

3.1.5 Comparisons of KIN and KPH approaches with measurements

As mentioned above, no direct measurement of the oligomer fraction of SOA is available at ground based measurement stations. However, we can assess the role of oligomer formation processes in improving model-measurement comparisons, knowing that the organic fraction of atmospheric aerosols is usually underestimated by models (Heald et al., 2011). In this section, we present the comparison of CHIMERE organic carbon (OC) mass concentration in the PM₁₀ fraction of aerosols, obtained with 4 different model configurations (REF, KIN and KPH in both modes) with measurements obtained at two EMEP background sites : the rural stations of Harwell in the United Kingdom (100km west of London) and Melpitz in Eastern Germany (150km south of Berlin). Figure 10 presents these comparisons for the period July 20th - August 3rd 2006, the statistical data (mean bias (MB), normalized mean bias (NMB), root mean square error (RMSE), normalized root mean square error (NRMSE) and correlation coefficient (R)) being given in Table 2.

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

The pH-dependent approaches have shown to cause a fast and intense production of oligomers that may induce such a short-time variability in the SOA fraction of the aerosol. Here, though, there is no quantitative impact of this process on the OC mass concentration level all along the period, whatever the site. Such results could be expected in the deliquescent configuration, since we concluded that the simulated relative humidity was too low to permit the transport of oligomers over long distances. But it appears that the metastable mode, which promotes

oligomer persistence and its transport in the atmosphere, also doesn't significantly impact the organic carbon concentration at those sites. One possible explanation for this lack of effects is the non-inclusion of isoprene as an oligomer precursor in the KPH simulations, especially because the analysis of the model output reveals that 60 to 70% of KIN oligomers derived from isoprene at both stations. However, the conditions in which the KPH simulation was launched, and mainly the K_H value used for the BiA0D species in conjunction with the variability of the aerosol pH, could also account for the low production of oligomers in remote continental areas of Europe.

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

4 Discussions and Conclusions

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

4.1 Oligomer formation from isoprene

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

4.2 Further developments for oligomer formation dynamics

On a broader level, the difficulty of restituting faithfully oligomer yields and SOA formation dynamics comes from the diversity of the phenomena that drive SOA formation in the atmosphere. It is indeed clear now that oligomerization processes, which may produce up to 50% of SOA on the average, rely on both the volatility of the multiple SVOCs and their

reactivity in the condensed phase, which is controlled by a series of oxidation, association and fragmentation reactions that can be kinetically described.

One important issue is thus our ability to describe in an appropriate manner the variety of SVOC behaviors in the gas and condensed phase in an AQM. As for K_H values, we have discussed the fact that the representation of SVOC partitioning in models for now is not highly accurate. Most 3D models indeed use one single K_H value to account for the behavior of a complex mixture of SOA precursors, and this format clearly prevents the model to reconstitute the full diversity of the gas/particle partitioning of individual compounds in time and space. This is all the more important because the results we obtained with CHIMERE showed that oligomer concentrations present a considerable sensitivity to the K_H value selected for the biogenic surrogate species that produces SOA. Similarly, when simulating chemistry in the aerosol phase, the allocation of distinct kinetic constant values for the reactivity of the condensed oligomer precursors would be valuable. Kalberer et al. (2006) effectively observed disparities in the temporal evolution of the aerosol molar mass while studying the oxidation of trimethylbenzene, α -pinene and isoprene. Taking this into account would probably have increased the OC short-time variability of the KIN method. However, increasing the degree of refinement of a modeling approach through a differentiation of individual behaviors is not always a good solution. The more refined the scheme becomes, the more difficult it is to collect the details about organic compound reactivity, making it difficult to set up the approach in a 3D model. As an example, the KPH approach proposes to consider the specific formation of oligomers from the polymerization of aldehydes only, that may happen through diverse acid-catalyzed reactions. Although it is evident that the consideration of only one single polymerization pathway constitutes a limitation for the quantitative simulation of SOA production from ambient organic precursors, this hypothesis has the advantage of proposing a well-identified process which can be adjusted in the model in terms of intensity, and upon the environmental conditions, from experimental knowledge about this reaction. However, in this approach, isoprene oxidation products (ISOPA) could not be considered as oligomer precursors, due to the fact that the KPH approach is only applicable to aldehydes and that there is no detail about the structural properties of the ISOPA surrogate species in the current CHIMERE chemical scheme. Including all or part of this species in the oligomerization process would thus have introduced an indeterminate uncertainty in our simulations. The outcome of this is a severe underestimation of the modeled OC compared with Harwell and Melpitz observation, that was – at least partly – attributed to the non inclusion of isoprene in

