Response to reviewer comments for the manuscript: **Understanding and constraining global secondary organic aerosol amount and size-resolved condensational behavior** by **D'Andrea et al.**

We would like to thank the anonymous reviewers for the overall positive and insightful comments on the manuscript. The original comments are in italics and the response to each comment is directly below the comment. We will submit a revised version of the manuscript and figures with the changes outlined below.

Response to review 1:

In the manuscript by D'Andrea et al., the influence of secondary organic aerosol formation on aerosol number size distributions is investigated by a series of sensitivity tests made using a global aerosol model with detailed aerosol microphysics. The paper is very clearly written and thereby easy to follow. I do not find any scientific or technical errors in the paper. Since the topic investigated in this paper is highly relevant for modeling and understanding both global and regional SOA formation, and ultimately atmospheric cloud condensation nuclei production, I am in favor of accepting this paper for publication after some revisions explained in more detail below.

First of all, I do not think that the title of the paper correctly reflects its contents. The investigation does contribute to understanding and constraining size-resolved condensation behavior but, in my opinion, it does relatively little to constrain the secondary organic aerosol amount. I suggest that the author consider modifying the title somehow.

We have changed the title to reflect the above comment to "Understanding global secondary organic aerosol amount and size-resolved condensational behavior "

Second, I do not fully understand why the considered particle size regimes vary from section to section. For example, in sections 3.1 and 3.2 authors have chosen N3, N10, N40 and N80, which is fine when investigating changes in both nucleated particles and CCN. However, in model-measurement comparison N3 has been dropped of and N150 is used instead. The Abstract and Conclusions sections discuss only particles larger than 40 nm (N40), providing only a partial view on the results obtained from the whole analyses.

This should have been stated explicitly in the paper, but was not. When understanding the role of SOA in the growth of particles to CCN sizes, it is important to illustrate the behavior with plots of N3, N10, N40 and N80. However, in the model-measurement comparisons of the full size distribution, it is important to include N150 since the addition of extra SOA had a significant impact on the model output in this size range. In the MASS-XSOA simulations, the mass is going directly to the larger particles, hence having little impact on increasing the number of 150 nm particles by growth from smaller sizes. However, in the SURF-XSOA simulations, the mass is going to particles smaller than 150 nm and growing them to sizes greater than 150 nm. This increases N150 and more accurately matches measurements. While N40 and N80 are likely more appropriate proxies for CCN in most clouds, N150 is an important constraint on the shape of size distributions. Although N3 is important in investigating nucleation, in size distribution shape analysis N3 behaves enough like N10 that we felt it was acceptable to remove it from the model-measurement comparison. Additionally, many of the observed size distributions did not include measurements below 10 nm. Therefore, we include N150 in the model-measurement comparisons rather than N3.

We have included the following text into section 3.4 of the manuscript: "N150 was included in this figure since the additional SOA and changes in the condensational behavior of SOA caused significant changes to the number of particles larger than 150 nm. This change in N150 had a large impact on the shape of the size distribution. In contrast, N3 in size distribution shape analysis behaves enough like N10 and with most of the observations starting around 10 nm, N3 was removed from the model-measurement analysis."

Finally, I think that the authors should discuss, and preferably also provide some guidance for, future model development and model-measurement comparisons regarding atmospheric SOA formation. How would the authors prioritize large-scale model development aiming to improve the SOA treatment when considering the balance between accuracy and computationally costs? Which other quantities, besides aerosol number size distribution, should be compared when evaluating SOA models and which kind of comparisons are feasible at current state and near future?

We agree that some ideas for future studies should be included in the manuscript. The following text has been included into the conclusions section of the manuscript to address this: "Future studies could use size-resolved composition from state of the art instruments to further constrain SOA; it is important to not only get the size distribution correct, but it is important to get the composition correct too. More sophisticated SOA schemes involving SOA volatility and chemistry may further improve size distributions; however, combining these SOA schemes with aerosol microphysics is computationally expensive. "

Response to review 2:

