We thank both reviewers for their comments. We have revised the manuscript based on their comments and queries and provided a point-by-point response below. Reviewer comments are in *italic*, our response is in red and excerpts from the manuscript reflecting changes are in *italic blue*.

Reviewer 1

The manuscript by Jathar et al. summarizes results from a new modeling approach to characterize SOA formation in southern California. In this study, the volatility basis set along with updated VOC emission profiles and speciations are used in a chemical transport model to quantify SOA formation in the region and separate the contributions from diesel and gasoline sources. The topic is of high relevance given the interest in recent years in investigating SOA formation in urban areas from IVOCs and understanding the contribution of gasoline and diesel sources to SOA. The paper is well- written and organized, and the figures are of high quality. The only flaw in the structure of the manuscript is that the conclusion section is missing. I have a few technical and minor editorial comments listed below. Once these concerns are addressed, I support publishing the manuscript.

We agree with the reviewer's comment. To state the conclusions from the paper, we add a conclusion section to the manuscript:

"Conclusions:

In this work, we developed an updated version of the CMAQ model that included revised estimates of (i) VOC and IVOC SOA precursors from gasoline and diesel sources and (ii) experimentally constrained parameterizations for SOA production from IVOCs. Predictions of OA mass concentrations from the updated model (VBS-IVOC) slightly under-predicted daily-averaged, filter-based measurements at CSN sites in California during May and June 2010 (fractional bias=-23% and fractional error=43%) but were a factor of three lower than aerosol mass spectrometer-based measurements made at Pasadena as part of the CalNex campaign. The Pasadena site may have been influenced by local sources and transport not captured by the model at a 4 km resolution. We recommend future modeling studies to be performed at higher resolution.

When compared to a Traditional model of OA in CMAQ that includes a non-volatile treatment of POA and no SOA from IVOCs, the VBS-IVOC model produced different spatial patterns of OA with lower (~50%) concentrations in source regions but higher (~20-40%) concentrations away from the sources. The VBS-IVOC model in comparison to the Traditional model improved predictions of the sources and composition of OA. These findings are consistent with previous comparisons between Traditional- and VBS- models and highlight the importance of the use of an OA model that includes semi-volatile and reactive POA and SOA formation from IVOCs.

Predictions of OA from the VBS-IVOC model are similar to those from a recently released research version of CMAQ (VBS) that included semi-volatile POA and SOA formation from IVOCs (Woody et al., 2016). The predictions of these two models were similar for three reasons. First, the VOC and IVOC updates in this work, surprisingly, did not substantially alter the total emissions of SOA precursors in southern California (although the VOC-IVOC composition was different between the two models for gasoline sources). Second, mobile sources only accounted for slightly more than one-third of the total OA in southern California and hence updates to the emissions and SOA production from mobile sources had a limited influence on the total OA burden. And third, and most important, was that both models predicted that multigenerational aging of vapors in equilibrium with OA was a major source of SOA. Both models used similar aging mechanisms that are conceptually based on the work of Robinson et al. (2007), which assumed a constant reaction rate constant and only allowed for the formation of functionalized, *lower-volatility products. However, reaction rates may vary with C* and O:C of the OA and fragmentation reactions can be increasingly important at longer time scales (Kroll et al., 2011). Existing aging mechanisms have not been constrained with laboratory data. This implies that the OA predictions, despite the substantial new data, are poorly constrained as one moves downwind of source regions. Murphy and Pandis (2009) report improved model performance when aging reactions are turned off for biogenic SOA. Recently, Jathar et al. (2016) proposed that laboratory chamber experiments that are used to parameterize SOA production may already include products from some aging reactions, raising concerns about double counting. Although some work has been done to understand the aging of biogenic SOA (Donahue et al., 2012;Henry and Donahue, 2012)}, future laboratory work needs to be directed in understanding the role of aging of OA vapors formed from anthropogenic sources on the mass and properties of OA.*

For the first time, we compared model predictions to ambient measurements of IVOCs. The new VBS-IVOC model better predicted the ambient IVOC concentrations compared to the Traditional and VBS models. This suggests that the updated model reasonably simulated the emissions, transport and chemistry of IVOCs from mobile sources. However, the model representation of IVOCs from non-mobile sources remains poorly constrained and needs to be explored through future emissions, laboratory and modeling studies.

Finally, the VBS-IVOC model predicted that mobile sources accounted for 30-40% of the OA in southern California, with half of the OA being SOA. The diurnal variation of OA in Pasadena supports the hypothesis that substantial OA is produced through photochemical reactions vs. primary emissions_(Hayes et al., 2013). Gasoline-powered sources contributed 13 times more OA than diesel-powered sources and sensitivity simulations indicated that these findings were robust to changes in diesel emissions. Model predictions suggested that half of the mobile source SOA was formed from the oxidation of IVOCs, which demonstrates the importance of including IVOCs as an SOA precursor. However, the relative contribution of VOCs and IVOCs to SOA formation was sensitive to the inclusion of aging reactions. While both laboratory and field evidence indicate that aging is an important atmospheric process, it is unclear if and by how much aging enhances OA over regional scales and whether aging chemistry varies by precursor and source (Jathar et al., 2016). For these reasons, the relative importance of VOC and IVOC SOA precursors and the source apportionment presented here is a first estimate and will likely evolve as we develop better models to simulate the dependence of aging on SOA formation.”.

2. P4, L22: Are the emission profiles of non-road gasoline sources assumed to be the same as on-road vehicles tested on the UC cycle? Also how are their emissions rates defined? Measurements in European cities in recent years have shown high amounts of SOA are formed from small (2- and 4-stroke gasoline engines). How are such emissions characterized for S. Cal?

In this work, we only change the emissions profiles for mobile sources, not the magnitude of the emissions. The existing emissions inventory already accounts for the large differences in emissions rate between, for example 2-stroke and on-road gasoline sources. The NMOG speciation is assumed to be the same for on- and off-road gasoline sources. This assumption is supported by the results from May et al. (2014) who show that the NMOG speciation for 2-stroke off-road gasoline engines was consistent with that of on-road gasoline engines but found that the 4-stroke off-road gasoline engines produced more IVOC emissions. We should note that May et al. (2014) only quantify the NMOG speciation from a set of eight lawn and garden equipment engines, which may not be representative of the diversity found across the off-road sector. The on- and off-road equivalence in terms of the NMOG speciation is not a bad assumption but may need to be examined in detail by future work.

Emissions rates for off-road sources were calculated using MOVES (Baker et al., 2015). Platt et al. (2014) (the study the reviewer seems to be referring to) and Gordon et al. (2013) found that the production factors of SOA for 2- and 4-stroke gasoline engines were 2-3 orders of magnitude higher than those for light-duty vehicles. However, they showed that most of the SOA produced could be explained by the emissions and oxidation of aromatic compounds and did not find IVOCs to be an important precursor of SOA.

We have made a note about the points raised in this discussion in the section that talks about the gasoline and diesel contributions to OA: "*Platt et al. (2014) and Gordon et al. (2013) have recently argued that off-road sources, especially those powered using two-stroke engines, can be a large contributor to fine particle pollution in cities. In the inventory of Baker et al. (2015), which is used in this work, off-road sources contributed to ~40% of the NMOG and ~40% of the POA emissions from mobile sources. Given their substantial emissions, it is critical then that emissions rates from these sources be accurately represented in large-scale models. Only one study so far has reported VOC and IVOC emissions profiles from off-road engines. May et al. (2014) have found that two-stroke off-road gasoline engines had similar emissions profiles as on-road gasoline engines, but that the four-stroke off-road gasoline engines had much higher IVOC fractions than on-road gasoline engines. However, Platt et al. (2014) have shown that most of the SOA produced from two-stroke off-road gasolines engines can be explained by the emissions and oxidation of aromatic compounds and they did not find IVOCs to be an important precursor of SOA. In our work, we have assumed that the VOC speciation, IVOC fraction of NMOG, and the SOA parameterization for IVOCs were identical between the on- and off-road mobile sources. Given the uncertainties, these assumptions may need to be examined in detail in future work.* ".

3. P5, L 38-39: Why are biogenic SOA not aged similarly to other species?
The reason for not aging biogenic SOA is based on the modeling studies performed by Murphy and Pandis (2009) and Lane et al. (2008) where they observe that the aging of biogenic SOA results in the over-prediction of OA in the eastern United States. Additionally, Jathar et al. (2016) based on the extrapolation of chamber data suggest that aging reactions may double count SOA production and over-predict the importance of aging reactions in the atmosphere. The laboratory evidence for this is mixed. Donahue et al. (2012) show that OH oxidation of α-pinene SOA enhances SOA production while Henry and Donahue (2012) show that the OH oxidation combined with photolysis of the SOA products can result in destruction of SOA. We acknowledge this uncertainty for aging of biogenic (and anthropogenic) SOA in the manuscript: "*Murphy and Pandis (2009) report improved model performance when aging reactions are turned off for biogenic SOA. Recently, Jathar et al. (2016) proposed that laboratory chamber experiments that are used to parameterize SOA production may already include products from some aging reactions, raising concerns about double counting. Although some work has been done to understand the aging of biogenic SOA (Donahue et al., 2012;Henry and Donahue, 2012)}, future laboratory work needs to be directed in understanding the role of aging of OA vapors formed from anthropogenic sources on the mass and properties of OA.*".

4. P6, L2-3: It is mentioned that 10% of POA is shifted to SOA; is that because of POA aging or in addition to that?
The transfer of 10% of the POA mass to the SOA basis set is done as part of the aging reactions. The text is edited as follows: "*Finally, the aging reactions also shift a portion (~10%) of the POA vapors to the anthropogenic SOA basis set to maintain O:C ratios (Koo et al., 2014).*".

5. Sec 3.1 and Fig 2: How are "episodes" defined? Also are these data limited to the boundary layer? Please clarify.
The word 'episode' is used here to define the time period for which the model simulations are run. The time period simulated is chosen to coincide with the CalNex measurements. Since the word 'episode' is not required (and may create confusion), we have dropped it from the manuscript and the supporting information. For instance, the caption for Figure 1is edited to: "*Figure 1: Total emissions from May 4 to June 30, 2010 for POA, BTEX (aromatics), ALK5 (long alkanes) and IVOCs for gasoline and diesel sources in the Los Angeles and Orange Counties for the three OA models: Traditional, VBS and VBS-IVOC.* ". The data presented in this work in Figures 1 through 6 are all limited to the surface/boundary layer to be consistent with the measurements.

6. P6, L29: Isn't OM/OC ratio of 1.6 too low for SOA dominated regions and too high for POA dominated regions? Could uncertainties in this ratio also affect the comparison in Fig. 3a?
We agree with the reviewer that the OM:OC ratio in the atmosphere spans a large range (~1.4-2.3) and depends on the source, composition, and photochemical age of the OA. This uncertainty obviously affects the model-measurement comparison in Figure 3(a). Our choice of a value of 1.6 is based on typical values used in the literature to convert filter-based OC measurements. This value is consistent with the average OM:OC ratio of 1.7 (with an uncertainty of ±30%) calculated by Hayes et al. (2013) from a detailed comparison of AMS based OA measurements with filter based OC measurements at Pasadena. We edit the manuscript to improve the discussion around the use of the 1.6 value: "*The CSN measurements need to be multiplied by an OM:OC ratio to account for the non-carbon species associated with organic carbon (Turpin and Lim, 2001). While ambient OM:OC ratio vary from 1.4 and 2.3 (Aiken et al., 2008), we use a constant value of 1.6 in this work based on previous estimates used for filter-based measurements (e.g., (Cappa et al., 2016)). This value is consistent with the OM:OC ratio of 1.7±0.5 estimated by Hayes et al. (2013) in Pasadena.*".

7. Fig 4. It is surprising the total POA from gasoline is more than that of diesel. Based on fuel-based emission factors of POA (Ban Weiss et al. 2008) and fuel use data, one expects the reverse. Are the emission factors used in this study significantly different than Ban Weiss et al.?

The reviewer is correct. If one uses the emission factor and POA:BC ratios for $PM_{2.5}$ from Ban-Weiss et al. (2008) for gasoline and diesel on-road sources (0.07 and 1.4 g kg-fuel^{-1} and 0.71 and 2 respectively) and combines it with fuel use in the Los Angeles and Orange counties (46,000 tons day^{-1} of gasoline and 5,300 tons day^{-1} of diesel), we get POA emissions of 1.9 and 2.5 tons day^{-1} for on-road gasoline and diesel sources respectively. In our work POA emissions, which are consistent with emissions from the EMFAC mobile source inventory for 2010, are 3.9 and 2.0 tons day^{-1} for on-road gasoline and diesel sources respectively. This indicates that the on-road gasoline POA in our work is a factor of 2 higher than that estimated using the Ban-Weiss et al. (2008) data. If we use the findings from Ban-Weiss et al. (2008), the mobile POA fraction in Figure 4 will be reduced and deteriorate the comparison with the measured HOA fraction. However, the Ban-Weiss et al. (2008) data will not dramatically change the conclusions made from Figure 6 about the gasoline and diesel contributions to OA. We add the following sentence to address this comment: "*Comparison of the POA predictions from the VBS-IVOC model to ambient measurements made by Ban-Weiss et al. (2008) suggests that the on-road gasoline POA in the model may be over-predicted by a factor of 2, although this under-prediction does not significantly change the gasoline/diesel contribution to OA.*".

