Atmos. Chem. Phys. Discuss., 8, S3745–S3758, 2008
www.atmos-chem-phys-discuss.net/8/S3745/2008/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “A computationally-efficient secondary organic aerosol module for three-dimensional air quality models” *by* P. Liu and Y. Zhang

P. Liu and Y. Zhang

Received and published: 16 June 2008

Reply to Referee #2

General comments

The representation of SOA is an important part of modeling PM2.5 in atmospheric chemical transport models and it is also computationally expensive. The Liu and Zhang paper presents general areas (calculation of activity coefficients, solving SOA partitioning equations) where CPU calculation time in aerosol models can be reduced. Simulations are performed in a box model in which species concentrations are set at initial values to represent urban and rural conditions with either high or low biogenic VOC concentrations. Runs are performed for 24 hours with only gas and aerosol-phase

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

chemistry (no emissions, transport, or deposition). The optimization of particular parameters is relevant to MADRID 2. The optimized version of MADRID 2 represents significant speed-up over base case simulation while sacrificing some accuracy.

We thank the reviewer for the overall positive assessment of this manuscript. Detailed responses to specific comments and changes incorporated in the revised manuscript are summarized below.

Specific comments

1. Page 7089, lines 1 through 5: Are the hydrophobic and hydrophilic categories mutually exclusive? Are there any OCs that would be included in both hydrophobic and hydrophilic categories?

Reply:

Yes, the hydrophobic and hydrophilic categories are mutually exclusive. No OCs are included in both hydrophobic and hydrophilic categories. If an organic species shows affinity for both organic and aqueous phases, it is chosen as either hydrophobic or hydrophilic, due to the lack of experimental data on thermodynamic properties of mixed organic-inorganic aqueous solutions (Pun et al., 2002).

This has been clarified in the revised paper, see page 4, lines 1-4 from the bottom.

2. Page 7090, line 5: Do hydrophilic compounds form SOA if water is not present? More detail on the hydrophilic SOA model would be helpful.

Reply:

Yes, the hydrophilic compounds are considered to form SOA if water is not present, following the absorption mechanism that is similar to the hydrophobic compounds. This has been indicated in the revised paper. A more detailed description of hydrophilic module has been added in the revised paper, see page 6, second paragraph.

3. Page 7091, line 3-5: How much error does holding Mom constant over the time-step

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

introduce?

Reply:

We use a time step of 1-minute, which is among the smallest time steps used in current 3-D models. While a smaller time step can be used for box model studies, its use in 3-D models is usually too expensive to afford, so the use of 1-minute as a time step to derive the SOA parameterization is adequate in our study.

To address the reviewer’s comment on potential errors by holding Mom constant over the time step, we reduced the time step from 1-minute to 30-sec., the percentage deviations for major gas species and total PM are -10.6 to 3.0, -8.3 to 11.9, -8.3 to 12.1 and -8.2 to 4.2 for rural HBG, rural LBG, urban HBG, and urban LBG conditions, respectively. The CPU time increases by a factor of 2 under all conditions. Such errors may increase when the time step is further reduced, however, the use of time step less than 1-minute is currently not realistic for 3-D model simulations, as stated previously.

4. Page 7091, line 26: Should urban and rural air have the same NMHC speciation? Probably not. Comment on using the same distribution for rural and urban air. In Table 1, indicate which NMHCs use the Griffin distribution.

Reply:

We agree that using the same NMHC speciation for urban and rural conditions may not be very accurate. On the other hand, most current studies use the same NMHC speciation for all atmospheric conditions because of lack of data. We are not an exception. For example, Griffin et al. (2002) used the same speciation to split total NMHCs into a number of species for the entire domain including both urban and rural areas. Pun et al. (2003) also used the same speciation over the entire simulation domain for their modeling of an episode from the Nahville/Wstern Tennessee study. The limitation has been indicated in page 9, lines 3-5.