In this work, the authors examine methods of secondary organic aerosol (SOA) condensation in the global chemical transport model, GEOS-Chem, and the implications for particle size distributions. The base model forms SOA by assuming a 10% yield of aerosol from monoterpene emissions. The condensational behavior of that aerosol was assumed to be either mass (thermodynamic, MASS) or surface area (kinetic, SURF) based. A second set of simulations added 100 Tg/yr to the preexisting 19 Tg/yr of SOA and reexamined the impacts of mass and surface area based behavior on particle size distributions. A third set of simulations added corrections to the surface area uptake and did not significantly affect aerosol size distributions compared to the second set of simulations. Adding 100 Tg/yr of SOA in both the mass and surface area based parameterizations generally significantly improved model-measurement agreement for particle number distributions. Best agreement with observations was found for the surface area condensational behavior with an extra 100 Tg/yr of SOA. The paper is well written and it is easy to understand the author's method. The manuscript should be suitable for publication after addressing the following comments.

1. The authors discuss the idea of thermodynamic vs. kinetic condensational behavior on page 18974. Could the authors better clarify/distinguish between equilibrium/kinetic uptake and nonvolatile/semivolatile aerosol?

We agree that the idea of thermodynamic vs. kinetic condensational behavior is not described in enough detail in the manuscript. The following text was added to the Introduction to address this: "In summary, thermodynamic condensational behavior assumed that the gas-particle partitioning reaches equilibrium instantly when means that the net particle condensation is proportional to the particle mass. This assumes SOA to be semi-volatile (e.g. $C^* \sim 1$ μg m^{-3}) where the SOA mass reaches thermodynamic equilibrium quickly and partitions into the pre-existing aerosol mass. Kinetic condensational behavior is limited by gas-phase-diffusional growth and thus vapors condense kinetically proportional to the aerosol surface area. This assumes SOA to be effectively non-volatile (e.g. $C^* < 10^{-3}$ μg m^{-3}). This is explored in detail in Riipinen et al., 2011 and Pierce et al., 2011."

The definition of thermodynamic behavior used here seems to assume equilibrium of semivolatile SOA. The kinetic behavior assumes nonvolatile SOA and diffusion-limited growth. Is it possible to examine deviations from equilibrium and volatility separately?

Yes, you are correct here. Thermodynamic condensation does assume equilibrium of semivolatile SOA and kinetic condensation assumes nonvolatile SOA. The text included above has been added to the introduction to clarify this. It is possible to explore deviations from these two assumptions; however, this requires the explicit simulation of both volatility and the size distribution, which is very computationally expensive. It was done for specific locations in a box model in Pierce et al., 2011, and the effective volatility was found to be very low and consistent with the kinetic assumption.

Is it possible to get good model agreement if semivolatile aerosol (or aerosol spanning a continuum of volatility) is taken up by a parameterization accounting for diffusion and volatility (presumably the diffusion term is always present, it is just more or less important at times)?

Yes, but a large fraction of the SOA would need to be very low volatility (i.e. C* <= 1E-3). This was explored in Pierce et al., 2011. To explicitly simulate both volatility (e.g. through a volatility basis set) and the size distribution in a 3D model is computationally expensive and not currently feasible in our group.

2. Except for one metric in one size range (LMB, N40), the MASS-XSOA simulation is significantly improved compared to MASS-BASE. Does that indicate the assumption of equilibrium condensational behavior is less of a problem than getting the overall rate of SOA formation correct (in terms of implications for size distributions)?

There is definitely improvement from MASS-BASE to MASS-XSOA, however there is also an improvement in all metrics from MASS-BASE to SURF-BASE. This indicates that the assumption of volatility is also an important parameter. However, to most accurately represent size distributions in our work, assumptions to both the condensational behavior and the SOA formation rate must be correct. The following text has been added to the last paragraph of section 3.4 in the manuscript to address this: “There is a significant improvement in most metrics when the additional SOA was included (i.e. from MASS-BASE to MASS-XSOA); however, there is also a significant improvement in all metrics when kinetic condensation was assumed instead of thermodynamic condensation (i.e. MASS-BASE to SURF-BASE). This indicates that both the amount and condensational behavior of SOA are important in order to accurately represent size distributions. However, it appears…“

Is the observational agreement with MASS vs SURF specific to the amount of mass added? (What happens if you add 150 or 200 Tg/yr?)

