

Reply to reviewers:

To reply to the overall comments and to evaluate the ability of SOAP to model condensation/evaporation more thoroughly, we added a comparison of the implicit method of SOAP for the treatment of particle-phase diffusion with an explicit method (where the particle is discretized with 100 layers and the exchange between layers is represented explicitly according to the Ficke law). When performing this comparison, we found a problem with the condensation of low-volatile compound, which were strongly affected by the kinetic of diffusion in the external layer whereas diffusion in this layer should not limit condensation.

The kinetic of condensation was then very low at low diffusion even if the compound was non-volatile. We therefore added an external layer subject to condensation/evaporation only. The solver of SOAP was also modified by inhibiting condensation/evaporation depending on the diffusion effect on concentrations. The implicit method of SOAP now agrees well with the explicit method. The details of the modifications and comparisons have been added to the paper.

Reply to reviewer 1:

*As noted in the original review, the concept of a flexible SOA module for use in chemical transport modeling is attractive, but not without rigorous testing and validation. While references were added, particularly to the introduction and methodology, they are still lacking in the presentation of results. The authors may want to consider splitting the paper and reserving presentation of the dynamic option until comparisons with a model such as KM-GAP have been made. That the diffusion coefficients are the same in each layer and the concentrations in each layer are independent of one another are particularly concerning; also concerning is that compounds allowed to partition into the aqueous and/or organic phases cannot partition between phases (for the latter, comparisons with work of e.g., Zuend and Seinfeld would be appropriate). The abstract does not strongly distinguish the work from other published work, including one of the major conclusions (e.g., the importance of non-ideality). The presentation quality has been improved, but there are still several grammatical errors that in some cases strongly affect the clarity of the work. The discussion of molecular surrogates/structures is still confusing.*

The topic of this paper is the development of a new model for the partitioning of secondary organic aerosol and not to discuss the effect of activity coefficients on the formation of secondary aerosol. We strongly disagree that the importance of non-ideality is one of the major conclusions of this article as it is not the subject. Conclusions on activity coefficients were added to the abstract according to previous comment of the reviewer even though it was not the objective of the paper. Conclusions on activity coefficients are removed from the introduction. The importance of non-ideality and other phenomena will be studied into greater details in future studies on the 3D application of SOAP to be able to conclude on their importance.

A validation of the implicit method of SOAP has now been added by comparison to an explicit method.

“That the diffusion coefficients are the same in each layer”: as explained and discussed in the text, this is a simplified model. We think that this simplified model is appropriate for our study as there is currently, no method to estimate the organic-phase diffusion coefficient. We may think in further studies about how to remove this assumption in our algorithm.

“and the concentrations in each layer are independent of one another are particularly concerning”. The layers are not completely independent of one another, as each of them interacts with the gas-phase simultaneously. Furthermore, the “bulk” condensation/evaporation rate of the particle is distributed over all layers depending on the diffusion. Although, this is a simplified implicit approach to represent efficiently the condensation/evaporation/diffusion of organic compounds, the comparisons to the explicit method are very satisfactory.

We are quite confused with the statement “concerning is that compounds allowed to partition into the aqueous and/or organic phases cannot partition between phases” whereas multiphase partitioning is one of the main objectives of SOAP.

Concerning the discussion on molecular surrogates/structures, “Semi-volatile organic compounds are represented by surrogate compounds” is added to the text. Molecular structures are assigned by the user to each surrogate compound, and a default structure is provided for each surrogate. This approach is very common when modeling volatile or semi-volatile organic species in air-quality models, as all organic species may not be explicitly modeled.

Reply to Reviewer 2:

***Conceptual Issues:***

*1. Page 12, line 16: I am afraid I find this second assumption seriously flawed considering the goal of the model. The authors use the word "layer" almost exclusively to discuss these regions of each particle that are separated from each other in the model. However, the only sense they are "layered" can be found in the parameterization of their diffusion timescales, which are based on their volumes, not their order. In my opinion, a critical aspect of their "layered-ness" is from inner layers being shielded from the gas-phase by the outer layers. If I'm not mistaken, the authors have now implicitly defined their layers to be detached regions, each one pseudoconnected to both the gas phase and the core. At the same time, they assert that the particles are axially symmetric. Although I disagree with this concept, they have made it clear in their discussion what the model assumes, and the reader can make up their own mind. It seems like an alternative could be achieved where the mass transfer due to condensation/evaporation in an inner phase is inhibited not just by its diffusion but also by the layers outside of it..*

Although the layers are indeed quite independent in terms of fluxes, they are connected to the gas phase via the characteristic time of diffusion of each layer. Furthermore, the layers are connected by the redistribution of organic compounds between nearby layers to keep the volume of layers unchanged. The composition of the other layers can have an effect on the exchange between layers but this effect is missing as discussed in the text because compounds go directly from the gas-phase to the layer (or from the layer to the gas phase). However, it is

a good idea to inhibit condensation/evaporation by the layers outside it, and we will investigate this in future work.

