

We thank Reviewer #1 for their efforts in reviewing our manuscript. Responses below.

Recent research has indicated that stabilized Criegee Intermediates (sCI) could play an important role in atmospheric oxidation of e.g. SO₂. In this manuscript by Pierce et al., the authors implement sCI+SO₂ chemistry into the global aerosol model GEOS-Chem. The main focus of the work is on the effect of the additional SO₂ oxidation pathway on cloud condensation nuclei (CCN) concentrations. The manuscript is well written, concise and with clear conclusions. The manuscript should be published after addressing the following comments.

1) The main conclusion of the manuscript is clear, and maybe expected: additional sulfuric acid has little effect on CCN concentrations in regions where most of the particle growth is due to organics. This result should of course be somewhat sensitive to model parameters such as nucleation rate and the assumed size of emitted primary particles. With e.g. lower activation nucleation coefficient you should have less nucleation, less competition for growing vapours, and maybe the CCN-sensitivity to sCI+SO₂ might be higher? If possible, the authors should include a sensitivity simulation with modified nucleation parameters (or primary emission diameter), or at least add some discussion on the issue.

Yes, there would be *some* sensitivity of these conclusions to the nucleation scheme or primary emissions assumptions, the changes in the sensitivity of CCN to CI+SO₂ chemistry will be 2nd-order (e.g. we added 100 Tg SOA yr⁻¹ for extra growth of the particles and the sensitivity of CCN to CI+SO₂ had a relative change of a few percent). Regardless, the reviewer is certainly correct that we certainly haven't tested the full parameter space and we should address this.

We have added the following text to the article: “Similarly, we did not test the sensitivity to CCN changes to CI+SO₂ chemistry under different nucleation-rate, primary-emissions or deposition assumptions; however, while uncertainties in each of these assumptions affect the CCN predictions, their effect on the sensitivity of CCN to CI+SO₂ chemistry is likely minimal (as was the case with the XTRA-SOA simulations, where CCN changed greatly due to the additional SOA, but the sensitivity of CCN to CI+SO₂ chemistry did not greatly change).”

2) The description of the sensitivity tests with additional SOA should be more clear: is the SOA mass artificially increased (with emissions correlated with CO), or are some precursor emissions increased? It seems that SOA formation is increased in a way that XSOA experiments do not provide more sCI, but only more particle growth?

This is correct. In Section 2.1, we had written, “The extra SOA in the XSOA cases has no effect on the CI chemistry.”, but this is easy to miss and perhaps easy to misinterpret. We have re-written this as “The extra SOA in the XSOA cases is added as condensable material in the grid boxes where CO is emitted. This extra SOA does not contribute to additional CI formation or alter the gas-phase chemistry scheme in any way.” and added a sentence later in the same paragraph, “Because the extra SOA in the XSOA cases have no impact on the CI chemistry, the BASE-CI and XSOA-CI cases have the same CI budgets (described in the next section).”

For the caption of Table 2 (CI budget), we changed “Sources and sinks of CIs in the BASE-CI and XSOA-CI simulations.” to “Sources and sinks of CIs in the BASE-CI and XSOA-CI simulations (same for both simulations).” Similarly, for Figure 1, we had mentioned that the rates of CI production are for both the BASE-CI and XSOA-CI simulation. We have added an additional “(same for both

simulations)”.

In the discussion of Figure 2, we had written, “Figure 2 shows the global relative contributions to the various SO₂-loss pathways as predicted by GEOS-Chem for the BASE and BASE-CI cases (XSOA and XSOA-CI, respectively, gave identical results).” And the caption already reads, “Figure 2. Fractional contributions of SO₂-loss pathways predicted for the BASE and BASE-CI simulations (XSOA and XSOA-CI simulations give the same respective SO₂ budgets).”

Thus, there were several different places where we had mentioned that the extra SOA had no effect on the CI chemistry, but we have added additional discussion for clarity in several places.

3) Is the GEOS-Chem originally missing H₂SO₄ if compared against observations? As the implemented chemistry seems to induce large changes in H₂SO₄ concentrations, it might help the reader to know if this initial effect is towards a better direction for model performance.

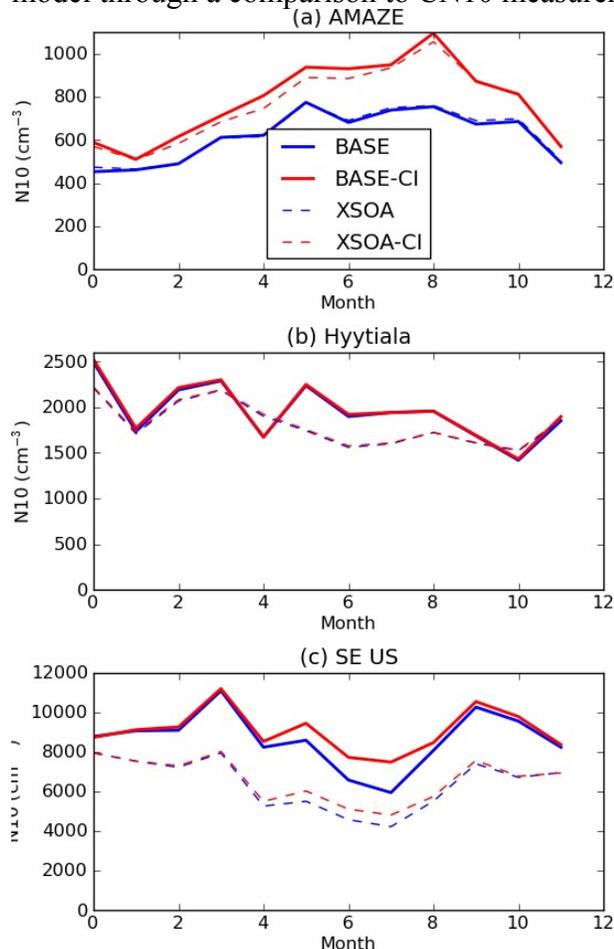
We had intended to do this comparison, and we have added the following paragraph to the manuscript to describe why we have not done it (and we defer to the Boy et al. (2012) study as the current best use of this technique).

“It would be useful to evaluate the model-predicted H₂SO₄ concentrations against field observations (e.g. at Hyytiälä, Finland where these observations has been performed over extended time periods (Riipinen et al., 2011)) to determine if the CI+SO₂ chemistry improves modeled H₂SO₄ concentrations. However, (1) the model overpredicts H₂SO₄ by a factor of 2 at Hyytiälä even without CI+SO₂ chemistry (likely because the large model grid box also includes cities and source regions, and there are uncertainties in the condensation sink), and (2) the modeled H₂SO₄ is more sensitive to the condensation sink (80% reduction in H₂SO₄ concentrations at Hyytiälä due to the addition of the extra 100 Tg of SOA per year in the XSOA simulation) than the CI+SO₂ chemistry (25% increase in H₂SO₄ at Hyytiälä). Similarly, uncertainties in the accommodation coefficient and primary emissions would also cause uncertainties in the condensation sink. Thus, we were not able to not gain any useful information about CI+SO₂ chemistry on improving H₂SO₄ concentrations in our model. On the other hand, the study of Boy et al. (2012), which simulated the local conditions explicitly with constrained condensation sinks and SO₂ concentrations, did predict that CI+SO₂ chemistry was needed for the closure of H₂SO₄ concentrations. This is no evidence from our current study to either support or refute their conclusions, and we defer to their study as the current best estimate of the role of CI+SO₂ in generating H₂SO₄.”

4) The same for CN: does the inclusion of sCI+SO₂ chemistry improve for example the intra-annual variation profiles of total particle number? The additional chemistry would likely increase the magnitude of the seasonal cycle, which could already be overestimated by the model? The two chosen locations (Hyytiälä and AMAZE) might not reveal the whole picture of the effect. Unfortunately, the effect seems to be largest in areas with very little observations. Maybe at least an additional station could be included from Eastern US, where the effect can reach 15% for CN?

We plotted the season cycle in CN 10 at the AMAZE site, Hyytiälä and the SE US (Northern Alabama) for the 4 simulations below. There is some effect on the magnitude of the season cycle at the AMAZE site and the SE US. However, this season cycle will also be sensitive to the season cycle of biomass burning emissions and SOA near these two sites. Considering that the change in the season cycle due to the addition of CI is not substantial, we do not believe that we can constrain the CI+SO₂ in the

model through a comparison to CN10 measurements.



5) While 1-year simulations are likely enough for the annual CN/CCN calculation, the AIE is somewhat sensitive to the modeled cloud fields. The approach here uses climatological cloud fields and prescribed updraft velocities, and considers only the cloud albedo effect, which could underestimate the total aerosol indirect effect related to *sCI*+*SO2*. With the presented changes in CCN concentration, the indirect aerosol effect is likely small, but Section 3.5 should include an uncertainty range for AIE, and discussion on the limitations of the approach.

We have examined the sensitivity to the assumed updraft velocity on AIE, similar to what was done in Spracklen et al. (2011a). The table below shows the AIE due to including of CI+SO2 chemistry for the BASE and XSOA cases.

Updraft velocity (m s ⁻¹)	Annual mean first aerosol indirect effect (W m ⁻²) due to inclusion of CI chemistry	
	BASE	XSOA
0.1	-0.025	-0.028
0.2	-0.031	-0.034
0.3	-0.031	-0.036
0.4	-0.030	-0.035

0.5
MEAN*

-0.030
-0.029

-0.033
-0.033

To the methods section we now have, “As a base assumption, we assume a uniform updraft velocity of 0.2 m s^{-1} , but test values between 0.1 and 0.5 $0.2\text{--}0.5 \text{ m s}^{-1}$ to test the sensitivity to this.”

In the Section 3.5, we now have, “When the updraft velocities are varied between 0.1 and 0.5 m s^{-1} , the range of AIE was -0.025 to -0.031 W m^{-2} for the BASE case (and -0.028 to -0.036 W m^{-2} for XSOA).”

Regarding the sensitivity to prescribed cloud fields, a recently submitted paper (Rap et al., 2013) using the GLOMAP aerosol microphysics model with the same AIE technique evaluated the differences in AIE when year-2000 cloud fields were used rather than the 1983-2008 climatology used here (Table A1, Rap et al., 2013). The authors found that using the two different cloud climatologies introduced variation in the AIE of less than 5%, across a number of natural aerosol sources. We now address this in the paper.

Indeed the total AIE due to CI+SO₂ could be larger if cloud lifetime effects were included. We have added to the methods section, “As we only quantify the cloud albedo AIE sensitivity to CI+SO₂ chemistry, the total AIE (when cloud lifetime effects are included) may be larger.” In Section 3.5, we have added, “As these estimates are only for the cloud albedo AIE, the total AIE may be higher if aerosol lifetime effects were included.”

5) The aerosol indirect effect (Section 3.5) varies significantly from model to another. It would be useful for the reader to know some baseline for aerosol indirect effect in the GEOS-Chem, such as anthropogenic aerosol indirect forcing since pre-industrial, even if this can be found from the included references.

We have not done the aerosol indirect forcing since the pre-industrial time period in GEOS-Chem TOMAS. Additionally, this would not likely be useful for getting a baseline sensitivity of AIE. The variability in pre-industrial-to-present-day radiative forcing between models will not only be dependent on the model AIE sensitivity to CCN changes but also to the time-dependent aerosol emissions/processes in the models. Thus a model that shows a relatively large PI-PD RF change may not show a relatively large AIE sensitivity to a process change in PD simulations. Regardless, because the CI+SO₂ sensitivities are an order-of-magnitude smaller than many other sensitivities, model-to-model variation likely is not an issue.

6) Could some future aspect be included in the conclusions: if assuming a significant decrease in global anthropogenic SO₂ emissions (50-90%) and a simultaneous increase in the biogenic VOC emissions (induced by climate warming), what would happen to the CN or CCN sensitivity to sCI+SO₂?

To the conclusion we have added, “Additionally, a warmer future climate could bring additional biogenic alkene emissions, which may increase the fraction of SO₂ that is oxidized by CIs. However, additional biogenic alkenes may also yield more SOA. Additional SOA coupled with potential future reductions in SO₂ emissions would mean that H₂SO₄ would be even less important for ultrafine particle growth, and the sensitivity of CCN to CI+SO₂ chemistry could be even less than in the present day.”

References:

Rap, A., Spracklen, D. V., Bellouin, N., Carslaw, K. S., Schmidt, A., Scott, C. E., Mann, G. W.,(2013).
"Natural aerosol direct and indirect radiative effects." *Geophysical Research Letters*, submitted.