This was not tested since the addition of 100 Tgyr^{-1} of anthropogenically controlled SOA was found in both Spracklen et al., 2011 and Heald et al., 2011 using different methods. Using 100 Tgyr^{-1} also brought the statistical metrics closer and including more SOA would likely overestimate the number of CCN-sized particles. Based on the log-mean bias of N80 going from -0.078 in SURF-BASE to 0.008 in SURF-XSOA, it is likely that adding more SOA would likely cause too many CCN-sized particles in polluted regions in our model framework. This may be good to look at in the future; however, these simulations are computationally heavy and time intensive.

3. Figure 6 of Riipinen et al. 2011 indicates the kinetic model significantly increases the number of particles in the 10^{-8} to about $3x10^{-8}$ m diameter range. Figure 8 of this work indicates that the SURF-BASE and MASS-BASE are very similar with SURFBASE often being lower. Can the authors comment on why they are different?

Figure 6 in Riipinen et al. 2011 is a snapshot in time during a single nucleation and growth event. Our work is averaged over all times where particles grow to diameters larger than 30 nm and will feed back on nucleation rates via and increased condensation sink (i.e. more growth = reduced nucleation). In Riipinen et al. 2011, the nucleation rates were fixed, and the timing of the snapshot was such that the growing nucleation mode was centered at 20 nm.

4. Page 18982, Line 1-14, can more explanation of why these changes are seen be added? In particular, why are some decreases in N3 seen in Figure 5?

The following text has been added to section 3.2 of the manuscript: "In some regions downwind of biogenically active regions, N3 decreases by more than 10%. The increased ultrafine particle growth in the biogenically active regions causes an increase in the coagulational sink for small particles and they are removed more quickly, therefore causing a deficiency in N3. As the air masses move over oceanic regions away from these regions, relatively few emitted or nucleated ultrafine particles are available to replace the lost N3."

Minor comments:
1. Why does sulfuric acid decrease when switching from SURF-BASE to SURF-XSOA (Figure 4)?

This is explained in paragraph 2 of section 3.1. The global decrease in sulfuric acid vapor is due to the increase in the condensation sink from the increase in larger particles when the additional SOA is added to the model. The following text has been added to the manuscript to clarify this: "There is a global decrease in sulfuric acid vapor of 18.8% (larger near many anthropogenic CO source regions) with the inclusion of the additional SOA since the condensation of sulfuric acid vapor increases with the increased number of large particles (increased condensation sink)."

2. Page 18973, line 2-4, awkward sentence.

The sentence has been changed to the following: "Measurements of the submicron particle composition throughout the continental boundary layer show 20 – 90% of the aerosol is organic, and much of this organic aerosol is SOA (Jimenez et al., 2009)."

References:

Heald, C. L., Coe, H., Jimenez, J. L., Weber, R. J., Bahreini, R., Middlebrook, A. M., Russell, L. M., Jolleys, M., Fu, T.-M., Allan, J. D., Bower, K. N., Capes, G., Crosier, J., Morgan, W. T., Robinson, N. H., Williams, P. I., Cubison, M. J., DeCarlo, P. F., and Dunlea, E. J.: Exploring the vertical profile of atmospheric organic aerosol: comparing 17 aircraft field campaigns with a global model, Atmos. Chem. Phys., 11, 12673-12696, doi:10.5194/acp-11-12673-2011, 2011.

Pierce, J. R., Riipinen, I., Kulmala, M., Ehn, M., Petäjä, T., Junninen, H., Worsnop, D. R., and Donahue, N. M.: Quantification of the volatility of secondary organic compounds in ultrafine particles during nucleation events, Atmos. Chem. Phys., 11, 9019-9036, doi:10.5194/acp-11-9019-2011, 2011.

Riipinen, I., Pierce, J. R., Yli-Juuti, T., Nieminen, T., Häkkinen, S., Ehn, M., Junninen, H., Lehtipalo, K., Petäjä, T., Slowik, J., Chang, R., Shantz, N. C., Abbatt, J., Leaitch, W. R., Kerminen, V.-M., Worsnop, D. R., Pandis, S. N., Donahue, N. M., and Kulmala, M.: Organic condensation: a vital link connecting aerosol formation to cloud condensation nuclei (CCN) concentrations, Atmos. Chem. Phys., 11, 3865-3878, doi:10.5194/acp-11-3865-2011, 2011.

