Response to reviewer #1

ACP-2014-122: "Volatility basis-set approach simulation of organic aerosol formation in East Asia: implication for anthropogenic-biogenic interaction and controllable amounts" by H. Matsui et al.

We thank the reviewer very much for reading our paper carefully and giving us valuable comments. We have revised our paper by taking into account the reviewer's suggestions. Detailed responses to individual comments are given below.

Major points:

1) Page 6210, lines 18 – 26, Uncertainties of simplicity in our VBS model

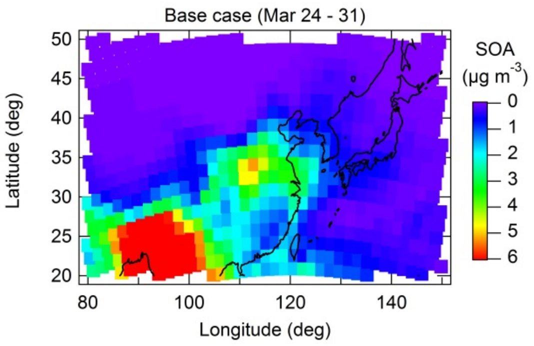
Reviewer's comment:

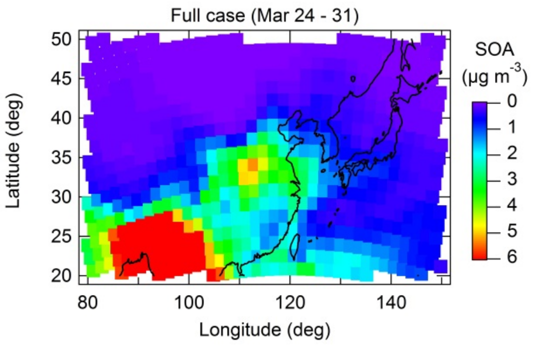
This simplification is a promising solution to a vexing problem in modeling OA in large-scale CTMs and maintaining some amount computational efficiency. The authors explain the approach well enough, but don't mention the possible numerical consequences. Much of the OA loading is admittedly accumulation mode, but not all. I would expect much of the POA material to be at low sizes, more characteristic of combustion processes. Moreover, the authors are working with an on-line, coupled MET/CTM; what impact does this simplification have for cloud activation? Are there any previous examples of a model trying this approach? The authors should, at the very least, warn the reader that the effects of this approach are very uncertain.

Response:

We conducted a simulation without the simplicity of the VBS model during 21-31 Mar 2009. In this simulation, OA size distribution is calculated for each of the VBS species (53 species x 8 size bins). Aerosol-phase (interstitial) and cloud-phase (in-cloud) aerosols and their size distributions are calculated separately for each VBS species. From the comparison between this sensitivity simulation including full representation of OA species and the base case simulation with the simplicity, the uncertainties in the estimation of SOA mass concentrations in the base simulation were estimated to be about 20% (as a total effect of OA formation, activation, and removal processes). The correlation coefficient (R^2) of SOA spatial distribution (at about 1 km) between the two simulations was 0.96, suggesting that the performance of OA distributions is good enough in the base case simulation (figures below).

We have clarified these conclusions in the revised manuscript (Sec. 2.3).





2) Page 6211, lines 1 – 10, Uncertainties in S/IVOC emissions

Reviewer's comment:

The assumption of (SVOC+IVOC)/POA = 7.5 is very uncertain and claiming consistency with the Mexico City studies is not enough for justification. Are there any volatility measurements from East Asia to even get a small peek at how reliable this assumption might be? Are the combustion activities (i.e. vehicle types, energy usage, etc) similar enough between all of East Asia and Mexico City to warrant such an assumption without exploring its uncertainty? I would expect to see some kind of sensitivity study focusing on this parameter. The disclaimer at the end of Section 2 (that these uncertainties were discussed in Tsimpidi et al. (2010)) does not quite hold up since that work focused on entirely different geographical scales, energy generation profiles, and soci-economic contexts. Moreover, noting that POA emissions were constrained with measurements, it is very likely that some of the POA measured consisted of semivolatile compounds. If this is the case, then multiplying POA by 3 to get the SVOC emissions would overpredict POA concentrations. Should not the POA emissions be rescaled to account for this?

Response:

Since we could not find a good reference for S/IVOC emissions over East Asia, we examined the sensitivity of the treatment of S/IVOC emissions by conducting two sensitivity simulations. A sensitivity simulation with the increase in SVOC (C* ranging from 10^3 to 10^{-2} µg m^{-3}) emissions by a factor of 2 enhanced total OA and SOA concentrations by 25% and 45%, respectively. Another sensitivity simulation with the increase in IVOC (C* ranging from 10^6 to 10^4 µg m^{-3}) emissions by a factor of 2 enhanced total OA and SOA concentrations by 20% and 15%, respectively. These results suggest OA concentrations are moderately sensitive to the treatment of S/IVOC emissions over East Asia. We have added these results to the revised manuscript (Sec. 2.3).

The modifications of POA emissions based on measurements were applied to the simulations in and around Tokyo only. We do not use these modifications in the simulations over East Asia. We have clarified this point in the revised manuscript (Sec. 3.1).

