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 a- 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 restitute 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 NH3 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 NH3 emissions in our simulations is the season. NH3 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: Hi instead of Hi 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 Knote 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 partioning 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 restitute 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 pysicochemical 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 (BiA0D) » family, and they are accounted for by a surrogate SOA compound which 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 α-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 α-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 condense aerosol phase, in order to evaluate the magnitude of the differentials between the model results in each configuration.

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 increases.*

'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 10ˆ7 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 restitute 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'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 KH 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.

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Oligomer formation in the troposphere: from experimental knowledge to 3-D modeling

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Abstract

The organic fraction of atmospheric aerosols has proven to be a critical element of air quality and climate issues. However, its composition and the aging processes it undergoes remain insufficiently understood. This work builds on laboratory knowledge to simulate the formation of oligomers from biogenic secondary organic aerosol (BSOA) in the troposphere at the continental scale. We compare the results of two different modeling approaches, a 1st-order kinetic process and a pH-dependent parameterization, both implemented in the CHIMERE air quality model (AQM), to simulate the spatial and temporal distribution of oligomerized SOA over western Europe. Our results show that there is a strong dependence of the results on the selected modeling approach: while the irreversible kinetic process leads to the oligomerization of about 50 % of the total BSOA mass, the pH-dependent approach shows a broader range of impacts, with a strong dependency on environmental parameters (pH and nature of aerosol) and the possibility for the process to be reversible. In parallel, we investigated the sensitivity of each modeling approach to the representation of SOA precursor solubility (Henry's law constant values). Finally, the pros and cons of each approach for the representation of SOA aging are discussed and recommendations are provided to improve current representations of oligomer formation in AQMs.

1 Introduction

Due to their fast evolution in the troposphere and their continuous interaction with the ambient gas phase, atmospheric aerosols present a highly variable chemical composition in space and time (Q. Zhang et al., 2007). They comprise large quantities of inorganic species such as nitrates and sulfates, but they also contain an organic fraction (organic aerosol, OA), made of condensed semi-volatile organic species presenting a wide range of oxidation degrees (Jimenez et al., 2009). Part of this OA comes from the emission of particulate organic compounds into the atmosphere during combustion processes: it is called Primary Organic Aerosol (POA). However, away from combustion emission sources, most of the OA arises from the oxidation of gas-phase organic species, making up the secondary organic aerosol (SOA), which may represent up to 70 % of OA on a mass basis (Kanakidou et al., 2005). The diversity in size and composition of atmospheric aerosols induces major differences in their physicochemical properties (Molnar et al., 2001; Kanakidou et al., 2005). These properties affect their impact on the radiative balance of the atmosphere (Stier et al., 2007; Paredes-Miranda et al., 2009) and their adverse health effects (Fuzzi et al., 2006). Thus, not only the total aerosol mass, but also their size distribution and their chemical content are of crucial importance for atmospheric issues. Although major scientific advances have been made during the last decade, the composition and the aging processes of the organic aerosol fraction remain insufficiently understood (e.g., Volkamer et al., 2006).

As a consequence, Air Quality Models (AQMs), despite significant progress, still have difficulties to quantitatively reproduce the observed particulate matter (PM) levels and gradients, and continue to underestimate the formation of SOA in the troposphere, from cities to remote areas (Shrivastava et al., 2011; Ervens et al., 2011; Petetin et al., 2014). In this regard, the chemistry of organics in the aqueous condensed phase remains poorly characterized. Thanks notably to atmospheric simulation chamber data, new processes have been integrated into AQMs so as to fill the gap between models and observations. These processes include for example the addition of new precursors (e.g., Y. Zhang et al., 2007), the treatment of SOA hygroscopicity (e.g., Pun, 2008) and aqueous chemistry SOA formation pathways (e.g., Carlton et al., 2008). In doing so, oligomerization was highlighted as one of the most important identified processes of SOA evolution. Laboratory studies indeed showed that oligomerization could be a quantitatively important evolution pathway for aqueous condensed species, and may greatly contribute to a better understanding of SOA aging (e.g., Kalberer et al., 2004; Jang et al., 2005; Trump and Donahue, 2014, and references therein). In particular, modeling studies have shown that the oligomerization of biogenic oxidized com-

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pounds happens to be a significant source of secondary organic aerosols (Aksoyoglu et al., 2011).

Based on these experimental results, two distinct approaches aiming at representing oligomerization into AQMs have initially been developed. One approach, described by Carlton et al. (2010), proposes to represent the formation of oligomers observed in simulation chambers by using a first-order rate constant for all organic compounds. In parallel, Pun and Seigneur (2007) developed a pH-dependent oligomer formation, based on the experimental data of Jang et al. (2005), which applies only to the aldehyde species dissolved in the aerosol aqueous phase. More recently, Trump and Donahue (2014) also used an equilibrium approach to model oligomer formation within the volatility-basis set (VBS) formulation. Although these approaches rely on two very different concepts, they both aim to produce oligomers in the aerosol phase from the particle-phase reactions of condensed semi-volatile organic species, using empirical relationships. These parameterizations have been implemented in several AQMs such as CAMx (www.camx.com), CMAQ (http://www.cmaq-model.org) and Polyphemus (http://cerea.enpc.fr/polyphemus/index.html) in order to improve the simulated SOA concentration fields. Several modeling studies including these new parameterizations were conducted (Pun and Seigneur, 2007; Carlton et al., 2010; Aksoyoglu et al., 2011; Couvidat et al., 2012); it came out that oligomerization of biogenic oxidation products is mostly responsible for SOA formation and that the implementation of this process in AQMs reduces the discrepancy between the PM simulated mass and measurements in Europe and North America. However, although enhanced operational SOA modeling is needed, there still are no in situ measurements of oligomers that would increase our understanding of their formation and either allow the validation of these approaches or enable further refinement of the models. As an example, Pun and Seigneur (2007) indicated that their approach may overestimate the role of water in this process, as it is not currently known whether all liquid water present in aerosols is available to interact with organic compounds. Furthermore, as the two methods diverge both on the set of species submitted to oligomerization and on the nature of the driving parameters (kinetic constant vs. equilibrium relationship), we also can expect the modeled distribution of simulated oligomers to differ between the two approaches.

To our knowledge, these approaches have not yet been compared in a same model. Such an initiative seems warranted, first to identify the range of uncertainties that these two parameterizations induce in the model outputs, but also to define how these parameterizations influence our understanding of SOA production in time and space. Thus, this work aims at investigating the representation of oligomerization that is provided by operational models. It consists in a model sensitivity study using, in turn, each oligomerization approach presented above to quantify the production of organic PM over Europe in the lower troposphere through continuous simulation. Moreover, it includes a study of the impact of the Henry's law constant computation for complex organic species, which is considered as a key parameter in representing the multiphase behavior of organic compounds in the atmosphere (Raventos et al., 2010). This study was conducted with the CHIMERE AQM (www.lmd.polytechnique.fr/chimere) at the continental scale over Europe during a summer period covering July and August 2006. The simulated SOA yields as well as the oligomer spatial and temporal distribution obtained in each model configuration are compared, so as to learn about the corresponding approaches.

This work is divided into three parts. First, the methodology and the model configurations are presented. Next the influence of the Henry' law constant on gas-particle partitioning, as well as the impact of each parameterization on the SOA budget are discussed. Finally, we discuss the assets and limitations of both oligomer modeling approaches and provide recommendations for future work.

2 Methodology and model set-up

2.1 Model set-up

This study uses the CHIMERE AQM, which is designed to produce daily forecasts of ozone, PM and other pollutants and to conduct pollution event analyses and research studies in atmospheric chemistry (Menut et al., 2013). The model may be run from the regional to the continental scale, with horizontal resolutions ranging from 1 to 100 km. CHIMERE is used daily for operational air quality forecasts in 9 different regions of France and Europe. In this context, model performance is assessed every day via the comparison of the model output with atmospheric measurements, which also provides the basis for the ongoing improvement of CHIMERE. CHIMERE uses the MELCHIOR2 gas-phase chemical scheme (120 reactions among 44 gaseous species), which is adapted from the original EMEP mechanism and is a reduced version of the MELCHIOR1 mechanism, obtained by Carter's surrogate molecule method (Carter, 1990). The gas-phase chemical mechanism for SOA production has been described in detail by Pun et al. (2006) and Bessagnet et al. (2008).

In CHIMERE, a sectional aerosol module provides the evolution of the concentrations of 7 particulate groups of species: primary PM, nitrate, sulfate, ammonium, biogenic SOA, anthropogenic SOA, and water (Schmidt et al., 2001; Bessagnet et al., 2004, 2009). The size distribution of aerosol particles is represented using 8 size sections ranging from 10 to 40 µm. Physical processes taken into account are coagulation (Gelbard and Seinfeld, 1980), condensation via absorption (Nenes et al., 1998; Pun et al., 2006) and nucleation for sulfuric acid (Kulmala et al., 1988). The equilibrium concentrations of inorganic species are computed by the thermodynamic module ISORROPIA (version 1.7) presented in Nenes et al. (1988). The distribution of secondary organic species between the gas and particulate phases is calculated using Raoult's law with a temperature-dependent partitioning coefficient as described by Pankow (1994) for hydrophobic species and using Henry's law for hydrophilic species (Pun et al., 2006). In this version of the CHIMERE model, SOA formation is processed through the oxidation of 5 biogenic gaseous precursor species (isoprene, α-pinene, β-pinene, limonene, ocimene and humulene) and 4 anthropogenic precursor species (benzene, toluene, trimethylbenzene and a species accounting for C4-C10 alkanes). As for condensable species, both hydrophilic (condensation following Henry's law) and hydrophobic (condensation following Raoult's law) behaviors are considered, they are represented by:

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- six hydrophilic surrogate species including an anthropogenic non-dissociative species (AnA0D), an anthropogenic once-dissociative species (AnA1D), an anthropogenic twice-dissociative species (AnA2D), a biogenic non-dissociative species (BiA0D), a biogenic once-dissociative species (BiA1D) and a biogenic twice-dissociative species (BiA2D). The pAnA*D and pBiA*D species stand for the part of the surrogate species that is present in the particulate phase

- three hydrophobic species comprising two anthropogenic species with low and moderate saturation vapor pressures (AnBlP and AnBmP) and a biogenic species with a moderate saturation vapor pressure (BiBmP)

- two water soluble surrogate species that account for the isoprene oxidation products (ISOPA1, ISOPA2). The oxidation of isoprene is adapted from the formulation prescribed by Kroll et al. (2006) and Y. Zhang et al. (2007).

Note that if – for any time step and grid cell – the modeled aerosol is not deliquescent, the gas-aerosol partition of the hydrophilic species will then be driven by their saturation vapor pressure. That is, their condensation will follow Raoult's law.

In the model, horizontal advection is calculated using the Van Leer second-order scheme and boundary layer turbulence is represented as a diffusion phenomenon, following Troen and Mahrt (1986). Vertical winds are diagnosed through a bottom-up mass balance scheme. Dry deposition is coded as in Wesely (1989) and photolytic rates are attenuated using liquid water or relative humidity. Finally, the numerical time solver uses the TWOSTEP method (Verwer, 1994).

The 2006 annual anthropogenic emissions from the EMEP (European Monitoring and Evaluation Programme) database (Vestreng et al., 2005) at a resolution of $0.5^\circ \times 0.5^\circ$ have been used (http://www.emep.int). They include CO, NH_3, NMVOC, NO_x, SO_x, and PM emissions for the 10 anthropogenic activity sectors of the SNAP nomenclature. The emission values are disaggregated into individual chemical species and at an hourly time step according to IER (Eber et al., 1994) recommendations, and are spatially distributed over our simulation domain using a kilometric land use database (http://glcf.umiacs.umd.edu). Biogenic emissions have been computed with the MEGAN model (Guenther et al., 2006). Climatologic LMDZ (Hauglustaine et al., 2004) model output data were used for boundary conditions. Finally, the mesoscale model MM5 (Dudhia et al., 1993) was used to generate hourly meteorological fields for CHIMERE over a European domain covering our simulation domain, with a horizontal resolution of 54 km and using 32 levels in the vertical direction from the surface to 10 hPa.

A European domain extending from 6° W to 20° E in longitude and from 38 to 54° N in latitude (see Fig. 1) was defined for this study: its size allows tracking and studying large European city plumes and the domain includes our study area, which is western Europe. The horizontal resolution is 0.23° × 0.20°. For the vertical resolution, we used 8 levels of decreasing resolution from the ground level up to 500 hPa, the first model layer being 50 m thick. The simulation domain and its grid are illustrated in Fig. 1. The simulation period covers two months (July and August) in the summer of 2006. The simulation was run with a spin-up period (15 days) prior to the periods of interest in order to ensure that emissions and secondary pollutants are realistically distributed over the domain at the beginning of the evaluation period.

2.2 Oligomer parameterizations

This section describes the implementation of oligomer production in CHIMERE using the two existing parameterizations and their associated hypotheses.

2.2.1 Kinetic approach

The first approach (called hereafter KIN) is based on the hypothesis that oligomer formation may be represented through a kinetic process (Morris et al., 2006; Carlton et al., 2010). This hypothesis is supported by a series of smog chamber experiments conducted by Kalberer et al. (2004), where an important fraction of organic aerosol mass was shown to be composed of oligomers. The authors reported that, after 20 h of processing, 50 % of the total organic aerosol mass was transformed into oligomers. From this result, Morris et al. (2006) proposed the use of a first-order rate constant $k_1 = 9.6 \times 10^{-6}\,\mathrm{s}^{-1}$ to account for the oligomerization formation process, corresponding to a half-life of 20 h for organic species in the particulate phase. In this approach, biogenic and anthropogenic species are all potential oligomer precursors. However, due to low amounts of anthropogenic SVOC from the oxidation of classic precursors (toluene, xylene, trimethylbenzene. . .) over Europe, the production of anthropogenic oligomer could be negligible (Aksoyoglu et al., 2011).

To transcribe this approach in the model, we have allocated a first-order oligomer production kinetics to all the hydrophobic and hydrophilic surrogate species (AnA0-1-2D and BiA0-1-2D, AnBlP, AnBmP, BiBmP, ISOPA1 and ISOPA2) of the CHIMERE aerosol module. Preliminary simulations with CHIMERE confirmed the precedent findings, i.e. a very low budget of oligomers of anthropogenic origin (concentrations reach $10^{-3}\,\mathrm{ng\,m^{-3}}$ at the maximum over the domain) compared with biogenic oligomers (which concentrations reach a few $\mathrm{\mu g\,m^{-3}}$ for oligomers over many continental areas).

Thus, for simplification, only the 6 biogenic surrogate species (BiA0D, BiA1D, BiA2D, BiBmP, ISOPA1 and ISOPA2) were considered here (gas-phase chemical scheme for SOA formation is available in Table 6 of Menut et al., 2013). Furthermore, as will be discussed below, our study will focus on monoterpenes, a common species of both modeling approaches. To that end, a new species family called BiOLG, representing the total sum of oligomerized pBiA*D compounds, was introduced in CHIMERE. It accounts for oligomer formation from the oxidation of monoterpenes only and will be the basis for the intercomparison of the two approaches.

In this empirical parameterization, oligomerization is considered as an irreversible process. This approach has the advantage of simplicity, as it proposes a similar chemical reactivity for all organic oligomer precursors in the particulate phase (hydrophilic and hydrophobic species), one single chemical pathway for oligomer formation, and only one type of oligomer product. However, the drawback of this method is that it does not account for the details of the gas-phase SVOC speciation, for the variability of the aerosol nature (deliquescent aerosol or not), nor for ambient parameters such as pH. Thus, it may lead to biases in the quantitative estimation of oligomer and OA production. Moreover, owing to the choice of a kinetic approach with a half life of 20 h, oligomer production is expected to be dominant away from source areas (except in the presence of severe anticyclonic conditions), enhancing the role of pollutant transport.

2.2.2 pH-dependant approach

The second approach (called here KPH) combines the laboratory works of Jang et al. (2005) – who showed that the polymerization of aldehydes may happen through a variety of acid-catalyzed reactions – and the observations of Gao et al. (2004) – who indicated that at least 10 % of the total organic aerosol mass is converted into oligomers due to the formation of organic acids in the aerosol. From these results, Pun and Seigneur (2007) developed an equation for the calculation of the gas-to-particle partitioning constant of semi-volatile aldehydes. It represents their increased partitioning toward the aqueous phase due to acidity:

$$K_{\mathrm{p,\,eff},\,i} = K_{\mathrm{p},\,i}\left[1 + K_{0,\,\mathrm{eff},\,i,\,\mathrm{ref}}\cdot\left(\frac{C_{\mathrm{H^+}}}{C_{\mathrm{H^+},\,\mathrm{ref}}}\right)^{1.91}\right] \quad (1)$$

where $K_{\mathrm{p,\,eff},\,i}$ is the effective partitioning coefficient of the ith compound between the gas phase and the aerosol aqueous phase; $K_{\mathrm{p},\,i}$ is its standard partitioning coefficient – calculated for non-acidic conditions – and $C_{\mathrm{H^+}}$ represent the aqueous concentration of hydronium ions. In this approach, $C_{\mathrm{H^+},\,\mathrm{ref}}$ is set to 10^{-6} mol L^{-1} and $K_{0,\,\mathrm{eff},\,i,\,\mathrm{ref}}$ stands for the value of 0.1 found by Gao et al. (2004) under the $C_{\mathrm{H^+},\,\mathrm{ref}}$ conditions. According to the results of Jang et al. (2005), aldehydes appear to be more reactive than ketones by two orders of magnitude. To simplify the parameterization, Pun and Seigneur (2007) considered as a first approximation that only aqueous aldehydes undergo oligomerization. In our model, it is equivalent to assuming that only BiA0D surrogates can lead to oligomer formation. Such a consideration derives from the fact that isoprene oxidation products in CHIMERE are not associated with a given molecular structure. Thus, oligomerization processes could not be attributed to isoprene surrogates without more chemical details here, using the KPH approach. Our study then focuses on what can be learned from oligomerization modeling approaches on the basis of monoterpene surrogate reactivity.

~~Unlike the first approach, oligomerization is treated here as a reversible process. It is important to note that this approach only indirectly accounts for oligomer production. Indeed, to account for their aqueous reactivity, Eq. (1) alters the solubility of organic species, which in turn changes their particle-to-gas ratio and simulates their accumulation in the particulate phase. Thus, no model species is added to represent the aqueous oligomers.~~ This is why it is necessary to perform two types of simulations to estimate the effect of the oligomerization process: a reference case – called hereafter REF – and a scenario case (KPH). The differences in the pBiA0D concentration fields between the two simulations represent aqueous oligomerization in the KPH approach:

$$[\text{Oligomers}] = [\text{pBiA0D}]_{\text{KPH}} - [\text{pBiA0D}]_{\text{REF}} \tag{2}$$

To implement this approach in the model and ensure the robustness of the modified partitioning constant value, it was necessary to adequately account for the acidity of the deliquescent particles. The particle pH is calculated in CHIMERE by an online coupling with the ISORROPIA model (http://nenes.eas.gatech.edu/ISORROPIA) that solves the transition between solid and aqueous phases through the estimation of the deliquescent relative humidity. However it is also possible to run ISORROPIA in a metastable configuration, which considers that aerosols remain in a liquid state, thus avoiding the transfer of dissolved BiA0D ~~towards~~ the gas phase ~~under conditions of low relative humidity, thus~~ favoring oligomer persistence ~~and~~ its transport in the atmosphere.

This alternative is taken into account for the evaluation of the KPH approach. ISORROPIA model also provides – for each cell and at every time step of the model calculation – particle water content and ion species equilibrium concentrations. At the end of the ISORROPIA computation, we constrained the particle pH to a range of values between 2 and 6. The upper limit of 6 allows us to be consistent with the parameterization and to avoid partitioning constant values lower than that of the reference (see Eq. 1). The lower limit was set for numerical reasons, as the transfer of the concerned organic species to the aqueous phase becomes total under a pH of 2.

2.3 Module implementation

As mentioned in the previous section, isoprene oxidation products could not considered as oligomer precursors in the pH-dependent approach, due to the absence of structural information on these species in the gaseous chemical scheme. A refined chemical scheme for isoprene oxydation in CHIMERE is under development (Couvidat and Seigneur, 2011) and will be included later in the model. Pending this future model develoment, we focus here on a comparative evaluation of oligomerization of monoterpene oxidation products using the two parameterizations described above. Nevertheless, the absence of molecular structure allocation for ISOPA1 and ISOPA2 (model oxidation products of isoprene) is not a limiting factor for the kinetic approach. Thus, considerations about the relative importance of kinetic oligomer production from monoterpenes and isoprene will be presented in the result section.

One important issue in SOA production is the influence of the gas-particle partition of semi-volatile species on the final model results, whether under dry or wet conditions. However, since this work focuses on the reactivity of hydrophilic compounds, we specifically addressed the issue of Henry's constant values, K_H. By affecting the fraction of the semi-volatile species that partition into the aqueous phase, this constant directly impacts the quantitative production of the organic aerosol fraction. Furthermore, the reliability of K_H values is known to be low for complex compounds of atmospheric interest~~, especially for highly soluble species (Raventos et al., 2010). In order to observe the effect of refining these values in the different approaches, we ran the model with different sets of K_H values. To that end, the group contribution method of Suzuki et al. (1992) that is used by default in CHIMERE to produce K_H values at 298 K was replaced by a new group contribution approach called GROMHE, developed by Raventos~~

~~et al. (2010). This approach, which is based on the molecular structure of the molecule, was shown to be more reliable than the standard methods for complex organic compounds of atmospheric interest.~~ By default, the molecular structure selected for BiA0D in CHIMERE is that of pinonaldehyde, a 10-carbon-atom molecule with an oxo group and an aldehyde group, while BiA1D and BiA2D are respectively based on norpinic acid (9-carbon-atom molecule with a carboxy group and an oxo group) and on pinic acid (9-carbon-atom molecule with two carboxy groups). Table 1 summarizes the default structure properties and molar masses, as well as the partitioning and saturation pressure characteristics used in CHIMERE for the 3 hydrophilic surrogates that lead to oligomer production from monoterpenes.

In order to evaluate the importance of considering a given molecular structure for each of these surrogate species, we computed different K_H values for them, corresponding to the different molecular structures they implicitly account for. The importance of investigating K_H values for our study is demonstrated in the next section (Sect. 3.1.1). Then, following the discussion of the results of the standard oligomerization approaches, we will discuss the results of additional oligomerization simulations conducted using a range of possible K_H values. These sensitivity tests are presented in detail in Sect. 3.2.

3 Results

3.1 Model approaches for oligomer formation

3.1.1 Precursor partitioning in the reference case

In order to examine the gas-particle partition of the model surrogates, we report in Fig. 2 the average concentration fields of the hydrophilic and hydrophobic surrogates simulated by CHIMERE in the reference case for the period 20 July–3 August 2006. This figure indicates that BiA1D is the highest hydrophilic contributor to the organic aerosol mass concentration, while BiA0D remains quasi-exclusively in the gas phase. However, among the monoterpene surrogates, the hydrophobic species BiBmP is the largest contributor to the organic aerosol mass concentration. On average, hydrophilic and hydrophobic species account for 25 and 75 % of this organic aerosol mass concentration, respectively.

As the impact of the K_H partitioning constant value is likely to be important for the formation of oligomers, we focused on gaseous hydrophilic species and on the processes governing their transfer toward the particulate phase. To that end, we analyzed two different situations. In the first one, the aerosol is treated as a deliquescent aerosol where the distribution of the hydrophilic species between the gas and the condensed phases is driven by Henry's law. In the second one, we consider a dry aerosol where the partition of hydrophilic species is driven by Raoult's law.

For the deliquescent aerosol situation, we calculated the partitioning coefficient as described by Mouchel-Vallon et al. (2013), where the fraction of the surrogate species in the aqueous phase is obtained as follows:

$$\xi^i = \frac{C_a^i}{C_a^i + C_g^i} = \left(1 + \frac{1}{H^i RTL}\right)^{-1} \tag{3}$$

In this equation, C_a^i and C_g^i represent (in $\mu g\,m^{-3}$) the concentration of species i in the particulate and gas phases respectively; H_i is the Henry's law constant (in $M\,atm^{-1}$); R is the ideal gas law constant; T is the temperature, and L is the liquid water content (LWC) of the aerosol (in cm^3 liquid water cm^{-3} air). We set the liquid water content value within the 10^{-11}–10^{-12} range of values proposed by Engelhart et al. (2011) for a deliquescent aerosol.

For a dry aerosol we used an equation similar to Eq. (3), which has been shown to apply equally to the organic compounds that condense into an organic phase (e.g., Donahue et al., 2009; Valorso et al., 2011). There, M_w stands for the mean organic aerosol molar mass (set to $250\,g\,mol^{-1}$ based on Robinson et al. (2007), C_{OA} represents the total organic aerosol mass concentration (µg m^{-3}) and P_{vap} is the saturation vapor pressure (atm) and considering an ideal mixture.

$$\xi^i = \frac{C_{\mathrm{a}}^i}{C_{\mathrm{a}}^i + C_{\mathrm{g}}^i} = \left(1 + \frac{M_{\mathrm{w}} P_{\mathrm{vap}}}{C_{\mathrm{OA}} RT} 10^6\right)^{-1} \qquad (4)$$

Figure 3 illustrates the gas-particle partition of the three semi-volatile compounds considered in our work for the two distinct situations. The fraction of the compound present in the particulate phase (represented by ξ_i values) is plotted as a function of K_{H} for a deliquescent aerosol under typical atmospheric liquid water content situations (upper graph), and as a function of P_{vap} in the case of a dry organic aerosol with C_{OA} ranging from low (0.1 µg m^{-3}) to high (10 µg m^{-3}) atmospheric concentrations (lower graph). This figure shows how the magnitude of the condensation process increases with the K_{H} value (Fig. 3a) and decreases with the saturation vapor pressure (Fig. 3b). To analyze these results, each graph can be split into 3 parts.

For deliquescent aerosols:

- ~~When the Henry's law constant value is lower than 10^7 M atm^{-1} (part I) or greater than 10^{13} M atm^{-1} (part III), then whatever the value of LWC, the equilibrium is either totally in favor of the gas phase (part I, insoluble compounds) or in favor of the particulate phase (part III, soluble compounds), respectively.~~

- For intermediate K_{H} values (part II), the mass of the semi-volatile species is shared between the two phases. In this area, partitioning towards the aqueous phase is an increasing function of LWC values.

