

We are grateful to the referees who proposed interesting discussions on several points of our works. Following their comments, we extended our bibliography research and did some supplementary work (in particular, we propose now a model-measurement comparison and a point on VBS) and we increased the level of accuracy of several sections in the paper. We also answer all their comments and seize the opportunity to make our points clear and justify our choices and approaches.

It is quite important to note that this work aims at investigating what can be understood from the use of existing oligomer parameterizations in Air Quality models, and that we do not try to promote these parameterizations. We intend to determine if these approaches produce significant AOS levels, to what extent their results converge or not, and what are their greater strengths, weaknesses and sensitivities to input parameters. Thus, whenever the referees indicate that the modeling approaches for oligomer formation are far too simplistic, we do agree. But then, it becomes even more important to estimate the (positive or negative) impact of their use on model results, the parameters that make them weak, and the need for further scientific developments.

## REFEREE #1

**More discussion is needed about the differences between the approach used in this work and oligomer formation within the VBS formulation as described by Trump and Donahue (2014)**

*The works of Trump and Donahue do bring interesting areas for improvement for the representation of oligomer formation in 3D models. Although the VBS approach is different from classic AQM chemical schemes (mainly because VBS does not rely on the description of the structure of the species of interest), the principles of oligomer formation considered there are quite similar as the ones we study. The results of Trump and Donahue (2014) were already considered when working on the interpretation of our results. However, according to your recommendations, an explicit discussion of this approach was added in our discussion section.*

*Oligomer formation in the VBS approach aims at restituting experimental SOA yields, through a description of the phase partitioning equilibrium of various VOC oxidation products from a given volatility bin. Additionally, a condensed-phase reactivity is added, on the basis of a second-order association rate constant for the monomer and a first-order dissociation rate constant for the dimer. This last value is set from observations of the evaporation of SOA from  $\alpha$ -pinene on the scale of a few hours. Doing this, they propose a combination of a KPH-style approach and a condensed-phase KIN approach, but clearly addressing the issue of reversibility.*

*It is worthy to mention that the authors do indicate that this approach is highly simplified and not realistic (only a single volatility class of condensed products reacts, regardless of the structure of precursors, and forming only carboxylic acid dimers). The stated goal of their work is (just like here) to identify what kind of chemistry this experiment-based approach produces and how it helps understanding/representing oligomers. They also confirm that the sophistication of the approach would require advances in the knowledge of SOA yields and oligomer production dynamics.*

*Despite the choice of simplifying assumptions, an interesting result of this approach is the simulation of a two-stage evaporation (monomers evaporate rapidly upon dilution while only a modest drop in oligomer concentration is simulated due to the equilibrium dynamics) that may help reproducing recent observations of delayed SOA evaporation. Also, the “irreversible oligomerization” limit (high ratio dimerization/evaporation) definitely appears not compatible with the observed mass-yield behavior.*

**Meteorological model: Authors should mention which MM5 version was used. Horizontal resolution of MM5 was given as 54 km (page 9236, lines 3-7). The resolutions of CHIMERE domains on the other hand, were 0.5 deg x 0.5 deg and 0.23 deg x 0.20 deg. Was MM5 used with another**

**projection, not lat-lon? Was MM5 horizontal resolution for the mother domain same as the CHIMERE mother domain? Authors must describe how they generated meteorological fields for the nested domain with a resolution of 0.23 deg x 0.20 deg.**

*MM5 was used with longitude/latitude format. CHIMERE model uses only a bilinear interpolation subroutine in the meteo interface. However all technical details, not really essential for this paper, are presented in details in CHIMERE documentation (<http://www.lmd.polytechnique.fr/chimere/>) and in Menut et al., (2013) (<http://www.geosci-model-dev.net/6/981/2013/>).*

**Emissions: Resolution of anthropogenic emissions is very coarse (0.5 deg.). Do biogenic emissions have the same coarse resolution? Maps showing biogenic emissions (isoprene, monoterpenes, sesquiterpenes separately) during the modeling period should be shown in order to understand the locations of BSOA precursor emissions. Fig. 8b (SOA from monoterpenes) and Fig. 9 (right) (SOA from monoterpenes and isoprene) suggest that isoprene and monoterpene emissions have the same distribution (SOA concentration increases at the same locations due to addition of isoprene emissions). Is that true? Authors should discuss the influence of horizontal resolution of biogenic emissions on the distribution of biogenic SOA produced from isoprene and monoterpenes.**

*You are right, diffuse anthropogenic emissions are obtained at a coarse resolution of 0.5 deg. However, they are redistributed inside each CHIMERE grid cell as a function of urbanization density, via a specific CHIMERE redistribution algorithm used routinely for air quality analysis and forecast. As for the biogenic emissions, they are calculated at a base resolution of 1km from the MEGAN model (<http://lar.wsu.edu/megan/>) and aggregated over each CHIMERE grid cell. So a test about biogenic emission resolution is pointless here. The equations of the MEGAN model definitely differentiate isoprene, monoterpene and sesquiterpene emissions. However, considering the diversity of vegetation at the scale of 0.2-0.23 degrees, it is statistically probable that all types of biogenic compounds are emitted in large quantities in each CHIMERE rural cell. Thus, it is expected that biogenic emission maps (and even more so, those of secondary oxidation products such as SOA) at a 0.2(3)° resolution do not reconstitute the fineness of the isoprene and monoterpene emission distribution. The reason of what you observe is thus the effect of modeling air mass dynamics at a classic continental resolution, and not a problem of coarse or non-discriminating biogenic inventory.*

**The number of biogenic precursors was given as 5 (page 9234, line 25), but the following list has 6 names (isoprene, alpha-pinene, beta-pinene, limonene, ocimene and humulene). The focus of the study is on monoterpenes. However, humulene is a sesquiterpene. It is not very clear whether BiBmP refers to the sesquiterpene surrogate. Does Fig. 9 include the sesquiterpene BSOA? As it is given in the paper, BSOA from monoterpenes means from alpha-pinene, beta-pinene, limonene and ocimene. What about BSOA from humulene (a sesquiterpene)? Authors should explain how they treated sesquiterpenes in their formulations.**

*Sorry, it was a mistake. Humulene emissions are not calculated in this model version and thus it's not a SOA precursor. The gas-phase chemical for SOA formation used in this model version is also available in Menut et al., (2013) (cf Table 6 - <http://www.geosci-model-dev.net/6/981/2013/>).*

*The particle size range was given as 10-40 micrometer (page 9234, line 16). If this is correct, then it means only the coarse fraction was modeled. Authors should explain it and give the particle size range the results refer to.*

*Sorry it was a typo. The particle size range is 10nm-40µm. It was corrected.*

**Fig. 2: Two figures g and h are missing.**

*Numbering of the figures was corrected.*

**Fig 3: Upper panel: Two red points for BIA0D on the blue line have to be described.**

*We remove these two points because they were misleading.*

**Fig. 4** When is the “daily maxima”? Highest oligomers are over the Adriatic Sea. In Fig. 6 d however, it looks very different at 05 UTC.

*The time of the daily maxima does not exist, as the daily maximum is the highest concentration simulated in a grid cell during the day. Thus the time is different from one grid cell to another. Figure 4 allows visualizing the highest local values for the oligomer species but it has no temporal consistency. So there is no link between figure 4 and figure 6. Furthermore, the color scales are different.*

**Fig 6:** The choice of 05 UTC to analyze precursor and oligomer concentrations has to be explained. Most of the biogenic emissions are higher around noon and boundary layer develops during late morning hours.