3) Uncertainties in controllable fraction estimate

Reviewer's comment:

As seen in Fig. 8a and Fig. 10, the large controllable fraction estimate is significantly related to the huge OPOA concentrations present when anthropogenic aging is turned on, as the authors point out. This is hugely uncertain. It is probably an upper limit and should be stated somewhere.

Response:

As the reviewer suggested, we have added a description that S/IVOCs emissions and their aging rates have large uncertainties currently to the discussion of controllable fraction estimate in section 5.2.

4) Model performance versus other parameters

Reviewer's comment:

In general, the authors rely heavily on timeseries comparisons to evaluate the output from the model. Table 5 presents statistical evidence of mixed results. Figure 5 though, begins to address other types of comparisons that may be more telling for the capabilities of this model. Seeing as how there is only one take home point from Fig. 5 (that the model with aging performs much better than that without aging), I wonder if there are more comparisons along "chemical coordinates" that would be helpful here. For instance, why didn't the authors look at model performance versus temperature, time of day, black carbon or CO concentrations, precipitation, OOA/OA ratio, etc to try to characterize the ability of the model to predict SOA relative to its ability to predict other model components (in addition to sulfate)? As an example, comparing OA to sulfate allowed the authors to attempt to control for photochemical activity, while comparing to black carbon would control for some important anthropogenic and biomass burning emissions.

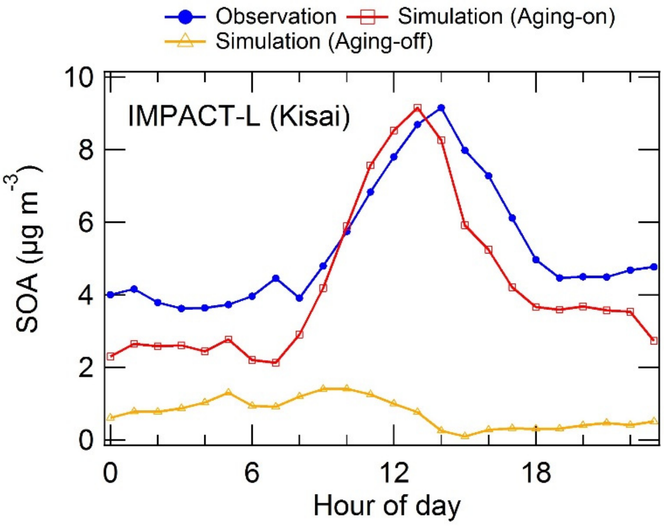
Response:

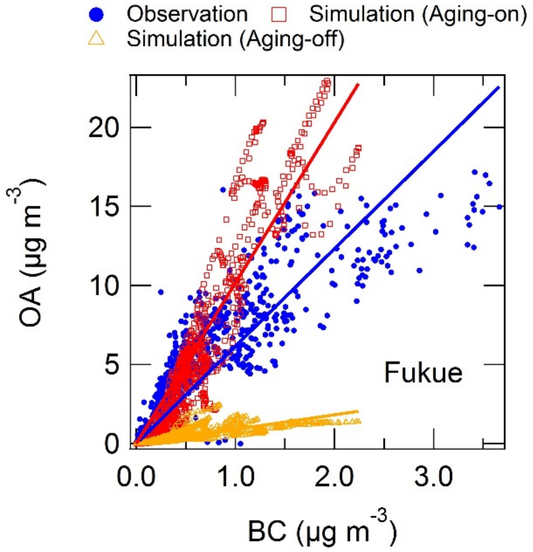
Since meteorological field (temperature, wind, water vapor mixing ratio) is nudged by the NCEP-FNL data, synoptic-scale meteorological variations and related aerosol transport processes are well captured by WRF-chem. Our previous simulation using similar model settings showed that observed precipitation and its spatial distributions were generally reproduced by WRF during the simulation period (Oshima et al., 2013). We have added these descriptions to the revised manuscript (section 3.2).

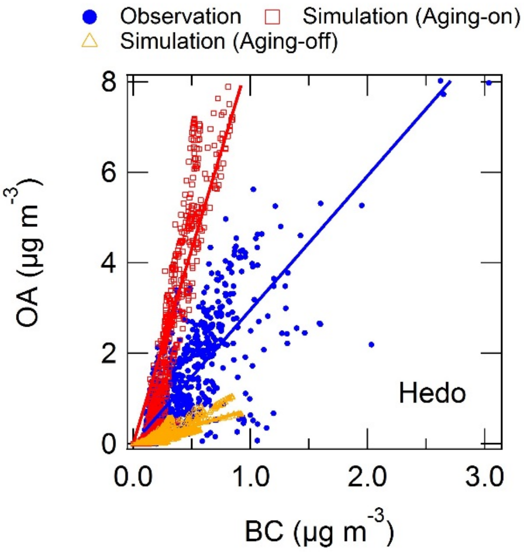
We have added the comparison of BC mass at Fukue and Hedo sites to evaluate model performance of primary aerosol species. We have added figures (Figures 6a and 6b) and statistics (Table 5) of BC in the revised manuscript.