Spracklen, D. V., Carslaw, K. S., Poschl, U., Rap, A., and Forster, P. M.: Global cloud condensation nuclei influenced by carbonaceous combustion aerosol, Atmos. Chem. Phys., 11, 9067–9087, doi:10.5194/acp-11-9067-2011, 2011a.

Spracklen, D. V., Jimenez, J. L., Carslaw, K. S., Worsnop, D. R., Evans, M. J., Mann, G. W., Zhang, Q., Canagaratna, M. R., Allan, J., Coe, H., McFiggans, G., Rap, A., and Forster, P.: Aerosol mass spectrometer constraint on the global secondary organic aerosol budget, Atmos. Chem. Phys., 11, 12109-12136, doi:10.5194/acp-11-12109-2011, 2011b.

Response to review 3:

The authors present a model study exploring sensitivities of SOA characteristics (amount and condensational behavior) to changes in CCN number concentrations. Specifically, they explore differences in the number concentration of particles with cutoff diameters of 3, 10, 40, and 80 nm with the latter two being proxies for CCN. They find that a surface-based distribution of SOA mass leads to best results in terms of statistical parameters if model results are compared to measurements at various locations in the US and Europe. Other parameterizations such as a SOA mass distribution based on preexisting aerosol mass or size-dependent growth rates for small particles lead either to a bias in predicted CCN number concentration or have little effect, respectively.

Overall, this model study provides an important step towards a better representation of SOA formation and particle growth in global (and likely smaller scale) models. The paper is very clearly written and easy to follow. I have only some minor comments that should be taken into account before the manuscript can be accepted for publication in ACP.

1) The conclusions are mostly a summary of the model results. There is nothing wrong with this fact; however, I am missing somewhat a conclusive recommendation for future model studies. Do the authors recommend that only surface-controlled ('kinetic condensation') should be used in models? In the beginning, they say that the truth is likely a combination of both thermodynamic and kinetic condensation. How should that transition be handled in models?

For future models, the condensation of SOA would be some mixture between kinetic and thermodynamic condensation and could be determined through further constraints. Riipinen et al. 2011 explores a 50/50 case between the two, but in this study we chose to explore the two limiting cases (a 50/50 case was tested, but the results were similar to the kinetic case). The addition of more sophisticated SOA schemes may further improve simulations of size distributions and further constrain models. The following text was added to the manuscript to address this: "Future studies could use size-resolved composition from state of the art instruments to further constrain SOA; it is important to not only get the size distribution correct, but it is important to get the composition correct too. More sophisticated SOA schemes involving SOA volatility and chemistry may further improve size distributions; however, combining these SOA schemes with aerosol microphysics is computationally expensive. "

2) One proxy for CCN is N40, i.e. the number concentration of particles with diameter < 40 nm. Some information might be useful under what circumstances these particles might indeed be activated not cloud droplets. Using a typical hygroscopicity for SOA of ï ¸An = 0.1, the critical supersaturation is >1% for a 40 nm particle. How frequent are ´ such relatively high supersaturations around the globe?

We believe the reviewer meant to say that N40 is the number of particles with diameter > 40 nm. High supersaturations, such as >1% may be achieved for faster updraft rates (e.g. >1 m/s) and/or for clean aerosol distributions. In this study we used two proxies for CCN to address this issue. N80 represents approximately 0.2% supersaturation. We use these two proxies because they provide information on the CCN changes for high- and low-superaturation clouds.

3) Overall, the authors should carefully go through the manuscript and define all symbols and terms, even if they are common within the model community (e.g., BL, Fuchs surface area, C, NH, SH, etc).*

The terms have been more clearly defined in the manuscript.