This method should give a good estimation of the capacity of the particle to absorb compounds and such simple algorithm is necessary to be able to represent particle-phase diffusion efficiently so that it can be used in air quality models.

*2. There is still an unresolved issue with section 2.3.8. I mentioned previously that if the authors are assuming that the "surface of particles is probably covered partially by both the organic matter and partially by the aqueous phase", then I would expect an angular-dependent concentration gradient to emerge in the gas phase at the surface of the drop. This would not affect the bulk gas-phase concentrations (as the authors interpreted my statements previously), but would have an affect near the surface where vapor pressure and  $D_{air}$  control the steepness or shallowness of the gradient moving away from the surface to the bulk phase. For this simple model, this approximation may not hurt much, but I think it is worth mentioning in the text.*

The following section was added to the text:

“Finally, the model assumes that there is no gradient of the gas-phase concentrations near the interface with the particle. If the particle is divided into two separated regions (one aqueous and one organic), an angular gradient of gas-phase concentrations could influence the condensation of compounds into the two regions. To address properly this phenomenon, the particle and the gas phase at the vicinity of the particle should be discretized as a function of the angular gradient. However, due to the high diffusivity of organic compounds in the gas phase, the diffusion of organic compounds around the particle should be very fast compared to the kinetic of condensation and therefore, this assumption should have a low effect on condensation/evaporation.”

*3. In Figure 2, why is the magnitude of the morphology factor less for layer 3 than for layer 2? I assume here that layer 1 is the closest to the core, and layer 3 is the furthest, but this could be wrong. In any case, I would expect the layers to have consistently increasing or decreasing effect depending on which order they fall in the particle. I suspect this has to do with how big the individual layers are?*

The position of layers inside the particle has been added to the caption so that the figure can be read without referring to the text. The morphology factor corresponds to the effect of the solid core on morphology factors. The fact that the morphology factor is higher for the second layer means that the solid core has a lower effect on the characteristic time of this layer.

It is difficult to compare morphology factors between them because the layers have different volumes (and different characteristic times) and so it is not straightforward to compare the global effect.

*4. I do not see a change to Figure 3, but looking at it again, I am able to understand it better. How about changing the name of the box on the left to "Calculate Evolution for Species with Characteristic times lower than  $t_{eq}$  (assume equilibrium)" and the box on the right to "Calculate Evolution of Species with Characteristic times higher than  $t_{eq}$  (assume dynamic)". This is if I understand the boxes correctly. I still do not get why the dynamic box has a box for "equilibrium" inside it. Is it for calculating particle-phase transfers during the time step? Again, no output arrow.*

There is an “equilibrium” box inside the dynamic because evolution for cases at equilibrium is recomputed at every time step (as mentioned in the text). Equilibrium was changed to "Calculate Evolution of Species with Characteristic times lower than  $\tau_{eq}$ ".

**Technical Issues:**

*p3, l2-3: Please add reference for human health, visibility and climate change impacts of particles.*

References added.

*p6, l3: It may be worth adding a little more information here for the reader. Specifically, does the model require every size section to have the same number of layers available to it?*

“Furthermore, each bin can be separated into several phases and several layers.” Changed to “Furthermore, each bin can be separated into several layers (the number of layers being the same for each bin) and several phases (the number of phases can change from one bin/layer to another bin/layer).”

*p14, eq 31: Please define  $\alpha_{layer}$  after this first introduction of it. Can the authors give some description of what it is exactly? If I understand it right, it is proportional to the effect the organic phase has on the bulk  $D_{org}$ .*

Done.

*p15, l7: Too many significant figures for the values of  $\alpha$ .*

Changed.

*p25, l3: For how long should the mass of layers must stay constant? Across a time step? Throughout the simulation?*

“Throughout the simulation.” Added in the text.

*Tables 1 and 3.: Perhaps my pdf is malfunctioning, but this does not appear to be a table.*

Changed.

*p28, l14: What size distribution features were used for these test cases? How many bins, etc?*

Informations added in the text.

