

# Oligomer formation in the troposphere: From experimental knowledge to 3D modeling

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## Abstract

The organic fraction of atmospheric aerosols has proven to be a critical element of air quality and climate issues. However, its composition and the aging processes it undergoes remain insufficiently understood. This work builds on laboratory knowledge to simulate the formation of oligomers from biogenic secondary organic aerosol (BSOA) in the troposphere at the continental scale. We compare the results of two different modeling approaches, a 1<sup>st</sup>-order kinetic process and a pH-dependent parameterization, both implemented in the CHIMERE air quality model (AQM), to simulate the spatial and temporal distribution of oligomerized SOA over western Europe. We also included a comparison of OC concentrations at 2 EMEP stations. Our results show that there is a strong dependence of the results on the selected modeling approach: while the irreversible kinetic process leads to the oligomerization of about 50% of the total BSOA mass, the pH-dependent approach shows a broader range of impacts, with a strong dependency on environmental parameters (pH and nature of aerosol) and the possibility for the process to be reversible. In parallel, we investigated the sensitivity of each modeling approach to the representation of SOA precursor solubility (Henry's law constant values). Finally, the pros and cons of each approach for the

1 representation of SOA aging are discussed and recommendations are provided to improve  
2 current representations of oligomer formation in AQMs.

3

## 4 **1 Introduction**

5 Due to their fast evolution in the troposphere and their continuous interaction with the  
6 ambient gas phase, atmospheric aerosols present a highly variable chemical composition in  
7 space and time (Zhang et al., 2007a). They comprise large quantities of inorganic species such  
8 as nitrates and sulfates, but they also contain an organic fraction (organic aerosol, OA), made  
9 of condensed semi-volatile and low volatility organic species presenting a wide range of  
10 oxidation degrees (Jimenez et al., 2009). Part of this OA comes from the emission of  
11 particulate organic compounds into the atmosphere during combustion processes: it is called  
12 Primary Organic Aerosol (POA). However, away from combustion emission sources, most of  
13 the OA arises from the oxidation of gas-phase organic species, making up the secondary  
14 organic aerosol (SOA), which may represent up to 70% of OA on a mass basis (Kanakidou et  
15 al., 2005). The diversity in size and composition of atmospheric aerosols induces major  
16 differences in their physicochemical properties (Molnar et al., 2001; Kanakidou et al., 2005).  
17 These properties affect their impact on the radiative balance of the atmosphere (Stier et al.,  
18 2007; Paredes-Miranda et al., 2009) and their adverse health effects (Fuzzi et al., 2006). Thus,  
19 not only the total aerosol mass, but also their size distribution and their chemical content are  
20 of crucial importance for atmospheric issues. Although major scientific advances have been  
21 made during the last decade, the composition and the aging processes of the organic aerosol  
22 fraction remain insufficiently understood (e.g., Volkamer et al., 2006).

23 As a consequence, Air Quality Models (AQMs), despite significant progress, still have  
24 difficulties to quantitatively reproduce the observed particulate matter (PM) levels and  
25 gradients, and continue to underestimate the formation of SOA in the troposphere, from cities  
26 to remote areas (Shrivastava et al., 2011; Ervens et al., 2011; Petetin et al., 2014). In this  
27 regard, the chemistry of organics in the aqueous condensed phase remains poorly  
28 characterized. Thanks notably to atmospheric simulation chamber data, new processes have  
29 been integrated into AQMs so as to fill the gap between models and observations. These  
30 processes include for example the addition of new precursors (e.g., Zhang et al., 2007b), the  
31 treatment of SOA hygroscopicity (e.g., Pun, 2008) and aqueous chemistry SOA formation  
32 pathways (e.g., Carlton et al., 2008). In doing so, oligomerization was highlighted as one of  
33 the most important identified processes of SOA evolution. Laboratory studies indeed showed

1 that oligomerization could be a quantitatively important evolution pathway for aqueous  
2 condensed species, and may greatly contribute to a better understanding of SOA aging (e.g.,  
3 Kalberer et al., 2004; Jang et al., 2005; Trump and Donahue, 2014 and references therein). In  
4 particular, modeling studies have shown that the oligomerization of biogenic oxidized  
5 compounds happens to be a significant source of secondary organic aerosols (Aksoyoglu et  
6 al., 2011).

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

1 equilibrium relationship), we also can expect the modeled distribution of simulated oligomers  
2 to differ between the two approaches.

3

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

19

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

25

## 26 **2 Methodology and model set-up**

### 27 **2.1 Model set-up**

28 This study uses the CHIMERE AQM, which is designed to produce daily forecasts of ozone,  
29 PM and other pollutants and to conduct pollution event analyses and research studies in  
30 atmospheric chemistry (Menut et al., 2013). The model may be run from the regional to the  
31 continental scale, with horizontal resolutions ranging from 1 to 100 km. CHIMERE is used  
32 daily for operational air quality forecasts in 9 different regions of France and Europe. In this

1 context, model performance is assessed every day via the comparison of the model output  
2 with atmospheric measurements, which also provides the basis for the ongoing improvement  
3 of CHIMERE. CHIMERE uses the MELCHIOR2 gas-phase chemical scheme (120 reactions  
4 among 44 gaseous species), which is adapted from the original EMEP mechanism and is a  
5 reduced version of the MELCHIOR1 mechanism, obtained by Carter's surrogate molecule  
6 method (Carter, 1990). The gas-phase chemical mechanism for SOA production has been  
7 described in detail by Pun et al. (2006) and Bessagnet et al. (2008).

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

- 25 - six hydrophilic surrogate species including an anthropogenic non-dissociative species  
26 (AnA0D), an anthropogenic once-dissociative species (AnA1D), an anthropogenic  
27 twice-dissociative species (AnA2D), a biogenic non-dissociative species (BiA0D), a  
28 biogenic once-dissociative species (BiA1D) and a biogenic twice-dissociative species  
29 (BiA2D). The pAnA\*D and pBiA\*D species stand for the part of the surrogate species  
30 that is present in the particulate phase
- 31 - three hydrophobic species comprising two anthropogenic species with low and  
32 moderate saturation vapor pressures (AnBIP and AnBmP) and a biogenic species with  
33 a moderate saturation vapor pressure (BiBmP)

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

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

7  
8 In the model, horizontal advection is calculated using the Van Leer second-order scheme and  
9 boundary layer turbulence is represented as a diffusion phenomenon, following Troen and  
10 Mahrt (1986). Vertical winds are diagnosed through a bottom-up mass balance scheme. Dry  
11 deposition is coded as in Wesely (1989) and photolytic rates are attenuated using liquid water  
12 or relative humidity. Finally, the numerical time solver uses the TWOSTEP method (Verwer,  
13 1994).

14  
15 The 2006 annual anthropogenic emissions from the EMEP (European Monitoring and  
16 Evaluation Programme) database (Vestreng et al., 2005) at a resolution of  $0.5 \times 0.5^\circ$  have  
17 been used (<http://www.emep.int>). They include CO, NH<sub>3</sub>, NMVOC, NO<sub>x</sub>, SO<sub>x</sub>, and PM  
18 emissions for the 10 anthropogenic activity sectors of the SNAP nomenclature. The emission  
19 values are disaggregated into individual chemical species and at an hourly time step according  
20 to IER ([http://www.ier.uni-stuttgart.de/index\\_en.html](http://www.ier.uni-stuttgart.de/index_en.html)) recommendations, and are spatially  
21 distributed over our simulation domain using a kilometric land use database  
22 (<http://glcf.umiacs.umd.edu>). Biogenic emissions have been computed with the MEGAN  
23 model (Guenther et al., 2006) using a land use database of 1km resolution and hourly  
24 meteorological parameters from the MM5 model (see below) for the calculation of the various  
25 biogenic VOC emission flux intensity and temporal evolution (<http://lar.wsu.edu/megan/>).  
26 Climatologic LMDZ (Hauglustaine et al., 2004) model output data were used for boundary  
27 conditions. Finally, the mesoscale model MM5 (Dudhia et al., 1993) was used to generate  
28 hourly meteorological fields for CHIMERE over a European domain covering our simulation  
29 domain, with a horizontal resolution of 54 km and using 32 levels in the vertical direction  
30 from the surface to 10 hPa.

31  
32 A European domain extending from  $6^\circ$  W to  $20^\circ$  E in longitude and from  $38^\circ$  N to  $54^\circ$  N in  
33 latitude (see Figure 1) was defined for this study: its size allows tracking and studying large  
34 European city plumes and the domain includes our study area, which is western Europe. The

1 horizontal resolution is  $0.23^\circ \times 0.20^\circ$ . For the vertical resolution, we used 8 levels of  
2 decreasing resolution from the ground level up to 500 hPa, the first model layer being 50 m  
3 thick. The simulation domain and its grid are illustrated in Figure 1. The simulation period  
4 covers two months (July and August) in the summer of 2006. The simulation was run with a  
5 spin-up period (15 days) prior to the periods of interest in order to ensure that emissions and  
6 secondary pollutants are realistically distributed over the domain at the beginning of the  
7 evaluation period.

8

## 9 **2.2 Oligomer parameterizations**

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

### 12 **2.2.1 Kinetic approach**

13 The first approach (called hereafter KIN) is based on the hypothesis that oligomer formation  
14 may be represented through a kinetic process (Morris et al., 2006; Carlton et al., 2010). This  
15 hypothesis is supported by a series of smog chamber experiments conducted by Kalberer et al.  
16 (2004), where an important fraction of organic aerosol mass was shown to be composed of  
17 oligomers. The authors reported that, after 20 hours of processing, 50% of the total organic  
18 aerosol mass was transformed into oligomers. From this result, Morris et al. (2006) proposed  
19 the use of a first-order rate constant  $k_1 = 9.6 \times 10^{-6} \text{ s}^{-1}$  to account for the oligomerization  
20 formation process, corresponding to a half-life of 20 h for organic species in the particulate  
21 phase. In this approach, biogenic and anthropogenic species are all potential oligomer  
22 precursors. However, due to low amounts of anthropogenic SVOC from the oxidation of  
23 classic precursors (Toluene, Xylene, Trimethylbenzene...) over Europe, the production of  
24 anthropogenic oligomer could be negligible (Aksoyoglu et al., 2011).

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

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

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

## 20 **2.2.2 pH-dependant approach**

21 The second approach (called here KPH) combines the laboratory works of Jang et al. (2005) -  
22 who showed that the polymerization of aldehydes may happen through a variety of acid-  
23 catalyzed reactions - and the observations of Gao et al. (2004) - who indicated that at least  
24 10% of the total organic aerosol mass is converted into oligomers due to the formation of  
25 organic acids in the aerosol. From these results, Pun and Seigneur (2007) developed an  
26 equation for the calculation of the gas-to-particle partitioning constant of semi-volatile  
27 aldehydes. It represents their increased partitioning toward the aqueous phase due to acidity:

$$28 \quad K_{p,eff,i} = K_{p,i} \cdot \left[ 1 + K_{0,eff,i,ref} \cdot \left( \frac{C_{H^+}}{C_{H^+,ref}} \right)^{1.91} \right] \quad (1)$$

29 where  $K_{p,eff,i}$  is the effective partitioning coefficient of the  $i^{th}$  compound between the gas  
30 phase and the aerosol aqueous phase;  $K_{p,i}$  is its standard partitioning coefficient - calculated



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

13 The KPH approach only artificially reproduces oligomer production. Indeed, the reactivity in  
14 the particulate phase that leads to the consumption of dissolved organic species is restituted by  
15 an increase in the value of their effective partitioning coefficient, according to Equation (1).  
16 As a consequence, oligomerization is treated here as a fully reversible process. Furthermore,  
17 this approach does not require any new model species to represent the aqueous oligomers.  
18 This is why it is necessary to perform two types of simulations to estimate the effect of the  
19 oligomerization process: a reference case - called hereafter REF - and a scenario case (KPH).  
20 The differences in the pBiA0D concentration fields between the two simulations represent  
21 aqueous oligomerization in the KPH approach:

$$22 \quad [\text{Oligomers}] = [\text{pBiA0D}]_{\text{KPH}} - [\text{pBiA0D}]_{\text{REF}} \quad (2)$$

23 To implement this approach in the model and ensure the robustness of the modified  
24 partitioning constant value, it was necessary to adequately account for the acidity of the  
25 deliquescent particles. The particle pH is calculated in CHIMERE by an online coupling with  
26 the ISORROPIA model (<http://nenes.eas.gatech.edu/ISORROPIA>) that solves the transition  
27 between solid and aqueous phases through the estimation of the deliquescent relative  
28 humidity. However it is also possible to run ISORROPIA in a metastable configuration,  
29 which considers that aerosols remain in a liquid state under conditions of low relative  
30 humidity, thus avoiding the transfer of dissolved BiA0D back to the gas phase and favoring  
31 oligomer persistence as well as its atmospheric transport. This alternative is taken into  
32 account for the evaluation of the KPH approach.

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

### 8 **2.3 Module implementation**

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

19 One important issue in SOA production is the influence of the gas-particle partition of semi-  
20 volatile species on the final model results, whether under dry or wet conditions. However,  
21 since this work focuses on the reactivity of hydrophilic compounds, we specifically addressed  
22 the issue of Henry's constant values,  $K_H$ . By affecting the fraction of the semi-volatile species  
23 that partition into the aqueous phase, this constant directly impacts the quantitative production  
24 of the organic aerosol fraction. Furthermore, the reliability of  $K_H$  values is known to be low  
25 for complex compounds of atmospheric interest, especially for highly soluble species  
26 (Raventos et al., 2010). In order to observe the effect of refining these values in the different  
27 approaches, we ran the model with different sets of  $K_H$  values. To that end, the group  
28 contribution method of Suzuki et al. (1992) that is used by default in CHIMERE to produce  
29  $K_H$  values at 298 K was replaced by the GROMHE group contribution approach. This method  
30 was developed by Raventos et al. (2010). It is based on the molecular structure and was  
31 shown to be more reliable than the standard methods for the complex organic compounds of  
32 atmospheric interest. In this context, an issue that must be addressed is that of the ideality of

1 aqueous solutions. Indeed, due to the presence of inorganic salts at high concentrations, it is  
2 highly probable that the aqueous aerosol phase is non-ideal, which may affect Henry's law  
3 constants by one to two orders of magnitude. This phenomenon can be taken into account  
4 using Setschenow coefficients (Wang et al., 2015). However, figuring out the existing  
5 uncertainty on the aerosol aqueous phase composition, and the fact that the uncertainty in the  
6 estimation of Henry's law constants using the group contribution approach may be about at  
7 least one order of magnitude (Raventos et al., 2010), we have considered that the correction  
8 brought by Setschenow coefficients would have a second-order effect, most probably poorly  
9 controlled due to the lack of accuracy on the aqueous phase description and the margin of  
10 uncertainty on the coefficients themselves. This is why we did not include a non-ideality  
11 correction in the  $K_H$  evaluation process. In any case, the sensitivity tests that we conducted  
12 during these works will allow us to assess the necessary degree of sophistication on Henry's  
13 law constant values, and to identify areas for improvement.

