Atmos. Chem. Phys. Discuss., 10, C9622–C9633, 2010
www.atmos-chem-phys-discuss.net/10/C9622/2010/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "SOSA – a new model to simulate the concentrations of organic vapours and sulphuric acid inside the ABL – Part 1: Model description and initial evaluation" *by* M. Boy et al.

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Received and published: 11 November 2010

"SOSA – a new model to simulate the concentrations of organic vapours and sulphuric acid inside the ABL – Part 1: Model description and initial evaluation"

Michael Boy, et al.

First of all we want to thank both reviewers for their very constructive comments to improve the quality of this manuscript. Following we will respond to each single comment. Most statements are in the way that we will use the advice and correct the manuscript as recommended or add the requested item. In some cases we did not agreed completely with the reviewers and we will point or explain our opinion more clearly.

Detailed item-by-item response of the reviewer comments:

Referee 1:

* Application of a 1D-model requires a rather homogeneous surface to prevent disturbances by slanted wind pattern to affect the results. In this respect the field forest site SMEAR II in Hyytiälä is exemplary. Has the model been tested at other sites/conditions, too?

Not until now but in the near future we plan to set up the model for the Manitou forest station in the front range of the Colorado Rockies in Colorado, USA.

* How much detail and how many errors have been omitted by averaging for 30 min? I am aware that the usual data collection uses this time frame, but what about the model? What is the necessary time resolution essentially required?

The gas concentrations in Hyytiälä are measured every 6 minutes and met-data are of course achieved with a much higher resolution. The model runs with a time step of 10 s for the meteorology and 60 s for the chemistry, but to include this high temporal resolution as input for all the input variables for several years would lead to a huge input memory. In the model runs we linear integrate between the 30-minute values and ignore short time peaks of certain parameters for the gas concentrations. The met-data are only used for the nudging and in this case are not crucial for the predictions.

* p. 18613/18614: Please check the variable(s) $A\varphi$ (p. 18613, eq. 12) and $A\Phi$ (p. 18614, l.5). Are these two identical or not?

Corrected, it should be $A\varphi$

* It seems that the nudging is essential. Interpolation has been made for datasets of every 6 hs. Would there be a benefit in increasing this for the results? How far the model deviates in the absence of nudging, thus for prognosis?

The model results depend on many factors. Even with given profiles of air temperature in free atmosphere (above ABL height) and geostrophic wind, the solution will be depend on the selected surface moisture (values that are not well known for area affecting footprint of measurements). Under given isolation this value will dictate the Bowen ratio and as such heat flux value and in its turn all characteristics in the ABL. We mentioned in the paper that our task is reproducing measured characteristics as close as possible to decrease the uncertainties in the calculation of the chemical species and for this reason the nudging procedure was applied. In our opinion the answer to your question can be considered as a separate issue for investigation mostly concerning model sensitivity study. But this has been done in a number of studies with SCADIS referred in the paper.

* The vegetation is known to have a slightly elevated temperature compared to the atmosphere. How is this treated in the model? I know that a model cannot capture everything but this would have strong effects on the emissions!

This is true only partly, namely such situation is typical only for fair weather in midday time. The model capture this effect solving balance equations for sunlit and shade leaves. The procedure is described in a study referred in the paper (e.g. Sogachev et al., 2002).

* What is the "negligible" deviation for a chemistry time-step of 60 s? It Would be nice to show a plot for deviations or agreement for the time-steps between 5-300 s with respect to chemistry. That would strengthen the arguments more and help others to use the approach later on.

One figure with a short interpretation with time-steps 10, 30, 60, 120, 300 and 1000 s will be included in the final version of the manuscript.

* p. 18620, l.17f: Please write all the listed monoterpenes correctly: (alpha-pinene, beta-pinene, limonene, carene, sabene and camphene).

Will be corrected in the final version

* Please make a very important comment on using two exemplary monoterpene schemes for the complex mixture and its effects on inorganic chemistry. Since the entire mixture of monoterpene species represent reaction rate constants with the individual oxidants varying by about 4-5 orders of magnitude this is essential for closing OH budgets, ozone and NOx-cycles etc. This interferes strongly with the supposed implementation of new particle formation and its link to OH.

There is a misunderstanding by the reviewer; we used for the first order reaction of the monoterpenes all the single reaction rates corresponding to each monoterpene. For alpha- and beta-pinene we used the complex MSM-mechanism because for other mono-terpenes these codes are not available until now. However, the OH-sink term concerning terpenes should be correct and only the second-reactions-sink includes an underestimation. Parallel to this article we are nearly ready to submit one paper where we present the OH-reactivity modeled with SOSA. The results show that for several organic compounds including alpha-, beta-pinene, methane and others the OH-sink-term for second order reaction is below 10 % in comparison with the first-order reactions of organic and inorganic compounds. We will point this more out more clearly in the final version of the manuscript to avoid further misunderstanding.

* In general the model is a very interesting tool to study the important aspects such as missing OH-reactivity (OH-sink). However, the assumption of two selected monoterpenes I suppose only a single one of them can only represent the determination of the uncertainty range due to monoterpenes, not the exact pin down of the product k(X+OH)*X!!! This uncertainty taking into account the actual mixture and reactivity of the monoterpenes should be given for later investigations.

Already answered in the last comment

* Text comments on Fig.4: The Deviations between PTR-MS measurements (Rinne et al., 2005) and MEGAN approximations are nothing special. The empirical approach ("simplification") by Guenther et al. (2006) is just an empirical relationship, not a strict

plant physiological approach! Thus 8-14% are quite OK. One should keep in mind the different atmospheric lifetimes of the different monoterpenes e.g. from camphene to limonene. This will certainly affects the vertical and horizontal pattern simulated and its intercomparison with ambient measurements. Please take this into account when discussing Fig. 4.

Yes this is correct but as the PTRMS only measures the sum of the all monoterpenes and in the comparison we add up the single monoterpenes with consideration of their lifetime including the different reaction rates the results should be the same and as mentioned by the referee the 8-14 % difference is surprisingly good.

* Fig.4: Plotting a logarithmic vertical axis would be beneficial. Moreover the indication of the measured values inter-compared with would allow a direct visualization of the statements made. This can be either by averages as made for the modeling output or by individual days. If this is supposed to be shifted to a supporting online information, OK.

We tried and compared the 2 figures (linear and logarithmic) and came all to the final result that a logarithmic plotting for the vertical axis is not improving but more decreasing the visible message of the figure and came to the conclusion that we will prefer to keep the figure at it is. Also considering that the x-axis is in logarithmic scale the visualization of the comparison with the PTRMS data would not be visible (just one line on top of the other).

* The nighttime effects of the vertical monoterpene profile reduction includes not only physical, chemical and meteorological mechanisms but partially compensates each other. I.e. chemical reactions with NO3 at nighttime do express at different and usually less intense speed than with OH at daytime resulting in a longer atmospheric lifetime. The mixture of individual monoterpenes might also change throughout the day depending on the source terms and pools emptied for emission. At night the plants surface is expected to be wet (high humidity) and thus has different properties than during

daytime. How is this being treated in the model?

The arguments of the referee are complete correct and we would be happy if we could include some kind of daily profile for single monoterpene standard emission potentials (SEP). However, these input values are not available at the moment and facing the lag of a really well established seasonal SEP-profile we believe that it will take a long time until this will be available. However, in the model MEGAN we calculate of course the emission activity based on changing meteorological conditions which, however, not differs between the single monoterpenes. Also the wet surface of the plants in the night times are not considered until now in the model because the knowledge how this will influence the emission of the plants is still far away from being complete.

* The remarks on nucleation mode particles and the shape of organic vapours as well as sulfuric acid and OH are worth a comment: Since OH (in combination with the atmospherically rather stable SO2) is the basic source of H2SO4 the profile essentially depends on the sink terms. If short lived any compounds originating by an OH-related reaction will display the same behaviour and thus act as a good marker for OH. The monoterpenes emitted from the biosphere display certainly a notable vertical profile due to their source only at the surface and their chemical degradation with increasing distance from the emission site. Monoterpenes however are not directly involved in particle formation and growth but their oxidation products. Thus, the rate of reaction with ozone and the one with OH will display different behaviour with the latter most likely similar to H2SO4. The similarity of nucleation mode particles with monoterpenes is an interesting phenomenon but is to be considered similar to a correlation with SO2 if multiple oxidation pathways needed to be considered, that haven't to be.

In this point I not complete agree with the referee and want him to have a look at one paper we published parallel at ACPD (Lauros et al, 10, 20005-20033) with the model MALTE which includes the aerosol dynamic code UHMA. In this paper we should it comparison with measured vertical particle number concentrations that a only on sulfuric acid based nucleation theory in comparison with a sulfuric acid and monoterpene-

OH reaction based theory shows a complete different picture specially at the entrainment zone and above. In SOSA until now we do not have aerosol dynamic included but the clear difference in modeled H2SO4 concentrations with measured vertical particle concentrations is obvious. As soon as monoterpenes included in any nucleation theorem the vertical profile will be shifted to a more realistic way with much lower values of new formed particles above the ABL as measured in many field campaigns.

* It would be beneficial to see a clear mechanism related vertical profile to distinguish. However, this is currently not available. But if so the complexity of the process might interfere because a multiple step related nucleation process is feasible complicating the intercomparison of simulation and reality.

At the moment, as mentioned we do not understand the formation mechanism, however as pointed out in the manuscript participation of one compound which is emitted from the canopy or soil is favorable.

* Conclusions: Reduce the starting paragraph. Challenges of 1D-models are apparent as well as the need but missing of meteorological as well as chemical values to run the code. Interesting would be the intercomparison of H2SO4 on the vertical scale to provide a base for mechnistic tests. Also the future implementation of the UHMA code (Korhonen et al., 2004) is highly encouraged and an excellent idea.

Yes if the referee could provide us with measured vertical profiles of H2SO4 we are very happy. The implementation of UHMA in SOSA will be finished until the end of this year.

Referee 2:

* p. 18609, line 4: I suspect that the ozonolysis of sesquiterpene leads to the formation of low-volatile oxidation products (but not to “very volatile” ones). The low volatility of these products favour their involvement in gas-to-particle conversion.

Yes this is correct and we will use the words low-volatile in the final version

* p. 18612-18613, Eqs. (5)-(7), (9): To avoid confusion with standard deviation of velocity components (see Fig. 1e) I recommend the use of α for the Prandtl and Schmidt numbers (instead of $\sigma{-1}$), respectively, as introduced in the original paper of Sogachev et al. (2002). Please check the paramerisation of the Prandtl number according to Eq. (5) for the case Ri > 0. It does not agree with the formulation in the original paper.

For two-equation models using σ for the Schmidt and Prandtl numbers is more general, thus we prefer still use this notation. Sogachev et al. (2002) used another closure model. However, to avoid confusion of the reader, we still keep subscripts for different variables. In fact, in figure 5e we used such subscripts to remark standard deviations of different velocity components (σu,v,w). There is no any restricted parameterizations for σH,Q and as such we used better one from our point of view. However, because the idea used this kind of dependency and basic constant 1.35 was originally proposed by Businger et al-. 1971 we just a slightly change in the reference to this paper as (e.g. Businger et al., 1971).

* p. 18613, Eqs. (7), (14): Define or correct the parameter C-w2.

There was the mistake in reproduction of equation. It should be Cw2 -. Corrected.

* p. 18613, Eq. (12): I found the canopy parameterisation very interesting. The ansatz to define ST contains additional predictive parameters, such as the scalar properties of the sunlighted and shaded part of the canopy. Are the sunlit properties derived from an energy balance equation, the shaded ones from a diagnostic parameterisation? I recommend to add a few sentences to explain the closure of the canopy parameterisation, at least in a qualitative way.

Temperature of sunlit and shaded part of leaves solved from energy balance equation at each grid levels considered in the model. Predictive parameter in the model is air temperature, thus both temperatures of leaves fraction as well as their incellular moisture are defined from diagnostic equation using information about turbulence regime inside canopy and incoming radiation at each levels. We insist to keep our paper as short as possible, because it is not simple to describe all parameterization in a few words, but we provide references.

* p. 18614, lines 5, 7: Use correct style Aφ and φ (instead of AΦ and Φ). ... φ is the placeholder for the atmospheric value of the scalar.

Corrected, it should be Aφ

* p. 18614, lines 9-11: Although described in the original paper of Sogachev et al. (2002), I recommend to add at least the physical unit of the integral exchange coefficients [m/s]. I have not re-derived the parameterisation equations, but at least I have checked their consistency by the physical units.

We add dimensionality in the text for clarity.

* p. 18618, Fig. 1: (a) This figure shows the beta distribution (18), i. e., the abscissa depicts f = Ah/LAI. (c) The abscissa shows the normalised momentum flux, i. e., u'w'/u*. Please add overline. (e) The measured values refer to the standard deviations of u, v, and w. To which velocity component the (predicted) solid lines refer? Owing to the dominant contribution of the vertical velocity variance to the TKE and the strong correlation between TKE and the plot in Fig. 1(e), I guess σw is depicted.

The figure and its caption were corrected. In figure 1e, lines show the values (2/3 TKE)0.5, that equals σu,v,w for homogeneous turbulence, assumed in two-equation models.

* p. 18619, line 28: The 1D model is per se not able to capture atmospheric fronts, which are defined by strong horizontal in homogeneities.

To compensate drawback of 1D model we used nudging procedure. It allows getting atmospheric parameters inside forest and above from measurements..

* p. 18620, line 1: Replace "definition of R" by "determination of R".

Corrected

* p. 18620, lines 17-28, Fig. 4: From the presentation of time averaged vertical profiles (averaging over one month) I tentatively concluded, that the monoterpene precursors did not reveal any burst-like behavior. What can the authors say about the diurnal variation of monoterpenes over the plant canopy? (Please check the annotations of chemical compounds.)

We please the referee to give some more explanation for this statement. There are no precursors for monoterpenes because they are emitted from the forest. Yes there is a diurnal variation of this compound with highest concentrations at night resulting from decreases vertical mixing. The annotations of the monoterpenes will be corrected in the final version of the manuscript.

* p. 18621, lines 9-13: I recommend the use of the notion "vertical gradient" in connection with the correct unit: "... vertical gradient of -2.15×109 cm-3 per ABL thickness", or "decrease of ... over the whole ABL" etc.

Correct and we will change the unit to vertical gradient of -2.15x109 cm-3 per ABL thickness.

* p. 18621, line 25: Maybe "an inversion was located at about 1100-1200 m".

Correct will be changed in the final version

* p. 18621, line 26: Either "surface layer" (Prandtl layer) or "mixed layer". Here, maybe "lower part of the ABL below 600 m".

Corrected to "lower part of the ABL below 600 m".

* p. 18622, lines 1-17, Fig. 5: The authors insinuate "strong evidence, that the amount of newly formed particles detected at sizes above 3 nm are more related to the concentrations of organic molecules than to the concentrations of sulphuric acid inside and above the ABL." I recommend the direct inclusion of the cited Figure 9 of O'Dowd et al. (2009) in the present paper. While the particle concentration around noon seems to be correlated with the mixed layer height (not shown but stated in the paper, see next

item), there is obviously no jump of the sulphuric acid profile at the mixed layer height, i. e., sulphuric acid concentration scales with OH concentration. Is the sulphuric acid evolution influenced by any other reacting agents than OH? Seemingly, local ground sources of sulphur dioxide do not play any role. Here, I refer also to the specific comment nb. 13 on p. C7305 of the first reviewer.

The direct inclusion of the figure from the manuscript by O'Dowd et al. is not possible because we do not have the figure and do not want to add another co-author only for a figure which was already published. Sulfuric acid production depends on the concentration of OH and SO2, however because of its very fast condensation onto the particle phase the sink term has to be calculated as precise as possible. Concerning the source for SO2 we just can say that there are not local sources for SO2 from the canopy or soil. This compound is a more anthropogenic gas with a lifetime of several weeks and long-range transport from north or southern Europe are the main origin of SO2 over Hyytiälä.

* p. 18622, line 23: Please add the criterion for the determination of the mixed layer height. It is obviously not a predictive property. This is of importance because of the "excellent agreement with the measurements of vertical particle profile"! What is the vertical grid resolution at this height?

We add criteria for definition of ABL height in figures caption. The text of the paper was slightly corrected because the resolution here was not enough (about 50m) to catch exact value of 604 m (actually measurements cannot also indicate this with such accuracy).

* p. 18623, line 22: "cannot"

Will be corrected

* Figures: The annotations in nearly all figures are too small in the ACPD format. Figures should be enlarged.

We will increase the font size of all annotations in the final figures

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 18607, 2010.