*Indeed, if we wanted to have a maximum of oligomer precursors in the gas phase, we would have considered the late morning or early afternoon hours. However, we chose this timestep because it allowed showing both dry and wet aerosols, and proposed a wide range of pH values. Thus, we could view in parallel the concentration fields of the gas precursor, the potentially accumulated oligomers (from the day before) in the condensed phase, and the instantaneous aerosol properties. This permitted us to conclude that there were periods of time when reversibility due to pH and RH conditions was the driving parameter of the KPH approach, and that the conditions unfavorable to the retention of oligomers in the condensed phase were met over the largest part of Europe.*

**High precursor concentration and deliquescent aerosol with low pH favour oligomerization. Precursor concentrations are very low over the Mediterranean but oligomers are high - just because of low pH? Is such a low pH (around 1, Fig. 6 b) reasonable? This needs to be discussed more clearly.**

*Henningan et al., (2015) evaluated different models and proxy methods to estimate the aerosol pH, and showed that the ISORROPIA model is one of the most suitable methods to estimate it. We added this reference in our paper. It partly supports the low pH calculated during our simulation, but the values are also supported by the few existing experimental pH characterizations, as mentioned in the text.*

**In Fig 6b, pH seems to be 3.5 around the Benelux area which has the highest NH<sub>3</sub> emissions in Europe and therefore acidity is expected to be neutralized. Is it reasonable to have such a low pH in that area?**

*In the literature, there are few aerosol pH values so it is difficult to answer such a question. However, from our findings we believe that 3.5 may not be considered as a quite low pH value, as among the rare observations, most of them show an even lower pH value (we clearly talk about the aerosol pH and not cloud droplet pH). Furthermore, one reason why Benelux would not be affected by intense NH<sub>3</sub> emissions in our simulations is the season. NH<sub>3</sub> emissions are linked with agricultural processes and present a maximum in spring and autumn, and a minimum in summer.*

**Fig. 7:** Location of the grid cell for the time series should be given

*It was added in the legend of the figure.*

**Fig 8 d and e:** Relative concentrations show highest contribution of oligomers over the seas. Authors might consider to show absolute contributions.

*Absolute concentrations of oligomers under different formats and obtained with different model configurations were shown and discussed in several figures (4, 5 and 6). Here, the point is more the characterization of the share of oligomer production in the whole BSOA formation process. This is why we have made the choice to show relative contributions. Furthermore, over the sea (ie far from sources), the relative contributions are quite high, and the absolute BSOA is low. This allows understanding that : 1) for the KIN approach, a unique fate for most of BSOA precursors (90% is probably unreasonable and 2) for the KPH approach, there is surely an excessive role of relative humidity on BSOA through oligomer stability away from emission sources.*

**Page 9236, lines 8-11: Authors must describe how the boundary conditions for the European domain were generated.**

*The boundary conditions of the continental domain are climatological (10 years average) model data obtained from global simulations conducted with LMDz. One value per month is given for each pollutant considered in this process. They have demonstrated a high consistency for air quality simulations over continental domains (except maybe for the restitution of punctual dust episodes from African deserts and their impact on Southern Europe), as the borders are located away from the main anthropogenic centers, thus in rather homogeneous atmospheric zones, and as the atmospheric composition is rapidly dominated by local emissions when air masses enter the domain.*

**Page 9240, line 6: replace “.. could not considered” with “.. could not be considered”**

**Page 9242, eq 3:  $H_i$  instead of  $H_i$  as in line 18**

**Page 9242, lines 23-25: indicate the Eq. 4 at the end of the sentence.**

**Page 9242, line 26: (set .... Robinson et al. (2007))**

**Page 9246, line 9: ..smoother gradients (Fig. 5)**

**Page 9246, line 11: ..previously. (remove (Fig 5))**

*It was corrected.*

## REFeree #2

1.a)

**In many recent studies, it has been discussed that for aerosol Henry's law constants are not directly applicable since the aqueous solutions are not ideal. Recently, correction factors, e.g. the Setschenov coefficient, have been applied. Therefore using a constant Henry's law constant for all conditions seems an oversimplification. This should be at least briefly discussed.**

*It is now discussed in the paper.*

1.b)

**The sensitivity to the Henry's laws constant is not new and has been investigated previously in a regional model. The novelty of the current study as compared to a previous one (Knote et al., 2015) should be discussed.**

