

Interactive comment on “Modelling organic aerosol over Europe in summer conditions with the VBS-GECKO parameterization: sensitivity to secondary organic compound properties and IVOC emissions” by Victor Lannuque et al.

Anonymous Referee #2

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Lannuque et al. report on findings from simulations performed with a chemical transport model over Europe. They find that the VBS-GECKO model to simulate organic aerosol (OA) chemistry and gas/particle partitioning, which they argue is more physically-based, provides slight improvements in model performance. They also performed sensitivity simulations but, except for the inclusion of intermediate volatility organic compound (IVOC) emissions in urban areas, find the model results to exhibit low sensitivity to ranges explored in the input values.

This study adds to the growing literature on predicting the formation, composition, and

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properties of secondary organic aerosol (SOA) on regional scales. SOA is an important, yet uncertain, component of PM_{2.5} and hence the study is well motivated. The VBS-GECKO model undertakes a novel approach to modeling OA where it leverages chemical detail from GECKO but in a heavily parameterized form. However, I have several concerns with the model detail provided in the manuscript and the interpretation of the simulation results (outlined below). I am hesitant to recommend publication in ACP at this point. I have made some major and minor comments for the authors to consider.

Major comments:

1. POA and SVOC: Throughout the manuscript, the use of the terms POA and SVOC is unclear. For example, on page 4, lines 21-24, the authors describe the SVOC/POA ratio used in this work. What does this mean? Are those the SVOCs in the gas-phase ratioed against the POA in the particle phase? If yes, how does the statement on line 21, ‘POA from emission inventories are considered as SVOC’ make sense? Also, is the ratio used to just determine the SVOC emissions and that the POA and SVOC are then repartitioned in the model? Also, a more elaborate justification of the source-resolved SVOC/POA ratios is warranted. A sentence saying ‘This factor was shown to give satisfactory results’ is insufficient.

2. POA: How is the POA dealt with in VBS-GECKO or is the POA formulation borrowed from H₂O? If yes, I am a little concerned that the POA volatility distribution used in this work relies on that reported in Robinson et al. (2007). The Robinson parameterization is from a small off-road diesel engine and is probably not very representative of the gasoline- and diesel-powered sources in Europe. There has been significant amount of experimental (e.g., May et al., 2013a,b,c, Louvaris et al., 2017) and modeling (e.g., Woody et al., 2016, Jathar et al., 2017; Akherati et al., 2019) work since the Robinson paper in parameterizing and applying the POA volatility by source. While I would like to see these parameterizations be used in the base simulations, at the very least, insight from earlier work needs to be included as a sensitivity study to show the influence of source-resolved POA volatility on regional OA mass concentrations.

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3. VBS-GECKO parameterization: The description for the OA model is incomplete (confusing at times) and needs to be significantly improved. Here are a few examples to help restructure this section: (i) How are IVOCs dealt with and what surrogates are used to model their SOA formation? (ii) How are IVOC emissions developed? (iii) Does this section describe the treatment of SVOCs too and if yes, what surrogates are used? I am concerned that the manuscript treats SVOCs and IVOCs interchangeably. (iv) How is the NO_x dependence modeled? I am guessing that the ratios that are being talked about discuss the branching ratio between RO₂ and NO and RO₂ and HO₂. Are there separate VBSs for products formed at different NO_x levels? How are species formed at a high (low) NO_x level then aged or transformed when they react further at a low (high) NO_x level? All of these have implications on how results in the sensitivity section (4.3) are interpreted. (v) It is unclear whether each precursor gets a separate 7-bin VBS. Does it? If yes, the properties of the VBS bins remain the same but the mass yields are different? (vi) How is partitioning modeled for a given species between the organic and aqueous phases? Presumably, aqueous refers to the water associated with inorganic aerosol. Also, what about water uptake by the organic species itself? (vii) How are the saturation vapor pressures (P_{sat}) for the VBS species determined? The P_{sat} values are changed in the sensitivity simulations. A change in the P_{sat} values by an order of magnitude should dramatically change the SOA produced. Wouldn't this affect the evaluation of GECKO predictions against chamber or flow reactor measurements? In fact, an evaluation of GECKO predictions was not discussed at all. Again, these have implications on how results in the sensitivity section (4.4) are interpreted. Finally, I think I understand very generally how GECKO is used to determine the mass yields and properties of the VBS product species but since this is the main contribution of this work, it would be better to provide a paragraph length description of how this is done and what those parameterizations represent.

4. Sensitivity simulations for ageing: I have major concerns in how the sensitivity simulations were performed and the interpretation drawn from the model predictions. Perhaps, some of these concerns stem from a lack of transparency in how the VBS-

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GECKO parameterizations were developed and how ageing was modeled. For example, if the VBS-GECKO parameterizations are constrained to predictions from GECKO, which already includes ageing, why are another set of ageing reactions modeled in CHIMERE? In fact, how is ageing defined? Is it defined as the transformation past the time period, the GECKO simulations were run for? Also, if there is a need to model additional ageing, what is the justification for such a high KOH? Is this KOH value constrained? If yes, against what laboratory or field data? How is ageing modeled in VBS-GECKO? Does it use the 'bulldozer' mechanism of Robinson et al. (2007)? There is evidence that this type of ageing mechanism may overestimate SOA production in regional models (e.g., refer to Lane et al. (2008) for biogenic SOA and Jathar et al. (2016) for all SOA) and might require explicit modeling of fragmentation reactions (Shrivastava et al., 2013; 2015). Finally, the conclusion that 'aging rates are likely not a major source of uncertainty' needs to be framed in context of how it is modeled in this work and findings from earlier work.

5. IVOC simulations: I am not sure how varying the IVOC fraction of NMVOC represents a changing fleet. Presumably, the NMVOC emissions as part of the inventory already represent a fixed fraction of gasoline versus diesel sources. A changing fleet (e.g., more diesel and less gasoline) would reduce the total NMVOC emissions from mobile sources since diesels emit less NMVOC than gasoline per mile driven. So, a higher IVOC fraction could still result in a lower IVOC emission. Either this is part has not been described well or the emissions simulations are not accounting for changing total NMVOC emissions with a changing fleet. Also, it needs to be stated that these emissions are only being applied to mobile sources and also only to tailpipe emissions (i.e., not evaporative emissions). Is that right? 6. Grammar and style: There are numerous grammatical mistakes in the manuscript and the style could be improved too to enhance readability.

Minor comments:

1. Page 2, lines 5-9: Can this first paragraph include newer citations when discussing

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OA and SOA?

2. Page 2, line 19: The SOA in chamber experiments rarely represents oxidation products after a single oxidation step. Rephrase.
3. Page 2, paragraph starting on line 16: This could benefit from reviewing the literature on a few other types of SOA modeling. For example, Jathar et al.'s (GMD, 2015) use of the statistical oxidation model. Or Li et al.'s (AE, 2015) use of the master chemical mechanism. In other words, there aren't just two approaches to model SOA but rather several methods that span a continuum in complexity.
4. Page 4, line 10: Is the particle size resolution too low to separate PM1 from PM2.5? Wouldn't numerical diffusion add uncertainty to how PM is split in that 1 to 2.5 μm region?
5. Page 4, line 22: The extensive emissions work done with open burning suggests that residential burning should have a lower SVOC/POA ratio than other anthropogenic combustion sources.
6. Section 2.2.2: To clarify, each precursor species in Table 1 gets a separate 7-bin VBS?
7. Page 5, line 16: Rephrase 'VBS-GECKO considers the formation of 7 volatility bins'.
8. Page 5, line 28: How is RRR calculated in CHIMERE?
9. Page 6, line 24: evaluated 'by' comparing.
10. Page 6, lines 24-32: Is there a reason for sub-selecting 7 stations for comparing the time series. What not do a comparison at all available sites? Can details about how the OA is measured (e.g., filter followed by OC/EC, AMS) added to this paragraph?
11. Page 7, line 14: Please comment on whether regulatory agencies use the Boylan and Russell (2006) criteria when evaluating model output. My sense is that they do not.

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12. Page 7, lines 20-25: What is the primary reason for differences in the ref versus VBS-GECKO simulations for OA mass concentrations (e.g., source treatment, chemistry)? It is important to discuss this since the VBS-GECKO leads to slightly better model performance.
13. Page 7, line 30: Is this the Pearson r ? If yes, please use the small letter ' r '? If not, please specific what correlation coefficient this is. Can you comment on the value of r ? How does it compare to r from earlier regional modeling work (e.g., Ahmadov et al., JGR, 2012; Baker et al., ACP, 2015; Murphy et al., ACP, 2017)? It would be good to contrast the model skill across different geographical regions (i.e., United States versus Europe). To me an r^2 of 0.25 doesn't sound that good. Does it?
14. Figure 3: It would improve interpretation of the data if the site location was specified in the panel instead of using the station number?
15. Page 9, line 8: I thought a VBS species could condense in both the organic and aqueous phases depending on the organic and aqueous partitioning coefficients respectively. If not, how is this treatment in the reference model handled? Perhaps, there is a need for a table that talks about the different model configurations?
16. Page 9, line 24: Where is Benelux? Is this location significant? If yes, please specify. Please also do so anywhere else results from a specific location are discussed.
17. Figure 5: General comment: Given the very small differences in panels (a) and (d), at what percent level would one be able to say with confidence that there were differences in model predictions? In other words, what is the precision in the model?
18. Section 4.1: The results presented in this section are sensitive to the amount of aerosol water available? How well is aerosol water modeled when compared to measurements? In fact, how well is inorganic aerosol modeled when compared to measurements?
19. Page 9, line 33: What does 'slightly' mean? Can you be quantitative?

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20. Page 11, line 4: What does 'free NO_x' mean?
21. Page 11, line 5: What does 'whatever' mean?
22. Page 12, line 21: I am not sure why IVOCs would ever be in the particle phase. In the hot exhaust, IVOCs are likely to be in the vapor phase. When hot exhaust is diluted and cooled, the IVOCs probably don't have enough time to condense and then evaporate.
23. Page 13, lines 1-13: Are the IVOCs described here referred to as SVOCs in the lines following this section (lines 14-31)? This was quite confusing.
24. Page 13, lines 14-31: I was hoping this would be covered in the methods section.
25. Figure 14: Could these also include the measurements?
26. Page 15, lines 15-21: Are newly discovered pathways for SOA from autooxidation reactions and acid-catalyzed pathways included? If not, could these be cited here to provide context?
27. Page 17, line 6: I do not recollect where the volatility of the OA was discussed and how the authors conclude that LVOC and ELVOC make up most of the OA.

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