14 By default, the molecular structure selected for BiA0D in CHIMERE is that of  
15 pinonaldehyde, a 10-carbon-atom molecule with an oxo group and an aldehyde group, while  
16 BiA1D and BiA2D are respectively based on norpinic acid (9-carbon-atom molecule with a  
17 carboxy group and an oxo group) and on pinic acid (9-carbon-atom molecule with two  
18 carboxy groups). Table 1 summarizes the default structure properties and molar masses, as  
19 well as the partitioning and saturation pressure characteristics used in CHIMERE for the 3  
20 hydrophilic surrogates that lead to oligomer production from monoterpenes.

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

## 28 **3 Results**

### 29 **3.1.1 Precursor partitioning in the reference case**

30 In order to examine the gas-particle partition of the model surrogates, we report in Figure 2  
31 the average concentration fields of the hydrophilic and hydrophobic surrogates simulated by

1 CHIMERE in the reference case for the period July 20 - August 3, 2006. This figure indicates  
 2 that BiA1D is the highest hydrophilic contributor to the organic aerosol mass concentration,  
 3 while BiA0D remains quasi-exclusively in the gas phase. However, among the monoterpene  
 4 surrogates, the hydrophobic species BiBmP is the largest contributor to the organic aerosol  
 5 mass concentration. On average, hydrophilic and hydrophobic species account for 25% and  
 6 75% of this organic aerosol mass concentration, respectively.

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

14

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

$$18 \quad \xi^i = \frac{C_a^i}{C_a^i + C_g^i} = \left(1 + \frac{1}{H_i R T L}\right)^{-1} \quad (3)$$

19 In this equation,  $C_a^i$  and  $C_g^i$  represent (in  $\mu\text{g m}^{-3}$ ) the concentration of species  $i$  in the  
 20 particulate and gas phases respectively;  $H_i$  is the Henry's law constant (in  $\text{Matm}^{-1}$ );  $R$  is the  
 21 ideal gas law constant;  $T$  is the temperature, and  $L$  is the liquid water content (LWC) of the  
 22 aerosol (in  $\text{cm}^3$  liquid water per  $\text{cm}^3$  air). We set the liquid water content value within the  
 23  $10^{-11}$ - $10^{-12}$  range of values proposed by Engelhart et al. (2011) for a deliquescent aerosol.

24

25 For a dry aerosol we used an equation similar to equation (3), which has been shown to apply  
 26 equally to the organic compounds that condense into an organic phase (Eq. 4) (e.g., Donahue  
 27 et al., 2009; Valorso et al., 2011). There,  $M_w$  stands for the mean organic aerosol molar mass  
 28 (set to  $250 \text{ g mol}^{-1}$  based on Robinson et al. (2007)),  $C_{OA}$  represents the total organic aerosol  
 29 mass concentration ( $\mu\text{g m}^{-3}$ ) and  $P_{\text{vap}}$  is the saturation vapor pressure (atm) and considering an  
 30 ideal mixture.

$$31 \quad \xi^i = \frac{C_a^i}{C_a^i + C_g^i} = \left(1 + \frac{M_w P_{\text{vap}}}{C_{OA} R T} 10^6\right)^{-1} \quad (4)$$

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

10

11 For deliquescent aerosols:

- 12 - When the Henry's law constant value is lower than  $10^7 \text{ Matm}^{-1}$  (part I) or greater than  
13  $10^{13} \text{ Matm}^{-1}$  (part III), then considering the selected range of LWC values, the  
14 equilibrium is either in favor of the gas phase (part I, not significantly present in the  
15 aqueous phase) or in favor of the particulate phase (part III, highly soluble  
16 compounds), respectively.
- 17 - For intermediate  $K_H$  values (part II), the mass of the semi-volatile species is shared  
18 between the two phases. In this area, partitioning towards the aqueous phase is an  
19 increasing function of LWC values.

20 Similarly, for dry aerosols:

- 21 - The partition is completely in favor of the aerosol phase (low volatility compounds –  
22 part 1) or towards the gas phase (volatile compounds – part 3) whatever the  $C_{OA}$  for  
23 saturation vapor pressures that are lower than  $10^{-13} \text{ atm}$  or greater than  $10^{-6} \text{ atm}$ ,  
24 respectively.
- 25 - For intermediate values (part 2, shaded area), partitioning towards the condensed  
26 phase increases with increasing  $C_{OA}$ .

27 The main conclusions that can be drawn from these graphs are the following. First, over this  
28 set of atmospheric situations, and whatever the nature of the aerosol - BiA0D never  
29 contributes significantly to OA formation. Indeed,  $\xi_{\text{BiA0D}}$  values reach a maximum of 0.3% in  
30 the most favorable combination (dry aerosol,  $C_{OA} = 10 \mu\text{g m}^{-3}$ ). Second,  $\xi_{\text{BiA1D}}$  and  $\xi_{\text{BiA2D}}$   
31 values respectively range from 1.7 to 14.4% and from 1.5 to 12.9% for a deliquescent aerosol,

1 and span the 3.30-77.4% and the 4.9-83.9% ranges in the presence of a dry aerosol. Thus,  
2 BiA1D and BiA2D are likely to sweep a wide range of partitioning states in the presence of a  
3 dry aerosol, while their  $K_H$  value are too low to account for a substantial transfer to the  
4 aqueous aerosol phase in the presence of a deliquescent aerosol. One should note, however,  
5 that in the dry aerosol model (Equation 4), the activity coefficients are assumed to be unity; in  
6 other words, one does not account for interactions among organic species. Since hydrophobic  
7 and hydrophilic species have significantly different molecular structures, one could anticipate  
8 that including the activity coefficients in the model would reduce the absorption of the  
9 hydrophilic species in the hydrophobic organic phase or even lead to the formation of a  
10 separate organic phase (Couvidat and Sartelet, 2015). Therefore, the values given for the  
11 partition of hydrophilic aerosol should be seen as upper limits. Considering those 2 elements,  
12  $K_H$  appears to be an influential parameter for BiA\*D species, its modulation - with regard to  
13 the effective solubility of the surrogates – being likely to strongly enhance the oligomer  
14 production efficiency when the aerosol is deliquescent and when the residual gas fraction of  
15 the surrogate is not negligible. A species such as BiA0D, which currently remains mostly  
16 gaseous in the standard version of the model, may thus be particularly sensitive to the  
17 reference value of its Henry's law partitioning constant.

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

### 22 **3.1.2 Oligomer production from the oxidation of monoterpenes**

23 CHIMERE simulations were launched in the reference, KIN, and KPH configurations (both  
24 modes) for the two periods of interest defined above. The quantitative differences in the  
25 concentrations of the simulated biogenic oligomers, as well as their spatial and temporal  
26 features, were investigated. As mentioned previously, we focused on the comparison between  
27 the BiOLG (KIN approach) and the  $p\text{BiA0D}_{\text{KPH} - \text{REFERENCE}}$  (KPH approaches) concentration  
28 fields.

29 Figure 4 presents the oligomer daily concentration maxima simulated by CHIMERE from the  
30 oxidation of monoterpenes for both parameterizations and for one representative day of the  
31 simulated period. It highlights large differences in the oligomer concentration fields produced  
32 in each approach, both in terms of intensity and spatial distribution. Indeed we can see that,

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

22 When averaging our results over the whole summer period, we observe no significant change  
23 in the location of high oligomer concentrations, though concentration values are logically  
24 lower than hourly peaks, and concentration fields show smoother gradients (Fig. 5). However  
25 what is interesting is that the quantitative trends differ from those predicted previously.  
26 Indeed, the KIN parameterization produces the highest average oligomer concentrations that  
27 range from  $0.1$  to  $0.4 \mu\text{g m}^{-3}$  over most of the simulation domain. This approach forms well-  
28 mixed secondary plumes similar to those of other long-lived atmospheric oxidants such as  
29 ozone, with maxima over Central Europe and Mediterranean areas. On the contrary, KPH  
30 oligomers only slightly exceed  $0.1 \mu\text{g m}^{-3}$  (in both deliquescent and metastable modes),  
31 except over small regions of the Adriatic Sea and over northern Spain areas where they reach  
32 a value  $0.3 \mu\text{g m}^{-3}$  in the deliquescent mode. It is noticeable that, due to the persistence of an  
33 aqueous phase, the metastable mode produces higher oligomer concentrations over the entire

1 domain. However, the difference remains moderate in terms of absolute mass concentration.  
2 This feature confirms the lack of oligomer mass accumulation in the KPH approach that was  
3 observed in the spatial analysis of hourly maps. It indicates that, beyond the question of  
4 relative humidity, favorable conditions for oligomers production in the KPH approach are not  
5 often met along time. The conditions of the process reversibility thus have to be more  
6 precisely identified and understood, for both modes of this approach.

### 7 **3.1.3 Driving parameters of both approaches**

8 We explored these differences in order to identify the parameters driving production, transport  
9 and decomposition of oligomers over continental areas for both approaches. First, the  
10 parameters describing the aerosol properties together with the BiA0D partition were plotted  
11 over the domain and analyzed for a given time step of the simulation. Then we investigated  
12 the temporal evolution of the BiA0D partition and oligomer formation at one grid point of the  
13 domain in the 3 CHIMERE configurations.

14 Figure 6 presents the nature (humid or dry) and the pH of the aerosol simulated over Europe  
15 for 24 July 2006 at 5:00 UTC, in relation with BiA0D concentration fields. The similarity of  
16 the aerosol type (dry or humid, Figure 6a) determined by ISORROPIA and of the oligomer  
17 concentration fields (Figure 6d) indicates that the existence of a deliquescent aerosol is not  
18 ensured in all grid cells and proves to be a discriminatory parameter for oligomer production  
19 in the simulations. Figure 6 also emphasizes the role of pH in this process. In northern Spain,  
20 significant oligomer formation is observed in the presence of both a wet aerosol and a very  
21 acidic aqueous phase (pH around 2.5), although this is not a region where the concentrations  
22 of BiA0D are high. On the contrary, over Great-Britain, where there is no significant oligomer  
23 formation, CHIMERE predicts the presence of a deliquescent aerosol, low gaseous BiA0D  
24 concentrations and a pH value around 4. These results place the pH threshold for a significant  
25 oligomer production from BiA0D at a value comprised between 3 and 4. Our previous  
26 calculations indicate that the fraction of BiA0D in the aerosol phase remains lower than 1%  
27 for a pH of 4, but reaches up to 6% - 39% for a pH of 3, considering a LWC in the  $10^{-11}$  to  
28  $10^{-12}$  range ( $\text{cm}^3$  water  $\text{cm}^{-3}$ ). This exponential relationship supports the local formation of  
29 high oligomers concentration peaks in Figure 6 (d), with regards to the conditions shown in  
30 Figures (a) and (b). Clearly, although the presence of the precursor is the first requirement for  
31 oligomer production, it is not a determining parameter of the structure of oligomer  
32 concentration fields. As the modeled pH strongly impacts the rate and the intensity of



1 oligomer formation, its robustness was questioned. Although no direct measurements of the  
2 pH of the aerosol have been realized yet, our calculations are consistent with previous  
3 experimental studies reporting strongly acidic fine particles (Ludwig and Klemm, 1990;  
4 Herrmann, 2003; Keene et al., 2004). Our results are also consistent with the work of Xue et  
5 al. (2011), which is based on chemical composition and meteorological data collected at a  
6 suburban site in Hong Kong and which estimated the aerosol pH to range between -1.87 and  
7 3.12. Despite the uncertainty that cannot be fully removed on the modeled pH value, we  
8 didn't consider necessary to run other assessment methods, on the basis of the recent works of  
9 Henningan et al. (2015) who affirm that thermodynamic models like ISORROPIA are more  
10 adapted to estimate the aerosol pH than proxy methods such as the ones using ion balance and  
11 ratios.

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

17 In the KIN approach, BiOLG progressively accumulates in the air mass and shows a  
18 smoothed concentration curve along time. Furthermore, oligomer concentrations are not  
19 strongly correlated with the presence of gaseous precursors due to the time required for the  
20 kinetic formation process. In the KPH approach, oligomer concentrations are highly variable,  
21 showing intense peaks that alternate with periods of near-zero content in the particle phase. It  
22 is noted that the black curve (KPH, metastable mode) present high values on 22 and 23 July  
23 that are not observed for the results of the deliquescent mode. These events are not either  
24 correlated with a specific origin of the air mass (analysis not shown here) or with a given  
25 BiAOD concentration threshold, but both take place during shaded periods and can therefore  
26 be attributed to the limiting effect of a dry aerosol in the deliquescent mode. However, from  
27 the co-variability of pBiAOD concentrations in shaded and non-shaded areas, it appears that  
28 the existence of a deliquescent aerosol is not the only driving parameter of this  
29 formation/evaporation cycle. Indeed, sharp decreases in the particulate fraction of BiAOD are  
30 simultaneously observed whatever the aerosol physic state (see 21 – 22 and 24 July for  
31 instance), which implies that pH variability also plays a decisive role in the calculations,  
32 during a large part of the day. During these periods, the pH was indeed comprised between 4  
33 and 6, thus being the principal limitation for BiAOD storage in the particulate phase. Thereby,

1 whatever the selected mode (deliquescent or metastable), there is no continental transport of  
2 oligomers due to fast and quantitative release processes. It results in the simulation of short  
3 duration peaks, accounting for local production from emissions.

4 Finally, Figure 7 reveals the recurrent loss of particulate BiAOD in northern Spain during the  
5 period of study, mostly during daytime periods. It shows an average duration of 2 to 6 hours  
6 for the oligomer peak events, which is quite short in view of the time required for pollutant  
7 mixing and transport in the troposphere. Therefore, these local phenomena cannot affect PM  
8 mixing ratios over large areas and for extended time periods. As the transfer of BiAOD to the  
9 gas phase from the aerosol is frequent and total in the KPH approach, its consistency has to be  
10 considered. This process appears to be highly dependent both on the pH variability - which  
11 has been poorly measured up to now – and on the  $K_H$  change (from Equation (1)) required to  
12 significantly alter the partition of BiAOD between the 2 phases. That is, the choice of the  
13 reference  $K_H$  value may be of primary importance. Such findings question the relevance of  
14 simulating a low-constrained reversibility for the formation of oligomers in 3D models.

