Atmos. Chem. Phys. Discuss., 10, C13008–C13019, 2011
www.atmos-chem-phys-discuss.net/10/C13008/2011/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Modeling organic aerosols in a megacity: comparison of simple and complex representations of the volatility basis set approach" *by* M. Shrivastava et al.

Anonymous Referee #1

Received and published: 31 January 2011

General comments

This paper is within the scope of ACP and I think that it deserve publication but only after a substantial revision.

[However, I am not sure the paper is well suited *for the special issue* (Megacities: air quality and climate impacts from local to global scales) since it does not really deal very much with air quality or climate impacts; it is a paper describing model development that maybe, in the long run, can lead to a model applicable for climate impact studies on larger scales (but for that more model development is needed, e.g., wet deposition and fragmentation reactions are missing in the version presented here).]

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

The paper describes a modification of the WRF-Chem model to include VBS based treatment of organic aerosol. A “standard” 9-species VBS scheme (with some changes in assumed oxygen uptake per oxidation generation) is tested and a simplified 2-species VBS is developed and compared to the 9-species VBS. A sensitivity test of the anthropogenic S/IVOC emissions is also performed. Ground based and aircraft measurements from the MILAGRO 2006 campaign are used for evaluation.

In my opinion, the paper does not give any new clear insights into the issue of organic aerosols in the Mexico City region compared to the large number of MILAGRO papers already published. Still, the implementation of a VBS-OA scheme in WRF-Chem and, especially, the development of the simplified 2-species VBS scheme may be interesting enough to justify publication in ACP.

Since very few scientific conclusions are drawn in the paper, I think it needs to be condensed into a much shorter paper. It is now about 50 pages of text + 5 Tables + 15 Figures (most of them with several panels). In my opinion this is far too long! The authors should focus on the actual conclusions they can draw from their work and rewrite the paper to be of an appropriate length. If the authors want to publish “everything” from their evaluations/comparisons they should do this as a technical report and not in a peer-reviewed scientific journal. For most readers, too long papers are not useful. I think most readers of scientific literature would agree that the shorter a paper can be written and still contain the important findings the better.

I suggest that the authors rethink the manuscript and restructure and condense it to a much shorter, more interesting paper. Maybe half the length would be reasonable for ACP. The best option would probably be a complete rewriting of the paper but if the authors are unwilling to do that it may be possible to adjust the paper by cutting out a number of whole sections and a careful “focussing” of the text (removing/rewriting unnecessary sentences). Also, if you want to keep lots of Figures it may be better to put them in Supplementary material.

Specific comments

Partly due to the length of the manuscript I may have missed some specific problems but here is at least a start.

Page 30209, lines 4-5: “Dzepina et al. (2010) recently reported. . .”
The sentence is difficult to understand, partly because the Dzepina-paper referred to is still not published (in review according to the reference list; and I have only been able to find an abstract for the paper); if I understand it correctly the Tsimpidi et al. (2010) mechanism does include SI-SOA and, if that is the case, the sentence does not make sense to me. In general I think the authors should try to limit the referencing of a paper “in review”; the Dzepina et al. (2010) paper is referred to three times in the manuscript.

Chapter 2 Model description:
Although I think this paper in general is far too long, the section about the introduction of semi/intermediate-volatility OA into the MOSAIC aerosol dynamics module is very short and very few details are given. If this really is the first time SI/SOA is coupled to the MOSAIC module it would be interesting to know some more details about how this was done (e.g., what extra modifications/assumptions are needed for the organic components, accommodation coefficients, impact on water uptake, etc); on page 30216, lines 22-27 you write: “The detailed treatment of OA has been fully integrated with the inorganic MOSAIC aerosol module in WRF-Chem, thus constituting a state-of-the-art representation of processes leading to organic and inorganic aerosol formation in the atmosphere. This detailed modeling approach in WRF-Chem is necessary to understand the suite of complex physical and chemical interactions between biogenic SOA formation, anthropogenic OA and inorganic species.” But you give no details about how you have you have treated these “complex physical and chemical interactions” between the OA and the inorganic species. If the details are mostly technical and not interesting to the general reader they could be presented in Supplementary material to the article.

A general question regarding the comparisons of model concentrations to AMS-data:

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

How are the size-distributed OA concentrations compared to the AMS-measurements? Are only the two smallest size bins included or also the third (0.625 – 2.5μm, dry diameter)? Is hygroscopic growth taken into account?

Page 30211, line 6: The SAPRC-99 reference is not correct. The link is not working. Please update to a correct reference for the mechanism. Also the comment in the reference is a bit strange: "last updated 30 March 2010"? As far as I understand the SAPRC-99 mechanism was replaced by SAPRC-07 in January 2010, so I wonder if there were any updates to SAPRC-99 in March 2010?