*The paper of Knöte et al., 2015 deals with the effect of Henry's law constant on the dry deposition of SVOCs, and its impact on SOA concentrations (that decrease due to the lack of precursors when dry deposition is enhanced). Indeed, as they use a VBS approach, their model does not take into account  $K_H$  values for the gas/particle partitioning of SVOCs, but only for dry deposition, according to the Wesely parameterization. Thus, they do not give information on the influence of  $K_H$  on the transfer of SVOCs to the particulate phase for SOA production, which is our focus here.*

2.a)

*We agree with the referee's comment, about the oversimplification of oligomer production when considering a first order process. However, in the absence of further experimental data, the “KIN approach” had the advantage of proposing a simple way to reconstitute the “total observed” oligomer quantities. And because it is very likely that this approach cannot fully reproduce the sensitivity of oligomer formation to the variability of the aerosol water content, it is quite interesting to observe the features of oligomer production in a model from this approach, compared with more sophisticated modeling approaches.*

2.b)

*A point about the role of oligomer aging was added in our document (section 4).*

3.a)

*On the basis of the reviewer's recommendations, we have extended our bibliography about measurements, conducted a comparison between our model results and some measurements, and finally added a section named « Comparisons of KIN and KPH approaches with measurements » in the paper. This element is also mentioned in the abstract and introduction, and used for discussion in the conclusion section.*

3.b)

*We didn't use ion ratio as a proxy, following the recommendations of Henningan et al., 2015 (ACP) who consider that the best estimation for aerosol pH - despite existing uncertainties – is provided by thermodynamical models and not ion balance and ratios that are misleading and should be avoided.*

3.c)

*Following the expectations of the reviewer, we proceeded to a model-measurement comparison. The results are fully described in section the new section 3.1.5.*

**3.d) Please, give references for the occurrence of deliquescence in the atmosphere. To my understanding, the vast majority of all ambient aerosol particles are in their metastable state as their efflorescence relative humidity is suppressed to very low values due to the complex mixtures of organics and inorganics. Therefore, I think the scenario of dry aerosol particles in the atmosphere is unrealistic.**

*It is highly probable that an approach not considering the metastable state is a poor representation of reality. However, the frequency of the situations allowing the evaporation of particles in the atmosphere is not given and the consistency of considering this in AQMs is still under debate.*

*In the literature there are some laboratory studies of the behavior of aerosols having an aqueous phase containing one or more organic compounds (ex Zardini et al., 2008) which indicate that aerosols may actually undergo a metastable state. However the deliquescence and efflorescence thresholds of such particles are not well known and the studied particles are often binary mixtures of organic and inorganic solutes. As for in situ observations, Ansari and Pandis (2000) showed that considering both deliquescent and metastable paths for the partitioning of nitrate in Southern California was essential at low nitrate aerosol concentrations, although not significant for high concentrations. Fountoukis et al. (2009) also indicate that – for particle concentrations under conditions characteristic of Mexico City – organics can promote thermodynamically stable water down to very low RH and that it may serve as an important constraint for 3D AQMs. On the reverse, Moya et al. (2002) showed that the assumption of metastable state for sub-micrometer particles may introduce large errors when  $RH < 60\%$ , highlighting the importance of deliquescence predictions at low RH. Similarly, Mikhailov et al. (2013) – from the analysis of atmospheric aerosols – indicate that under a RH level of about 70%, organic species may not be completely dissolved in the aqueous phase and may also coexist in a solid aerosol phase (eutonic state). Although this doesn't imply the reversibility of the transfer of the organic species to the particulate phase (as it is considered in the KPH approach), a possible inhibition of oligomer production in low RH conditions is thus likely.*

*In our study we propose the implementation, one after another, of an approach based on the deliquescence of the aerosol and an approach based on the possibility of a metastable state for the aerosol, with an efflorescence threshold set to zero. This procedure makes it possible to isolate - by comparison - the effect of atmospheric humidity over a continent on the accumulation of oligomers in SOA using such modeling approaches. Depending on the sensitivity of our results to the threshold values, we can appreciate the importance of knowing and well representing the  $RH_D$  and  $RH_E$  thresholds in a model (and to discuss the choice of  $RH_E$ , the relevance of the set to 0 ... ) which is an important element of the robustness of the KPH modeling approaches.*

3.e)



The SOA chemical scheme, and thus the budget of aldehydes in the particulate phase, relies on Pun et al. studies. Pun et al. (2006) have proposed a representation of SOA physicochemical properties based on the grouping of all identified SOA species into a more tractable set of surrogate SOA species. In this scheme, the compounds that have a carbonyl group are included in the « Biogenic Hydrophilic Nondissociative SOA Compounds (BiAOD) » family, and they are accounted for by a surrogate SOA compound whose molecular structure includes 10 carbon atoms with an oxo group and an aldehyde group.