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

### 32 **3.1.4 Oligomer to organic aerosol ratio in summer**

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

7 When considering monoterpenes as the only oligomer precursors, the implementation of a  
8 kinetic approach (Figure 8, left and central upper graphs) results in a significant increase (+1-  
9  $2 \mu\text{g m}^{-3}$ ) of the average OA mass concentration inside the plume. Although the general  
10 structure of the plumes is not changed, the kinetic production of oligomers leads to the  
11 presence of significant  $BSOA_{\text{terp}}$  values over an area that is much broader than in the  
12 reference case. On the opposite, the KPH approach in deliquescent mode (Figure 8, right  
13 upper graph) does not modify the average mass concentration and spatial distribution of  
14  $BSOA_{\text{terp}}$ . The same conclusion can be drawn from the metastable version of KPH (not shown  
15 here). In terms of ratios, the OA fraction that remains under the form of oligomers (Figure 8,  
16 lower graphs representing pOLG to  $BSOA_{\text{terp}}$  ratio) represents 20 to 50% of the organic  
17 aerosol mass originating in monoterpenes over all the continental areas in the KIN approach.  
18 It is due to the stabilization of a very large proportion of biogenic organic species in the  
19 condensed phase under the form of oligomers. However, extreme values of this ratio are  
20 simulated over marine areas (see the purple color, meaning that approximately 80% of  
21  $BSOA_{\text{terp}}$  is under the form of oligomers). This phenomenon can be explained by a  
22 combination of two factors. First, irreversible and continuous oligomer formation is the only  
23 possible chemical evolution pathway for condensed biogenic species in this version of the  
24 model. Second, in our model, marine areas are very little influenced by fresh organic  
25 emissions, which tend to favor the omnipresence of an aged OA over the sea. This is probably  
26 wrong, as high contributions of primary organic matter to the marine aerosol were predicted.  
27 However, they are not taken into account in our simulations (Ovadnevaite et al., 2011).  
28 Furthermore, such a high degree of OA conversion to oligomers has never been reported in  
29 the literature. Although it is limited on that point, it may be partly unrealistic to simulate a  
30 single fate for all biogenic organics present in the particulate phase. Despite this statement,  
31 the absolute OA concentration simulated over the sea remains low ( $<0.2 \mu\text{g m}^{-3}$ ), thereby  
32 limiting the impact of this potential bias in the model. As regards KPH simulations, the model  
33 indicates (as expected) a very low average contribution of oligomers to the mass of  $BSOA_{\text{terp}}$

1 over continental areas, except in the north of Spain – where the contribution of oligomers  
2 represents 10 to 20% of the SOA mass concentration – and over marine areas where it  
3 sometimes exceeds 40%. Over continental areas, the oligomer fraction is shown to be  
4 insignificant because of the frequent reversal of the formation process due to wide pH  
5 variations (see above).

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

14 These results highlight the importance of closer identifying the oxidation products of the main  
15 atmospheric BVOCs, as well as their structure and reactivity. In particular, questions still  
16 arise about the way the evolution of condensed isoprene derivatives should be represented.  
17 Indeed, the assumption of Carlton et al. (2010), which states that the formation of oligomers is  
18 driven by a same first-order rate constant whatever the oxidation products, is questionable.  
19 First, because this parameterization derives from the evolution of cyclic compounds in  
20 chamber experiments, which is the case of  $\alpha$ - and  $\beta$ -pinene, the 2 most common  
21 monoterpenes, but not of isoprene and its derivatives. The oxidation of isoprene by hydroxyl  
22 radicals leads to the formation of methyl vinyl ketone and methacrolein (Pandis et al., 1991,  
23 Paulot et al., 2009), which in turn produce tetrols and methylglyceric acid (Claeys et al., 2004;  
24 Surratt et al., 2006; Kleindienst et al., 2009) that are aliphatic compounds. Although oligomer  
25 formation from the oxidation of isoprene has been shown to occur in smog chambers (e.g.,  
26 Sato et al., 2011; Nguyen et al., 2011a, 2011b; Liu et al., 2012a; Tan et al., 2012; Lin et al.,  
27 2014), the oligomer formation process is likely to differ significantly from that from  
28 aromatics as measured by Kalberer et al. (2004) Second, because this kinetic constant only  
29 stands for an average reactivity as Kalberer et al. (2004), during their experiments, could only  
30 observe the fact that 50% of the total organic mass was converted to oligomer-like species.  
31 Such results cannot establish whether all aromatic compounds had undergone oligomerization  
32 following the same pathway or if its evolution was only attributable to a specific set of

1 compounds. Applying this parameterization to a large set of biogenic species may cause an  
2 incorrect assessment of the contribution of oligomers to the total SOA budget.

### 3 **3.1.5 Comparisons of KIN and KPH approaches with measurements**

4 As mentioned above, no direct measurement of the oligomer fraction of SOA is available at  
5 ground based measurement stations. However, we can assess the role of oligomer formation  
6 processes in improving model-measurement comparisons, knowing that the organic fraction  
7 of atmospheric aerosols is usually underestimated by models (Heald et al., 2011). In this  
8 section, we present the comparison of CHIMERE organic carbon (OC) mass concentration in  
9 the PM<sub>10</sub> fraction of aerosols, obtained with 4 different model configurations (REF, KIN and  
10 KPH in both modes) with measurements obtained at two EMEP background sites : the rural  
11 stations of Harwell in the United Kingdom (100km west of London) and Melpitz in Eastern  
12 Germany (150km south of Berlin). Figure 10 presents these comparisons for the period July  
13 20<sup>th</sup> - August 3<sup>rd</sup> 2006, the statistical data (mean bias (MB), normalized mean bias (NMB),  
14 root mean square error (RMSE), normalized root mean square error (NRMSE) and correlation  
15 coefficient (R)) being given in Table 2.

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

29 The pH-dependent approaches have shown to cause a fast and intense production of oligomers  
30 that may induce such a short-time variability in the SOA fraction of the aerosol. Here, though,  
31 there is no quantitative impact of this process on the OC mass concentration level all along  
32 the period, whatever the site. Such results could be expected in the deliquescent configuration,

1 since we concluded that the simulated relative humidity was too low to permit the transport of  
2 oligomers over long distances. But it appears that the metastable mode, which promotes  
3 oligomer persistence and its transport in the atmosphere, also doesn't significantly impact the  
4 organic carbon concentration at those sites. One possible explanation for this lack of effects is  
5 the non-inclusion of isoprene as an oligomer precursor in the KPH simulations, especially  
6 because the analysis of the model output reveals that 60 to 70% of KIN oligomers derived  
7 from isoprene at both stations. However, the conditions in which the KPH simulation was  
8 launched, and mainly the  $K_H$  value used for the BiA0D species in conjunction with the  
9 variability of the aerosol pH, could also account for the low production of oligomers in  
10 remote continental areas of Europe.

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

### 13 **3.2 Sensitivity to the $K_H$ value**

14 From the model results presented in figures 4 to 7, we found that the amplitude of oligomer  
15 formation was potentially strongly dependent on the reference  $K_H$  value of BiA0D, whatever  
16 approach is taken. Yet, the solubility of Bia0D has to be considered as an uncertain  
17 parameter. First because Bia0D accounts for 11 monoterpenes oxidation products, which  
18 partition differently and may be poorly approximated via a unique  $K_H$  value. Second, because  
19 it is recognized that, regardless of the group contribution approach used, uncertainties in the  
20 estimation of  $K_H$  grow when solubility exceeds  $10^4 \text{ Matm}^{-1}$ , due to a lack of experimental  
21 measurements (Raventos et al., 2010). This is an important issue as all the 11 species  
22 represented by pinonaldehyde all have a solubility greater than that of pinonaldehyde itself  
23 ( $K_H=4.97 \times 10^4 \text{ Matm}^{-1}$ ). This is notably the case of hydroxypinonaldehyde  
24 ( $K_H=3.26 \times 10^7 \text{ Matm}^{-1}$ ), ketolimonoaldehyde ( $K_H = 1.7 \times 10^8 \text{ Matm}^{-1}$ ) or 2-hydroxy-3-iso-  
25 propyl-6-oxo-heptanal ( $K_H=2.5 \times 10^6 \text{ Matm}^{-1}$ ). Consequently, it appears warranted to consider  
26 the possibility for the BiA0D Henry's law constant to vary by several orders of magnitude.  
27 Thus, in order to evaluate the robustness of each approach to this input parameter, sensitivity  
28 tests to the solubility of the BiA0D species were conducted with CHIMERE.

#### 29 **3.2.1 Influence on the surrogate partitioning properties**

30 In view of surrogate properties presented in Figure 3a, our sensitivity study focused on the  
31 transition area, that is the  $4 \times 10^8 - 4 \times 10^9 \text{ Matm}^{-1}$  range of  $K_H$ , which allows accounting for the

1 solubility of all the potential oxidation products mentioned before, while providing estimates  
2 of the impact of correcting the global BiA0D  $K_H$  value. In this range, we considered 3 specific  
3  $K_H$  values for BiA0D ( $4.97 \times 10^4$ ,  $4 \times 10^8$  and  $4 \times 10^9 \text{ Matm}^{-1}$ ). Before conducting the sensitivity  
4 tests in CHIMERE, we evaluated the influence of  $K_H$  on the partitioning coefficient of  
5 BiA0D, using the same graphs as in section 2, over the whole range of possible pH values and  
6 with a liquid water content of  $10^{-11} \text{ cm}^3 \text{ water cm}^{-3}$ . The results are presented in Figure 11.  
7 The reference value ( $K_H = 4.97 \times 10^4 \text{ Matm}^{-1}$ , black curve of Figure 11) corresponds to the left  
8 part of Figure 3a, that is a quite null value of the partitioning coefficient. Here, we can see that  
9 only an acidic aqueous phase ( $\text{pH} < 4$ ) allows the quantitative formation of oligomers. When  
10 increasing  $K_H$  to a value in the  $4 \times 10^8$  to  $4 \times 10^9 \text{ Matm}^{-1}$  range, we enter the second area of  
11 Figure 3a, where the particulate fraction of BiA0D becomes significant for a LWC of  
12  $10^{-11} \text{ cm}^3 \text{ water cm}^{-3}$ ). There, a significant formation of SOA takes place from neutral  
13 conditions with 10% to 52% of BiA0D being in the condensed phase, depending on the  $K_H$   
14 value. For a pH of 5, particulate fraction reaches 48% and 90% in favor of the aerosol phase,  
15 for  $K_H = 4 \times 10^8 \text{ Matm}^{-1}$  and  $4 \times 10^9 \text{ Matm}^{-1}$  respectively. However, in this transition area, the  
16 partition of the surrogate species remains strongly influenced by the liquid water content.  
17 Such results underline the threshold condensation phenomenon for this range of  $K_H$  values.  
18 Also, such a sensitivity of BiA0D solubility to the  $K_H$  value may have important  
19 consequences for the results of the KPH approach (whatever the mode considered). Indeed,  
20 considering the highest  $K_H$  value instead of the standard one, at  $\text{pH} = 6$ , in the reference  
21 simulations, causes the reference particulate fraction of BiA0D to increase from 0 to 52%  
22 (with  $\text{LWC} = 10^{-11} \text{ cm}^3 \text{ water cm}^{-3}$ ). The impact of implementing a pH-dependent approach  
23 will thus be lower and the resulting speciation of the OA material will show a much lesser  
24 proportion of oligomers.

### 25 **3.2.2 Impact on the simulated oligomer concentration fields**

26 The sensitivity tests were launched with CHIMERE in the reference, KIN and KPH  
27 configurations (in both deliquescent and metastable modes) using each time a different  $K_H$   
28 value, as mentioned in the previous section. The average simulated oligomer concentrations  
29 fields are shown in Figure 12 for the KIN (left), KPH deliquescent (center) and KPH  
30 metastable (right) approaches.

31 In the KIN approach, we observe that an increase in the value of the Henry's law constant  
32 value (from top to bottom, left column) induces an increase in average simulated oligomer

1 concentrations, due to the low solubility of the BiA0D species in the standard configuration,  
2 which was identified as a limiting parameter for the kinetic production of oligomer in the  
3 condensed phase. However, this dependency is non linear. The increase of  $K_H$  by almost 4  
4 orders of magnitude (from  $4.97 \times 10^4$  to  $4 \times 10^8 \text{ M atm}^{-1}$ ) induces approximately the same  
5 response as a further increase by one order of magnitude (from  $4 \times 10^8$  to  $4 \times 10^9 \text{ M atm}^{-1}$ ),  
6 that is,  $+0.1$  to  $+0.2 \mu\text{g m}^{-3}$  over Italy and the Adriatic Sea in each case. Clearly, there is a low  
7 effect of  $K_H$  variability under a threshold located around  $10^8$ - $10^9 \text{ M atm}^{-1}$  in the simulated  
8 atmospheric conditions

9 The interpretation of the model behavior is more complex in the KPH configuration. As stated  
10 above, the KPH parameterization affects the partition between the gas and particulate phases,  
11 and oligomer concentrations are accounted for by an increment in the quantities of the  
12 condensed surrogate BiA0D. For the deliquescent mode, when  $K_H$  is set to  $4 \times 10^8 \text{ Matm}^{-1}$   
13 (Figure 12e), oligomer concentrations increase over continental areas by  $0.1$  to  $0.2 \mu\text{g m}^{-3}$  on  
14 the average, compared with the simulation using the standard  $K_H$  value (figure 12b). Indeed,  
15 as the solubility of Bia0D becomes higher, the decrease in pH required to form particulate  
16 material is reduced. Thus, even for pH values around 4-5, the partitioning of BiA0D towards  
17 the aerosol phase is favored. In this configuration, the oligomer maxima are located over the  
18 continent and not over the Adriatic, which means that the spatial and temporal evolution of  
19 SOA is substantially modified by the choice of the default  $K_H$  value. When shifting again the  
20  $K_H$  value by one order of magnitude ( $4 \times 10^9 \text{ Matm}^{-1}$ ; Figure 12h), we observe a decrease in the  
21 oligomer concentrations compared with Figure 12e. This result illustrates the fact that, in this  
22 configuration, the default BiA0D partition is much in favor of the particulate phase, and that  
23 there is no significant effect of further increasing the  $K_H$  value through Equation (1).  
24 However, in these 3 simulations, the total SOA mass from hydrophilic biogenic species (not  
25 shown, corresponding to pBiA0D dissolved by default + the incremental fraction due to the  
26 effect of Equation (1) on  $K_H$ ) increases from the low to the high  $K_H$  value scenario. As regards  
27 the metastable mode, the absolute increase in the oligomer concentration due to acidity is  
28 significantly higher than in the deliquescent mode (see the concentration scale) due to the fact  
29 that, in this configuration, there is no parameter (such as RH) able to set back to zero the  
30 quantity of oligomer present in the condensed phase. There, as for the deliquescent mode, the  
31 spatial and temporal features of oligomer production are profoundly altered by the assignment  
32 of the BiA0D  $K_H$  value. Knowing the complex composition of this surrogate species, it is a  
33 major difficulty in the implementation of the KPH approach.



1 Finally, whatever the choice of BiA0D solubility, the location and the spatial extent of  
2 oligomer formation remain different in the 3 configurations of CHIMERE. While the kinetic  
3 production of oligomer species leads to a diffuse plume with maximum values in the  
4 Mediterranean and over Southern Europe, while the highest concentrations are observed over  
5 forested areas of central Europe - thus closer to biogenic sources - in the KPH approaches  
6 where instantaneous oligomer production is simulated. This result draws our attention to the  
7 impact of the oligomer formation rate on the distribution of SOA in continental plumes,  
8 especially considering the diversity of relevant SOA precursors in the BiA0D species. Finally,  
9 it is worth noting however that the high  $K_H$  scenario of the metastable KPH mode makes little  
10 sense, as the KPH approach is based on the possibility for OA formation to depend on the  
11 specificities of the aerosol aqueous phase, which is no longer the case in figure 12e and 12h.