Page 30213, lines 25-26: The anthropogenic emissions inventory includes traffic emissions and municipal trash burning.
What about other anthropogenic emissions?

Page 30214, lines 1-4: "Also, municipal trash burning is expected to have similar OA spectra as fresh vehicular emissions dominated by hydrocarbon-like OA (HOA) with also some similarities with BBOA (Mohr et al., 2009); hence organic OA emissions from these sources are lumped together"
What sources are lumped together? Trash-burning and vehicular emissions? Or Trash-burning and BBOA?

Page 30214, lines 12-13: "Emission factors were taken from multiple sources (Andreae and Merlet , 2001; M. O. Andreae, personal communications, 2008)"
This is not clear (and definitely not reproducible). I suggest that the details are specified in Supplementary Material.

Page 30216, lines 5-8: "Isoprene and terpene emissions calculated by the NEI emissions inventory for Mexico domain are removed to avoid double counting of biogenic emissions (already calculated by MEGAN model within the domain)."
There is no reference to the NEI emissions inventory?
Why did you choose to use MEGAN emissions of isoprene also in the parts of the domain where you had another emission inventory that also included the anthropogenic

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

isoprene? Was it impossible to combine the information in order to keep the, potentially important, anthropogenic isoprene emissions?

2.1.2.2 V-SOA formation

You specify from where you have taken the SOA-yields for the AVOCs (Tsimpidi et al. and Hildebrandt et al.) but not for the BVOCs. I guess the ISOP, TERP and SESQ SOA yields were taken from Tsimpidi et al.?

Page 30219, lines 2-4: “The reaction rates of various VOC species with the OH radicals in Eq. (5) are already present within the SAPRC-99 mechanism, as a part of gas-phase chemistry”
I can not find any SESQ reactions in SAPRC-99. What reaction rates were used for sesquiterpenes? Also, how did you treat SOA formation from ozonolysis? And what about reactions with NO_3-radicals? Here you only mention reactions with OH-radicals.

Chapter 2.2 Condensed 2-species OA mechanism

Since this mechanism is constructed for computational efficiency I wonder why you have not neglected the 4 gas phase SI-SOA species, 4 of the 8 gas phase POA species and 16 of the 32 aerosol phase POA species (the low volatility species will remain in the aerosol phase under most atmospheric conditions and the high volatility species will be in the gas phase)?

2.2.2.2 V-SOA

Page 30222, lines 25-26 (and Table 5): You state: “The SOA yields for alkane and olefin species are chosen to be equal to the yields corresponding to species with C* of 1 μgm-3 in the 4-product VBS from Tsimpidi et al. (2010).”
When I compare your Table 5 with the Tsimpidi′s Table 2 it looks as if you have used the C*=1 μgm-3 values for the olefin species but not for the alkanes; for ALK4 and 5 you seem to use Tsimpidi′s values for the C*=10 μgm-3 species. Please correct the text and explain the reason for your different choices for the ALK and OLE species.

Page 30223, lines 5-6: “to ensure atmospherically relevant conditions”

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

Not a major point, but I would not say that you "ensure" atmospherically relevant conditions when using the smog chamber data from Ng et al. Relative humidities in the experiments are very low and even if you choose the experiments with the lowest aerosol generated it is still fairly high concentrations compared to the ambient atmosphere. Also, the Ng experiments only provide SOA yields for the OH-reaction. What do you assume for ozonolysis and reactions with NO_3?

Page 30223, lines 9-11: Biogenic V-SOA is found to be a factor of 5 lower than what Hodzic et al. (2009) calculates and as a reason you give "mainly due to lower biogenic emissions in this work".
But you have used MEGAN for biogenic emissions and Hodzic et al. also used the MEGAN model for biogenic emissions? So how can biogenic emissions differ so much that the difference in BSOA is a factor of five? I guess there must be other more important reasons? On page 30216 you state that you have neglected the Anthropogenic isoprene in your run (and that the anthropogenic isoprene could be a factor of 5 higher than the biogenic isoprene at the T0 site) but missing Anthropogenic isoprene should not have a significant impact on Biogenic SOA and you also quote that the largest contribution to biogenic SOA in the Mexico City basin is due to regional isoprene (>60%) produced upwind on the coastal area and advected into the city.
It is also not clear if the factor of five difference in BSOA (compared to Hodzic et al.) is for all of the model domain or only at certain site(s).

Page 30223, lines 23-24: "Also, the computational burden of handling the cloud processes would be unnecessarily excessive."
This statement is a bit worrying; if you want to be able to use the model for larger scale modelling or longer time periods and/or wetter regions you really have to include wet deposition. How much would the computational burden increase by including wet deposition?