We also examined the diurnal variation of SOA at Kisai and the relationship of OA/BC at Fukue and Hedo to confirm the model performance (figures below). The model performance of SOA diurnal variations at Kisai is much improved by considering aging processes. The performance of OA to BC ratios is also improved by aging processes at Fukue and Hedo, while the ratios are overestimated at both sites. This overestimation may suggest the overestimation of aging processes and/or S/IVOCs emissions in our model, though the uncertainties in AMS measurements may also contribute the discrepancy between measurements and model simulations (section 3.2). Since these conclusions are similar to those obtained by SOA/O_3 plots (Komaba and Kisai) and OA/SO_4 plots (Fukue and Hedo) and are already described in the text, we do not add these figures to the manuscript. The correlation between SOA and temperature was not good during IMPACT ($R^2 = 0.19$ at Kisai, not shown).

Observed OOA/OA ratio was estimated to be greater than 95% at Fukue and Hedo (Zhang et al., 2007). Simulated SOA/OA ratio was 84% at Fukue and 83% at Hedo, suggesting that our model simulations tend to underestimate the fraction of SOA to total OA at these measurement sites. We have added these descriptions to the revised manuscript.







5) OA concentrations and size information in model, controllable PM

Reviewer's comment:

I was surprised in general that the OA concentrations were so low, given the notoriety of Beijing and other East Asian cities. They seem to compare approximately similar to results obtained for the US (Lane et al., ES&T, 2008) and Europe (Fountoukis et al., 2011). Are these results only including PM_1 concentrations, in order to be more comparable to the AMS results? I recommend it be stated very clearly what size cutoff is being used so reader's know how to contextualize the results. Since the authors are taking the next step to quantify a "controllable" fraction of OA, I think it would be very beneficial to mention the up-to-date estimates for average total particulate matter concentrations in various parts of the region. Readers in the general aerosol community will be interested to know what impact controlling these sources would have on the total loading (at different sizes), not just that of the OA.

Response:

In our previous study during the CARE-Beijing-2006 campaign, observed OC concentrations were 6.3 μg m^{-3} and observed POC and SOC concentrations were estimated to be 3.9 and 2.4 μg m^{-3} at Beijing in summer 2006 (Matsui et al., 2009). Therefore, we do not think simulated OA concentrations are too low in and around Beijing, though the period is not the same between the CARE-Beijing measurements and our simulations.

In section 4, particles smaller than 1 μm in dry diameter are used for comparisons with AMS measurements. In section 5, we use bulk OA mass concentrations (40 nm – 10 μm). We have clarified this size cutoff information in the revised manuscript.

We estimated controllable amounts of $PM_{2.5}$ over East Asia. The fraction of controllable $PM_{2.5}$ was estimated to be 92% on domain and period average, though dust and sea salt from natural sources are not considered in this study. We have added this result to the revised manuscript. Since OA is the focus of this study, we do not add a figure for $PM_{2.5}$.

Minor points:

6) Page 6205, lines 15 – 25

Reviewer's comment:

Not all "traditional" models underestimated OA and/or SOA concentrations using the Odum approach. For example, see Simpson et al. (2007) where OA was modeled over Europe. Many would argue that the underestimation could just as likely have come from using unrealistically low yields, rather than from not including aging or using the VBS.

Response:

We have revised the text at Page 6205 line 18 from "Using this approach" to "Using these coefficients" to consider the reviewer's comment.

7) Page 6205, line 28

Reviewer's comment:

I would strongly urge the authors to refrain from using the acronym SIVOCs and instead refer to both groups separately, i.e. "SVOCs and IVOCs." While I understand the motivation for streamlining the terminology in the manuscript, it is my opinion that combining these terms will lead to confusion and doesn't add much value.

Response:

We have revised the abbreviation SIVOC as the reviewer suggested. Since the abbreviation S/IVOC is used in some previous studies (e.g., Hodzic et al., 2010; Shrivastava et al., 2011), we used this abbreviation in the revised text.

8) Page 6207

Reviewer's comment:

The authors present a nice discussion of previous work. However, they leave out an emerging concept that I would expect to be important for future work with this model: the role of "anthropogenic water" (Carlton and Turpin, 2013). Improving the model with an aqueous formation pathway and repeating all of the experiments is well outside the scope of this manuscript, which already discusses a lot of issues. I would expect, however, to see this pathway discussed in the introduction though, and I would expect the results to be discussed at some point in the context of this possibly important interaction. Figure 6 suggests that there is plenty of sulfate around. Would a large interaction seem plausible? To what magnitude?

Response:

We have added some description on Carlton and Turpin (2013) to section 5.2 in the revised manuscript: "Carlton and Turpin (2013) suggested aerosol water produced in anthropogenic aerosols (e.g., SO_4) would enhance biogenic SOA mass concentrations in the eastern U. S. through aqueous-phase chemistry. This process is not considered in our model but could be a potentially important mechanism to enhance controllable OA amounts further in East Asia because SO_4 and OA generally have similar spatial distribution over East Asia."

9) Page 6211, lines 14 – 16,

Reviewer's comment:

I'm glad to see the authors point to the uncertainties inherent in dry deposition parameterizations. Please also mention for the reader what has to be assumed physically to effect a change in the dry deposition velocity by a factor of 2. I assume solubility is driving this calculation? If so, what is the range of solubilities that results in a factor of 2 difference?