*p33, l1: Perhaps replace "interesting" with "compelling"?*

Changed.

**Grammatical Issues:**

*p2, l25: ...some compound"s" Changed*

*p3, l17: "or" no phase separation. Changed*

*p4, l3-4: It's hard to understand this sentence exactly. One word was missing. Changed.*

*p5, l9-10: I recommend removing "if for example, the ... negligible" since the information in parentheses following seems to make the point perfectly clear. Changed.*

*p10, l5: ...hydrophobic (condense "into" both phases). Changed.*

*p12, l22: May I suggest reqrting "interface with the gas phase" to "gas-phase interface"?*  
Changed.

*p13, l3: Please remove "of" to read "no kinteic transfer of compounds" Changed.*

Reply to reviewer 3:

**Major comments:**

*1. Section 2.1 Overview: In this section the authors should thoroughly describe the processes contained in the new model. On the contrary, they keep comparing their model with other models throughout the section. This makes it difficult for the reader to follow what are the exact*

*processes included in SOAP if he/she is not well aware of the processes contained in the other models as well. I recommend including three main parts on this section. The first part (couple of paragraphs) should be self contained and describe the processes included in SOAP without referring to any other models. In the second part (one paragraph) they should make a quick comparison with the processes included (or not included) in the other models as well. They should also add one last paragraph (third part) where they can highlight the novel aspects of SOAP.*

The Overview has been rewritten:

“SOAP is based on the surrogate approach where SOA species are divided into three types: hydrophilic species (which condense only into an aqueous phase when the concentration of water in aerosols is higher than  $0.01 \text{ ug m}^{-3}$ ) and hydrophobic species (which condense only into an organic phase due to their low affinity with water) or both (condense on both phases) as chosen by the user. The model can represent the non-ideality of aerosols (interactions between organic compounds and interactions between organic and inorganic compounds represented via activity coefficients), hygroscopicity, phase separation and formation of SOA following an equilibrium approach or a dynamic approach.

Semi-volatile organic compounds are represented by surrogate compounds. To represent the non-ideality of aerosols, molecular structures are assigned by the user to each surrogate compound. A default structure is provided for each surrogate. This structure is used to compute the non-ideality of aerosols via activity coefficients. If the user specifies that a compound is both hydrophilic and hydrophobic, the repartition between phases is done according to the value of activity coefficients. However, the user can decide that a compound is only hydrophilic or only hydrophobic (for example alkane or lowly oxidized compounds are probably not absorbed by the aqueous phase of particles). Moreover, if there is no compound that is both hydrophilic and hydrophobic, the condensation into the organic phase can be solved separately from the condensation into the aqueous phase. The system is then uncoupled. On the opposite, if there is at least one compound which is both hydrophilic and hydrophobic, the condensation into the organic phase and the condensation into the aqueous phase must be solved simultaneously. The system is then coupled and consumes more CPU time. The user may prefer an uncoupled system for 3D application due to higher time efficiency.

To compute SOA formation, two different approaches can be used to model gas/particle partitioning: the equilibrium approach and the dynamic approach. In the equilibrium approach, aerosols are assumed to be at thermodynamic equilibrium with the gas phase. The model uses then a method of Newton-Raphson to efficiently compute the partitioning of each compound between the gas and particle phases. In the dynamic approach, the dynamic of the condensation and particle diffusion of organic compounds is treated with a multi-layer representation of OA (the organic mass is divided into several layers having different characteristic times to reach equilibrium). In this method, the particle size distribution is divided into sections (inside a section/bin, all particles are assumed to have the same diameters). Inside a bin, compounds condense into the aqueous phase or/and the organic phases. Furthermore, each bin can be separated into several layers (the number of layers being the same for each bin) and several phases (the number of phases can change from one layer to another layer).

SOAP is based on the methodology of the models H<sup>2</sup>O and AEC. However, as described above several processes were added. The model can have species that can condense on both the organic phase and the aqueous phase (like in MPMPO), can compute the effects of the interactions between inorganic and organic compounds on the condensation of organics, phase separation of the organic aerosol, and dynamic formation of SOA. The dynamic approach developed in this study is a simplified approach to take into account particle-phase diffusion with a low number of layers, and to keep the computation time as low as possible to

be used in 3D air quality models. It does not describe particle-phase diffusion as thoroughly as KM-GAP (Shiraiwa et al., 2012).”

*2. Section 2.2.2 Page 9: SOAP assumes that the total (organic and inorganic) amount of water computed by SOAP should be at least equal to the amount of water given by ISORROPIA. However, as they mention later, organic species can enhance or reduce the water absorption by aerosols. Wouldn't it be more valid to just accept the water content calculated by SOAP (even if it's lower from ISORROPIA's) as ISORROPIA is called prior to SOAP and does not include organics? Moreover, they should include a small discussion about the major differences on the parameterizations used by ISORROPIA and SOAP to compute water. It is not very clear why it is scientifically valid to accept the SOAP calculations when the water content is larger than ISORROPIA's but to accept the ISORROPIA calculations when it is not. Please discuss the rationale behind this assumption.*

We modified the manuscript to explain the reasons that made us prefer the choice made in the paper:

“We chose here to assume that the amount of water should at least be equal to the amount of water given by ISORROPIA, although it would be possible to keep the amount of water computed by SOAP even when lower than the amount of water computed by ISORROPIA. However, if the amount of water given by SOAP is significantly lower than ISORROPIA, this would induce changes in the amount of inorganics in the aerosol. As the amount of inorganics may not be recomputed after SOAP, we considered that amount of water is at least equal to the amount of water given by ISORROPIA, the amount of water being recomputed only to provide a better estimate of the amount of water when water absorption are mainly due to organics. The best way to deal with this dilemma would be to fully couple inorganic and organic aerosol formation.”

As for the differences of parameterizations, the following sentence was added to the text:

“SOAP computes the amount of water using the water activity computed by the thermodynamic models UNIFAC and AIOMFAC whereas ISORROPIA computes the amount of water using the ZSR correlation (Robinson and Stokes, 1965).”

*3. Section 2.2.4: An explanation of how the exact compound concentrations in the different organic aerosol phases are determined is missing. Are the components first condensed in the organic phase and then are separated in more than one phases (using some kind of factors?) or the phase separation is performed in prior and the components are condensed on the different phases (using equations 14-24 with more than just one  $A_{p,i}$ )? Moreover, what exactly are the differences between the several organic phases?*

The differences between the organic phases are simply differences of composition. The text is modified to provide more information by adding equations 26 and 27 (equations 21 And 22 generalized to several organic phases).

4. Section 3.3 Page 32 first paragraph: I do not agree with the use of value 0.5 for the accommodation coefficient. It is well known that for accommodation coefficients between 0.1 and 1, the mass transfer rate is high and not sensitive to the exact value used. The authors have to use a lower value, certainly lower than 0.01, to limit the effect of mass transfer to the organic phase. You can refer to Figure 12.13 of Pandis and Seinfeld (2006) for choosing the appropriate a value that will allow you to test the effect of diffusion in the organic phase.

Changing the effect of the accommodation coefficient has only a limited effect compared to the effect of the particle-phase diffusion on which we want to focus. It does not strongly impact our results. We chose to present results with an accommodation coefficient of 0.01 based on results of other studies (values between 0.1 (Saleh et al., 2013) and 0.001 (Lee et al., 2011)). The user can easily modify this choice of accommodation coefficient.

5. Section 3 Results: The authors should add an evaluation of the model by comparing the model results against measurements from the period covered by their test cases. There is no way to prove the credibility of their model if they will not evaluate it. If measurements are not available, they have to compare it at least against a more comprehensive dynamical model (i.e., KM-GAP). They mention on the conclusion section that they will do this on a future study but the evaluation is certainly needed at this point, either against measurements (preferred) or at least against other models.

A section on the validation of the model with comparisons to the results of an explicit method was added in the text.

#### **Minor comments**

1. Throughout the manuscript the authors are using the organic phase either on singular form (i.e., diffusion in the organic phase) or on plural form (i.e., condense into the organic phases). You have to be consistent throughout the text, so my recommendation would be to use the plural form since the model can have more than one organic phases and use the single form only in cases you have only one organic phase (i.e., specifically in section 2.2.1 and 2.2.2, or on some results for the POA and SOA compounds)

Changed.

2. Page 4 line 22: Can you add the threshold used for humidity below which condensation to aqueous phase is not allowed?

Changed.

3. Page 5 lines 1-2: Can you add all the new processes added in SOAP and not just an example?

Overview has been Changed.

4. Page 5 line 17: Difference from what? See also the first major comment where I suggest adding the comparison of SOAP process with other models in a separate paragraph.

Overview has been changed.

5. Pages 5 line 28 to page 6 line 2: Are there any maximum values of bins, phases, and layers that the user is allowed to distribute the organic compounds? How do these numbers affect the overall performance of the model? Are there any recommended (optimal) values to be used as default?

There are no particular maximum values. It is up to the user to specify those values according to what the user wants to do.

6. Page 6 lines 7 and 8: Please change the “gas phase and an organic phase” into “gas and organic phases”

We wrote it this way to emphasize that there is only one organic phase. “An organic phase” is changed to “one organic phase”

7. Page 13 lines 7-17: This paragraph is confusing. It is not clear in which parts the authors discuss about the processes contained on their model or processes that are well known but are omitted from their model. Please rephrase the whole paragraph

The paragraph was rephrased:

For example, in case of evaporation of the aqueous phase (which could be due to a strong change of the relative humidity), this assumption can create some evaporation/recondensation issues in the model (compounds evaporate and recondense after some time into the organic phase according to condensation/evaporation fluxes). Actually, a part of organic compounds should go directly from the aqueous phase to the organic phase. It could also be possible that if an aqueous phase and an organic phase coexist into the same particle that organic compounds do not condense directly from the gas phase into the organic phase (because the kinetic is too slow) but condense first into the aqueous phase and then go from the aqueous phase to the organic phase (if it is quicker for a compound to condense into the organic phase by this pathway). However, it can also be argued that if there is an aqueous phase (the relative humidity is too high), the organic phase may not be significantly viscous and therefore high organic-phase diffusion coefficient should be used.

8. Table 4: There is no information, anywhere in the manuscript, about what these compound names stand for. You should include a description of them somewhere in the text or in this table.

A table of description of compounds was added.

9. Figures 1-3 and Tables 1-4 are not referred in the text at all.

After checking the text, each table and Figure are referred in the text.

### **Typos:**

1. Page 2 line 15: Add “(OA)” after “organic aerosol” Changed

2. Page 2 line 17: Erase “(OA)” after “aerosol” Changed

3. Page 2 line 23: Rephrase “preliminary” with “the results of this study” Changed

4. Page 3 line 8: Add “(3D)” after “three dimensional” Done.

5. Page 3 line 18: Replace “organic aerosol” with “OA” Done.

6. Page 4 lines 3-4: A verb is missing from the sentence Changed

7. Page 4 line 11: Add a comma after “air quality models” Done.

8. Page 4 line 16-17: Please change the last sentence to “This paper describes the SOAP model and the results of several test cases” Changed.

9. Page 4 line 18: You may want to replace “development” with “description”

The paper really presents the development of a new model. It is not a simple description which was already presented somewhere else.

10. Page 5 line 26: Erase the comma and add “in order” before the “to be used” and replace “in” with “by” Changed

11. Page 6 line 6: Change the “are now described” with “are described below” Changed.

12. Page 9 line 2: Add “(i.e., ISORROPIA)” after the “inorganic model” Done.

13. Page 9 line 2: Add Replace “for the inputs of” with “as input to” Done.

14. Page 9 line 3: Erase “(for example ISORROPIA)” Done.

15. Page 24 lines 2-3: Erase the “partially by” before the “aqueous phase” Done.

16. Page 25 line 11: Add “interface” before the “layer” Done.

17. Page 25 line 12: Replace “are” with “remain” Done.



18. Page 29 lines 14-16: Replace “tables 5 and 6 show respectively with and without the ideality assumption the concentrations of organic aerosol for both test cases formed from the various precursors as well as the concentrations of water.” with “tables 5 and 6 show the concentrations of organic aerosol for both test cases formed from the various precursors as well as the concentrations of water, with and without the ideality assumption, respectively.” Changed.
19. Page 29 line 16: Erase the word “here” Done.
20. Page 29 lines 26-27: Move the “in the biogenic case” in line 27 after the “their concentrations” in line 26 Changed.
21. Page 30 line 5: Replace “result of previous study (Couvidat et al., 2012)” with “results of Couvidat et al. (2012)” Changed.
22. Page 30 line 14: Erase “of” after “change” Changed.
23. Page 30 line 27: Replace comma with “and” after the “BiA2D” Changed.
24. Page 32 line 14: Replace “much slower to reach equilibrium” with “reaching equilibrium much slower” Done.
25. Figure 3: An output arrow is missing Done.
26. Figures 4-7: Replace “equal to tenth the concentrations” with “equal to one tenth of the concentrations” Done.
27. Table 8: Replace “saturation” with “separation” on the titles of second and third columns Done.