Chapter 3.1
Page 30226, line 2 (and Figure 1): "Figure 1 shows . . . total SOA surface

concentrations. . .”
Is this correct? Does Figure 1 show only SOA (that is, not including POA)?

Page 30226, lines 22-26. The discussion about the B-V-SOA predictions is repeated in some more detail than above; see my comments above also for this part (if >60% of the BSOA is due to regional isoprene, produced upwind and advected into the city how can there be a factor of 5 lower BSOA at both T0 and T1 in this study compared to Hodzic et al. if the regional isoprene emissions are from MEGAN in both cases?). And, do you consider Anthropogenic isoprene as a source of Biogenic SOA? This is a bit strange I think and, if it is so, it needs to be pointed out in the text.

Page 30227, lines 13-14: CO measurements are taken from a “nearby operational monitoring site”
How near is this operational monitoring site? And does it have a similar character as the T0-site (closeness to major emission sources, geographical features etc). I find it a bit strange that you choose to almost exclusively present the model measurement comparisons for OA in terms of enhancement ratios with respect to CO (considering that you do not have CO measurements at T0 and the discussion in section 3.2.2 about the complicated interpretation of night-time CO data leading to “more uncertainties during night as compared to day-time”).
I would have preferred to see more straightforward comparisons of modelled OA to measured OA.

Page 30228, lines 18-20: “Model peaks do not result from night-time chemistry with O_3 or NO_3 radicals, since night-time chemistry leading to SOA formation is not represented in WRF-Chem.”
Does this mean that you do not include SOA formation from, e.g., ozonolysis of terpenes? Ozonolysis is estimated to be an important SOA-source (see, e.g., Capouet et al., JGR 2008). Why did you not include night-time SOA-chemistry in the model simulations?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Page 30229, line 7: “consistent with the underprediction of SOA/ΔCO in Fig. 3d” What do you mean by this? I guess this part of the sentence could just be skipped?

Page 30230, line 9 (and Figure 4): What is included in BBOA in Figure 4? Only primary BBOA or also oxidised BB-SI-SOA? Is BB-V-SOA included in the WRF-Chem model (and, if so, is it included in BBOA in Figure 4 or is it included in some of the other V-SOA fractions)?

Page 30230, line 22: How do you handle the vertical emission distribution for BBOA (and other emissions)? Do you use some plume-rise calculation scheme for hot emissions?

Figure 4c: Observed concentrations are missing in the Figure. I definitely think that observed concentrations should be included here!

Page 30232, lines 15-17: You state that the agreement between case 3 and 2 is “very interesting” and still you do not show the results for case 3. . . If it really is very interesting you should perhaps consider illustrating these similarities (instead of a number of other less interesting plots)?

Page 30233, lines 1-16: I do not think that this section contains very interesting results and I do not see why it is included in the chapter about results at the T0-site (since it discusses results along flight tracks and not city center measurements). Also, it is difficult to see the details in Figures 5c and 5d (and if they are to be included I think you should change the x-axis to local time instead of UTC, or at least mention the time difference between local time and UTC in the figure caption).

Chapter 3.4
What particle size is evaluated at the T2 site (PM2.5? PM10?)
Since the measurements at T2 are OC/EC measurements I do not understand why you first convert the observations to “TOTOA” using an assumed OM/OC ratio of 1.4? This just introduces a big, unnecessary, uncertainty into the comparison. You could

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

easily compare your calculated OC concentrations to the observed OC. This needs to be changed. What OM/OC ratio does your model give at T2?

Figure 7c. The curve showing measurements looks surprisingly spiky, for being a 24-day average of AMS-measurements. How did you calculate the averages? Is it 24-day averages of hourly mean concentrations? (I guess that the AMS-data have a very high time-resolution and that you, in principle, could calculate a more continuous curve?) The model curves look much more continuous and seem to have higher resolution than 1h? The same question is also valid for Figure 6. Several of the AMS-curves look a bit “unsmooth”; are these curves also 24-day averages and why are they not calculated with higher time resolution than 1h?

Chapter 3.5
The AMS-data used in the comparisons are 10s-data. What time resolution is the model calculated concentrations? What about the temporal variation of emissions in the model? Do you use hourly variations in emissions or something more sophisticated? I am not surprised that the model does not show the same scatter as a set of 10s AMS data. In itself, this does not highlight “significant uncertainties in representation” of temporal (or spatial) variation of emission sources. You could never expect a 3D-emission inventory to have a 10s-time resolution and I do not think that Figures 8a-d, and the long discussion about them in the manuscript, are very interesting (thus I think this (page 30236-30237) is one of the parts that can be removed from the manuscript; or moved to the supplementary if the authors prefer that). Did you prepare similar scatterplots for 10s-AMS data for any of the surface measurements (and did that show similar differences in scatter)?
Figure 9 is much more interesting since it compares the different model versions to each other and to the measurements.

