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Atmospheric
Chemistry
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Discussions

# *Interactive comment on* "Aerosol ageing in an urban plume – implications for climate and health" *by* P. Roldin et al.

**P. Roldin et al.**

pontus.roldin@nuclear.lu.se

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We appreciate the comments by the referee which have especially helped to clarify confusing and missing information in the manuscript as well as improve our sensitivity studies.

First we want to clarify which changes in the model that we have performed after considering the comments from referee #1 and referee #2 as well as the comments on the companion paper (Roldin et al., 2010). The changes concern the organic gas to particle partitioning and we have rewritten chapter 2.2.2 and 2.4 in Roldin et al., 2010 (the model description paper). The updated organic gas to particle partitioning is described in the separate document called: "Gas to particle partitioning of organic compounds in ADCHEM".

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 therefore we 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 $\mu$g/m3 instead of C*=10-4 and C*=1011 $\mu$g/m3 which was the range we used for the model runs presented so far.

2) The 2-product model (not used in this paper but in Roldin et al., 2010) 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 37 surrogate species (35 for SOA and 2 for POA). In the same way as for 2D-VBS model, the 2-product model keeps track of all 37 species in each particle size bin. However, since the number of organic compounds is fewer (37 instead of 11X10=110) this model is faster. Another advantage is that each of these 37 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).

Owing to these changes and the additional comment from referee #1 dealing with how we choose model cases, we are currently re-running the model for all possible cases.

1. Section 2.1 Page 18736: The ToF-AMS measurements were used to test the accuracy of the ADCHEM model in describing the aerosol chemical composition. As these measurements were not conducted at the time of the modeled period the authors should also mention which was the simulation period and also comment on the expected uncertainties by evaluating the model with these measurements (especially if the simulations was not during the October and March). In addition, it is not clear

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whether the gas phase concentration measurements were held during the simulation period.

Yes, we fully agree with the referee that we should provide a discussion about the uncertainty of evaluating the model with the ToF-AMS measurements and that we should clearly describe which the simulation period is. The gas phase concentration measurements were conducted during the simulation period, and this we will clearly state in the updated version of the paper. Certainly, we expect that the gas to particle partitioning and formation rate of e.g. nitrate and condensable organic compounds can change as a result of varying meteorological conditions. Therefore, we expect to see differences in the chemical composition between different time periods. However, the AMS data still gives a representative picture of the relative concentration of different compounds in different size classes and hence, it is of great value for the evaluation of modeled chemical composition.

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?)

*It is correct that no information is given concerning how these different schemes (size structure methods, SOA-models and coupled or uncoupled condensation schemes) can affect the results and why the method described in the last paragraph of this section (Page 18739, lines 1-8) was selected to serve as basecase. We agree with the referee that this information should be given as a short text and we will also add a reference to the companion paper by Roldin et al. (2010) which addresses these questions in

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detail.

**In Roldin et al. (2010) 18 different model runs were performed according to the list given below. These model runs were designed to study the sensitivity of the results to different aerosol dynamic processes, vertical and horizontal mixing, size structure method, 2-product model or 2D-VBS, semi-volatile or non-volatile POA emissions, with or without IVOC emissions and with uncoupled or coupled condensation of acids. It is true that no information is given about sensitivity analysis in this paper. We will write a sentence in the current paper, which explains that the sensitivity test can be found in the companion paper (Roldin et al., 2010). The referee has requested sensitivity tests for the SOA formation. As a response to the request of the referee, we will extend this list of sensitivity runs. We will include separate model runs with SVPOA, but no IVOC emissions, SVPOA and IVOC emissions and model runs where the SVPOA is assumed to in equilibrium with the gas phase directly after the emissions or entirely found in the particle phase and then partly evaporating upon ageing. From Roldin et al., 2010:

“If not otherwise specified the full-stationary structure with 200 size bins was used, condensation/evaporation was solved as an uncoupled process, both vertical and horizontal mixing was considered, the 2D-VBS method was used for the partitioning of organic compounds between gas and particle phase, POA was assumed to be non-volatile and IVOC emissions were not considered.”

“1. All processes included (base case) 2. Full-stationary structure with 50 size bins 3. Full-stationary structure with 25 size bins 4. Moving-center structure with 25 size bins 5. Moving-center structure with 10 size bins 6. Combination of full-stationary and moving-center with 25 size bins 7. Coupled condensation 8. 2-product model used for SOA production 9. No aerosol dynamic processes 10. No dry deposition 11. No coagulation 12. No condensation growth 13. No wet deposition 14. Doubled mixing height. 15. Doubled horizontal turbulent diffusivity 16. 1-D model (without horizontal mixing) 17. With SVPOA and IVOC emissions 18. Unity mass accommodation coefficients”

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***We found that the nitrate particle content was lower when treating the acid and base condensation as coupled since the particles were not fully acid neutralized for the uncoupled condensation model runs. Therefore we used the uncoupled condensation of acid and base for the basecase simulations. We will add an explanation why we used uncoupled condensation.

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

*We agree with the referee that it is not clear how the organic aerosols coming from the oxidation of the Semi-volatile POA and the intermediate VOC are treated. We will give a short description about this and add a reference to Roldin et al. (2010) for a more detailed description of the 2D-VBS (see the separate document called: "Gas to particle partitioning of organic compounds in ADCHEM"). The POA and IVOCs are added to the 2D-VBS channels with C* between 10-2 and 106 $\mu$g/m3 and O:C-ratio equal to zero. As a consequence, these compounds are treated in the same manner as any other organic compounds, with a reaction rate equal to 3*10-11 cm3/molecules for OH oxidation if they are found in the gas phase.

**The IVOCs and POA are not directly lumped together with the ASOA and BSOA precursors since none of those compounds are found in the 2D-VBS channels with C* between 10-2 and 106 $\mu$g/m3 and O:C-ratio equal to zero. In the updated model version all traditional ASOA and BSOA precursors (BTX, monoterpenes and isoprene) are first oxidized in the gas phase before they are included in the 2D-VBS and therefore no one of them will fall into the 2D-VBS channels with O:C-ratio equal to zero (see the separate document called: "Gas to particle partitioning of organic compounds in ADCHEM"). However when the IVOCs and POA compounds are oxidized they will be

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mixed with the ASOA and BSOA compounds since the model only use one 2D-VBS for all organic compounds and not separate 2D-VBS for BSOA, ASOA and POA+IVOCs.

*** Yes, a short description of the 2D-VBS should be added and the 2D-VBS and 2-product model should be described in more detail in Roldin et al., 2010 (see the separate document called: “Gas to particle partitioning of organic compounds in ADCHEM”).

4. Page 18738 line 6: Please provide a reference for the chemical mechanism used. This reference will be added. The original kinetic code is from EMEP and described in Pirjola and Kulmala (1998).

5. Page 18738 lines 14-16: *How the high NOx/HO2 is defined? Moreover, depending on the value of the NOx/HO2 ratio, does the model follow one of the two reaction pathways (NO vs HO2) or a combination of those two?**I would also recommend to provide a table with the SOA-yields used under the high and low NOx/HO2 ratios.

*Yes, thank you. This information is missing and should be added both in this manuscript and in Roldin et al. (2010). The model always follows both the pathway where the ASOA precursors react with OH followed by reaction with NO and where they react with OH followed by reactions with HO2. Hence, the answer is that the model follows a combination of the two reaction pathways.

**This information will be provided in a new figure called Fig. S2, which is included as supplementary material to Roldin et al. (2010). We will provide a reference to this figure (The figure can be found in the separate document: “Gas to particle partitioning of organic compounds in ADCHEM”).

6. Section 2.7: I found this exercise very interesting. Based on these results, instead of using the measured size distribution at Vavihill as representative upwind Malmo conditions, you could use 8% higher particle number concentrations than the measured background values at Vavihill.