Response:

We do not use and assume a certain value of solubility or Henry's law constant for S/IVOC and OVOC species used in this study. So, we cannot estimate the range of solubility for them. The dry deposition velocity of S/IVOC and OVOC species is assumed to be that of HNO_3 (V_{HNO3}) in this study. In the sensitivity simulations, we used the values of 2 x V_{HNO3} and 0.5 x V_{HNO3} as the dry deposition velocity of S/IVOC and OVOC species.

10) Page 6211, lines 18 – 24,

Reviewer's comment:

I did not quite understand what the authors have chosen to do for in-cloud aerosol. Is there a separate size distribution for this material? Does the model simulate regeneration of aerosols after cloud drop evaporation? If so, is the chemical composition information (i.e. fractional contribution of ASOA, BSOA, POA, etc) maintained through the process of activation/uptake followed by evaporation/regeneration? Table 3 suggests that in-cloud aerosol is modeled explicitly, but it is unclear how this works.

Response:

In WRF-chem, interstitial (aerosol-phase) and in-cloud (cloud-phase) aerosols are treated separately for all aerosol species (5 inorganic species, BC, OA, and dust) and size bins to calculate in-cloud aerosol formation, regeneration, and wet removal processes. Therefore, OA size distribution is calculated separately for aerosol-phase and cloud-phase in our model. The model considers the increase in total OA (sum of all VBS species) through aerosol regeneration after cloud evaporation. Since the information of each VBS species is not calculated for in-cloud aerosols in our model, chemical composition (mass fraction of each VBS species) of regenerated OA is assumed to be that of interstitial OA at the same three-dimensional grid cell.

We have added these descriptions to the revised manuscript (section 2.2).

11) Section 4.3,

Reviewer's comment:

Section 4.3 is a little light for such a deep topic. Could the authors add some discussion about the choices of aging rate constants? Do they believe these bound the possibilities of aging rate constants in East Asia or just probe the space as in previous work? In many past studies, different aging rate constants were applied to SOA and POA. The authors also explore some past assumptions that ASOA and BSOA age with different rate constants. However, it appears as if they always age anthropogenic POA and SOA compounds similarly. Is there a composition effect when increasing or decreasing the rate constant? More specifically, Table 6 shows that increasing the rate constant by a factor of 4 enhances OPOA concentrations more relative to ASOA. I take it this is because there is a huge source of OPOA material sitting at intermediate volatility? It could be helpful to discuss this result in the context of previous studies that had far less fractional contribution of OPOA to the total (i.e. Tsimpidi et al., 2010; Fountoukis et al., 2011) using 4 x 10^{-11} cm^3 $molec^{-1}$ s^{-1}. Is this pointing to overzealous emissions? Please consider moving the last two paragraphs of section 5.1.1 to section 4.3.

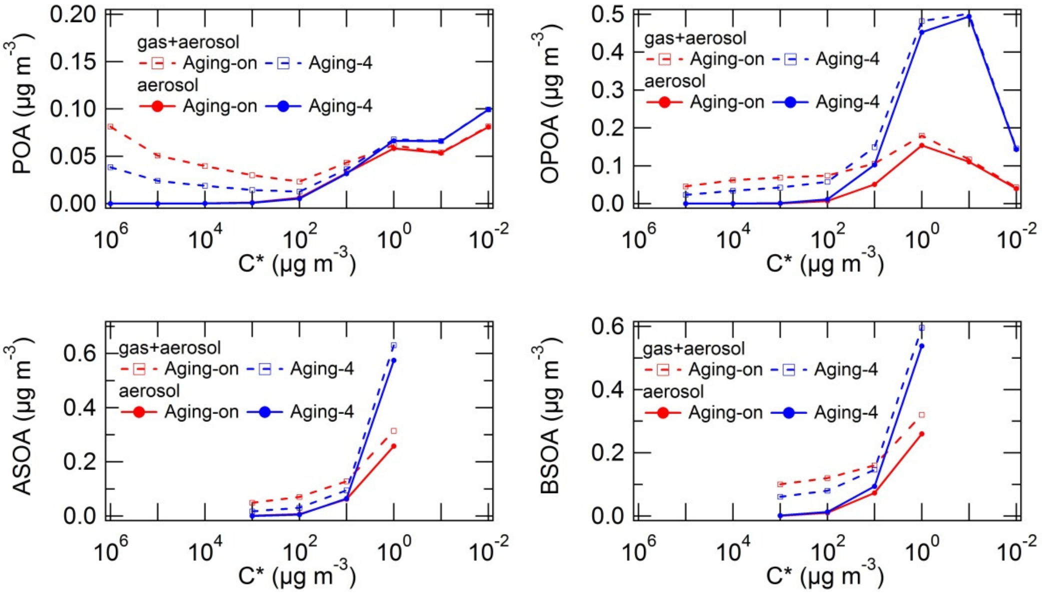
Response:

The aging rate constants in section 4.3 (merged to section 4.2 in the revised manuscript) were chosen based on the treatment of other studies (typical range of VBS simulations). We do not have the information of S/IVOC aging rate suitable for the East Asian region.

We conducted three additional sensitivity simulations (POA-4, ASOA-4, and BSOA-4; shown by bold in the following table) to understand the increase in OA concentrations from the Aging-on to the Aging-4 simulation. OPOA increase from the Aging-on to the Aging-4 simulation was mostly due to faster aging processes of primary and secondary S/IVOCs (because POA and OPOA are about the same between the POA-4 and Aging-4 simulations). ASOA (BSOA) increase from the Aging-on to the Aging-4 simulation was due to faster aging processes of both anthropogenic OVOCs (biogenic OVOCs) and S/IVOCs. The contribution of S/IVOCs aging processes to ASOA and BSOA increases was estimated to be about one-third of total increases in ASOA and BSOA concentrations from the Aging-on to the Aging-4 simulation.

Simulation	Aging rate				Concentrations			
	POA	OPOA	ASOA	BSOA	POA	OPOA	ASOA	BSOA
Aging-on	1e-11	1e-11	1e-11	1e-11	0.236	0.369	0.333	0.346
Aging-4	4e-11	4e-11	4e-11	4e-11	0.275	1.223	0.661	0.654
POA-4	**4e-11**	**4e-11**	**1e-11**	**1e-11**	**0.256**	**1.200**	**0.400**	**0.418**
ASOA-4	**1e-11**	**1e-11**	**4e-11**	**1e-11**	**0.259**	**0.374**	**0.553**	**0.354**
BSOA-4	**1e-11**	**1e-11**	**1e-11**	**4e-11**	**0.252**	**0.379**	**0.350**	**0.551**

As the reviewer suggested, increasing the rate constant by a factor of 4 enhances OPOA concentrations (increase by a factor of 3.3) more relative to ASOA (increase by a factor of 2). Since both primary and oxygenated S/IVOCs concentrations in high volatility (C^* of $10^6 - 10^2$ μg m^{-3}) are lower in the Aging-4 simulation (figures below), these IVOCs and their aging processes (including the 7.5% increase in mass for an oxidation, section 2.2) may contribute to the difference in enhancement between OPOA and ASOA.



We discuss the data at measurement sites in section 4 and the results over the whole domain in section 5. In section 4.3 (section 4.2 in the revised manuscript), we use model results at Fukue and Hedo. Since the contents in the last two paragraphs of section 5.1.1 are the discussions over the whole domain, we do not move the two paragraphs to section 4.

12) Page 6221, line 15,

Reviewer's comment:

Using the aggregated OM:OC ratio of 1.6 seems unnecessary here given the model detail available. The authors have enough information to use 1.4 for the POA and 2.0 (or even 2.2) for SOA species, as an example. This would better reflect the oxygenated nature of the SOA. Of course, if I understand the model-measurement comparison correctly, then the model will underestimate the measurements to an even greater extent. Also, in line 16, "OA concentrations" should read "OC concentrations" I think.

Response:

In this paragraph, all the observed OC values were converted to OA. The conversion of OC to OA is used because total organics (OA) are discussed throughout this paper. As the reviewer pointed out, the conversion of simulated OA to simulated OC is another way for comparison between measurements and model simulations. We think either comparison is OK because the comparison in this paragraph is rough (for example, simulation period is different between observation and model simulation). Even if we use higher OC-to-OA conversion rate of 1.9 (instead of 1.6), its impact on the statistics is small (the underestimation at Hong Kong and Bangkok is changed from 60 – 70% to 65 – 75%).

13) Figure 6 and Section 3.2,

Reviewer's comment:

What was the collection efficiency for the AMS in this data and what effect does that have on the comparisons?

Response:

The collection efficiency was assumed to be 0.5 at Fukue and 1.0 at Hedo (Takami et al., 2005, 2007). We clarified these values in the revised manuscript. The observed OA concentrations at Hedo are the lower limit in terms of the collection efficiency. This might be a reason why simulated OA concentrations agree well at Fukue but are overestimated at Hedo.

14) Figure 7,

Reviewer's comment:

Please consider adding a panel for OPOA distribution to the left side. Even though there won't be one for the right side, it is instructive for the reader to see the contribution of this species. I was surprised the bars for OPOA were so high in Fig. 8.

Response:

As the reviewer suggested, we have added panels for OPOA to Figure 7 in the revised manuscript.

15) Table 6 and Figure 7,

Reviewer's comment:

How was the boundary layer height determined for this calculation? When the authors write "~1 km", are they implying that they chose a fixed number of WRF-CHEM layers and used that for the entire analysis, or was the number of layers allowed to fluctuate with meteorology? If so, was temperature or vertical mixing used to diagnose this behavior? If done incorrectly, this could certainly bias the results. Why not use the bottom layer concentration to compare to the measurements, for instance?

Response:

The height of "~ 1 km" means a fixed number of WRF-chem layers (layer number of 8, sigma level of 0.895). The layer 8 is used for the analysis over East Asia (section 5). The lowest layer is used for the comparison with surface measurements (section 4). We clarified this point in the revised manuscript.

Technical points:

Reviewer's comment:

Page 6205, line 15: Please revise to read "parent VOCs (for example, isoprene and …)" since these are not the only compounds used for modeling SOA sources.

