Atmos. Chem. Phys. Discuss., 10, C15137–C15148, 2011
www.atmos-chem-phys-discuss.net/10/C15137/2011/

Atmospheric
Chemistry
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Discussions

Interactive comment on "Development and evaluation of the aerosol dynamic and gas phase chemistry model ADCHEM" *by* P. Roldin et al.

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Received and published: 4 May 2011

First of all we would like to clarify which changes in the model that we have performed after considering the comments from referee #1 as well as the comments on the companion paper (Roldin et al., 2010). The changes concern the organic gas to particle partitioning which is described in Sect. 2.2.2 and 2.4 and new model results from 2D-VBS and two-product model simulations are presented in Sect. 4.2.1.

1) The 2D-VBS model has been changed and it now tracks all the 2D-VBS surrogate species in every size bin. Running this model with 200 size bins is however computationally expensive and we therefore changed to 100 size bins between 1.5 and 2500 nm in diameter. We have also decreased the number of 2D-VBS bins from 11X16 to 11X10. This is possible since we no longer consider the non-oxidized SOA-precursors

in the VBS (e.g. benzene, toluene and xylene) but only their generally less volatile oxidation products. The volatility distribution in the VBS is now between C*=10-2 and C*=107 μg/m3 instead of C*=10-4 and C*=1011 μg/m3 which was the range we used for the model runs presented so far.

2) The 2-product model has been changed. It no longer uses the 2-product yield parameterizations from experimental work in smog chambers. Instead, it keeps track of each 2-product model surrogate species (2 products for each oxidation reaction). In total this gives 40 surrogate species (35 for SOA, 2 for POA non-oxidized POA, 2 for non-oxidized IVOCs and 1 for oxidized POA and IVOC products). In the same way as for 2D-VBS model, the 2-product model keeps track of all 40 species in each particle size bin. However, since the number of organic compounds is fewer (40 instead of 11X10=110) this model is faster. Another advantage is that each of these 40 products can be traced back to the original non-oxidized molecules and therefore it is possible to distinguish between ASOA, BSOA and POA. This is not possible with the 2D-VBS which keeps track of the O/C-ratio (an indirect measure of the origin of the organic compounds).

Answers to referee #1

1. Page 18668 line 20: ". . .for 13 different compounds. . ." I assume these are aerosol compounds. Please specify.

Yes, it is aerosol compounds and we clarify this in the new manuscript on page 8, line 22-25. Now with the updated 2D-VBS model the number of different aerosol particle compounds is 8 for the inorganic compounds and 110 for all the organic compounds, in total 118 aerosol particle compounds.

2. Section 2.2.4 2nd paragraph: Does it rain simultaneously with the same rainfall intensity to all of the 20x20 grids? Please explain.

Yes, for the selected case study it does. We specify this on page 39, line 3-4 in the

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updated manuscript.

In the model we always assume that the rainfall intensity is uniform in the horizontal direction perpendicular to the air mass trajectory and the rainfall only occur below the estimated cloud base. The estimated cloud base is derived from the vertical RH profiles along the trajectory. For the simulated case study the RH was however never near 100 % within the model domain (up to 2000 ma..g.l.). Hence, for the modeled case study the cloud base was above the model domain and the rainfall affected all 20x20 grids with the same intensity. How the model estimates the position of the clouds and the cloud thickness is described on page 17, line 22-29 and on page 18, line 1-3. We have also included a description of how the model treats the wet deposition removal on page 15, line 22-25.

3. Section 2.2.6 line 27: Please provide a reference for the cloud droplet size distribution parameters (diameter and σ).

Yes, thank you for clarifying this to us. We have included a motivation of the selected cloud droplet distribution and a reference in the text on page 18, line 4-14. For the final simulations we changed the cloud droplet mode diameter from 20 μm to 10 μm because this value is in better agreement of what we have found in the literature about realistic droplet sizes distributions (see e.g. Rogers and Yau, 1989).

4. Page 18678 line 10: “. . .Eqs. (5) and (4)” should be “. . .Eqs. (5) and (6)”

Yes, thank you we have changed this in the text.

5. Section 2.4 2nd paragraph: The authors suggest that an advantage of the two product theory against the VBS scheme is that using the latter you have to lump all the organics based on their volatility and therefore loosing the individual characteristics of the VOCs (i.e. specific yields, molecular weights etc.). I assume that when the model use the VBS theory, the VOCs are lumped on the high volatility bins (10ËĘ7-10ËĘ11) and then they participate in the same chemical reactions using the same parameters

in each of the volatility bins. If that is the case then I suggest using some speciation for the VOCs and then only lumping the oxidation products of each VOC (and not the VOCs themselves) depending on their volatility and O/C ratio. In that way you can still have different VOCs participating in different chemical reactions with different characteristics. Moreover, using this treatment, the volatility bins will be reduced from 10ËĘ11 to 10ËĘ6 as all the products of the oxidation of the VOCs will be distributed in lower volatility bins.

Yes, thank you for these good suggestions. We have adapted them and changed the 2D-VBS model accordingly (see section 2.4.2 on page 28). The 2D-VBS now considers the species specific first oxidation step before the oxidation products are included into the 2D-VBS. We have thereby been able to decrease the upper volatility bin to 10ˆ7 μg/m3.

6. Page 18685 line 22: I found the low limit of the volatility distribution (C* = 10ËĘ-4) extremely low. Based on figure 7 the total OA concentration never goes below 2 μg m-3. Therefore, the organics that are distributed at the 4 first volatility bins (10ËĘ-4 - 10ËĘ-1) are always in the aerosol phase. Probably a higher low limit at 10ËĘ-1 or 10ËĘ-2 would be enough to describe the phase state of these species.

Yes, thank you we have now changed so that the first volatility bin starts at 10-2 μg/m3 (see line 5, page 28).

7. Page 18686 lines 16-26: What is the change on the O/C ratio and the saturation concentration after each aging reaction?

Yes, thank you for this good question. This was definitely not clear in the submitted manuscript. We have clarify this in the new manuscript where we include a table that describes the probability functions of adding 1, 2 or 3 oxygen atoms after each oxidation reaction and the probability functions for how much these added oxygen atoms change the saturation concentration (see Table 1 and section 2.4.3 on page 29, line 25-29 and on page 30, line 1-14).

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8. Page 18687 lines 18-22: The discussion here is not in accordance with what was stated on the Eqs. 14 and 15.

Yes, thank you for clarifying this error to use. Equation 14 was used for high NOx conditions and eq. 15 for low NOx conditions and not the other way around as was written in Eq. 14 and 15. With the updated version of the 2D-VBS model Eq. 14 (now Eq. 15) is used both for low and high NOx conditions and the difference between the low and high NOx conditions is instead considered with the first oxidation step before the compounds are included in the 2D-VBS. This is described on page 30, line 15-28 and on page 31, line 1-15.

9. Table S3: The SVPOA emission fractions at 10ËĘ5 and 10ËĘ6 volatility bins should be equal to zero.

Yes, thank you we have changed this in the table.

Answers to referee #2

1. In several places, the authors mentioned that the model is developed for detailed studies from local scale to regional or global scale. ADCHEM is a Lagrangian model and air masses in different grid boxes may have quite different trajectories. As I understand, the model follows one single trajectory for the whole domain and it is not clear how accurate the results will be after a few days of air mass travel. The authors need to explain why the model can be used for regional or global scale.

Yes, thank you for addressing this issue. In the new version of the manuscript we do not state that ADCHEM should be used for global scale. A discussion about the scales which ADCHEM is appropriate for and under which meteorological conditions the assumption of following one air mass trajectory is not suitable is found on page 3, line 23-27, page 10, line 1-28.

2. Model input (Section 3.2). This session should be expanded to provide more details on how vertical profiles of meteorology parameters are obtained and used to drive the

model. Could the authors provide a figure showing such profiles? Do these parameters change horizontally? Since the vertical profiles are used, I assume that wind speed at least vary with height. Then, different air masses in the domain travelled different distance during a given period of time. How do you deal with this in the model? What about the wind shear? Have you considered the effect of wind shear on mixing? The authors refer to Roldin et al. (2010) for more information but I could not find much of such information there either. Anyway, this one is the model description paper and it is necessary to provide such information here.

Yes, we agree that we should include a more detailed description about the meteorological data and how it is used in the model. We do this in the updated manuscript on page 35, line 7-21. We have also include Fig. S2 in the supplementary material which gives examples of temperature and relative humidity profiles at a few places along the air mass trajectory downwind of Malmö. We have also clarified in the text that the meteorological conditions which we use do not change horizontally perpendicular to the air mass trajectory which ADCHEM follows (page 35, line 16-17). We have also included Fig. S1 in the supplementary material which illustrate how different HYSPLIT air mass trajectories which start at different altitudes over Malmö are diverged from each other due to wind shear. We also clearly clarify that since ADCHEM is a Lagrange model it only follows one air mass trajectory and does not consider the wind shear induced divergence of the air mass trajectories at different altitudes (see page 3, line 23-27 and page 10, line 1-11). This is an important disadvantage with Lagrange models compared to Eulerian models. ADCHEM do however consider how the wind shear and buoyant convection influenced the turbulent diffusivity in the horizontal and vertical direction. This is clarified in the updated manuscript on page 9, line 13-21.

3. Compared to 0-D Lagrangian box-models, one advantage of the ADCHEM model is its 2-D spatial distributions. The figures presented show the vertical spatial variations but no figure was given to show the horizontal variations. I think that it will be useful to demonstrate the capability of the ADCHEM model by presenting one or two figures

showing the horizontal spatial variations of key species. One good example will be the concentrations of particles in the whole domain (2-D vertical-horizontal cross section) at selected times (or locations).

Yes, certainly it would be good to demonstrate how the particle number concentration changes in the horizontal and vertical direction perpendicular to the air mass trajectory. We have included such a figure displaying the particle number concentration within the whole 2D-model domain at a few different distances downwind of Malmö (see Fig. 6 and the describing text on page 40, line 15-29, on page 41, line 1-5 and on page 48, line 8-15).

4. The authors stated that "the particle number size distribution in the center of the urban plume from Malmo is mainly affected by dry deposition, coagulation and condensation". What about nucleation? Nucleation is well known to occur frequently in Europe and is a key process controlling particle number concentration. It appears that nucleation was not important for the case study presented here. Have the authors looked into cases where significant nucleation occurred? If yes, how well was the modeling doing for such cases?

No for the urban plume studies performed with the model we have not considered any cases with significant homogeneous new particle formation. The maximum new particle formation rate for the selected case study was approximately 1 cm-3 of 1.5 nm stable clusters. Still, these particles did not have any significant influence on the particle number concentration for particle larger than 5 nm in diameters. This is likely since the growth rate of these particles was too low for them to escape the coagulation sink. We have added a discussion about this in the text where we state that the uncertainty concerning the influence from homogeneous nucleation is especially large since the growth rate of these particles depend strongly on the concentrations of low-volatile organic compounds which we do not know the concentration of. Therefore it is possible that ADCHEM significantly underestimated the growth rate of the smallest particles (see page 39, line 24-28 and on page 40, line 1-7).

5. Page 18668, line 23 and below. Could you explain in more detail how this scheme (usage of an inert specie) is related to the diffusion of model tracers?

Yes, we try to clarify this in the new version of the manuscript on page 8, line 25-27. The use of an inert specie is possible since the transport of compounds by turbulent diffusivity in contrast to e.g. molecular diffusion is independent of the properties of the individual species. The mixing of the inert specie therefore describes the air mass transport between different gird cells. Since we use operator splitting and first consider the mixing and then the species specific processes (e.g. coagulation, dry deposition and chemical reactions) the general air mass transport between the grid cells is the only information which is required.

6. Page 18668, lines 11-14. How sensitive is the result to assumed concentration gradient values in the upper boundary? How you treat the mixing around the horizontal boundary?

Yes thank you for this important question. We have also run the model without any concentration gradient as upper boundary conditions. However since the atmosphere above the boundary layer is stable the mixing in the vertical direction is very slow. Therefore this had insignificant influence on the concentrations within the boundary layer. Near the upper boundary conditions the concentrations do however become higher if using a zero gradient. Unfortunately we have no measurements on gas or particle concentrations in the vertical direction for the studied case study. We have included a discussion about this in the updated manuscript on page 9, line 22-27.

As horizontal boundary condition we assume that the concentration gradient is zero (=0). We clearly write this in the updated manuscript on page 9, line 27-28.

7. Page 18676, line 18. It appears that the output from HYSPLIT model is used heavily in the ADCHEM model. It is necessary to give a reasonable description of the HYSPLIT model and its uncertainties.

Yes you are right. Since the HYSPLIT model rely on relatively coarse meteorological input data (1°x1°) the local wind field may differ considerably from what is predicted by the HYSPLIT model (see page 7, line 25-28 and page 8, line 1-3). Therefore we used wind direction measurements at 24 mag.l. from a meteorological mast in Malmö to verify the HYSPLIT air mass trajectory. For the selected case study the air mass trajectory agreed within 5° with these measurements. We have added this information to the manuscript on page 8, line 8-12. Unfortunately, we have not been able to find any document concerning the model uncertainties with the HYSPLIT model. We do however referee in the text to the comprehensive trajectory model intercomparison by Stohl et al., 2001 which compared three different air mass trajectory models and concluded that close to the surface the average horizontal position deviations may be up to 10% for 48 hour backward trajectory simulations (see page 8, line 4-8).

Answers to referee #1 on the companion paper

2.Page 18739, 1st pagragraph: How is SOA condensation done? I could not find the following details in the other Roldin paper on ACPD.* Do you track the 11x16 2DVBS surrogate species in every size bin, or do you just track the total mass of the 11x16 2D-VBS species aerosol organic phase without size information? **If you do track the organic composition at each size, do you solve condensation kinetically by solving the diffusion equation for each aerosol size section and each 2D volatility bin, or do you just assume that each size instantaneously goes to equilibrium with the gas phase? Full kinetic condensation seems very computationally demanding for 11x16 2D volatility bins, 200 size sections and 20x20 gridboxes considering the range of volatilities make condensation a very stiff system of differential equations. ***However, kinetic condensation may predict very different size-dependent growth rates due to SOA condensation than assuming instantaneous equilibrium or just tracking the bulk SOA mass (see comment #7). This is a tricky problem. If you are performing full kinetic condensation of the 2D-VBS onto each size section, please give details because this would be very useful.

For the results presented in the ACPD manuscript we did not track the surrogate species in every size bin, just the total mass of every condensing species. However after reading the comments by the referee we decided to update the model and now it tracks all 2D-VBS species in each size bin. The referee points out that this is computationally more demanding especially for the coagulation algorithm. Therefore we have decided to only use 100 size bins between 1.5 and 2500 nm in diameter. As a consequence the model performs with approximately the same speed as previously with 200 size bins. With the new model version, it is only the first step oxidation products from the SOA-precursors (e.g. benzene, toluene and xylene) which are included in the 2D-VBS and not the more volatile non-oxidized compounds. With this change it was possible to decrease the number of 2D-VBS bins from 11X16 (176) to 11X10 (110) with C between 10-2 to 107 μg/m3 instead of 10-4 to 1011 μg/m3 (see Sect. 2.4.2).

**The condensation/evaporation is solved kinetically in our model. However, we normally use the wording “diffusional limited condensation/evaporation” to describe this. Hence, we understand how the referee could have missed this information. In order to avoid confusion, we have added the term “kinetic” to describe the condensation (see page 14, line 6-15).

We have not previously tracked the organic compounds in each size bin. But, we have updated our model for this purpose. Since, we have additionally changed other model descriptions as suggested by other referee comments, we needed to rewrite section 2.4.

*** Yes we agree and we hope we have illustrated this with the updated model description (Sect. 2.4) and the results presented in Sect. 2.4.1. (Fig 12).

7. Page 18752, line 12-14: The details of how SOA condensation is done (see comment #2) may have implications into your organic mass size distribution. If SOA is low volatility (C* _< 1E-1 or 1E-2), it will condense to the Fuchs-corrected aerosol surfacearea distribution and will not re-evaporate on a timescale shorter than what you

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are modelling. If SOA is more semi-volatile, individual molecules will re-condense and reevaporate quickly and the net condensation will be proportional to the aerosol mass distribution. This means that semi-volatile SOA will net-condense onto larger sizes than low-volatility SOA. Depending on how condensation is done (and what volatilities your SOA has if you condense using a fully kinetic condensation scheme) you can get large variability in the predicted organic size distribution.

Yes, thank you for describing this clearly to us. This is indeed very interesting and important to mention in the text (see page 14, line 8-12, page 46, line 6-30, page 47, line 1-3, Fig. 12 and page 49, line 1-11). This is a large advantage of the updated model which keeps track of each 2D-VBS compound in each size bin and in the gas phase and then solves the condensation/evaporation separately for each of these compounds.

Answers to referee #2 on the companion paper

2. Section 2.2 Page 18737: The authors provide a brief description of the different schemes that the model can use to simulate the aerosol dynamics, the SOA formation, and the condensation/evaporation of the inorganic components. However, there are no indications of how these different schemes can affect the results and why the methods described in the last paragraph of this section (Page 18739, lines 1-8) were selected to serve as basecase. An analysis of the sensitivity of the results to these assumptions would be appropriate along with a more detailed discussion for the selected schemes (i.e. the uncoupled condensation of acids was chosen. Are there any indications that the particles during the simulations are not acid neutralize?)

The referee has requested sensitivity tests for the SOA formation. As a response to the request of the referee, we have extended the list of sensitivity runs (see page 37). We have now included separate model runs with non-volatile POA instead of semi-volatile POA, no IVOC emissions, no BVOC emissions and no BTX emissions.

3. Page 18737 2nd Paragraph: *It is not clear how the model treats the organic

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aerosols coming from the oxidation of the Semi-volatile POA and the intermediate VOC when the 2D-VBS is used. **Are they lumped with the ASOA? ***Moreover, it would be helpful to provide the ageing reaction rate and an explanation of the way that the organic aerosols shift their position in the 2D matrix after each oxidation (what's the depletion on their volatility? What's the increase on the O:C ratio?).

*** The 2D-VBS model description on page 28, line 24 until page 31, line 23 now describe how the organic molecules shift their position in the 2D-VBS after each oxidation step.

References

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