All SOA yields and properties of this scheme are based on experimental studies that have provided molecular information on the SOA products of  $\alpha$ -pinene oxidation by ozone and OH, along with the associated stoichiometric coefficients and SOA yields, and on the high gas-phase yields of four identified molecular products for the oxidation of  $\alpha$ -pinene by nitrate radicals.

Although the model parameters for each gaseous precursor were derived to obtain the same SOA mass as in the experiment, the model may only account for a subset of all the gas oxidation products because minor products were not coded. However, in the case of the pinenes, the missing mass consists mostly of volatile compounds, including formaldehyde and acetone.

The base model was tested against smog chamber data, and some adjustments have been made to improve the model performance. For further details, we refer you to Pun et al., 2006.

3.f)

Clearly, there is high debate regarding the role of acidity in the formation of oligomers. Peltier et al. (2007) indicate that they did not find any evidence of acid-catalyzed SOA formation in their measurements, while other studies do interpret observations as the result of acid-catalyzed SOA formation (REFERENCES). Without new experiments we can't - and we don't intend to - arrive at any certainty on this issue.

As mentioned in the text, Equation 1 is derived from laboratory works that propose an interpretation of oligomer production based on the existence of acid-catalyzed reactions. Thus, it artificially shifts the gas/particle balance when the pH of the particle changes. In our works, this school of thought is simply set against a kinetic approach that ignores the composition of the condensed aerosol phase, in order to evaluate the magnitude of the differentials between the model results in each configuration.

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### **Minor comments**

**It should be noted somewhere that oligomerization is only considered in the aqueous phase of aerosol particles, and that chemistry in clouds is not included** – It is now specified in the introduction.

**SOA is also made up of low volatility organics.** It's added in the introduction.

**Did the study really report that the 'total organic aerosol mass was converted into oligomers' or the precursor mass? I.e. did the organic aerosol mass increase or not?** - It's obviously a mistake. We are talking about the precursor mass. Thus, the organic aerosol mass doesn't necessarily increase.

**'Eq (1) alters the solubility : : ' is poor wording. Please, reword.** We corrected this paragraph.

**I am confused. I thought that ISORROPIA is included in CHIMERE and calculates the liquid water content** - You are right: for 3D simulations we used isorropia on-line coupled with CHIMERE (for each timestep and grid cell). However, here we just conducted a 0D study with a fixed LWC value.

**Species with  $10^{-7}$  M/atm are not 'insoluble'. For example, in the presence of clouds, they are mostly present in the aqueous phase** - Yes, the term is abusive. As we focus only on aerosols and not clouds, we only consider low LWCs. In those conditions, species with  $10^{-7}$  M/atm are not significantly

present in the aqueous phase, and will not be considered among the soluble species of interest. It is noted in the text.

**'Discrepancy' implies that one model is 'more correct' than the other. However, I think both parameterizations are very crude assumptions. Wording should express that the current results are all not representative for the atmosphere.** There surely is one version of the model that provides a better representation of oligomer production, even if both are supposed to be crude. However, using the word "discrepancy", we didn't wish to imply that one model was particularly correct and that the other one was wrong. As the meaning of "discrepancy" is "conflict, disagreement", it fits the comparison between model and measurements and we kept it. As for the model-model comparisons, we changed this word to "divergency".

**'observed' implies 'ambient measurements'. Is this really meant here or rather 'predicted'?** You're right. It's predicted.

**What is meant by 'KH correcting factor'?** It's the change in KH induced by the pH dependence. We clarified this in the text.

**Again, 'observed' or 'predicted'?** Predicted.

**Not clear how the 'dependence on RH was removed'** - The metastable mode ensures the permanent presence of an aqueous phase in the aerosol. Thus, there is no more effect of having low RH values on oligomers. We clarified this in the text.

**'Initial' implies that this value might change over the course of the simulation. Is this true?** – No, it means that each simulation is made on the basis of one specific value, initially chosen among the whole range of possible solubilities. As this adjective was misleading, we removed it from the sentence.

« As rapid oligomer formation was observed in laboratory experiments, imposing a minimum value for KH could be a substitute to oligomer formation processes (which require the addition of chemical reactions) and reduce significantly the size of chemical scheme in AQMs. » **I do not understand this sentence. If only KH were to be used to present oligomer formation, the modules for AQM might be simpler. However, it is obvious that also particle phase reactions need to be added. Such addition, makes such a module quite complex** –We do agree (and it's already noted in the paper) that realistic parameterizations for oligomer production should include particle phase reactions. However, in the KPH approach, such a simplistic approximation is made for the aldehyde surrogates. And artificially increasing the  $K_H$  value of some SOA precursors may have an equivalent impact on SOA formation in the model.

Again, we are not suggesting that modifying the gas-to-particle equilibrium is equivalent to reconstitute the behavior of the molecules in the condensed atmospheric phase. We just consider the possibility for those approaches to produce more acceptable SOA levels than running a model that ignores oligomer formation. Indeed, AQ models focus on the production of acceptable concentration fields for relevant species (here SOA) and aim at finding a simplified representation of atmospheric chemistry for this purpose. In this objective, even simple parameterizations may offer a very good compromise when they induce a realistic behavior of the species of interest, under the usual range of environmental conditions. This is what we test.

**The study by Wang et al., 2010, referred to nucleation of particles that is enhanced in the presence of organics. This is a completely different scenario...** This was indeed not consistent. We modified the text and removed the reference.

**All the cited studies here refer to bulk aqueous phase experiments. Therefore, they could not give quantitative conclusions about the importance of these oligomerization pathways in the atmosphere. The follow-up study by Ervens et al shows clearly that these processes likely only contribute marginally to ambient SOA. In addition the same study discussed that under atmospheric conditions, likely there is no oxygen limitation.**

The discussion and conclusion section was rewritten on the basis of the comments of all referees. In particular, the sentence refereeing to Ervens's study was removed as indeed it was not focusing on a major process.

**The indices on the symbols are very blurry in a too small font.** Figure3 was produced again, with larger fonts.

**This figure by itself is very misleading. At the very least, it should be noted that it only refers to Eq.-1. Usually  $K_H$  values increase with increasing pH due to dissociation of acids.** The legend was clarified.

## REFEREE #3

1)

The biogenic emissions are calculated at a base resolution of 1km from the MEGAN model and aggregated over each CHIMERE grid cell. The equations of the MEGAN model propose equations for the calcul of isoprene, monoterpene and sesquiterpene emission fluxes upon time, depending on meteorological features. It was specified in the text. However, the model is well-known and the text is accompanied by the reference of a paper (and a web link) so we didn't expand its description. You are right, biogenic emission maps may be of interest. However, it is expected that biogenic emission maps at a 0.2° resolution do not restitute the fineness of the emission distribution and may look like BVOC oxidation product (BiA\*D) maps, without bringing new information. This is why we decided not to increase the size of the paper with the maps.

2)

The pH can be negative if  $H^+$  concentrations are too high, which is problematic for our calculations. We set a limit at 2 as the transfer to the particulate phase of SVOCs is already total at this value and there is no need to produce higher  $K_H$  values. Nevertheless, these values are consistent with others studies (like the recent paper of Henningan et al., 2015). And there is no problem with the fact that this limit is reached because it remains consistent with the literature. As it is pointless, we didn't investigate the places and times when the limit was reached.

3)

You are right. This required a long supplementary work, and it now done in a new section.

4)

It was corrected.