

First of all, we would like to thank the reviewers for their comments. The response to the comments are showed after each comment (in italics).

Anonymous Referee #1

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The Couvidat et al. manuscript reports on a series of parameterizations implemented in a model for secondary organic aerosol (SOA). Model simulation results are compared with experimental data obtained from the Euphore chamber, using both anthropogenic and biogenic precursors. The model used is the SOAP model, which uses surrogate compounds for each precursor that best reproduce the bulk properties of the SOA formed (e.g., O/C and H/C ratios). SOAP model parameterizations are developed for anthropogenic and biogenic precursors, and to represent oligomerization and acid catalyzed uptake of aldehydes. Sensitivity of model simulations to increased particle viscosity and vapor wall loss are considered. While there are some complex processes that are well represented in the model, and these complex processes are treated in a single model framework, the manuscript lacks clear direction. The objectives of the modeling are not clear, nor are the scientific contributions. Development of SOA models has been rapidly advancing over the last 20 years; parameterizations for all of the processes described in this manuscript have been developed and applied. The application of different parameterizations is not particularly novel, nor does it clearly advance the state of the science. It is suggested that this manuscript undergo major revisions prior to publication. The manuscript may be improved by focusing on one of the parameterizations (e.g., oligomerization) and comparing more rigorously to other model parameterizations and a broader suite of published studies. The manuscript should also be read carefully for clarity and grammatical errors. This will also improve the manuscript and increase its potential impact.

We agree that the introduction and the goals need to be clearer. The introduction was rewritten to emphasize the fact that this study is part of an update of the H₂O mechanism using the molecular surrogate approach and that the paper aim at developing (and also evaluating) a SOA mechanism including various processes which are often not taken into account together. We think that only taking into account oligomerization would significantly decrease the interest of the study (and would not have been possible without reformulating the H₂O mechanism). Moreover, our knowledge oligomerization has been scarcely in 3D air quality models as well as the impact of viscosity or the dynamic uptake of aldehyde onto acidic aerosols.

Comments:

The mechanism parameters for aromatics were developed largely from chamber studies that are now 10+ years old. For at least some of the compounds of interest, more recent data are available. For example: Hildebrandt et al., ACP 2015 (toluene) and Li et al., ACP 2016 (aromatics, low NO_x). The same is true of the parameters used to represent oligomerization. See for example, Kundu et al., ACP 2016 (oligomers from limonene). There may be good reasons for using the particular studies/data chosen, but those reasons should be articulated.

This work was initiated a few years ago when the article of Li et al. 2016 was not published and the algorithms are fitted on published Odum's curves data (Hildebrandt et al. do not report any Odum

Curve). Although some of the data used came from old chamber studies, we think that those data are not outdated. As for oligomerization, some parameterizations for 3D modeling were already based on the same experiments of Kalberer. A comparison of the results between these parameterizations is even done in the study. Moreover, no quantitative data are present in Kundu et al. 2012 on the evolution of molar masses with time (that were needed for the development of the model).

Abstract, lines 6-7: replace "were" with "where"

Corrected

p.3, line 20: It is recommended that the authors be more specific about the ranges of conditions covered by the experiments, particularly for atmospherically-relevant conditions that are outside the available datasets.

The range of conditions covered by each of the experiments were summarized in Tables 1 and 2. A sentence is added to refer to these tables, in case this was not enough visible in the text.

p.5, line 3-4: Chamber data studies are referenced twice.

The sentence was reformulated.

p. 7, lines 27-30: How are "short", "big", and "bigger" oligomers defined?

Definitions are added into the text.

Short oligomers: oligomers of 2 to 4 monomers blocks that can be formed quickly during the first hours

Big oligomers: more than 4 blocks of monomers

Bigger oligomers: oligomers with higher molar masses

p. 11, lines 11-15: Can more be said about the underlying reasons for differences between the model simulations in this work with those of Santiago et al. 2012? Particularly from the perspective of describing the likely processes in the experimental studies.

There could be many reasons for the differences between the two studies as the box models used are very different: dynamic approach vs the equilibrium approach, comparison to uncorrected with simulation of depositions to wall vs comparison to corrected values without simulating deposition and how the mechanism in itself was developed or how CMAQ treat the partitioning of secondary organic aerosol. A comparative study would be needed to compare the code of the two models and the data used.

p. 11, lines 31-33: It is suggested that this section be rewritten to clarify that the model simulations are over/under predicting in different chemical regimes. It is not clear as written.

The paragraph was rewritten to improve clarity.

p. 15: The discussion of the consideration of vapor wall loss is incomplete and perhaps misleading. The measurement/model agreement will reflect both the model parameterizations (as indicated), but also the experimental conditions. In this case, underestimation by inclusion of vapor wall loss may largely be due to the fact that vapor wall loss was negligible in the Euphore chamber under the experimental conditions. There is not good scientific support for broadly applying a 3-fold decrease in SVOC volatility and a single vapor wall loss parameterization for all SOA models developed using the

Odum approach as applied to all Teflon chamber studies. The extent of wall loss involves competing kinetic processes, and will be highly dependent on the chamber and the experimental conditions

Due to the uncertainty on the parameter, we initially intended to simply investigate what could be the impact of vapor losses and how it could impact SOA. A value for the vapor loss rate for Euphore is now estimated. Moreover, a mistake producing too much wall deposition was also found and corrected. Section 3.4 as changed.

Anonymous Referee #2 Received and published: 29 March 2018

Couvidat et al. develop updates to a secondary organic aerosol (SOA) model and report their findings on how those updates perform against chamber SOA measurements made with mixtures of biogenic and anthropogenic precursors. They find that, in general, the updates help improve the model-measurement comparison but offer nuanced insights on the role of NO, oligomerization, vapor wall losses, reactive uptake of pinonaldehyde, and particle phase on SOA formation.

The area of study undertaken by the authors is very important, that of understanding the processes that determine the formation, composition, evolution, and properties of SOA from oxidation of organic precursors. Findings here will help develop simplified mechanisms for atmospheric models. However, the manuscript in its current form does not do well in communicating the methods and, in some cases, the results and implications of the modeling efforts (see some comments below for details). What makes the manuscript even harder to understand is that there are numerous grammatical mistakes and phrasing/style issues. These need to be fixed before the manuscript can be reviewed again, in addition to achieving the quality desired in a journal like Atmospheric Chemistry and Physics. Although I believe this is important and novel work, I cannot make a judgement at this point based on the manuscript submitted for review. Hence, I do not recommend publication in ACP until the issues I discuss below are resolved, the presentation quality is significantly improved, and the manuscript is sent out for review again.

Major Comments:

1. Details on experimental methods and data: There is very little description of the experimental methods used to provide context to the modeling in this work. For example, how big is the Euphore facility? Given the size, was it correct to use the same wall loss rate as that used by the Caltech chamber to model vapor wall losses? Was it a Teflon chamber? What was the motivation to use a mix of precursors instead of using a single precursor? Were these photooxidation experiments or ozonolysis experiments (especially for the biogenic mixture)? Was an OH precursor used and if yes, which one? What photochemical ages were achieved? Was ozone produced? If yes, how much? Were these experiments seeded? What instrumentation was used to measure aerosol mass concentrations? How were the data corrected for wall losses? What are the uncertainties in the measurement data? Answers to these questions and more that bear relevance to the modeling need to be provided as part of section 2.1.

Yes, it's true that more information would help to introduce this study. The section 2.1 has been rewritten to provide more information about all these questions.

2. Details on modeling methods: Various details of the modeling approach are missing that make it hard to understand the simulated processes. For example, (page 4, lines 30-32), why was the wall loss

rate for vapors used in this work based on the Caltech chamber. A vapor wall loss rate could be estimated for the Euphore facility based on the calculations laid out in the supporting information of Zhang et al. (PNAS, 2014). Why was this not done? Also, the vapor wall loss rate only defines the loss rate of vapors. The affinity of these compounds to stick to the walls was modeled by Zhang et al. (PNAS, 2014) and later shown by Krechmer et al. (ES&T, 2016) to be a function of the vapor pressure of the species. Was this modeled similarly? In the mechanism section (page 5, lines 1-31), the abbreviations for the different species are obvious but it would be worthwhile to explicitly specify them, e.g., API is never defined. Perhaps, include this information in the tables as a legend. Why is only the number mean used to model particle size and not use the entire aerosol size distribution?

We added more information on the computation of vapor wall losses in section 3.4. Vapor wall losses were calculated similarly to Krechmer et al. and Zhang et al.

Due to the uncertainty on the parameter, we initially intended to simply investigate what could be the impact of vapor losses and how it could impact SOA. A value for the vapor loss rate for Euphore is now estimated. Moreover, a mistake producing too much wall deposition was also found and corrected. Section 3.4 has changed.

The abbreviations are now defined in the text and in the table for the mechanisms.

The following sentence was also added into the text:

“As modeling properly nucleation and coagulation of particles would be needed to simulate adequately the size distribution of particles, particles were gathered inside a single diameter bin.”

3. Structure, grammar, phrasing, and style: In terms of structure, I did not understand the order of the figures. I would recommend that the figure numbers be ordered in the order they show up in the manuscript. Further, the grammar, phrasing and style could be significantly improved. Here is a sample of mistakes I found just in Section 3.3 on page 13: (a) line 8: ‘they dynamic of the uptake’, (b) line 18: ‘specific of the compound’, and (c) line 18-19: ‘probably provides a good estimate and order of magnitude.’. The manuscript is littered with such mistakes.

The order of figures was changed, following the reviewer advices.

Several mistakes and grammar errors were corrected. A spell check by the editors will be asked for to track any remaining mistakes.

Minor comments:

1. Page 2, line 13: Consider citing the chemical transport model study of Cappa et al. (ACP, 2016) that simulated the influence of vapor wall losses on organic aerosol (OA) mass concentrations in urban areas.

Reference added.

2. Page 2, line 14: Jathar et al. (ACP, 2016) have showed – similar to the findings in this work – that oligomerization may not play an important role in affecting SOA mass concentrations but may change the SOA composition. Consider citing.

Reference added.

3. Page 3, line 17: How big is the Euphore facility?

Details were added in section 2.1. The volume of Euphore is 202 m³.

4. Page 4, line 29: *What does chamber is closed mean?*

“closed” replaced by “enclosed by the retractable steel housing.” Explanation are added in section 2.15. Page 5, line 23-29: *Are the different O:Cs possibly from differences in OA mass concentrations in the different experiments?*

The mean O/C may indeed change for different concentrations of OA. However, the precursors and the chemical regimes are probably the most important elements. The range of H/C and O/C from the cited studies are obtained from a variety of conditions with various organic aerosol loading.

6. Page 11, line 7-8: *Is particle number or mass used to determine particle wall loss rates? Why are the particle wall loss rates different for with and without oligomerization?*

In these simulations, the wall deposition rate was constrained to reproduce with the model the decrease of SOA volume concentrations (measured with the SMPS) during the last hours of the experiments. As the computed evolution of SOA concentrations during the last hours can be slightly different with or without oligomerization, the wall deposition rate used with and without oligomerization are different.

7. Page 11, line 28: *Could the differences in SOA formation be explained as a function of the VOC/NO_x ratio expressed in ppbC/ppb, similar to previous work?*

The following sentence was added to justify the use of the chemical regime ratio

The chemical regime ratio was used instead of the VOC/NO_x because in this study a mixture of VOC (and not a single VOC) was present in the chamber. The chemical regime ratio takes into account the reactivity of the compounds and can therefore be used to compare different experiments with different mixtures of VOC.

8. Page 12, line 17: *Use ‘fragmentation’ instead of ‘fractionalization’.*

Corrected

9. Page 14, line 7-8: *Sentence is unclear and needs more explanation.*

“For non-viscous aerosols, deposition of particles to wall can lead to the evaporation of SVOC due to a decrease of the absorbing mass.” Replaced by “For non-viscous, deposition of particles to the walls lead to a decrease of the absorbing mass (mass of the organic aerosol). As the gas/particle partitioning is proportional to the absorbing mass, SVOC will evaporate to maintain the gas/particle partitioning whereas this evaporation will be limited for a viscous aerosol.”

10. Page 14, line 14-15: *What figure shows a factor of 3 difference for the simulation that includes the loss of vapors to the walls.*

Reference to the figure added.

11. Page 14, line 23: *What do stoichiometric coefficients mean here?*

Detail added.

Simulating secondary organic aerosol from anthropogenic and biogenic precursors: comparison to outdoor chamber experiments, effect of oligomerization on SOA formation and reactive uptake of aldehydes

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Abstract.

New parameterizations for the formation of organic aerosols ~~have been~~ were developed. These parameterizations cover SOA formation from biogenic and anthropogenic precursors, NO_x dependency, oligomerization and the reactive uptake of pinonaldehyde. ~~Those parameterizations are based on available experimental results~~ These parameterizations were implemented in a
5 box model where the condensation/evaporation of semi-volatile organic compounds was simulated by the Secondary Organic Aerosol Processor (SOAP) model to take into account the dynamic evolution of concentrations.

The ~~effects of those parameterizations are tested against various~~ parameterizations were tested against several experiments carried out in previous studies ~~inside the outdoor chamber Euphore~~ in the EUPHORE outdoor chamber. Two datasets of experiments were used : the anthropogenic experiments (~~were where~~ SOA is formed mainly from a mixture of toluene,
10 1,3,5-trimethylbenzene and o-xylene) and the biogenic experiments (~~were where~~ SOA is formed mainly from α -pinene and limonene).~~SOA formation inside the chamber is simulated by using the Secondary Organic Aerosol Processor (SOAP) model to take into account the dynamic evolution of concentrations.~~

When assuming no wall deposition of organic vapors, satisfactory results were obtained for the biogenic experiments and for
most of the anthropogenic experiments. However, ~~the~~ a decrease of SOA concentrations (up to 30%) was found when taking
15 into account wall deposition of organic vapors (with the parameters of Zhang et al. (2014)). The anthropogenic experiments seem to indicate a complex NO_x dependency that could not be reproduced by the model. Oligomerization was found to have a strong effect on SOA composition and could have a strong effect on the formation of SOA. The uptake of pinonaldehyde (which is a high volatility SVOC) onto acidic aerosol was found to be too ~~slow to occur~~ to be significant under atmospheric conditions~~but less volatile or more reactive aldehydes could react in acidic aerosols~~.
20 Pun and Seigneur (2007) used in some air quality models may lead to an overestimation of SOA concentrations. Less volatile or more reactive aldehydes could nevertheless react with acidic aerosols.

~~However, taking into account wall deposition of organic vapors (with the parameters of Zhang et al. (2014)) lead to a~~

strong underestimation of SOA concentrations. This feature is consistent with the fact that the SOA mechanisms are based on environmental chamber data. This underestimation could however be corrected by decreasing the volatility of SVOC by a factor 3. The effect of particle viscosity was also estimated. Low changes in concentrations were Regarding viscosity, a low effect of viscosity on SOA concentrations was estimated by the model, although a decrease of SVOC evaporation was found when taking ~~into account SOA viscosity, although taking it into account~~ lead to a decrease of SVOC evaporation and prevent changes in concentration due, as well as a lower sensitivity of concentrations to changes of temperature during the experiments.

1 Introduction

Because of the effect of fine particles on human health (WHO, 2003) and ecosystems (Kanakidou et al., 2005), ~~it is necessary to develop models able to predict particle formation in order to evaluate its impact and to evaluate~~ the use of models have become a common practice to evaluate impacts and mitigation strategies. ~~As particulate~~ Particulate organic matter (OM) represents a large fraction of the total fine particulate mass, typically between 20 and 60% (Kanakidou et al., 2005; Yu et al., 2007; Zhang et al., 2007), ~~efforts have to be made to represent OM as accurately as possible in models. Secondary Organic Aerosols (SOA) represents most of OM with the secondary fraction (secondary organic aerosols, SOA) representing most of it (90% according to the best estimate of Kanakidou et al. (2005)).~~ Therefore, efforts have to be made to represent OM as accurately as possible in models.

Numerous models have been developed to simulate OM in 3D air quality models (Schell et al., 2001; Donahue et al., 2006, 2011; Pun et al., 2002; Couvidat et al., 2012; Griffin et al., 2003; Jathar et al., 2015; Tulet et al., 2006; Carlton et al., 2010; Menut et al., 2013). Most of these models use simple parameterizations based on SOA yields estimated from smog chamber experiments conducted under specific conditions, which can be different from atmospheric conditions (low humidity, specific NO_x conditions) ~~based on chamber experiment results even if several studies (Zhang et al., 2014, 2015; Bian et al., 2015) showed that gas wall deposition of organic vapors could lead.~~ Nevertheless, SOA yields from chamber experiments have traditionally been estimated considering particle wall-losses, but not gas wall-losses. Several studies (Zhang et al., 2014, 2015; Bian et al., 2015; Cappa indicate that this fact could have led to a strong underestimation of SOA yields. ~~Moreover, SOA parameterizations need to take into account the effects of NO_x concentrations or oligomerization as those effects have been shown to greatly affect the level of~~ SOA predicted by models (e.g. Ng et al. (2007a, b); Pun and Seigneur (2007); Couvidat and Seigneur (2011); Hall IV and Johnston (2011)). ~~Therefore, it is necessary to develop parameterizations gathering all these phenomena. Moreover,~~ On the other side, none of these models take into account all the the whole complexity of the processes involved in organic aerosol formation (non-ideality, multi-phase partitioning, viscosity of the aerosol, phase separation, aging, oligomerization and organosulfate formation, effects of NO_x concentrations, etc...). ~~Some of these processes were treated in the Secondary Organic Aerosol Processor (SOAP)(Couvidat and Sartelet, 2015), a 0D model that can be used to take into account non-ideality, multi-phase partitioning, phase separation and the viscous state of OM, that can highly affect the level of SOA predicted (e.g. Ng et al. (2007a, b); Pun and Seigneur (~~)). Therefore, the development of parameterizations addressing these aspects can provide insights about the SOA formation processes, and improve current model estimates.

Oligomer formation has been addressed in some modeling studies. This process may be important for organic aerosol as it can transform semi-volatile and volatile organic compounds into less volatile compounds. Trump and Donahue (2014) studied the effect of oligomerization on the dynamic of organic aerosol formation. Pun and Seigneur (2007) developed a parameterization for the oligomerization of aldehydes by increasing ~~the partitioning coefficient of aldehydes~~their partitioning toward
5 the particle. This parameterization (treating oligomerization with an equilibrium constant) have been used in Couvidat et al. (2012) to increase ~~the partitioning of SOA formation from~~ pinonaldehyde. High aerosol concentrations were simulated with this parameterization. However, Liggio and Li (2006b) showed that the uptake of pinonaldehyde onto acidic aerosol is a slow process and that this process could be due to oligomerization but also to organosulfate formation. Carlton et al. (2010) used a simple first-order rate constant of oligomerization for all organic compounds based on the results of Kalberer et al. (2004).
10 ~~Lemaire et al. (2015) compared all these approaches~~ Jathar et al. (2016) used the parameterization of Carlton et al. (2010) and showed that, depending on the mechanism, it could have a strong effect or not on SOA formation. In all the cases, the authors found a strong effect on composition (or volatility distribution). Lemaire et al. (2015) compared these different approaches for oligomerization and emphasized the need to simulate properly oligomerization in air quality models.

~~In this study, several parameterizations are developed and the results of the model are tested against SOA formation (from biogenic and anthropogenic precursors) experiments performed in the outdoor chamber Euphore. The parameterizations developed concern the oxidation mechanisms of biogenic (α -pinene, limonene) and anthropogenic (toluene, trimethylbenzene) precursors, oligomerization and the dynamic uptake of pinonaldehyde onto acidic aerosols. Several approaches have been used to represent SOA formation in 3D air quality models. Most of these approaches have in common that they are based on results from smog chamber experiments but differ in the methodology for lumping organic compounds and the treatment of the processes involved in SOA formation. Among these approaches, the Volatility Basis Set (VBS) approach (Donahue et al., 2006; Robinson et al., 2007) has been widely used (Lane et al., 2008; Shrivastava et al., 2008; Murphy and Pandis, 2009; Shrivastava et al., 2011; Han et al., 2016). It uses a basis set where Semi-Volatile Organic Compounds (SVOC) are distributed on an equally spaced logarithmic scale for volatility (volatility bins). Aging was treated in the VBS by assuming a shift of volatility per aging step (gas-phase oxidation creates a change of volatility bins). A 1.5D VBS (Koo et al., 2014) and a 2D VBS (Donahue et al., 2011) were also developed to take into account changes in the oxidation degree.~~

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~~The goal of~~ Another approach used in 3D air quality models is the molecular surrogate approach (Pun et al., 2002, 2006; Griffin et al., 2006). In this approach, surrogate compounds (that gather a large number of SVOC with similar thermodynamic properties) are associated with molecular structures to extrapolate SOA formation from smog chambers to the atmosphere. In the molecular surrogate approach, several processes, which are often not taken into account in the other approaches can be readily estimated (e.g., absorption into an aqueous phase, hygroscopicity, non-ideality) and can be treated explicitly in the model. Based on this methodology, the Secondary Organic Aerosol Processor (SOAP) (Couvidat and Sartelet, 2015) was developed to simulate the gas/particle partitioning of SVOC by taking into account non-ideality (by considering the interactions between organic and inorganic compounds), multi-phase partitioning, phase separation, hygroscopicity and the viscous state of organic aerosols. It was recently implemented in the CHIMERE air quality model (Couvidat et al., 2018) to simulate the gas/particle partitioning of SVOC formed with the H₂O mechanism (Couvidat et al., 2012). However, in H₂O, a simplified aging mechanism was only

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applied for the first step of oxidation of anthropogenic primary SVOC due to lack of information and SVOC were supposed to be only hydrophilic (condense only the aqueous phase of particles) or only hydrophobic (condense only the organic phase of particles).

In order to create a SOA mechanism that could be implemented in 3D air quality models and that considers the main phenomena involved in SOA formation (non-ideality, multi-phase partitioning, viscosity of the aerosol, phase separation, aging, oligomerization, effects of NO_x concentrations), the aim of this study is to ~~evaluate how several processes and parameterizations could affect SOA modeling. In a first part, a new SOA mechanism developed with a common methodology improve and update the H_2O mechanism for the formation of SOA from the oxidation of monoterpenes and aromatics by reconsidering some of the assumptions made in the development of this mechanism (no aging, compounds only hydrophilic or only hydrophobic, use of the parameterization of Pun and Seigneur (2007)).~~ The update of the mechanism was done based on SOA yields (~~available in the literature with the methodology of Odum et al. (1996)~~) ~~is tested~~; an aging mechanism was added; SVOC surrogate are assumed to be able to condense on both the aqueous phase and the organic phase; parameterizations for oligomerization and uptake of pinonaldehyde were also developed. The new SOA mechanism was tested against the experiments carried out inside the EUPHORE outdoor chamber under conditions different from the conditions under which it was developed (mixture of different compounds, non-controlled temperature). In a second part, the effect of particle phase reactions ~~is was~~ investigated. For that purpose, a parameterization for oligomerization was developed ~~in this study~~ to evaluate the impact of ~~oligomerization and the results given by this process. The results obtained with the equilibrium based parameterization of Pun and Seigneur (2007) is were also~~ compared to the results given by a dynamic parameterization based on the results of Liggio and Li (2006b) for the uptake of pinonaldehyde onto acidic aerosol. ~~The results of these two parameterizations are compared to results from SOA formation experiments in SOA concentrations simulated with these parameterizations were compared to measured concentrations from experiments in the~~ presence of SO_2 (that ~~lead leads~~ to the formation of ~~an acidic aerosol acidic aerosols~~). Finally, the effects of low diffusion inside the particle due to high viscosity and of wall losses of organic vapors ~~are~~ ~~were also~~ studied.

2 Method

~~New~~ ~~The new~~ parameterizations described hereafter ~~are were~~ developed and tested against experiments that were ~~previously carried out~~ ~~carried out in previous studies~~ inside the outdoor chamber ~~Euphore~~ ~~EUPHORE~~ in Valencia.

2.1 Experimental datasets

EUPHORE is a 204 m^3 hemispherical Teflon outdoor chamber located in Valencia, (CEAM), Spain. The chamber is surrounded by a retractable steel housing, which can be opened or closed to control the time of exposure to sunlight. The housing also serves to protect the chamber from rain and strong winds. The floor of the reactor consists of aluminum panels covered with Teflon, with a cooling system designed to compensate the heating of the chamber caused by solar irradiation. Two high-powered mixing fans (with an air flow of $4000 \text{ m}^3/\text{h}$), located on the floor of the chamber, are used to ensure the homogeneous mixing

of reactants and products. The EUPHORE facility is described in detail in Volkamer et al. (2001).

The experiments used for the comparison between the model and experiments have been published in previous studies (Vivanco et al., 2011, 2013). The ~~Euphore facility is described in Volkamer et al. (2001). Although, the experimental experiments used in this study were initially planned to increase the experimental information regarding SOA formation and to be mainly used in model performance evaluation processes. As most of the studies at that time were focused on the oxidation of individual organic gases or simple mixtures of them, those experiments constitute a contribution to the experimental database on SOA formation, by considering the oxidation of different mixtures of organic precursors. Although the experimental~~ dataset was designed for model evaluation purposes, it was not designed to evaluate the model developed in this study. ~~Vivanco et al. (2016); Santiago et al. (2012b)~~ Vivanco et al. (2016) and Santiago et al. (2012b) used these experiments to evaluate simple parameterizations existing in several air quality models. The experiments may not cover all the range of values covered by the model for some parameters, especially for relative humidity (RH) which was lower than 40% for all experiments. ~~Experimental conditions are described in Tables 1 and 2.~~

OH was formed by HONO photolysis. Ozone was formed throughout the experiment and often reach concentrations around 200 ppb. However, at the start of the experiments where concentrations of ozone are lower, monoterpenes will react mainly with OH radicals. As almost all the monoterpenes reacted during the first hour of the reaction, monoterpenes can be considered to react both with OH and O₃. Calculations carried with RACM2 showed that 10 to 70% of the monoterpenes should have reacted with O₃. For experiments B4 and B5 with very low relative humidities (around 10%), most of the monoterpenes reacted with OH (around 90%). OH photo-oxidation time (determined for a concentration of 1.5×10^6 molecules cm⁻³) was determined to range from a few hours to more than a day.

Two datasets of experiments are used: (i) the anthropogenic experiments where SOA is formed from the oxidation of toluene (TOL), 1,3,5-trimethylbenzene (TMB) and to a lesser extent o-xylene and octane and (ii) the biogenic experiments where SOA is formed from α -pinene (API) and limonene (LIM) and ~~limonene and~~ to a lesser extent isoprene. Experimental conditions for the anthropogenic and biogenic experiments are described respectively in Tables 1 and 2. For the biogenic dataset, two experiments were carried out in presence of SO₂ to evaluate the parameterization of Pun and Seigneur (2007). Due to its low SOA yield, SOA from isoprene oxidation should not represent ~~more than a few percent~~ a significant amount of total SOA.

Although octane is a precursor of SOA and is present in the anthropogenic experiments, SOA formation from octane oxidation was not taken into account in this study as Vivanco et al. (2016) showed with an experiment in the same chamber that octane lead to an insignificant amount of SOA. Due to its low yield (0.5% according to Lim and Ziemann (2005)), octane SOA should not represent more than a few percent of total SOA.

PM volume concentrations were measured with a Scanning Mobility Particle Sizer Spectrometer (SMPS). ~~Data are not corrected for wall losses as deposition of particles is taken into account in the model.~~

2.2 Model development

Secondary organic aerosols inside the chamber were simulated by coupling the gas-phase mechanism RACM2 (Goliff et al., 2013) with the SOAP model (Couvidat and Sartelet, 2015) to compute the dynamic formation of SOA. RACM2 was used because it has been shown to perform well for oxidant formation (Kim et al., 2009). To represent the chemical evolution of SVOC, RACM2 was modified to take into account the formation of the surrogate species according to the mechanisms described hereafter. The ROS2 algorithm (Verwer et al., 1999) was used to solve the chemical kinetic equations.

SOAP is a model designed to be modular with user options depending on the computation time. SOAP uses the molecular surrogate approach to estimate several properties and parameters (hygroscopicity, absorption into the aqueous phase of particles, activity coefficients and phase separation) and to evaluate the partitioning of organic compounds between one or several organic phases (the number of organic phases is determined by Gibbs energy minimization) and the inorganic phase. It accounts for the influence of interactions between organic and inorganic compounds by using the AIOMFAC algorithm (Zuend et al., 2008, 2011; Zuend and Seinfeld, 2012). Secondary inorganic aerosol formation was added to the SOAP model by using the equilibrium parameters of ISORROPIA v2.1 (Fountoukis and Nenes, 2007).

Currently, SOAP assumes that inorganic aerosols are metastable liquids and therefore does not take into account efflorescence or deliquescence processes. This assumption could be wrong in presence of ammonia due to the low humidity inside the chamber, as ammonium sulfate would probably be solid ~~for humidities lower than the~~ as the humidity in the chamber (below 40%) is always far below the deliquescence relative humidity (80% at 298K). However, no ammonia was present ~~for any in these~~ experiments and SO₂ was only introduced for two experiments. For those two experiments, SO₂ oxidation will lead to sulfuric acid formation which remains liquid over the full RH range (Seinfeld and Pandis, 1998).

Several experimental data were used to constrain the model. Temperature and relative humidity measurements inside the chamber were used as inputs for the model. SMPS measurements were used to compute the mean diameter of particles. ~~The diameter of particle was used to compute the kinetic of condensation/evaporation/diffusion and the Kelvin effect by the dynamic approach of SOAP~~ As modeling properly nucleation and coagulation of particles would be needed to simulate adequately the size distribution of particles, particles were gathered inside a single diameter bin. The mean diameter of particles was constrained to provide the model with a realistic estimation of the diameter without modeling the nucleation in SOAP. ~~The diameter of particle is used to compute the kinetic rate of condensation/evaporation/diffusion and the Kelvin effect by the dynamic approach of SOAP.~~

The model results were compared to non-corrected (according to wall losses) results. Wall deposition of particles was simulated via first order loss rate parameter constrained to reproduce the loss of particles during the last hours of the experiment when the chamber was ~~losed~~ enclosed by the retractable steel housing.

Wall losses of vapors were not taken into account due to the lack of information on deposition onto ~~Euphore~~ EUPHORE walls. However, in the last section, the effect of vapor wall losses on SOA formation in the chamber was investigated by taking into account vapor wall losses according to parameters estimated (~~Zhang et al., 2014~~) for the Caltech chamber by Zhang et al. (2014)

2.2.1 SOA Mechanism

A new mechanism was developed for SOA formation from toluene (TOL), xylene (XYL) and trimethylbenzene (TMB). Parameters were fitted ~~based~~ on data issued from ~~various-several~~ studies under low and high NO_x conditions: Ng et al. (2007b) for Toluene SOA, ~~Ng et al. (2007b); Cocker III et al. (2001) for Xylene SOA and~~ Cocker III et al. (2001) for ~~TMB-TMB SOA~~ and the results from both studies for for Xylene SOA. No information was found on SOA formation from TMB oxidation under low-NO_x conditions, therefore, the stoichiometric coefficient from the low-NO_x conditions for xylene was used. Similarly to Vivanco et al. (2016), the low-NO_x condition yield are used only if radicals formed from the oxidation of the precursors react at least twice with the HO₂ radical, to prevent high formation of low-NO_x SOA under intermediate NO_x conditions. Molecular structures (used by SOAP to estimate several properties and to compute activity coefficients) were selected based on the results of Im et al. (2014) by selecting the compound with a similar volatility, formed in the largest quantity and ensuring the best reproduction of the O/C and H/C ratios. Reactions and properties of surrogate species are shown in Tables 3 and 7.

For monoterpenes, the mechanism of Pun et al. (2006) was updated using results from more recent studies. For SOA formation from α -pinene, β -pinene and limonene ozonolysis, the mechanism is based on the parameterizations described in Lee et al. (2011) for high and low NO_x conditions. The API + OH reaction is based on the results of Svendby et al. (2008) whereas for the LIM + OH reaction, the yield of BiA2D was optimized to give the better-best results. Reactions and properties of surrogate species are shown in Tables 3 and 7.

The terpene + NO₃ yields are based on Fry et al. (2014).

In the surrogate SOA approach, results of the model may depend on the choice of the surrogate structure to represent SOA formation. Although different VOCs form different compounds (or the same compounds in different quantities), this approach gather lumps together species that have similar properties (like saturation vapor pressure) and are expected to have similar chemical structure. For example, first-generation aldehyde products from terpene oxidation were represented by the surrogate species BiA0D. Moreover, the compounds were selected (based on the best information available on SOA products) to reproduce the mean properties of SOA and of the O/C and H/C ratios. Kim et al. (2014) showed that the mean O/C and H/C ratios are respectively around 0.34-0.36 and 1.4-1.5 for SOA from α -pinene and limonene respectively. The selected surrogates give a O/C between 0.3 and 0.44 and a H/C between 1.55 and 1.6. For TOL SOA, the chosen surrogates give a O/C ratio (between 0.71 and 0.8) and H/C ratio (between 1.14 and 1.6) similar to the reported values by Schilling (2015) (between 0.7 and 0.8 for O/C and between 1.2 and 1.6 for H/C). For TMB SOA, Sato et al. (2012) indicate a O/C ratio around 0.4-0.6 and a H/C around 1.5-1.7. The chosen surrogates reproduce the O/C ratio (between 0.38 and 0.55) but seem to underestimate the high H/C ratio (between 1.13 and 1.44 due to the low H/C of the AnIP2 compound). However, for AnIP2, a better molecular structure having a similar O/C ratio and saturation vapor pressure could not be found.

The mechanism of Couvidat and Seigneur (2011) was used to simulate SOA formation from isoprene.

2.2.2 Oligomerization

Carlton et al. (2010) developed a parameterization for oligomerization based on a simple first-order rate constant of oligomerization. Based on the results of Kalberer et al. (2004) indicating 50% of polymers after 20h in TMB SOA, Carlton et al. (2010) determined a kinetic constant of $9.6 \times 10^{-6} \text{ s}^{-1}$. However, this number was obtained with a laser desorption ionization–mass spectrometry (LDI-MS) by taking all compounds with m/z higher than 400 (with m s-the ion mass and z is its the ion charge) and may not take into account small oligomers (dimers or trimers that may be formed more rapidly). Kalberer et al. (2004) and Kalberer et al. (2006) also studied the oligomer fraction based on a volatility tandem differential mobility analyzer (VTDMA) giving the remaining volume fraction of particles at different temperatures. They found that for TMB SOA, the remaining fraction at 100°C after 5h ranges from 50% to 62% and is composed of small oligomers or very low volatility organic compounds. The remaining fraction at 100°C can even reach ~~and~~ 80% to 90% after 25h. Based on this results and assuming that the remaining fraction is mainly composed of small oligomers and that oligomerization is irreversible, the first-order constant of oligomerization should be around $3.85 \times 10^{-5} \text{ s}^{-1}$ to take into account small oligomer formation.

However, Roldin et al. (2014) showed that oligomerization should involve second order reversible reactions like esterification, hemiacetalization, aldolization, peroxyhemiacetalization. The equilibrium of these reactions are unfavored by humid conditions and the kinetic reaction is catalyzed under acidic conditions. Indeed, oligomer formation by esterification was reported in the case of isoprene SOA (Surratt et al., 2006). In this study, oligomerization is represented ~~like~~ by a reversible process which is mainly due to mechanisms like esterification, unfavored by humid conditions. Oligomers are represented by simple species to know if “monomer blocks” are present mainly as oligomers or as monomers. If a monomer block from a compound reacts with another monomer block (from the same compound or from another compound), the compound will be converted from monomer to oligomer. The parameterization currently does not take into account different kinetic rate parameters between each combination of compounds due to lack of data. It assumes that a compound A reacting with itself will have the same kinetic parameter than a compound B reacting with itself and will have the same value when compounds A and B react together.

Oligomerization is represented by a simple “reduced” reaction:



with A a monomer compound, A_{oligo} the monomer blocks of compound A inside oligomers, m_{oligo} the number of monomer blocks inside oligomers, k_{oligo} the kinetic rate parameter of oligomerization and $k_{reverse}$ the kinetic rate parameter of the reverse reaction. If more data ~~are were~~ available, the parameterization could be improved to take into account different kinetic rate parameters of oligomerization per combination.

30 The net flux of oligomerization J_{oligo} is computed using activities instead of concentrations for two main reasons. First, chemical rates are more consistent with thermodynamic equilibrium by computing rates using activities. Second, some studies (Madon and Iglesia, 2000; Rahimpour, 2004) express-expressed the need to compute chemical rates using activities and ~~show~~

that it gives better results showed that better results are obtained for non-ideal systems.

$$J_{oligo} = -\frac{dX_{a,monomer}}{dt} = k_{oligo}a_{a,monomer} - k_{reverse}a_{a,oligomer} \quad (2)$$

with $X_{a,monomer}$ the molar fraction of compound a, $a_{a,monomer}$ the activity on a molar fraction basis of compound a and $a_{a,oligomer}$ the activity on a molar fraction basis of the oligomer formed from compound a.

5 The kinetic rate of oligomerization k_{oligo} is computed as follows:

$$k_{oligo} = k_{oligo}^{max}a_{monomer} \quad (3)$$

with k_{oligo}^{max} the maximum kinetic rate parameter for oligomerization, and $a_{monomer}$ the sum of monomer activities.

To calculate the reverse kinetic rate parameter, the computation is based on the equilibrium oligomerization constant K_{oligo}^{eq} . The equilibrium constant for oligomerization (due to esterification or a similar oligomerization mechanism) is computed with:

10

$$K_{oligo}^{eq} m_{oligo}^{-1} = \frac{a_{a,oligomer}a_{H_2O}^{m_{oligo}-1}}{a_{a,monomer}a_{monomer}^{m_{oligo}-1}} \quad (4)$$

At equilibrium, the rate of oligomerization is zero. Therefore,

$$\frac{k_{oligo}^{max}}{k_{reverse}} = \frac{a_{a,oligomer}/m_{oligo}}{a_{monomer}a_{a,monomer}} = \frac{(K_{oligo}^{eq})^{m_{oligo}-1}a_{monomer}^{m_{oligo}-2}}{a_{H_2O}^{m_{oligo}-1}} \quad (5)$$

To represent oligomerization, k_{oligo}^{max} , m_{oligo} and K_{oligo}^{eq} were estimated based on the results of Kalberer et al. (2006). In this study, the molar masses of heavy molecules in SOA from several precursors were measured using matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). To do that, we represented explicitly the formation of oligomers up to tetramers from a single monomer using the kinetic rate parameter and the equilibrium constant for oligomerization to simulate the evolution of mass averaged molar mass of oligomers (which cannot be simulated with our reduced parameterization for oligomerization because the molar mass of oligomers does not vary with this parameterization). The equilibrium constant of oligomerization K_{oligo}^{eq} and the oligomerization constant $k_{oligo}^{max,extended}$ of the extended parameterization were fitted so that the evolution as a function of time of the weight average molar mass of oligomers during the first hours of the experiment is reproduced by the model as shown by Fig. 1. A molar mass of the TMB SOA monomer of 155 g/mol was chosen so that the molar mass of TMB SOA is between 140 and 170 g/mol based on Im et al. (2014). m_{oligo} and k_{oligo}^{max} are chosen so that the molar averaged mean molar mass and the total mass of oligomers (with oligomers and monomers) of the reduced and the extended parameterizations are were similar. The reduced parameterization values found for k_{oligo}^{max} , m_{oligo} and K_{oligo}^{eq} were respectively $2.2 \times 10^{-4} \text{ s}^{-1}$, 3.35 and 2.94 for TMB SOA. k_{oligo}^{max} is in the same order of magnitude as the kinetic rate parameter reported for the reaction acetaldehyde and methanol by Roldin et al. (2014): $4.9 \times 10^6 \text{ a}[\text{H}^+] \text{ M h}^{-1}$ ($\text{a}[\text{H}^+]$ being the activity of H^+), which should be around $6 \times 10^{-4} \text{ s}^{-1}$ on an activity basis for a pH of 4.6 (order of magnitude of pKa for carboxylic acids).

This reduced parameterization only takes into account the formation of short oligomers (oligomers of 2 to 4 monomers blocks that can be formed quickly during the first hours) but should give a good insight on the impact of oligomerization on

SOA formation. Formation of short oligomers can impact SOA formation by transforming monomers and increasing the condensation of semi-volatile compounds onto the particle. However, big oligomers (more than 4 blocks of monomers) formation should affect less SOA formation as it should mainly lead to the transformation of oligomers into bigger oligomers (oligomers with higher molar masses). Big oligomers could affect indirectly the partitioning of monomers by increasing the mean molar mass of the organic phase; the partitioning constant of monomers being inversely proportional to the mean molar mass.

This parameterization also gives good results for the isoprene SOA oligomerization using a molar mass of 120 g/mol. This molar mass corresponds to the molar mass of methyl glyceric acid, which was shown to undergo oligomerization by esterification). For α -pinene, Kalberer et al. (2006) did not find any significant temporal evolution of oligomer molar masses, which is consistent with a dimer formation who-that cannot react further and therefore parameters for oligomerization of α -pinene SOA cannot be evaluated.

The results for SOA oligomerization from TMB and isoprene for the extended and reduced parameterizations are shown in Fig. 1. For the formation of dimers from α -pinene, we used the same parameters except for-that m_{oligo} is set to 2 to limit the formation of oligomers to dimers. DePalma et al. (2013) confirmed that particle-phase dimer formation is possible. However, Kristensen et al. (2014) studied the formation of 4 dimers and determine-determined that for those 4 dimers are not formed from particle-phase reaction but through gas-phase reactions of the stabilized Criegee Intermediate formed from the ozonolysis of α -pinene. It could then be possible that in the case of α -pinene not all the oligomers are formed via particle-phase reactions.

In this study, the second order parameterization was used for simulations. In case of the oligomerization inside an aqueous acidic phase, a kinetic rate of $8.76 a[H^+]$ should be used to take into account the effect of acidity on oligomerization.

2.2.3 Uptake of pinonaldehyde onto acidic aerosols

Several studies (Liggio and Li, 2006a, b) reported an uptake of pinonaldehyde onto acidic aerosols higher than what could be predicted by assuming equilibrium between the gas and particle phases and no chemical reaction inside the particles. This phenomenon is attributed to oligomer and/or organosulfate formation. Gao et al. (2004b) reported a similar phenomenon for various aldehydes. To represent this phenomenon, Pun and Seigneur (2007) developed a parameterization by computing an effective Henry's law constant H_{eff} for aldehyde compounds:

$$H_{eff} = H \left(1 + 0.1 \left(\frac{a(H^+)}{10^{-6}} \right)^{1.91} \right) \quad (6)$$

where H is the monomer Henry's law constant of the compound, and $a(H^+)$ is the activity of protons in the aqueous phase. As fine particles are generally very acidic (Ludwig and Klemm, 1990; Keene et al., 2004), uptake of pinonaldehyde will in fact appear to be an irreversible process, even though the parameterization is formulated as a reversible process. Using this parameterization for pinonaldehyde in 3D air quality models leads to very high concentrations of SOA from monoterpenes (Couvidat et al., 2012).

However, this parameterization does not take into account the uptake kinetic rate of aldehydes. Liggio and Li (2006b) measured the uptake rate coefficients for various acidities of the aerosols. The authors showed that the uptake of pinonaldehyde onto aerosols can only be significant for very high acidities (which can be reached with low ammonia concentration and at low

humidities). Based on these results, a parameterization for the chemical evolution of pinonaldehyde has been developed in this study:

$$BiA0D_{part} \xrightarrow{k_{trans}} \text{Non volatile products} \quad (7)$$

with $BiA0D_{part}$ the amount of pinonaldehyde inside the particle and k_{trans} (in s^{-1}), the kinetic rate of BiA0D transformation inside the particle into a product assumed non-volatile. Liggio and Li (2006b) did not evaluate a kinetic rate of pinonaldehyde transformation inside the particle but a kinetic of uptake. However, the kinetic of uptake can be linked to the kinetic of transformation by assuming equilibrium between the gas and particle phases:

$$k_{uptake} = k_{trans} K_{aq} A Q \quad (8)$$

with K_{aq} the partition coefficient of pinonaldehyde between the gas phase and the particle and AQ the particle mass.

As in Liggio and Li (2006b), the pH of particles and activities of compounds were computed with AIOMFAC (Zuend et al., 2008, 2011; Zuend and Seinfeld, 2012; Ganbavale et al., 2015) according to experimental conditions. The estimated flux of transformation based on the results of Liggio and Li (2006b) was plotted against several variables to find the variables exhibiting the best correlations. m_{H^+} the molality of ion H^+ and $a_{HSO_4^-}^{(m)}$ the activity as a molality basis of ion HSO_4^- were found to be the best variables with high correlation coefficients (0.98 for m_{H^+} and 0.92 for $a_{HSO_4^-}^{(m)}$) with the chemical flux of transformation pinonaldehyde J_{trans} inside the particle. Fig. 2 shows J_{trans} (in s^{-1}) as a function of m_{H^+} (in mol/kg) and $a_{HSO_4^-}^{(m)}$ (in mol/kg).

Two possible parameterizations can therefore be used to take into account the possible transformation of pinonaldehyde in the particle phase: the H^+ -dependent parameterization and the HSO_4^- -dependent parameterization. For the H^+ -dependent parameterization, the kinetic rate is computed as:

$$k_{trans} = 2.01 \times 10^{-7} \times \exp(0.297 m_{H^+}) \quad (9)$$

whereas the HSO_4^- -dependent parameterization is computed with:

$$k_{trans} = 1.53 \times 10^{-7} a_{HSO_4^-}^{(m)} \quad (10)$$

In that case, we assume-assumed that the reaction leads to the formation of the organosulfate formed from pinonaldehyde.

The H^+ -dependent parameterization could be representative of an oligomerization mechanism catalyzed by H^+ ion. However, in that case, the uptake of pinonaldehyde should be seen as a reversible pathway with-which also depends on the humidity of the experiments. The HSO_4^- -dependent parameterization could be representative of organosulfate formation and therefore pinonaldehyde should in that case act as a sink for sulfates due to the reaction between sulfates and pinonaldehyde.

2.3 Aging mechanism

To test the influence of aging on SOA formation, an aging mechanism was developed. The aging of BiA0D is based on the results of Chacon-Madrid and Donahue (2013) who studied SOA formation from pinonaldehyde oxidation. SOA formation

from BiA1D is based on the SOA yield from the oxidation of pinonic acid as measured by Müller et al. (2012). For the aging of BiA2D, the parameterizations of Jathar et al. (2015) were used to determine the amount of functionalization and the decrease of volatility due to aging. Nopinone, which is formed from the oxidation of β -pinene was shown to form a significant amount of SOA and low-volatility products (Sato et al., 2016). Nopinone was included in the mechanism. SOA yields from nopinone oxidation was based on Mutzel et al. (2016). The yields of formation of nopinone were based on Hakola et al. (1994) for the reaction of β -pinene with OH and O₃ and on Hallquist et al. (1999) for the reaction of β -pinene with NO₃. Kinetics for aging were taken from the Master Chemical Mechanism v3.3.1 (Jenkin et al., 1997; Saunders et al., 2003).

For the aging of aromatic SOA compounds, the parameterizations of Jathar et al. (2015) were used to determine the amount of functionalization and the decrease of volatility due to aging. According to this study, oxidation of aromatics should mainly lead to the addition of one oxygen atom. For simplification purposes, we assumed that aging of aromatic SOA leads to the addition a single hydroxy group.

Table 6 shows the aging mechanism used in this study.

This simple mechanism ~~was developed~~ is used here in order to be able to assess the capacity to form oligomers and of the reactive uptake of pinonaldehyde in the long-term formation of SOA.

2.4 Long-term SOA formation simulations

The experimental conditions (low relative humidity, oxidation over a few hours, high organic mass loading) are probably very different from typical ambient conditions. To evaluate more precisely the potential effect of oligomerization, SOA formation from the oxidation of α -pinene, toluene and TMB over 3 days of evolution with an organic mass loading of 5 $\mu\text{g m}^{-3}$ ~~from the oxidation of α -pinene, toluene and TMB~~ was simulated for various humidities with or without oligomerization. The simulated effect of oligomerization is compared to the simulated effect of aging on SOA formation. Octane and NO_x concentrations are set in order to reproduce a level of OH concentrations similar to summer conditions (around 0.001 ppb during daytime). The diurnal cycle was simulated by computing the evolution of the zenith angle at Valencia as a function of local time. This diurnal profile was simulated to take into account that oxidation and aging slow down during night (due to the low concentrations of radicals) whereas oligomerization continues. On the other hand, the relative humidity was assumed constant (whereas under ambient conditions relative humidity probably ~~have~~ has a diurnal profile) ~~and the~~ The structures of pinonic acid for simulations with α -pinene and of AnRP2 for simulations with toluene and TMB oxidation are used for the structure of the organic loading. Those simulations are not representative of atmospheric conditions but can be used to illustrate the effect of long-term oligomerization on SOA formation. For simulations with oligomerization, the fraction of monomers inside the aerosol is assumed to be one, i.e., the aerosol is assumed to be mainly constituted by monomers that can react with absorbed compounds. These simulations provide therefore information on the maximal effect that oligomerization can have on SOA yields.

3 Results

The simulated degradation of precursors is illustrated in Figures S1 and S2 in supplementary materials. Whereas the mechanism was able to reproduce the degradation of VOC during the beginning of the experiments, medium-term oxidation of toluene seems to be underestimated for some experiments (A1, A3, A4 and A7). Due to this, medium-term formation of toluene SOA may be underestimated.

3.1 Comparison with measurements

Figures 3 and 4 show ~~respectively~~ the results of the model for the biogenic experiments without SO₂ and the anthropogenic experiments respectively. Simulated SOA composition for simulations considering oligomerization are illustrated in Supplementary Materials in Figures S3 (biogenic experiments) and S4 (anthropogenic experiments). In these simulations, the wall deposition rate was constrained to reproduce ~~the loss of particles with the model the decrease of SOA volume concentrations (measured with the SMPS)~~ during the last hours of the ~~experiment when the chamber was closed as described in section 2.2. Therefore~~ experiments. Because the computed evolution of SOA concentrations during the last hours can be slightly different with or without oligomerization, the wall deposition rate used with and without oligomerization are different. To examine the effect of the wall deposition rate, the formation of SOA with oligomerization was also simulated with the deposition rate as computed by the simulation without oligomerization to ensure that effect of changes on deposition remain low.

For the biogenic experiments, the model gives good results with or without oligomerization for all experiments with slightly better results without oligomerization for experiment B5 and slightly better results with oligomerization for experiment B1. The experiments B2, B3, B4 and B5 have previously been modeled by ~~Santiago et al. (2012b)~~ Santiago et al. (2012a) using a box model version of two air quality models: CMAQ (Carlton et al., 2010) and Chimere (Menuet et al., 2013). The authors found a significant overestimation of modeled SOA which was not found with the model used in this study.

For the anthropogenic experiments, the model gives satisfactory results (with or without oligomerization) for experiment A1, A3, A6 and A7 but overestimates concentrations by 30-40% for A2 and A5 and underestimates concentrations by 25% for A8 and A9.

Concentrations for experiment A4 are overestimated by a factor 2. However, experimental conditions for experiment A4 are close to those of experiment A1, except ~~for HONO concentrations which~~ that HONO concentrations are two times higher than for experiment A4. The model gives similar results for A1 (for which the model gives satisfactory results) and A4. It could not explain why concentrations were so different between these two experiments. One possibility is that anthropogenic SOA formation is inhibited at high HONO concentrations.

The alternation of overestimation and underestimation events could be related to differences in chemical regimes. To compare the chemical regimes of the experiments, a ratio representative of the chemical regime (called hereafter “chemical regime ratio”) was computed with the sum of VOC concentrations multiplied by their reactivity with OH divided by NO_x concentra-

tions:

$$C_r = \frac{\sum_i k_{OH,i} C_i}{C_{NO_x}} \times 10^{10} \quad (11)$$

with C_r the chemical regime ratio, C_i the concentration in ppb of each VOC and C_{NO_x} the concentration in ppb of NO_x , $k_{OH,i}$ the reactivity with OH in molecule⁻¹ cm³ s⁻¹. 10^{10} is a factor set so that the values are close to unity. The chemical regime ratio was used instead of the VOC/ NO_x because in this study a mixture of VOC (and not a single VOC) was present in the chamber. The chemical regime ratio takes into account the reactivity of the compounds and can therefore be used to compare different experiments with different mixtures of VOC.

It appears that depending on the chemical regime ratio, the model may overestimate or underestimate the concentrations. Indeed, for the experiments with a low chemical regime ratio (experiments A8 and A9 which have ~~respectively~~ ratios of 0.13 and 0.7) ~~underestimate SOA concentrations~~, whereas ~~experiments that overestimate concentrations (experiments A2 and A5) have a~~ respectively SOA concentrations are underestimated. On the contrary, SOA concentrations experiments with high chemical regime ratio (~~the ratios are~~ experiments A2 and A5 with respectively ratios equal to 2.2 and 1.64) ~~Other experiments (except are overestimated. Except for A4) have a chemical regime ratio~~, the model gives satisfactory results for the other experiments (having chemical regime ratios between 0.77 and 1.05 ~~and give satisfactory results~~). It may indicate a more complex NO_x dependency than what is represented in the model.

3.2 Effect of oligomerization on SOA formation

~~According to the model, the~~ For the biogenic and anthropogenic experiments ~~show~~, a low effect of ~~the~~ oligomerization on SOA ~~mass in the chamber formation was simulated~~ as shown by Figures 3 and 4. Concentrations are indeed similar with and without oligomerization with low differences compared to the amount of SOA. Although the amount of SOA does not significantly change, the composition of SOA is strongly affected by oligomerization. Indeed, the oligomer content (in mass) at the end of the experiment varies from 68% to 78% for the biogenic experiments and from 38% to 58% for the anthropogenic experiments with a similar range of humidity (between 0.4% and 37%). For a 55% relative humidity, Gao et al. (2004a) determined for α -pinene that the oligomer content of SOA could be well over 50%. This result is consistent with the results of our parameterization as an oligomer content around 60% was simulated for such an humidity.

The results of long-term SOA formation simulations are shown in Figures 5, 6 and 7. Without taking into account aging, oligomerization leads to a significant increase of concentrations after 3 days of evolution even at high humidity. Increase factors due to oligomerization are 2.5 for α -pinene, 2.0 for toluene and 6.2 for TMB for a relative humidity of 30% and are 1.8 for α -pinene, 1.4 for toluene and 3.3 for TMB for a relative humidity of 70%. Oligomerization is therefore a process that could significantly affect long term SOA formation.

Assuming aging leads to a slight decrease of SOA mass due to ~~fractionalization~~ fragmentation for toluene SOA or an increase of concentrations due to functionalization for TMB and α -pinene SOA. However, the effect of aging on SOA formation simulated here seems less important than the effect of oligomerization.

The different parameterizations of oligomerization are also compared in Fig. 5: the equilibrium second order reaction pa-

parameterization developed in this study, the first order complete reaction of Carlton et al. (2010) with a kinetic rate parameter of $9.6 \times 10^{-6} \text{ s}^{-1}$ (halftime of 20h) and a kinetic rate parameter of $3.85 \times 10^{-5} \text{ s}^{-1}$ (halftime of 5h). The three different parameterizations have different impact on SOA formation. The first order parameterization with a kinetic rate parameter of $9.6 \times 10^{-6} \text{ s}^{-1}$ has a low impact on SOA yield-yields except after a few days of oligomerization. With the kinetic rate parameter of $3.85 \times 10^{-5} \text{ s}^{-1}$, the increase of SOA yield-yields can be significant after 10 hours, ~~for~~. For RH=70% the SOA yield increases by 72% after one day. The second order parameterization gives a faster SOA production. However, this figure shows the maximal effect of the second-order parameterization (molar fraction of oligomers of 1). Depending on conditions, the second order parameterization ~~could~~ may only have a low impact on SOA concentrations and the formation of oligomers could rapidly reach an equilibrium.

10 Depending on the conditions, oligomerization could also lead to a decrease of SOA concentrations as the partitioning is inversely proportional to the mean molar mass of organic aerosols (Pankow, 1994), which will increase with the oligomer formation. Increasing ~~by a factor 2~~ the mean molar mass lead by a factor 2 leads to a decrease around 40% of the SOA formed without oligomerization, indicating that the partitioning of monomers are sensitive to the value of the mean molar mass.

3.3 Uptake of pinonaldehyde onto acidic aerosols

15 The pH and HSO_4^- parameterizations and the parameterization of Pun and Seigneur (2007) assuming equilibrium are compared and evaluated against experiments B6 and B7 where α -pinene and limonene are oxidized in the presence of SO_2 . The oxidation of SO_2 leads to the formation of sulfuric acid and therefore to acidic aerosols. The amount of SOA formed with each parameterization is compared to the results of the experiments (Fig. 8).

The parameterization of Pun and Seigneur (2007) leads to a significant overestimation of SOA concentrations. With this parameterization, BiAOD is entirely absorbed by the acidic aerosol. On the contrary, using the pH and HSO_4^- parameterizations which take into account the dynamic of the uptake, no significant formation of SOA is formed by this pathway ~~and~~. The two parameterizations give almost the same results than assuming no uptake.

Pinonaldehyde was found to be too volatile to form significant SOA by this pathway. The long-term formation of SOA by this pathway is tested with the simulation described in the previous section but in the presence of $2 \mu\text{g}/\text{m}^3$ of sulfuric acid. Fig. 5 shows that even at low humidity (RH=30%), the amount of SOA formed is not significant after 3 days of evolution. Therefore, SOA formation from the reactive uptake by acidic acid of pinonaldehyde probably does not contribute significantly to SOA formation.

However, it could be possible that aldehyde compounds less volatile than pinonaldehyde react and form significant amount of SOA by this pathway. To test this hypothesis, we assumed that organosulfate could be formed from the compounds AnRP1 and AnRP2 (which have an aldehyde group in their molecular surrogate structure) using the HSO_4^- parameterization. The kinetic ~~should be specific of~~ rate parameter should depend on the compound but the HSO_4^- parameterization probably provides a good ~~estimate and order of magnitude~~ estimation of this phenomenon. Fig. 9 shows the amount of organosulfate that would be formed by this pathway for a humidity of 70% from the oxidation of toluene. Long-term organosulfate formation seems possible by this pathway (even at high humidity) as significant amount of organosulfate (13 to 18% of SOA) is formed

with this assumption and that a significant mass of aldehydes has been converted into organosulfates. However, ~~this process~~ if high concentrations of ammonia are present in the atmosphere, pH will increase and HSO_4^- will decrease. In case of high concentrations of ammonia, the kinetic rate could be too low for this process to be significant. This process would need for sulfate to not be fully neutralized by ammonia.

5

3.4 Investigation of the effect of particle-phase diffusion and wall losses of organic vapors

To evaluate the effect of the particle phase viscosity on SOA formation, the SOAP model was run for a particle-phase ~~coefficient~~ diffusion-diffusion coefficient of 2×10^{-16} molecules/cm²/s which correspond to the order of magnitude of values determined for toluene SOA at low humidities (Song et al., 2016).

10 To investigate wall losses of organic vapors, wall losses were treated as in Zhang et al. (2014) by using a first-order wall loss rate ~~coefficient for vapors of 2.5 ×~~ and the organic aerosol equivalent wall (set to 10 mg/m³ following Zhang et al. (2014)). According to McMurry and Grosjean (1985), the wall vapor loss rate k_w can be computed with the following formula:

$$k_w = \frac{A}{V} \frac{\frac{a_w c}{4}}{1 + \frac{\pi}{2} \frac{a_w c}{4 \sqrt{k_e D_{gas}}}} \quad (12)$$

15 with A/V the surface on volume ratio of the chamber (equal to 1 m⁻¹ for EUPHORE), a_w the mass accommodation coefficient of organic vapors onto the wall, c is the mean thermal speed of the molecules, k_e is the coefficient of eddy diffusion, D_{gas} is the molecular diffusivity.

20 As the mixing is carried out by two fans with a flux of 4000 m³/h, the characteristic time for the mixing inside the chamber is estimated to be around 90 s for EUPHORE and k_w is estimated to be around 10^{-4} s⁻¹ was used as in Zhang et al. (2014) (value determined for the Teflon chamber of Caltech) . Effect- . Following Zhang et al. (2014), the kinetic of evaporation of compounds from the wall $k_{w,off}$ is computed with:

$$k_{w,off} = \frac{k_w}{K_{p,w} C_w} \quad (13)$$

with $K_{p,w}$ the gas/wall partition coefficient (chosen equal to the gas/particle partition coefficient) and C_w equivalent wall OA concentration (set to 10 000 $\mu\text{g m}^{-3}$).

25 The effects of the particle-phase viscosity and of wall losses of vapor is illustrated in Fig. 10 for ~~experiment~~ experiments A5, A7 and B1. Results for other experiments (biogenic and anthropogenic) are similar to ~~this experiment~~ these experiments and are illustrated in Supplementary Materials in figures S5 and S6.

30 Generally, similar results are obtained between non-viscous and viscous aerosols. Assuming viscous aerosols can lead to an increase of SOA concentrations due to the limitation of evaporation with low diffusion. As found by Couvidat and Sartelet (2015), condensation of low volatility compounds is possible without diffusing into the particle by condensing at the gas/particle interface. The condensation of low volatility compounds can create a layer onto which more volatile compounds

can condense to respect Raoult's law at the interface. However, viscosity can prevent the evaporation of those more volatile compounds by preventing their diffusion from the core of the particle to the interface. For non-viscous aerosols, deposition of particles to ~~wall can lead to the evaporation of SVOC due to~~ the walls lead to a decrease of the absorbing mass (mass of the organic aerosol). As the gas/particle partitioning depends on the absorbing mass, SVOC will evaporate to maintain the gas/particle partitioning whereas this evaporation will be limited for a viscous aerosol.

Assuming viscous aerosols can also lead to a decrease of SOA sensitivity to ~~change~~ changes of conditions during the experiments. For example, experiment A5 is characterized by a decrease of the temperature during the experiment ~~that lead~~ leading to a decrease of volatility. Whereas concentrations increase when assuming non-viscous aerosols, concentrations seem unaffected by the change of temperature when assuming viscous aerosols (as compounds are absorbed by the core of particles with a slow kinetic rate). The shape of modeled SOA concentration curve is closer to measurement when assuming viscous aerosols.

Taking into account wall losses of vapors leads to a ~~strong~~ decrease of SOA concentrations (as illustrated in Fig. 10), particularly for the anthropogenic experiments (decrease ~~up to a factor 3~~ between 8 and 30%) due to the lower organic aerosol loading compared to the biogenic experiments. ~~The fact that the model underestimates SOA formation when assuming that vapors can condense onto the wall chamber is not not surprising as the~~ As the developed mechanism is based on the methodology of Odum et al. (1996) by using experimental results from Teflon chambers, it could be possible that the parameters of the mechanism (saturation vapor pressures and stoichiometric coefficients for the formation of SVOC) are biased. As stronger organic aerosol loading favors condensation onto organic aerosol over condensation onto walls, wall losses of vapor may produce a shift in apparent volatilities; the organic aerosol formed in chambers may appear more volatile than it should be. For both the biogenic and anthropogenic experiments, results can be corrected by decreasing the saturation vapor pressures by ~~a factor 3~~ 20% as better or similar results could be obtained than without taking into account wall losses of organic vapors. These results indicate that volatility determined by the use of Odum's curves ~~could be overestimated by a significant factor~~ may be slightly overestimated. However, wall deposition of organic vapors could also lead to an underestimation in the SOA mechanism of stoichiometric coefficients.

25 4 Conclusions

Several parameterizations were developed in this study. First, the chemical mechanism of Couvidat et al. (2012) was updated. The performance of the new mechanism was evaluated by comparison to experimental results from previous studies carried out in the ~~Euphore~~ EUPHORE chamber in Valencia. Second, parameterizations to take into account oligomerization and the uptake of pinonaldehyde onto acidic aerosols were developed. Finally, the effects of particle viscosity and wall deposition of vapors were investigated.

Without taking into account wall losses of vapors, good performances are obtained for the biogenic experiments. However, the experiments used for the comparison have high organic aerosol loading (between 50 and 150 $\mu\text{g}/\text{m}^3$) whereas low aerosol ~~loading~~ loadings are more representative of atmospheric conditions. More experiments at low organic aerosol loading could

be carried out to provide more information. Good performances are also obtained for most of the anthropogenic experiments. However, the experiments with the lower TMB/NO_x chemical regime ratio underestimates concentrations by 30 % whereas the experiments with the higher TMB/NO_x chemical regime ratio overestimates concentrations by 30 %. This could indicate a more complex NO_x chemistry than what is taken into account inside the model. However, this discrepancy could be due to the
5 difficulty to simulate properly radicals inside the chamber under some conditions. More experiments should be carried out to confirm these results and improve the NO_x dependency inside the model.

Oligomerization was shown to have little impact on SOA mass during experiments. However, oligomerization was found to influence composition as a large part of SOA is constituted (more than 50% for biogenic experiments) by oligomers in simulations, especially at low humidity. Moreover, even at high humidities ~~under representative atmospheric conditions~~, simu-
10 lations indicate that oligomerization could increase substantially organic aerosol concentrations. However, more efforts should be deployed to improve this parameterization. Indeed, this parameterization represents a “bulk oligomerization” and does not account for differences in the reactivity of monomers. This parameterization could nonetheless be useful to study the effect of oligomerization in 3D air quality models.

The uptake of pinonaldehyde was found to be too slow to contribute significantly to the formation of organic aerosols and
15 that the approach of Pun and Seigneur (2007) greatly overestimates the effect of the particle acidity on SOA formation. However, it could be possible that the uptake of aldehydes less volatile than pinonaldehyde (or more reactive) is strongly influenced by the particle acidity leading to the formation of oligomers or organosulfate. However, the uptake of aldehydes could reach an equilibrium and not be irreversible as assumed in this study. Experiments are needed to confirm those points.

Taking into account wall losses of organic vapors with the parameters of Zhang et al. (2014) leads to a ~~significant underestimation~~
20 ~~of SOA concentrations up to a factor 3. This feature is not surprising as the mechanism developed in this study was based on decrease that could reach 30%. As the developed mechanism is based on the methodology of Odum et al. (1996) by using experimental results from Teflon chambers and the Odum methodology (Odum et al., 1996) which do not take into wall losses of vapors. This underestimation~~, it could be possible that the parameters of the mechanism (saturation vapor pressures and stoichiometric coefficients for the formation of SVOC) are biased. This decrease could however be ~~corrected~~ compensated by
25 decreasing the volatility of SVOC by ~~a factor 3~~ 20%.

However, the experimental conditions do not cover the full range of RH whereas the model shows that RH may strongly influence SOA yields which is consistent with the results of Healy et al. (2009). More experiments need to be carried out at high humidity to confirm the effect of humidity and to validate performances of the model under these conditions.

Finally, these parameterizations should be implemented in a 3D air quality models to evaluate their impact on SOA forma-
30 ~~on air quality~~. Oligomerization should especially be studied into ~~greater~~ great details as it could lead either to an increase or a decrease (by increasing the mean molar mass that would lead to a decrease of the partitioning constant of monomers) of SOA concentrations. Moreover, different parameterizations of oligomerization could lead to very different results. It is therefore important to determine experimentally the chemical mechanisms involved in SOA formation: first order or second order reaction, complete or equilibrium reaction.

35

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Table 1. Initial concentrations in ppb, temperature (T) in Kelvin and relative humidity in % for biogenic experiments.

Experiment	Isoprene	α -pinene	Limonene	NO	NO ₂	HONO	SO ₂	T	RH
B1	107	66	58	34	128	99	0	302-307	0.5-3
B2	92	50	50	48	0	87	0	298-300	30-26
B3	122	71	40	41	0	53	0	297-300	19-22
B4	0	63	65	32	0	101	0	294-298	8-13
B5	99	59	53	150	0	307	0	295-297	8-11
B6	87	50	51	244	89	40	513	295-300	15-19
B7	55	79	76	198	0	165	461	302-305	20-30

Table 2. Initial concentrations in ppb, temperature (T) in Kelvin and relative humidity in % for anthropogenic experiments. SO₂ was not present for those experiments.

Experiment	Toluene	Xylene	TMB	Octane	NO	NO ₂	HONO	T	RH
A1	102	22	153	85	19	0	99	299-305	10-16
A2	200	49	300	155	23	0	75	302-305	9-18
A3	48	11	106	42	23	0	71	302-307	6-14
A4	98	24	160	79	37	0	156	297-307	6-13
A5	97	21	146	81	4	8	52	297-308	7-14
A6	93	22	146	78	21	0	94	300-308	0.4
A7	107	26	160	89	21	0	89	306-309	7-10
A8	116	29	19	10	57	0	119	302-305	15-18
A9	81	21	118	65	31	0	90	299-303	28-37

Table 3. Reactions leading to SOA formation^a from α -pinene (referred as API), β -pinene (referred as BPI) and limonene (referred as LIM).

Reaction	Kinetic rate parameter (molecule ⁻¹ .cm ³ .s ⁻¹)
API + OH \rightarrow 0.30 BiA0D + 0.40 BiA2D + OH	$1.21 \times 10^{-11} \times \exp(\frac{440}{T})$
API + O ₃ \rightarrow APIO3RAD + O ₃	$5.00 \times 10^{-16} \times \exp(\frac{-530}{T})$
APIO3RAD + HO ₂ \rightarrow 0.024 BiA3D + 0.15 BiA2D + 0.38 BiA1D + HO ₂	$4.10 \times 10^{-13} \times \exp(\frac{790}{T})$
APIO3RAD + NO \rightarrow 0.085 BiA2D + 0.24 BiA1D + NO	$8.8 \times 10^{-13} \times \exp(\frac{180.2}{T})$
API + NO ₃ \rightarrow 0.70 BiA0D + NO ₃	$1.19 \times 10^{-12} \times \exp(\frac{-490}{T})$
BPI + OH \rightarrow 0.07 BiA0D + 0.08 BiA1D + 0.06 BiA2D + 0.27 NOPINONE + OH	$2.38 \times 10^{-11} \times \exp(\frac{357}{T})$
BPI + O ₃ \rightarrow 0.09 BiA0D + 0.022 BiA3D + 0.045 BiA2D + 0.20 BiA1D + 0.17 NOPINONE + O ₃	1.50×10^{-17}
BPI + NO ₃ \rightarrow 0.02 BiA0D + 0.21 BiNIT + 0.02 NOPINONE + NO ₃	2.51×10^{-12}
LIM + OH \rightarrow 0.35 BiA0D + 0.15 BiA2D + OH	$4.20 \times 10^{-11} \times \exp(\frac{401}{T})$
LIM + O ₃ \rightarrow LIMO3RAD + O ₃	$2.95 \times 10^{-15} \times \exp(\frac{783}{T})$
LIMO3RAD + HO ₂ \rightarrow 0.14 BiA3D + 0.44 BiA2D + 0.42 BiA1D + HO ₂	$4.10 \times 10^{-13} \times \exp(\frac{790}{T})$
LIMO3RAD + NO \rightarrow 0.14 BiA3D + 0.5 BiA2D + 0.36 BiA1D + NO	$8.8 \times 10^{-13} \times \exp(\frac{180.2}{T})$
LIM + NO ₃ \rightarrow 0.69 BiA0D + 0.28 BiNIT + NO ₃	1.22×10^{-11}

^a Oxidants may be present as both reactants and products so that a reaction added to RACM2 will not affect the original photochemical oxidant concentrations. MO₂ and ACO₃ are ~~respectively~~ the methylperoxy radical and the peroxyacetyl radical respectively. A is either NO, NO₃, MO₂ or ACO₃.

Table 4. Reactions leading to SOA formation^a from toluene (referred as TOL).

Reaction	Kinetic rate parameter (molecule ⁻¹ .cm ³ .s ⁻¹)
TOL + OH → ... + 0.25 TOLP + OH	$1.80 \times 10^{-12} \times \exp(\frac{355}{T})$
TOLP + HO ₂ → TOLlowNO _x + HO ₂	$3.75 \times 10^{-13} \times \exp(\frac{980}{T})$
TOLP + A → TOLhighNO _x + A	A = NO: $2.70 \times 10^{-12} \times \exp(\frac{360}{T})$ A = NO ₃ : 1.2×10^{-12} A = MO ₂ : $3.56 \times 10^{-14} \times \exp(\frac{708}{T})$ A = ACO ₃ : $7.40 \times 10^{-13} \times \exp(\frac{765}{T})$
TOLlowNO _x + OH → TOLlowNO _x RAD + OH	6.90×10^{-11}
TOLhighNO _x + OH → TOLlowNO _x RAD + OH	6.90×10^{-11}
TOLlowNO _x RAD + HO ₂ → 0.697 AnPER + HO ₂	See TOLP + HO ₂ reaction
TOLlowNO _x RAD + A → 0.131 AnRP2 + 0.324 AnIP1 + A	See TOLP + A reaction
TOLhighNO _x RAD + HO ₂ → 0.131 AnRP2 + 0.324 AnIP1 + HO ₂	See TOLP + HO ₂ reaction
TOLhighNO _x RAD + A → 0.131 AnRP2 + 0.324 AnIP1 + A	See TOLP + A reaction

^a Oxidants may be present as both reactants and products so that a reaction added to RACM2 will not affect the original photochemical oxidant concentrations. MO₂ and ACO₃ are ~~respectively~~ the methylperoxy radical and the peroxyacetyl radical respectively. A is either NO, NO₃, MO₂ or ACO₃.

Table 5. Reactions leading to SOA formation^a from xylene (referred as XYL) and ~~trimethylbenzene~~1,3,5-trimethylbenzene (referred as TMB).

Reaction	Kinetic rate parameter (molecule ⁻¹ .cm ³ .s ⁻¹)
XYL + OH → ... + 0.274 XYLP	$1.70 \times 10^{-11} \times \exp(\frac{116}{T})$
XYLP + HO ₂ → XYLlowNOx + HO ₂	See TOLP + HO ₂ reaction
XYLP + A → XYLhighNOx + A	See TOLP + A reaction
XYLlowNOx + OH → XYLlowNOxRAD + OH	6.90×10^{-11}
XYLhighNOx + OH → XYLlowNOxRAD + OH	6.90×10^{-11}
XYLlowNOxRAD + HO ₂ → 0.611 AnPER + HO ₂	See TOLP + HO ₂ reaction
XYLlowNOxRAD + A → 0.0529 AnRP1 + 0.344 AnIP2 + A	See TOLP + A reaction
XYLhighNOxRAD + HO ₂ → 0.0529 AnRP1 + 0.344 AnIP2 + HO ₂	See TOLP + HO ₂ reaction
XYLhighNOxRAD + A → 0.0529 AnRP1 + 0.344 AnIP2 + A	See TOLP + A reaction
TMB + OH → ... + 0.274 TMBP	5.67×10^{-11}
TMBP + HO ₂ → TMBlowNOx + HO ₂	See TOLP + HO ₂ reaction
TMBP + A → TMBhighNOx + A	See TOLP + A reaction
TMBlowNOx + OH → TMBlowNOxRAD + OH	6.90×10^{-11}
TMBhighNOx + OH → TMBlowNOxRAD + OH	6.90×10^{-11}
TMBlowNOxRAD + HO ₂ → 0.611 AnPER + HO ₂	See TOLP + HO ₂ reaction
TMBlowNOxRAD + A → 0.0117 AnRP1 + 0.250 AnIP2 + A	See TOLP + A reaction
TMBhighNOxRAD + HO ₂ → 0.0117 AnRP1 + 0.250 AnIP2 + HO ₂	See TOLP + HO ₂ reaction
TMBhighNOxRAD + A → 0.0117 AnRP1 + 0.250 AnIP2 + A	See TOLP + A reaction

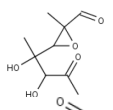
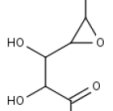
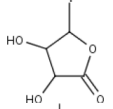
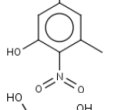
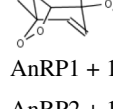
^a Oxidants may be present as both reactants and products so that a reaction added to RACM2 will not affect the original photochemical oxidant concentrations. MO₂ and ACO₃ are ~~respectively~~ the methylperoxy radical and the peroxyacetyl radical respectively. A is either NO, NO₃, MO₂ or ACO₃.

Table 6. Aging mechanism of SVOCs^a.

Reaction	Kinetic rate parameter (molecule ⁻¹ .cm ³ .s ⁻¹)
BiA0D + OH → RA0D + OH	9.0×10^{-12}
RA0D + HO ₂ → BiA1D + HO ₂	$5.20 \times 10^{-13} \times \exp(\frac{980}{T})$
RA0D + NO → 0.6 BiA1D + 0.075 BiA3D + NO	$7.50 \times 10^{-12} \times \exp(\frac{290}{T})$
BiA1D + OH → 0.061 BiA3D + OH	1.12×10^{-11}
BiA2D + OH → 0.4 BiA3D + OH	7.29×10^{-12}
NOPINONE + OH → 0.16 BiA3D + OH	1.55×10^{-11}
AnRP1 + OH → 0.26 AnRP1a + OH	6.0×10^{-12}
AnRP2 + OH → 0.06 AnRP2a + OH	6.0×10^{-12}
AnIP1 + OH → 0.04 AnIP1a + OH	6.0×10^{-12}
AnIP1a + OH → Volatile products + OH	6.0×10^{-12}
AnIP2 + OH → 0.48 AnIP2a + OH	6.0×10^{-12}
AnIP2a + OH → 0.38 AnIP2b + OH	6.0×10^{-12}

^a Oxidants may be present as both reactants and products so that a reaction added to RACM2 will not affect the original photochemical oxidant concentrations. MO₂ and ACO₃ are ~~respectively~~ the methylperoxy radical and the peroxyacetyl radical respectively.

Table 7. Properties of the different surrogate SOA species.

Surrogate	Molecular structure	MW ^a	P ⁰ ^b	ΔH _{vap} ^c
AnRP1		202	1.01×10^{-7}	50
AnRP2		160	2.68×10^{-7}	50
AnIP1		132	2.36×10^{-6}	50
AnIP2		167	1.24×10^{-5}	50
AnPER		190	non-volatile	-
AnRP1a	AnRP1 + 1 group OH	218	non-volatile	-
AnRP2a	AnRP2 + 1 group OH	176	non-volatile	-
AnIP1a	AnIP1 + 1 group OH	148	1.36×10^{-7}	50
AnIP2a	AnIP2 + 1 group OH	183	2.58×10^{-7}	50
AnIP2b	AnIP2a + 1 group OH	199	5.39×10^{-9}	50
BiA0D	pinonaldehyde	168	1.0×10^{-3}	50
BiA1D	pinonic acid	184	5.61×10^{-5}	50
BiA2D	pinic acid	186	1.67×10^{-6}	50
BiA3D	3-methyl-1,2,3-butanetricarboxylic acid	202	non-volatile	-

^a Molecular weight [g.mol⁻¹]

^b Saturation vapor pressure [torr] at 298K

^c Enthalpy of vaporization [kJ.mol⁻¹]

Kinetic of transformation of pinonaldehyde as a function of m_{H^+} the molality of ion H^+ (left) and $a_{HSO_4^-}^{(m)}$ the activity as a molality basis of ion HSO_4^-

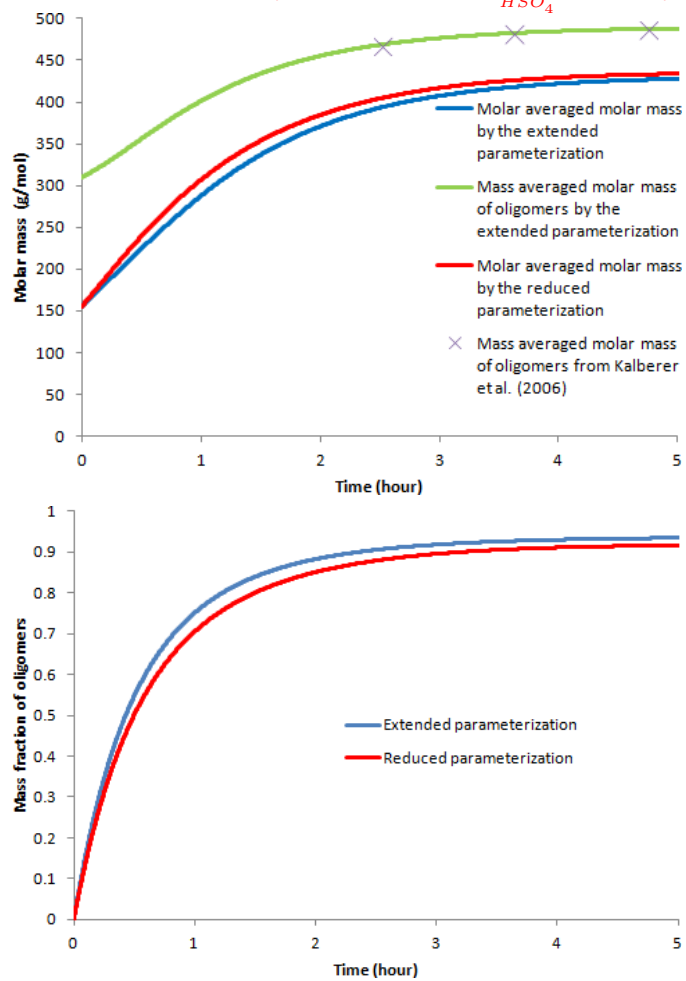


Figure 1. Temporal evolution of molar masses (top) and of the mass fraction of oligomer (down) for the extended and reduced parameterizations.

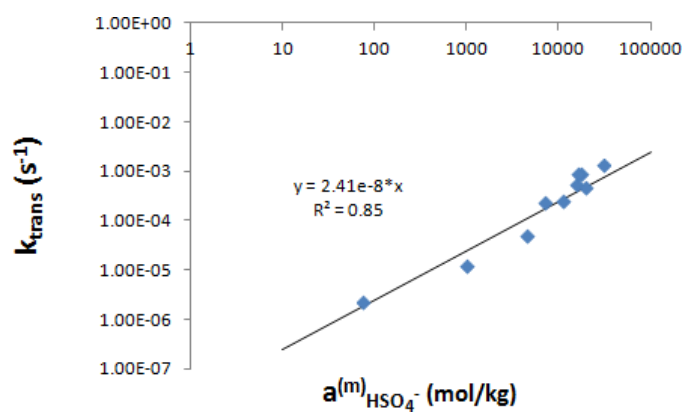
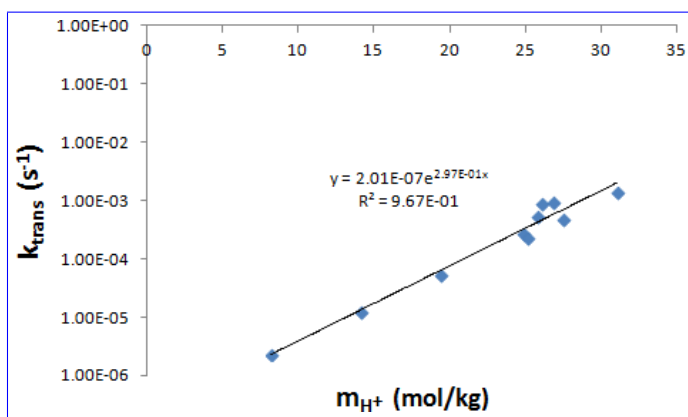


Figure 2. Kinetic rate of transformation of pinonaldehyde as a function of m_{H^+} , the molality of ion H^+ (left) and $a_{\text{HSO}_4^-}^{(m)}$, the activity on a molality basis of ion HSO_4^- (right).

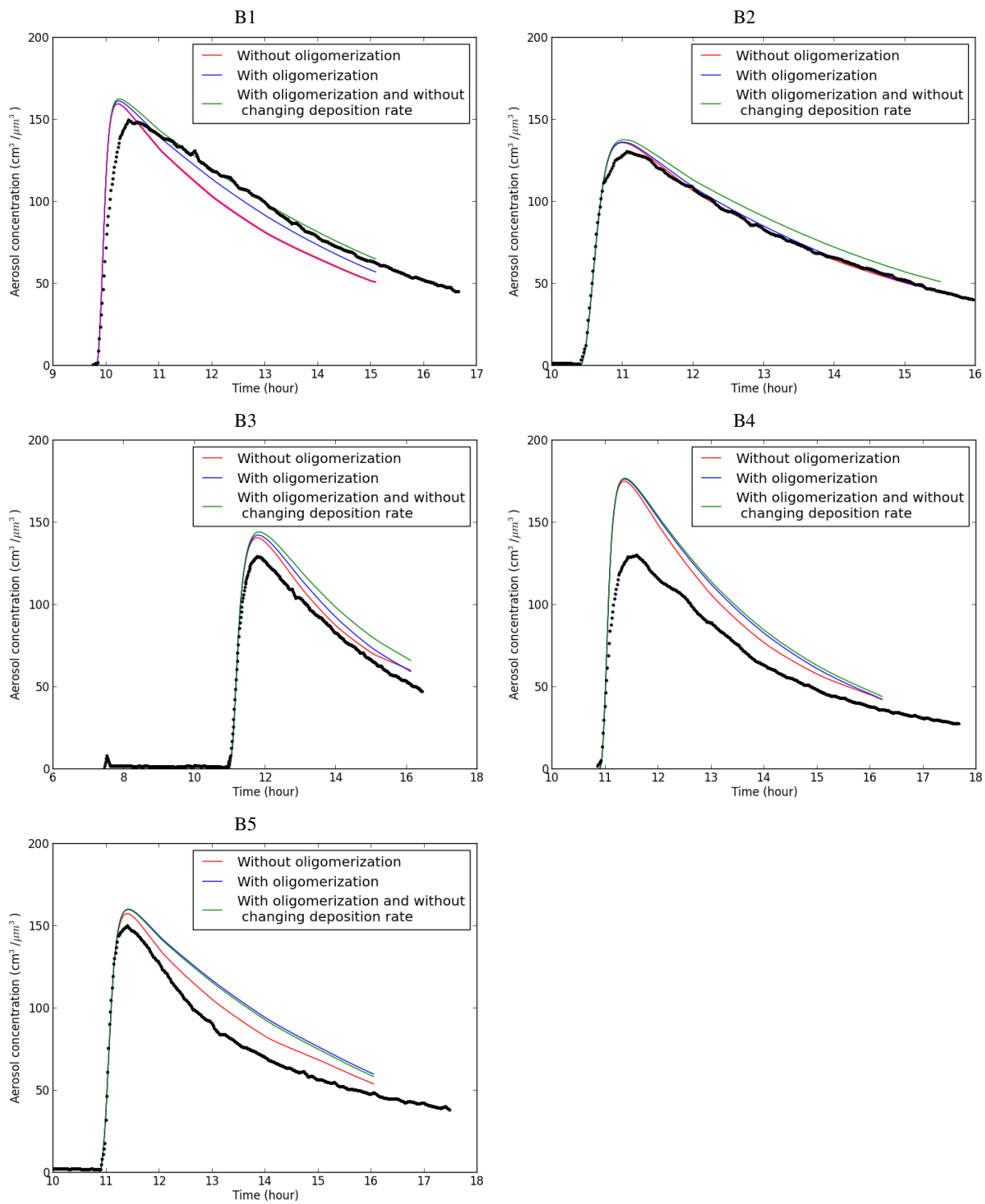


Figure 3. Aerosol concentration formation for the biogenic experiments without SO_2 . Black lines correspond to SMPS measurements.

B6-B7 Aerosol concentration formation for the biogenic experiments with SO₂. Black lines correspond to SMPS measurements.

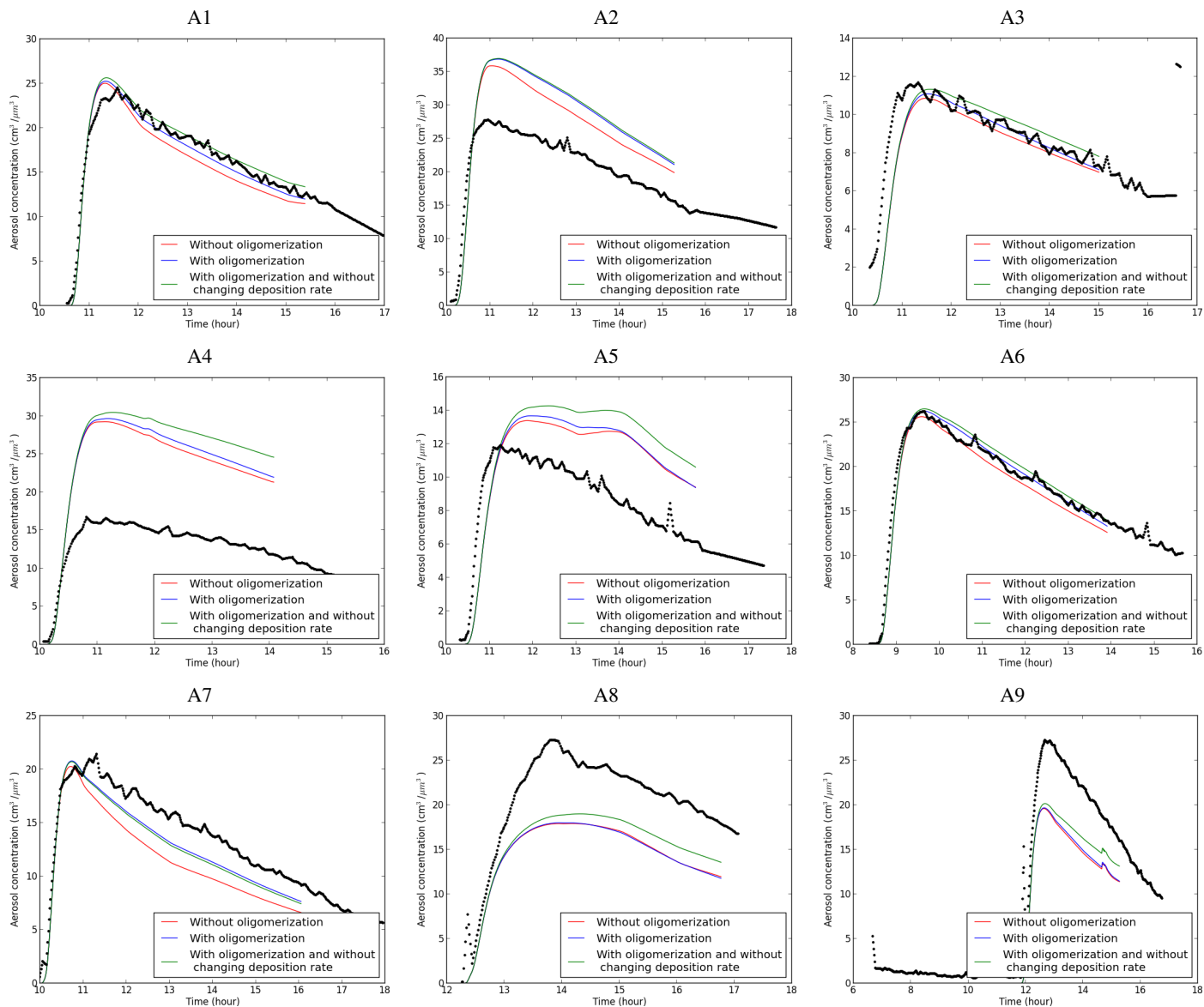


Figure 4. Aerosol concentration formation for the anthropogenic experiments. Black lines correspond to SMPS measurements.

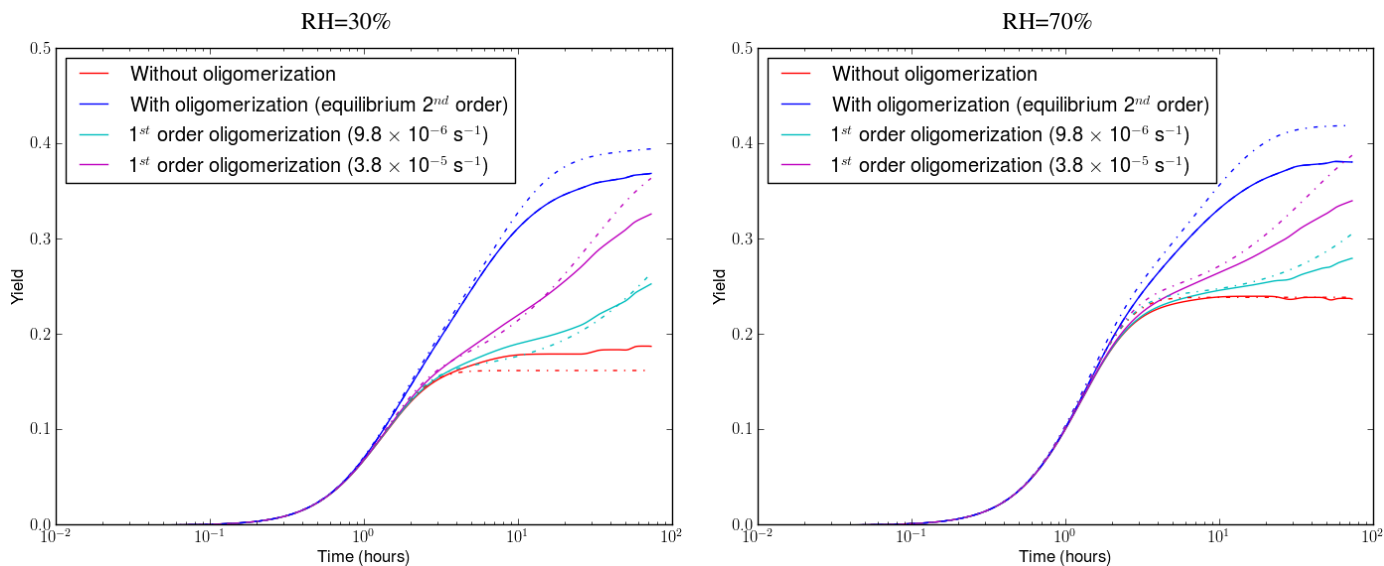


Figure 5. Evolution of the SOA yield from α -pinene oxidation as a function of time for an organic mass loading of $5 \mu\text{g m}^{-3}$. Solid lines correspond to SOA formation with aging. Dashed lines (-) correspond to SOA formation without aging.

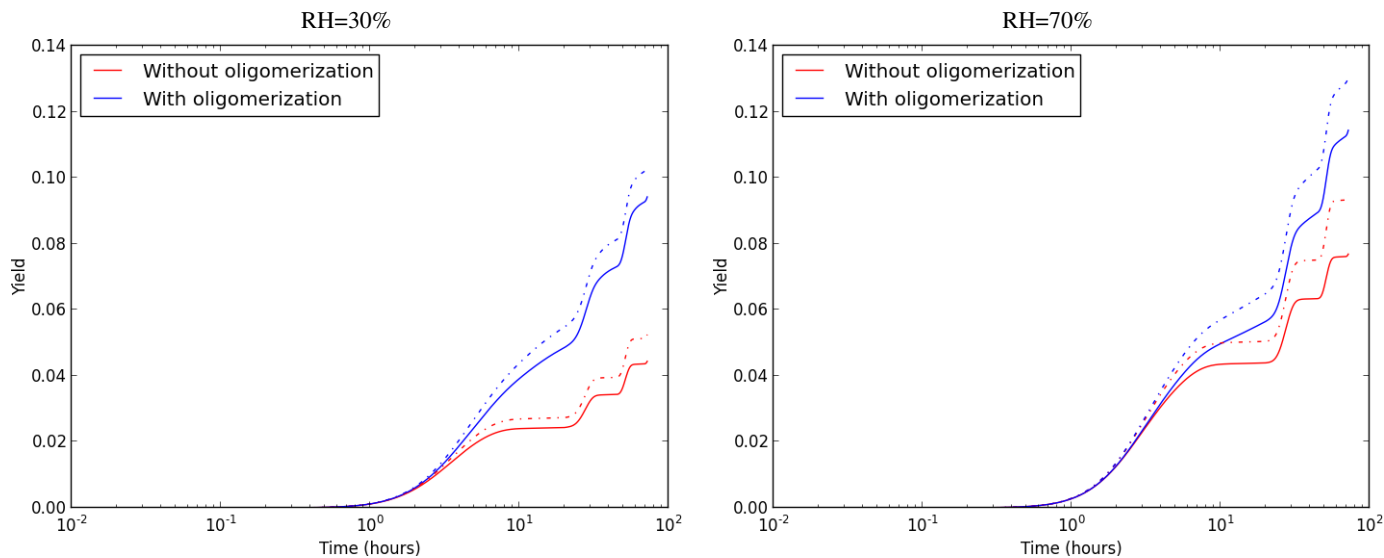


Figure 6. Evolution of the SOA yield from toluene oxidation as a function of time for an organic mass loading of $5 \mu\text{g m}^{-3}$. Solid lines correspond to SOA formation with aging. Dashed lines correspond to SOA formation without aging.

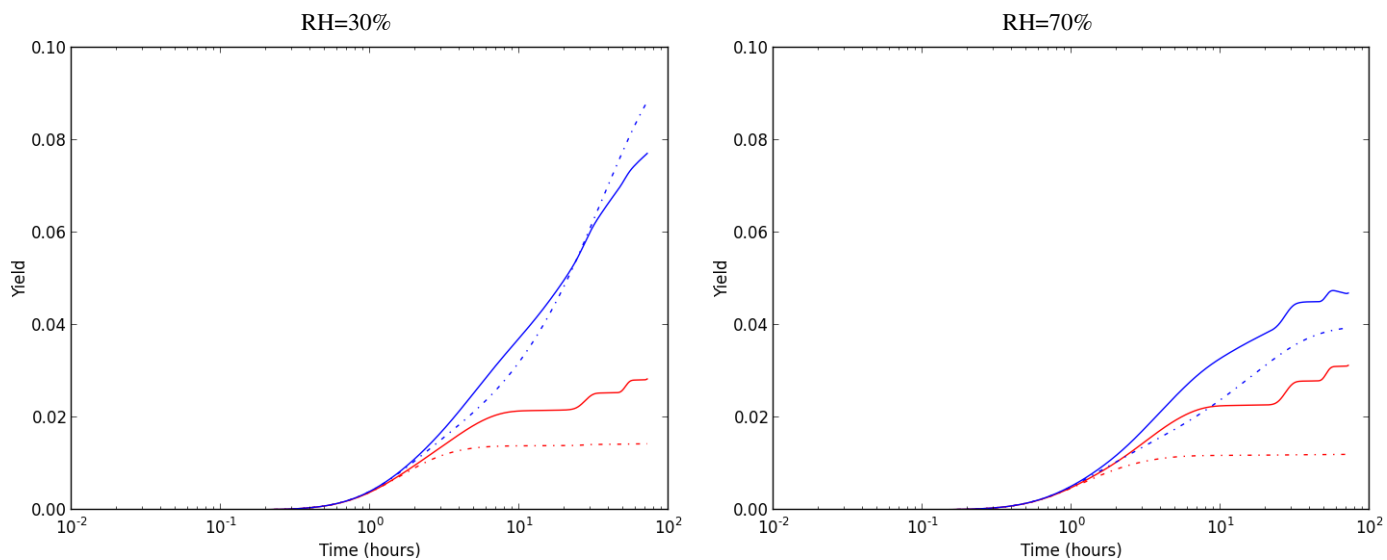


Figure 7. Evolution of the SOA yield from trimethylbenzene oxidation as a function of time for an organic mass loading of $5 \mu\text{g m}^{-3}$. Solid lines correspond to SOA formation with aging. Dashed lines correspond to SOA formation without aging.

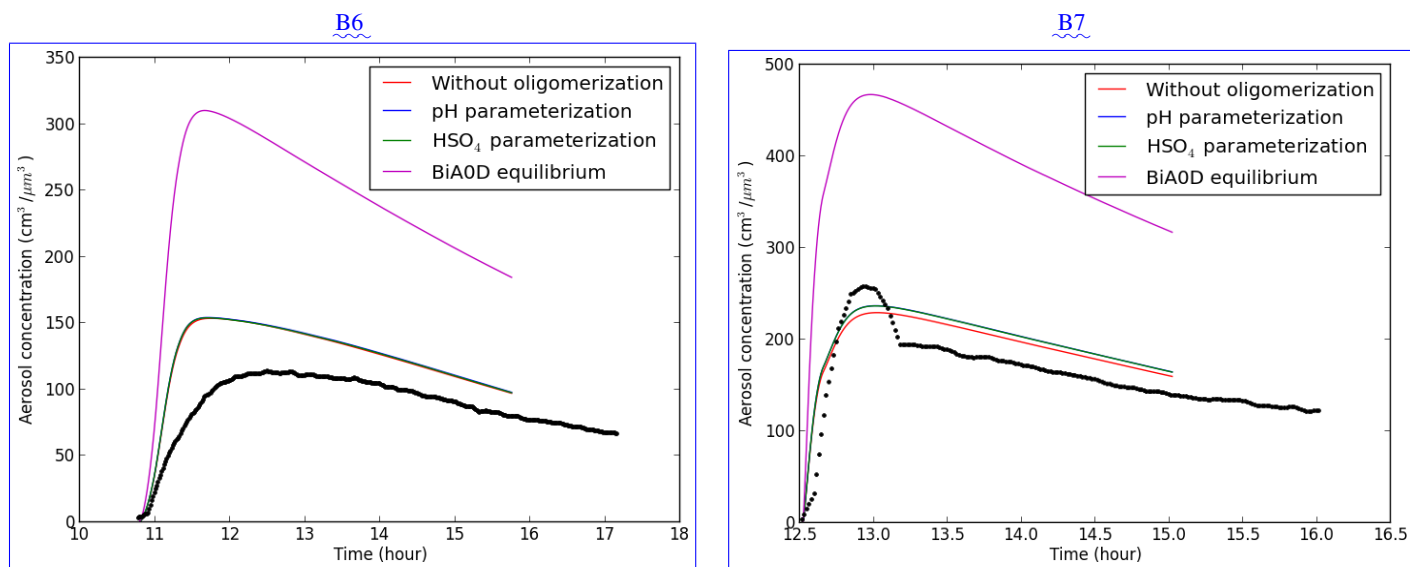


Figure 8. Aerosol concentration formation for the biogenic experiments with SO_2 . Black lines correspond to SMPS measurements.

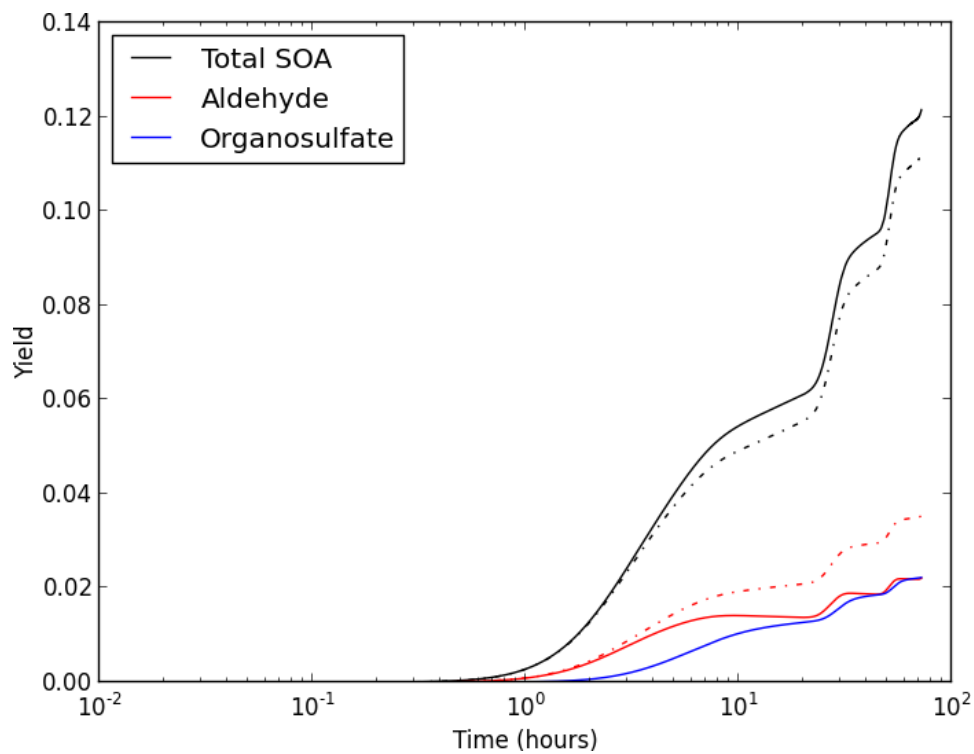


Figure 9. Yield of formation of SOA, aldehydes and organosulfates with (solid lines) or without (dashed lines) the conversion of aldehydes into organosulfates as a function of time for an organic mass loading of $5 \mu\text{g m}^{-3}$ with $2 \mu\text{g m}^{-3}$ of sulfates.

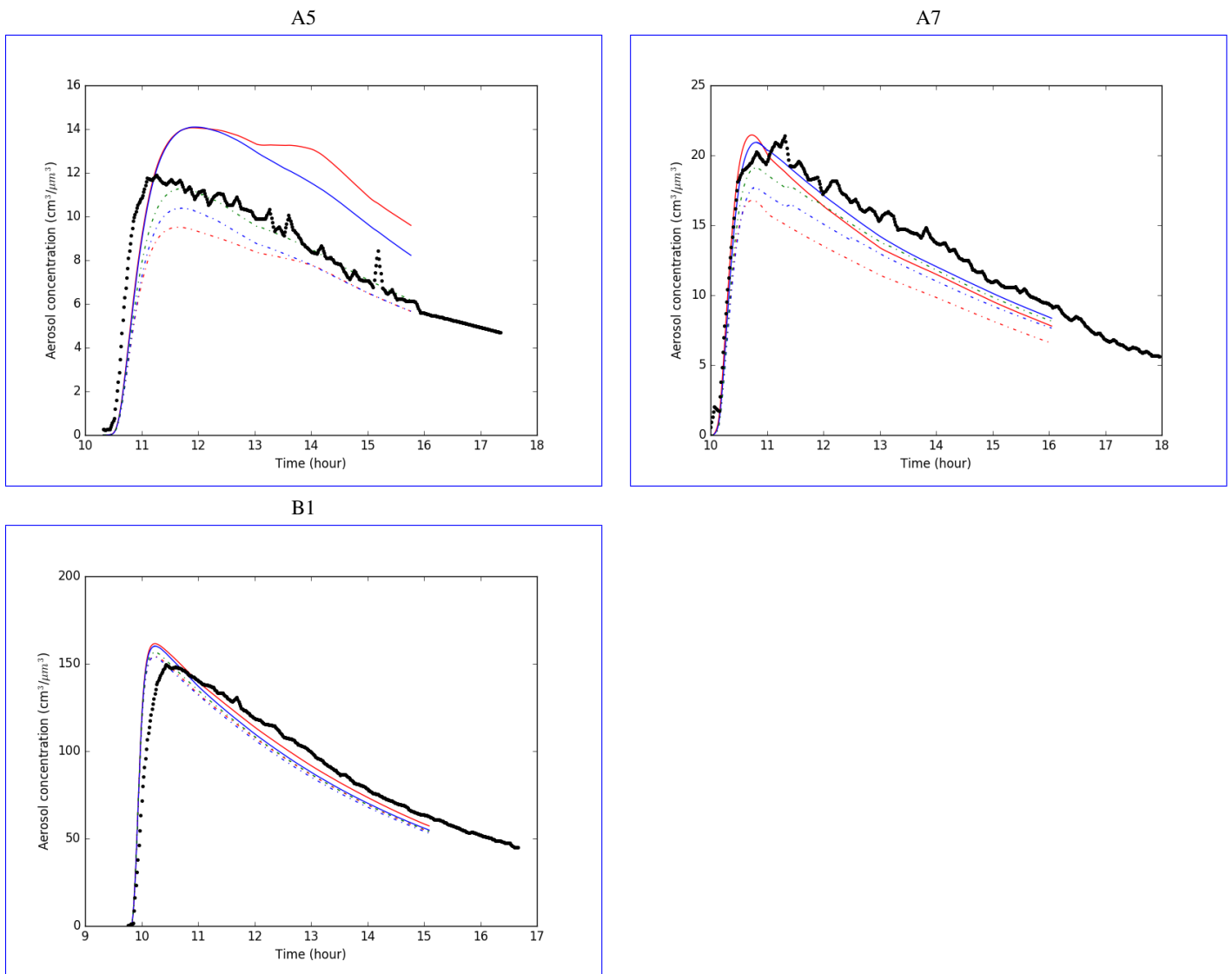


Figure 10. Effect of viscosity and gas wall losses on SOA concentrations for several experiments. The black line corresponds to SMPS measurements, the red lines correspond to modeled SOA concentrations for the non-viscous aerosol assumption, the blue lines correspond to modeled SOA concentrations for the viscous aerosol assumption, and the green line correspond to modeled SOA concentrations for the viscous aerosol assumption with a decrease by a factor 3-20 % of volatility. Solid lines corresponds to simulations assuming no gas wall losses, dotted lines with gas wall losses.