Page 30240, lines 2-6: The sentence starting by “Because both total OA and SOA are overpredicted. . . ” is rather confusing and I think that it should be rephrased (or it could also be removed since it just describes some ideas about how to try to tune the model

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

to get better results).

Figures 10 and 11: These figures need much better figure captions. I think it should be possible to get some idea of what is shown from the figure caption without having to search the text for the section that deals with it.

Figure 10 b and d: Case 1 and Case 3 give almost identical results, which I find very surprising since these two cases are so different. Please explain this (I guess that there may be an erroneous labelling in the Figure; in Figure 10c Case 2 and Case 3 are rather similar (as expected))

Chapter 3.6, about Non-fossil carbon fraction, contains no interesting information and I think it should be excluded from the paper. The available observations give somewhat conflicting results and the model results presented in this paper are not (at this stage) useful for resolving the issue. You use some rough estimates of the fraction of non-fossil carbon in the “urban carbon” and states “15% of biogenic SOA is PBAP”, which I do not understand at all; do you consider 15% of the biogenic secondary organic aerosol to be Primary Biological Aerosol Particles? What exactly do you mean by this? Also, the biomass burning emissions in this study are apparently too low and, according to the authors, the B-V-SOA is too low and to handle this, the fraction of non-fossil carbon is adjusted by increasing B-V-SOA by a factor of 5! Since the whole chapter 3.6 is unimportant for the main conclusions of this paper (and since it is does not give any additional conclusions/results and seems to be mostly rather rough “guess-work”) I think that it should not be included.

Figure 12. I think this should also be removed (partly because I think the whole chapter about non-fossil carbon should be excluded and partly because I do not understand why it is interesting to show diurnal variations of fNF anyway).

This also means that I suggest that you remove the discussion-section, starting on Page 30246, line 25 and ending on Page 30247, line 5. This part also clearly shows that the whole chapter about non-fossil carbon can be excluded without loss of content “the overall conclusion is unclear. . .”

Chapter 3.7, which contains a comparison between the WRF-Chem and CHIMERE models, could also be removed from the paper with no loss of essential information. The differences between the two models are large (different emissions, different chemistry schemes, different VBS-schemes, different meteorological drivers) which makes comparisons of results rather difficult to interpret and, to be honest, I do not think the comparison presented in Chapter 3.7 and Figures 13-15 gives any useful/interesting information.

Page 30246, lines 23-24: “Dry deposition of S/IVOC vapors downwind would reduce SOA formation bringing model predictions closer to AMS PMF analysis”
But in chapter 2.3 you state that dry deposition is calculated for all gas-phase SOA precursor species? Did you NOT include dry deposition of S/IVOC in the gas phase?

Page 30248, lines 21-23: “The computational expense can be reduced further if sources of organic aerosols and O:C ratios are not required.”
This is true also for the 9-species VBS (not only the 2-species).
Also, it would be interesting to know how much the expense would be reduced by these simplifications (though I can not see that you would be willing to neglect the O:C ratios in many applications).

To save space (and for ease of comparison) I suggest that Tables 3 and 5 are combined into a single table.

Technical corrections

Page 30219, line 20: “Table 2” should be: Table 3

Page 30219, line 25: “Table 1” should be: Table 2

Page 30220, line 13-15: the sentence about POA(a) and SI-SOA(a) is a bit strange; I thought that the authors nomenclature was that (a) meant aerosol-phase (that is particulate)? If so, it does not make sense to write that POA(a) and SI-SOA(a) would remain in the aerosol phase under most atmospheric conditions... The POA(a) with C*=1E5 μgm-3 will not stay in the aerosol phase under most atmospheric conditions.

Page 30231, line 6: across the depth of the boundary layer

Page 30231, line 19: of the boundary layer

Page 30238, line 4: of the 2-species VBS

Page 30238, line 6: lower than the other 2 modelling cases

Page 30239, lines 21-24: The sentence starting with “These include V-SOA” could be removed since the definitions are given (several times) earlier in the paper.

Page 30240, lines 26-27: as compared to the other two cases

Page 30240, line 28: suggests revising the SVOC

Page 30241, line 1: or the volatility distribution of the emissions

Page 30246, line 7: In addition, models need to capture

Page 30247, line 12: difficulty . . . the AMS collection efficiency

Page 30248, line 12: to a 9-species

Page 30265, last sentence: as discussed in the text.

A general style comment: I think many sections in the text are too long. This makes the text unnecessarily difficult/tedious to read. In many cases it would be easy to just split the long sections into several parts (but I think the paper needs to be condensed/rewritten anyway so perhaps the overly long sections will disappear then). One of many examples of very long sections is starting on Page 30247, line 6 and ends on Page 30248, line 1.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 30205, 2010.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper