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Interactive Comment

Interactive comment on "Kinetic multi-layer model of gas-particle interactions in aerosols and clouds (KM-GAP): linking condensation, evaporation and chemical reactions of organics, oxidants and water" *by* M. Shiraiwa et al.

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Referee General Comment:

This manuscript describes development of a kinetic model simulating gas and particle phase mass transport and chemical reactions. Developing such a model is timely and the manuscript is for the most part easy to follow. I have, however, a number of suggestions / concerns that should be addressed before the manuscript can be considered for publication in ACP;

Response:

We thank Anonymous Referee #1 for the review and the positive evaluation of our manuscript. The constructive suggestions for improvement are very welcome and will be implemented upon revision. Detailed responses to the individual comments are given below.

Referee Comment 1:

Chapter 2, model description, is on the whole quite long and could be condensed somewhat. Some specific suggestions on this: - Equations 11-13 are quite basic and probably unnecessary - The chapter is filled with equations of the form J=k*[Z]. Perhaps it is not necessary to write explicitly out the specific equation for each combination of subscripts. - The description of equations of chemical reactions on pages 33697-33699 and then again on p. 33701 are largely similar and the latter could be mostly omitted.

Response:

We agree that model description is indeed long and some equations are basic. However, we would like to keep all equations because explicit listing of equations and formulations makes very clear for readers how mass fluxes and chemical reactions are treated and concentrations are calculated in the model. Referees #2 and #3 as well as other interested colleagues asked for more rather than less information.

Referee Comment 2:

Some information on the model should however, be added and/or clarified: Chapter 3.1 mentions that equations are solved in Matlab, chapter 3.2 does not mention anything of such nature and chapter 3.3 mentions Matlab and even the ODE solver used. As the paper presents the new model KM-GAP, this kind of technical information should be described in some detail, and already before chapter 3.

Response:

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In the presented results, the equations are solved using an ODE solver in Matlab. We will add the below sentence in the beginning of chapter 3 in the revised manuscript.

"In this study the coupled differential equations were solved in Matlab software with an ode23tb solver, which integrates a system of differential equations using second and third order Runge-Kutta formulas."

Referee Comment 3:

On p. 33693 (and onwards) it is mentioned that KM-GAP treats each species semivolatile and the distinction between volatile and non-volatile compounds is removed in KM-GAP. Yet the example in section 3.3 implies that the compounds can still be treated as volatile or non-volatile. This feature bears clarification.

Response:

KM-GAP does not depend on restricting assumptions and pre-definition of volatility (volatile or non-volatile) and it can treat species of any volatility using the actual vapor pressure. In the simulation shown in section 3.3, the vapor pressure of oleic acid and other reaction products are assumed to be 0, i.e., for simplicity they are regarded as effectively non-volatile. This simplifying assumption can be removed by inserting actual or estimated vapor pressures of all involved species, which we intend to do in more detailed follow-up studies.

Referee Comment 4:

The authors should discuss the validity of ideal mixture assumption (Eq. 6) for the thin layers of material they are dealing with.

Response:

In chemical transport models ideal mixing is assumed in most cases. Recently, the experimental study by Hildebrandt et al. (2011) suggests quasi-ideal mixing of SOA at equilibrium. Moreover, the assumption of ideality can be removed in KM-GAP if

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activity coefficients are available. We will add the following sentences after eq(16) in the revised manuscript.

"The ideal mixing assumption is also employed in practically all chemical transport models, and a recent experiment is consistent with pseudo-ideal mixing of anthropogenic and biogenic SOA compounds at equilibrium (Hildebrandt et al., 2011). Note that the assumption of ideality can be relaxed in KM-GAP if activity coefficients are available."

Referee Comment 5:

Eq. 22 suggests that 1) the presence of adsorbates always decreases the surface accommodation coefficient compared to an adsorbate-free surface and 2) any accommodation takes place only as the incoming molecule meets a molecule of its own species. These two assumptions are worth mentioning.

Response:

Estimation of αs,Zi is based on a Langmuir adsorption model in which all adsorbate species compete for a single type of non-interfering sorption sites on the quasi-static surface. The presence of adsorbates usually decreases the accommodation coefficient when compared to an adsorbate-free surface. Accommodation takes place if incoming molecules meet a surface site which is not occupied by adsorbate molecules. We will clarify this point by adding the following sentence to the revised manuscript.

"Estimation of αs,Zi is based on a Langmuir adsorption model in which all adsorbate species compete for a single type of non-interfering sorption sites on the quasi-static surface (Pöschl et al., 2007)."

Referee Comment 6:

Eq. 26: is the bulk diffusion coefficient used for the transport between sorption and quasi-static surface layer the liquid or gas phase coefficient?

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Response: It is the condensed phase bulk diffusion coefficient as specified in the equation as Db,Zi (but not Dg,Zi).

Referee Comment 7 & 8:

Continuing from previous comment: the use of diffusion coefficient and bulk diffusion concepts in general seems dubious at best when the situation is such that molecules are moving distances of the order of their own diameter. Could the authors comment on this?

Furthermore, the form J=k*[Z] for the transport equation combined with the estimate for a transport rate coefficient k obtained with Fick's 1st law (e.g. Eq.26) looks unusual: 1) how exactly is Eq. 26 derived? 2) the concentration gradient looks to be between the concentration in a specific layer and a vacuum instead of a difference between the neighboring layers? Also, the subscripts of k in Eqs. 26 and 27 seem to be backwards compared to the notation given in appendix A.

Response:

Based on Fick's 1st law of diffusion, the net flux of Zi from sorption layer to quasi-static surface layer (Js,ss,net) can be described as follows (C is bulk concentration and x is distance)

Js,ss,Zi,net = -Db * dC / dx = -Db * (([Zi]s/ δZi) – ([Zi]ss/ δZi)) / δZi

The net flux is described by

Js,ss,Zi,net = Js,ss,Zi - Jss,s,Zi = ks,ss,Zi [Zi]s – kss,s,Zi [Zi]ss

Comparing these two equations leads to eq(26). Note that eq(27) is not obtained by this direct comparison, because ks,ss is affected by the vapor pressure of Zi as described in the manuscript. Another way to treat bulk diffusion is to directly solve the partial differential equation of Fick's second law. We showed in the appendix of an earlier study (KM-SUB, Shiraiwa et al., 2010) that the two methods agree well, confirming

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that validity of our method and showing that the multi-layer kinetic flux formalism of our model converges with the continuum flux formalism of Fick's law. The subscripts of k in eq(26) and (27) are correct and consistent with Table A1.

Referee Comment 9 & 10:

The transport rate coefficient from quasi-static surface layer to first bulk layer given in Eq. 35 has an added curiosity: if one plugs in Eq. 35 the bulk-to-quasi static coefficient as given by Eq. 34, one sees that the surface-to-bulk coefficient depends on the thickness of the first bulk layer. This appears counterintuitive, why would transport from the surface to bulk depend on the arbitrary, purely computational choice of number of bulk layers. Could the authors comment on this?

The very next equation, Eq. 36, however gives another expression for the transport rate coefficient for quasi-static surface to bulk transport which doesn't make of use of the bulk layer thickness. Even if the subscript b1, denoting 1st bulk layer, of Eq. 35 is changed to b for Eq. 36, it is clear that the two coefficients are the same as any transport from surface to bulk is to bulk layer one by construction of the model. The right hand sides of the two equations are however only equal when the thickness of the first bulk layer is one effective molecular diameter. This discrepancy requires explanation, and specifically it needs to be made clear which expression the model uses.

Response:

Indeed the rate coefficient of transport from the surface into first bulk layer depends on the layer thickness, because the average distance that molecules have to travel increases with the layer thickness. This treatment is the key for multi-layer model approach and this is why the simulation results are not affected by the arbitrary choice of number of bulk layers (Shiraiwa et al., 2010). The overall transport flux from surface to "bulk" is calculated using eq(37), which does not depend on the layer thickness, but this flux is not used to calculate the flux into a certain layer. It is used only to calculate

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the bulk accommodation coefficient which should not depend on the arbitrary choice of layer thickness. We will add the following sentence for clarification and revise the manuscript accordingly.

"Note that the physical parameters kss,b,Zi, Jss,b1,Zi, and αb,Zi do not depend on the bulk layer thickness, whereas the model parameters kss,b1,Zi and Jss,b1,Zi vary with the bulk layer thickness."

Referee Comment 11:

In the sentence starting on line 17 on p. 33701 it is mentioned that an adequately large number of bulk layers is required to ensure that the assumption that each bulk layer is homogeneously mixed. As bulk diffusion is used to describe the fluxes between layers, there is necessarily a limit on how small a layer can be for the diffusion treatment to be reasonable. The authors should comment on this also, and how the two requirements can be reconciled.

Response:

Physically, the lower limit of layer thickness is the molecular diameter. Choosing a smaller thickness is not a problem numerically, but physically it does not make sense. The upper limit of layer thickness for a reasonable treatment of bulk diffusion depends on the bulk diffusivity and the time step used in the simulation (Shiraiwa et al., 2011). With low bulk diffusivity in (semi-)solid matrices, the equilibration mixing time is long so that small layer thickness should be used. Whereas the high bulk diffusivity in liquid matrices, large layer thickness may be sufficient as equilibration mixing time is short. We will clarify by adding below sentences in section 2.3 in the revised manuscript.

"The lower limit of physically meaningful layer thickness corresponds to the molecular diameter of the involved chemical species, and the upper limit for correct treatment of bulk diffusion depends on the diffusivity. In (semi-)solid matrices with low diffusivity, the mixing times are long and concentration gradients can be steep, so that relatively

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thin layers should be used (>10 layers) (Shiraiwa et al., 2011a). In liquid matrices with high diffusivity, the mixing times are short and concentration gradients are small, so that relatively thick layers can provide sufficient resolution (<10 layers) (Shiraiwa et al., 2011a)."

Referee Comment 12:

Continuing on the assumption of homogeneously mixed bulk layers: the authors could comment in chapter 3.3 on how reasonable this assumption is for runs with fewer number of layers (n=5) especially if the assumption is not valid, since they report that the observed results do not change when going from 5 to 200 layers.

Response:

We could go below 5, but then we lose the information of bulk concentration profile. To reproduce the experimental data, one layer is actually sufficient as already shown in the KM-SUB paper (Fig, 2a, Shiraiwa et al., 2010). This is because the degradation kinetics of oleic acid are limited by surface accommodation of ozone, and the bulk diffusion (10-7 cm2 s-1) of oleic acid is fast. For high resolution and to avoid the congestion of the concentration profile plot (Fig. 5), we use a high number of layers.

Referee Comment 13:

In general, it would be good if the authors could demonstrate the sensitivity of their results to the various simplifying assumptions, most importantly: 1) ideal mixing; 2) use of diffusion coefficient as a measure for transport over a layer with molecular thickness. This could be done by a set of sensitivity simulations where the related quantities are varied within a reasonable range.

Response:

As mentioned in the response to Referee Comments 7&8, point 2) was validated by comparison with a partial differential equation method (Shiraiwa et al., 2010). We intend to test the validity of the ideal mixing assumption in follow-up studies, by applying

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KM-GAP to a system for which activity coefficients are available.

Referee minor corrections:

- Eq. 14: in accordance to the notation used elsewhere in the paper subscript X should be Z

- Line 17 on p. 33696: “as described below in Eq. 18” should read “as described above in Eq. 14”

- Line 8 on p. 33697 “i.e. H2O” should probably read “e.g. H2O”, unless the authors suggest H2O to be the only adsorbate species

- Line 9 on p. 33698: subscript bs should be ss

- Line 23 on p. 33699 (Eq. 33): subscript bs should be b1

- Line 3 on p. 33701: psi in parentheses is redundant for this sentence

- Line 20 on p. 33704: “in units of g g-1” is an odd way to say that the ratio is unitless

Response:

Thanks for pointing out these corrections. We will correct them in the revised manuscript. For mass fractions, the unit g g-1 is recommended by IUPAC, so we would like to keep it as is.

References:

Hildebrandt, L., Henry, K. M., Kroll, J. H., Worsnop, D. R., Pandis, S. N. and Donahue, N. M.: Evaluating the Mixing of Organic Aerosol Components Using High-Resolution Aerosol Mass Spectrometry, Environ. Sci. Technol., 45, 6329-6335, 2011.

Pöschl, U., Rudich, Y. and Ammann, M.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions - Part 1: General equations, parameters, and terminology, Atmos. Chem. Phys., 7, 5989-6023, 2007.

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Shiraiwa, M., Pfrang, C. and Pöschl, U.: Kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB): the influence of interfacial transport and bulk diffusion on the oxidation of oleic acid by ozone, Atmos. Chem. Phys., 10, 3673-3691, 2010.

Shiraiwa, M., Ammann, M., Koop, T. and Pöschl, U.: Gas uptake and chemical aging of semisolid organic aerosol particles, Proc Natl Acad Sci USA, 108, 11003-11008, 2011.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 33689, 2011.