Similarly, for dry aerosols:

- The partition is completely in favor of the aerosol phase (low volatility compounds – part 1) or towards the gas phase (volatile compounds – part 3) whatever the C_{OA} for saturation vapor pressures that are lower than 10^{-13} atm or greater than 10^{-6} atm, respectively.

- For intermediate values (part 2, shaded area), partitioning towards the condensed phase increases with increasing C_{OA}.

The main conclusions that can be drawn from these graphs are the following. First, over this set of atmospheric situations, and whatever the nature of the aerosol – BiA0D never contributes significantly to OA formation. Indeed, ξ_{BiA0D} values reach a maximum of 0.3 % in the most favorable combination (dry aerosol, $C_{\mathrm{OA}} = 10\,\mu\mathrm{g\,m}^{-3}$). Second, ξ_{BiA1D} and ξ_{BiA2D} values respectively range from 1.7 to 14.4 % and from 1.5 to 12.9 % for a deliquescent aerosol, and span the 3.30–77.4 % and the 4.9–83.9 % ranges in the presence of a dry aerosol. Thus, BiA1D and BiA2D are likely to sweep a wide range of partitioning states in the presence of a dry aerosol, while their K_{H} value are too low to account for a substantial transfer to the aqueous aerosol phase in the presence of a deliquescent aerosol. One should note, however, that in the dry aerosol model (Eq. 4), the activity coefficients are assumed to be unity; in other words, one does not account for interactions among organic species. Since hydrophobic and hydrophilic species have significantly different molecular structures, one could anticipate that including the activity coefficients in the model would reduce the absorption of the hydrophilic species in the hydrophobic organic phase or even lead to the formation of a separate organic phase (Couvidat and Sartelet, 2015). Therefore, the values given for the partition of hydrophilic aerosol should be seen as upper limits. Considering those 2 elements, K_{H} appears to be an influential parameter for BiA*D species, its modulation – with regard to the effective solubility of the surrogates – being likely to strongly enhance the oligomer production efficiency when the aerosol is deliquescent and when the residual gas fraction of the surrogate is not negligible. A species such as BiA0D, which currently remains mostly gaseous in the standard version of the model, may thus be particularly sensitive to the reference value of its Henry's law partitioning constant.

It is thus important to determine how uncertainties in the K_{H} value influence the results and efficiency of the two oligomer production approaches. For this purpose, we conducted sensitivity tests to the refinement of the most uncertain K_{H} values, taking into account the structure of the model species and of its components.

3.1.2 Oligomer production from the oxidation of monoterpenes

CHIMERE simulations were launched in the reference, KIN, and KPH configurations (both modes) for the two periods of interest defined above. The quantitative differences in the concentrations of the simulated biogenic oligomers, as well as their spatial and temporal features, were investigated. As mentioned previously, we focused on the comparison between the BiOLG (KIN approach) and the pBiA0D$_{\mathrm{KPH-REFERENCE}}$ (KPH approaches) concentration fields.

Figure 4 presents the oligomer daily concentration maxima simulated by CHIMERE from the oxidation of monoterpenes for both parameterizations and for one representative day of the simulated period. It highlights large differences in the oligomer concentration fields produced in each approach, both in terms of intensity and spatial distribution. Indeed we can see that, using the KIN approach, the highest oligomer concentrations reach about 0.80 µg m^{-3} over southeastern Europe (Fig. 4a) while in both KPH configurations the peak values are highly localized (not necessary in the same areas according to the mode used) and may exceed 1 µg m^{-3} (Fig. 4b and c), with local peaks around 1.50 µg m^{-3} (not visible on the color scale). The same ~~discrepancies~~ between the KIN and the KPH model configurations are observed for every day of the summer period, with daily concentration maxima spanning the 0.30–1 µg m^{-3} and the 0.80–2.50 µg m^{-3} ranges, respectively. In terms of hourly peaks, we can learn from the KPH results that there are areas of high gaseous precursor concentrations where BiA0D solubility is (at least transiently) strongly enhanced by local reductions in pH. According to Fig. 3 the decline in pH has to be greater than 3 or 4 units with regard to the reference value of 6, so as to increase the BiA0D partitioning constant by several orders of magnitude and allow the massive transfer of the species to the particulate phase. Such conditions appear to be met off the eastern Italian and over well-delimited forested continental areas of northern Spain notably. From the elevated peak values, it seems likely that the formation of oligomers proceeds by rapid changes in the BiA0D partitioning. In return, the inhomogeneity of oligomer concentration fields suggests a recurring evaporation of the particulate aerosol component in the deliquescent mode and/or the instability of low pH values. As for the KIN approach, we can see that the time required for the kinetic process as well as the irreversible nature of the coded process allow the presence of large regional oligomer plumes with smooth concentration gradients, as well as the presence of significant amounts of this species over the entire domain.

When averaging our results over the whole summer period, we observe no significant change in the location of high oligomer concentrations, though concentration values are logically lower than hourly peaks, and concentration fields show smoother gradients. However what is interesting is that the quantitative trends differ from those observed previously (Fig. 5). Indeed, the KIN parameterization produces the highest average oligomer concentrations that range from 0.1 to 0.4 $\mu g\,m^{-3}$ over most of the simulation domain. This approach forms well-mixed secondary plumes similar to those of other long-lived atmospheric oxidants such as ozone, with maxima over Central Europe and Mediterranean areas. On the contrary, KPH oligomers only slightly exceed 0.1 $\mu g\,m^{-3}$ in both deliquescent and metastable modes, except over small regions of the Adriatic Sea and over northern Spain areas where they only reach up to 0.3 $\mu g\ m^{-3}$ in the deliquescent mode. It is noticeable that, due to the persistence of an aqueous phase, the metastable mode produces higher oligomer concentrations over the entire domain. However, the difference remains moderate in terms of absolute mass concentration. This feature confirms the lack of oligomer mass accumulation in the KPH approach that was observed in the spatial analysis of hourly maps. ~~Beyond this, it indicates that favorable conditions for oligomers production are not often met along time.~~ The conditions of the process reversibility have to be more precisely identified and understood, for both modes of the KPH approach.

3.1.3 Driving parameters of both approaches

We explored these differences in order to identify the parameters driving production, transport and decomposition of oligomers over continental areas for both approaches.

First, the parameters describing the aerosol properties together with the BiA0D partition were plotted over the domain and analyzed for a given time step of the simulation. Then we investigated the temporal evolution of the BiA0D partition and oligomer formation at one grid point of the domain in the 3 CHIMERE configurations.

Figure 6 presents the nature (humid or dry) and the pH of the aerosol simulated over Europe for 24 July 2006 at 05:00 UTC, in relation with BiA0D concentration fields. The similarity of the aerosol type (dry or humid, Fig. 6a) determined by ISORROPIA and of the oligomer concentration fields (Fig. 6d) indicates that the existence of a deliquescent aerosol is not ensured in all grid cells and proves to be a discriminatory parameter for oligomer production in the simulations. Figure 6 also emphasizes the role of pH in this process. In northern Spain, significant oligomer formation is observed in the presence of both a wet aerosol and a very acidic aqueous phase (pH around 2.5), although this is not a region where the concentrations of BiA0D are high. On the contrary, over Great-Britain, where there is no significant oligomer formation, CHIMERE predicts the presence of a deliquescent aerosol, low gaseous BiA0D concentrations and a pH value around 4. These results place the pH threshold for a significant oligomer production from BiA0D at a value comprised between 3 and 4. Our previous calculations indicate that the fraction of BiA0D in the aerosol phase remains lower than 1 % for a pH of 4, but reaches up to 6–39 % for a pH of 3, considering a LWC in the 10^{-11} to 10^{-12} range ($\mathrm{cm^3\,water\,cm^{-3}}$). This exponential relationship supports the local formation of high oligomers concentration peaks in Fig. 6d, with regards to the conditions shown in Fig. 6a and b. Clearly, although the presence of the precursor is the first requirement for oligomer production, it is not a determining parameter of the structure of oligomer concentration fields. As the modeled pH strongly impacts the rate and the intensity of oligomer formation, its robustness was questioned. Although no direct measurements of the pH of the aerosol have been realized yet, our calculations are consistent with previous experimental studies reporting strongly acidic fine particles (Ludwig and Klemm, 1990; Herrmann, 2003; Keene et al., 2004). Our results are also consistent with the work of Xue et al. (2011), which is based on chemical composition and meteorological data collected at a suburban site in Hong Kong and which estimated the aerosol pH to range between −1.87 and 3.12.

In order to address the temporal variation of the aerosol properties related with oligomer formation, concentration time series for BiA0D (reference simulation – blue line) and for oligomers (KIN approach – red line, KPH approach – green line for the deliquescent mode, black line for the metastable mode) have been plotted in Fig. 7 for a given grid cell in northern Spain for the period from 20 to 24 July.

In the KIN approach, BiOLG progressively accumulates in the air mass and shows a smoothed concentration curve along time. Furthermore, oligomer concentrations are not strongly correlated with the presence of gaseous precursors due to the time required for the kinetic formation process. In the KPH approach, oligomer concentrations are highly variable, showing intense peaks that alternate with periods of near-zero content in the particle phase. It is noted that the black curve (KPH, metastable mode) present high values on 22 and 23 July that are not observed for the results of the deliquescent mode. These events are not either correlated with a specific origin of the air mass (analysis not shown here) or with a given BiA0D concentration threshold, but both take place during shaded periods and can therefore be attributed to the limiting effect of a dry aerosol in the deliquescent mode. However, from the co-variability of pBiA0D concentrations in shaded and non-shaded areas, it appears that the existence of a deliquescent aerosol is not the only driving parameter of this formation/evaporation cycle. Indeed, sharp decreases in the particulate fraction of BiA0D are simultaneously observed whatever the aerosol physic state (see 21–22 and 24 July for instance), which implies that pH variability also plays a decisive role during a large part of the day. During these periods, the pH was indeed comprised between 4 and 6, thus being the principal limitation for BiA0D storage in the particulate phase. Thereby, whatever the selected mode (deliquescent or metastable), there is no continental transport of oligomers due to ~~evaporation~~ processes. It results in the simulation of short duration peaks, accounting for local production from emissions.

Finally, Fig. 7 reveals the recurrent loss of particulate BiA0D in northern Spain during the period of study, mostly during daytime periods. It shows an average duration of 2 to 6 h for the oligomer peak events, which is quite short in view of the time required for pollutant mixing and transport in the troposphere. Therefore, these local phenomena cannot affect PM mixing ratios over large areas and for extended time periods. As the transfer of BiA0D to the gas phase from the aerosol is frequent and total in the KPH approach, its consistency has to be considered. This process appears to be highly dependent both on the pH variability – which has been poorly measured up to now – and on the K_H ~~correcting factor necessary to~~ alter the partition of BiA0D between the 2 phases. That is, the choice of the reference K_H value may be of primary importance. Such findings question the relevance of simulating a low-constrained reversibility for the formation of oligomers in 3-D models.

From these results, three key points can be inferred. First, the structure of oligomer concentration fields is driven both by the kinetic constant rate and by average pBiA*D concentrations in the KIN approach, while it mainly depends on the physical and chemical areosol properties in the KPH approach. In that latter approach, the formation of large quantities of oligomers appears to be conditional on the presence of a deliquescent aerosol and of strong acidity, sufficient initial particulate material, and possibly high radical levels for the oxidation of biogenic VOCs. However, most of the differences between this equilibrium approach and the kinetic one may be reduced by considering a greater stability (better constrained reversibility) in the pH-dependent oligomerization process. The relevance of taking this into consideration in 3D models will be discussed in the last part of this article. Second, the total mass of simulated oligomers, as well as their participation in the organic fraction of the aerosol, is clearly specific to the adopted approach. This is quantitatively described in Sect. 3.1.4. Finally, we have shown that the default solubility to BiA0D is a determining element of the model results in the KPH approach. As it affects the default quantities of BiA0D (and other oligomer precursors) in the aerosol, it may also play a major role in the results of the KIN approach. As the allocation of this parameter is quite uncertain, the sensitivity of the model results to K_H will be investigated in Sect. 3.2.

3.1.4 Oligomer to organic aerosol ratio in summer

In a second step, we estimated the contribution of the modeled oligomers to the biogenic secondary organic aerosol (BSOA) budget. For this analysis, we first considered the ratio of oligomers arising from monoterpenes only to the so-called $BSOA_{terp}$ (fraction of SOA induced by both hydrophilic and hydrophobic species from monoterpenes, Fig. 8) and then, using the KIN approach only, all biogenic (isoprene included) oligomers (Fig. 9) and total BSOA.

When considering monoterpenes as the only oligomer precursors, the implementation of a kinetic approach (Fig. 8, left and central upper graphs) results in a significant increase (+1–2 $\mu g\,m^{-3}$) of the average OA mass concentration inside the plume. Although the general structure of the plumes is not changed, the kinetic production of oligomers leads to the presence of significant $BSOA_{terp}$ values over an area that is much broader than in the reference case. On the opposite, the KPH approach in deliquescent mode (Fig. 8, right upper graph) does not modify the average mass concentration and spatial distribution of $BSOA_{terp}$. The same conclusion can be drawn from the metastable version of KPH (not shown here). In terms of ratios, the OA fraction that remains under the form of oligomers (Fig. 8, lower graphs representing pOLG to $BSOA_{terp}$ ratio) represents 20 to 50 % of the organic aerosol mass originating in monoterpenes over all the continental areas in the KIN approach. It is due to the stabilization of a very large proportion of biogenic organic species in the condensed phase under the form of oligomers. However, extreme values of this ratio are simulated over marine areas (see the purple color, meaning that approximately 80 % of $BSOA_{terp}$ is under the form of oligomers). This phenomenon can be explained by a combination of two factors. First, irreversible and continuous oligomer formation is the only possible chemical evolution pathway for condensed biogenic species in this version of the model. Second, in our model, marine areas are very little influenced by fresh organic emissions, which tend to favor the omnipresence of an aged OA over the sea. This is probably wrong, as high contributions of primary organic matter to the marine aerosol were ~~observed~~ However, they are not taken into account in our simulations (Ovadnevaite et al., 2011). Furthermore, such a high degree of OA conversion to oligomers has never been reported in the literature. Although it is limited on that point, it may be partly unrealistic to simulate a single fate for all biogenic organics present in the particulate phase. Despite this statement, the absolute OA concentration simulated over the sea remains low ($< 0.2\,\mu g\,m^{-3}$), thereby limiting the impact of this potential bias in the model. ~~In~~ regards to KPH simulations, the model indicates (as expected) a very low average contribution of oligomers to the mass of $BSOA_{terp}$ over continental areas, except in the north of Spain – where the contribution of oligomers represents 10 to 20 % of the SOA mass concentration – and over marine areas where it sometimes exceeds 40 %. Over continental areas, the oligomer fraction is shown to be insignificant because of the frequent reversal of the formation process due to wide pH variations (see above).

Isoprene oxidation products are a major contributor (around 50 % in our simulations) to the total SOA mass. Therefore, when their potential for oligomerization is considered in KIN, they significantly contribute to this aged organic fraction. Indeed, as can be seen in Fig. 9, when isoprene surrogates are included in the OA aging process, the average BSOA mass fraction increases by 2 to $4\,\mu g\,m^{-3}$ over the whole eastern and southern areas of our domain. In these areas, its total concentrations reach 3 to $6\,\mu g\,m^{-3}$. The largest increases are obtained over Italy, as well as over the Mediterranean and Adriatic Seas, where the recirculation of continental air masses possibly favors air mass aging under low dispersion conditions.

These results highlight the importance of closer identifying the oxidation products of the main atmospheric BVOCs, as well as their structure and reactivity. In particular, questions still arise about the way the evolution of condensed isoprene derivatives should be represented. Indeed, the assumption of Carlton et al. (2010), which states that the formation of oligomers is driven by a same first-order rate constant whatever the oxidation products, is questionable. First, because this parameterization derives from the evolution of cyclic compounds in chamber experiments, which is the case of α- and β-pinene, the 2 most common monoterpenes, but not of isoprene and its derivatives. The oxidation of isoprene by hydroxyl radicals leads to the formation of methyl vinyl ketone and methacrolein (Pandis et al., 1991; Paulot et al., 2009), which in turn produce tetrols and methylglyceric acid (Claeys et al., 2004; Surratt et al., 2006; Kleindienst et al., 2009) that are aliphatic compounds. Although oligomer formation from the oxidation of isoprene has been shown to occur in smog chambers (e.g., Sato et al., 2011; Nguyen et al., 2011a, b; Liu et al., 2012a; Tan et al., 2012; Lin et al., 2014), the oligomer formation process is likely to differ significantly from that from aromatics as measured by Kalberer et al. (2004) Second, because this kinetic constant only stands for an average reactivity as Kalberer et al. (2004), during their experiments, could only observe the fact that 50 % of the total organic mass was conversed to oligomer-like species. Such results cannot establish whether all aromatic compounds had undergone oligomerization following the same pathway or if its evolution was only attributable to a specific set of compounds. Applying this parameterization to a large set of biogenic species may cause an incorrect assessment of the contribution of oligomers to the total SOA budget.

3.2 Sensitivity to the K_H value

From the model results presented in Figs. 4 to 7, we found that the amplitude of oligomer formation was potentially strongly dependent on the reference K_H value of BiA0D, whatever approach is taken. Yet, the solubility of Bia0D has to be considered as an uncertain parameter. First because Bia0D accounts for 11 monoterpenes oxidation products, which partition differently and may be poorly approximated via a unique K_H value. Second, because it is recognized that, regardless of the group contribution approach used, uncertainties in the estimation of K_H grow when solubility exceeds $10^4\,\mathrm{M\,atm^{-1}}$, due to a lack of experimental measurements (Raventos et al., 2010). This is an important issue as all the 11 species represented by pinonaldehyde all have a solubility greater than that of pinonaldehyde itself ($K_H = 4.97 \times 10^4\,\mathrm{M\,atm^{-1}}$).

This is notably the case of hydroxypinonaldehyde ($K_H = 3.26 \times 10^7\,M\,atm^{-1}$), ketolimonoaldehyde ($K_H = 1.7 \times 10^8\,M\,atm^{-1}$) or 2-hydroxy-3-iso-propyl-6-oxo-heptanal ($K_H = 2.5 \times 10^6\,M\,atm^{-1}$). Consequently, it appears warranted to consider the possibility for the BiA0D Henry's law constant to vary by several orders of magnitude. Thus, in order to evaluate the robustness of each approach to this input parameter, sensitivity tests to the solubility of the BiA0D species were conducted with CHIMERE.

3.2.1 Influence on the surrogate partitioning properties

In view of surrogate properties presented in Fig. 3a, our sensitivity study focused on the transition area, that is the 4×10^8–$4 \times 10^9\,M\,atm^{-1}$ range of K_H, which allows accounting for the solubility of all the potential oxidation products mentioned before, while providing estimates of the impact of correcting the global BiA0D K_H value. In this range, we considered 3 specific K_H values for BiA0D (4.97×10^4, 4×10^8 and $4 \times 10^9\,M\,atm^{-1}$). Before conducting the sensitivity tests in CHIMERE, we evaluated the influence of K_H on the partitioning coefficient of BiA0D, using the same graphs as in Sect. 2, over the whole range of possible pH values and with a liquid water content of $10^{-11}\,cm^3\,water\,cm^{-3}$. The results are presented in Fig. ~~10~~. The reference value ($K_H = 4.97 \times 10^4\,M\,atm^{-1}$, black curve of Fig. ~~10~~) corresponds to the left part of Fig. 3a, that is a quite null value of the partitioning coefficient. Here, we can see that only an acidic aqueous phase (pH < 4) allows the quantitative formation of oligomers. When increasing K_H to a value in the 4×10^8 to $4 \times 10^9\,M\,atm^{-1}$ range, we enter the second area of Fig. 3a, where the particulate fraction of BiA0D becomes significant for a LWC of $10^{-11}\,cm^3\,water\,cm^{-3}$). There, a significant formation of SOA takes place from neutral conditions with 10 % to 52 % of BiA0D being in the condensed phase, depending on the K_H value. For a pH of 5, particulate fraction reaches 48 and 90 % in favor of the aerosol phase, for $K_H = 4 \times 10^8$ and $4 \times 10^9\,M\,atm^{-1}$ respectively. However, in this transition area, the partition of the surrogate species remains strongly influenced by the liquid water content. Such results underline the threshold condensation phenomenon for this range of K_H values. Also, such a sensitivity of BiA0D solubility to the K_H value may have important consequences for the results of the KPH approach (whatever the mode considered). Indeed, considering the highest K_H value instead of the standard one, at pH = 6, in the reference simulations, causes the reference particulate fraction of BiA0D to increase from 0 to 52 % (with LWC = 10^{-11} cm^3 water cm^{-3}). The impact of implementing a pH-dependent approach will thus be lower and the resulting speciation of the OA material will show a much lesser proportion of oligomers.

3.2.2 Impact on the simulated oligomer concentration fields

The sensitivity tests were launched with CHIMERE in the reference, KIN and KPH configurations (in both deliquescent and metastable modes) using each time a different K_H value, as mentioned in the previous section. The average simulated oligomer concentrations fields are shown in Fig. ~~11~~ for the KIN (left), KPH deliquescent (center) and KPH metastable (right) approaches.

In the KIN approach, we observe that an increase in the value of the Henry's law constant value (from top to bottom, left column) induces an increase in average simulated oligomer concentrations, due to the low initial solubility of the BiA0D species, which was identified as a limiting parameter for the kinetic production of oligomer in the condensed phase. ~~However, this dependency exhibits a threshold phenomenon, as the increase of K_H by almost 4 orders of magnitude (from 4.97×10^4 to 4×10^8 M atm^{-1}) induces approximately the same response (0.1 to 0.2 µg m^{-3} of increase over Italy and the Adriatic Sea) as a further increase by one order of magnitude (4×10^8 to 4×10^9 M atm^{-1}).~~

The interpretation of the model ~~results~~ is more complex in the KPH configuration. As stated above, the KPH parameterization affects the partition between the gas and particulate phases, and oligomer concentrations are accounted for by an ~~increase~~ in the quantities of the condensed surrogate BiA0D. For the deliquescent mode, when K_H is set to 4×10^8 M atm^{-1} (Fig. ~~11~~e), oligomer concentrations increase over continental areas on average by 0.1 to 0.2 µg m^{-3} compared with the simulation using the

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standard K_H value (Fig. ~~11~~b). Indeed, as the solubility of Bia0D ~~grows,~~ the decrease in pH required to form particulate material is reduced. Thus, even for pH values around 4–5, the partitioning of BiA0D towards the aerosol is ~~increased~~. When shifting again the K_H value by one order of magnitude ($K_H = 4 \times 10^9$ M atm^{-1}, Fig. ~~11~~h), we observe a decrease in the oligomer concentrations compared with Fig. ~~11~~e. ~~This result illustrates the fact that the modification of the BiA0D partition creates less oligomer when~~ ~~K_H exceeds a given threshold. Indeed, the fraction of BiA0D in the condensed phase is by default substantial and there is thus no significant effect of adding an oligomer production parameterization. However, the total pBiA0D mass (already dissolved + produced from the modification of~~ ~~K_H) increases with~~ ~~K_H, from the top (Fig. 11b) to the bottom (Fig. 11h) scenario. As regards the metastable mode, the absolute increase in the oligomer concentration due to acidity is significantly higher than in the deliquescent mode (see the concentration scale that is 4 times larger compared with the KIN and KPH deliquescent maps) as the dependence upon relative humidity was removed. However, the same conclusions as for the deliquescent mode can be drawn.~~

~~Finally, whatever the initial choice of BiA0D solubility, the location and the spatial extent of oligomer formation remain different in the 3 configurations of CHIMERE. While the kinetic production of oligomer species leads to a diffuse plume reaching many remote areas of Europe, the highest concentrations of oligomers are definitely observed close to biogenic source areas in the KPH approaches. It is worthy to note that the KPH metastable configuration – associated with high~~ ~~K_H values for BiA0D – also allows the formation of large continental plumes, which is not observed in the deliquescent mode. This last configuration makes little sense, as the KPH approach is based on the possibility for OA formation to depend on the specificities of the aerosol aqueous phase which is no longer the case in Fig. 11c and h. However, as the plumes differ from those of the KIN approach, it brings our attention on the importance of oligomer formation rate from gaseous precursors, and on the number/types of precursors.~~

~~4 Discussions and conclusions~~

~~In view of oligomer concentrations simulated by CHIMERE using two different approaches, several points need to be discussed.~~

~~First, the oligomer concentrations in both approaches are highly influenced by the initial value of K_H. Yet 3-D models use one single value of this parameter to account for the behavior of a complex mixture of SOA precursors and this parameter is unable to restitute entirely the variability of the gas/particle partitioning of all these compounds in time and space. It is interesting to see that allocating a high default value to K_H allows an immediate transfer of SVOCs into the condensed phase and thus increase significantly the organic aerosol concentration in continental plumes. As rapid oligomer formation was observed in laboratory experiments, imposing a minimum value for K_H 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. However, this choice may affect the spatio-temporal distribution of organic aerosol as can be deduced from the large differences between the KIN and KPH oligomer plumes. It thus appears necessary to refine the Henry's law constant values of the SVOCs of atmospheric interest.~~

~~Second, improvements and developments could be considered for each approach. As for the KIN parameterization, it would be important to propose distinct values for the kinetic constants of the various oligomer precursors, in particular as Kalberer et al. (2006) have shown disparities in the temporal evolution of the aerosol molar mass considering the oxidation of trimethylbenzene, α-pinene and isoprene. Regarding KPH, one single oligomerization pathway is represented for all environmental conditions. This is one main limitations of the approach. Furthermore, its dependence on the nature and state (deliquescent or metastable) of the aerosol, as well as its pH – all determined by the ISORROPIA model – is probably overestimated.~~

~~But, more significantly, the two approaches differ on the irreversible (KIN) or reversible (KPH) property of the oligomerization process which, from our findings, is~~

~~one key point of this process. According to a recent study of Wang et al. (2010), the heterogeneous reactions forming oligomers on nanoparticules may be at least partially irreversible, as their persistence in the particulate phase upon water evaporation should be effective due to their their low volatility and their high molecular weight (Wang et al., 2010; Ervens et al., 2011; Liu et al., 2012b). This assumption is supported by the recent works of Hall and Johnston (2012a) who investigated the thermal stability of a SOA matrix including 50 % of oligomeric species formed by the ozonolysis of α-pinene: the authors concluded that, at ambient temperatures, oligomeric species should be nonvolatile by structure. These observations cannot be reproduced with the KPH-deliquescent approach as the production of OA is canceled right after each phase of water evaporation or pH increase. In the light of the recent experimental results mentionned above, a potential improvement of the KPH approach could be the addition of reactive uptake in aerosol, as for the KIN parameterization. Indeed, it is now recognized that organic compounds may undergo chemical reactions in the particle phase by both non-oxidative and oxidative reactions that lead to the formation of semi-volatile compounds and even non-volatile compounds in the case of high molecular weight species (Kroll and Seinfeld, 2008; Kroll et al., 2009). Furthermore, through laboratory experiments conducted on ozonolysis of α-pinene, oligomer formation would be driven by reactive uptake rather than by the partition of monomers between both phases (Hall and Johnson, 2012b). Nevertheless, this reactive uptake being observed within seconds (Heaton et al., 2007; Hall and Johnson, 2012b) it appears more realistic to represent the oligomerization process in two steps: a first fast step modifying directly the partitioning of monomers to represent the rapid formation of oligomers before the stabilization of the OA formed through a reactive uptake. Currently, the KIN approach does not allow this initial step.~~

~~In view of all these elements, a KPH-like approach using a metastable mode and considering a reactive uptake with partial reversibility could be a suitable parameterization to represent the formation of oligomers from monoterpenes. However the determination of the aerosol mode is not an obvious choice (Fountoukis et al., 2009). Moya~~

~~et al. (2002) have shown that considering a metastable mode for PM_1 (where organic matter is mainly present) leads, under low relative humidity conditions ($< 60\,\%$), to significant errors in the concentrations of the inorganic species which indirectly determine the aerosol pH and thus oligomers formation. The authors conclude that it is essential to consider a deliquescent mode for low relative humidity.~~

~~Concerning isoprene, we have mentioned the fact that it is recognized as an important precursor of SOA through its first generation products, methacrolein (MACR) and methyl vinyl ketone (MVK) (Pandis et al., 1991; Carlton et al., 2009). During recent experimental studies these compounds have been detected as important oligomer precursors in the condensed phase (El Haddad et al., 2009; Liu et al., 2012b; Renard et al., 2013). Renard et al. (2015), for instance, investigated the formation of oligomers through the photooxidation of MVK into a photoreactor. This study revealed that considering only a first-order rate constant to represent the formation of oligomers is not appropriate. Indeed, they highlighted that the oxidation of MVK by OH (in the condensed phase of a deliquescent aerosol) is governed by a kinetic competition between functionalization and oligomerization, depending on the precursor initial concentration. Furthermore, even if the oxidation mechanisms in the condensed phase are assumed to be the same as in the gas phase, the branching ratio in favor of highly oxidized monomers seems to be more important than in the gas phase (Kroll and Seinfeld, 2008). Furthermore, based on the laboratory experiments of Renard et al. (2015), Ervens et al. (2015) developed a chemical mechanism for the oligomerization of MVK and MACR in a deliquescent aerosol. Using a multiphase box model, they underlined the potential key role of MVK to oxygen concentration ratio in the oligomerization rate, under atmospherically relevant conditions. Thus, the oligomerization process of isoprene derivatives constitutes a complex atmospheric multiphase process where a kinetic approach is probably relevant to represent the initial formation of oligomers, but a second-order rate constant would be more suitable than the current first-order rate constant to represent the oxidation of first-generation isoprene products by $OH_{(aq)}$. However, further experimental work about MVK and MACR aqueous reactivity is needed to consolidate the~~

~~experimental findings before implementing such chemical schemes in AQMs. As an example, Ervens et al., (2015) proposed a k_{oligo} of 2.50×10^{-12} molec cm^{-3} s^{-1} for the single oxidation reaction of MVK (or MACR) by hydroxyl radical to form oligomers, but they recommend being cautious with this value due to the fact that the kinetics could be different when considering different atmospheric conditions (LWC, $OH_{(aq)}$, MACR, MVK concentrations. . .).~~

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Table 1. Properties of the biogenic hydrophilic and hydrophobic surrogate SOA species used in the simulations conducted with the CHIMERE model.

Surrogate species	Molecular Structure	Molar Mass ($g\,mol^{-1}$)	Henry's law constant[1] ($M\,atm^{-1}$ at 298 K)	Saturation vapor pressure[2] (atm)	Considered in KIN[3]	Considered in KPH[3]
BiA0D	Pinonaldehyde	168	4.97×10^{4}	3.55×10^{-7}	Yes	Yes
BiA1D	Norpinic acid	170	6.85×10^{8}	2.86×10^{-10}	Yes	No
BiA2D	Pinic acid	186	6.03×10^{8}	1.88×10^{-10}	Yes	No
BiBmP	C15 oxo aldehyde	236	10^{-2}	3.97×10^{-9}	Yes	No

[1] The Henry's law constants are calculated with the group contribution approach, GROMHE.

[2] Pun et al. (2006).

[3] Surrogate undergoing oligomerization.

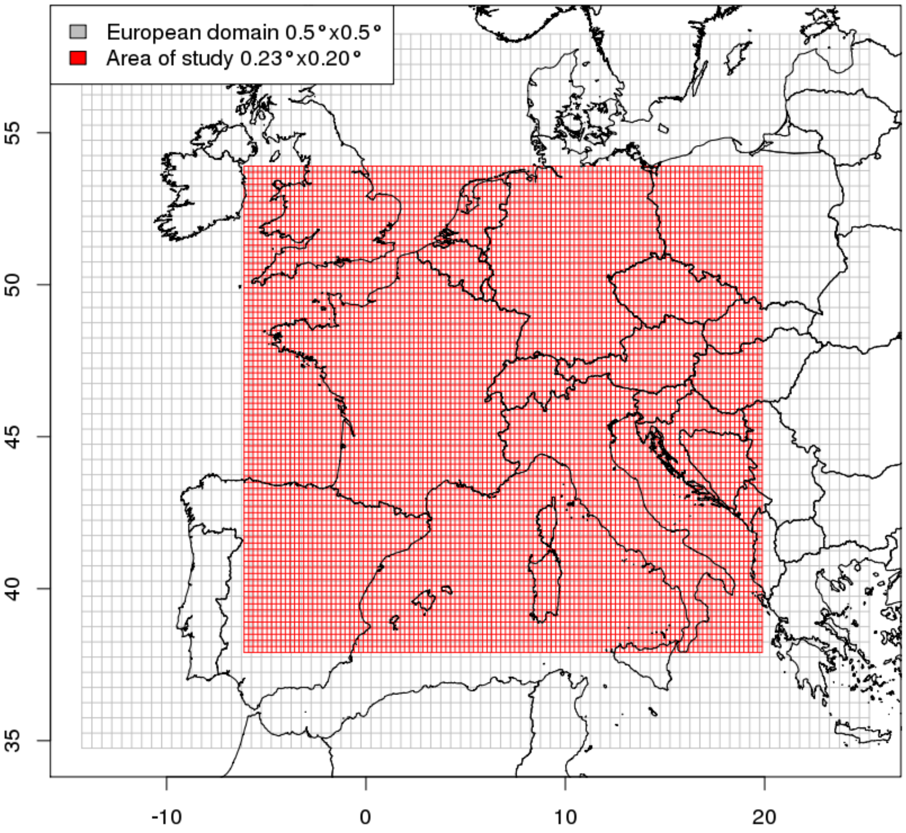

Figure 1. In red, gridded domain used for the air quality simulations, having a horizontal resolution of 0.23° × 0.20°. In black, large-scale domain used to provide boundary conditions (horizontal resolution of 0.5° × 0.5°).

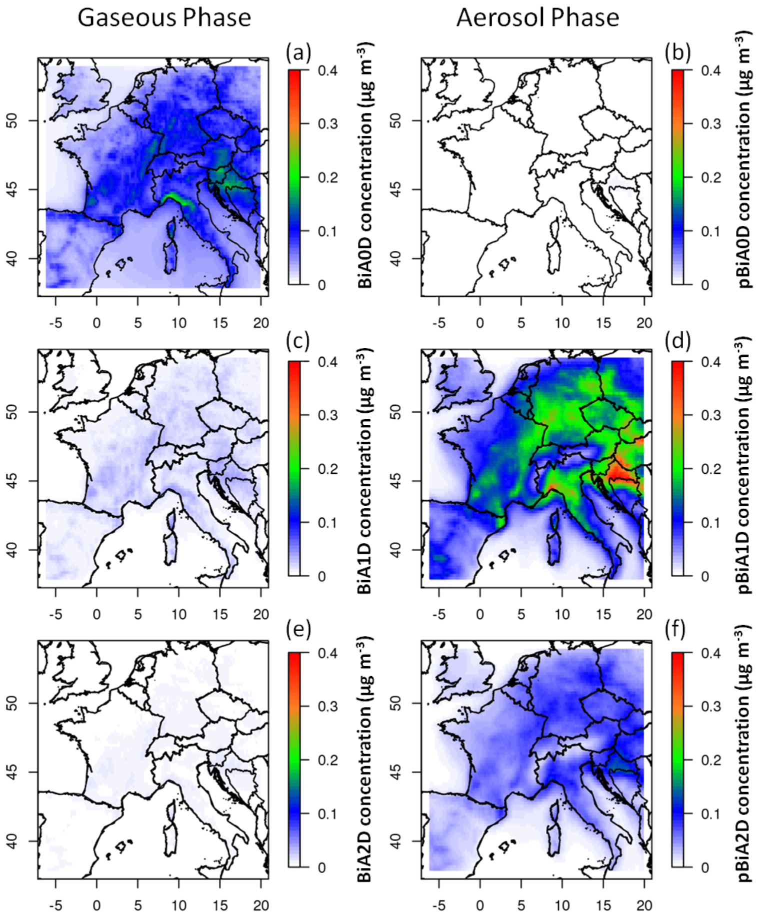

Figure 2. Mass concentration fields of BiA0D (**a** and **b**), BiA1D (**c** and **d**), BiA2D (**e** and **f**) and BiBmP (**g** and **h**) in the gas (left) and particulate (right) phases, modeled by CHIMERE and averaged over 20 July–3 August 2006.

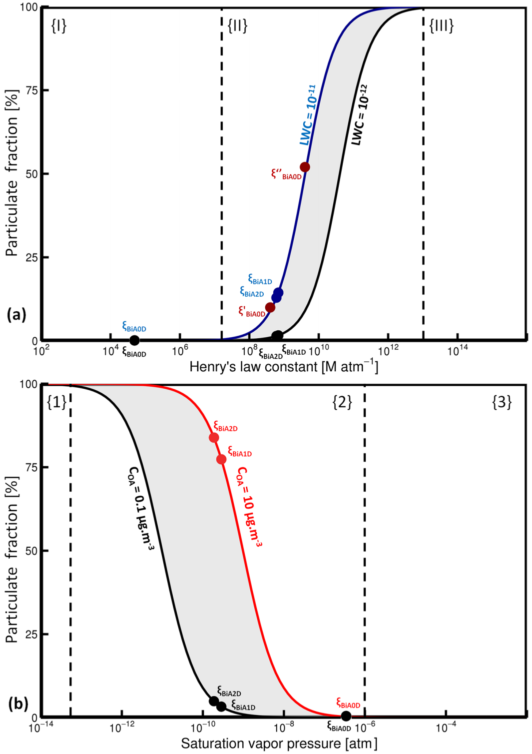

Figure 3. Particulate fraction as a function of Henry's law constant (upper figure) and as a function of saturation vapor pressure (lower figure). The partition of each surrogate is represented by the colored dots for different conditions of organic aerosol mass concentration. Shaded areas represent the range of typical atmospheric condition.

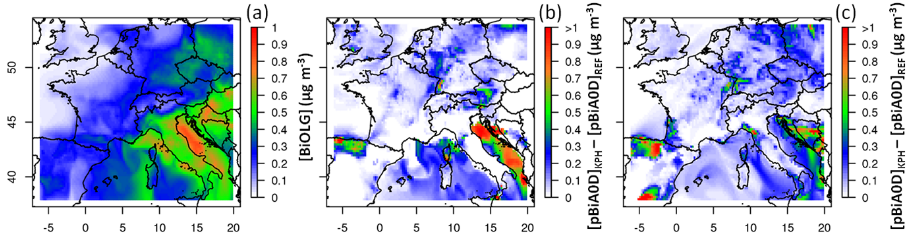

Figure 4. Oligomer daily maxima modeled with the two modeling approaches, using 3 different CHIMERE configurations for oligomer formation: KIN **(a)**, KPH Deliquescent **(b)** and KPH Metastable **(c)** for 24 July 2006.

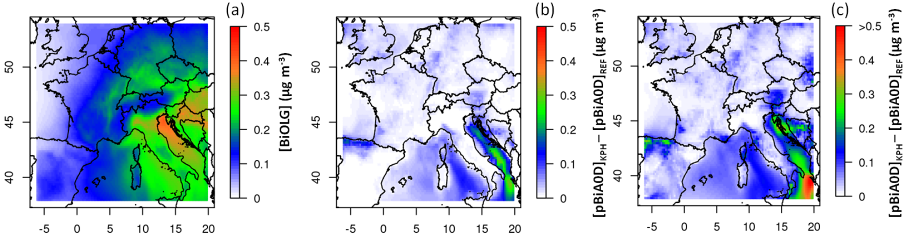

Figure 5. Average modeled oligomer concentration fields from monoterpenes in the KIN **(a)** and KPH configurations considering both deliquescent **(b)** and metastable mode **(c)** for the period of 20 July–3 August 2006.

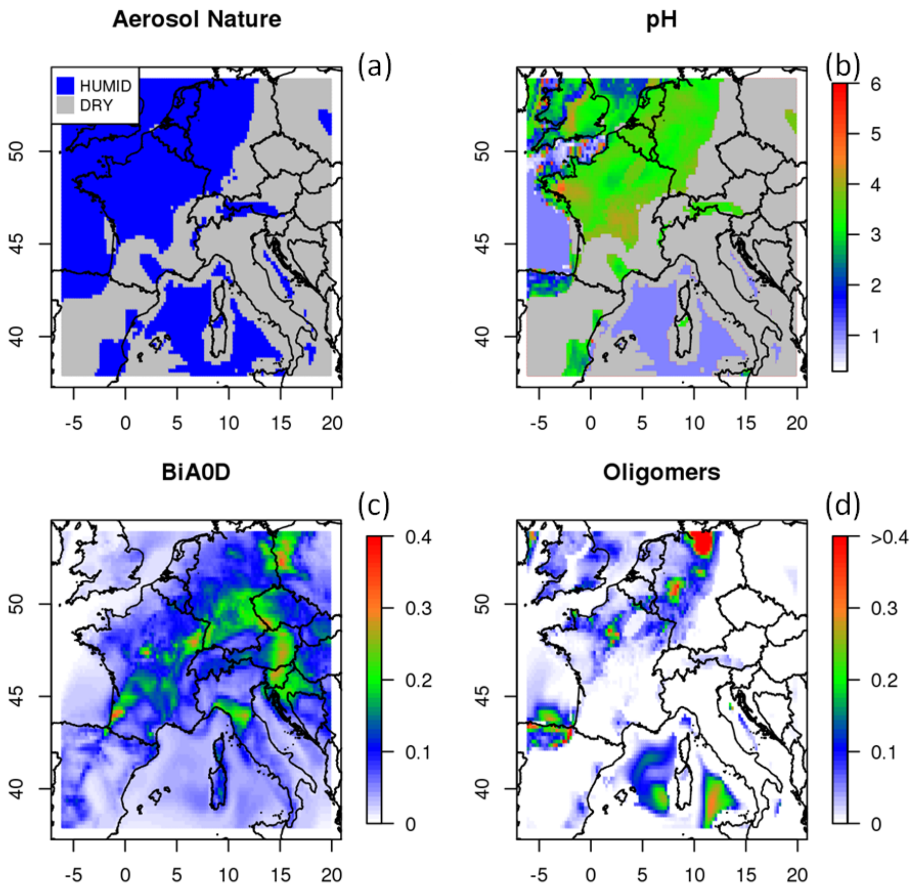

Figure 6. CHIMERE results for 24 July 2006 at 05:00 UTC: nature (humid or dry) of the aerosol **(a)**, pH of the aqueous phase **(b)**; BiA0D precursor concentration fields in the gas phase for the reference simulation ($\mu g\,m^{-3}$) **(c)** and oligomer concentrations ($\mu g\,m^{-3}$) **(d)** obtained with the KPH approach.

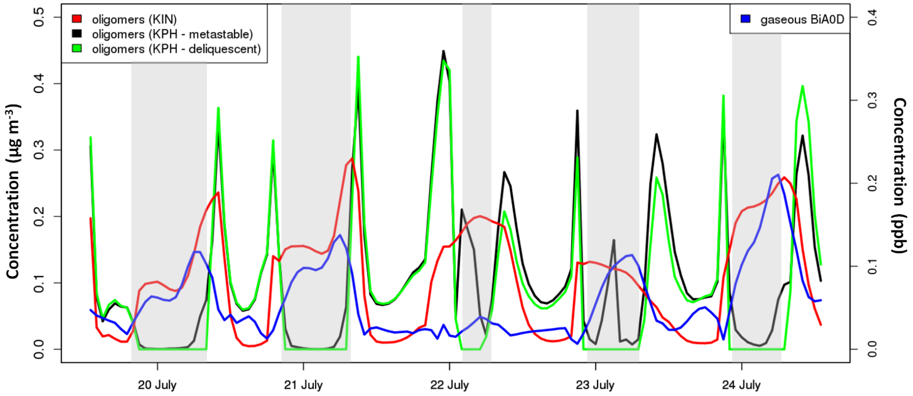

Figure 7. Time series of BiA0D concentrations (ppb) in the reference simulation (blue line), the KIN (red line) oligomer concentrations (µg m^{-3}), and the KPH oligomer concentrations (µg m^{-3}) in the deliquescent mode (green line) and in the metastable mode (black line), as simulated with CHIMERE for the 20–24 July 2006 period. The shaded areas correspond to the presence of a dry aerosol in the deliquescent configuration.

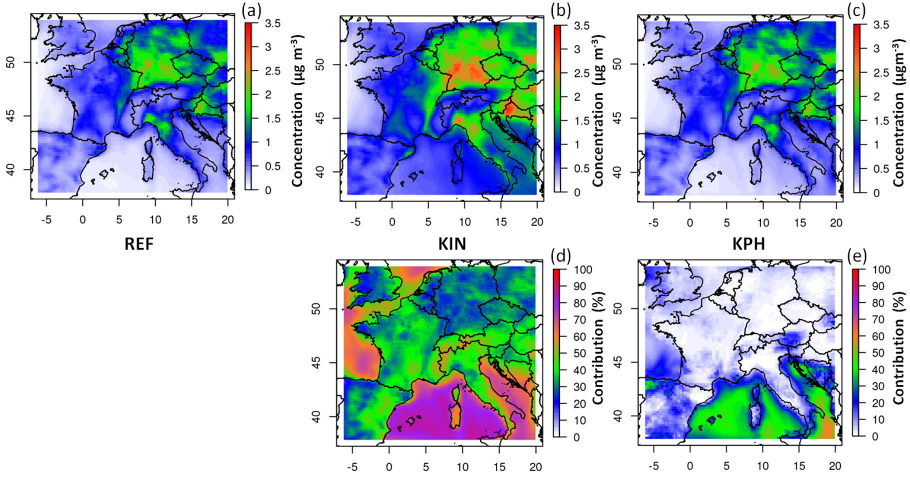

Figure 8. Modeled average BSOA concentration from monoterpenes simulated in the reference case (left), from the KIN approach (center) and from the KPH approach in the metastable mode (right) for the period 20 July–3 August 2006. Lower graph: contribution of oligomers to $BSOA_{terp}$.

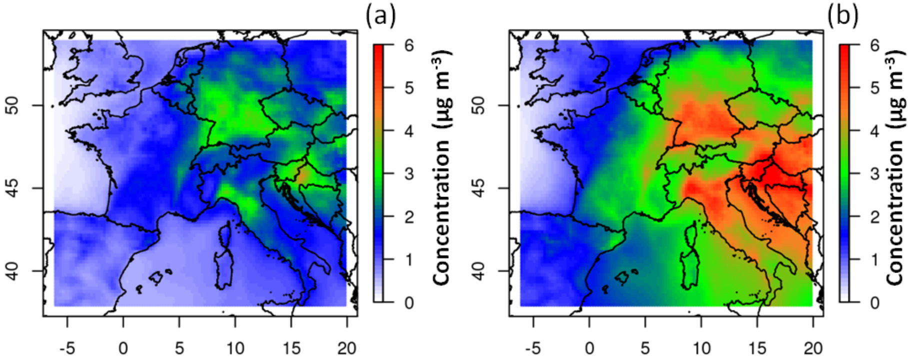

Figure 9. Modeled average BSOA concentration from isoprene and monoterpenes in the reference case (left) and from the KIN approach (right) for the period 20 July–3 August 2006.

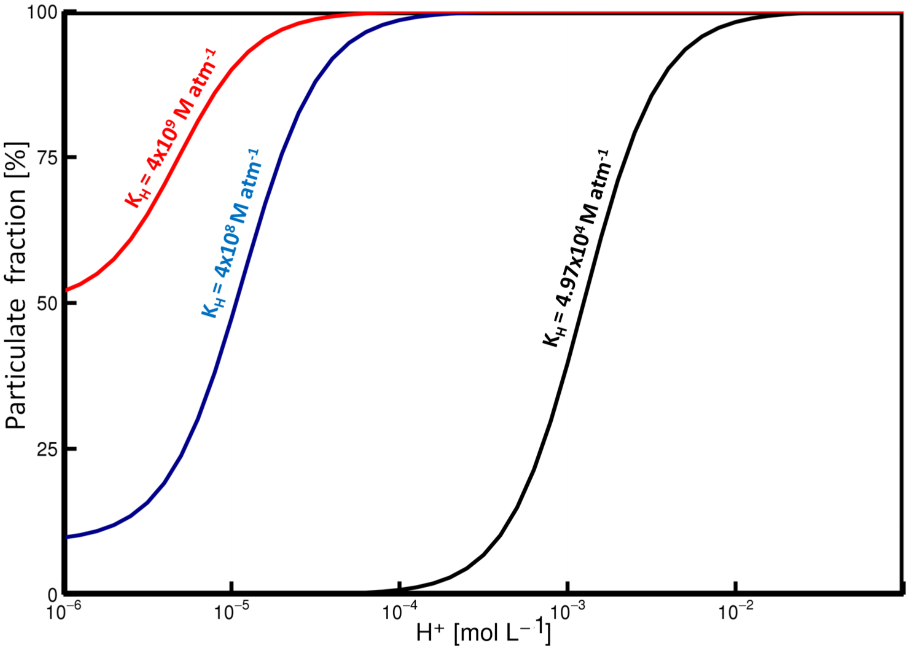

Figure ~~10~~. Evolution of the particulate fraction of a given species as a function of H$^+$ concentration, for 3 different values of its Henry's law constant $K_\mathrm{H} = [4.97 \times 10^4;\ 4 \times 10^8;\ 4 \times 10^9\,\mathrm{M\,atm^{-1}}]$ at a LWC of 10^{-11} cm^3 water cm^{-3}.

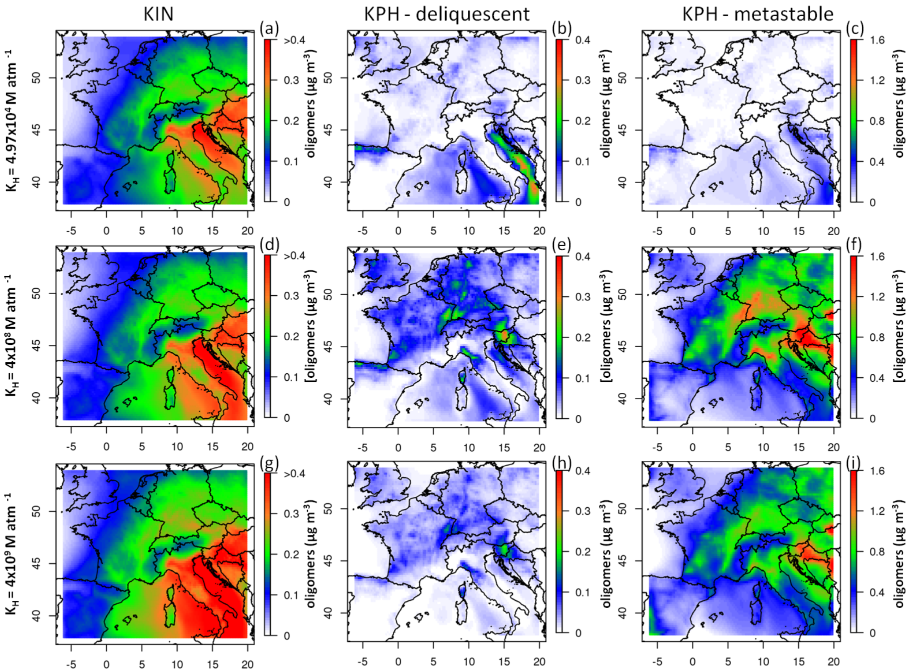

Figure ~~11~~. Mean modeled oligomer concentrations from monoterpenes hydrophilic surrogates (thus without BiBmP) for both approaches: KIN (left), KPH deliquescent (center) and KPH metastable mode (right) over 20 July–3 August 2006. The simulations are conducted using for BiA0D the following K_H values: 4.97×10^4 M atm^{-1} (top, **a**, **b** and **c**), 4×10^8 M atm^{-1} middle, (**d**, **e** and **f**) and 4×10^9 M atm^{-1} (bottom, **g**, **h** and **i**).

3.1.5 Comparisons of KIN and KPH approaches with measurements

As mentioned above, no direct measurement of the oligomer fraction of SOA is available at ground based measurement stations. However, we can assess the role of oligomer formation processes in improving model-measurement comparisons, knowing that the organic fraction of atmospheric aerosols is usually underestimated by models (Heald et al., 2011). In this section, we present the comparison of CHIMERE organic carbon (OC) mass concentration in the PM_{10} fraction of aerosols, obtained with 4 different model configurations (REF, KIN and KPH in both modes) with measurements obtained at two EMEP background sites : the rural stations of Harwell in the United Kingdom (100km west of London) and Melpitz in Eastern Germany (150km south of Berlin). Figure 10 presents these comparisons for the period July 20th - August 3rd 2006, the statistical data (mean bias (MB), normalized mean bias (NMB), root mean square error (RMSE), normalized root mean square error (NRMSE) and correlation coefficient (R)) being given in Table 2.

Globally, whatever the configuration, the modeled OC is severely underestimated at both stations. Nevertheless, the KIN approach provides an increase in the OC mass concentration of about 1 µg m^{-3}, which reduces significantly the gap between model and measurements, both at Harwell and Melpitz sites. According to Table 2, the mean bias is reduced from -1.10 to -0.82 µg m^{-3} (Harwell) and from -2.71 to -1.82 µg m^{-3} (Melpitz) compared with the reference simulation, but the correlation coefficient remains the same (around 0.5 and 0.7, respectively). This is due to the fact that the impact of the kinetic-dependent production of oligomers is quite little time-dependent and thus doesn’t allow the restitution of the peaks observed along the period and missed by CHIMERE in its reference configuration. Thus, this approach rather provides an increase in the OC background level and doesn’t position oligomers as likely to account for the short-time variability of OC in summer. This result highlights the importance of ensuring the consistency of the process kinetics, and intensity (which is K_H-dependant).

The pH-dependent approaches have shown to cause a fast and intense production of oligomers that may induce such a short-time variability in the SOA fraction of the aerosol. Here, though, there is no quantitative impact of this process on the OC mass concentration level all along the period, whatever the site. Such results could be expected in the deliquescent configuration, since we concluded that the simulated relative humidity was too low to permit the transport of oligomers over long distances. But it appears that the metastable mode, which promotes oligomer persistence and its transport in the atmosphere, also doesn’t significantly impact the organic carbon concentration at those sites. One possible explanation for this lack of effects is the non-inclusion of isoprene as an oligomer precursor in the KPH simulations, especially because the analysis of the model output reveals that 60 to 70% of KIN oligomers derived from isoprene at both stations. However, the conditions in which the KPH simulation was launched, and mainly the K_H value used for the BiA0D species in conjunction with the variability of the aerosol pH, could also account for the low production of oligomers in remote continental areas of Europe.

The sensitivity of oligomer parameterizations to the K_H input parameters is investigated in the next paragraph.

4 Discussions and Conclusions

Given the dissimilarities between the oligomer concentration fields simulated with CHIMERE using two different approaches, and considering the sensitivity tests that were conducted, the principles that guide the different approaches must be discussed, and further developments have to be considered.

4.1 Oligomer formation from isoprene

First of all, the fate of isoprene in the condensed phase shall be examined, as isoprene has been recognized as a major SOA precursor through its first generation products methacrolein (MACR) and methyl vinyl ketone (MVK) (Pandis et al., 1991; Carlton et al., 2009), which were found to be important oligomer precursors in the condensed phase (El Haddad et al., 2009; Liu et al., 2012b, Renard et al., 2013). On this specific point, the study of Renard et al. (2015) based on the photooxidation of MVK into a photoreactor revealed that considering only a first-order rate constant to represent the formation of oligomers is not appropriate, as the oxidation of MVK by OH was (in the condensed phase of the deliquescent aerosol) governed by a kinetic competition between functionalization and oligomerization, which depends on the precursor initial concentration. Furthermore, the branching ratio in favor of highly oxidized monomers seems to be more important in the condensed phase than in the gas phase (Kroll and Seinfeld, 2008), thus favoring the formation of a stable OA. A multiphase box model study conducted by Ervens et al. (2015) based on the laboratory experiments of Renard et al. (2015) underlined a potential key role of the MVK-to-oxygen concentration ratio in the oligomerization rate under atmospherically relevant conditions. Thus, in the case of isoprene, the formation of oligomers via the oxidation by $OH_{(aq)}$ in the condensed phase may well be represented by a kinetic approach based on a second-order rate constant. The authors propose a k_{oligo} of 2.50 x 10^{-12} molec cm^{-3} s^{-1} for the single oxidation reaction of MVK and MACR by OH_{aq}, but they recommend being cautious with this value as the kinetics may differ within the variety of atmospheric conditions (LWC, $OH_{(aq)}$, MACR, MVK concentrations…).

4.2 Further developments for oligomer formation dynamics

On a broader level, the difficulty of restituting faithfully oligomer yields and SOA formation dynamics comes from the diversity of the phenomena that drive SOA formation in the atmosphere. It is indeed clear now that oligomerization processes, which may produce up to 50% of SOA on the average, rely on both the volatility of the multiple SVOCs and their reactivity in the condensed phase, which is controlled by a series of oxidation, association and fragmentation reactions that can be kinetically described.

One important issue is thus our ability to describe in an appropriate manner the variety of SVOC behaviors in the gas and condensed phase in an AQM. As for K_H values, we have discussed the fact that the representation of SVOC partitioning in models for now is not highly accurate. Most 3D models indeed use one single K_H value to account for the behavior of a complex mixture of SOA precursors, and this format clearly prevents the model to restitute the full diversity of the gas/particle partitioning of individual compounds in time and space. This is all the more important because the results we obtained with CHIMERE showed that oligomer concentrations present a considerable sensitivity to the K_H value selected for the biogenic surrogate species that produces SOA. Similarly, when simulating chemistry in the aerosol phase, the allocation of distinct kinetic constant values for the reactivity of the condensed oligomer precursors would be valuable. Kalberer et al. (2006) effectively observed disparities in the temporal evolution of the aerosol molar mass while studying the oxidation of trimethylbenzene, α-pinene and isoprene. Taking this into account would probably have increased the OC short-time variability of the KIN method. However, increasing the degree of refinement of a modeling approach through a differentiation of individual behaviors is not always a good solution. The more refined the scheme becomes, the more difficult it is to collect the details about organic compound reactivity, making it difficult to set up the approach in a 3D model. As an example, the KPH approach proposes to consider the specific formation of oligomers from the polymerization of aldehydes only, that may happen through diverse acid-catalyzed reactions. Although it is evident that the consideration of only one single polymerization pathway constitutes a limitation for the quantitative simulation of SOA production from ambient organic precursors, this hypothesis has the advantage of proposing a well-identified process which can be adjusted in the model in terms of intensity, and upon the environmental conditions, from experimental knowledge about this reaction. However, in this approach, isoprene oxidation products (ISOPA) could not be considered as oligomer precursors, due to the fact that the KPH approach is only applicable to aldehydes and that there is no detail about the structural properties of the ISOPA surrogate species in the current CHIMERE chemical scheme. Including all or part of this species in the oligomerization process would thus have introduced an indeterminate uncertainty in our simulations. The outcome of this is a severe underestimation of the modeled OC compared with Harwell and Melptiz observation, that was – at least partly – attributed to the non inclusion of isoprene in oligomer precursors when running CHIMERE with the KPH configuration. Similarly, we have seen that the dependence of the model results upon (i) the state (deliquescent or metastable) of the aerosol, and (ii) its inorganic composition and pH, constitute a key challenge for the implementation of the KPH approach. In this respect, there is a necessity to define a parameterization focusing on the restitution of a unique parameter (such as the dynamics of global SOA yields), and relying on an irreducible set of parameters and processes, provided that it allows the model to perform satisfactorily with regard to existing measurements. For this purpose, *in situ* atmospheric oligomer measurements conducted at various distances from the sources would be absolutely necessary to assign a representative average value for the K_H of the SVOC surrogate species - as our results showed that the rate and intensity of the SVOC transfer to the aerosol phase give the SOA plumes their shapes.

Another path of research would be to impose a minimum value for the transfer of a given biogenic SVOC species to the aqueous phase, in order to quantitatively restitute rapid oligomer formation without significantly increasing the size of the chemical scheme in the AQM. Then, kinetically adjusted chemical reactions simulating both the oligomer formation and release should be added to control the stability of this organic fraction in the aerosol. Indeed, the definitive character of the formation of oligomers is the key to a correct representation of their total mass and dynamics of formation, as was shown by our comparative study of irreversible (KIN) and reversible (KPH) oligomerization processes at the continental scale.

How can we improve the representation of oligomer stability in the modeling approaches investigated here? The literature does not give a straightforward answer to the question of oligomerization reversibility. Several observations and experiments reported in the literature point to the irreversibility – at least partial – of the oligomerization process. According to a recent study of Liu et al., (2012b), the formation of oligomers from methacrolein and methyl vinyl ketone (isoprene oxidation products) is irreversible. This assumption is supported by the recent works of Hall and Johnston (2012a) who investigated the thermal stability of a SOA matrix including 50% of oligomeric species formed by the ozonolysis of α-pinene: the authors concluded that, at ambient temperatures, oligomeric species should be nonvolatile by structure. However, Trump and Donahue (2014) report discording results about SOA mass yields in these experiments, that point to an oligomerization process that would be reversible under specific conditions (dilution, temperature), which is probably a good compromise in the interpretation of all laboratory experiments.

Considering these elements, the kinetic approach that represents oligomer formation as the only possible fate for the relevant condensed organics may lead to a significant overestimation of the oligomer fraction in the aerosol. Thus, it should at least take into account a possible loss of SOA by evaporation, due notably to fragmentation processes (Renard et al., 2015). Indeed, organic compounds in the particulate phase have shown to be submitted to a variety of non-oxidative and oxidative reactions leading to the formation of both semi-volatile and non-volatile compounds, depending on their final molecular weight (Kroll and Seinfeld, 2008; Kroll et al., 2009). Furthermore, the absence of reversibility in the kinetic approach makes it little adaptable to laboratory observations such as the evaporation of SOA from α-pinene on the scale of a few hours (Grieshop et al., 2007). On the reverse, the high SOA mass yields obtained from the oxidation of biogenics SVOCs cannot be reproduced using the KPH-deliquescent approach, as SOA formed this way is permanently released due to aerosol water evaporation or pH increase. Whatever the model configuration, our works have shown that the oligomerization reversibility proposed by the KPH approach was difficult to set-up and control in an AQM. Therefore, considering (i) the laboratory experiments conducted by Hall and Johnson (2012b) on the ozonolysis of α–pinene, which indicated that oligomer formation would be driven by reactive uptake rather than by the partition of monomers between both phases and (ii) the fact that this reactive uptake may be observed within seconds (Heaton et al., 2007; Hall and Johnson, 2012b), it appears more realistic to propose a representation of the oligomerization process in two stages: a first fast step modifying directly the monomer partitioning so as to represent the rapid formation of oligomers (not permitted by the KIN approach only), and a stabilization step consisting of a kinetic uptake of the OA previously formed (not adjustable in a KPH approach). Trump and Donahue (2014) have recently proposed a comprehensive but simplified vision of reversible oligomerization that effectively combines a partitioning equilibrium and a condensed-phase kinetic reactivity, and that clearly addresses the issue of reversibility. This vision was built from the VBS approach, a modeling technique relying on SVOC volatility bins rather than on identified chemical species to represent the progressive formation of SOA from gaseous organic compounds upon atmospheric oxidation processes (Robinson et al., 2007). The works of Trump and Donahue propose a detailed analysis of an expanded VBS version taking into account oligomer formation dynamics in a quite similar way as here: namely, the description of the equilibrium phase partitioning of various VOC oxidation products from a given volatility bin, and a kinetic-dependent reactivity in the condensed phase where the association of 2 identical particulate monomers compete with the dissociation of the dimers thus formed. The ratio of those two rate constants makes a dimerization formation equilibrium. There, major simplifying assumptions are made. They mainly stem from the fact that only one single volatility class of condensed products reacts, and that this class reacts in its entirety - regardless of the structure of precursors - to form carboxylic acid dimers. Indeed, representative equilibrium constants for the dimerization reaction were derived from laboratory works on dicarboxylic acid dimers formation. Finally, it is stressed by the authors that neither of the simplifications considered in this approach is likely to be realistic, and that the stated goal of their work is only to identify what type of chemistry this method produces and how it helps understanding/representing oligomers in the atmosphere. Despite such simplifications, the authors show that their approach allows restituting experimental SOA yields for different initial OA conditions, as well as SOA formation dynamics. A particularly interesting result of this approach is the simulation of a two-stage SOA 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. Through sensitivity tests to the condensed phase reactivity kinetics, this approach also outlines that an irreversible oligomerization process (high dimerization to evaporation kinetic ratio) would definitely appears incompatible with the observed SOA mass-yield behaviors.

As for conventional modeling approaches relying on molecule structural properties, and based on these findings, a KPH-like approach considering a further reactive uptake - with partial reversibility or fragmentation so as to fit the observations about the hysteresis of SOA formation and evaporation - could be a suitable parameterization to represent the formation of oligomers from monoterpenes. Even so, the determination of the aerosol mode (deliquescent/metastable) is not an obvious choice. Although Fountoukis et al. (2009) concluded from plume studies that organics could promote thermodynamically stable water down to very low RH, Moya et al. (2002) have shown that considering a metastable mode for PM_1 (where organic matter is predominantly present) leads, under low relative humidity conditions (<60%), to significant errors in the concentrations of the inorganic species which indirectly determine the aerosol pH and thus oligomers formation. Similarly, Mikhailov et al. (2013) found – from the analysis of atmospheric aerosols – 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. These studies both conclude to the importance of considering a deliquescent mode for low relative humidity conditions.

Beyond the fundamental lack of *in situ* data required to evaluate oligomer and SOA concentration fields produced by AQMs, new advances are expected from further laboratory works to improve the accuracy of SOA formation processes in the models. In particular, as has been indicated by Trump and Donahue (2014), any sophistication of oligomer formation approaches would require advances in the knowledge of SOA yields and oligomer production dynamics. Such experiments would allow building relevant thermodynamical and chemical schemes that simulate the dynamics of SVOC capture, their reactivity in the condensed phase as well as their further potential for atmospheric release, to be implemented in AQMs.

Table 2. Statistical results for organic carbon (OC) simulation (reference, KIN approach, KPH deliquescent and metastable approaches).

OC (µg m^{-3})	MB	NMB (%)	RMSE	NRMSE (%)	R
GB36 – Harwell					
REF	-1.10	-77.7	1.33	94.2	0.53
KIN	-0.82	-57.8	1.11	78.6	0.53
KPH – Deliquescent aerosol	-1.09	-76.8	1.32	93.5	0.52
KPH – Metastable aerosol	-1.08	-76.4	1.32	93.1	0.53
DE44 - Melpitz					
REF	-2.71	-76.0	3.00	83.6	0.70
KIN	-1.82	-51.0	2.11	59.2	0.70
KPH – Deliquescent aerosol	-2.70	-75.7	2.97	83.3	0.70
KPH – Metastable aerosol	-2.67	-74.7	2.93	82.2	0.72

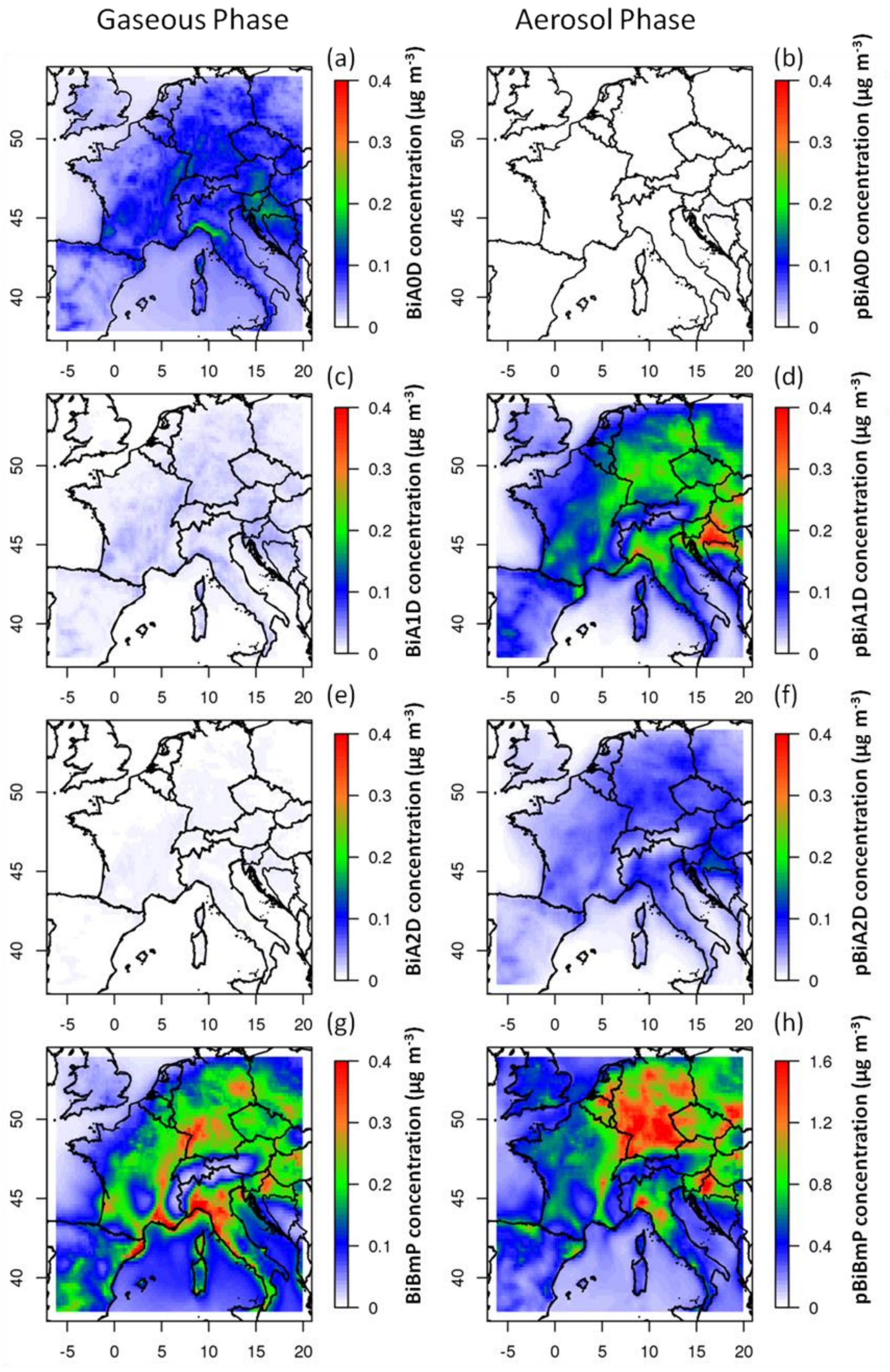

Figure 1. Mass concentration fields of BiA0D (a and b), BiA1D (c and d), BiA2D (e and f) and BiBmP (g and h) in the gas (left) and particulate (right) phases, modeled by CHIMERE and averaged over July 20 - August 3 2006.

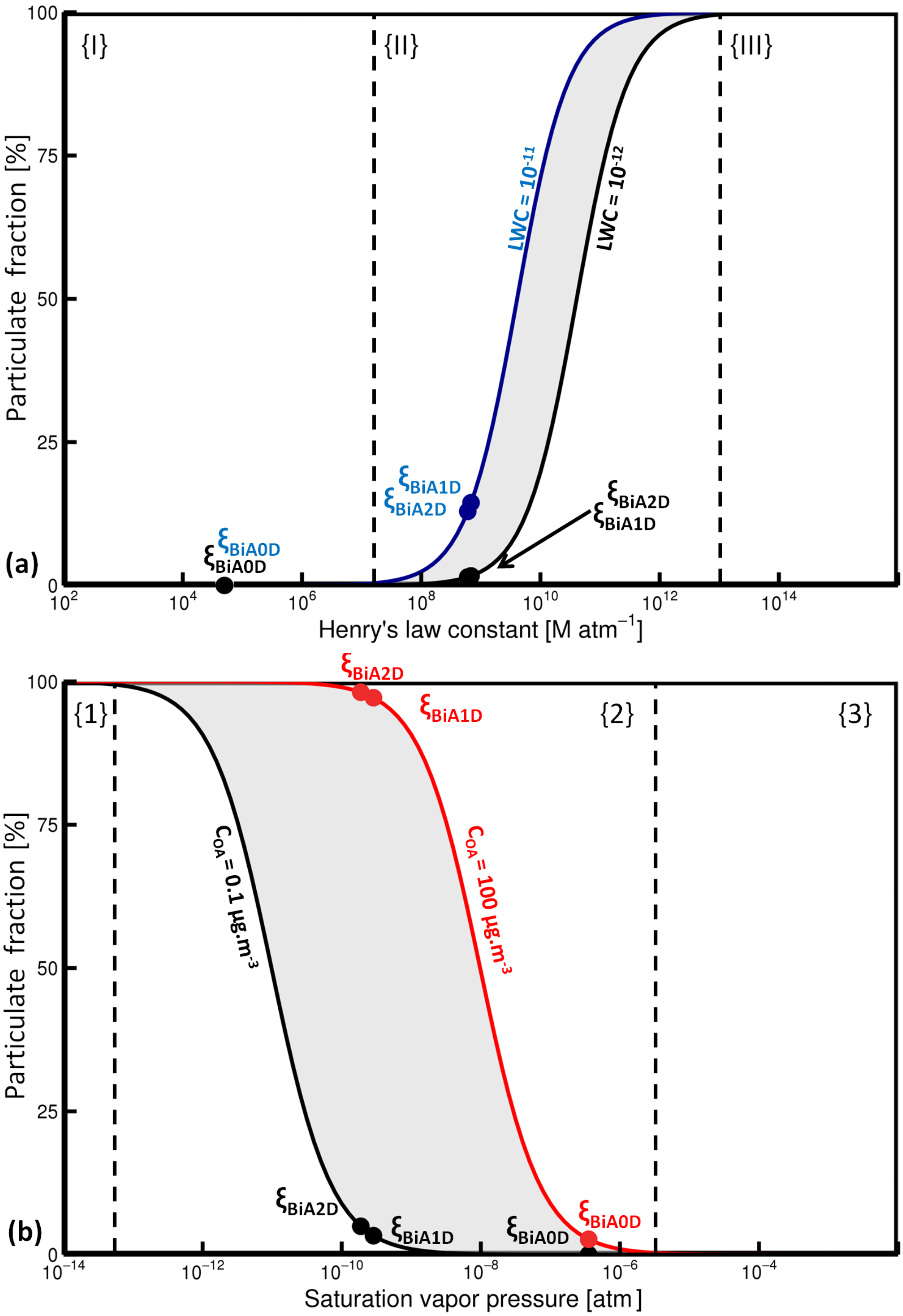

Figure 2. Particulate fraction as a function of Henry's law constant (upper figure) and as a function of Saturation vapor pressure (lower figure). The partition of each surrogate is represented by the colored dots for different conditions of organic aerosol mass concentration. Shaded areas represent the range of typical atmospheric condition.

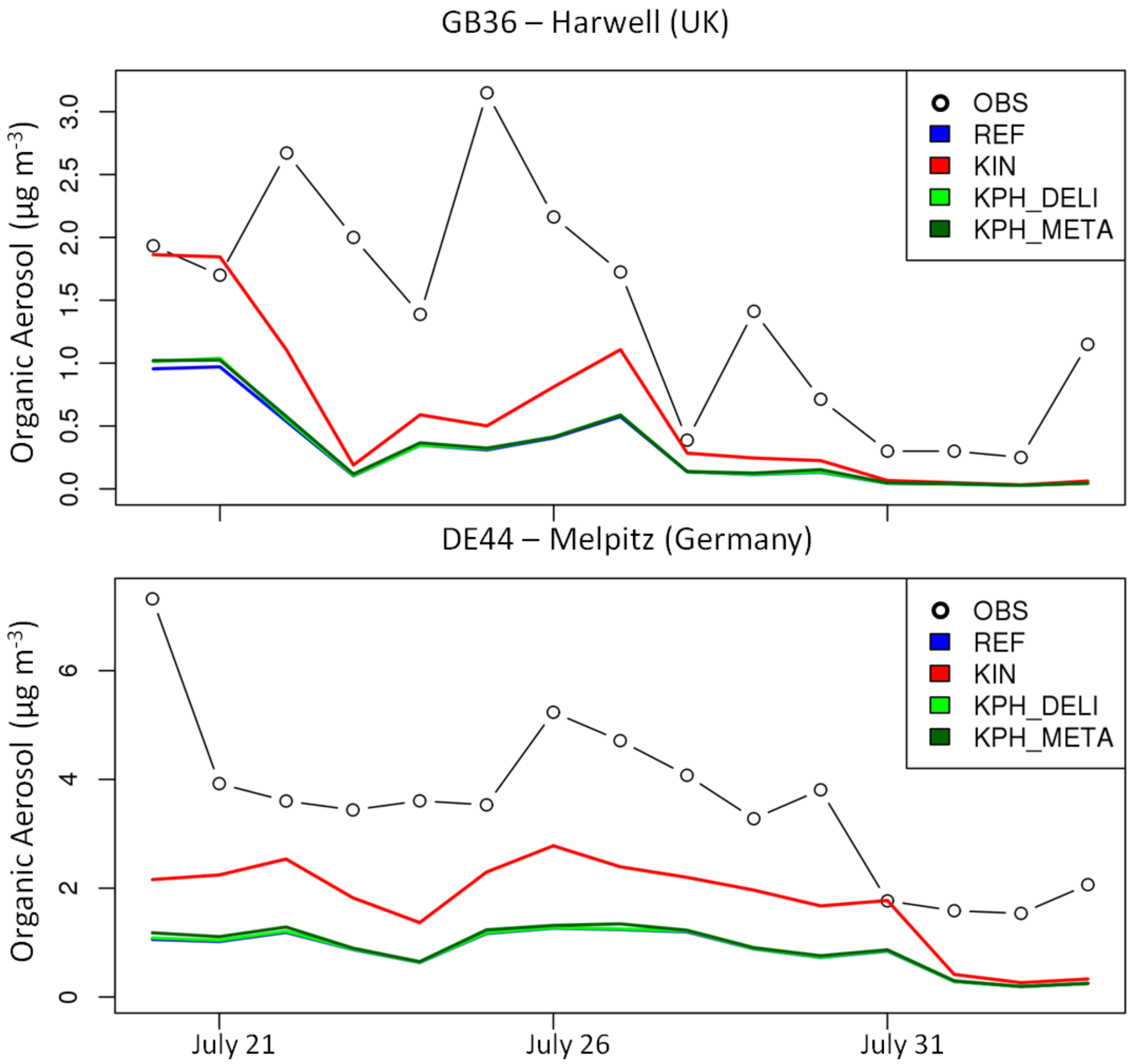

Figure 10. Comparisons of OC measurements (circles) with simulated OC in PM_{10} obtained in the reference simulation (blue), using the kinetic approach configuration (red), and using both KPH approaches - either in deliquescent or metastable mode (green and darkgreen curves respectively) at the Harwell (UK, top) and Melpitz (Germany, bottom) sites during the month of July 2006.