In addition, while it is clear what the authors mean, some of the rather colloquial expressions should be *corrected, e.g.: p. 18972, l. 4: CCN number concentration (not simply 'CCN') p. 18979, l. 8: "Each site measures: : :" should be replaced by "At each site, it is measured: : :" (or similar – the sites do not perform the measurements) p. 18982, l. 2 (and other places): "the annual-average BL percent change in N3, N10, N40 and N80" might imply that BL changes. It might be better to use " the annual-average percent change in N3, N10, N40 and N80 throughout the BL" (or similar) p. 18983, l. 4: Be more specific and explain what is meant here by 'aerosol microphysics'*

The expressions have been clarified throughout the manuscript. Also, to clarify aerosol microphysics the following text was included in the manuscript: "(nucleation, condensation, coagulation and other processes that shape the aerosol number, size and composition)"

4) Some more explanation of the sensitivity of the CCN number concentration to SOA amount (Sect. 3.1) should be given: - Can the decrease of sulfuric acid with an added SOA condensation sink be explained by a faster particle removal?

The sulfuric acid is in the vapor phase, therefore the increasing rate of condensation of sulfuric acid (to the larger condensation sink) is what is causing the decrease in concentration. A faster particle removal rate would lower the condensation sink and lead to an increase in sulfuric acid vapor concentration. To be clear in the text that we are talking about sulfuric acid *vapor*, we have changed the manuscript to explicitly state "vapor" at several points in the text.

The fact that fewer ultrafine particles exist in the SURF-XSOA case might appear somewhat counterintuitive. Is it because growth rates are so quick and thus all ultrafine particles are nearly immediately converted into N40 or larger? Please clarify.

There are two reasons why there are decreases in ultrafine particles: (1) the decrease in sulfuric acid concentration (due to the increased condensation) suppresses nucleation, and (2) the increase in N40 and N80 increases the coagulational sink for small particles and they are removed more quickly.

5) End of Section 3.4: In order to better evaluate the order of magnitude of additional effects that impact CCN number concentration, could you give some approximate (percentage) uncertainties introduced by effects such as uncertainties in nucleation, primary emission etc?

We agree that it is important to include approximate uncertainties with the various processes mentioned. The following text has been added to section 3.4 of the manuscript to address this: "A recent global model uncertainty study by Lee et al., 2013 find that the relative uncertainties to global mean CCN number concentrations vary between model parameters. The relative uncertainty to CCN (from -2σ to 2σ) due to accumulation mode dry deposition, Aitken mode dry deposition, anthropogenic SOA emissions, biogenic SOA emissions and boundary layer nucleation are approximately 40%, 18%, 20%, 12% and 5% respectively (Lee et al., 2013)."

Minor/technical comments

p. 18977, l. 3: What is meant by 'emission size'?

By emission size we refer to the size of the emitted particles. This is rather vague in the text and therefore the manuscript has been updated with the following text to eliminate this confusion: "We note that the predicted size distributions and uncertainty ranges in this paper are sensitive to the nucleation scheme, emissions fluxes and size of emitted particles (e.g. Pierce et al. 2009c), but here we explore…"

p. 18977, l. 24: is this a completely empirical factor without any units?

Yes, it is. It is a size-dependent scaling factor from 0-1. The following text has been added to the manuscript to clarify this: "…where k is an empirical unitless condensation scale factor…"

p. 18978, l. 10: In the previous section, it is 18 Tg year-1

This has been fixed in the current version of the manuscript. The flux should be 19 Tg yr^{-1}.

p. 18979, l. 22: Why are N3 excluded from this analysis? Are there fewer measurements to compare with available? If so, say so.

Text has been added to section 3.4 of the manuscript to address this issue: "N150 was included in this figure since the additional SOA and changes in the condensational behavior of SOA caused significant changes to the number of particles larger than 150 nm. This change in N150 had a large impact on the shape of the size distribution. In contrast, N3 in size distribution shape analysis behaves enough like N10 and with most of the observations start around 10 nm, N3 was removed from the model-measurement analysis."

p. 18980, l. 19: ': : :are the highest' (or 'sensitivity: : :is the highest')

Text has been updated to "…sensitivities of the size distribution to SOA are the highest."

p. 18985, l. 5: : : :are biased low

Text has been updated to: "…while the others are biased low by a larger magnitude."

Figure 9, caption: It might be useful to refer here to Table 3.

The following text has been added to the caption of Figure 9: "A summary of the statistics is compiled in Table 3."