In Table 1, the Griffin distribution is used for ETHE, ALKL, ALKM, ALKH, OLEL, OLEH, AROL, AROH, ISOP, BIOL, and BIOH, which has been added in the footnote in Table 1.

5. Page 7093, line 1: Why do rural HBG calculations take more time than urban HBG calculations?

Reply:

Compared with conditions with low biogenic VOCs, higher CPU costs are required under high biogenic VOCs conditions, due to the abundance of biogenic SOA precursors that are formed from the oxidation of their parent species and will partition into particulate phase. Such oxidation and partitioning are affected by concentrations of other relevant species such as anthropogenic SOA precursors and the total oxidation capacities. For example, aerosol-phase activity coefficients are a strong function of aerosol composition which is affected by their gaseous precursors. Under the rural HBG condition, the concentrations of anthropogenic SOA precursors such as lumped long chain alkanes (ALKH) (e.g., 0.075 ppb under rural HBG and 0.225 ppb under urban HBG), and other gases (NO2) (0.5 under rural HBG vs. 15 ppb under urban HBG) are relatively low, which affect the composition of species in the hydrophilic and hydrophobic modules. The rural HBG condition is more computationally-expensive than the urban HBG condition, because the calculation of activity coefficients for hydrophobic and hydrophilic SOA precursors using UNIFAC requires more significant CPU and the solution to their partitioning equations takes more time steps to converge under such conditions. For example, the UNIFAC subroutine is called by 5,710,164 times under the rural HBG condition and only 1,619,993 times under the urban HBG condition.

To address the reviewer’s comment, the reasons have been given in the discussion, see page 10, lines 1-3 from the bottom, and page 11, lines 1-6.

6. Page 7094, lines 4-17: Were other combinations of speed-up parameters examined or just the three solvers mentioned here?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Reply:

There maybe some misunderstanding here. We tested only one solver (instead of three) for partitioning equation but with three sets of solver parameters in order to identify a set of solver parameters with maximum speedup. The results shown in Figure 1 include results using the three sets of solver parameters. The results with other combinations of speed-up parameters are shown in Figure 2.

7. Page 7095, Section 3.4: The parameterization of activity coefficients is for the hydrophilic SOA only. Did you investigate parameterizing the activity coefficients for the hydrophobic SOA?

Reply:

Yes, we tested the parameterization of activity coefficients in the hydrophobic module using the same multiple regression method, but the results gave large deviations as compared with benchmark. This could be attributed to several reasons. First, the larger number of molecular entities and functional groups treated in the hydrophobic module than in the hydrophilic module (10 and 16 vs. 7 and 10) increases the uncertainties in the parameterization using the linear multiple regression approach. Second, the R program we used has a size limit for the input data, which limits the use of a very fine temperature interval for the hydrophobic module(i.e., we used 0.5 K for the hydrophilic module but 1.0 K for the hydrophobic module between 253 -313 K).

The hydrophilic module takes most CPU cost under the four conditions (65-97%). The parameterization of activity coefficients in the hydrophilic module therefore provides a major speedup. While the parameterization of activity coefficients in hydrophobic module may provide additional speedup, it is subject to the aforementioned uncertainties and introduces larger errors in the activity coefficient calculation. We therefore did not include it in this paper at this point. The speed-up of hydrophobic module using other methods certainly warrants further study in the future.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

These points have been added into discussions, see page 11, second paragraph and page 16, lines 1-4 from bottom, page 17, lines 1-9.

8. Page 7096, equation (3): Consider removing the c parameter from the equation and discussion since it is set to zero. Identify which species the subscripts stand for in Table 4. Why did you choose this parameterization over tabulated activity coefficients?

Reply:

In looking into the value of C, we double checked all independent variables used to derive the polynomial equation and found that the concentration of the 7th species was inadvertently considered as an independent species in the polynomial equation. Because the sum of the concentrations of the 7 species must be equal to 1, the concentration of the 7th species (i.e., water) depends on the sum of the six species, making it a dependent variable. With this update, the parameter c is actually non-zero, as shown in the updated Table 4. All the results (therefore conclusions) remain very similar with the updated parameterization.

In Table 4, a species subscript has been added to 1 to 6, i.e., as 1,j, to 6,j to identify the  values for each species, where the species indice i = 1 to 7, representing 5 hydrophilic surrogates, butandioic acid, and water. The five surrogates include propandioic acid (C2), dien-dioic acid with an aldehyde branch (C8), hydroxy-dien-dial (C8), hydroxy-carbonyl acid with one double bond (C9), hydroxy-carbonyl aldehyde (C10).

Both lookup table and polynomial fit are typical methods of speed up used in 3-D models for large amount of input data. For this particular speedup, the broad range of atmospheric chemical and physical conditions requires a look-up table with substantial amount of data for tabulated activity coefficients, resulting in a file size of several hundred megabytes to several gigabytes. In addition, some interpolation may still be needed when using lookup data if the simulated conditions lie between two points in the lookup table. Overall, we believe that the parameterization with a desirable accu-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

racy that is developed based on 1.16 Œ 108 simulations in our study is most efficient and user-friendly than tabulated activity coefficients.

9. Page 7097, line 2: What is the difference between MADRID 2 Fast and comb_all mentioned on the previous page?

Reply:

All speed-up methods used in comb_all are indeed used in MADRID 2_Fast, so there is no difference between MADRID 2_Fast and comb_all.

This has been clarified in the revised page 18, lines 8-9.

10. Page 7097, Section 3.5: Species concentrations (like NO) decrease to very low levels during simulations presumably due to the fact that emissions are turned off. What PM concentrations do you have at the end of 24-hour simulation? Since the VOCs are essentially oxidized during the 24 hours and aerosol is not removed by deposition, do SOA concentrations become unrealistically high? Have you run MADRID 2 Fast for 24 hours in CMAQ in one box with emissions, deposition, transport etc. turned on? How do the gas phase and PM concentrations compare to a base case simulation (with SMVGEAR and no optimization in the SOA module)? I know you mention in the conclusions that this will be put into CMAQ, but an initial examination of MADRID 2 Fast with CMAQ would be helpful since species concentrations would remain more realistic throughout the simulation.

Reply:

The limitation of the box model was stated clearly in the second sentence under section 2.2, namely, “Other atmospheric processes such as emissions, dilution, transport, removal, and aqueous-phase chemistry are not included in the box model”. So, it is not surprising that the mass concentrations of secondary PM2.5 accumulate over the simulation period. The reviewer is correct that lack of emissions in the box model helps explain very low NO, but this should not be a problem in

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

3-D models in which emissions of NOx are included.

In our box model testing, the total PM concentrations are 64.3, 24.2, 95.7, and 54.2 μg m-3 under the rural HBG/LBG and urban HBG/LBG, respectively, at the end of 24-hour simulations. SOA concentrations are high due to a continuous VOCs oxidation, i.e., 41.0, 2.6, 60.8, and 19.0 μg m-3 under the rural HBG/LBG and urban HBG/LBG, respectively, at the end of 24-hour simulations. While those values appear high under typical ambient conditions, they may still fall into range of the observed values. For example, Heald et al. (2008) reported that daytime mean total observed organic carbon concentrations range from 4 to 456 g m-3 over North America. Since the focus of the box model simulations is to explore various speed up methods for SOA calculation, the box model neglecting removal and transport processes but treating all major chemical and kinetic processes of aerosols should be adequate for our study.

To address the reviewer’s comments, we’ve tested CMAQ-MADRID 2_FAST against CMAQ-MADRID 2 for 24-hr and the results are realistic. The spatial distributions of daily mean absolute and percentage differences of simulated hourly O3 and 24-hr average PM2.5 by both simulations show negligible differences. For example, the absolute differences for O3 concentrations are from -0.02 to 0.02 ppb (with percentage differences of -0.07 to 0.1%), and those for PM2.5 concentrations are from -0.60 to 0.06 μg m-3 with percentage differences of -6.1 to 1.5%.