Page 6206, line 7: I would not consider OOA to be a "measure of SOA" in a strict sense, although I understand what the authors are getting at. Please consider rephrasing to something like "(OOA, thought to be analogous to SOA) concentrations" or "(OOA, likely reflective of SOA) concentrations".

Page 6206, line 20: Remove "of".

Page 6217, line 9-10: Please fix the units for 6.3×10^6 cm^3 and on the next line.

Fig. 5: Please, if possible, add the quantitative slopes of these lines to the figure in some way.

Fig. 8: The colors changing meaning between the panels is confusing. Please consider rearranging the bar graph so that simulation runs are grouped together and species are color coded. Then you could use the same colors that are used in panels b and c.

Page 6223, line 4: Please consider changing "ANaging" to "AN-aging" throughout the text.

Response:

We have revised the text and figures as the reviewer suggested.

Response to reviewer #2

ACP-2014-122: “Volatility basis-set approach simulation of organic aerosol formation in East Asia: implication for anthropogenic-biogenic interaction and controllable amounts” by H. Matsui et al.

We thank the reviewer very much for reading our paper carefully and giving us valuable comments. We have revised our paper by taking into account the reviewer’s suggestions. Detailed responses to individual comments are given below.

1) References

Reviewer’s comment:

The introduction is a very thorough discussion on the interest of the topic. While reading I got the sense that there were too many references there; although this is not a bad thing, since this is not a review article, I found it a bit distracting. The authors might want to reduce the number of references listed there, by maintaining the focus on the questions answered in the manuscript, rather than doing a full literature review of the topic.

Response:

We reduced the number of references in the revised manuscript as the reviewer suggested.

2) Introduction

Reviewer’s comment:

Although the statement in p. 6207, l. 6-8 is true for Asia when considered explicitly, the two studies of Pye et al and Jathar et al (referenced in the manuscript) were global, thus Asia was implicitly included. The statement is not adding any more value in the manuscript from what it currently has, and can easily be dropped. The fact that a regional model was used over Asia probably for the first time can then be stressed out in the following page, line 3: “We simulated…”.

Response:

We have deleted the sentence from the manuscript as the reviewer suggested.

3) Model description in section 3.1

Reviewer’s comment:

The model resolution (mentioned in section 3.1) and the aerosol solubility per volatility bin should be mentioned in section 2.1.

Response:

Since section 2.1 is the section for original WRF-chem model, we want to describe the model resolution and the treatment of VBS models in other sections. As the model resolution is different between the simulations in and around Tokyo (section 3.1) and those over East Asia (section 3.2), we need to describe them separately.

We have added the description about in-cloud scavenging of organic vapors in the revised manuscript: “In-cloud scavenging of organic vapors was calculated by assuming the aqueous-phase fraction of unity (all organic vapors are soluble)."

4) Kappa value

Reviewer's comment:

Why a constant kappa value was selected for all volatility bins, instead of a varying one?

Response:

We use a constant kappa value because it is the simplest treatment as a first step. We want to use more realistic treatment (e.g., increase of kappa with aging) and examine its sensitivity when we focus on removal processes and aerosol-cloud interactions in future studies.

5) Aqueous chemistry scheme

Reviewer's comment:

P. 6208 l. 24 mentions aqueous chemistry, but p. 6211 l. 27 says the opposite. Is the statement in p. 6208 about inorganic species only? Also, citing 5 papers for something that is not included in the model, is a good example of the excessive number of references used in the introduction, as I mentioned in the first comment.

Response:

Yes. In WRF-chem, aqueous chemistry for inorganic species is calculated. We have clarified this point in the revised manuscript.

We also reduce the number of references for SOA formation in aqueous phase as the reviewer suggested.

6) Aqueous SOA formation

Reviewer's comment:

In the same sentence, all these processes are also forming new OA mass from VOCs that in the current model state do not.

Response:

We have added the description that the processes form new OA mass from VOCs in the revised manuscript.

7) Uncertainties of VBS parameters

Reviewer's comment:

Please expand with a sentence or two on the "other uncertainties" mentioned in p. 6212, l. 20, as was done in p. 6211, l. 15-16.

Response:

We conducted sensitivity simulations on the treatment of S/IVOC emissions and wet deposition. The S/IVOCs-to-POA emission ratio of 7.5 used in this study is a highly uncertain parameter. We examined the sensitivity of the treatment of S/IVOC emissions by conducting two sensitivity simulations. A sensitivity simulation with the increase in SVOC (C* ranging from 10^3 to 10^{-2} µg m^{-3}) emissions by a factor of 2 enhanced total OA and SOA concentrations by 25% and 45%, respectively (period and domain average at an altitude of about 1 km). Another sensitivity simulation with the increase in IVOC (C* ranging from 10^6 to 10^4 µg m^{-3}) emissions by a factor of 2 enhanced total OA and SOA concentrations by 20% and 15%, respectively. These results suggest OA concentrations are moderately sensitive to the treatment of S/IVOC emissions over East Asia.

OA concentrations also have moderate sensitivity to the treatment of wet deposition of S/IVOCs and OVOCs. OA concentrations were increased by 25% in the simulation without wet deposition of S/IVOCs and OVOCs.

