

Author Responses to Referees and comments 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

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We thank the reviewers for their comments on the manuscript. We outline below responses to the points raised by each referee and summarize the changes made to the revised manuscript.

Responses to Referee 1

> 1. While VBS-Gecko is compared to Gecko_A, it's not clear how either of these compares to actual SOA observations. Simulating some lagrangian test cases from field measurements of SOA would have been helpful to understand the utility of these approaches.

The paper focuses on the development of the VBS-GECKO only. However, some observation/simulation comparisons for a few plume conditions were already performed in the past using the GECKO-A modeling tool (e.g. Lee-Taylor et al., 2011, 2015; Hodzic et al., 2013). Furthermore, the VBS-GECKO has been implemented in the chemistry-transport model CHIMERE and results compared with both in-situ measurements and other model outputs. Results show that the use of the VBS-GECKO parameterization slightly improves the performances of the model on OA concentrations compared to the current parameterization in CHIMERE. Detailed results will be included in a companion paper, to be submitted in ACPD (Lannuque et al., 2018).

> 2. A fixed set of yields are fit to different volatility bins in VBS-Gecko. But multigenerational aging e.g. functionalization/fragmentation reactions can change the VBS distributions, especially at longer timescales. Could use of fixed VBS-Gecko (which do not change with aging) yields be responsible for

the differences with explicit Gecko-A shown in Figure 8? I understand that the fixed yields are supposed to represent a fit to the entire dynamic evolution, but errors could be larger at longer timescales.

The sets of VBS-GECKO stoichiometric coefficients are optimized to reproduce both SOA formation and aging. As described in the paper (section 4.1), aging is described by gas phase reactions of the VBS-GECKO bins (VBx). All the coefficients of the precursor + oxidants and VBx+OH are fitted on simulations lasting 1, 2 or 5 days (depending on the lifetime of the precursor), based on GECKO-A generated chemical schemes involving 15 successive generations of non-radical compounds. VBS-GECKO should therefore represent the gas phase multigenerational aging on a time scale similar to SOA lifetime.

> 3. Condensed phase SOA processes as oligomerization can also alter volatility distributions, molar mass etc. How does VBS-Gecko or Gecko-A account for dynamic changes in SOA properties due to condensed phase chemistry?

The VBS-GECKO architecture depends directly on GECKO-A. Current version of the GECKO-A modeling tool ignores the aging process in the condensed phase, as stated in section 2.2 of the paper. Adding these processes explicitly require mechanistic and kinetic knowledge that still remain sparse. This is currently one of the main limits of the VBS-GECKO approach. Note that an empirically based parameterization could still later be added in VBS-GECKO to represent aging in the condense phase.

> 4. In Figure 2, why is the condensed mass of n-octadecane (red line) much higher than the other 2 precursors? Is this result supported by smog chamber measurements?

Octadecane have 10 and 8 carbon atoms more than o-xylene and α -pinene, respectively. The vapor pressure of octadecane oxidation products is therefore typically lower than products from o-xylene and α -pinene. Furthermore, less oxidation steps are required to form species of enough low volatility to condense, decreasing the formation of fragmented compounds (e.g. CO and CO₂). These results are in agreement with smog chamber studies showing a much higher yields for long chain alkanes than for mono-aromatics and terpenes (e.g. Lee et al., 2006; Lim and Ziemann, 2009; Li et al., 2016; Ng et al., 2007).

> 5. Mechanistically, why does maximum yield decrease as the number of methyl groups in aromatics increase?

For compounds having an identical number of carbon atoms, increasing the number of methyl groups is known to promote fragmentation (e.g. Aumont et al., 2013) and therefore to decrease SOA yields. However, increasing the size of the carbon skeleton also leads to lower volatility species and thus increases SOA yields (e.g. Lim and Ziemann, 2009). For the aromatic series, the increase of fragmentation outweighs the decrease of volatility of the parent compound. This trend is consistent with chamber observations (e.g. Li et al., 2016).