Yes, one could add 8 % higher particle number concentration than the measured background values at Vavihill and then you would get closer to the measured background values at Vavihill with the model. However, it is not a linear problem and the particle losses are varying with particle size. An exact agreement between the model and measurements at Vavihill would require that one runs the model many times until one finds the appropriate background values (trial and error). We agree that this is an interesting method to explore. However, the 8 % deviation is considerably lower than the uncertainty of the background particle number concentration, which is approaching 20 % (Page 18750, lines 8-9). Hence, for these case studies, we gain little in accuracy and we choose not to pursue this issue further.

7. Section 2.8: The authors should give more information for the simulation run without the anthropogenic gas emissions. In that case, are POA emissions treated as non-volatile? This would probably introduce an error in the estimated effect of the secondary aerosols as the concentration of POA would be increased. If the 2D-VBS theory is still used, how exactly the oxidation products of the low and semi-volatile organic compounds are being excluded? Part of OA is emitted and remains in the aerosol phase for its entire atmospheric life and therefore should be considered POA. Another part is emitted in the aerosol phase but it can evaporate in lower OA conditions and oxidized during its trip to Vavihill and re-condense in the aerosol phase forming SOA. Probably the correct way would be to allow the gas-particle partitioning of OA but ignore the ageing reactions.

Yes, we agree. We will extend the description about the simulation run without the anthropogenic gas emissions. The POA emissions were not treated as non-volatile for any of the simulations. The emissions of POA within the city which initially is in the particle phase were assumed to be equilibrated quickly between the gas and particle phase before reaching the urban background station in Malmö. The POA which then was detected in the particle phase will not continue to evaporate in any large extent after the city, but the POA which already has been evaporated will be able to condensate back onto the particles again. It was this pool of SVPOA which originally is in the particle phase but which was assumed to have been evaporated before reaching the urban background station that was removed for the simulation runs without anthropogenic gas phase emissions in Malmö. With this method you likely overestimate the condensation growth rate by organics since the POA will probably not have enough time to equilibrate from the street canyon until the urban background station in Malmö (just from a few minutes up to 1 hour). For the new model runs which we will perform we will not assume that the emitted POA is equilibrated quickly between the particle and gas phase. Instead we will assume that all POA initially is found in the particle phase and then part of it will slowly evaporate downwind Malmö. The POA will then be treated identically for the model runs with and without anthropogenic gas phase emissions in Malmö. The IVOC emissions (C* between 104 and 106 $\mu$g/m3) will however be removed over Malmö for the model runs without anthropogenic gas phase emissions in Malmö. In other words for the model runs without anthropogenic gas phase emissions the emissions of NOx, SO2, all alkenes, alkanes, CO, CH4, BTX and IVOCs will be removed. Everything else will be identical between the two model setups.

8. Page 18746 line 15: Please provide reference for the updraft velocity. In addition the authors should provide information for the values of the rest parameters that constrain the model results (i.e. accommodation coefficient).

We will provide a reference for the updraft velocity. Rogers and Yau, 1989 write that for typical stratus clouds the updraft velocity is a few tens of centimeters per second, while for cumulus clouds the updraft velocities are in the order of meters per second. We use an updraft velocity of 1 m/s for our cloud model. We will extend the adiabatic cloud parcel model description and provide information about the values for the important parameters. The mass accommodation coefficient of the condensing water and the thermal accommodation coefficient used to calculate the thermal conductivity of the latent heat release of evaporating water were set equal to one.

9. Page 18750 lines 8-9: This sentence implies that the authors have not actually cal-

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culated the ground number concentration error. Instead, they have assumed that this error should be less than 20%. If that is the case, I suggest adding a more comprehensive discussion about what led the authors to make such an assumption and also avoid referring in arbitrary numbers. Otherwise, please re-write this sentence in order to avoid this misunderstanding.

It is true that we have not provided a thorough explanation why we have assumed that the error should be maximum 20%. There are two uncertainties explaining why we chose this value. First, an instrumental error and second, an error appearing when choosing an appropriate background size distribution for Malmö. During a DMPS/SMPS intercomparison performed in the laboratory of the IFT at Leipzig, Germany it turned out that different measurement systems agreed within ±10 for the size range 20-200 nm diameter for a simulated aerosol size distribution with total particle number concentrations of a few thousands particles cm-3 (Wiedensohler, et al., 2010). Since our Vavihill instrument also contains similar components and similar inversion routines, which closely follow the protocol for measurement procedures employed at the intercomparison at IFT, we are confident that our own instrument would also have fallen within this ±10% error range if our system was to be included in the intercomparison. However, in background environments also particles below 20 nm diameter have a large influence on the total particle concentration. Also, the instrument control and maintenance is not as thoroughly supervised as in the lab at IFT and total number concentrations span over several magnitudes (Wiedensohler, et al., 2010). As mentioned above we also have an error arising from the choice of the background size distribution. Since we calculate the average of 26 different cases, we are however confident that the total uncertainty should not surpass the ±10% error by more than a few percent. With a conservative choice of uncertainty of ±20% we should therefore be on the safe side. A condensed version of this discussion has been added to the manuscript.

10. Page 18752 line 19: What is the physical meaning of the negative contribution (-0.01) of SA to the total PM2.5 mass?

The negative SA contribution occurs since the oxidizing capacity within the urban plume decreases (e.g. the OH and O3 concentration decreases) and therefore BVOCs, AVOCs, SO2 and NO2 are oxidized slower within the urban plume than outside. After a short distance downwind of Malmö this is however compensated by the higher concentrations of AVOCs, SO2 and NO2 within the urban plume compared to outside the urban plume. We will include a short explanation to the negative SA contribution in the article.

11. Figures 6, 7, 8: It would be interesting for these figures to display the modeled contributions of POA and SOA separately.

Yes we agree that this would be very interesting. However, with the present version of the model using 2D-VBS the organic compounds are not separated into POA, SOA , biogenic and anthropogenic. The organic compounds are only separated into different volatility (C*) and O:C-ratios. With the 2D-VBS it is possible to distinguish between non-oxidized POA (POA which stay in the particle phase and does not evaporate) and the rest of the organic compounds. So, at least this separation will be performed and illustrated with figures.

Technical corrections:

1. Page 18733 line 18: replace “Therefore is it important. . .” with “Therefore it is important. . .”

2. Page 18741 line 23: “. . .criteria 1 to 6. . .” should be “. . . criteria 1 to 5. . .”

3. Page 18742 Eq. (1): The Ctraffic(Dp) should be on the numerator.

4. Page 18745 line 13: insert comma after “Malmo”.

5. Page 18748 line 4: “Fig 4a and b” should be “Fig 3a and b”

We appreciate these corrections.

Reference list:

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Pirjola L. and Kulmala M. Modelling the formation of H2SO4-H2O particles in rural, urban and marine conditions. Atmos. Res., 46, 321-347, 1998.

Rogers R. R. and Yau M. K.. A Short Course in Cloud Physics 3rd Edition. Pergamon Press, Oxford, Great Britain ISBN: 0-08-034864-5, 1989.

Roldin P., Swietlicki E., Schurgers G., Arneth A., Lehtinen K. E. J., Boy M. and Kulmala M. Development and evaluation of the aerosol dynamic and gas phase chemistry model ADCHEM. Atmos. Chem. Phys. Discuss., 10, 18731-18780, 2010.

Wiedensohler A., Birmili W, Nowak A. et al.. Particle Mobility Size Spectrometers: Harmonization of Technical Standards and Data Structure to Facilitate High Quality Long-term Observations of Atmospheric Particle Size Distributions. Manuscript in preparation.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/10/C9916/2010/acpd-10-C9916-2010-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 18731, 2010.