## 12 **4 Discussions and Conclusions**

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

### 17 **4.1 Oligomer formation from isoprene**

18 First of all, the fate of isoprene in the condensed phase shall be examined, as isoprene has  
19 been recognized as a major SOA precursor through its first generation products methacrolein  
20 (MACR) and methyl vinyl ketone (MVK) (Pandis et al., 1991; Carlton et al., 2009), which  
21 were found to be important oligomer precursors in the condensed phase (El Haddad et al.,  
22 2009; Liu et al., 2012b, Renard et al., 2013). On this specific point, the study of Renard et al.  
23 (2015) based on the photooxidation of MVK into a photoreactor revealed that considering  
24 only a first-order rate constant to represent the formation of oligomers is not appropriate, as  
25 the oxidation of MVK by OH was (in the condensed phase of the deliquescent aerosol)  
26 governed by a kinetic competition between functionalization and oligomerization, which  
27 depends on the precursor initial concentration. Furthermore, the branching ratio in favor of  
28 highly oxidized monomers seems to be more important in the condensed phase than in the gas  
29 phase (Kroll and Seinfeld, 2008), thus favoring the formation of a stable OA. A multiphase  
30 box model study conducted by Ervens et al. (2015) based on the laboratory experiments of  
31 Renard et al. (2015) underlined a potential key role of the MVK-to-oxygen concentration ratio  
32 in the oligomerization rate under atmospherically relevant conditions. Thus, in the case of

1 isoprene, the formation of oligomers via the oxidation by  $\text{OH}_{(\text{aq})}$  in the condensed phase may  
2 well be represented by a kinetic approach based on a second-order rate constant. The authors  
3 propose a  $k_{\text{oligo}}$  of  $2.50 \times 10^{-12} \text{ molec cm}^{-3} \text{ s}^{-1}$  for the single oxidation reaction of MVK and  
4 MACR by  $\text{OH}_{\text{aq}}$ , but they recommend being cautious with this value as the kinetics may differ  
5 within the variety of atmospheric conditions (LWC,  $\text{OH}_{(\text{aq})}$ , MACR, MVK concentrations...).

## 6 **4.2 Further developments for oligomer formation dynamics**

7 On a broader level, the difficulty of restituting faithfully oligomer yields and SOA formation  
8 dynamics comes from the diversity of the phenomena that drive SOA formation in the  
9 atmosphere. It is indeed clear now that oligomerization processes, which may produce up to  
10 50% of SOA on the average, rely on both the volatility of the multiple SVOCs and their  
11 reactivity in the condensed phase, which is controlled by a series of oxidation, association and  
12 fragmentation reactions that can be kinetically described.

13 One important issue is thus our ability to describe in an appropriate manner the variety of  
14 SVOC behaviors in the gas and condensed phase in an AQM. As for  $K_{\text{H}}$  values, we have  
15 discussed the fact that the representation of SVOC partitioning in models for now is not  
16 highly accurate. Most 3D models indeed use one single  $K_{\text{H}}$  value to account for the behavior  
17 of a complex mixture of SOA precursors, and this format clearly prevents the model to  
18 reconstitute the full diversity of the gas/particle partitioning of individual compounds in time and  
19 space. This is all the more important because the results we obtained with CHIMERE showed  
20 that oligomer concentrations present a considerable sensitivity to the  $K_{\text{H}}$  value selected for the  
21 biogenic surrogate species that produces SOA. Similarly, when simulating chemistry in the  
22 aerosol phase, the allocation of distinct kinetic constant values for the reactivity of the  
23 condensed oligomer precursors would be valuable. Kalberer et al. (2006) effectively observed  
24 disparities in the temporal evolution of the aerosol molar mass while studying the oxidation of  
25 trimethylbenzene,  $\alpha$ -pinene and isoprene. Taking this into account would probably have  
26 increased the OC short-time variability of the KIN method. However, increasing the degree of  
27 refinement of a modeling approach through a differentiation of individual behaviors is not  
28 always a good solution. The more refined the scheme becomes, the more difficult it is to  
29 collect the details about organic compound reactivity, making it difficult to set up the  
30 approach in a 3D model. As an example, the KPH approach proposes to consider the specific  
31 formation of oligomers from the polymerization of aldehydes only, that may happen through  
32 diverse acid-catalyzed reactions. Although it is evident that the consideration of only one

1 single polymerization pathway constitutes a limitation for the quantitative simulation of SOA  
2 production from ambient organic precursors, this hypothesis has the advantage of proposing a  
3 well-identified process which can be adjusted in the model in terms of intensity, and upon the  
4 environmental conditions, from experimental knowledge about this reaction. However, in this  
5 approach, isoprene oxidation products (ISOPA) could not be considered as oligomer  
6 precursors, due to the fact that the KPH approach is only applicable to aldehydes and that  
7 there is no detail about the structural properties of the ISOPA surrogate species in the current  
8 CHIMERE chemical scheme. Including all or part of this species in the oligomerization  
9 process would thus have introduced an indeterminate uncertainty in our simulations. The  
10 outcome of this is a severe underestimation of the modeled OC compared with Harwell and  
11 Melptiz observation, that was – at least partly – attributed to the non inclusion of isoprene in  
12 oligomer precursors when running CHIMERE with the KPH configuration. Similarly, we  
13 have seen that the dependence of the model results upon (i) the state (deliquescent or  
14 metastable) of the aerosol, and (ii) its inorganic composition and pH, constitute a key  
15 challenge for the implementation of the KPH approach. In this respect, there is a necessity to  
16 define a parameterization focusing on the restitution of a unique parameter (such as the  
17 dynamics of global SOA yields), and relying on an irreducible set of parameters and  
18 processes, provided that it allows the model to perform satisfactorily with regard to existing  
19 measurements. For this purpose, *in situ* atmospheric oligomer measurements conducted at  
20 various distances from the sources would be absolutely necessary to assign a representative  
21 average value for the  $K_H$  of the SVOC surrogate species - as our results showed that the rate  
22 and intensity of the SVOC transfer to the aerosol phase give the SOA plumes their shapes.

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

32 How can we improve the representation of oligomer stability in the modeling approaches  
33 investigated here? The literature does not give a straightforward answer to the question of

1 oligomerization reversibility. Several observations and experiments reported in the literature  
2 point to the irreversibility – at least partial – of the oligomerization process. According to a  
3 recent study of Liu et al., (2012b), the formation of oligomers from methacrolein and methyl  
4 vinyl ketone (isoprene oxidation products) is irreversible. This assumption is supported by the  
5 recent works of Hall and Johnston (2012a) who investigated the thermal stability of a SOA  
6 matrix including 50% of oligomeric species formed by the ozonolysis of  $\alpha$ -pinene: the authors  
7 concluded that, at ambient temperatures, oligomeric species should be nonvolatile by  
8 structure. However, Trump and Donahue (2014) report discording results about SOA mass  
9 yields in these experiments, that point to an oligomerization process that would be reversible  
10 under specific conditions (dilution, temperature), which is probably a good compromise in the  
11 interpretation of all laboratory experiments.

12 Considering these elements, the kinetic approach that represents oligomer formation as the  
13 only possible fate for the relevant condensed organics may lead to a significant overestimation  
14 of the oligomer fraction in the aerosol. Thus, it should at least take into account a possible loss  
15 of SOA by evaporation, due notably to fragmentation processes (Renard et al., 2015). Indeed,  
16 organic compounds in the particulate phase have shown to be submitted to a variety of non-  
17 oxidative and oxidative reactions leading to the formation of both semi-volatile and non-  
18 volatile compounds, depending on their final molecular weight (Kroll and Seinfeld, 2008;  
19 Kroll et al., 2009). Furthermore, the absence of reversibility in the kinetic approach makes it  
20 little adaptable to laboratory observations such as the evaporation of SOA from  $\alpha$ -pinene on  
21 the scale of a few hours (Grieshop et al., 2007). On the reverse, the high SOA mass yields  
22 obtained from the oxidation of biogenics SVOCs cannot be reproduced using the KPH-  
23 deliquescent approach, as SOA formed this way is permanently released due to aerosol water  
24 evaporation or pH increase. Whatever the model configuration, our works have shown that the  
25 oligomerization reversibility proposed by the KPH approach was difficult to set-up and  
26 control in an AQM. Therefore, considering (i) the laboratory experiments conducted by Hall  
27 and Johnson (2012b) on the ozonolysis of  $\alpha$ -pinene, which indicated that oligomer formation  
28 would be driven by reactive uptake rather than by the partition of monomers between both  
29 phases and (ii) the fact that this reactive uptake may be observed within seconds (Heaton et  
30 al., 2007; Hall and Johnson, 2012b), it appears more realistic to propose a representation of  
31 the oligomerization process in two stages: a first fast step modifying directly the monomer  
32 partitioning so as to represent the rapid formation of oligomers (not permitted by the KIN  
33 approach only), and a stabilization step consisting of a kinetic uptake of the OA previously

1 formed (not adjustable in a KPH approach). Trump and Donahue (2014) have recently  
2 proposed a comprehensive but simplified vision of reversible oligomerization that effectively  
3 combines a partitioning equilibrium and a condensed-phase kinetic reactivity, and that clearly  
4 addresses the issue of reversibility. This vision was built from the VBS approach, a modeling  
5 technique relying on SVOC volatility bins rather than on identified chemical species to  
6 represent the progressive formation of SOA from gaseous organic compounds upon  
7 atmospheric oxidation processes (Robinson et al., 2007). The works of Trump and Donahue  
8 propose a detailed analysis of an expanded VBS version taking into account oligomer  
9 formation dynamics in a quite similar way as here: namely, the description of the equilibrium  
10 phase partitioning of various VOC oxidation products from a given volatility bin, and a  
11 kinetic-dependent reactivity in the condensed phase where the association of 2 identical  
12 particulate monomers compete with the dissociation of the dimers thus formed. The ratio of  
13 those two rate constants makes a dimerization formation equilibrium. There, major  
14 simplifying assumptions are made. They mainly stem from the fact that only one single  
15 volatility class of condensed products reacts, and that this class reacts in its entirety -  
16 regardless of the structure of precursors - to form carboxylic acid dimers. Indeed,  
17 representative equilibrium constants for the dimerization reaction were derived from  
18 laboratory works on dicarboxylic acid dimers formation. Finally, it is stressed by the authors  
19 that neither of the simplifications considered in this approach is likely to be realistic, and that  
20 the stated goal of their work is only to identify what type of chemistry this method produces  
21 and how it helps understanding/representing oligomers in the atmosphere. Despite such  
22 simplifications, the authors show that their approach allows restituting experimental SOA  
23 yields for different initial OA conditions, as well as SOA formation dynamics. A particularly  
24 interesting result of this approach is the simulation of a two-stage SOA evaporation  
25 (monomers evaporate rapidly upon dilution while only a modest drop in oligomer  
26 concentration is simulated due to the equilibrium dynamics) that may help reproducing recent  
27 observations of delayed SOA evaporation. Through sensitivity tests to the condensed phase  
28 reactivity kinetics, this approach also outlines that an irreversible oligomerization process  
29 (high dimerization to evaporation kinetic ratio) would definitely appears incompatible with  
30 the observed SOA mass-yield behaviors.

31 As for conventional modeling approaches relying on molecule structural properties, and based  
32 on these findings, a KPH-like approach considering a further reactive uptake - with partial  
33 reversibility or fragmentation so as to fit the observations about the hysteresis of SOA

1 formation and evaporation - could be a suitable parameterization to represent the formation of  
2 oligomers from monoterpenes. Even so, the determination of the aerosol mode  
3 (deliquescent/metastable) is not an obvious choice. Although Fountoukis et al. (2009)  
4 concluded from plume studies that organics could promote thermodynamically stable water  
5 down to very low RH, Moya et al. (2002) have shown that considering a metastable mode for  
6  $PM_{10}$  (where organic matter is predominantly present) leads, under low relative humidity  
7 conditions (<60%), to significant errors in the concentrations of the inorganic species which  
8 indirectly determine the aerosol pH and thus oligomers formation. Similarly, Mikhailov et al.  
9 (2013) found – from the analysis of atmospheric aerosols – that under a RH level of about  
10 70%, organic species may not be completely dissolved in the aqueous phase and may also  
11 coexist in a solid aerosol phase. These studies both conclude to the importance of considering  
12 a deliquescent mode for low relative humidity conditions.

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

## 21 **Acknowledgements**

22 This work was supported by the French national program PRIMEQUAL in the frame of the  
23 OLD-AIR project. The authors acknowledge the EBAS data providers and owners for the  
24 aerosol measurements at EMEP sites.

## 1 **References**

- 2 Aksoyoglu, S., Keller, J., Barmpadimos, I., Oderbolz, D., Lanz, V.A., Prevot, A.S.H.,  
3 Baltensperger, U.: Aerosol modelling in Europe with a focus on Switzerland during summer  
4 and winter episodes, *Atmos. Chem. Phys.*, 11, 7355-7373, doi: 10.5194/acp-11-7355-2011,  
5 2011
- 6 Bessagnet, B., Hodzic, A., Vautard, R., Beekmann, M., Cheinet, S., Honore, C., Liousse, C.,  
7 Rouil, L.: Aerosol modeling with CHIMERE - preliminary evaluation at the continental scale,  
8 *Atmospheric Environment*, 38, 2803-2817, doi: 10.1016/j.atmosenv.2004.02.034, 2004
- 9 Bessagnet, B., Menut, L., Curci, G., Hodzic, A., Guillaume, B., Liousse, C., Moukhtar, S.,  
10 Pun, B., Seigneur, C., Schulz, M.: Regional modeling of carbonaceous aerosols over Europe-  
11 focus on secondary organic aerosols, *Journal of Atmospheric Chemistry*, 61, 175-202, doi:  
12 10.1007/s10874-009-9129-2, 2008
- 13 Bessagnet, B., Menut, L., Curci, G., Hodzic, A., Guillaume, B., Liousse, C., Moukhtar, S.,  
14 Pun, B., Seigneur, C., Schulz, M.: Regional modeling of carbonaceous aerosols over Europe-  
15 focus on secondary organic aerosols, *Journal of Atmospheric Chemistry*, 61, 175-202, 2009
- 16 Carlton, A.G., Turpin, B.J., Altieri, K.E., Seitzinger, S.P., Mathur, R., Roselle, S.J., Weber,  
17 R.J.: CMAQ Model Performance Enhanced When In-Cloud Secondary Organic Aerosol is  
18 Included: Comparisons of Organic Carbon Predictions with Measurements, *Environmental*  
19 *Science & Technology*, 42, 8798-8802, doi: 10.1021/es801192n, 2008
- 20 Carlton, A.G., Wiedinmyer, C., Kroll, J.H.: A review of Secondary Organic Aerosol (SOA)  
21 formation from isoprene, *Atmos. Chem. Phys.*, 9, 4987-5005, 2009
- 22 Carlton, A.G., Bhave, P.V., Napelenok, S.L., Edney, E.D., Sarwar, G., Pinder, R.W., Pouliot,  
23 G.A., Houyoux, M.: Model Representation of Secondary Organic Aerosol in CMAQv4.7,  
24 *Environmental Science & Technology*, 44, 8553-8560, doi: 10.1021/es100636q, 2010
- 25 Carter, W.P.L.: A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic-  
26 Compounds, *Atmospheric Environment Part a-General Topics*, 24, 481-518, doi:  
27 10.1016/0960-1686(90)90005-8, 1990
- 28 Couvidat, F., Seigneur, C.: Modeling secondary organic aerosol formation from isoprene  
29 oxidation under dry and humid conditions, *Atmos. Chem. Phys.*, 11, 893-909, 2011

1 Couvidat, F., Debry, E., Sartelet, K., Seigneur, C. : A hydrophilic/hydrophobic organic (H<sup>2</sup>O)  
2 aerosol model : Developmentn evaluation and sensitivity analysis, Journal of Geophysical  
3 Research, 117, doi:10.1029/2011JD017214, 2012

4 Couvidat, F., Sartelet, K., The Secondary Organic Aerosol Processor (SOAP v1.0) model: a  
5 unified model with different ranges of complexity based on the molecular surrogate approach.  
6 Geosci. Model Dev., 8, 1111-1138, 2015.

7 Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J.,  
8 Guyon, P., Andreae, M.O., Artaxo, P., Maenhaut, W.: Formation of Secondary Organic  
9 Aerosol Through Photooxidation of Isoprene, Science, 2004

10 Donahue, N.M., Robinson, A.L., Pandis, S.N.: Atmospheric organic particulate matter: From  
11 smoke to secondary organic aerosol, Atmospheric Environment, 43, 94-106, 2009

12 Dudhia, J.: A nonhydrostatic Version of the Penn State-NCAR Mesoscale Model: Validation  
13 Tests and Simulation of an Atlantic Cyclone and Cold Front, Monthly Weather Review, 1993

14 El Haddad, I., Yao, L., Nieto-Gligorovski, L., Michaud, V., Temime-Roussel, B., Quivet, E.,  
15 Marchand, N., Sellegri, K., Monod, A.: In-cloud processes of methacrolein under simulated  
16 conditions - Part 2: Formation of secondary organic aerosol, Atmos. Chem. Phys., 9, 5107-  
17 5117, 2009

18 Ervens, B., Turpin, B.J., Weber, R.J.: Secondary organic aerosol formation in cloud droplets  
19 and aqueous particles (aqSOA): a review of laboratory, field and model studies, Atmos.  
20 Chem. Phys., 11, 11069-11102, 2011

21 Ervens, B., Renard, P., Ravier, S., Clément, J.L., Monod, A.: Aqueous phase oligomerization  
22 of methyl vinyl ketone through photooxidation - Part 2: Development of the chemical  
23 mechanism and atmospheric implications, Atmos. Chem. Phys., 15, 9109-9127, 2015

24 Fountoukis, C., Nenes, A., Sullivan, A., Weber, R., Van Reken, T., Fischer, M., Matias, E.,  
25 Moya, M., Farmer, D., Cohen, R.C., Thermodynamic characterization of Mexico City aerosol  
26 during MILAGRO 2006. Atmos. Chem. Phys., 9, 2141-2156, 2009.

27 Fuzzi, S., Andreae, M.O., Huebert, B.J., Kulmala, M., Bond, T.C., Boy, M., Doherty, S.J.,  
28 Guenther, A., Kanakidou, M., Kawamura, K., Kerminen, V.M., Lohmann, U., Russell, L.M.,  
29 Poschl, U.: Critical assessment of the current state of scientific knowledge, terminology, and



1 research needs concerning the role of organic aerosols in the atmosphere, climate, and global  
2 change, *Atmos. Chem. Phys.*, 6, 2017-2038, 2006

3 Gao, S., Ng, N.L., Keywood, M., Varutbangkul, V., Bahreini, R., Nenes, A., He, J.W., Yoo,  
4 K.Y., Beauchamp, J.L., Hodyss, R.P., Flagan, R.C., Seinfeld, J.H.: Particle phase acidity and  
5 oligomer formation in secondary organic aerosol, *Environmental Science & Technology*, 38,  
6 6582-6589, doi: 10.1021/es049125k, 2004

7 Gelbard, F., Seinfeld, J.H.: Simulation of Multicomponent Aerosol Dynamics, *Journal of*  
8 *Colloid and Interface Science*, 78, 485-501, doi: 10.1016/0021-9797(80)90587-1, 1980

9 Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.I., Geron, C.: Estimates of  
10 global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and  
11 Aerosols from Nature), *Atmos. Chem. Phys.*, 6, 3181-3210, 2006

12 Hall, W.A., Johnston, M.V.: Oligomer Content of  $\alpha$ -Pinene Secondary Organic Aerosol,  
13 *Aerosol Science and Technology*, 45, 37-45, 2011

14 Hall, W.A., Johnston, M.V.: The Thermal-Stability of Oligomers in Alpha-Pinene Secondary  
15 Organic Aerosol, *Aerosol Science and Technology*, 46, 983-989, 2012a

16 Hall, W.I.V., Johnston, M.: Oligomer Formation Pathways in Secondary Organic Aerosol  
17 from MS and MS/MS Measurements with High Mass Accuracy and Resolving Power,  
18 *Journal of The American Society for Mass Spectrometry*, 23, 1097-1108, 2012b

19 Hauglustaine, D., Hourdin, F., Jourdain, L., Filiberti, M.-A., Walters, S., Lamarque, J.-F.,  
20 Holland, E. : Interactive chemistry in the Laboratoire de Météorologie Dynamique general  
21 circulation model : Description and background tropospheric chemistry evaluation, *Journal of*  
22 *Geophysical Research-Atmospheres*, 2004

23 Heald, C.L., Coe, H., Jimenez, J.L., Weber, R.J., Bahreini, R., Middlebrook, A.M., Russell,  
24 L.M., Jolleys, M., Fu, T.-M., Allan, J.D., Bower, K.N., Capes, G., Crosier, J., Morgan, W.T.,  
25 Robinson, N.H., Williams, P.L., Cubison, M.J., DeCarlo, P.F., Dunlea, E.J. : Exploring the  
26 vertical profile of atmospheric organic aerosol: comparing 17 aircraft field campaigns with a  
27 global model, *Atmos. Chem. Phys.*, 11, 12673-12696, 2011

28

1 Hennigan, C.J., Izumi J., Sullivan, A.P., Weber, R.J., Nenes, A. : A critical evaluation of  
2 proxy methods used to estimate the acidity of atmospheric particles, *Atmos. Chem. Phys.*, 15,  
3 2775-2790, 2015

4 Herrmann, H.: Kinetics of Aqueous Phase Reactions Relevant for Atmospheric Chemistry,  
5 *Chemical Reviews*, 103, 4691-4716, 2003

6 Jang, M.S., Czoschke, N.M., Northcross, A.L.: Semiempirical model for organic aerosol  
7 growth by acid-catalyzed heterogeneous reactions of organic carbonyls, *Environmental*  
8 *Science & Technology*, 39, 164-174, doi: 10.1021/es048977h, 2005

9 Jimenez, J.L., Canagaratna, M.R., Donahue, N.M., Prevot, A.S.H., Zhang, Q., Kroll, J.H.,  
10 DeCarlo, P.F., Allan, J.D., Coe, H., Ng, N.L., Aiken, A.C., Docherty, K.S., Ulbrich, I.M.,  
11 Grieshop, A.P., Robinson, A.L., Duplissy, J., Smith, J.D., Wilson, K.R., Lanz, V.A., Hueglin,  
12 C., Sun, Y.L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn,  
13 M., Kulmala, M., Tomlinson, J.M., Collins, D.R., Cubison, M.J., Dunlea, E.J., Huffman, J.A.,  
14 Onasch, T.B., Alfarra, M.R., Williams, P.I., Bower, K., Kondo, Y., Schneider, J., Drewnick,  
15 F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami,  
16 A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J.Y., Zhang, Y.M., Dzepina, K., Kimmel,  
17 J.R., Sueper, D., Jayne, J.T., Herndon, S.C., Trimborn, A.M., Williams, L.R., Wood, E.C.,  
18 Middlebrook, A.M., Kolb, C.E., Baltensperger, U., Worsnop, D.R.: Evolution of Organic  
19 Aerosols in the Atmosphere, *Science*, 326, 1525-1529, doi: 10.1126/science.1180353, 2009

20 Grieshop, A.P., Donahue, N.M., Robinson, A.L.: Is the gas-particle partitioning in alpha-  
21 pinene secondary organic aerosol reversible?, *Geophysical Research Letters*, 34, L14810,  
22 doi:10.1029/2007g1029987, 2007

23 Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A.S.H., Fisseha, R.,  
24 Weingartner, E., Frankevich, V., Zenobi, R., Baltensperger, U.: Identification of polymers as  
25 major components of atmospheric organic aerosols, *Science*, 303, 1659-1662, doi:  
26 10.1126/science.1092185, 2004

27 Kalberer, M., Sax, M., Samburova, V.: Molecular Size Evolution of Oligomers in Organic  
28 Aerosols Collected in Urban Atmospheres and Generated in a Smog Chamber, *Environmental*  
29 *Science & Technology*, 40, 5917-5922, 2006

1 Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van  
2 Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y.,  
3 Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati,  
4 E., Stephanou, E.G., Wilson, J.: Organic aerosol and global climate modelling: a review,  
5 *Atmos. Chem. Phys.*, 5, 1053-1123, 2005

6 Keene, W.C., Pszenny, A.A.P., Maben, J.R., Stevenson, E., Wall, A.C.D.: Closure evaluation  
7 of size-resolved aerosol pH in the New England coastal atmosphere during summer, *Journal*  
8 *of Geophysical Research: Atmospheres*, 109, 2004

9 Kroll, J.H., Ng, N.L., Murphy, S.M., Flagan, R.C., Seinfeld, J.H.: Secondary Organic Aerosol  
10 Formation from Isoprene Photooxidation, *Environmental Science & Technology*, 40, 1869-  
11 1877, 2006

12 Kroll, J.H., Seinfeld, J.H.: Chemistry of secondary organic aerosol: Formation and evolution  
13 of low-volatility organics in the atmosphere, *Atmospheric Environment*, 42, 3593-3624, doi:  
14 10.1016/j.atmosenv.2008.01.003, 2008

15 Kroll, J.H., Smith, J.D., Che, D.L., Kessler, S.H., Worsnop, D.R., Wilson, K.R.: Measurement  
16 of fragmentation and functionalization pathways in the heterogeneous oxidation of oxidized  
17 organic aerosol, *Physical Chemistry Chemical Physics*, 11, 8005-8014, 2009

18 Kulmala, M., Laaksonen, A., Pirjola, L.: Parameterizations for sulfuric acid/water nucleation  
19 rates, *Journal of Geophysical Research-Atmospheres*, 103, 8301-8307, doi:  
20 10.1029/97jd03718, 1998

21 Lin, Y.-H., Budisulistiorini, S. H., Chu, K., Siejack, R. A., Zhang, H., Riva, M., Zhang, Z.,  
22 Gold, A., Kautzman, K. E., Surratt, J. D.: Light-absorbing oligomer formation in secondary  
23 organic aerosol from reactive uptake of isoprene epoxydiols, *Environmental Science &*  
24 *Technology*, 48, 12012-12021, 2014

25 Liu, Y., Monod, A., Tritscher, T., Praplan, A.P., DeCarlo, P.F., Temime-Roussel, B., Quivet,  
26 E., Marchand, N., Dommen, J., Baltensperger, U.: Aqueous phase processing of secondary  
27 organic aerosol from isoprene photooxidation, *Atmos. Chem. Phys.*, 12, 5879-5895, 2012b

28 Liu, Y., Siekmann, F., Renard, P., El Zein, A., Salque, G., El Haddad, I., Temime-Roussel,  
29 B., Voisin, D., Thissen, R., Monod, A.: Oligomer and SOA formation through aqueous phase

1 photooxidation of methacrolein and methyl vinyl ketone, *Atmospheric Environment*, 49, 123-  
2 129, 2012b

3 Ludwig, J., Klemm, O.: Acidity of Size-Fractionated Aerosol-Particles, *Water Air and Soil*  
4 *Pollution*, 49, 35-50, doi: 10.1007/bf00279508, 1990

5 Menut, L., Bessagnet, B., Khvorostyanov, D., Beekmann, M., Blond, N., Colette, A., Coll, I.,  
6 Curci, G., Foret, G., Hodzic, A., Mailler, S., Meleux, F., Monge, J.L., Pison, I., Siour, G.,  
7 Turquety, S., Valari, M., Vautard, R., Vivanco, M.G.: CHIMERE 2013: a model for regional  
8 atmospheric composition modelling, *Geosci. Model Dev.*, 6, 981-1028, 2013

9 Molnar, A., Meszaros, E.: On the relation between the size and chemical composition of  
10 aerosol particles and their optical properties, *Atmospheric Environment*, 35, 5053-5058, doi:  
11 10.1016/s1352-2310(01)00314-4, 2001

12 Moya, M., Pandis, S.N., Jacobson, M.Z., Is the size distribution of urban aerosols determined  
13 by thermodynamic equilibrium? : An application to Southern California. *Atmospheric*  
14 *Environment*, 36, 2349-2365, 2002.

15 Mouchel-Vallon, C., Brauer, P., Camredon, M., Valorso, R., Madronich, S., Herrmann, H.,  
16 Aumont, B.: Explicit modeling of volatile organic compounds partitioning in the atmospheric  
17 aqueous phase, *Atmos. Chem. Phys.*, 13, 1023-1037, doi: 10.5194/acp-13-1023-2013, 2013

18 Nenes, A., Pandis, S.N., Pilinis, C.: ISORROPIA: A new thermodynamic equilibrium model  
19 for multiphase multicomponent inorganic aerosols, *Aquatic Geochemistry*, 4, 123-152, doi:  
20 10.1023/a:1009604003981, 1998

21 Nguyen, T.B., Roach, P.J., Laskin, J., Laskin, A., Nizkorodov, S.A.: Effect of humidity on the  
22 composition of isoprene photooxidation secondary organic aerosol, *Atmos. Chem. Phys.*, 11,  
23 6931-6944, 2011a

24 Nguyen, T.B., Laskin, J., Laskin, A., Nizkorodov, S.A.: Nitrogen-containing organic  
25 compounds and oligomers in secondary organic aerosol formed by photooxidation of  
26 isoprene, *Environmental Science & Technology*, 45, 6908-6918, 2011b

27 Ovadnevaite, J., O'Dowd, C., Dall'Osto, M., Ceburnis, D.: Detecting high contributions of  
28 primary organic matter to marine aerosol: A case study, *Geophysical Research Letters*, doi:  
29 10.1029/2010GL046083, 2011

1 Pandis, S.N., Paulson, S.E., Seinfeld, J.H., Flagan, R.C.: Aerosol formation in the  
2 photooxidation of isoprene and  $\beta$ -pinene, *Atmospheric Environment. Part A. General Topics*,  
3 25, 997-1008, 1991

4 Pankow, J.F.: An Absorption-Model of Gas-Particle Partitioning of Organic-Compounds in  
5 the Atmosphere, *Atmospheric Environment*, 28, 185-188, doi: 10.1016/1352-2310(94)90093-  
6 0, 1994

7 Paredes-Miranda, G., Arnott, W.P., Jimenez, J.L., Aiken, A.C., Gaffney, J.S., Marley, N.A.:  
8 Primary and secondary contributions to aerosol light scattering and absorption in Mexico City  
9 during the MILAGRO 2006 campaign, *Atmos. Chem. Phys.*, 9, 3721-3730, 2009

10 Petetin, H., Beekmann, M., Sciare, J., Bressi, M., Rosso, A., Sanchez, O., Gherzi, V., A novel  
11 model evaluation approach focusing on local and advected contributions to urban PM<sub>2.5</sub>  
12 levels - application to Paris, France. *Geosci. Model Dev.*, 7, 1483-1505, 2014.

13 Paulot, F., Crouse, J.D., Kjaergaard, H.G., Kroll, J.H., Seinfeld, J.H., Wennberg, P.O.:  
14 Isoprene photooxidation: new insights into the production of acids and organic nitrates,  
15 *Atmos. Chem. Phys.*, 9, 1479-1501, 2009

16 Pun, B.K., Seigneur, C., Lohman, K.: Modeling secondary organic aerosol formation via  
17 multiphase partitioning with molecular data, *Environmental Science & Technology*, 40, 4722-  
18 4731, doi: 10.1021/es0522736, 2006

19 Pun, B.K., Seigneur, C.: Investigative modeling of new pathways for secondary organic  
20 aerosol formation, *Atmos. Chem. Phys.*, 7, 2199-2216, 2007

21 Pun, B.K.: Development and initial application of the sesquiversion of MADRID, *Journal of*  
22 *Geophysical Research-Atmospheres*, 113, 10, doi: 10.1029/2008jd009888, 2008

23 Raventos-Duran, T., Camredon, M., Valorso, R., Mouchel-Vallon, C., Aumont, B.: Structure-  
24 activity relationships to estimate the effective Henry's law constants of organics of  
25 atmospheric interest, *Atmos. Chem. Phys.*, 10, 7643-7654, doi: 10.5194/acp-10-7643-2010,  
26 2010

27 Renard, P., Siekmann, F., Gandolfo, A., Socorro, J., Salque, G., Ravier, S., Quivet, E.,  
28 Clément, J.L., Traikia, M., Delort, A.M., Voisin, D., Vuitton, V., Thissen, R., Monod, A.:  
29 Radical mechanisms of methyl vinyl ketone oligomerization through aqueous phase OH-

1 oxidation: on the paradoxical role of dissolved molecular oxygen, *Atmos. Chem. Phys.*, 13,  
2 6473-6491, 2013

3 Renard, P., Siekmann, F., Salque, G., Demelas, C., Coulomb, B., Vassalo, L., Ravier, S.,  
4 Temime-Roussel, B., Voisin, D., Monod, A.: Aqueous-phase oligomerization of methyl vinyl  
5 ketone through photooxidation - Part 1: Aging processes of oligomers, *Atmos. Chem. Phys.*,  
6 15, 21-35, 2015

7 Robinson, A.L., Donahue, N.M., Shrivastava, M.K., Weitkamp, E.A., Sage, A.M., Grieshop,  
8 A.P., Lane, T.E., Pierce, J.R., Pandis, S.N.: Rethinking Organic Aerosols: Semivolatile  
9 Emissions and Photochemical Aging, *science*, 315, 2007

10 Sato, K., Nakao, S., Clark, C.H., Qi, L., Cocker III, D.R.: Secondary organic aerosol  
11 formation from the photooxidation of isoprene, 1,3-butadiene, and 2,3-dimethyl-1,3-butadiene  
12 under high NO<sub>x</sub> conditions, *Atmos. Chem. Phys.*, 11, 7301-7317, 2011

13 Schmidt, H., Derognat, C., Vautard, R., Beekmann, M.: A comparison of simulated and  
14 observed ozone mixing ratios for the summer of 1998 in Western Europe, *Atmospheric  
15 Environment*, 35, 6277-6297, doi: 10.1016/s1352-2310(01)00451-4, 2001

16 Shrivastava, M., Fast, J., Easter, R., Gustafson Jr, W.I., Zaveri, R.A., Jimenez, J.L., Saide, P.,  
17 Hodzic, A., Modeling organic aerosols in a megacity: comparison of simple and complex  
18 representations of the volatility basis set approach, *Atmos. Chem. Phys.*, 11, 6639-6662,  
19 2011.

20 Stier, P., Seinfeld, J.H., Kinne, S., Boucher, O.: Aerosol absorption and radiative forcing,  
21 *Atmos. Chem. Phys.*, 7, 5237-5261, 2007

22 Suzuki, T., Ohtaguchi, K., Koide, K.: Application of Principal Components-Analysis to  
23 Calculate Henry Constant from Molecular-Structure, *Computers & Chemistry*, 16, 41-52, doi:  
24 10.1016/0097-8485(92)85007-1, 1992

25 Tan, Y., Lim, Y. B., Altieri, K. E., Seitzinger, S. P., Turpin, B. J.: Mechanisms leading to  
26 oligomers and SOA through aqueous photooxidation: insights from OH radical oxidation of  
27 acetic acid and methylglyoxal, *Atmos. Chem. Phys.*, 12, 801-813, 2012

1 Troen, I., Mahrt, L.: A Simple-Model of the Atmospheric Boundary-Layer - Sensitivity to  
2 Surface Evaporation, *Boundary-Layer Meteorology*, 37, 129-148, doi: 10.1007/bf00122760,  
3 1986

4 Trump, E.R., Donahue, N.M., Oligomer formation within secondary organic aerosols:  
5 equilibrium and dynamic considerations. *Atmos. Chem. Phys.*, 14, 3691-3701, 2014.

6 Valorso, R., Aumont, B., Camredon, M., Raventos-Duran, T., Mouchel-Vallon, C., Ng, N.L.,  
7 Seinfeld, J.H., Lee-Taylor, J., Madronich, S.: Explicit modelling of SOA formation from  $\alpha$ -  
8 pinene photooxidation: sensitivity to vapour pressure estimation, *Atmos. Chem. Phys.*, 11,  
9 6895-6910, 2011

10 Verwer, J.G.: Gauss-Seidel Iteration for Stiff ODEs from Chemical Kinetics, *SIAM Journal*  
11 *on Scientific Computing*, 5, 1243-1250, 1994

12 Vestreng, V., Breivik, K., Adams, M., Wagner, A., Goodwin, J., Rozovskiaya, O.,  
13 Pacyna, J.M.: Inventory Review 2005 – Emission Data reported to CLRTAP and under the  
14 NEC Directive – Initial review for HMs and POPs, EMEP/MS-CW, 2005

15 Volkamer, R., Jimenez, J.L., San Martini, F., Dzepina, K., Zhang, Q., Salcedo, D., Molina,  
16 L.T., Worsnop, D.R., Molina, M.J.: Secondary organic aerosol formation from anthropogenic  
17 air pollution: Rapid and higher than expected, *Geophysical Research Letters*, 33, 4, doi:  
18 10.1029/2006gl026899, 2006

19 Wang, C., Goss, K.-U., Lei, Y.D., Abbatt, J.P.D. and Wania, F.: Calculating Equilibrium  
20 Phase Distribution during the Formation of Secondary Organic Aerosol Using  
21 COSMO *therm*, *Environ. Sci. Technol.*, 49(14), 8585–8594, doi:10.1021/acs.est.5b01584,  
22 2015.

23 Xue, J., Lau, A.K.H., Yu, J.Z.: A study of acidity on PM(2.5) in Hong Kong using online  
24 ionic chemical composition measurements, *Atmospheric Environment*, 45, 7081-7088, 2011

25 Zhang, Q., Jimenez, J.L., Canagaratna, M.R., Allan, J.D., Coe, H., Ulbrich, I., Alfarra, M.R.,  
26 Takami, A., Middlebrook, A.M., Sun, Y.L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo,  
27 P.F., Salcedo, D., Onasch, T., Jayne, J.T., Miyoshi, T., Shimojo, A., Hatakeyama, S.,  
28 Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian,  
29 K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R.J., Rautiainen, J., Sun, J.Y.,  
30 Zhang, Y.M., Worsnop, D.R.: Ubiquity and dominance of oxygenated species in organic

1 aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, *Geophysical*  
2 *Research Letters*, 34, 6, doi: 10.1029/2007gl029979, 2007a

3 Zhang, Y., Huang, J.-P., Henze, D.K., Seinfeld, J.H.C.D.: Role of isoprene in secondary  
4 organic aerosol formation on a regional scale, *Journal of Geophysical Research: Atmospheres*,  
5 112, 2007b

6



1 Table 1. Properties of the biogenic hydrophilic and hydrophobic surrogate SOA species used  
 2 in the simulations conducted with the CHIMERE model. <sup>(1)</sup> The Henry's law constants are  
 3 calculated with the group contribution approach, GROMHE. <sup>(2)</sup> Pun et al., (2006).  
 4 <sup>(3)</sup> Surrogate undergoing oligomerization.

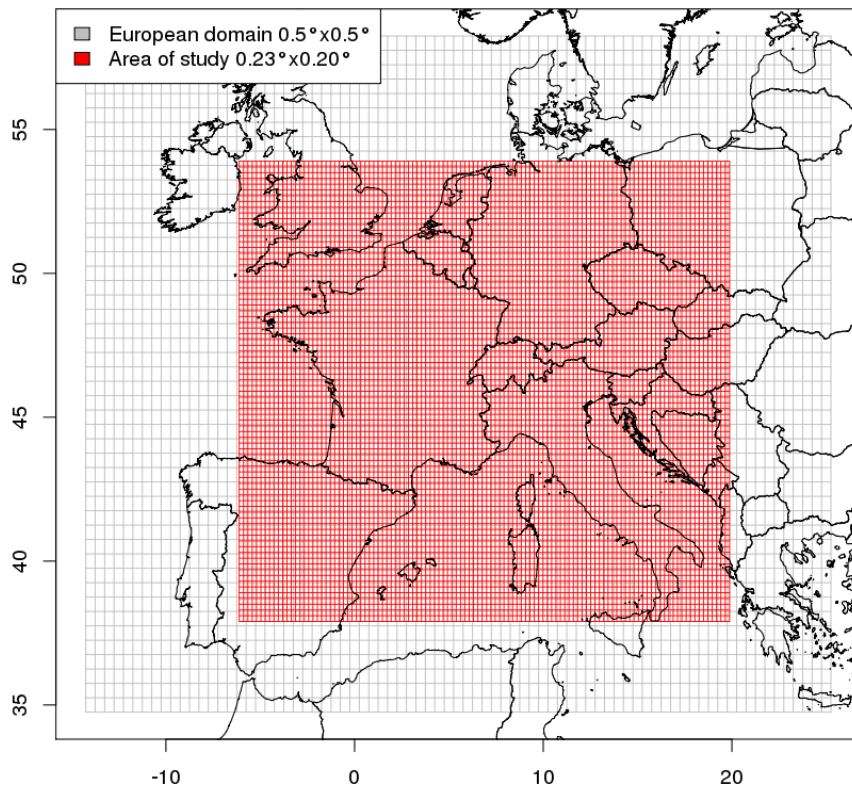
Surrogate species	Molecular Structure	Molar Mass (g mol <sup>-1</sup> )	Henry's law constant <sup>(1)</sup> (Matm <sup>-1</sup> at 298K)	Saturation vapor pressure <sup>(2)</sup> (atm)	Considered in KIN <sup>(3)</sup>	Considered in KPH <sup>(3)</sup>
BiA0D	Pinonaldehyde	168	4.97x10 <sup>4</sup>	3.55x10 <sup>-7</sup>	Yes	Yes
BiA1D	Norpinic acid	170	6.85x10 <sup>8</sup>	2.86x10 <sup>-10</sup>	Yes	No
BiA2D	Pinic acid	186	6.03x10 <sup>8</sup>	1.88x10 <sup>-10</sup>	Yes	No
BiBmP	C15 oxo aldehyde	236	10 <sup>-2</sup>	3.97x10 <sup>-9</sup>	Yes	No

5

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

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

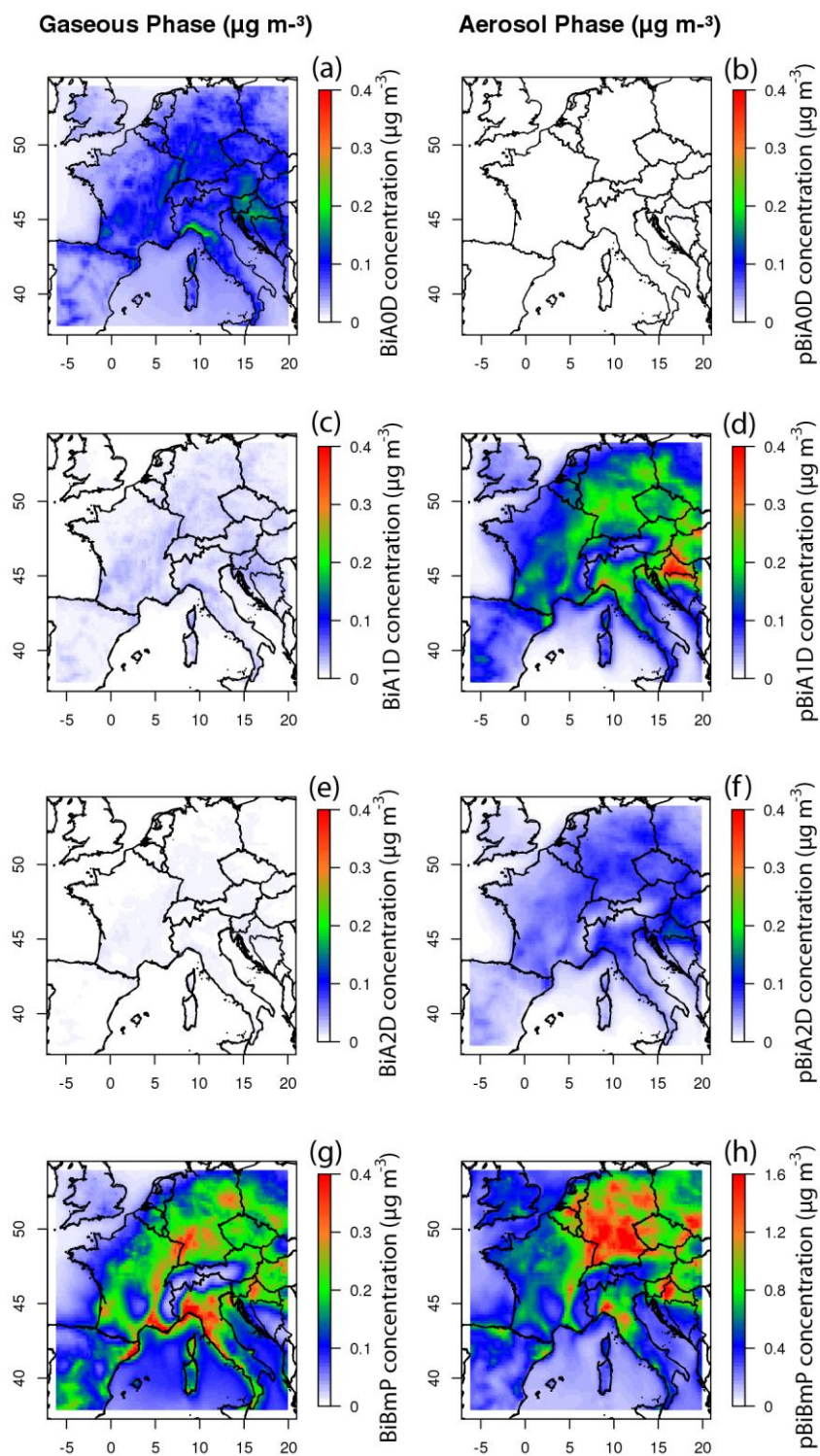
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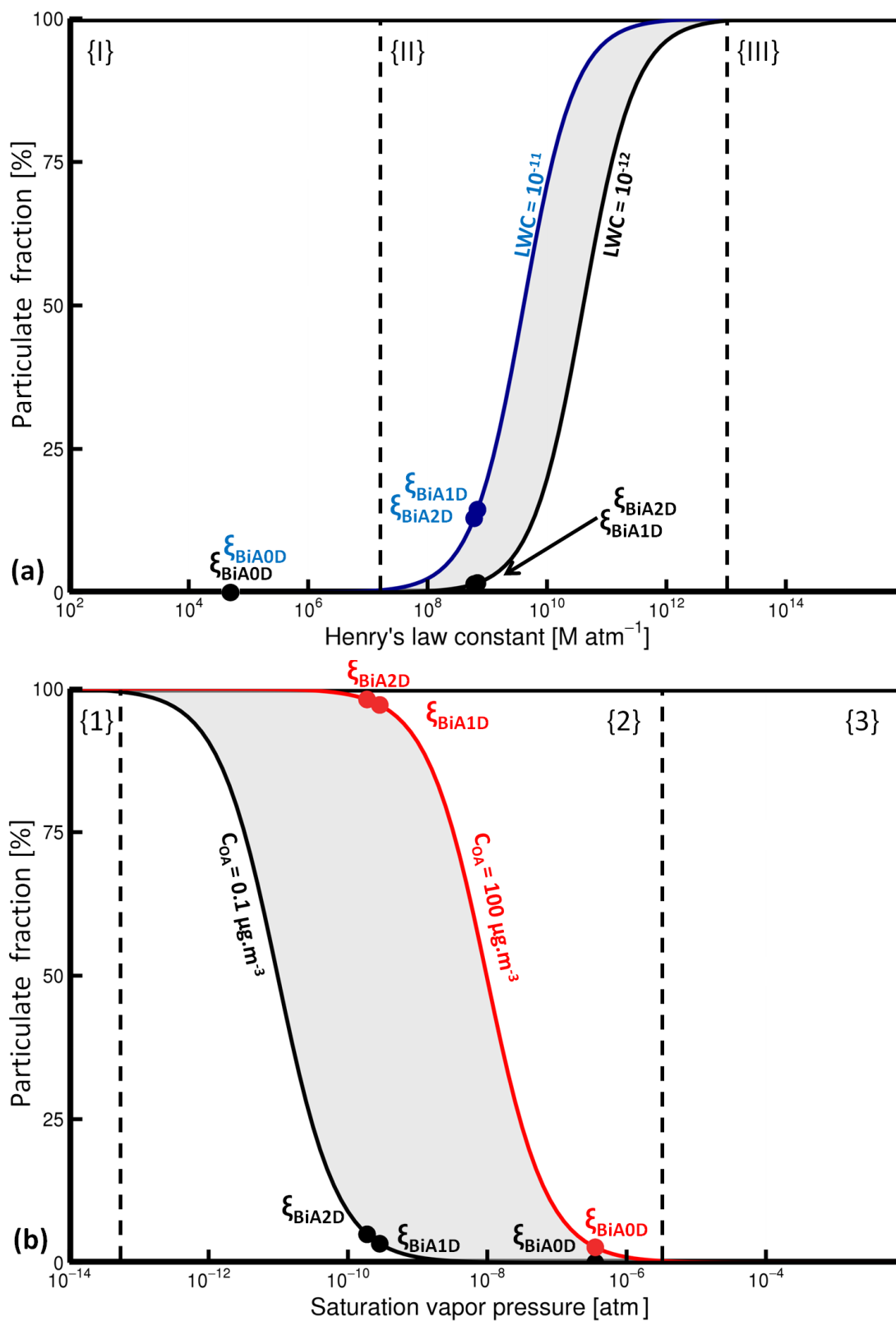
3 Figure 1. In red, gridded domain used for the air quality simulations, having a horizontal  
4 resolution of  $0.23^\circ \times 0.20^\circ$ . In black, large-scale domain used to provide boundary conditions  
5 (horizontal resolution of  $0.5^\circ \times 0.5^\circ$ ).