We have added these results to section 2.3 in the revised manuscript.

8) AMS analysis

Reviewer's comment:

What is the "custom solution procedure" in p. 6213, l. 23? Factor analysis?

Response:

We have revised the text as follows. "The oxygenated and hydrocarbon-like OA concentrations (OOA and HOA) were estimated by least-squares fits to the time series of OA using a linear combination of the time series of AMS-derived signals at mass-to-charge (m/z) ratios 44 and 57 (Zhang et al., 2005)."

9) The values of correlation coefficient

Reviewer's comment:

Same page bottom, please quantify "correlated well".

Response:

We have added the values of correlation coefficient. The revised text is "correlated well with HOA and OOA with slopes of 0.88–1.36 (R^2 of 0.76-0.85) and 0.97–1.41 (R^2 of 0.65-0.85), respectively".

10) Modification of emissions

Reviewer's comment:

The numbers mentioned at the bottom of p. 6214 apply to all simulations?

Response:

These modifications of emissions were applied to the simulations in and around Tokyo only. We do not use these modifications in the simulations over East Asia. We have clarified this point in the revised manuscript.

11) Dust and sea salt emissions

Reviewer's comment:

P. 6216, l. 2-3: This means that there are no dust and sea salt particles in the model, or they are offline?

Response:

Sea salt and dust emissions from natural sources are not considered in this study. We have clarified this point in the revised text. Dust (unidentified species) emissions from anthropogenic sources are considered based on the emission inventory of Streets et al.

12) Overestimation/underestimation of SOA in and around Tokyo

Reviewer’s comment:

The over/under estimation of results during day/night (p. 6217 middle) is very interesting. Does that mean that the aging is too fast, or there is very fast removal during night? Please say more about this.

Response:

The overestimation of SOA during daytime may be due to faster aging processes as the reviewer suggested. In addition, since we have no data to validate S/IVOCs in and around Tokyo, the treatment of S/IVOCs emissions may possibly contribute to this overestimation to some extent. The underestimation of SOA during nighttime may possibly be due to the underestimation of BSOA formation and/or its transport from suburbs. However, these are just speculations not solid conclusions.

13) SIVOCs and OVOCs in and around Tokyo

Reviewer’s comment:

SIVOCs and OVOCs must be considered for Tokyo (p. 6217 bottom) but OPOA only account for 6-7% in other places (next page, top). Does that happen due to the different precursors present in these sites?

Response:

At Komaba and Kisai sites (in and around Tokyo), OVOCs from anthropogenic sources are more important than oxygenated S/IVOCs. The aging processes of anthropogenic OVOCs play an important role to make the difference between the aging-on and aging-off simulations at Komaba and Kisai.

14) Two-bin-step aging scheme

Reviewer’s comment:

Section 4.3: why not using a 2-bin-step aging, as the new VBS schemes?

Response:

Adding a 2-bin-step aging scheme is not directly related to understanding the uncertainties of our VBS model and does not change the conclusions in this paper. When we need further computationally efficient scheme in the future, we make a 2-bin-step aging scheme and examine the performance of it then.

15) Volatility distribution in aging-on and aging-off simulations

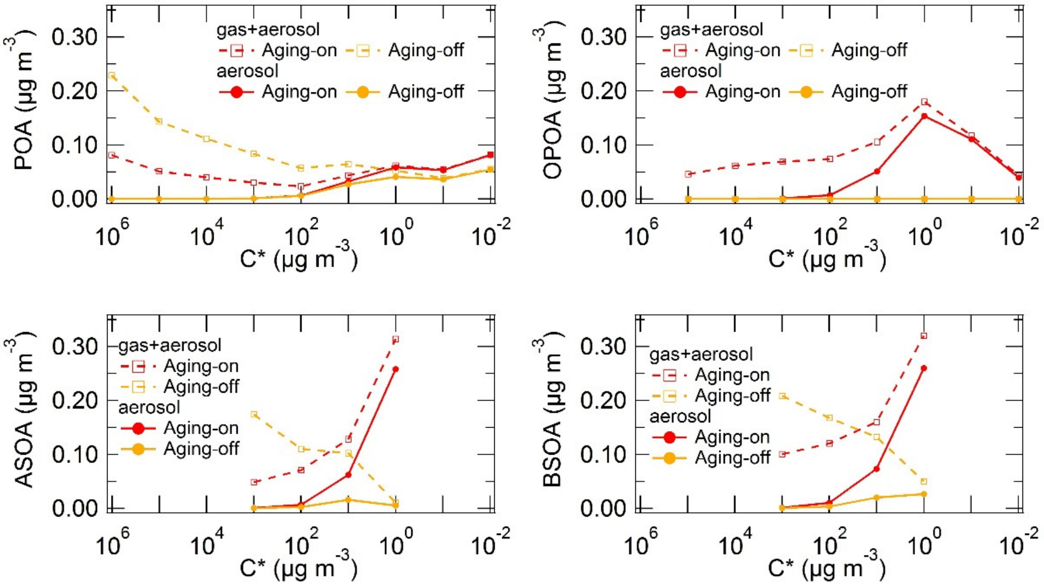
Reviewer’s comment:

P. 6221 bottom: Which volatility bins receive most of the mass? In aging-off it should be the same with emissions, but how about the aging-on experiments?

Response:

The figures shown below are the volatility distribution of POA (+ primary S/IVOCs), OPOA (+ secondary S/IVOCs), ASOA (+ anthropogenic OVOCs), and BSOA (+ biogenic OVOCs) (period- and domain-averaged concentrations at altitude of 1 km).

The concentrations of POA, ASOA, and BSOA categories (gas + aerosol) are higher at low volatilities and lower at high volatilities in the aging-on simulation (compared with the aging-off simulation). This result supports the description in the text.



16) Contribution of OH and other factors in estimating controllable OA fraction

Reviewer's comment:

P. 6225 top: A factor of 3 lower is impressive. Why not emit gas-phase species and neglect them when calculating the aerosols?

Response:

We conducted an additional sensitivity simulation to quantify the importance of the oxidant change (OH concentrations by a factor of 3) in the estimation of controllable OA concentrations. In this sensitivity simulation, we excluded emissions from combustion sources for aerosol species and SOA precursors (primary S/IVOCs, aromatics (ARO1 and ARO2), alkanes (ALK4 and ALK5), and olefins (OLE1 and OLE2)) without changing emissions for other gaseous species (CO, NO_x, SO_2, and other VOCs). Period-averaged OH concentrations in this sensitivity simulation were about the same as those in the base case simulation (the difference between two simulations was 7% for OH and 0.3% for HO_2 over East Asia). This sensitivity simulation reduced OA concentrations by 73% and BSOA concentrations by 42% over East Asia. These results suggest that the OH change by NO_x and VOCs has a large potential to increase controllable OA amounts over East Asia (from 73% to 87% for total OA and from 42% to 78% for BSOA).

We have added these descriptions to the revised manuscript (section 5.2).

17) Contribution of OH and other factors in estimating controllable BSOA

Reviewer's comment:

Same page, 2nd paragraph: this is an excellent result. Can you attribute that to oxidant changes (like in the previous paragraph) and larger mass of pre-existing particles?

Response:

Please see the response to comment (16).

18) Controllable OA fraction during other periods

Reviewer's comment:

Next page, 1st paragraph: Please expand this. Do you expect higher/lower contribution during other periods?

Response:

We have added the following sentence at the end of this paragraph based on the reviewer's question. "Since biomass burning emissions are highest during February-April over Southeast Asia and during March-May over China (Matsui et al., 2013a), higher fraction of controllable OA is expected in other seasons in terms of biomass burning emissions."

19) The definition of S/IVOCs

Reviewer's comment:

I am a bit confused on the POA/SIVOC explanation in Table 1. SIVOCs can be secondary, but they also form POA which are exclusively primary? This is not what Fig. 1 shows, where SIVOCs are only primary.

Response:

We have revised Fig. 1 to clarify that S/IVOCs in this figure are primary S/IVOCs. We have also revised the description of POA and S/IVOCs in Table 1.

20) Figure 5, fitting slope

Reviewer's comment:

Do the lines in Fig. 5 suggest faster aging than it should be? Also, why not have intercept (y=ax+b) when fitting the slopes?

Response:

Larger slopes in the model may suggest faster aging processes as the reviewer suggested, but we cannot conclude the reason of larger slopes from Fig. 5 only.

We calculated the slopes with intercept. At Kisai, y=0.12*x+2.0 for observation, y=0.20*x+0.06 for aging-on simulation, and y=0.017*x+0.38 for aging-off simulation. At Komaba, y=0.088*x+2.6 for observation, y=0.19*x+0.34 for aging-on simulation, and y=0.051*x+0.18. In this study, we want to use the slopes of y = ax (not y = ax +b) because the intercepts probably reflect night-time OA concentrations that are not related to photochemical activity in daytime.

21) Figure 9

Reviewer's comment:

I believe that the non-equal white piece on the 3rd pie and blue piece on the 4th pie in Fig. 9 show the non-linearity of the system, which is very interesting, and can be discussed a bit more.

Response:

We examined the details of the "white piece on the 3rd pie" and the "blue piece on the 4th pie" in Fig. 9. POA, OPOA, ASOA, BSOA concentrations in the "white piece on the 3rd pie" were 0.007, 0.012, 0.02, and 0.235 μg m^{-3}, respectively. POA, OPOA, ASOA, BSOA concentrations in the "blue piece on the 4th pie" were 0.196, 0.0, 0.038, and 0.241 μg m^{-3}, respectively. The results show the difference between the two pies is mostly due to the difference in POA concentrations not the non-linearity of SOA formation.

22) Technical corrections

Reviewer's comment:

(a) P. 6206, l. 26: factor OF 5.

(b) P. 6212, l. 17: delete second "also".

(c) Same page, l. 2-3, delete "in and around Tokyo".

(d) Fig. 8, 10, 11 legend: no need to mention the sigma levels in parentheses.

Response:

(a), (b), and (d): We have revised the text as the reviewer suggested.

(c): We do not delete "in and around Tokyo" at P6212, l.26-27 because it is necessary.