oligomer precursors when running CHIMERE with the KPH configuration. Similarly, we have seen that the dependence of the model results upon (i) the state (deliquescent or metastable) of the aerosol, and (ii) its inorganic composition and pH, constitute a key challenge for the implementation of the KPH approach. In this respect, there is a necessity to define a parameterization focusing on the restitution of a unique parameter (such as the dynamics of global SOA yields), and relying on an irreducible set of parameters and processes, provided that it allows the model to perform satisfactorily with regard to existing measurements. For this purpose, *in situ* atmospheric oligomer measurements conducted at various distances from the sources would be absolutely necessary to assign a representative average value for the K_H of the SVOC surrogate species - as our results showed that the rate and intensity of the SVOC transfer to the aerosol phase give the SOA plumes their shapes.

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

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

Considering these elements, the kinetic approach that represents oligomer formation as the only possible fate for the relevant condensed organics may lead to a significant overestimation of the oligomer fraction in the aerosol. Thus, it should at least take into account a possible loss of SOA by evaporation, due notably to fragmentation processes (Renard et al., 2015). Indeed, organic compounds in the particulate phase have shown to be submitted to a variety of non-oxidative and oxidative reactions leading to the formation of both semi-volatile and non-volatile compounds, depending on their final molecular weight (Kroll and Seinfeld, 2008; Kroll et al., 2009). Furthermore, the absence of reversibility in the kinetic approach makes it little adaptable to laboratory observations such as the evaporation of SOA from α -pinene on the scale of a few hours (Grieshop et al., 2007). On the reverse, the high SOA mass yields obtained from the oxidation of biogenics SVOCs cannot be reproduced using the KPH-deliquescent approach, as SOA formed this way is permanently released due to aerosol water evaporation or pH increase. Whatever the model configuration, our works have shown that the oligomerization reversibility proposed by the KPH approach was difficult to set-up and control in an AQM. Therefore, considering (i) the laboratory experiments conducted by Hall and Johnson (2012b) on the ozonolysis of α -pinene, which indicated that oligomer formation would be driven by reactive uptake rather than by the partition of monomers between both phases and (ii) the fact that this reactive uptake may be observed within seconds (Heaton et al., 2007; Hall and Johnson, 2012b), it appears more realistic to propose a representation of the oligomerization process in two stages: a first fast step modifying directly the monomer partitioning so as to represent the rapid formation of oligomers (not permitted by the KIN approach only), and a stabilization step consisting of a kinetic uptake of the OA previously formed (not adjustable in a KPH approach). Trump and Donahue (2014) have recently proposed a comprehensive but simplified vision of reversible oligomerization that effectively combines a partitioning equilibrium and a condensed-phase kinetic reactivity, and that clearly addresses the issue of reversibility. This vision was built from the VBS approach, a modeling technique relying on SVOC volatility bins rather than on identified chemical species to represent the progressive formation of SOA from gaseous organic compounds upon atmospheric oxidation processes (Robinson et al., 2007). The works of Trump and Donahue propose a detailed analysis of an expanded VBS version taking into account oligomer formation dynamics in a quite similar way as here: namely, the description of the equilibrium phase partitioning of various VOC oxidation products from a given volatility bin, and a kinetic-dependent reactivity in the condensed phase where the association of 2 identical particulate monomers compete with the dissociation of the dimers thus formed. The ratio of

those two rate constants makes a dimerization formation equilibrium. There, major simplifying assumptions are made. They mainly stem from the fact that only one single volatility class of condensed products reacts, and that this class reacts in its entirety - regardless of the structure of precursors - to form carboxylic acid dimers. Indeed, representative equilibrium constants for the dimerization reaction were derived from laboratory works on dicarboxylic acid dimers formation. Finally, it is stressed by the authors that neither of the simplifications considered in this approach is likely to be realistic, and that the stated goal of their work is only to identify what type of chemistry this method produces and how it helps understanding/representing oligomers in the atmosphere. Despite such simplifications, the authors show that their approach allows restituting experimental SOA yields for different initial OA conditions, as well as SOA formation dynamics. A particularly interesting result of this approach is the simulation of a two-stage SOA evaporation (monomers evaporate rapidly upon dilution while only a modest drop in oligomer concentration is simulated due to the equilibrium dynamics) that may help reproducing recent observations of delayed SOA evaporation. Through sensitivity tests to the condensed phase reactivity kinetics, this approach also outlines that an irreversible oligomerization process (high dimerization to evaporation kinetic ratio) would definitely appears incompatible with the observed SOA mass-yield behaviors.

As for conventional modeling approaches relying on molecule structural properties, and based on these findings, a KPH-like approach considering a further reactive uptake - with partial reversibility or fragmentation so as to fit the observations about the hysteresis of SOA formation and evaporation - could be a suitable parameterization to represent the formation of oligomers from monoterpenes. Even so, the determination of the aerosol mode (deliquescent/metastable) is not an obvious choice. Although Fountoukis et al. (2009) concluded from plume studies that organics could promote thermodynamically stable water down to very low RH, Moya et al. (2002) have shown that considering a metastable mode for PM_{10} (where organic matter is predominantly present) leads, under low relative humidity conditions (<60%), to significant errors in the concentrations of the inorganic species which indirectly determine the aerosol pH and thus oligomers formation. Similarly, Mikhailov et al. (2013) found – from the analysis of atmospheric aerosols – that under a RH level of about 70%, organic species may not be completely dissolved in the aqueous phase and may also coexist in a solid aerosol phase. These studies both conclude to the importance of considering a deliquescent mode for low relative humidity conditions.

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

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

OC ($\mu\text{g m}^{-3}$)	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

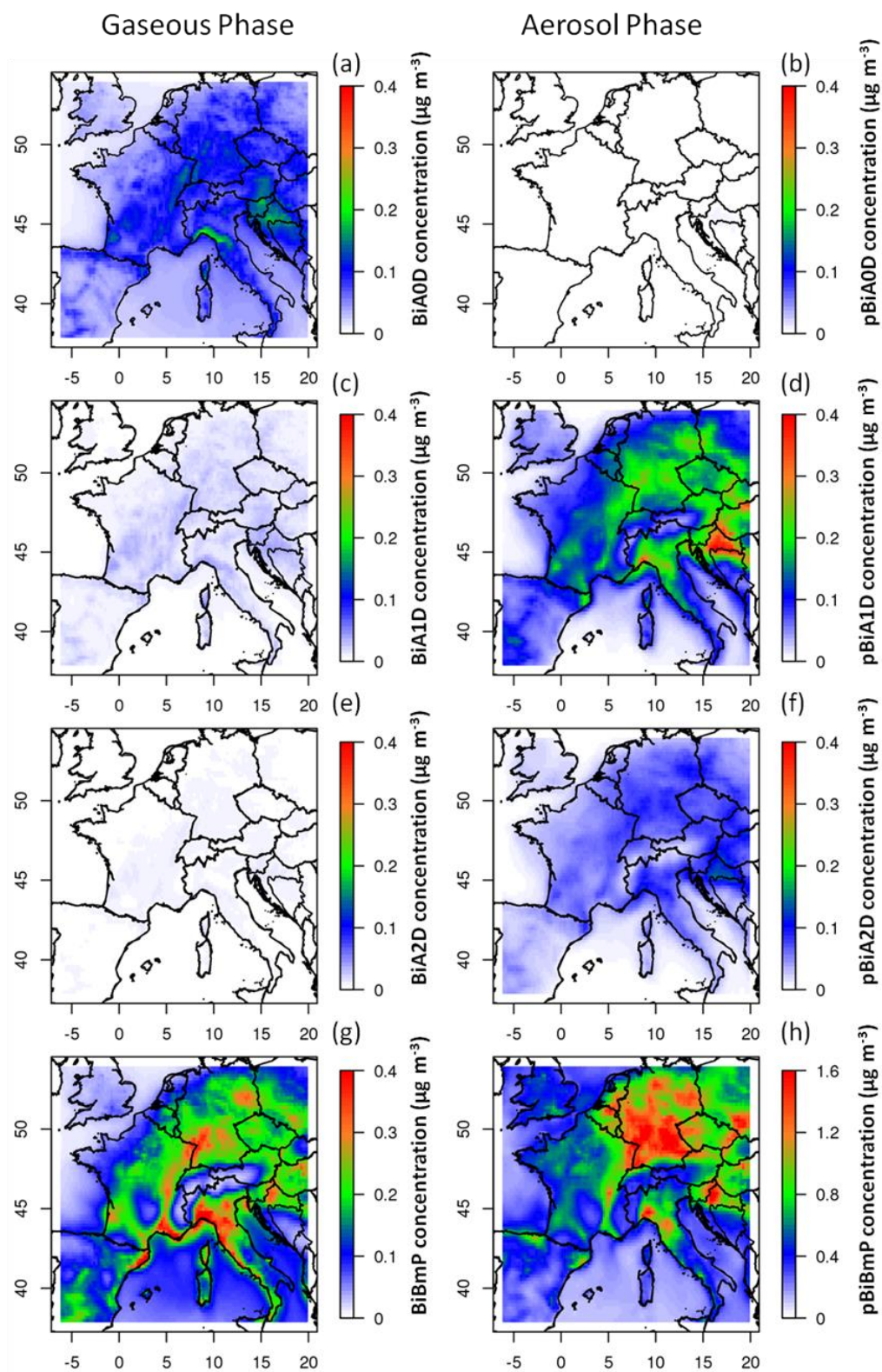


Figure 1. Mass concentration fields of BiA0D (a and b), BiA1D (c and d), BiA2D (e and f) and BiBmP (g and h) in the gas (left) and particulate (right) phases, modeled by CHIMERE and averaged over July 20 - August 3 2006.

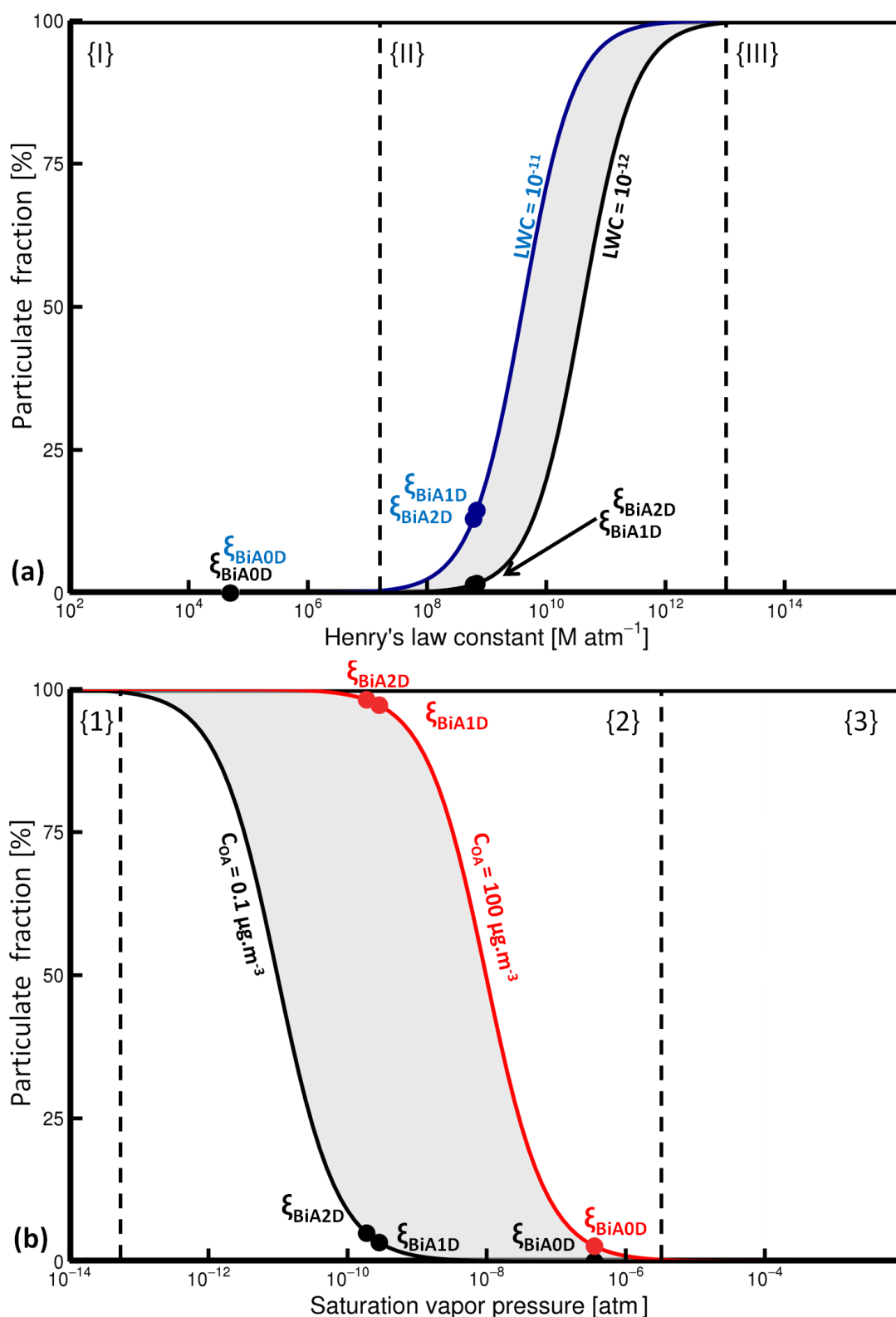


Figure 2. Particulate fraction as a function of Henry's law constant (upper figure) and as a function of Saturation vapor pressure (lower figure). The partition of each surrogate is represented by the colored dots for different conditions of organic aerosol mass concentration. Shaded areas represent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

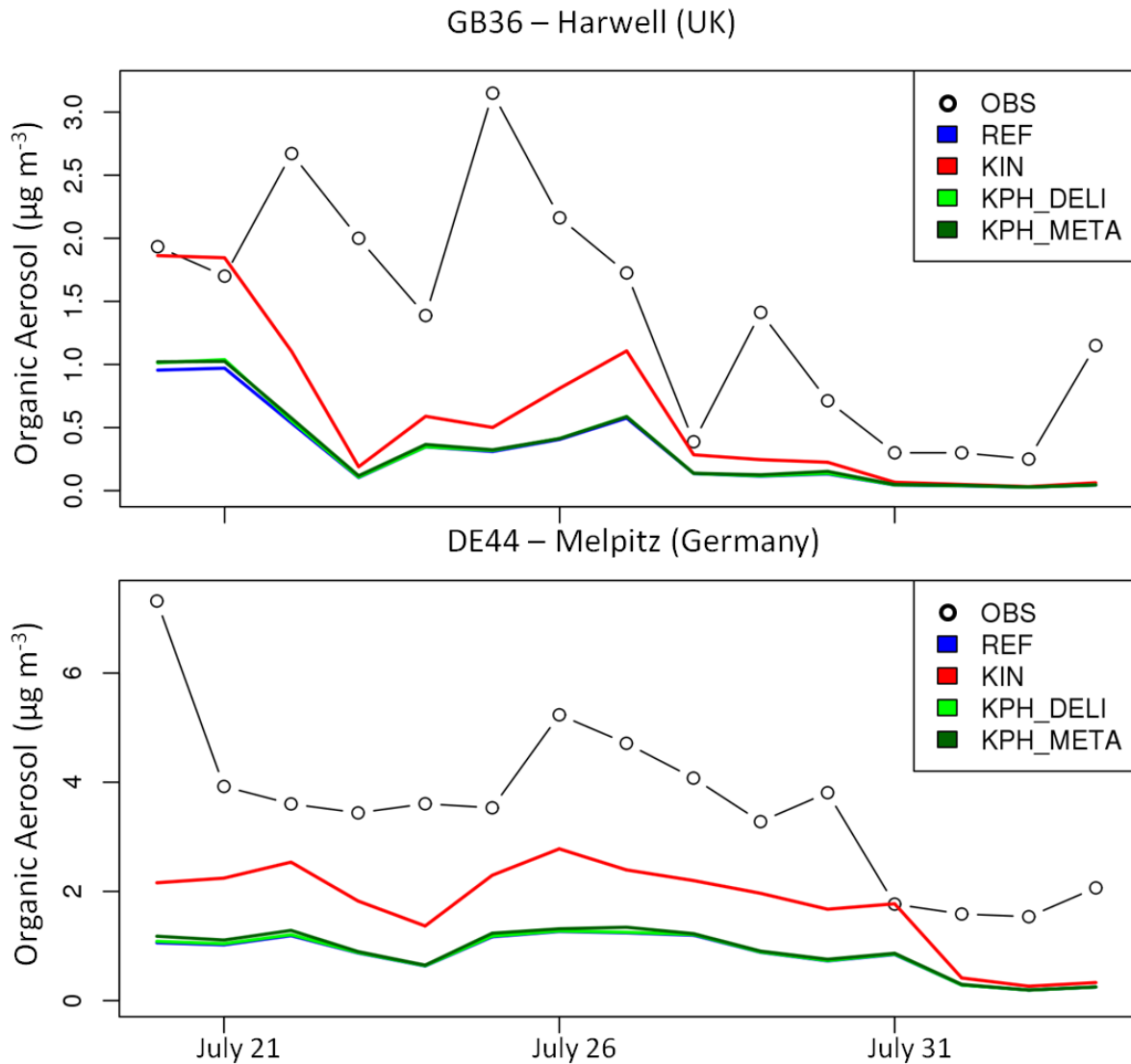


Figure 10. Comparisons of OC measurements (circles) with simulated OC in PM_{10} obtained in the reference simulation (blue), using the kinetic approach configuration (red), and using both KPH approaches - either in deliquescent or metastable mode (green and darkgreen curves respectively) at the Harwell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