> 6. *The enthalpies of vaporization are assumed to be NO_x-independent and only depend on volatility bins. However, volatility of SOA is NO_x-dependent. See Xu et al. 2014. Could the authors comment on how NO_x-dependent volatility affects their assumptions of SOA properties e.g. enthalpies of vaporizations and molar mass?*

In VBS-GECKO, SOA volatility is NO_x-dependent owing to the different sets of stoichiometric coefficients for various levels of NO_x (see section 4.3.1). Indeed, the relative contribution of different volatility bins in SOA production changes according to the NO_x conditions. The estimation method of Nannoolal et al. (2008) is used to calculate both the enthalpies of vaporization and the vapor pressure of the species. This method leads to a strong correlation between the two parameters (see Fig. 5) and justify the use of a mean vaporization enthalpy per volatility bin. Moreover, molar masses and enthalpies of vaporization have been fixed before fitting the coefficients to allow compensation of possible biases. Results of the fits at 298 and 270 K show that the approach captures well the sensitivity of SOA to temperature. Finally, even though vaporization enthalpies are fixed, the overall SOA volatility (and their sensitivity to temperature changes via the prescribed vaporization enthalpies) depends on the concentration of each bin, which is NO_x dependent.

> 7. *Why do terpene SOA yields show the strongest sensitivity to temperature and pre-existing organic aerosol mass?*

Figure 3 shows that a high sensitivity of SOA yields to temperature and pre-existing organic aerosol mass is a common feature for precursors having a skeleton with 8-12 carbon atoms. For these precursors, SOA contributors fall mostly in the VB4 and VB5 bins, i.e. with a saturation vapor pressure in the 10⁹-10¹¹ atm range. Gas/particles partitioning of these bins are the most sensitive to temperature and pre-existing organic aerosol mass.

> 8. *I recommend adding references to some recent review papers in the context of challenges in SOA measurements and modeling in the Introduction e.g. (Ng et al. 2017, Shrivastava et al. 2017).*

The two references were added.

Reponses to Referee 2

> In regard to the initial condition simulations, it is stated that the NO_x and HO_x concentrations are typical of chemical characteristics of low- to high-NO_x environments (p. 4, l. 16) and it was found that for NO levels > 1 ppb most of the RO₂ reacts with NO_x. 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 NO_x and HO_x 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?

We do not fully agree that our simulated levels of HO₂, RO₂ for the various prescribed NO_x concentrations (and therefore RO₂+NO vs RO₂+HO₂ reaction rates) strongly differ from other atmospheric simulations results. The various models typically use a similar NO_x/HO_x/NO_x/CO/CH₄ chemistry, which is also used to define our modeling scenario (see section 2.1). Depending on the scenarios (from remote to urban), an additional simplified organic “module” is used as a proxy for the key contribution of VOC in the chemistry of the HO_x pool. Trend and magnitude of the simulated HO₂ versus NO_x concentration (see figure 1) appears to be consistent with observations, e.g. Stone et al. (2012) (see Fig. 9 of Stone et al., 2012). Furthermore, the calculated reaction rate ratio α for the various NO concentrations (now denoted RRR, see below) agree fairly well with those presented by Henze et al., 2008 (see for example the Fig. 4 of Henze et al., 2008).

Two levels of NO_x are considered in the parameterization of Henze et al. (2008) and Barsanti et al. (2013): either a high or a low NO_x case. In the VBS-GECKO parameterization, 5 distinct levels of NO_x are considered, selected to cover the full range of α (or RRR) values (see section 4.3.1) and accounting for the nonlinear relationship between these 2 parameters. Our approach also avoid the issues of associating “experimental low/high-NO_x conditions” with “atmospheric low/high-NO_x conditions”, as presented by Barsanti et al. (2013) in their article.

> 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?

A mean molecular weight of 250 g mol⁻¹ was only set to the seed (i.e. preexisting) OA to compute the gas/particle partitioning of the species according to the Raoult’s law, as described page 5 of the paper. This value is used in all the simulations performed in this study. The pre-existent OA is not further taken in account in the analysis (as in Fig. 5) and to set the properties of the various bins (VBx). Furthermore, deposition is ignored for organic matter (gas and particles). Mean Henry’s law coefficient H^{eff} are computed for the various bin (see table 2) for the later application of the parameterization in 3D models (where H^{eff} is usually a required parameter in deposition module). In the current version of the model, effect of Relative Humidity RH on the partitioning of organic species

is ignored. In the box model, RH only contributes to the HO_x chemistry (in particular for the production of OH from O₃ photolysis)

> *In defining the seven VBS bins, the same properties are assigned to each bin, regardless of the precursor. In the case of the k_{OH} 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.*

Indeed, the distribution of Henry's coefficient within each bin spans several orders of magnitude. Representing this additional information would require the development of 2 dimensional VBS, to capture both the volatility and solubility distributions. This is out of the scope of the present parameterization. However, a clear trend is observed for the mean H^{eff} , increasing as volatility decrease. This trend is not specific to α -pinene but is also found for the other precursors (note that results shown in Fig. 5 only represent the distributions of properties at a given time for 3 simulations among 1010 simulations lasting five days). The mean H^{eff} was computed for each bin, based on all training simulations performed for all the alkane parent compounds (see page 9). As stated above, H^{eff} values are not used for the box model simulations performed in this study but provided for the application of VBS-GECKO in 3D chemical transport model. In a second article in preparation (Lannuque et al., 2018), VBS-GECKO is implemented in a chemical-transport model and the sensitivity of simulated SOA concentrations to Henry's law Constants is examined (including effect on both partitioning and deposition). First results show a weak sensitivity on simulated SOA concentration to variation of H^{eff} .

> *On p. 7, l. 31-32 it is stated that the species formed at high NO_x have a molar mass that is ≈ 100 g mol⁻¹ higher than at low NO_x. 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.*

The statement concerning the “100 g mol⁻¹” has been removed. Indeed, that statement is more qualitative than quantitative.

> **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.*

The term “ α ratio” has been replaced by “RRR” for “reaction rate ratio” of RO₂ to remove all ambiguity.

> p.2, line 16: *"Theirs" should be "their". What does "their" refer to? This is awkward as written (description of SOA parameterization).*

Done. "Their" refers to "secondary organic species".

> *Line 19: I don't think that Cappa and Wilson 2012 use decadal volatility bins. This should be checked.*

Yes, Cappa and Wilson 2012 don't use decadal volatility bins (a miss placed reference) the references was removed.

The other editorial recommendations were taken into account in the manuscript. Thanks for the suggested corrections.

Other comments:

> *Estimation of ODE parameters for a system of equations is a challenging problem. Can you please provide details as to how the BObyQA method was applied for this particular problem? Were any idealized tests (i.e. solving the ode's with known parameters and then using the numerical solutions to retrieve the parameters) performed for typical conditions to test the robustness and accuracy of the fitting approach in estimating parameters of the ODEs?*

The ODE solving method applied is the “lsoda” function provided in the “deSolve” R package. The BObyQA optimization method applied in this study is a non-modified “BObyQA” function provided in the “nloptr” R package. The BObyQA method offers the possibility to constrain the coefficients (here bounds are set to 0-1 for the stoichiometric coefficients and 0-100 for the photolysis factors, see section 4.3.1). No idealized test has been performed. Nevertheless, many different optimization methods have been tested on simpler cases before selecting the method. These tests were performed on single simulation, using a C14 alkane as the parent compound, without temperature, NO_x or C_{oa} variations. Various configuration of VBS-GECKO were then tested, including different number of bins. The BObyQA was found to be especially robust, providing the same set of optimized coefficients for different sets of initial coefficients used to start the iteration process. The consistency of the set of ODE and its ability to capture SOA formation was systematically examined during the progressive design of the VBS-GECKOA parameterization.

> *Are the learning scenario data publicly available?*

The dataset is now available online on Zenodo website (URL: <https://zenodo.org/record/1402601>).

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