (red). In the simulation, the ambient conditions are kept constant during each month. For the first month of each trajectory, the CN concentrations (dotted) are chosen based on Campbell and Deshler (2014). In the following months, the simulated CN concentrations (solid) are the result of only coagulation and air volume compression, as there is no gaseous sulfuric acid present.



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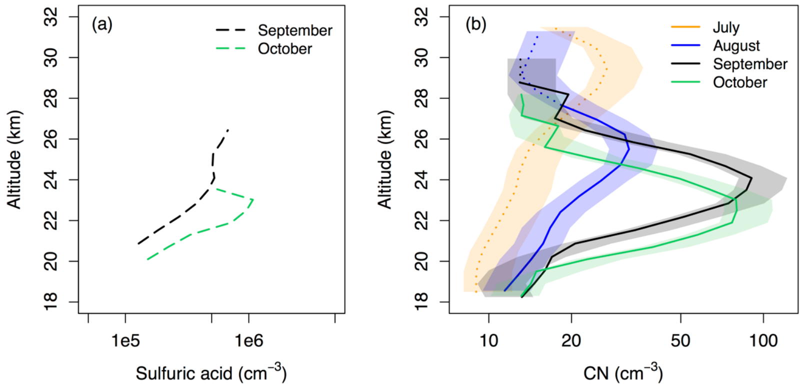
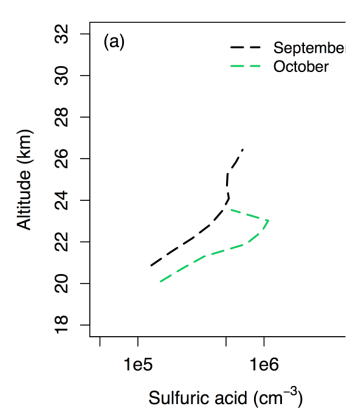


Figure 3: CN layer gaseous sulfuric acid profiles (a) and the simulated CN using these profiles (b). We derive the sulfuric acid if the simulated CN concentrations in Fig. 2b are too low without gaseous sulfuric acid being present and therefore nucleation and condensational growth are needed to simulate the CN layer. As in Fig. 2b, the dotted lines are the initial CN based on observations



Gelöscht:

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and the solid lines are the simulated CN. The uncertainty ranges of the measured CN from Campbell and Deshler (2014) are shown as shaded areas for comparison.

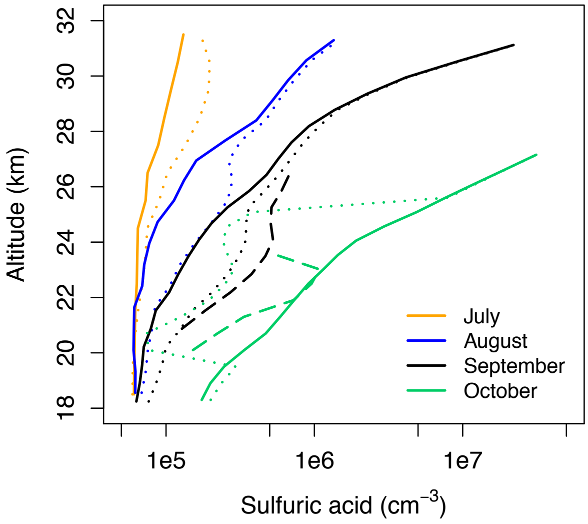


Figure 4: Combination of the nucleation threshold sulfuric acid profiles from Fig. 1b (solid) and the CN layer sulfuric acid profiles from Fig. 3a (dashed). Additionally, we show sulfuric acid profiles that cause a CN increase in our CN simulation of Fig. 3b (dotted) which should represent upper limits of the Antarctic winter stratospheric sulfuric acid outside the CN layer.

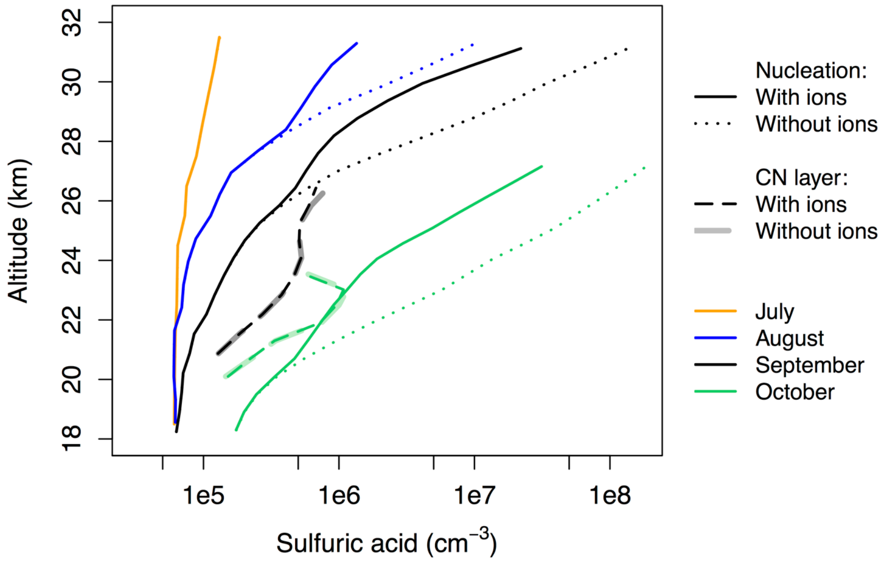


Figure 5: Comparison of the nucleation threshold sulfuric acid profiles derived including ion-induced nucleation (solid lines) and without simulating ions (dotted lines). At low sulfuric acid concentrations the derived profiles do not change. The CN layer profiles also hardly change (thick dashed lines; grey and light green are without ions and black and green are with ions, but they are almost identical).

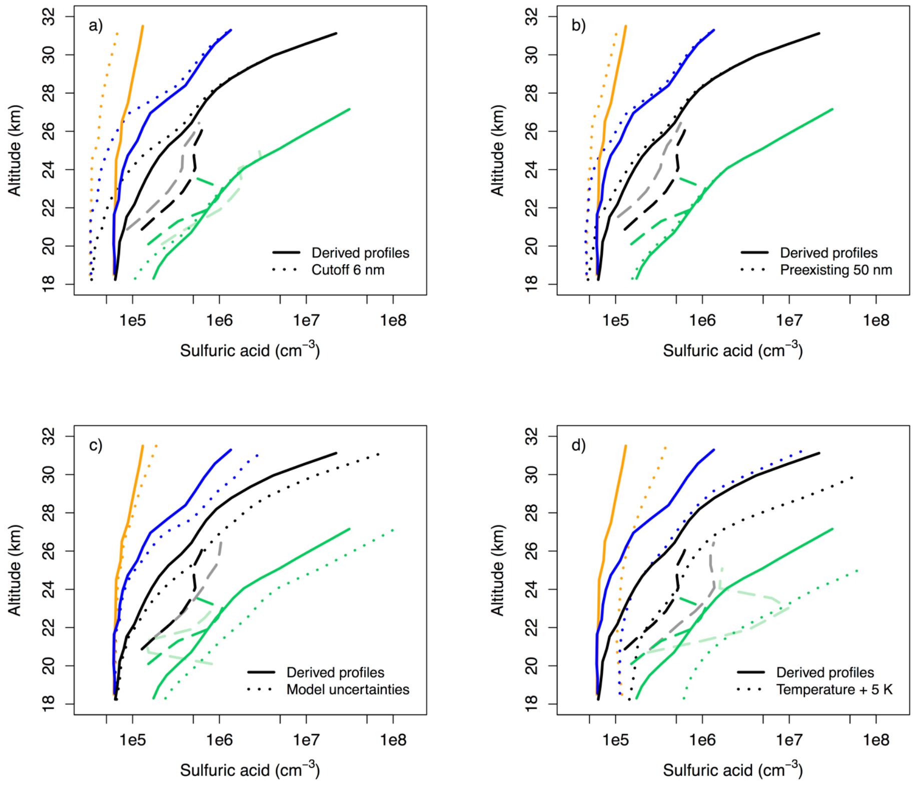
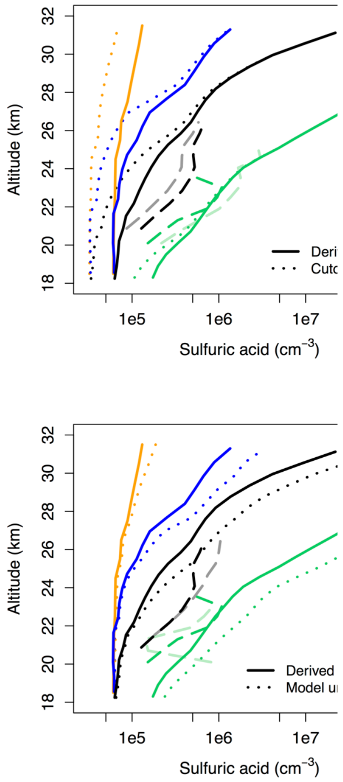


Figure 6: Sensitivity studies varying (a) CN counter cutoff size, (b) preexisting particle size, (c) model thermochemical and dynamic parameters, and (d) temperature, to estimate the uncertainties of the derived sulfuric acid profiles. As in Fig. 5, the solid and dark dashed lines show the nucleation threshold and CN layer formation profiles as presented in Fig. 4. The dotted and light dashed lines show the changed profiles according to the sensitivity tests.



Gelöscht:

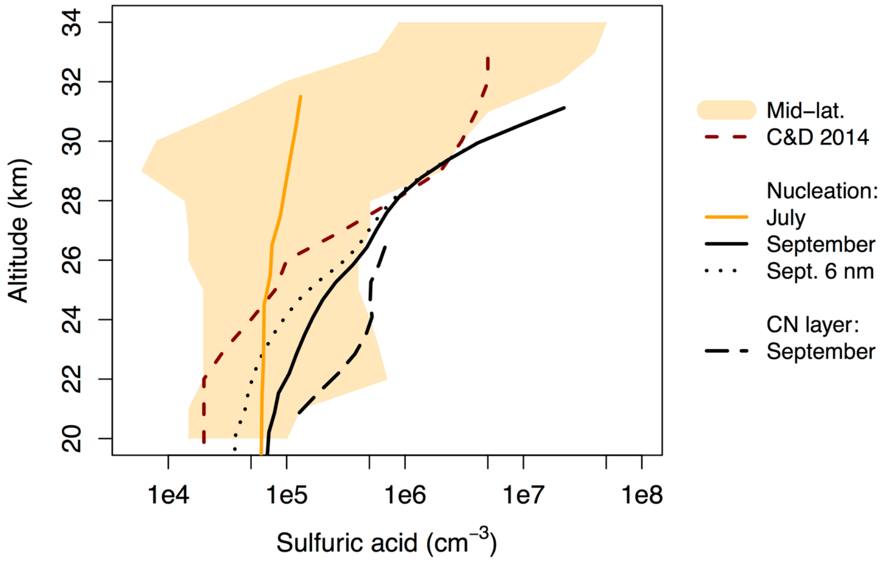
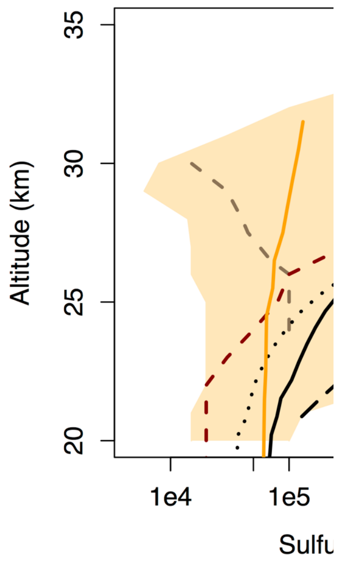


Figure 7: Comparison of our derived Antarctic sulfuric acid profiles (nucleation threshold: solid, CN layer: long dashed) with the derived profile from Campbell and Deshler (2014) (dark red, short dashed) and mid latitude measurements and modeling of Arnold et al. (1981), Reiner and Arnold (1997), Schlager and Arnold (1987), Viggiano and Arnold (1981), and Mills et al. (2005) (shaded area). The September nucleation threshold profile for nucleation and growth to a lower cutoff of 6 nm from Fig. 6a is also included (black dotted).

Gelöscht:



Gelöscht: **), inferred Arctic sulfuric acid from measurements in January presented by Krieger and Arnold (1994) (brown, short dashed),**

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As the next step we study

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that is necessary for a CN increase. The reason are small particles that still exist from the nucleation event in September and just have to grow above the counting threshold. Therefore, a CN increase requires less sulfuric acid than the nucleation of new particles in our reference case.

The

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Note, however, that the sulfuric acid in the CN layer in October is quite uncertain as the sensitivity studies below show. Additionally, it is only needed when we try to reproduce the measured CN as a monthly mean. Campbell and Deshler (2014) note that most measurements were performed between late August and early October. If the measured CN are representative for the beginning of October, the derived sulfuric acid should be lower or might not be necessary at all.

In September above the CN layer at ~28 km, too many CN are simulated even without sulfuric acid being present (Fig.

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If the August CN at ~31 km would be about a third lower, the simulated CN in September and October would be in the measurement range. Similarly, the simulated CN in September at ~20 km are a little higher than the observations. Note, however, that we assume no sulfuric acid. If there were some sulfuric acid present, it would condense on the existing CN, increase their size and coagulation efficiency, which would result in lower CN concentrations.

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forms at sulfuric acid concentrations where ion-induced nucleation does

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have to nucleate there, but only particles that formed already in September but remained smaller than the CN-counter threshold have to grow to explain the observations

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are too low and the negative clusters recombine too fast for ion-induced nucleation to occur at significant levels. However, nucleation would be dominated by ion-induced nucleation if it occurred at slightly higher temperatures. We derived sulfuric acid concentrations for