

Response to anonymous Referee #2 comments:

R2.1) The paper presented by Shrivastava et al. compares organic aerosol simulations with different configurations of the WRF-CHEM model, including the VBS (volatility basis set) approach (i.e. Robinson et al., 2007) with extensive observations from the MILAGRO campaign. The results are satisfactory, within the known uncertainties of models. A reduced formulation of the VBS method with a reduced number of volatility bins is developed: differences with the standard formulation are acceptable (i.e. within or lower than differences with observations). In my opinion, the paper deserves publication in ACP after substantial revision. The paper presents an extensive model to observation comparison, for the example of Mexico City and the MILAGRO campaign. AMS derived organic carbon fraction measurements from various urban, peri-urban and aloft sites and from aircraft are taken into account, in addition to the O:C ratio and the fraction of fossil carbon. General conclusions are an underestimation of HOA (primary organic aerosol) and an overestimation of OOA (secondary organic aerosol) downwind of the megacity. Reasons for these discrepancies are discussed and related mainly to uncertainties in emissions, and in the parametrisations of the secondary aerosol formation. In addition, a reduced scheme of the VBS method is presented and evaluated. This is a useful analysis, as current implementations of the standard VBS methods in 3D models are calculation time and memory consuming. However, the paper is very long (73 pages in ACPD format). Comparison to measurements are described in great detail, which makes it difficult for the reader to keep track of the all different analysis. There is a strong need for substantially shortening the paper (say, by about a factor of two). This would much strengthen the papers major conclusions.

The paper is much shortened now as suggested by the two reviewers. A large fraction of the text and 7 figures are moved to the supporting information. We hope that the reviewer finds this satisfactory.

R2.2) The conclusions section could be extended, in order to give the reader a synthetic view over all observed differences at different sites / platforms. A synthetic table of results could be added. There would be a need for finding statistical metrics allowing quantifying model to observation differences. The validity of the reduced VBS method compared to the standard one should be addressed in a more formal way. For the given set of measurements, the reduced method seems to perform as well as the standard one, both types of simulations are rather similar. This is an encouraging, significant result, but which would become more pertinent if put on a more quantitative basis (again, this is a question of statistical metrics).

We have included statistical metrics for the 3 modeling scenarios in Table 3. The metrics include HOA, OOA and BBOA comparisons at the T0 and T1 ground sites. Statistics summarizing all flights are shown in the form of box plots in Figure 9.

R2.3) There is also a need to thoroughly discuss the limits, in terms of environmental conditions, under which the reduced VBS formalisms is still valid. Sure, air pollution conditions between an urban site inside Mexico city and the Gulf of Mexico are different, but still most of

the discussed measurements are impacted by Mexico city emissions. A useful extension of the paper would be to compare the standard and the reduced configuration for idealized cases, for example by varying both the emission strength and by analyzing OA components as a function of the chemical age.

We agree. But this could be the subject of an entire study by itself. In addition, this topic has been explored in great detail for Mexico City in recent publications, see for example Figures 6,8, SI-8, and SI-21 of Dzepina et al. (2009) and Figures 3 and S4-S6 of Dzepina et al. (2011). Both reviewers have indicated that the paper is already long; therefore it makes sense to perform such an analysis in a future paper rather than increase the length of the present paper.

R2.4) Another concern is about emissions. In particular, primary OA emissions are increased by a factor of three in order to take into account the additional SVOC emissions. Reference to Hodzic et al. (2010) and Tsimpidi et al., 2010 is made to justify the application of this factor. In Hodzic et al. (2010), page 5496, it is argued: “: : . we assumed that approximately one third of the total emitted urban POA mass is in the aerosol phase under average ambient conditions found in Mexico-City (average OA concentration of 20 ug/m³). Based on this assumption, total semivolatile plus aerosol phase emissions of organic species (POA+SVOC) were determined by multiplying the POA emission fluxes by a factor of 3. However, in order to determine this factor, it is NOT the ambient OA concentrations which need to be known, but those present during the emission factors measurements used for the emission cadastre. These concentrations are likely to be much larger than 20 ug/m³! In the initial approach by Robinson et al. (2007), they are assumed to be 10000 ug/m³ for emission over the US, which leads to a multiplicative factor of one. In addition, SVOC are partly retained by the quartz filters often used for the OA emission measurements. If this happens, the SVOC emissions are already included in the aerosol phase emission factors. In conclusion, despite the fact the reference to peer reviewed is made, this multiplicative factor needs to be justified in much more detail. Especially, knowledge on the construction of the emission inventory is needed, in order to correctly interpret it in the framework of the VBS emissions. Note that the application of this multiplicative factor also directly impacts the formation of secondary organic aerosol formation (more precisely SI-VOC) from SVOC and IVOC oxidation. So all major results of this paper are affected by the choice of this factor. If this factor cannot be enough justified, then an alternative strategy would be following Dzepina et al., 2009, to use HOA measurements to scale HOA+SVOC emissions. After taking into account these major criticisms, which will require substantial revision, the paper should be a useful contribution to ACP.

Again the main objectives of this paper are developing a condensed 2-species VBS mechanism and evaluating it extensively against the 9-species VBS to establish its utility for large scale applications in climate models. For this we chose to use the same emissions for both 9-species and 2-species VBS. While issues about uncertainty of S/IVOC emissions are well justified, they have been sufficiently acknowledged in the paper. Using the same emissions permits a more direct comparison with previous modeling work for Mexico City as well. The emission issues do not affect the main goals and conclusions in this paper. The suggestion by the reviewer to scale HOA measurements for HOA+SVOC is also subject to uncertainties. Doing this correctly in a 3D model requires HOA measurements at sufficient spatial and temporal resolution, or else

spatial/temporal interpolation will produce significant uncertainties. So we choose not to go down the path of using HOA measurements to scale HOA+SVOC emissions in this paper.

R2.5) Specific remarks :Page 30211 line 4: “Aerosol phase species for higher volatility ($>10^{**4}$ ug m⁻³) could be neglected with little effect on OA predictions, but were included for completeness. Doesn't depend this statement on the reaction time and thus on the spatial scale of the simulation ?

We do not understand what the reviewer means here. We are talking about neglecting aerosol phase of the higher volatility species, which will be negligible. Reaction times and spatial scales will affect the gas phase part of these species and will always be included. See response to comments by Referee number 2 and his suggestions on further improving computational efficiency of 2-species VBS on this.

R2.6) Page 30228 : The comparison between the 9 and 2 bin scheme is done here for the actual conditions of the Milagro campaign. For these conditions, the comparison seems fine. However, it would be interesting to test the validity of this comparison also under a broader range of conditions.

We agree. But that will be subject of a future study for another paper. As stated previously, we will not perform such a sensitivity study in the interest of space, given the request from both reviewers to substantially shorten the paper.

R2.7) Page 30326 and other places: “HOA is significantly under-predicted aloft over Mexico City and immediately downwind of city. HOA predictions improve at farther downwind locations (CO mixing ratios lower than 250 ppb). SOA predictions in Fig. 8b and d show the reverse trend as compared 20 to HOA. SOA predictions are much better over the city and immediate downwind locations, but SOA is over-predicted as compared to AMS OOA at more remote downwind locations.” If OA emissions would be further increased to match HOA, then OOA would be even more overestimated by simulations. Is that right ?

Yes that is right. However, there are missing processes such as fragmentation reactions, a more accurate representation of dry deposition, etc., which are not included here. As discussed in the main text, an accurate representation of all physical and chemical processes affecting SOA formation is needed to get right answers for the right reasons.

R2.8) Page 30244, line 17: “WRF-Chem using online meteorology as discussed earlier which is more useful for simulating event periods, while CHIMERE uses offline meteorology through MM5.” Why ? Because updated meteorology is available for transport and chemistry calculations at every time step in a, online model, but needs to be interpolated (often from hourly output) in off line models : : .. But does this effect play a role in the current simulations?

The reviewer is correct regarding why these differences can arise. We have not done the simulations required to show the differences between offline and online calculations for this case, which is beyond the scope of this study. There have been previous studies describing how

differences in chemistry at specific times and locations can be attributed to online and offline meteorology (see Grell et al. reference below) and it is beyond the scope of this study to quantify this effect. More importantly, online meteorology is required to simulate aerosol-cloud-radiation feedback mechanisms that we intend to perform with the VBS treatment of SOA in the future. We have altered this sentence to point to previous papers on this subject.

Grell, G.A., R. Knoche, S.E. Peckham, and S.A. McKeen, 2004: Online versus offline air quality modeling on cloud-resolving scales. *Geophys. Res. Lett.*, 31, article number L16177