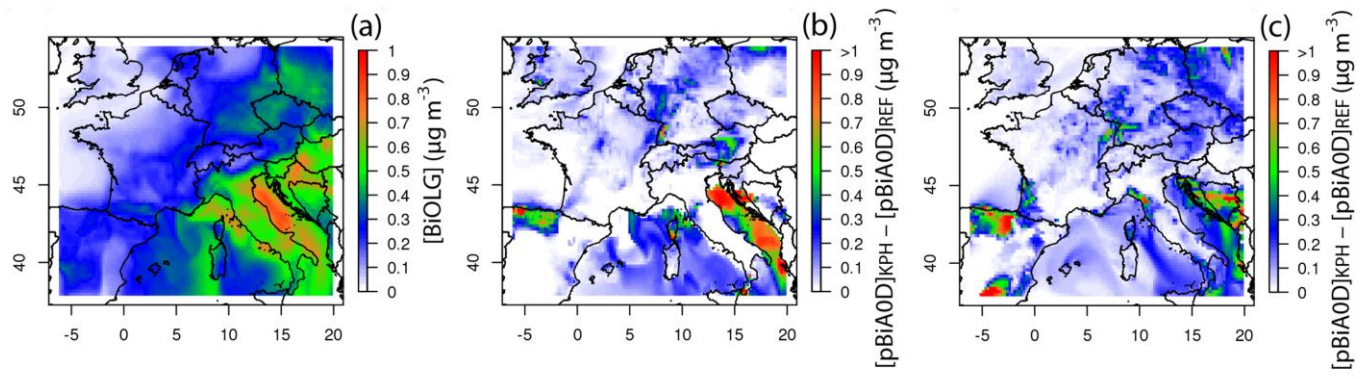
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3 Figure 2. Mass concentration fields of BiA0D (a and b), BiA1D (c and d), BiA2D (e and f)  
 4 and BiBmP (g and h) in the gas (left) and particulate (right) phases, modeled by CHIMERE  
 5 and averaged over July 20 - August 3 2006.

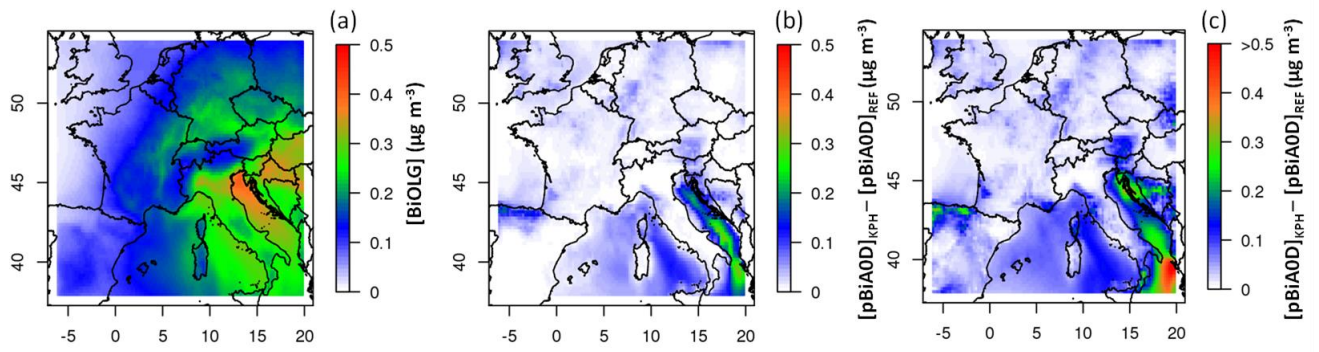


1  
 2 Figure 3. Particulate fraction as a function of Henry's law constant (upper figure) and as a  
 3 function of Saturation vapor pressure (lower figure). The partition of each surrogate is  
 4 represented by the colored dots for different conditions of organic aerosol mass concentration.  
 5 Shaded areas represent the range of typical atmospheric condition.



1  
2

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

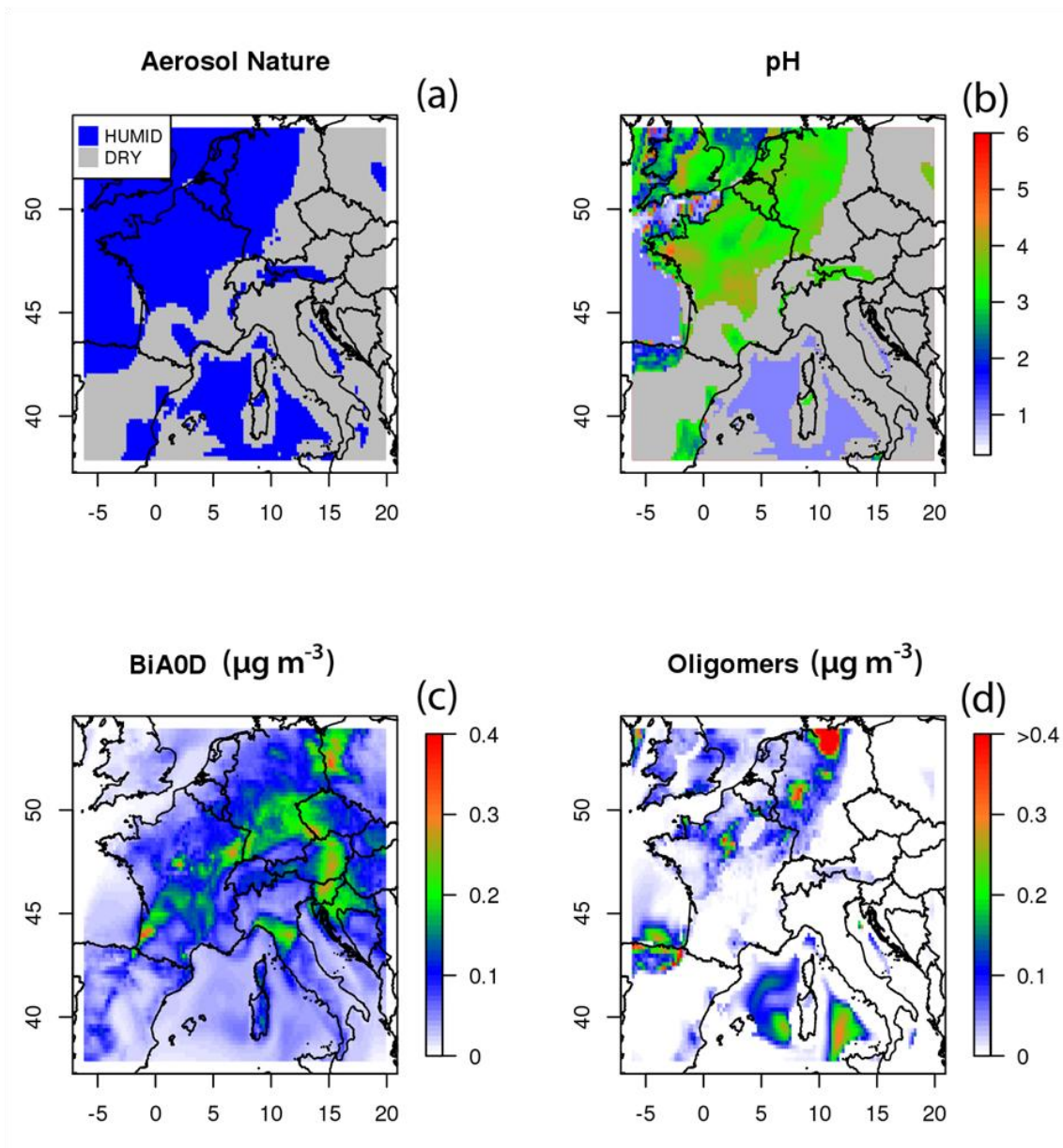


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3 Figure 5. Average modeled oligomer concentration fields from monoterpenes in the KIN (a)  
 4 and KPH configurations considering both deliquescent (b) and metastable mode (c) for the  
 5 period of July 20-August 3 2006.



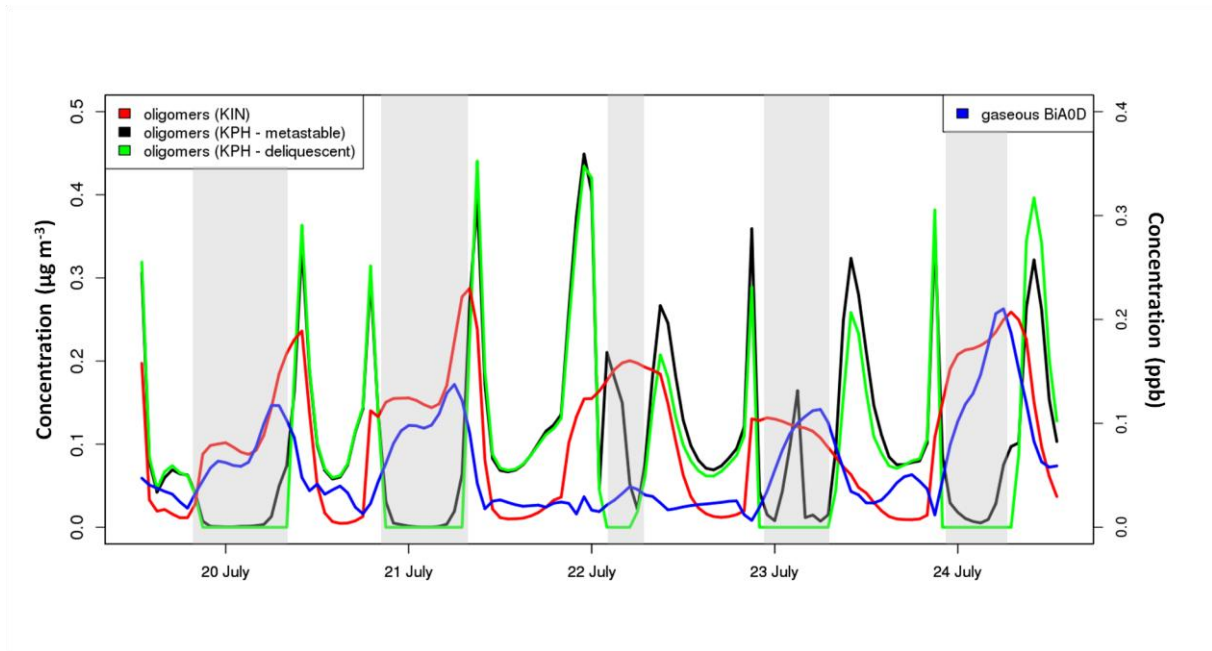


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3 Figure 6. CHIMERE results for 24 July 2006 at 5:00 UTC: nature (humid or dry) of the  
 4 aerosol (a), pH of the aqueous phase (b); BiAOD precursor concentration fields in the gas  
 5 phase for the reference simulation ( $\mu\text{g m}^{-3}$ ) (c) and oligomer concentrations ( $\mu\text{g m}^{-3}$ ) (d)  
 6 obtained with the KPH approach.

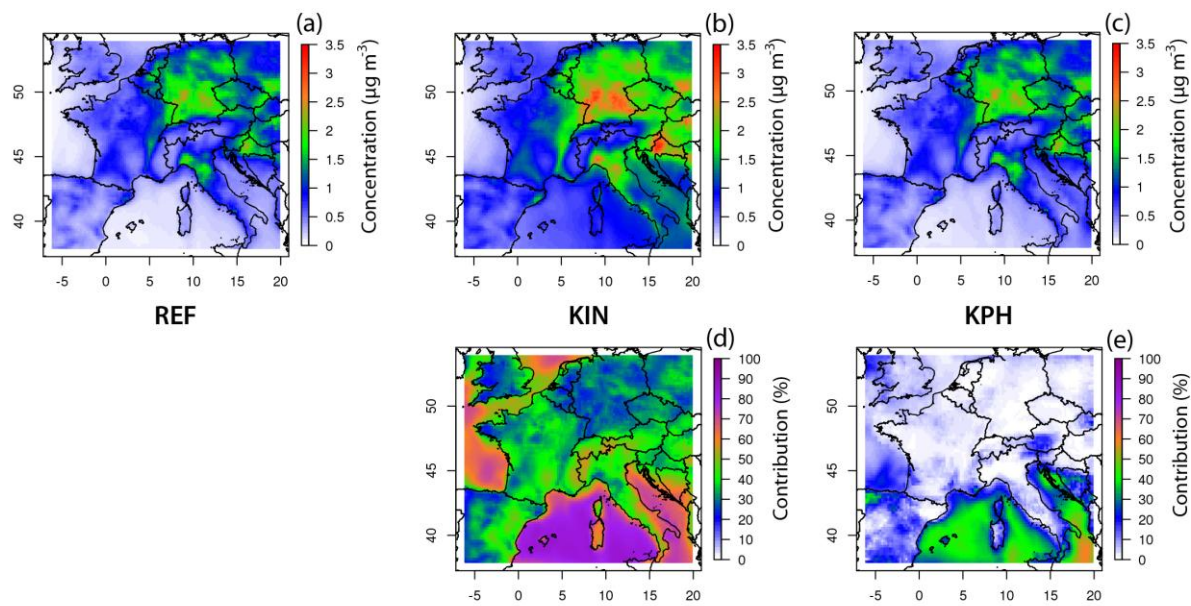




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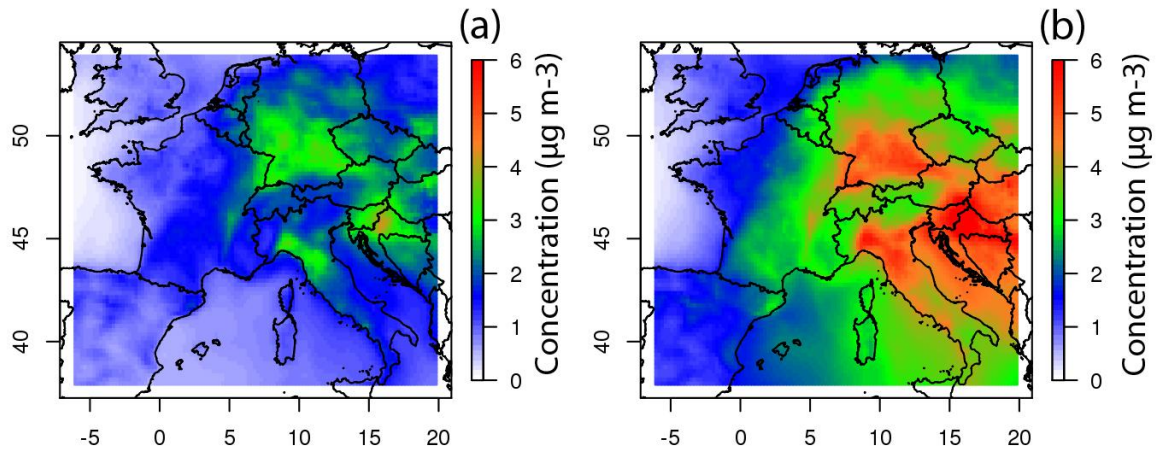
3 Figure 7. Time series of BiA0D concentrations (ppb) in the reference simulation (blue line),  
 4 the KIN (red line) oligomer concentrations ( $\mu\text{g m}^{-3}$ ), and the KPH oligomer concentrations  
 5 ( $\mu\text{g m}^{-3}$ ) in the deliquescent mode (green line) and in the metastable mode (black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



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

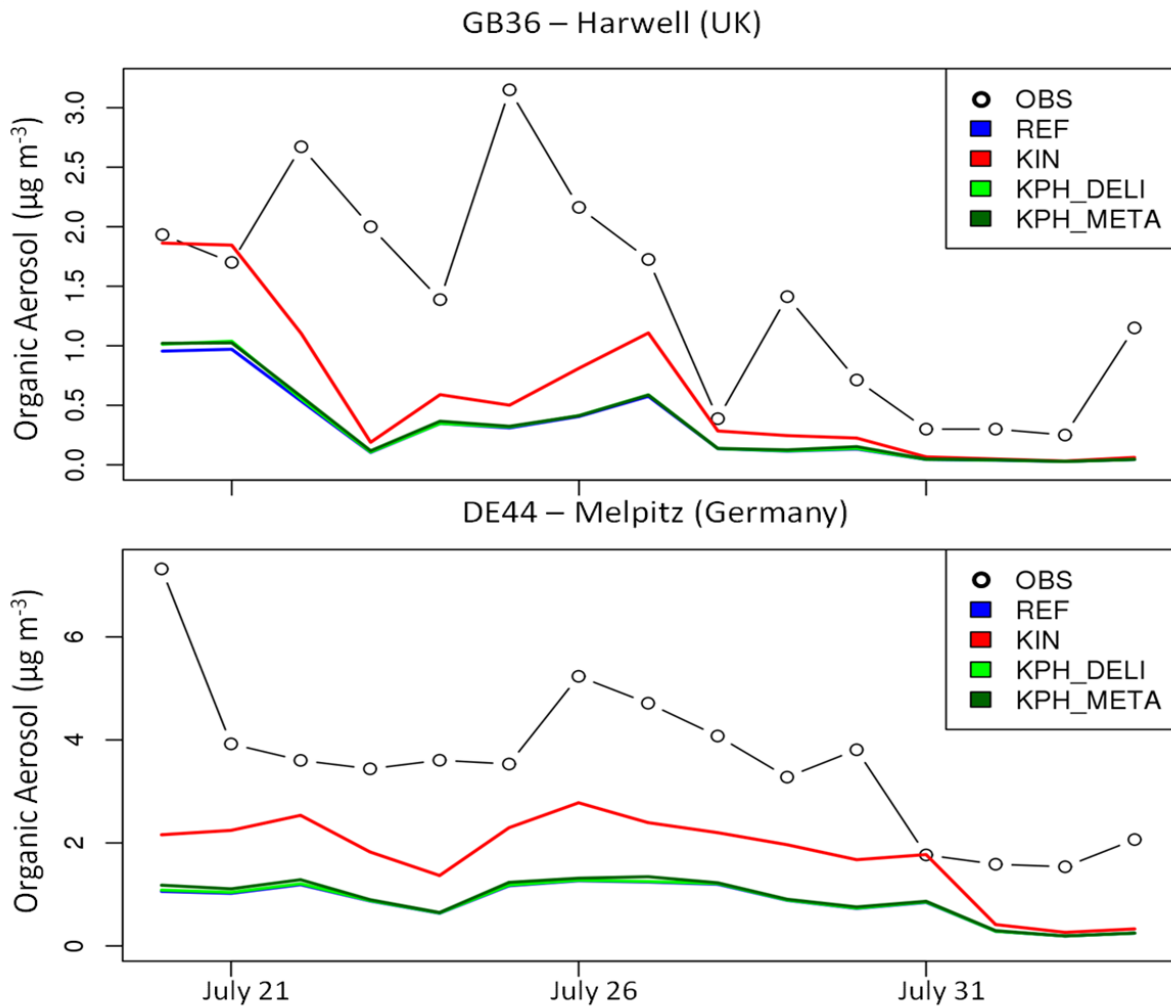


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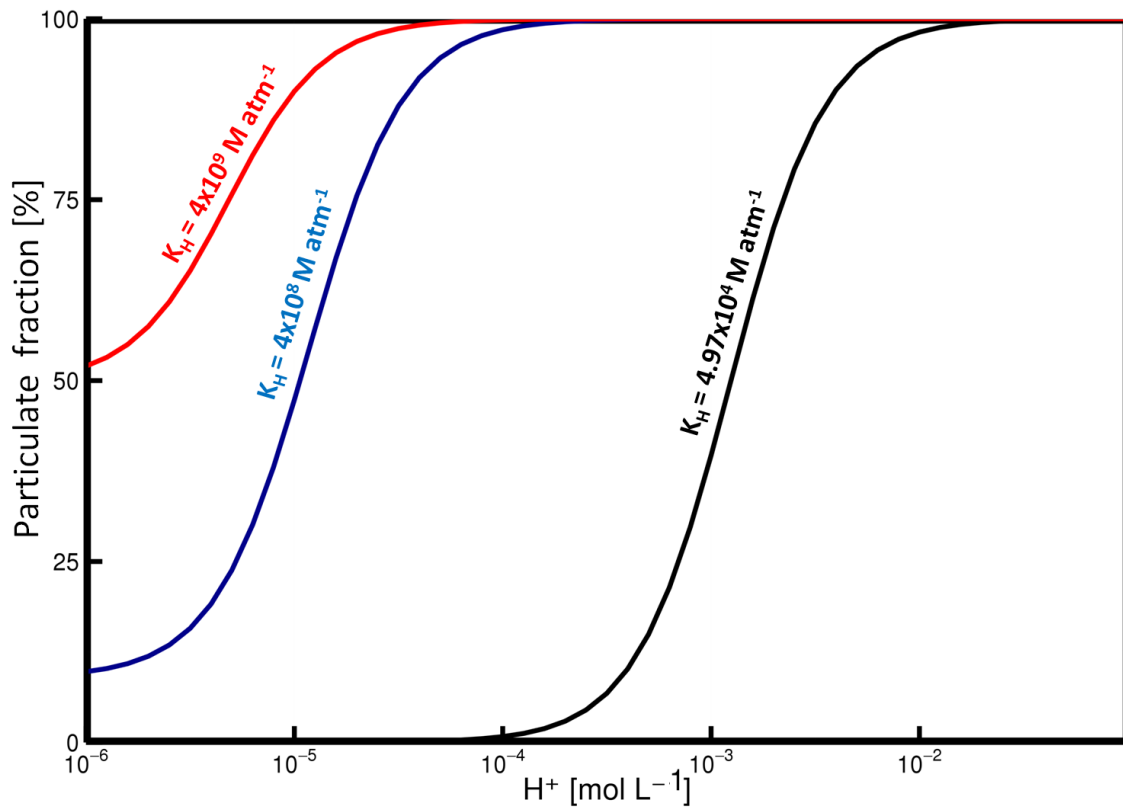
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3 Figure 9. Modeled average BSOA concentration from isoprene and monoterpenes in the  
4 reference case (left) and from the KIN approach (right) for the period July 20 - August 3,  
5 2006.

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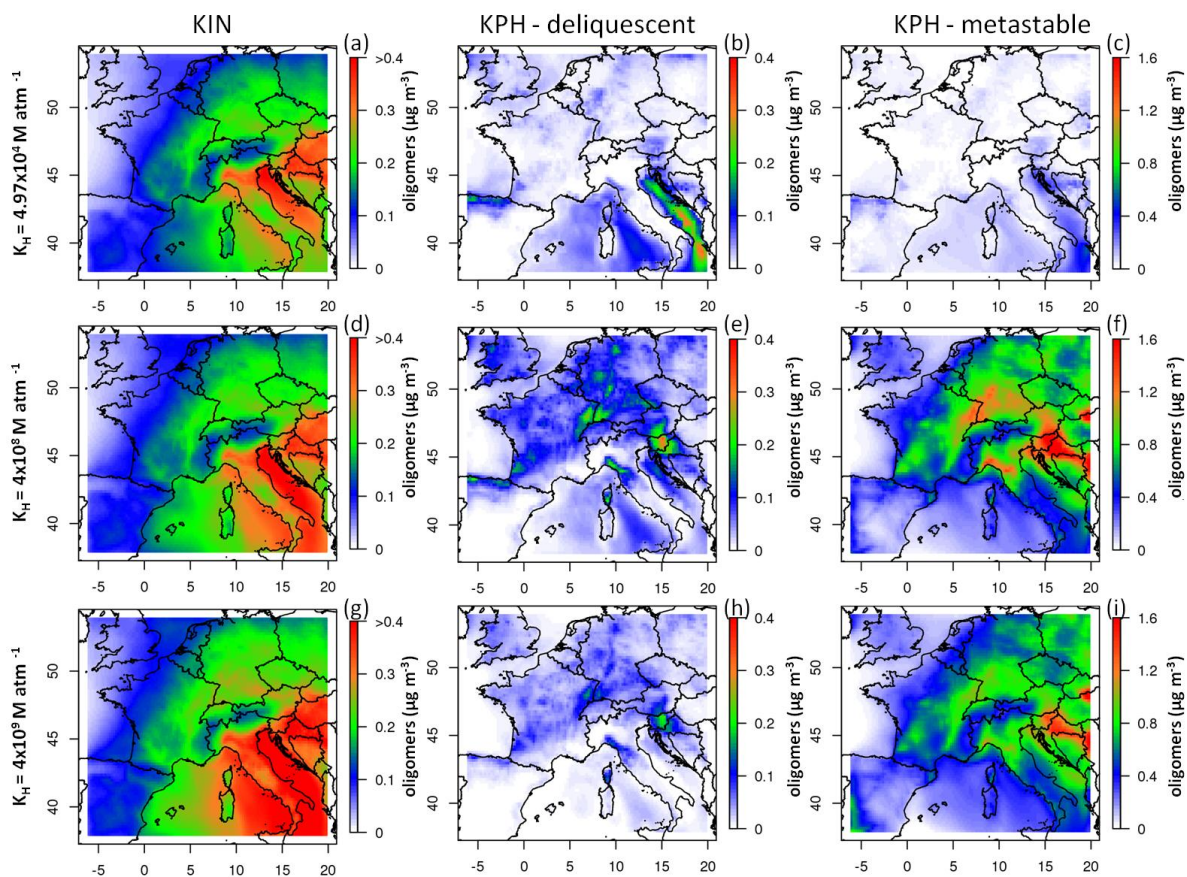
1  
 2 Figure 10. Comparisons of OC measurements (circles) with simulated OC in PM<sub>10</sub> obtained in  
 3 the reference simulation (blue), using the kinetic approach configuration (red), and using both  
 4 KPH approaches - either in deliquescent or metastable mode (green and darkgreen curves  
 5 respectively) at the Harwell (UK, top) and Melpitz (Germany, bottom) sites during the month  
 6 of July 2006.



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2

3 Figure 11 - Evolution of the particulate fraction of a given species as a function of H<sup>+</sup>  
 4 concentration according to the equation (1), for 3 different values of its Henry's law constant  
 5  $K_H = [4.97 \times 10^4; 4 \times 10^8; 4 \times 10^9 \text{ Matm}^{-1}]$  at a LWC of  $10^{-11} \text{ cm}^3 \text{ water cm}^{-3}$ .



1

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3 Figure 12. Mean modeled oligomer concentrations from monoterpenes hydrophilic surrogates  
 4 (thus without BiBmP) for both approaches: KIN (left), KPH deliquescent (center) and KPH  
 5 metastable mode (right) over July 20 - August 3, 2006. The simulations are conducted using  
 6 for BiA0D the following  $K_H$  values:  $4.97 \times 10^4 \text{ Matm}^{-1}$  (top, a, b and c),  $4 \times 10^8 \text{ Matm}^{-1}$  middle,  
 7 ( $4 \times 10^9 \text{ Matm}^{-1}$  (bottom, g, h and i).