These results have been added in page 19, lines 8-11.

11. Figure 3d: PM deviates by almost 20% under some conditions. Is any of this deviation due to the inorganics? What PM concentration (in μg/m3) does the largest deviation correspond to?

Reply:

In Figure 3d, the large deviations of 15% in PM2.5 occur at high RHs such as 80%, and are associated with both organics and inorganics: the hydrophilic SOA and ammonium (e.g., their deviations are -34.1% and -30.6%, respectively, under the rural HBG condition with an RH of 80% and a temperature of 313 K). Others inorganics such as sulfate and nitrate have less deviations (-0.4% to 0.3% and -1.3% to 0.0%, respectively).

The largest deviation corresponds to relatively high PM2.5 concentrations. For example, PM2.5 concentrations change from 55.1 in MADRID 2 to 37.2 μg m-3 in MADRID 2_FAST under the rural HBG condition with an RH of 80% and a temperature of 313 K. Higher RH can result in a higher effective Henry’s law constant that subsequently favors the hydrophilic SOA formation. The extra water associated with hydrophilic OC causes additional partitioning of the inorganics to the aqueous phase (Pun et al., 2002). So MADRID 2_FAST under such conditions may cause the deviations in both hydrophilic SOA and inorganics, especially ammonium, as compared with the case without any speed-up.

The above points have been added in the discussion, see page 18, line 1 from the bottom, and page 19, lines 1-7.

Technical corrections

Paper should have been edited more thoroughly for errors and clarity before submission. 1. Page 7086, line 24 through page 7087, line 1: Rewrite sentence The formation of SOA . . . condensable products. for clarity

Reply:

This sentence has been rewritten, see page 2, first paragraph.

2. Page 7087, line 4: Replace posts with poses

Reply:

The typo has been corrected.

3. Page 7087, line 22: Are hydrophilic compounds treated in MADRID 1 or are they

treated using something other than Henry’s law? Please clarify sentence.

Reply:

The hydrophilic compounds are not treated in MADRID 1, but they are treated based on the Henry’s Law only in MADRID 2. This has been clarified, see page 3, the first paragraph.

4. Page 7087, line 16 through 20: Rewrite sentence First, both . . . derived by Pankow et al. 1994. for clarity

Reply:

This sentence has been rewritten, see page 3, first paragraph.

5. Page 7088, line 1: Replace SOA module with the SOA module

Reply:

The suggested change has been corrected.

6. Page 7088, line 4: Rename section

Reply:

The section has been renamed as “Model description”.

7. Page 7088, line 19: Replace SOA module with the SOA module

Reply:

The suggested change has been corrected. .

8. Page 7089, line 13, 20: Equation 1 & 2 citation should be Pankow not Pun/Zhang.

Reply:

The citation for Equations 1 and 2 has been corrected as “Pankow et al. (1994a, 1994b)”.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

9. Page 7090, line 3: Replace stop with continue

Reply:

The suggested change has been corrected.

10. Page 7091, line 6: Replace condition with conditions

Reply:

The suggested change has been corrected.

11. Page 7091, line 11: Replace , with :

Reply:

The suggested change has been corrected.

12. Page 7092, line 26: Replace second with seconds

Reply:

The suggested change has been corrected.

13. Page 7093, lines 6-9: Rewrite sentence

Reply:

The sentence has been rewritten.

14. General comment: MAXIT and MAXITS are both used. Pick one name. Also Mom sometimes has a bar over it and sometimes does not.

Reply:

MAXITS should be used. MAXIT has been replaced by MAXITS throughout the paper.

and denote different variables:

Mom (μgm-3 air) is the sum of concentrations of primary (non-volatile) organic

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

carbon (semivolatile) in the particulate phase that serve as the organic absorbing medium.

is the average molecular weight of the organic absorbing medium.

To avoid confusion, Mom has been changed to MTOM.

