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Interactive comment on "Exploration of the influence of environmental conditions on secondary organic aerosol formation and organic species properties using explicit simulations: development of the VBS-GECKO parameterization" *by* Victor Lannuque et al.

Anonymous Referee #2

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The Lannuque et al. manuscript reports on the use of the GECKO-A model (Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere) to develop Volatility Basis Set (VBS) parameterizations of secondary organic aerosol (SOA) formation for use in three-dimensional chemical transport models. Initial chemical conditions for the SOA simulations were generated by running GEKCO-A using fixed concentrations of CO and methane, and a range of NOx and O3 values. For a given O3 value, each NOx value leads to a steady-state OH and HO2 value, which are then used as

the chemical inputs for the SOA parameter optimization simulations (along with the CO, methane, NOx, and O3 values). Simulations were also conducted to consider a range of temperatures and photolysis rates (set by the solar zenith angle), as well as a range of pre-existing organic aerosol mass concentrations. The simulation results were used to then optimize the number and properties of the VBS bins, as well as the stoichiometric coefficients (leading to mass contributions) in each bin. A total of 7 bins were selected; the stoichiometric coefficients/concentration in each bin is a function of precursor and reaction conditions. The GECKO-VBS parameterization was evaluated against GECKO-A using a test set of simulations (independent of the optimization set). The GECKO-VBS parameterization represents general trends in SOA formation, and performs best in the majority anthropogenic precursor simulations; SOA is over-predicted in the majority biogenic precursor simulation with low NOx. The process for developing VBS parameterizations using GECKO-A was automated and should be of significant benefit to the community in the future.

In summary, GECKO-A is a unique modeling tool in its near-explicit representation of gas-phase chemistry. A complementary approach to experimentally-based methods for developing parameterizations of SOA is presented in this work. Some combination of GECKO-A type modeling as presented and experimental studies likely will lead to the best SOA parameterizations for three-dimensional model predictions. GECKO-A/-VBS model simulations additionally provide a unique metric against which to compare more chemically explicit gas- and particle-phase compositional data. This manuscript should be of great interest to the ACP readership. It is generally well written and easy to follow. Specific technical and editorial comments follow.

Technical: In regard to the initial condition simulations, it is stated that the NOx and HOx concentrations are typical of chemical characteristics of low- to high-NOx environments (p. 4, l. 16) and it was found that for NO levels > 1 ppb most of the RO2 reacts with NOx. This observed branching ratio is different than has been reported for regional (Barsanti et al., ACP, 2013, doi:10.5194/acp-13-12073-2013) and global

(Henze et al., ACP, 2008, https://www.atmos-chem-phys.net/8/2405/2008/) model simulations. This point is worth further discussion in the manuscript. Are the NOx and HOx concentrations truly representative of the ambient atmosphere? Under what limitations/conditions? What are the reasons that the GECKO-A model simulations of this branching ratio differ from those generated using a condensed gas-phase chemical mechanism? Is one more representative than the other? What are the implications for predicted SOA formation?

In the description of the treatment of partitioning (p. 5, l. 14-24), it is stated that 250 g mol-1 is used as the mean MW of the condensed phase. Is this for all of the GECKO simulations (e.g., GECKO-A and GECKO-VBS)? If so, why? Given that mean MW can be explicitly calculated and the MW distribution shown in Fig. 5 and related discussion (e.g., p. 9, l. 30) suggests a higher value is supported by the model simulations. What is the role of RH in the simulations? Does RH affect the partitioning constants (e.g., modify mean MW)? Or does it affect deposition?

In defining the seven VBS bins, the same properties are assigned to each bin, regardless of the precursor. In the case of the kOH values, as discussed in the manuscript, this is justifiable and unlikely to significantly affect the parameterizations or simulated SOA concentrations. However, the assignment of the Henry's Law Constants needs further discussion and justification. In Table 2, the effective Henry's Law Constants increase for each bin as volatility decreases. For the simulation results shown in Fig. 5, this trend only seems to hold for alpha-pinene (looking at the bin mean); further, between the precursors, the Henry's Law Constants (again, bin mean) vary by orders of magnitude between the precursors for the same volatility bin. Given that Henry's Law Constants are often used in wet and dry deposition parameterizations, this approach needs further consideration. In addition, in regard to the GECKO-A/GECKO-VBS comparisons, depending on the importance of dry deposition in the simulations, this may explain some of the disagreement.

On p. 7, l. 31-32 it is stated that the species formed at high NOx have a molar mass

that is $\sim$ 100 g mol-1 higher than at low NOx. Was this value calculated across all bins and all precursors? A visual inspection of Fig. S1 does not necessarily support this statement. Further, even if numerically true, it seems an unnecessary oversimplification (particularly since the Figure is in the supplement). The changes in molar mass seem to vary significantly between alpha values and across bins/precursors.

Editorial: It is recommend that the symbol beta be used to describe the reaction of RO2 with NO relative to HO2, as in Pye et al. (ACP, 2010, doi:10.5194/acp-10-11261-2010). The symbol alpha is confusing, particularly in the Supplementary Table S1, since alpha in SOA parameterizations is historically used to represent the stoichiometric coefficients.

It is also recommended that since the abbreviation OA for organic aerosol is introduced, it should be used throughout the manuscript (see for example lines 26-31 on p. 12).

Abstract-line 29: "dynamic" should be "dynamics". The discussion of the VBS-GEKCO performance is awkward as written. Maybe just, "In evaluating the ability of VBS-GECKO to capture the temporal evolution of SOA mass, the mean relative error is less than 20% compared to GEKCO-A."

p.2, line 16: "Theirs" should be "their". What does "their" refer to? This is awkward as written (description of SOA parameterization). Line 19: I don't think that Cappa and Wilson 2012 use decadal volatility bins. This should be checked. Line 30: "influences" should be "influence"

p. 6, line 16: "growths" should be "increases"

p. 8, line 22: "redistributing" should be "redistributes"

p. 11, line 3: "performed on" should be "performed for" p. 12, line 19: It is suggested that "do however not" be reworded as "do not, however, partition"; line 31: "lesser" should be "less"

p. 13, line 19: add "respectively" after scenario; line 31: It is suggested that "species

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was arbitrary" be replaced with "species was arbitrarily set to the same"

p. 15, line 9: "aromatics compounds" should be "aromatic compounds"; line 22-23: It is suggested that "NOx levels dependence of SOA formation" be replaced with "The dependence of SOA formation on NOx levels is represented. . ."