8.P8, L20: Since absolute amounts of the predicted IVOCs are in fact half of the measured values, why the emission ratios of IVOCs were not adjusted to match the measurements? Couldn't this also be the reason why the predicted OA is so much lower than the HR-AMS values in Pasadena (P7, L40)? Related to this, with the additional amounts of IVOCs in runs summarized in Figure 6a, how does the OA comparison with the Pasadena measurements look?

We thank the reviewer for this comment since it led us to refine and simplify our analysis. Our initial thought was that the spatial resolution of the model at 4 km probably dispersed the pollutants too much and was insufficient to simulate the absolute concentrations at the Pasadena ground site where the CalNex measurements were made. We therefore ratioed the IVOC measurements with CO for the model evaluation to account for the effects of dispersion. However, the correct quantity to compare, as others have used in the past (Woody et al., 2016), is the ratio of IVOC to ΔCO. However, as Woody et al. (2016) have pointed out, the ΔCO predictions are a factor of two to low compared to the ΔCO measurements and could mean that the CO emissions in the model might be a factor of two too low. We should note however, that the daily-averaged CO mixing ratios are only about 25% lower than the measurements at Pasadena. Since the intent here is to evaluate the IVOC concentrations and not evaluate the model's ability to predict CO (an under-prediction in CO does not necessarily suggest an under-prediction in non-methane organic gas (NMOG) emissions, a fraction of which – for combustion sources – is assumed to be IVOCs), we replot Figure 5 (see below) with absolute concentrations of IVOCs. While the total IVOC concentrations are under-predicted by ~35%, the new presentation of the data does not change the conclusions made in the manuscript. The text is edited based on the above-mentioned changes as follows: "*Gasoline and diesel IVOC concentrations (3.9 μg m^{-3}) from the VBS-IVOC model were 35% lower when compared to the hydrocarbon IVOCs concentrations measured by Zhao et al. (2014) (6 μg m^{-3}). In contrast predictions from the VBS model are a factor of 4 lower than the measurements, which highlights the improved representation of IVOCs in the VBS-IVOC model. The under-prediction of VBS-IVOC could partly be a result of the inability of the model with a 4 km horizontal resolution to capture the location-specific concentrations at Pasadena. The model-measurement comparison suggests that the VBS-IVOC model reasonably simulates the emissions, transport and chemistry of IVOCs from mobile sources. Furthermore, the VBS-IVOC model predicts that the majority of the hydrocarbon IVOCs originate from gasoline sources. Coincidentally, the predicted IVOC sum for other anthropogenic sources and biomass burning (4.3 μg m^{-3}) compared well with the measured oxygenated IVOCs (4.1 μg m^{-3}).*".

The additional amounts of IVOCs were only added for diesel-powered sources in Figure 6(a) to examine the sensitivity of IVOC emissions estimates on the gasoline-diesel OA split. Since all of these simulations only marginally change the diesel OA contribution, these would not have any effect on the model-measurement comparison in Figure 3b. This point is discussed in the Section *Discussion on Gasoline versus Diesel O*A: "*A factor of 5 increase in IVOC emissions only results in a 0.025 μg m^{-3} increase in total OA mass concentration. Therefore, uncertainty in the diesel IVOC emissions does not appear to alter the model-measurement comparison discussed earlier.*".

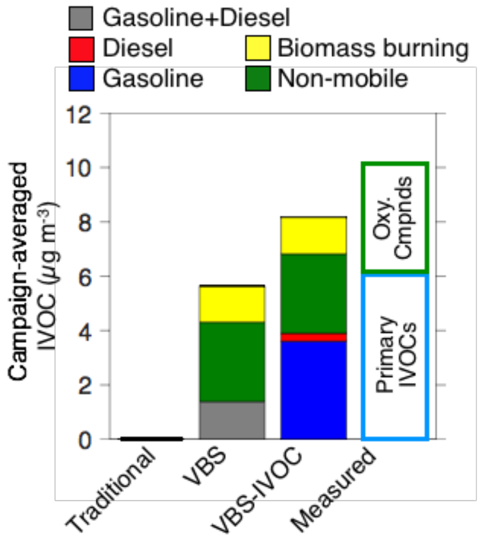

Figure 5: Comparison of predicted and measured campaign-averaged IVOC concentrations at the Pasadena ground site. Measured concentrations are from Zhao et al. (2014). Here, both model predictions and measurements only include primary IVOCs. The predictions of IVOCs also include primary vapors in equilibrium with POA.

9. P11, L10-13: Is the low-NOx regime expected to be present downwind, i.e., in Inland Empire or just over the ocean? Measurements over the land in S. Cal usually show NO levels at ~100s of pptv which is much higher than the threshold for low-NOx conditions, given typical HO2 mixing ratios. Because of this, I don't think low-NOx conditions are common in S. Cal and therefore applying only the high-NOx SOA yields to VOCs/IVOCs should not change total SOA formation.

We agree with the reviewer that when considering the precursor contributions at Pasadena, the NO_x dependence probably does not help explain differences between the 3D model predictions from this work and the box model predictions from (Jathar et al., 2014). This is because the NO levels are probably high enough that most of the SOA formation proceeds through the high NOx pathway. We thank the reviewer for this comment and we edit the text to only consider the effect of aging to explain the difference in the 3D and box model results: "*Figure 6(a) resolves the OA contributions based on the precursor class at the Pasadena site. The VBS-IVOC model predicts that IVOCs, particularly from gasoline vehicles, form almost as much SOA as VOCs (long alkanes and single-ring aromatics). This is in contrast to Jathar et al. (2014), who found that unspeciated precursors (or IVOCs) were approximately a factor of 4 larger than VOCs in forming SOA in chamber experiments. One possible explanation for this difference is that Jathar et al. (2014) did not account for the effects of continued aging of IVOC oxidation products on OA concentrations*".

10. Minor comments: P3, line 9 and P5, L31 miss references

Those references were accidently added by EndNote. They have been removed.

P6, L28: Mention that HR- AMS measurements were made in Pasadena.

We modify the sentence to mention Pasadena: "*Figure 3(b) compares predictions of daily-averaged OA concentrations to measurements made using a high-resolution aerosol mass spectrometer (HR-AMS) in Pasadena (*Hayes et al., 2013*)*".

Fig 3: Define in the caption what f.b. and f.e refer to.

The following text is added to the caption: “*f.b. is the fractional bias* ($\frac{1}{N}\sum_{i=1}^{N}\frac{P-M}{\frac{P+M}{2}}$) *and f.e. is the fractional error* ($\frac{1}{N}\sum_{i=1}^{N}\frac{|P-M|}{\frac{P+M}{2}}$)*; P is the predicted value, M is the measured value and N is the sample size.*”.

11. P7, L27-28: remove “in” from “note that in the VBS model. . ..” and remove () around Woody et al.
The text is corrected.

12. P7, L31-33: sentence is unclear and needs to be rephrased
We revise the sentence to: “*It is unclear if the predicted non-mobile, non-cooking and non-biomass burning POA (which in Pasadena accounts of ~9% of the OA) should be added to the SOA predictions before being compared with the OOA factor derived from the ambient tdata. The non-mobile, non-cooking and non-biomass burning POA (or anthropogenic (other) POA) category here includes sources such as stationary fuel combustion (e.g., natural gas combustion), surface coatings (e.g., metal coating), mineral processes (e.g., concrete production), road dust and managed burning (e.g., prescribed burns).*”.

13. P9, L 19: add on: “. . .limited effect ON the SOA burden “.
The text is corrected.

Reviewer 2

This manuscript incorporated new experimentally derived inputs to improve the simulation of OA in southern California in the CMAQ model. The authors focused primarily on treatments of intermediate volatility organic compounds (IVOC) from gasoline and diesel sources, implementing updated estimates of emissions and updated parameterizations of SOA formation. They evaluated the simulated results against measurements during the CalNex campaign. Overall, the authors found the updated model performed well at reproducing the (CSN) observed bulk OA concentrations at several locations in S. California. The updated model significantly underestimated OA concentrations when compared to HR-AMS measurements at Pasadena. However, the updated model showed significant improvement at reproducing the OA composition and IVOC compositions at Pasadena. Model simulations showed that gasoline sources contribute about much more OA then diesel sources do due to the former’s much larger SOA production. They showed that this conclusion is robust, even when the uncertainty in diesel IVOC emissions is considered. In my view, this paper represents a good step in improving model representation of SOA formation under the VBS framework. Many current models use VBS, but the inputs to these models are highly uncertain, particularly for IVOC emissions and chemistry. I think the authors did a nice job at incorporating as much new experimentally-derived inputs as possible into their VBS model. The result is an updated, useful, and at least partially validated, model that the community can continue to build on. I recommend publication after minor revision.

1. Abstract: "The updated model, despite substantial differences in emissions and chemistry, performs similar to a recently released research version of CMAQ." This sentence is unclear. What is the "research version of CMAQ"? I assume it is the CMAQ used by Woody et al., without updated treatments to IVOC?
Yes, the reviewer is correct and we edit the abstract to be more clear: “*The updated model, despite substantial differences in emissions and chemistry, performed similar to a recently*

released research version of CMAQ (Woody et al., 2016) that did not include the updated VOC and IVOC emissions and SOA data.".

2. Figure 3: Are there CSN measurements at Pasadena that can be compared to the HR- AMS measurements? Also, why not compare model results to PMF analysis of the AMS measurement? I see this is done as a campaign average in Figure 4. But perhaps doing this comparison in Figure 3b would shed lights on why the high concentration days were more severely underestimated by the model. Might be worth a try.
Unfortunately, there are no CSN sites in or near Pasadena. However, there were co-located filter measurements performed by research groups other than those using the HR-AMS at Pasadena. Hayes et al. (2013) perform a comprehensive comparison of the HR-AMS data against the filter measurements (described in the supporting information) and find that the HR-AMS data were generally consistent with the filter measurements and there was no indication that the HR-AMS data are over-estimating OA mass concentrations. Woody et al. (2016) compare hourly-averaged model predictions from CMAQ against PMF factors from the HR-AMS data and make the following conclusions: (i) cooking OA concentrations compare well with AMS-COA during the morning but are under-predicted in the afternoon and late night, (ii) non-cooking POA concentrations compare well with AMS-HOA but are under-predicted during the afternoon, and (iii) predicted SOA concentrations capture diurnal trends in OOA but are consistently a factor of 5 lower during all times of the day. Since the model predictions of OA mass concentrations and diurnal profiles in this work did not change dramatically when compared to Woody et al. (2016), the findings described earlier apply here. We add a short discussion about this in the text: "*Before discussing the normalized composition predicted by the VBS-IVOC model, we briefly describe the findings from Woody et al. (2016) who carefully compared the predictions of absolute concentrations of the VBS model to the PMF factors estimated from the ambient HR-AMS measurements. Woody et al. (2016) found that (i) the predicted cooking-related OA concentrations compared well with the COA factor during the morning but were low in the afternoon and late night, (ii) non-cooking POA concentrations compared well with the HOA factor except during the afternoon when it was underpredicted, and (iii) predicted SOA concentrations match the diurnal profile of the OOA factor but were but was a factor of 5 lower during all times of the day."*.

3. Minor comments: There seems to be problems with the insertion of some citations (e.g., page 5, line 31 'ENREF_20').
The citations is fixed in the revised manuscript.

4. Figure S3: The caption should read "Comparison of campaign-averaged predictions of the VBS model of Woody et al. (2016) and VBS-IVOC model".
The text is corrected in the revised supporting information.

References

Aiken, A. C., DeCarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., and others: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, Environ. Sci. Technol, 42, 4478--4485, 2008.

Baker, K. R., Carlton, A. G., Kleindienst, T. E., Offenberg, J. H., Beaver, M. R., Gentner, D. R., Goldstein, A. H., Hayes, P. L., Jimenez, J. L., Gilman, J. B., de Gouw, J. A., Woody, M. C., Pye, H. O. T., Kelly, J. T., Lewandowski, M., Jaoui, M., Stevens, P. S., Brune, W. H., Lin, Y. H., Rubitschun, C. L., and Surratt, J. D.: Gas and aerosol carbon in California: comparison of measurements and model predictions in Pasadena and Bakersfield, Atmos. Chem. Phys., 15, 5243-5258, 10.5194/acp-15-5243-2015, 2015.

Ban-Weiss, G. A., McLaughlin, J. P., Harley, R. A., Lunden, M. M., Kirchstetter, T. W., Kean, A. J., Strawa, A. W., Stevenson, E. D., and Kendall, G. R.: Long-term changes in emissions of nitrogen oxides and particulate matter from on-road gasoline and diesel vehicles, Atmospheric Environment, 42, 220-232, 2008.

Cappa, C. D., Jathar, S. H., Wexler, A. S., Seinfeld, J., and Kleeman, M. J.: Simulating secondary organic aerosol in a regional air quality model using the statistical oxidation model – Part 2: Assessing the influence of vapor wall losses, Atmospheric Chemistry & Physics, 16, 3041-3059, 2016.

Donahue, N. M., Henry, K. M., Mentel, T. F., Kiendler-Scharr, A., Spindler, C., Bohn, B., Brauers, T., Dorn, H. P., Fuchs, H., Tillmann, R., Wahner, A., Saathoff, H., Naumann, K.-H., Möhler, O., Leisner, T., Müller, L., Reinnig, M.-C., Hoffmann, T., Salo, K., Hallquist, M., Frosch, M., Bilde, M., Tritscher, T., Barmet, P., Praplan, A. P., DeCarlo, P. F., Dommen, J., Prévôt, A. S. H., and Baltensperger, U.: Aging of biogenic secondary organic aerosol via gas-phase OH radical reactions, Proceedings of the National Academy of Sciences, 109, 13503-13508, 10.1073/pnas.1115186109, 2012.

Gordon, T. D., Tkacik, D. S., Presto, A. A., Zhang, M., Jathar, S. H., Nguyen, N. T., Massetti, J., Truong, T., Cicero-Fernandez, P., Maddox, C., Rieger, P., Chattopadhyay, S., Maldonado, H., Maricq, M. M., and Robinson, A. L.: Primary Gas- and Particle-Phase Emissions and Secondary Organic Aerosol Production from Gasoline and Diesel Off-Road Engines, Environ. Sci. Technol., 47, 14137-14146, 2013.

Hayes, P. L., Ortega, A. M., Cubison, M. J., Froyd, K. D., Zhao, Y., Cliff, S. S., Hu, W. W., Toohey, D. W., Flynn, J. H., Lefer, B. L., Grossberg, N., Alvarez, S., Rappenglück, B., Taylor, J. W., Allan, J. D., Holloway, J. S., Gilman, J. B., Kuster, W. C., de Gouw, J. A., Massoli, P., Zhang, X., Liu, J., Weber, R. J., Corrigan, A. L., Russell, L. M., Isaacman, G., Worton, D. R., Kreisberg, N. M., Goldstein, A. H., Thalman, R., Waxman, E. M., Volkamer, R., Lin, Y. H., Surratt, J. D., Kleindienst, T. E., Offenberg, J. H., Dusanter, S., Griffith, S., Stevens, P. S., Brioude, J., Angevine, W. M., and Jimenez, J. L.: Organic aerosol composition and sources in Pasadena, California, during the 2010 CalNex campaign, Journal of Geophysical Research: Atmospheres, 118, 9233-9257, 10.1002/jgrd.50530, 2013.

Henry, K. M., and Donahue, N. M.: Photochemical aging of α-pinene secondary organic aerosol: effects of OH radical sources and photolysis, The Journal of Physical Chemistry A, 116, 5932-5940, 2012.

Jathar, S. H., Gordon, T. D., Hennigan, C. J., Pye, H. O. T., Pouliot, G. A., Adams, P. J., Donahue, N. M., and Robinson, A. L.: Unspeciated organic emissions from combustion sources and their influence on the secondary organic aerosol budget in the United States, Proceedings of the National Academy of Sciences, 111, 10473-10478, 2014.

Jathar, S. H., Cappa, C. D., Wexler, A. S., Seinfeld, J. H., and Kleeman, M. J.: Simulating secondary organic aerosol in a regional air quality model using the statistical oxidation model – Part 1: Assessing the influence of constrained multi-generational ageing, Atmospheric Chemistry & Physics, 16, 2309-2322, 2016.

Koo, B., Knipping, E., and Yarwood, G.: 1.5-Dimensional volatility basis set approach for modeling organic aerosol in CAMx and CMAQ, Atmospheric Environment, 95, 158-164, 2014.

Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E., Mazzoleni, L. R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb, C. E., and Worsnop, D. R.: Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol, Nature Chemistry, 3, 133-139, 2011.

Lane, T. E., Donahue, N. M., and Pandis, S. N.: Simulating secondary organic aerosol formation using the volatility basis-set approach in a chemical transport model, Atmospheric Environment, 42, 7439-7451, 2008.

May, A. A., Nguyen, N. T., Presto, A. A., Gordon, T. D., Lipsky, E. M., Karve, M., Gutierrez, A., Robertson, W. H., Zhang, M., Chang, O., Chen, S., Cicero-Fernandez, P., Fuentes, M., Shiou-Mei, H., Ling, R., Long, J., Maddox, C., Massetti, J., McCauley, E., Na, K., Pang, Y., Rieger, P., Sax, T., Truong, T., Vo, T., Chattopadhyay, S., Maldonado, H., Maricq, M., and Robinson, A. L.: Gas- and particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles, Atmospheric Environment, 88, 247–260, http://dx.doi.org/10.1016/j.atmosenv.2014.01.046, 2014.

Murphy, B., and Pandis, S.: Simulating the formation of semivolatile primary and secondary organic aerosol in a regional chemical transport model., Environ. Sci. Technol., 43, 4722-4728, doi:10.1021/es803168a, 2009.

Platt, S. M., Haddad, I. E., Pieber, S. M., Huang, R. J., Zardini, A. A., Clairotte, M., Suarez-Bertoa, R., Barmet, P., Pfaffenberger, L., Wolf, R., Slowik, J. G., Fuller, S. J., Kalberer, M., Chirico, R., dommen, J., astorga, C., Zimmermann, R., Marchand, N., Hellebust, S., Temime-Roussel, B., Baltensperger, U., and Prévôt, A. S. H.: Two-stroke scooters are a dominant source of air pollution in many cities, Nature communications, 5, 2014.

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking organic aerosols: Semivolatile emissions and photochemical aging, Science, 315, 1259-1262, 2007.

Turpin, B., and Lim, H.: Species contributions to PM2. 5 mass concentrations: Revisiting common assumptions for estimating organic mass, Aerosol Science and Technology, 35, 602--610, 2001.

Woody, M. C., Baker, K. R., Hayes, P. L., Jimenez, J. L., Koo, B., and Pye, H. O. T.: Understanding sources of organic aerosol during CalNex-2010 using the CMAQ-VBS, Atmospheric Chemistry and Physics, 16, 4081-4100, 2016.

Zhao, Y., Hennigan, C. J., May, A. A., Tkacik, D. S., de Gouw, J. A., Gilman, J. B., Kuster, W., Borbon, A., and Robinson, A. L.: Intermediate-volatility organic compounds: a large source of secondary organic aerosol, Environ. Sci. Technol., 2014.

Chemical Transport Model Simulations of Organic Aerosol in Southern California: Model Evaluation and Gasoline and Diesel Source Contributions

Shantanu H. Jathar[1], Matthew Woody[2], Havala O. T. Pye[2], Kirk R. Baker[2], and Allen L. Robinson[3]

[1] Mechanical Engineering, Colorado State University, Fort Collins CO 80525
[2] US Environmental Protection Agency, Research Triangle Park, NC, 27711
[3] Mechanical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213

Correspondence to: Shantanu H. Jathar (Shantanu.Jathar@colostate.edu) or Allen L. Robinson (alr@andrew.cmu.edu)

Abstract. Gasoline- and diesel-fueled engines are ubiquitous sources of air pollution in urban environments. They emit both primary particulate matter and precursor gases that react to form secondary particulate matter in the atmosphere. In this work, we updated the organic aerosol module and organic emission inventory of a three-dimensional chemical transport model, the Community Multiscale Air Quality Model (CMAQ), using recent, experimentally-derived inputs and parameterizations for mobile sources. The updated model includes revised volatile organic compound (VOC) speciation for mobile sources and secondary organic aerosol (SOA) formation from unspeciated intermediate volatility organic compounds (IVOC). The updated model was used to simulate quality in southern California during May and June 2010 when the California Research at the Nexus of Air Quality and Climate Change (CalNex) study was conducted. Compared to the traditional version of CMAQ, which is commonly used for regulatory applications, the updated model did not significantly alter the predicted organic aerosol (OA) mass concentrations but did substantially improve predictions of OA sources and composition (e.g., POA-SOA split), and ambient IVOC concentrations. The updated model, despite substantial differences in emissions and chemistry, performed similarly to a recently released research version of CMAQ (Woody et al., 2016) that did not include VOC and IVOC updates. Mobile sources are predicted to contribute 30-40% of the OA in southern California (half of which is SOA), making mobile sources the single largest source contributor to OA in southern California. The remainder of the OA is attributed to non-mobile anthropogenic sources (e.g., cooking, biomass burning) with biogenic sources contributing less than 5% to the total OA. Gasoline sources are predicted to contribute about thirteen times more OA than diesel sources; this difference is driven by differences in SOA production. The model predictions highlight the need to better constrain multi-generational oxidation reactions in chemical transport models.

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1 Introduction

Organic aerosol (OA) is a major component of atmospheric fine particulate matter (Jimenez et al., 2009). Source apportionment studies have historically attributed the majority of ambient OA in Southern California to motor vehicles emissions (Schauer et al., 1996), but analysis of data from the California Research at the Nexus of Air Quality and Climate Change (CalNex) study has led to conflicting conclusions about the overall contribution of motor vehicles to OA in southern California and the relative importance of gasoline versus diesel sources. Bahreini et al. (2012) hypothesized that the majority of OA in southern California was secondary organic aerosol (SOA) formed from emissions from gasoline powered-sources based on differences in weekday and weekend pollutant concentrations; Hayes et al. (2013) and Zotter et al. (2014) reached the same conclusion based on analysis of mass spectrometer and radiocarbon data respectively. In contrast, Gentner et al. (2012) concluded that diesel vehicles contributed more OA than gasoline vehicles based on a comprehensive speciation of SOA precursors present in gasoline and diesel fuels. Ensberg et al. (2014) proposed that observed levels of OA could be explained only if vehicle emissions were a minor source of SOA or that the SOA formation potential of vehicle emissions was significantly higher than that measured in laboratory studies. Finally, source-resolved chemical transport model (CTM) simulations predict that gasoline sources contribute approximately twice as much POA as diesel sources in southern California (Woody et al., 2016).

Research and regulatory efforts have historically focused on emissions of primary organic aerosol (POA) but recently the attention has shifted to secondary organic aerosol (SOA) since appears to dominate OA mass concentrations even in urban areas. Typical CTM treatments of OA assume non-volatile POA emissions and formation of SOA from "traditional" precursors (Carlton et al., 2010), which are speciated volatile organic compounds (VOCs) such as alkanes smaller than C_{12} single-ring aromatics, isoprene and mono- and sesquiterpenes. Robinson et al. (2007) proposed a new conceptual model for emissions and evolution of OA from combustion sources. Robinson et al. (2007) and subsequent work has demonstrated that: (1) POA emissions are semi-volatile and reactive (Grieshop et al., 2009;Huffman et al., 2009;May et al., 2013a;May et al., 2013b, c), (2) combustion sources emit substantial amounts of intermediate volatility organic compounds (IVOCs) that are efficient SOA precursors (IVOCs are higher carbon number species (C_{12+}) that are difficult to speciate using traditional gas chromatography mass spectrometry techniques due to the very large number of constitutional isomers and/or polarity of partially oxidized species (Jathar et al., 2014;Presto et al., 2011;Zhao et al., 2015;Hatch et al., 2015)) and (3) semi-volatile organic vapors in equilibrium with OA photo-chemically react or "age" in the atmosphere to form additional SOA (Miracolo et al., 2010). Recent state-of-the-science OA models have included these three processes, which improve model performance

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(Murphy and Pandis, 2009;Koo et al., 2014). These improvements, however, require simultaneous inclusion of all the above-mentioned processes; for example, inclusion of semi-volatile POA without SOA formation from IVOCs and aging reactions degrades model performance vis-à-vis total OA mass. However, the inputs required to represent these three processes are poorly constrained. For example, IVOC emissions from all sources are often assumed to be 1.5 times the POA emissions (Robinson et al., 2007;Shrivastava et al., 2008;Koo et al., 2014;Woody et al., 2016), based on measurements from two medium duty diesel vehicles (Schauer et al., 1999). New experimental data are needed to better constrain these processes.

Recently, a series of experiments investigated the SOA formation from gasoline vehicles, diesel vehicles and small off-road engines recruited from the California in-use fleet (Gordon et al., 2014a;Gordon et al., 2014b;Gordon et al., 2013). Jathar et al. (2014) analyzed these data to derive quantitative estimates of the IVOC emissions and their potential to form SOA after several hours of atmospheric oxidation. Here, we use the term IVOCs to represent the class of intermediate-volatility SOA precursors that remain unresolved at the molecular level using conventional GC-MS techniques; Jathar et al. (2014) referred to these as unspeciated organic compounds. We use the term VOCs to include the class of SOA precursors typically speciated using conventional GC-MS techniques (e.g., alkanes smaller than C_{12} and single ring aromatics). Jathar et al. (2014) derived separate parameterizations to account for SOA formation from IVOC emissions from gasoline and diesel sources for use in CTMs.

In this work, we use an updated version of CMAQ to simulate ambient OA from gasoline and diesel sources in southern California. The updates include new mobile source emissions profiles for VOCs (based on May et al. (2013b) and May et al. (2013c)) and include emissions and parameterizations for SOA production from IVOCs (based on Jathar et al. (2014)). Model predictions are evaluated using data collected during CalNex, compared to predictions of other models, and used to investigate the contribution of gasoline and diesel sources to ambient OA concentrations. This is the first time that a comprehensive set of gasoline and diesel source data have been used to develop source-specific IVOC inputs for a three-dimensional CTM. Earlier modeling efforts have relied on data that are almost a decade old (e.g., Koo et al. (2014)) and/or have used box models that may not accurately simulate horizontal and vertical transport and deposition (e.g., Hayes et al. (2015)). Hence, our work presents a step forward in improving the representation of sources, emissions and photochemical production of OA in large-scale models. This paper builds upon recent work by Baker et al. (2015) and Woody et al. (2016) who used different versions of CMAQ to simulate OA in California during May and June 2010.

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2 Methods

In this section, we provide a brief overview of CMAQ followed by more detailed descriptions of the OA model and emissions.

2.1 Chemical Transport Model

The CMAQ model version 5.0.2 was used to simulate air quality in California from May 4 to June 30, 2010, which coincides with the CalNex campaign (May–July 2010). Details about the application of this version to CalNex can be found in Baker et al. (2015) and Woody et al. (2016). Briefly, the model domain covered California and Nevada with a 4-km (317 x 236) grid resolution (Figure S.1). The vertical domain included 34 layers and extended to 50 mbar. Atmospheric gas-phase chemistry was simulated with the Carbon Bond 2005 (TUCL05) chemical mechanism (Yarwood et al., 2005;Whitten et al., 2010;Sarwar et al., 2012). Aerosol chemistry and partitioning was simulated using the aerosols 6 (AERO6) module with different models to represent OA (described below). United States anthropogenic emissions were based on the EPA's 2011v1 modeling platform (http://www.epa.gov/ttnchie1/net/2011inventory.html) and biogenic emissions were estimated using the Biogenic Emission Inventory (BEIS) version 3.14 model (Carlton and Baker, 2011). Gridded meteorological inputs for CMAQ and SMOKE were generated using version 3.1 of the WRF model (Skamarock et al., 2008). The first 11 days of the simulation were excluded from the analysis to minimize the influence of initial conditions. Boundary conditions were provided by a 36-km continental U.S. CMAQ simulation from the same time period.

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2.2 OA Model

The OA model used here builds on the volatility basis set (VBS) implementation in CMAQ (Koo et al., 2014) and is referred to as the VBS-IVOC model. The novel aspects of this work are the implementation of updated organic emissions profiles that explicitly account for IVOC emissions from gasoline and diesel sources and experimentally constrained parameterizations of Jathar et al. (2014) for the SOA production from these emissions.

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In the VBS-IVOC model, we extend the work of Baker et al. (2015) and Woody et al. (2016), both of which evaluated different OA models in CMAQ using the CalNex data. Baker et al. (2015) evaluated the standard OA module in CMAQ (Carlton et al., 2010). Woody et al. (2016) evaluated the VBS version of CMAQ as implemented by Koo et al. (2014), which treats POA emissions as semi-volatile and reactive treatment and accounts for SOA production from VOCs and IVOCs and their multigenerational oxidation or aged products. The VBS-IVOC model is the same as the VBS model of Woody et al. (2016) except for the treatment of gasoline and diesel sources. To facilitate direct comparison between the different models, all three studies

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(this work, Baker et al. (2015) and Woody et al. (2016)) use the same CTM (CMAQ v5.02), emissions inventory (except for the modifications described below) and meteorology inputs. However, Baker et al. (2015) used a different gas-phase chemical mechanism (SAPRC07b). We refer to the Baker et al. (2015) treatment of OA and the model results as the 'Traditional' model and we refer to the Woody et al. (2016) treatment of OA and the model results as the 'VBS' model.

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The VBS version of CMAQ includes four distinct volatility basis sets to separately track different classes of OA: anthropogenic POA, anthropogenic SOA, biogenic SOA, and biomass burning POA (Koo et al., 2014). The VBS-IVOC model extends CMAQ with three additional basis sets for POA from gasoline sources, diesel sources, and cooking activities to provide POA source apportionment (Woody et al., 2016). Each basis set has five volatility bins with different effective saturation concentrations (C*): non-volatile and logarithmically distributed bins from 10^0 to 10^3 µg m^{-3} at 298 K. The gas-particle partitioning of semi-volatile organic compounds in each basis set is assumed to be in equilibrium and to form a quasi-ideal solution with all of the OA.

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Emissions: In the VBS-IVOC model, we use emission inventories developed by Baker et al. (2015) and modified by Woody et al. (2016) for use with the VBS model. In this section we briefly describe the VBS inventory of Woody et al. (2016), focusing on the updates to gasoline and diesel organic emissions used in the VBS-IVOC model.

We (in the VBS-IVOC model) and Woody et al. (2016) use the same semi-volatile POA emissions. These were estimated by redistributing the non-volatile POA emissions of Baker et al. (2015) into the VBS. For gasoline and diesel exhaust and biomass burning, this redistribution is done using the source-specific volatility distributions of May and coworkers (May et al., 2013b, c;May et al., 2013a). Cooking emissions were redistributed using an approximation developed by Woody et al. (2016) based on thermodenuder measurements made with cooking emissions and ambient measurements made during MILAGRO (Huffman et al., 2009). For all other sources, the volatility distribution of Robinson et al.(Robinson et al., 2007) was used to map the existing POA emissions into the VBS.

In the VBS-IVOC model, we use new VOC speciation profiles for tailpipe emissions from gasoline and diesel sources (Table S.1). These speciation profiles are applied to the emissions inventory of Baker et al. (2015). Therefore, the VBS-IVOC model has the same mobile source emission rates as Baker et al. (2015) but with different organic speciation. For all gasoline sources (on and off-road), the VOC speciation is based on fleet-

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averaged data from May et al. (2014), which reports emissions of 202 unique species measured during chassis dynamometer testing of 68 light-duty gasoline vehicles operated over the Cold Unified Cycle (UC) using gasoline that met California summertime specifications (five of the vehicles were also run on the Freeway, Arterial and Hot UC cycles). For on- and off-road diesel vehicles, the VOC speciation is derived from the EPA SPECIATE profile for on-road heavy-duty diesel vehicles (Profile number 8774); the same diesel emissions profile is used in Baker et al. (2015) and Woody et al. (2016). All VOCs are mapped to CB05 model species using EPA's speciation tool, which lumps unique organic compounds to a representative model species that are similar in terms of based on reactivity and reaction chemistry (Eyth et al., 2006;Carter, 2008).

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For gasoline and diesel sources, we estimate the IVOC emissions in the VBS-IVOC model based on the gas-phase carbon-balance analysis of Jathar et al. (2014), who found that unspeciated organic compounds (assumed to be mainly IVOCs) contributed, on average, 25% and 20% of the non-methane organic gas (NMOG) emissions from gasoline and diesel vehicles respectively. IVOCs are included in the VBS-IVOC model by reapportioning the existing non-methane organic gas (NMOG) emissions between VOCs and IVOCs (effectively renormalizing the VOCs described above). Therefore, unlike previous VBS models such as Woody et al. (2016) where IVOC emissions are added to the NMOG emissions, no new NMOG emissions are added to the model for the gasoline and diesel sources. In addition, gasoline and diesel POA emissions in the C* bins of 10^3 and 10^4 µg m^{-3} (organic compounds that exist in the vapor phase in the atmosphere; 32% of gasoline and 35% of diesel POA emissions) are reclassified as IVOCs, consistent with the parameterization of Jathar et al. (2014).

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Following Robinson et al. (2007), IVOC emissions for all other sources (non-gasoline and diesel) were assumed to be 1.5 times the POA emissions (Woody et al. (2016) assumed this for all sources). Some of the IVOCs, as defined here, may already be included in the original emissions profile as ALK5 and UNK, however, Pye and Pouliot (2012) show that these emissions are very likely underestimated and, therefore, do not pose a serious problem of double counting SOA precursors.

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To illustrate the effects of these changes, Figure 1 plots the POA and SOA precursor emissions (BTEX (all aromatics), ALK5 (long alkanes) and IVOCs) from all gasoline and diesel sources in Los Angeles and Orange counties aggregated over the entire simulation period (May 4 to June 30, 2010). Table S.2 in the supplementary material lists the emissions for on- and off-road gasoline and diesel use, all other sources, and biogenic sources. Here, gasoline and diesel sources include both on- and off-road applications.

The magnitude of the POA emissions is identical between all three models with the exception that some of the POA emissions are reclassified as IVOCs in the VBS-IVOC model as described earlier. The BTEX emissions are identical between the Traditional and VBS models, but lower in the VBS-IVOC model because we have renormalized the NMOG emissions to account for IVOCs. The Traditional model does not include IVOC emissions. The IVOC emissions in the VBS-IVOC model are a factor of four higher for gasoline sources than in the VBS model of Woody et al. (ref), but 20% lower for diesel sources. Taken together, the BTEX, ALK5 and IVOC emissions (sum of all anthropogenic SOA precursors) are somewhat higher (40%) in the VBS-IVOC model compared to the VBS model for gasoline sources and slightly lower (5%) for diesel sources. Therefore, discounting for differences in reaction rate constants and SOA mass yields, we expect roughly similar SOA production from gasoline and diesel sources between the VBS and VBS-IVOC simulations. In all models, gasoline sources have substantially larger organic emissions than diesel sources (e.g. 3.7, 42, 35 and 16 times more POA, BTEX, ALK5 and IVOC for the VBS-IVOC model, respectively); therefore we anticipate much higher SOA production from gasoline sources than from diesel sources.

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SOA formation: SOA production from VOCs is simulated using the parameterizations of Murphy and Pandis (2009) except for toluene (Hildebrandt et al., 2009). SOA production from aromatics (toluene, xylene, and benzene), isoprene, and monoterpenenes have high- and low-NO_x yields; there is no NO_x dependence in the SOA yield from sesquiterpenes and IVOCs. Emissions profiles for VOCs, IVOCs and their SOA yields, specific to gasoline and diesel tailpipe emissions, are presented in Table S.1.

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IVOC emissions from gasoline and diesel sources are represented separately using two (one for gasoline and one for diesel) gas-phase species in the chemical mechanism (CB05-TUCL) and the parameterizations of Jathar et al. (2014) are used to estimate the SOA production from the IVOC oxidation. Briefly, the IVOCs react with the OH to form a set of semi-volatile products distributed in the VBS (Table S.1). The stoichiometric mass yields for each product were determined by fitting the SOA production measured in smog chamber experiments performed with diluted vehicle exhaust (Jathar et al., 2014). Following Woody et al. (2016), for all other sources (i.e. not gasoline and diesel) SOA production from IVOCs is based on the published yields for the SAPRC ARO2 model species from Murphy and Pandis (2009).

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SOA formed from VOCs and IVOCs is aged via reactions of the organic vapors with OH using a rate constant of 2 x 10^{-11} cm^3 $molecules^{-1}$ s^{-1}. These aging reactions form products with a vapor pressure reduced by one order of magnitude. Biogenic SOA is not aged. Semi-volatile POA vapors from all sources are aged using the scheme of Robinson et al. (2007) – gas-phase reactions with the hydroxyl radical (OH) using a rate constant of 4 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, which lowers volatility by an order of magnitude (Robinson et al., 2007). Finally, the aging reaction also shift a portion (~10%) of the particle-phase POA mass to the anthropogenic SOA basis set to maintain O:C ratios (Koo et al., 2014). OH is artificially recycled in the IVOC oxidation and all aging reactions to prevent double counting and impacts to the gas-phase chemistry of the underlying chemical mechanism (Koo et al., 2014). The rate constants used for the aging reactions is not well constrained and likely with C* and O:C.

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3 Results

Although the simulation domain covers the entire state of California, we focus our analysis on model predictions over southern California and the metropolitan area of Los Angeles. This region is the second most populated area in the US, has historically had severe air pollution problems, and was the focus of a major air quality campaign (CalNex) during the simulation period.

3.1 Spatial distribution of OA

Figure 2 shows maps of average predicted concentrations of total OA (POA+SOA) from the VBS-IVOC model for the following sources: (a) all, (d) gasoline, (e) diesel, (f) biogenic and (g) other. In addition, Figure 2 also plots the predicted ratios of (b) POA to OA and (c) SOA to OA. Average predicted concentrations of OA in southern California range between 1.5 and 3 μg m^{-3} with POA accounting for slightly more than half of the OA in source regions such as downtown Los Angeles (a 'source' region is defined as one with high anthropogenic emissions of species such as POA) and SOA dominating in non-source regions and off the coast.

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Gasoline sources are predicted to contribute ~35% of the inland OA while diesel sources contribute less than 3% (for details see Section 4). The predicted gasoline OA exhibits a slightly different spatial pattern than total OA, with higher downwind concentrations near Riverside than those near central Los Angeles, reflecting the importance of atmospheric production of SOA. As expected, biogenic SOA is more important outside of the urban areas contributing 5% of total OA in urban areas versus 10-20% in non-urban. Other OA contributes slightly more than half of all OA in the urban areas. Other OA is dominated by cooking POA, biomass burning POA and other anthropogenic SOA (see Figure 4 for contributions of these sources in Pasadena).

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3.2 Model Evaluation Using OA Mass and Composition Measurements

The VBS-IVOC model was evaluated using measurements made at the Chemical Speciation Network (CSN) and the CalNex Pasadena ground sites. Figure 3(a) compares predicted daily-averaged OA mass concentration to measurements of organic carbon (OC) made at six CSN sites in California (Fresno, Bakersfield, Central Los Angeles, Riverside, El Cajon and Simi Valley). Figure 3(b) compares predicted daily-averaged OA concentrations to measurements made using a high-resolution aerosol mass spectrometer (HR-AMS) in Pasadena (Hayes et al., 2013). The CSN measurements need to be multiplied by an OA:OC ratio to account for the non-carbon species associated with organic carbon (Turpin and Lim, 2001). While ambient OA:OC ratios can range between 1.4 and 2.3 (Aiken et al., 2008), we use a value of 1.6 in this work based on previous estimates used for filter-based measurements (e.g., (Cappa et al., 2016)). This value is consistent with the OA:OC ratio of 1.7±0.5 estimated by Hayes et al. (2013) in Pasadena.

Predictions from the VBS-IVOC model are slightly lower than the filter-based measurements at the CSN sites, similar to other studies (Simon et al., 2012). The fractional bias and fractional error versus CSN sites are -23% and 43%, respectively. At the CSN sites, predictions from the VBS-IVOC model are marginally better at the southern California sites (Central LA, Riverside, El Cajon, Simi Valley, Pasadena) than the central California sites (Fresno, Bakersfield). This may be due to sources related to oil and gas production and agricultural activity being more important in central California (Gentner et al., 2014).

Figure 3(b) indicates predictions from the VBS-IVOC model are a factor of three lower than the HR-AMS OA data at the Pasadena site. It is unclear why the model performs much better at numerous CSN sites than the Pasadena site. One possibility is that the Pasadena site is influenced by local sources and transport that is not captured by the model at a 4 km resolution.

OA mass concentrations are only one measure for evaluating model performance. Given the myriad sources of and complexity in SOA production, a model can predict the right absolute OA concentration for the wrong reason. Therefore, it is important to evaluate the model against OA composition. Figure 4 compares predicted POA and SOA mass fractions to results from a positive matrix factorization (PMF) analysis of HR-AMS measurements made in Pasadena (Hayes et al., 2013). Since the absolute OA concentrations as measured with the HR-AMS are under-predicted (Figure 3(b)), we focus on OA mass fractions. Mass fractions only allow for a qualitative comparison of the OA composition and any differences in the modeled and measured mass fractions cannot be interpreted as an under- or over-prediction in the absolute mass concentration.

Figure 4 compares model predictions to hydrocarbon-like OA (HOA), cooking OA (COA) and oxygenated OA (OOA) factors derived from the ambient HR-AMS data (Hayes et al., 2013). The AMS HOA factor is typically associated with POA from motor vehicles and other fossil fuel sources. Therefore, in this work, it

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is compared against predictions of POA from gasoline and diesel sources. The AMS COA factor is associated with primary cooking emissions and is compared against predictions of POA from cooking sources. The AMS OOA factor is associated with SOA and is compared against predictions of total SOA; the model did not resolve SOA by degree of oxygenation and hence we have not compared predictions to the individual HR-AMS-derived semi-volatile OOA (SV-OOA) and low-volatility OOA (LV-OOA) factors.

Before discussing the normalized composition predicted by the VBS-IVOC model, we briefly describe the findings from Woody et al. (2016) who carefully compared the predictions of absolute concentrations of the VBS model to the PMF factors estimated from the ambient HR-AMS measurements. Woody et al. (2016) found that (i) the predicted cooking-related OA concentrations compared well with the COA factor during the morning but were low in the afternoon and late night, (ii) non-cooking POA concentrations compared well with the HOA factor except during the afternoon when it was underpredicted, and (iii) predicted SOA concentrations match the diurnal profile of the OOA factor but were but was a factor of 5 lower during all times of the day.

Figure 4 shows that the VBS-IVOC model better predicts the POA-SOA split than the Traditional model. For the VBS-IVOC model, the POA-SOA split is 1:1 versus ~20:1 for the traditional model. The measurement-based factor analysis estimates a POA-SOA split of 1:2. For the Traditional model, SOA contributes less than 3% of the total OA.

In Figure 4, we show that the predicted gasoline+diesel POA fraction compares well with the HR-AMS HOA fraction while the predicted cooking POA fraction is over-predicted compared to the HR-AMS COA fraction; Woody et al. (2016) hypothesized that the VBS model (which has the same treatment for cooking OA as the VBS-IVOC) likely under-predicts cooking POA emissions based on a comparison of absolute cooking OA concentrations. For the VBS-IVOC model, about 6% of the OA is from biomass burning while Hayes et al. (2013) were unable to determine a biomass burning factor in their PMF analysis of ambient data. The SOA fraction predicted by the VBS-IVOC model is about 35% lower than the estimated OOA fraction. It is unclear if the predicted non-mobile, non-cooking and non-biomass burning POA (which in Pasadena accounts of ~9% of the OA) should be combined with SOA before being compared with ambient OOA factor. The non-mobile, non-cooking and non-biomass burning POA (or anthropogenic (other) POA) category here includes sources such as stationary fuel combustion (e.g., natural gas combustion), surface coatings (e.g., metal coating), mineral processes (e.g., concrete production), road dust and managed burning (e.g., prescribed

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burns). Unfortunately, the composition of the POA emitted from these sources is not well understood and needs to be investigated by future work.

Although predictions from the VBS-IVOC model are much better than the Traditional model for the POA-SOA split and the fractional source contribution/composition of OA, in Figure 3(b) we show that predictions from the VBS-IVOC model are substantially lower than the absolute concentrations measured by the HR-AMS. Future research should explore higher resolution simulations (<1 km) for the Los Angeles area, in addition to improving estimates of POA emissions (e.g., cooking) and improved representations for SOA formation (e.g., higher SOA yields when accounting for vapor wall-losses in chambers).

3.3 Model Evaluation Using IVOC Measurements

A novel aspect of the VBS models (VBS and VBS-IVOC) is that they track IVOCs, an important class of SOA precursors (Jathar et al., 2014). Campaign-averaged predictions of IVOC concentrations are compared in Figure 5 against IVOC measurements at the Pasadena ground site made by Zhao et al. (2014). This is the first time 3-D model predictions of IVOCs have been compared against ambient measurements.. The VBS-IVOC model does not simulate secondary production of IVOC species (for lack of data) and hence the model predictions in Figure 5 only include primary emissions of IVOCs. The IVOC measurements shown in Figure 5 are split into two categories: primary and oxygenated. Zhao et al. (2014) attribute the measured primary IVOCs to emissions from mobile sources (gasoline+diesel) and oxygenated IVOCs to primary sources and those formed in the atmosphere.

Predicted gasoline and diesel IVOC concentrations (3.9 μg m^{-3}) from the VBS-IVOC model are 35% lower than the primary IVOC concentrations measured by Zhao et al. (2014) (6 μg m^{-3}). This suggests that the VBS-IVOC model provides a reasonable representation of the emissions, transport and chemistry of IVOCs from mobile sources. Furthermore, the VBS-IVOC model predicts that the majority of the primary IVOCs originate from gasoline sources. The under-prediction could partly be a result of the inability of the model with a 4 km horizontal resolution to capture the location-specific concentrations at Pasadena. Coincidentally, the predicted IVOC for other anthropogenic sources and biomass burning (4.3 μg m^{-3}) compared well with the measured oxygenated IVOC (4.1 μg m^{-3}). Given the uncertainty in the model emissions of IVOCs for non-mobile sources (POAx1.5), the comparison with oxygenated IVOCs need to be explored in future work.

In contrast, predicted IVOC concentrations from the VBS model are a factor of 4 lower than the measurements, which highlights the improved representation of IVOCs in the VBS-IVOC model. The traditional model predicts essentially no IVOCs.

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3.4 Model Inter-comparison for OA

We compared predictions from the VBS-IVOC model to OA predictions from Baker et al. (2015) and Woody et al. (2016) who simulated air quality in California during CalNex. Figure S.2 presents maps of averaged concentrations and ratios of POA, SOA and total OA (POA+SOA) from the Traditional and VBS-IVOC models. The results are qualitatively similar to earlier VBS implementations (Fountoukis et al., 2014;Hodzic et al., 2010;Ahmadov et al., 2012;Shrivastava et al., 2011;Tsimpidi et al., 2009) and previous comparisons between VBS and Traditional-like models (Robinson et al., 2007;Shrivastava et al., 2008;Woody et al., 2016;Jathar et al., 2011). In the VBS-IVOC simulation, total OA concentrations are lower in source regions (~50%) but ~20-40% higher away from sources than the Traditional model. The decrease in source regions is due to POA evaporation while an increase away from sources results from enhanced SOA production. The OA predicted by the Traditional model is dominated by POA (1-3 µg m^{-3}) with very little SOA (0.2-0.4 µg m^{-3}) while the OA predicted by the VBS-IVOC model has equal proportions of POA and SOA.

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Figure S.3 compares predictions of the VBS and VBS-IVOC models, including average concentrations and ratios of POA, SOA and total OA (POA+SOA). The results are surprisingly similar. POA concentrations in the VBS-IVOC model are slightly lower (~10%) in source regions and lower still in non-source regions (~20%) than the VBS model. The SOA concentrations are nearly identical and both models predict more spatially uniform OA concentrations compared to the Traditional model. The modest differences in POA and SOA likely result from a combination of the following three reasons: (1) the magnitude of the total SOA precursor emissions in the VBS and VBS-IVOC models are basically the same (see BTEX, ALK5 and IVOC emissions data in Table S.2 for all sources), (2) gasoline and diesel sources contribute only 30%-40% of the predicted OA concentrations in southern California (see Section 5 for a detailed discussion) and (3) a majority of the SOA predicted in southern California arises from aging reactions.

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Although the VBS and VBS-IVOC models contain very different representations of mobile source emissions, these emissions contribute, on average, slightly more than one-third of the total OA in southern California (see Section 4). Therefore, the updates used in the VBS-IVOC model had a limited influence in affecting the overall OA burden. Strict regulations have dramatically reduced emissions from motor vehicles over the past three decades, which has both improved air quality and increased the relative importance of other sources (McDonald et al., 2015). For example, compared to mobile sources, cooking remains a possibly important, yet understudied, source of fine particle pollution in urban airsheds.

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The similarity between predictions from the VBS and VBS-IVOC models is also due to the importance of aging reactions. Both models use the same aging scheme applied to POA and SOA vapors (for more details, see Koo et al. (2014)) To quantify its contribution to predicted SOA concentrations, we ran the VBS-IVOC model with aging reactions turned off; these results are plotted in Figure S.4. Without aging, total predicted OA is nearly halved and SOA concentrations are significantly reduced (more than a factor of five in source regions, factor of 10 to 20 in terrestrial non-source regions and up to a factor of 40 over the ocean). Given that mobile sources contribute only about one-third of the total OA and that aging reactions significantly enhance OA concentrations, it appears that modest differences in the emissions and yield potential of SOA precursors between the VBS and VBS-IVOC models have a limited effect on the OA burden.

4 Gasoline versus Diesel Source Contributions to OA

Recent analyses of the CalNex data have led to conflicting conclusions about the contribution of gasoline and diesel sources to OA in southern California (Bahreini et al., 2012;Gentner et al., 2012;Ensberg et al., 2014;Hayes et al., 2013;Zotter et al., 2014;Hayes et al., 2015). The source-resolution implemented in the VBS-IVOC model allows for an assessment of the absolute and relative importance of gasoline and diesel sources to OA in southern California. In Figure 6, we plot the campaign-averaged OA concentrations attributable to gasoline and diesel use. The SOA production from VOCs emitted by gasoline and diesel sources was not tracked separately in the model. Here, the SOA from VOCs is estimated based on the contribution of gasoline and diesel sources to the emissions of VOC precursors (BTEX and ALK5) in Los Angeles and Orange counties.

In Pasadena, predictions from both VBS models show that gasoline sources contribute ~7 to 8 times more OA than diesel sources (Figure 6(a)), which is somewhat lower than other inland locations in southern California (Figure 6(b)). Domain-wide, the predicted gasoline contribution to OA is 10 to 20 times that of diesel. At Pasadena, predictions from the VBS-IVOC model show that gasoline contributes 20 times more SOA than diesel. Both VBS models predict that the combined (gasoline and diesel) POA-to-SOA split is ~1:3 implying that the contribution of gasoline and diesel sources to ambient OA strongly depends on SOA production and not directly-emitted POA. Based on results from the VBS-IVOC model, gasoline sources produce more SOA than POA (SOA~3.6xPOA) while diesel sources produce less SOA than POA (SOA~0.5xPOA).

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Moved down [1]: The aging reactions simulate the multigenerational gas-phase oxidation of vapors in equilibrium with OA. The aging mechanism used here is conceptually based on the work of Robinson et al. (2007) and only allows for the formation of functionalized, lower-volatility products. In essence, aging reactions, with enough time, will convert all semi-volatile vapors into particles. However, the mechanism assumes a constant reaction rate constant, which may vary with C* and O:C of the OA and does not account for fragmentation reactions, which should become increasingly important at longer time scales(Kroll et al., 2011). The reaction rate for aging and the effects of aging at longer time scales have not been constrained against laboratory data. This implies that the OA predictions, despite the substantial new data, become poorly constrained as one moves downwind of source regions. Murphy and Pandis (2009) have found that model predictions agree better with measurements when aging reactions are turned off for biogenic SOA. Recently, Jathar et al. (2016) have shown that aging reactions similar to those suggested in Robinson et al. (2007) might not be necessary since the laboratory chamber experiments that are used to parameterize SOA production already include products from the aging reactions happening inside the chamber. The work of Murphy and Pandis (2009) (for biogenics) and Jathar et al. (2016) suggests that including aging reactions in CTMs may double count SOA production and over-predict the importance of multigenerational gas-phase chemistry in the atmosphere. Although some work has been done to understand the aging of biogenic SOA (Donahue et al., 2012;Henry and Donahue, 2012), future laboratory work needs to be directed in understanding the role of aging of OA vapors formed from anthropogenic sources on the mass and properties of OA.

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Our predictions of the large contribution of gasoline vehicle exhaust to SOA are consistent with the weekday/weekend analysis of Bahreini et al. (2012) and qualitatively similar to the findings of Zotter et al. (2014) and Hayes et al. (2013). However, Hayes et al. (2015) predict a much larger contribution of diesel sources to SOA than this work (only1.5 to 2 times lower than gasoline), which can mostly be attributed to the differences in emissions inputs for S/IVOC emissions. (Hayes et al. (2015) estimate that 44-92% of the SOA arises from S/IVOCs). Hayes et al. (2015) estimated S/IVOC emissions by scaling POA emissions based on Schauer et al. (1999) and using the volatility distribution from Robinson et al. (2007). The POA scaling data are from two medium duty vehicles manufactured more than two decades ago and the volatility data are from a single diesel engine manufactured a decade ago. In contrast, our work uses a much more comprehensive dataset to determine S/IVOC emissions from gasoline and diesel sources. Finally, the emissions inventory (see Table S.1) suggests that the Traditional model (with a non-volatile POA and little SOA productions) would predict that gasoline sources contributes four times more OA than diesel sources.

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We also investigated the sensitivity of the VBS-IVOC predictions to uncertainty in diesel IVOC emissions. Zhao et al. (2015) recently directly measured the IVOCs from emissions of on-road diesel engines. They found that IVOCs could contribute up to 60% of the NMOG emissions, which is much greater than the 20% used here. To explore the implications of the findings of Zhao et al. (2015), we performed two additional sensitivity simulations with the VBS-IVOC model where we scale IVOC emissions from diesel sources by a factor of 3 and 5, which are effectively equivalent to IVOC-to-NMOG ratios of 0.6 and 1.0 respectively. For these simulations, additional IVOC mass is added to the inventory.

Results from the IVOC sensitivity simulations are also shown in Figure 6(a). We find that increasing the IVOC emissions proportionally increases the OA contribution from diesel sources. However, even if all of the NMOG emissions from diesel are IVOCs (an upper bound estimate), gasoline-related OA still dominates OA from diesel sources. A factor of 5 increase in IVOC emissions only results in a 0.025 μg m^{-3} increase in total OA mass concentrations and hence does not alter the previously discussed model-measurement comparison (Figure 3).

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Figure 6(c) shows the cumulative distribution for the fractional contribution of gasoline and diesel sources to total OA across southern California. Gasoline sources contribute much more to the total OA (median contribution of 35%) than diesel sources (median contribution of 2.6%) over southern California (Figure 6(c)). Together, mobile sources (gasoline and diesel use) contribute ~30-40% (10th-90th percentile) of the predicted OA concentration in southern California. Therefore, mobile sources remain the single most

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important source despite decades of increasingly strict emissions controls. The balance of the OA is from cooking POA (median contribution of 10%), biogenic SOA (median contribution of 10%) and all other anthropogenic sources (median contribution of 40%, which includes SOA from cooking sources). Gasoline sources are still predicted to be the largest single source category. This finding partially supports the conclusion of Ensberg et al. (2014) that mobile sources do not contribute the majority of OA in southern California and potentially explains why the updates only modestly changed the overall model predictions.

Figure 6(a) resolves the predicted OA concentration into POA and SOA precursor class at the Pasadena site. The VBS-IVOC model predicts that IVOCs, particularly from gasoline vehicles, form almost as much SOA as VOCs (long alkanes and single-ring aromatics). This is in contrast to Jathar et al. (2014), who found that IVOCs (referred to as unspecaited organics by Jathar et al.) were approximately a factor of 4 larger than VOCs in forming SOA in chamber experiments. One possible reason for this difference is that Jathar et al. (2014) did not account for the effects of atmospheric aging of IVOC oxidation products on OA concentrations. Simulations with the VBS-IVOC model with aging reactions turned off (discussed in Section 4.4) indicate that aging enhances VOC SOA by a factor of 14 but enhances IVOC SOA only by a factor of 3-5. The different enhancements is caused by different product distributions for VOC and IVOC SOA in volatility space. This underscores the uncertainty in the treatment of aging reactions.

Platt et al. (2014) recently argued that off-road sources, especially those powered using two-stroke engines, can be a large contributor to fine particle pollution in cities. In the inventory of Baker et al. (ref) used here, off-road sources contributed ~40% of the NMOG and ~40% of the POA emissions from mobile sources. Given their substantial emissions, it is critical that these sources be accurately represented in large-scale models. Unfortunately, only one study so far has reported VOC and IVOC emission profiles from off-road engines. May et al. (2014) found that two-stroke off-road gasoline engines have similar emissions profiles as on-road gasoline engines, but that the four-stroke off-road gasoline engines produced higher IVOC fractions than on-road gasoline engines. In our work, we have assumed that the VOC speciation, IVOC fraction of NMOG, and the SOA parameterization for IVOCs were identical between the on- and off-road mobile sources. This assumption may need to be examined in detail in future work.

5 Conclusions

In this work, we developed an updated version of the CMAQ model that included revised estimates of (i) VOC and IVOC SOA precursors from gasoline and diesel sources and (ii) experimentally constrained parameterizations for SOA production from IVOCs. Predictions of OA mass concentrations from the updated

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model (VBS-IVOC) slightly under-predicted daily-averaged, filter-based measurements at CSN sites in California during May and June 2010 (fractional bias=-23% and fractional error=43%) but were a factor of three lower than aerosol mass spectrometer-based measurements made at Pasadena as part of the CalNex campaign. We do not know why the model performs so much better at the CSN sites then the Pasadena site. One possibility is that the Pasadena site is influenced by local sources and transport not captured with a 4 km resolution. We recommend future modeling studies to be performed at higher resolution.

When compared to a Traditional model of OA in CMAQ that includes a non-volatile treatment of POA and no SOA from IVOCs, the VBS-IVOC model produced different spatial patterns of OA with lower (~50%) concentrations in source regions but higher (~20-40%) concentrations away from the sources. In comparison to the Traditional model, the VBS-IVOC model better predicted the sources and composition of OA. These findings are consistent with previous comparisons between Traditional- and VBS- models and highlight the importance of the use of an OA model that includes semi-volatile and reactive POA and SOA formation from IVOCs.

Predictions of OA from the VBS-IVOC model are similar to those from a recently released research version of CMAQ (VBS) that included semi-volatile POA and SOA formation from IVOCs (Woody et al., 2016). The predictions of these two models were similar for three reasons. First, the VOC and IVOC updates in this work, surprisingly, did not substantially alter the total emissions of SOA precursors in southern California (although the VOC-IVOC composition was different between the two models for gasoline sources). Second, mobile sources only accounted for slightly more than one-third of the total OA in southern California and hence updates to the emissions and SOA production from mobile sources had a limited influence on the total OA burden. And third, and most important, is that both models predict that multigenerational aging of vapors in equilibrium with OA is a major source of SOA. In addition, both models used similar aging mechanisms that are conceptually based on the work of Robinson et al. (2007), which assumed a constant reaction rate constant and only allowed for the formation of functionalized, lower-volatility products. However, reaction rates may vary with C* and O:C of the OA and fragmentation reactions can be increasingly important at longer time scales (Kroll et al., 2011). Existing aging mechanisms have not been constrained with laboratory data. This implies that the OA predictions, despite the substantial new data, are poorly constrained as one moves downwind of source regions. Murphy and Pandis (2009) report improved model performance when aging reactions are turned off for biogenic SOA. Recently, Jathar et al. (2016) proposed that laboratory chamber experiments that are used to parameterize SOA production may already include products from some aging reactions, raising concerns about double counting. Although some work has been done to understand the aging of biogenic SOA (Donahue et al., 2012;Henry and Donahue, 2012), future laboratory

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work needs to be directed in understanding the role of aging of OA vapors formed from anthropogenic sources on the mass and properties of OA.

For the first time, we compared model predictions to ambient measurements of IVOCs. The new VBS-IVOC model better predicted the ambient IVOC concentrations compared to the Traditional and VBS models. This suggests that the updated model reasonably simulated the emissions, transport and chemistry of IVOCs from mobile sources. However, the model representation of IVOCs from non-mobile sources remains poorly constrained and needs to be explored through future emissions, laboratory and modeling studies.

Finally, the VBS-IVOC model predicted that mobile sources accounted for 30-40% of the OA in southern California, with half of the OA being SOA. Gasoline-powered sources contributed 13 times more OA than diesel-powered sources and sensitivity simulations indicated that these findings were robust to changes in diesel emissions. The diurnal variation of OA in Pasadena supports the hypothesis that substantial OA is produced through photochemical reactions vs. primary emissions. Model predictions suggested that half of the mobile source SOA was formed from the oxidation of IVOCs, which demonstrates the importance of including IVOCs as an SOA precursor. However, the relative contribution of VOCs and IVOCs to SOA formation was sensitive to the inclusion of aging reactions. While both laboratory and field evidence indicate that aging is an important atmospheric process, it is unclear if and by how much aging enhances OA over regional scales and whether aging chemistry varies by precursor and source (Jathar et al., 2016). For these reasons, the relative importance of VOC and IVOC SOA precursors and the source apportionment presented here is a first estimate and will likely evolve as we develop better models to simulate the dependence of aging on SOA formation.

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6 References

Ahmadov, R., McKeen, S. A., Robinson, A. L., Bahreini, R., Middlebrook, A. M., de Gouw, J. A., Meagher, J., Hsie, E. Y., Edgerton, E., Shaw, S., and Trainer, M.: A volatility basis set model for summertime secondary organic aerosols over the eastern United States in 2006, Journal Of Geophysical Research-Atmospheres, 117, D06301, 2012.

Aiken, A. C., DeCarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., and others: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, Environ. Sci. Technol, 42, 4478--4485, 2008.

Bahreini, R., Middlebrook, A. M., de Gouw, J. A., Warneke, C., Trainer, M., Brock, C. A., Stark, H., Brown, S. S., Dube, W. P., Gilman, J. B., Hall, K., Holloway, J. S., Kuster, W. C., Perring, A. E., Prevot, A. S. H., Schwarz, J. P., Spackman, J. R., Szidat, S., Wagner, N. L., Weber, R. J., Zotter, P., and Parrish, D. D.: Gasoline emissions dominate over diesel in formation of secondary organic aerosol mass, Geophys. Res. Lett., 39, L06805, 10.1029/2011gl050718, 2012.

Baker, K. R., Carlton, A. G., Kleindienst, T. E., Offenberg, J. H., Beaver, M. R., Gentner, D. R., Goldstein, A. H., Hayes, P. L., Jimenez, J. L., Gilman, J. B., de Gouw, J. A., Woody, M. C., Pye, H. O. T., Kelly, J. T., Lewandowski, M., Jaoui, M., Stevens, P. S., Brune, W. H., Lin, Y. H., Rubitschun, C. L., and Surratt, J. D.: Gas and aerosol carbon in California: comparison of measurements and model predictions in Pasadena and Bakersfield, Atmos. Chem. Phys., 15, 5243-5258, 10.5194/acp-15-5243-2015, 2015.

Cappa, C. D., Jathar, S. H., Wexler, A. S., Seinfeld, J., and Kleeman, M. J.: Simulating secondary organic aerosol in a regional air quality model using the statistical oxidation model – Part 2: Assessing the influence of vapor wall losses, Atmospheric Chemistry & Physics, 16, 3041-3059, 2016.

Carlton, A. G., Bhave, P. V., Napelenok, S. L., Edney, E. O., Sarwar, G., Pinder, R. W., Pouliot, G. A., and Houyoux, M.: Model representation of secondary organic aerosol in CMAQv4. 7, Environ. Sci. Technol., 44, 8553-8560, 2010.

Carlton, A. G., and Baker, K. R.: Photochemical Modeling of the Ozark Isoprene Volcano: MEGAN, BEIS, and Their Impacts on Air Quality Predictions, Environmental Science & Technology, 45, 4438-4445, 10.1021/es200050x, 2011.

Carter, W. P.: Development of an improved chemical speciation database for processing emissions of volatile organic compounds for air quality models, Center for Environmental Research and Technology (CE-CERT), University of California, Riverside. http://www/. engr. ucr. edu/~ carter/emitdb, 2008.

Donahue, N. M., Henry, K. M., Mentel, T. F., Kiendler-Scharr, A., Spindler, C., Bohn, B., Brauers, T., Dorn, H. P., Fuchs, H., Tillmann, R., Wahner, A., Saathoff, H., Naumann, K.-H., Möhler, O., Leisner, T., Müller, L., Reinnig, M.-C., Hoffmann, T., Salo, K., Hallquist, M., Frosch, M., Bilde, M., Tritscher, T., Barmet, P., Praplan, A. P., DeCarlo, P. F., Dommen, J., Prévôt, A. S. H., and Baltensperger, U.: Aging of biogenic secondary organic aerosol via gas-phase OH radical reactions, Proceedings of the National Academy of Sciences, 109, 13503-13508, 10.1073/pnas.1115186109, 2012.

Ensberg, J. J., Hayes, P. L., Jimenez, J. L., Gilman, J. B., Kuster, W. C., de Gouw, J. A., Holloway, J. S., Gordon, T. D., Jathar, S., and Robinson, A. L.: Emission factor ratios, SOA mass yields, and the impact of vehicular emissions on SOA formation, Atmospheric Chemistry and Physics, 14, 2383-2397, 2014.

Eyth, A., Ran, L., Partheepan, R., Yarwood, G., Jimenez, M., and Rao, S.: New tools to generate spatial surrogate and speciation profile inputs to SMOKE, International Emission Inventory Conference, New Orleans, LA. Available at http://www/. epa. gov/ttn/chief/conference/ei15/session9/eyth. pdf, 2006.

Fountoukis, C., Megaritis, A., Skyllakou, K., Charalampidis, P., Pilinis, C., Denier Van Der Gon, H., Crippa, M., Canonaco, F., Mohr, C., and Prévôt, A.: Organic aerosol concentration and composition over Europe: insights from comparison of regional model predictions with aerosol mass spectrometer factor analysis, Atmospheric chemistry and physics, 14, 9061-9076, 2014.

Gentner, D., Ford, T., Guha, A., Boulanger, K., Brioude, J., Angevine, W., De Gouw, J., Warneke, C., Gilman, J., and Ryerson, T.: Emissions of organic carbon and methane from petroleum and dairy operations in California's San Joaquin Valley, Atmospheric Chemistry and Physics, 14, 4955-4978, 2014.

Gentner, D. R., Isaacman, G., Worton, D. R., Chan, A. W., Dallmann, T. R., Davis, L., Liu, S., Day, D. A., Russell, L. M., Wilson, K. R., Weber, R., Guha, A., Harley, R. A., and Goldstein, A. H.: Elucidating secondary organic aerosol from diesel and gasoline vehicles through detailed characterization of organic carbon emissions, Proceedings of the National Academy of Sciences, 109, 18318-18323, 2012.

Gordon, T. D., Tkacik, D. S., Presto, A. A., Zhang, M., Jathar, S. H., Nguyen, N. T., Massetti, J., Truong, T., Cicero-Fernandez, P., Maddox, C., Rieger, P., Chattopadhyay, S., Maldonado, H., Maricq, M. M., and Robinson, A. L.: Primary Gas- and Particle-Phase Emissions and Secondary Organic Aerosol Production from Gasoline and Diesel Off-Road Engines, Environ. Sci. Technol., 47, 14137-14146, 2013.

Gordon, T. D., Nguyen, N. T., May, A. A., Presto, A. A., Lipsky, E. M., Maldonado, S., Chattopadhyay, S., Gutierrez, A., Maricq, M., and Robinson, A. L.: Secondary Organic Aerosol Formed from Light Duty Gasoline Vehicle Exhaust Dominates Primary Particulate Matter Emissions, Atmospheric Chemistry & Physics, 14, 4461-4678, doi:10.5194/acpd-13-23173-2013, 2014a.

Gordon, T. D., Nguyen, N. T., Presto, A. A., Lipsky, E. M., Maldonado, S., Maricq, M., and Robinson, A. L.: Secondary organic aerosol production from diesel vehicle exhaust: impact of aftertreatment, fuel chemistry and driving cycle, Atmospheric Chemistry & Physics, 14, 4643-4659, doi:10.5194/acp-14-4643-2014, 2014b.

Grieshop, A., Miracolo, M., Donahue, N., and Robinson, A.: Constraining the volatility distribution and gas-particle partitioning of combustion aerosols using isothermal dilution and thermodenuder measurements., Environ. Sci. Technol., 43, 4750, 2009.

Hatch, L. E., Luo, W., Pankow, J. F., Yokelson, R. J., Stockwell, C. E., and Barsanti, K. C.: Identification and quantification of gaseous organic compounds emitted from biomass burning using two-dimensional gas chromatography–time-of-flight mass spectrometry, Atmospheric Chemistry and Physics, 15, 1865-1899, 2015.

Hayes, P., Carlton, A., Baker, K., Ahmadov, R., Washenfelder, R., Alvarez, S., Rappenglück, B., Gilman, J., Kuster, W., and de Gouw, J.: Modeling the formation and aging of secondary organic aerosols in Los Angeles during CalNex 2010, Atmospheric Chemistry and Physics, 15, 5773-5801, 2015.

Hayes, P. L., Ortega, A. M., Cubison, M. J., Froyd, K. D., Zhao, Y., Cliff, S. S., Hu, W. W., Toohey, D. W., Flynn, J. H., Lefer, B. L., Grossberg, N., Alvarez, S., Rappenglück, B., Taylor, J. W., Allan, J. D., Holloway, J. S., Gilman, J. B., Kuster, W. C., de Gouw, J. A., Massoli, P., Zhang, X., Liu, J., Weber, R. J., Corrigan, A. L., Russell, L. M., Isaacman, G., Worton, D. R., Kreisberg, N. M., Goldstein, A. H., Thalman, R., Waxman, E. M., Volkamer, R., Lin, Y. H., Surratt, J. D., Kleindienst, T. E., Offenberg, J. H., Dusanter, S., Griffith, S., Stevens, P. S., Brioude, J., Angevine, W. M., and Jimenez, J. L.: Organic aerosol composition and sources in Pasadena, California, during the 2010 CalNex campaign, Journal of Geophysical Research: Atmospheres, 118, 9233-9257, 10.1002/jgrd.50530, 2013.

Henry, K. M., and Donahue, N. M.: Photochemical aging of α-pinene secondary organic aerosol: effects of OH radical sources and photolysis, The Journal of Physical Chemistry A, 116, 5932-5940, 2012.

Hildebrandt, L., Donahue, N. M., and Pandis, S. N.: High formation of secondary organic aerosol from the photo-oxidation of toluene, Atmos. Chem. Phys. J1 - ACP, 9, 2973-2986, 2009.

Hodzic, A., Jimenez, J., Madronich, S., Canagaratna, M., DeCarlo, P., Kleinman, L., and Fast, J.: Modeling organic aerosols in a megacity: potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol formation, Atmospheric Chemistry and Physics, 10, 5491-5514, doi:10.5194/acp-10-5491-2010, 2010.

Huffman, J., Docherty, K., Mohr, C., Cubison, M., Ulbrich, I., Ziemann, P., Onasch, T., and Jimenez, J.: Chemically-resolved volatility measurements of organic aerosol from different sources, Environ. Sci. Technol., 43, 5351-5357, 2009.

Jathar, S., Farina, S., Robinson, A., and Adams, P.: The influence of semi-volatile and reactive primary emissions on the abundance and properties of global organic aerosol, Atmospheric Chemistry and Physics, 11, 7727-7746, doi:10.5194/acp-11-7727-2011 2011.

Jathar, S. H., Gordon, T. D., Hennigan, C. J., Pye, H. O. T., Pouliot, G. A., Adams, P. J., Donahue, N. M., and Robinson, A. L.: Unspeciated organic emissions from combustion sources and their influence on the secondary organic aerosol budget in the United States, Proceedings of the National Academy of Sciences, 111, 10473-10478, 2014.

Jathar, S. H., Cappa, C. D., Wexler, A. S., Seinfeld, J. H., and Kleeman, M. J.: Simulating secondary organic aerosol in a regional air quality model using the statistical oxidation model – Part 1: Assessing the influence of constrained multi-generational ageing, Atmospheric Chemistry & Physics, 16, 2309-2322, 2016.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., E, Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere, Science, 326, 1525-1529, 10.1126/science.1180353, 2009.

Koo, B., Knipping, E., and Yarwood, G.: 1.5-Dimensional volatility basis set approach for modeling organic aerosol in CAMx and CMAQ, Atmospheric Environment, 95, 158-164, 2014.

Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E., Mazzoleni, L. R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb, C. E., and Worsnop, D. R.: Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol, Nat Chem, 3, 133-139, http://www.nature.com/nchem/journal/v3/n2/abs/nchem.948.html - supplementary-information, 2011.

May, A. A., Levin, E. J. T., Hennigan, C. J., Riipinen, I., Lee, T., Collett, J. L., Jimenez, J. L., Kreidenweis, S. M., and Robinson, A. L.: Gas-particle partitioning of primary organic aerosol emissions: 3. Biomass burning, Journal of Geophysical Research: Atmospheres, 118, 2013JD020286, 10.1002/jgrd.50828, 2013a.

May, A. A., Presto, A. A., Hennigan, C. J., Nguyen, N. T., Gordon, T. D., and Robinson, A. L.: Gas-particle partitioning of primary organic aerosol emissions: (1) gasoline vehicle exhaust, Atmospheric Environment, 77, 128-139, 2013b.

May, A. A., Presto, A. A., Hennigan, C. J., Nguyen, N. T., Gordon, T. D., and Robinson, A. L.: Gas-particle partitioning of primary organic aerosol emissions: (2) Diesel vehicles, Environ. Sci. Technol., 47, 8288-8296, 2013c.

May, A. A., Nguyen, N. T., Presto, A. A., Gordon, T. D., Lipsky, E. M., Karve, M., Gutierrez, A., Robertson, W. H., Zhang, M., Chang, O., Chen, S., Cicero-Fernandez, P., Fuentes, M., Shiou-Mei, H., Ling, R., Long, J., Maddox, C., Massetti, J., McCauley, E., Na, K., Pang, Y., Rieger, P., Sax, T., Truong, T., Vo, T., Chattopadhyay, S., Maldonado, H., Maricq, M., and Robinson, A. L.: Gas- and particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles, Atmospheric Environment, 88, 247–260, http://dx.doi.org/10.1016/j.atmosenv.2014.01.046, 2014.

McDonald, B. C., Goldstein, A. H., and Harley, R. A.: Long-Term Trends in California Mobile Source Emissions and Ambient Concentrations of Black Carbon and Organic Aerosol, Environmental Science & Technology, 49, 5178-5188, 10.1021/es505912b, 2015.

Miracolo, M. A., Presto, A. A., Lambe, A. T., Hennigan, C. J., Donahue, N. M., Kroll, J. H., Worsnop, D. R., and Robinson, A. L.: Photo-Oxidation of Low-Volatility Organics Found in Motor Vehicle Emissions: Production and Chemical Evolution of Organic Aerosol Mass, Environ. Sci. Technol., 16305-16327, 2010.

Murphy, B., and Pandis, S.: Simulating the formation of semivolatile primary and secondary organic aerosol in a regional chemical transport model., Environ. Sci. Technol., 43, 4722-4728, doi:10.1021/es803168a, 2009.

Platt, S. M., Haddad, I. E., Pieber, S. M., Huang, R. J., Zardini, A. A., Clairotte, M., Suarez-Bertoa, R., Barmet, P., Pfaffenberger, L., Wolf, R., Slowik, J. G., Fuller, S. J., Kalberer, M., Chirico, R., dommen, J., astorga, C., Zimmermann, R., Marchand, N., Hellebust, S., Temime-Roussel, B., Baltensperger, U., and Prévôt, A. S. H.: Two-stroke scooters are a dominant source of air pollution in many cities, Nature communications, 5, 2014.

Presto, A. A., Nguyen, N. T., Ranjan, M., Reeder, A. J., Lipsky, E. M., Hennigan, C. J., Miracolo, M. A., Riemer, D. D., and Robinson, A. L.: Fine particle and organic vapor emissions from staged tests of an in-use aircraft engine, Atmospheric Environment, 45, 3603-3612, 2011.

Pye, H. O., and Pouliot, G. A.: Modeling the role of alkanes, polycyclic aromatic hydrocarbons, and their oligomers in secondary organic aerosol formation, Environ. Sci. Technol., 46, 6041-6047, 2012.

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking organic aerosols: Semivolatile emissions and photochemical aging, Science, 315, 1259-1262, 2007.

Sarwar, G., Simon, H., Bhave, P., and Yarwood, G.: Examining the impact of heterogeneous nitryl chloride production on air quality across the United States, Atmospheric Chemistry and Physics, 12, 6455-6473, 2012.

Schauer, J. J., Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T.: Source apportionment of airborne particulate matter using organic compounds as tracers, Atmospheric Environment, 30, 3837-3855, http://dx.doi.org/10.1016/1352-2310(96)00085-4, 1996.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 2. C-1 through C-30 organic compounds from medium duty diesel trucks, Environ. Sci. Technol., 33, 1578-1587, 1999.

Shrivastava, M., Fast, J., Easter, R., Gustafson Jr, W. I., Zaveri, R. A., Jimenez, J. L., Saide, P., and Hodzic, A.: Modeling organic aerosols in a megacity: comparison of simple and complex representations of the volatility basis set approach, Atmos. Chem. Phys., 11, 6639-6662, 10.5194/acp-11-6639-2011, 2011.

Shrivastava, M. K., Lane, T. E., Donahue, N. M., Pandis, S. N., and Robinson, A. L.: Effects of gas particle partitioning and aging of primary emissions on urban and regional organic aerosol concentrations, Journal of Geophysical Research-Atmospheres, 113, D18301, doi:10.1029/2007JD009735, 2008.

Simon, H., Baker, K. R., and Phillips, S.: Compilation and interpretation of photochemical model performance statistics published between 2006 and 2012, Atmospheric Environment, 61, 124-139, 2012.

Skamarock, W., Klemp, J., Dudhia, J., Gill, D., Barker, D., Duda, M., Huang, X.-Y., Wang, W., and Jordan, G.: A Description of the Advanced Research WRF Version 3. NCAR Technical Note, NCAR/TN–475+ STR, 2008.

Tsimpidi, A., Karydis, V., Zavala, M., Lei, W., Molina, L., Ulbrich, I., Jimenez, J., and Pandis, S.: Evaluation of the volatility basis-set approach for the simulation of organic aerosol formation in the Mexico City metropolitan area, Atmos. Chem. Phys, 10, 525-546, doi:10.5194/acp-10-525-2010, 2009.

Turpin, B., and Lim, H.: Species contributions to PM2. 5 mass concentrations: Revisiting common assumptions for estimating organic mass, Aerosol Science and Technology, 35, 602--610, 2001.

Whitten, G. Z., Heo, G., Kimura, Y., McDonald-Buller, E., Allen, D. T., Carter, W. P., and Yarwood, G.: A new condensed toluene mechanism for Carbon Bond: CB05-TU, Atmospheric Environment, 44, 5346-5355, 2010.

Woody, M. C., Baker, K. R., Hayes, P. L., Jimenez, J. L., Koo, B., and Pye, H. O. T.: Understanding sources of organic aerosol during CalNex-2010 using the CMAQ-VBS, Atmospheric Chemistry and Physics, 16, 4081-4100, 2016.

Yarwood, G., Rao, S., Yocke, M., and Whitten, G. Z.: Updates to the Carbon Bond chemical mechanism: CB05, ENVIRON International Corporation, Novato, CA, 2005.

Zhao, Y., Hennigan, C. J., May, A. A., Tkacik, D. S., de Gouw, J. A., Gilman, J. B., Kuster, W., Borbon, A., and Robinson, A. L.: Intermediate-volatility organic compounds: a large source of secondary organic aerosol, Environ. Sci. Technol., 2014.

Zhao, Y., Nguyen, N. T., Presto, A. A., Hennigan, C. J., May, A. A., and Robinson, A. L.: Intermediate volatility organic compound emissions from on-road diesel vehicles: chemical composition, emission factors, and estimated secondary organic aerosol production, Environ. Sci. Technol., 49, 11516-11526, 2015.

Zotter, P., El-Haddad, I., Zhang, Y., Hayes, P. L., Zhang, X., Lin, Y. H., Wacker, L., Schnelle-Kreis, J., Abbaszade, G., and Zimmermann, R.: Diurnal cycle of fossil and nonfossil carbon using radiocarbon analyses during CalNex, Journal of Geophysical Research: Atmospheres, 119, 6818-6835, 2014.

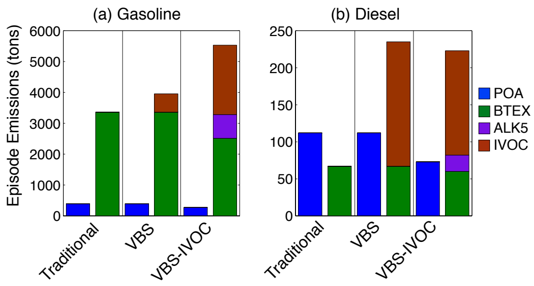

Figure 1: Total emissions from May 4 to June 30, 2010 for POA, BTEX (aromatics), ALK5 (long alkanes) and IVOCs for gasoline and diesel sources in the Los Angeles and Orange Counties for the three OA models: Traditional, VBS and VBS-IVOC.

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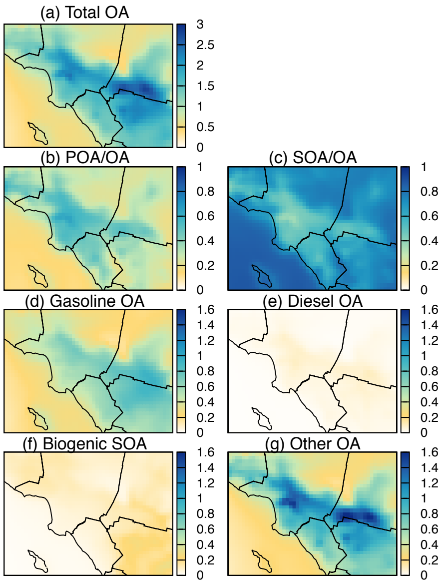

Figure 2: Averaged predictions from the VBS-IVOC model for (a) total OA (μg m^{-3}), (b) POA fraction, (c) SOA fraction, (d) total gasoline OA (μg m^{-3}), (e) total diesel OA (μg m^{-3}), (f) biogenic SOA (μg m^{-3}) and (g) other OA (μg m^{-3}) over southern California.

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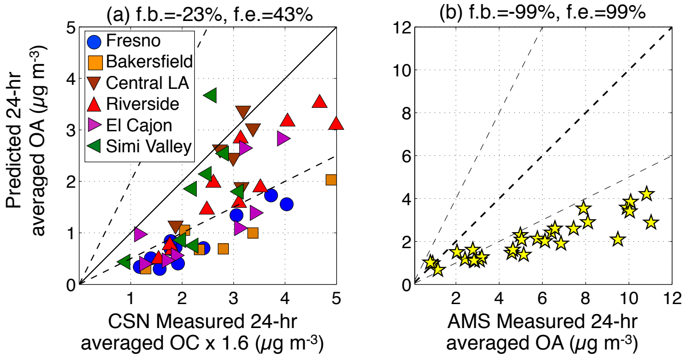

Figure 3: Scatter plot of VBS-IVOC OA predictions versus 24-hr measurements from (a) filters collected at sites in the Chemical Speciation Network (CSN) and (b) HR-AMS measurements at the Pasadena ground site during the CalNex campaign. In panel (a) the model-measurement comparison is for six sites in California (Fresno, Bakersfield, Central Los Angeles, Riverside, El Cajon and Simi Valley). f.b. is the fractional bias ($\frac{1}{N}\sum_{i=1}^{N}\frac{P-M}{\frac{P+M}{2}}$) and f.e. is the fractional error ($\frac{1}{N}\sum_{i=1}^{N}\frac{|P-M|}{\frac{P+M}{2}}$); *P* is the predicted value, *M* is the measured value and *N* is the sample size.

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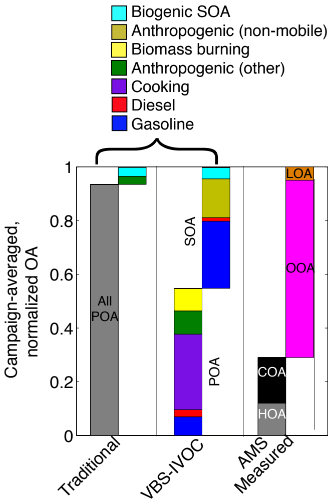

Figure 4: Averaged normalized composition of OA at the Pasadena ground site as predicted by the Traditional and VBS-IVOC models. Predictions are compared to PMF factors derived from ambient HR-AMS data collected in Pasadena Hayes et al. (2013).

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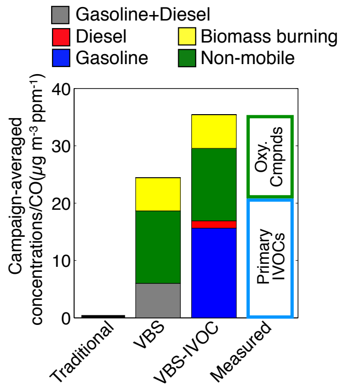

Figure 5: Comparison of predicted and measured average IVOC concentrations at the Pasadena ground site. Measured concentrations are from Zhao et al. (2014). The predicted IVOCs include primary vapors in equilibrium with POA. The data have been normalized by carbon monoxide (CO) concentrations to correct for any differences in mixing.

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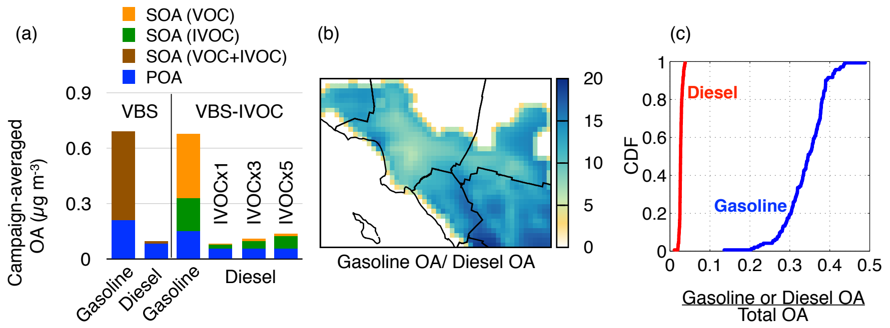

Figure 6: (a) VBS-IVOC predicted campaign-averaged OA concentrations attributable to gasoline and diesel sources at the ground site in Pasadena; the IVOCx1 result for diesel use is from the VBS-IVOC simulation, the IVOCx3 and IVOCx5 results are from separate sensitivity simulations where IVOC emissions from diesel are scaled by a factor of 3 and 5 respectively as described in the text. (b) Ratio of gasoline OA to diesel OA over southern California and (c) cumulative distribution functions that show the fractional contribution of gasoline plus diesel OA to total OA in southern California.

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reason could be attributed to the representation of aging reactions in the models, which

The aging reactions simulated the multigenerational gas-phase oxidation of vapors in equilibrium with OA. The aging mechanism used here iwas conceptually based on the work of Robinson et al. (2007), which assumed a constant reaction rate constant and only allowed for the formation of functionalized, lower-volatility products. In essence, aging reactions, with enough time, will convert all semi-volatile vapors into particles. However, the mechanism assumes a constant reaction rate constant,However, reaction rates which may vary with C* and O:C of the OA and does not account for fragmentation reactions, which should become can be increasingly important at longer time scales (Kroll et al., 2011). The reaction rate for aging and the effects of aging at longer time scales Neither of these have not been constrained against laboratory data. This implies that the OA predictions, despite the substantial new data, becomeare poorly constrained as one moves downwind of source regions. Murphy and Pandis (2009) have found that model predictions agree better with measurements when aging reactions are turned off for biogenic SOA. Recently, Jathar et al. (2016) have shown that aging reactions similar to those suggested in Robinson et al. (2007) might not be necessary since the laboratory chamber experiments that are used to parameterize SOA production already include products from the aging reactions happening inside the chamber. The work of Murphy and Pandis (2009) (for biogenics) and Jathar et al. (2016) suggests that including aging reactions in CTMs may double count SOA production and over-predict the importance of multigenerational gas-phase chemistry in the atmosphere. Although some work has been done to understand the aging of biogenic SOA (Donahue et al., 2012;Henry and Donahue, 2012), future laboratory work needs to be directed in understanding the role of aging of OA vapors formed from anthropogenic sources on the mass and properties of OA.