15. Page 7095, line 26: Rewrite sentence Multiple linear . . . process. for clarity

Reply:

This sentence has been rewritten, see page 15, lines 3-7 from the bottom.

16. Page 7097, line 16: Figure 4 is missing.

Reply:

It is not clear to us why this figure was missing, as it was included in our original submitted version. Nevertheless, it has been added back in the revised version.

17. Table 2: What do column headings Sect. 1 and Sect. 2 mean? Are they size sections? What sizes?

Reply:

Yes, they are particle size sections. A footnote on this has been added in Table 2 to clarify this.

18. Table 3: Is x the same as Ai (the aerosol phase concentration of species i)?

Reply:

Yes, it has been rewritten as Ai.

19. Table 3: Clarify the purpose of ALF.

Reply:

In the Line Search method, the ALF is the rate of the decrease of function values that

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

ensures the convergence in the calculations. In other words, the ALF helps to satisfy the Goldstein Amijo condition which guarantees the convergence of the algorithm. This has been clarified in Table 3.

20. Figure 3: Specify in the caption that MADRID 2 Fast is used.

Reply:

MADRID 2_Fast has been added in Figure 3 caption:

References

Griffin, R. J., Dabdub, D., Kleeman, M. J., Fraser, M. P., Cass, G. R., and Seinfeld, J. H.: Secondary organic aerosol 3. Urban/regional scale model of size- and composition-resolved aerosols, J. Geophys. Res., 107(D17), 4334, doi:10.1029/2001JD000544, 2002. Heald, C. L., A. H. Goldstein, J. D. Allan, A. C. Aiken, E. Apel, E. L. Atlas, A. K. Baker6, T. S. Bates, A. J. Beyersdorf, D. R. Blake, T. Campos, H. Coe, J. D. Crounse, P. F. DeCarlo, J. A. de Gouw, E. J. Dunlea, F. M. Flocke, A. Fried, P. Goldan, R. J. Griffin, S. C. Herndon, J. S. Holloway, R. Holzinger, J. L. Jimenez, W. Junkermann, W. C. Kuster, A. C. Lewis, S. Meinardi, D. B. Millet, T. Onasch, A. Polidori, P. K. Quinn, D. D. Riemer, J. M. Roberts, D. Salcedo, B. Sive, A. L. Swanson, R. Talbot, C.Warneke, R. J. Weber, P. Weibring, P. O. Wennberg, D. R. Worsnop, A. E.Wittig, R. Zhang, J. Zheng, and W. Zheng, Total observed organic carbon (TOOC) in the atmosphere: a synthesis of North American observations, Atmos. Chem. Phys., 8, 2007–2025, 2008. Hine, J., and P. K. Mookerjee: The intrinsic hydrophilic character of organic compounds: correlations in terms of structural contributions, J. Org. Chem., 40, 292-298, 1975. Pankow, J. F.: An absorption model of gas-particle partitioning of organic compounds in the atmosphere, Atmos. Environ, 28, 185-188, 1994a. Pankow, J. F.: An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol, Atmos. Environ, 28, 189-193, 1994b. Pun, B. K., Wu, S.-Y., Seigneur, C., Seinfeld, J. H., Griffin, R. J., and Pandis, S. N.: Uncertainties in modeling secondary organic aerosols: Three-dimensional modeling studies in

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Nashville/Western Tennessee, Environ. Sci. Technol., 37, 3647-3661, 2003. Pun, B. K., Griffin, R. J., Seigneur, C., and Seinfeld, J. H.: Secondary organic aerosol, 2. Thermodynamic model for gas/particle partitioning of molecular constituents, J. Geophys. Res., 107(D17), 4333, doi:10.1029/2001JD000542, 2002. Suzuki, T., K. Ohtaguchi, and K. Koide: Application of principal components analysis to calculate Henry’s constant from molecular structure, Comput. Chem., 16, 41-52, 1992.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 7085, 2008.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper