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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Explicit modeling of volatile organic compounds partitioning in the atmospheric aqueous phase" *by* C. Mouchel-Vallon et al.

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We thank the reviewers for their helpful comments on the manuscript. We outline below our responses to the points raised by each referee and summarize the changes made to the revised manuscript.

Response to Reviewer #1:

> Detailed comments: abstract line 11, does 2% refer to 2% of the total organic gas phase mass?

The sentence has been modified as follows: "The amount of dissolved organic matter

was found to be very low (yield less than 2% on a carbon atom basis) under a water content typical of deliquescent aerosols."

> p.24096 "lack of knowledge concerning the aqueous phase contribution to atmospheric chemistry (Ravishankara, 1997). This is a bit overstated. The community knows that sulfate aerosol is formed through aqueous chemistry and SOA can form. There are certainly open questions but the community knows it happens. ...eg. as the authors point out inorganic reactions in the aqueous phase have been studied extensively. The sentence should be worded more carefully.

We agree that our statement was overstated. The sentence has been modified to: "Aqueous phase is known to contribute to atmospheric processes (e.g. Seinfeld and Pandis, 2006)."

> P24097 line 15 - please provide units for "L". It is also important to note that Ervens and Volkamer have confirmed this through modeling as stated by the authors, ... but as applied to a series of laboratory experiments conducted under different conditions in different labs.

Unit used in this study for the liquid water content "L" is given p. 24100, l. 23. The sentence has been modified as follows: "Ervens and Volkamer (2010) modeled the SOA formation through aqueous phase processing of glyoxal, one of the oxidation products of isoprene. Their simulations based on observations in chamber experiments by Volkamer et al. (2009) have confirmed that there is a correlation between SOA mass increase and the liquid water content (denoted L hereafter)."

*> P24097 section "i", it's not just that highly soluble species are *expected* to be found in atmospheric waters, they *are*found. The review paper by Chebbi and Carlier explains this in detail.*

The sentence has been modified as follows: "Specifically, many secondary organic species formed during the gas phase oxidation of hydrocarbons are highly soluble and have been found in atmospheric water (e.g. Chebbi and Carlier, 1996; van Pinxteren et al., 2005; Sorooshian et al., 2007; Kawamura et al., 2010)."

> p.24098, line 6. There is a typo...constant"s" not constant

> p24099 "in details" should be "in detail"

It has been corrected in the manuscript.

> p. 24100, line 21: What species have $H > 10^{12}$?

Examples of such species are given in the results sections. Here, H is merely given as an upper limit above which a species should be in the aqueous phase at thermodynamic equilibrium and under typical atmospheric conditions. Estimation of this threshold value is straightforward from the partitioning equation (8) page 24110. The sentences are modified to introduce the partitioning equation in this paragraph.

> p.24101, The diffusivity number for the reference compound is provided for a temperature of 298K. The authors set T=278K in their model and use 278K for estimates of Heff values. What is a typical temperature for the (chemical) system in the atmosphere like the one studied here, and by how much would Dg (or kl?)change? How does the difference in temperature for the different parameters limit or confound the findings here?

Our study is limited to warm clouds. Hence, the temperature can typically vary from ≈ 288K (e.g. in a fog) to ≈ 250K. Our choice (278K) is purely arbitrary. In general, D_g is proportional to $T^{3/2}$ (e.g. Levine, 2009). Under this assumption, a 20 K decrease in temperature (from 298 to 278K) would therefore decrease D_g by approximately 10%. We ran sensitivity tests which show that such variation on Dg has no impact on the kinetics of the mass transfer.

> p. 24102, can the authors provide some brief details on how the acid/base equilibrium reactions are described kinetically and the influence of [H+] on phase partitioning?

Acid/base equilibrium reactions are enforced at each time step. In our model configuration, pH only affects the partitioning of carboxylic acids. Specifically, the effective Henry's law constant (H*) of acids increases with the pH. In this study, pH was set to 4.5, typical of clouds. Known gas-phase reactions do not lead to a large production of carboxylic acid and, as expected, our modeling results show a small contribution of carboxylic acid to the budget of organic compounds in the aqueous phase. We ran sensitivity tests at pH = 3 and pH = 6 which show no impact of pH variation on carbon distribution between phases.

The pH value used to perform the simulation was omitted in the section 2.3 devoted to initial conditions. The following sentence has been added section 2.3: "Partitioning of acids is pH dependent. The pH of the aqueous phase was set to a value of 4.5, typical of clouds (e.g. Brüggemann et al., 2005)."

> p.24102 what is the effect(s) of z=0.05? how sensitive are predictions to this value?

The mass accommodation alpha is a key parameter driving the rates of the mass transfer but does not modify the thermodynamic equilibrium. The deviation to the Henry's law equilibrium has been investigated. For our modeling conditions, species reach and sustain their equilibrium values on a short timescale. This finding is not surprising since no reactivity takes place in the aqueous phase to make the mass transfer a potential rate limiting step. In that case, α is not a sensitive parameter of the system. Furthermore, we ran sensitivity tests for isoprene simulations using different values of α (0.01, 0.05 and 0.5) assigned to all soluble compounds. As expected, no significant change was observed on the global carbon repartition and the organics functionalization.

> p. 24103 is an initial condition of [O3] = 40 ppb representative of areas where individual alkane concentrations are 10ppb? Can the authors provide an example that this is the case? The same O3 initial condition is used for all NOX scenarios? Can the authors justify this?

No attempt is made in this study to represent any specific areas or some representative conditions (cloud liquid water and constant irradiation are sustained for many days). As stated in the introduction, our goal is to explore how water soluble are the secondary species produced during the multigenerational oxidation of a given hydrocarbon. The simulations were therefore basically designed to sustain oxidation in the gas phase. Nevertheless, the distribution of the species (and therefore their partitioning to the aqueous phase) obviously depends on the environmental conditions, especially the NOx concentrations (as discussed in the manuscript). For 2 parent hydrocarbons (isoprene and a-pinene), the distribution of secondary organic species depends on the concentration ratio of the oxidants as well (OH and O3). Ozone and an OH source were therefore added in the initial conditions to allow both VOC+O3 and VOC+OH oxidation. A mixing ratio of 40ppb is representative of mid-latitude continental summer conditions. A constant OH source (1E7 radical/s) was added as a substitute of radical sources not taken into account in the simulations. For these conditions, isoprene is mostly oxidized by OH while a-pinene is oxidized by ozone and OH in about the same proportion, as stated page 24103, line 21. Finally, the same initial conditions were used for all the simulations to enable easier comparisons of the results.

A clarification has been added in section 2.3: "The objective is to simulate the evolution of different hydrocarbons in order to characterize the multiphase partitioning of their reaction products at different stages of the oxidation. No attempt is made here to represent a specific situation. The initial concentration of the precursor was set to 10 ppb. The simulations were run with constant environmental conditions. Temperature was fixed to 278 K. Photolysis frequencies were calculated for mid-latitude and for a solar zenith angle of 45° using TUV (Madronich and Flocke, 1997). NOx concentrations were held constant and three scenarios were considered corresponding to low NOx (0.1 ppb), intermediate NOx (1 ppb) and high NOx (10 ppb) conditions. For parent hydrocarbons bearing a double bond (isoprene and α-pinene), the distribution of secondary organic species depends on the concentration ratio of the oxidants as well (OH and O3). Ozone and an OH source were therefore added in the initial conditions to allow both VOC+O3 and VOC+OH oxidation. An initial mixing ratio of 40 ppb of O3

is used in the simulations and a constant OH source (10^7 radicals cm-3 s-1) was added as a substitute of radical sources not taken into account in the simulations."

> p.24104, line 12, number of liftetime"s"

It has been corrected in the manuscript.

> p.24104, how is 'tau', the lifetime defined? is it the chemical lifetime due to reaction with OH or does it combine OH/O3 and gas phase loss due to physical partitioning? is it the lifetime of the species in the gas phase or lifetime in the atmosphere prior to physical loss processes?

The lifetime τ is usually defined as:

$$C(\tau) \equiv C_0/e \tag{1}$$

where C_0 is the initial concentration of the species. In that case:

$$\ln\left(\frac{C_0}{C(t)}\right) = t/\tau \tag{2}$$

and we define the number of lifetimes N_τ :

$$N_\tau \equiv t/\tau = \ln\left(\frac{C_0}{C(t)}\right) \tag{3}$$

The concentration $C(t)$ of the parent hydrocarbon is known at each time step t. The number of lifetime is thus simply computed as $\ln\left(\frac{C_0}{C(t)}\right)$. It should be noted that the water solubility of the three precursors is negligible. The lifetime number account for any loss process of the parent hydrocarbon and therefore combines both OH and O3 loss for isoprene and a-pinene. As octane is not reactive towards O3, in this case τ is only due to reactivity with OH. This has been clarified in the paper as follows : " $N_\tau = ln\,(C_0/C(t)) = t/\tau$ (6)

where t is the simulated (physical) time, τ is the e-folding lifetime of the parent hydrocarbon (i.e. the time required to decrease its concentration by a factor $1/e$), C_0 and $C(t)$ its concentration at t_0 and t, respectively."

> p.24104, please change multifuntional "ones" to "species", "moieties" or another more specific word. can the authors define a specific range for "moderately soluble"?

The "moderately soluble" statement is simply an indication that we expect species that couldn't dissolve significantly in lower LWC conditions, to be found in water when LWC is higher. Paragraph 4.4 discussing Fig. 6-8 describes the solubility range of species contributing to the aqueous organic content. The paragraph has been modified as follows: "With such low water content, only the more soluble species contribute to the organic content of the aqueous phase, i.e. the more functionalized species. The top 10 contributors to the aqueous phase composition are C5 species bearing 4 functional groups each. For L set to a cloud value (Fig. 1b), less soluble species substantially contribute to aqueous phase organic mass. As a consequence, at the end of the simulation, 25% of the total carbon initially in the isoprene backbone is found in water."

> p. 24105, starting at Line 22. "dissolved organic matter is then likely subject to fast processing....this process is so far ignored in current atmospheric chemical models.' Is this statement accurate? The 3-dimensional photochemical models Geos-Chem (Fu et al., 2008) and CMAQ (Carlton et al., 2008) have some representation (simpliïňAed) of multiphase organic aqueous phase chemistry in their base versions.

We overstated that sentence. This paragraph has been modified as follows: "This dissolved organic matter is then likely subject to a fast processing which may significantly shape the ultimate oxidation budget. This process is taken into account in some recent atmospheric chemical models using simplified parameterizations. For example the CMAQ model (Carlton et al., 2008) and the Geos-Chem model (Fu et al., 2008; 2009) include SOA formation pathways through in-cloud oxidation of glyoxal and methylglyoxal, parameterized with laboratory experiments yields. However, these models cannot

take into account the progressive nature of the oxidation process and the large number of different species involved in the formation of aqueous organic carbon. Our results show that the dissolution of long chain organic species has a significant contribution to the aqueous phase organic content and therefore should be accounted for in models."

> Page 24106, Line 23 "Figure 2 shows that the dissolved organic content tends to increase with decreasing NOx concentration." This is a curious result. The authors state below (p. 24107) that "the degree of substitution of the organics ranges from 28% (low NOx scenario) to 38% (high NOx scenario)". Typically the more substituted an organic compound, the more soluble. Ervens et al. (2008) find that total solubility for an organic gas phase inventory is higher for low VOC:NOx (i.e., high NOx) and a paper currently in ACPD open discussion by Saylor shows results consistent with Ervens. Can the authors explain what appear to be discrepancies?

Indeed Ervens et al., 2008 show a strong dependence of the dissolved organic carbon to the VOC:NOx ratio but this study does not link this behavior to the functionalization degree of the organic carbon. Comparison between both studies is therefore not straightforward. The method used here to estimate Henry's law constants (Raventos-Duran et al., 2010) ascribes to nitrate and PAN moieties a much smaller contribution to the solubility of a given compound than those ascribed to hydroperoxide and carboxylic acid moieties. It can be hypothesized that even if "high-Nox" secondary organic products are more functionalized, they bear functional groups (nitrates for example) that make them less soluble than the comparatively lesser substituted "low-NOx" secondary organic products which bear highly soluble moieties (mainly hydroperoxides). In other words, a difunctional species produced in high-NOx conditions is likely less soluble than a difunctional species produced in low-NOx conditions. The mean substitution degree of the organic carbon therefore increases with the NOx concentration (but not the total dissolved organic carbon which show the opposite trend).

Response to Reviewer #2:

> A primary concern is that the authors attempt to estimate SOA formation in the aqueous phase while neglecting aqueous-phase reactions. This simplification is particularly problematic in aerosol water. The results of this study are inconsistent with recent lab and modeling studies showing significant SOA formation in aerosol water, driven by aqueous phase processes that are either neglected or inadequately represented here (Volkamer 2007, Lim 2005, Tan 2010, Surratt 2010, Galloway 2009, McNeill 2012, etc.) Therefore, it is suggested that the authors tailor the language of the paper to highlight their analysis of VOC solubility, which is novel and interesting, and eliminate (or at least heavily qualify) the estimates of SOA formation as this model is incomplete in that regard.

As announced in the title of the paper and stated in the introduction (p24099, l1), the aim of the paper is to examine the water solubility of the secondary species produced during the multigenerational oxidation of a given hydrocarbon. Water solubility is certainly not the unique factor controlling SOA production and reactivity in the aqueous phase likely play a key role. However, condensed phase reactivity and therefore SOA formation mechanisms are beyond the scope of this paper. Again, this paper is devoted to the air/water phase partitioning of secondary organic species and we purposefully ignore aqueous phase processes beyond those affecting the effective Henry's law coefficient (i.e. hydration of carbonyls and dissociation of carboxylic acid). This has been clarified at the end of the introduction:

"This study is devoted to the production of water soluble compounds from the gaseous oxidation of long chain hydrocarbons of atmospheric interest and the sensitivity of this dissolution to NOx levels. A fully explicit chemical mechanism is used to describe the oxidation of organics in the gas phase and their mass transfer to the aqueous phase. Note that chemical evolution in the condensed phase is not represented in this modeling framework. Aqueous phase reactivity has been shown as a key process in the production of SOA (e.g. Ervens et al., 2011) and estimation of SOA yields is beyond of the scope of this study."

We also discuss the limitation of our aerosol representation in the results part, before 3.2:

"The simulated organic content for aqueous aerosol conditions remains small for the three parent compounds considered in this study. However, we emphasize that the same uptake parameters are here applied for clouds and aerosols. As the composition of the inorganic material on which the liquid phase deliquesces is not simulated in the model, the effect of dissolved ions such as sulfate or chloride on uptake parameters cannot be represented. Recent studies have shown that when aerosol water is not considered as a dilute solution and is modeled accordingly, SOA yields are higher than SOA yields from in-cloud oxidation (e.g. Ervens et al. 2011). This can arise from the effect of dissolved ions on equilibrium and uptake values (e.g. Ip et al., 2009) and from the effects of higher concentrations which allow the formation of higher molecular weight species (e.g. Ervens et al., 2011 and references therein). Our results show that under conditions typical of a deliquescent aerosol, SOA formation cannot be explained only by phase partitioning and aqueous phase processes have to be taken into account. Nevertheless, under cloud like conditions, the three precursors yield substantial amounts of condensed organic matter even if aqueous phase processes are ignored."

It is reminded in the conclusion as well : "For $L = 1 \times 10^{-12}$ (i.e. aerosols water), only a small fraction of the secondary organic carbon is influenced by the aqueous phase. Note that this small partitioning toward the aqueous phase might be offset by chemical sinks in the condensed phase which were ignored in our model configuration (e.g. Surratt et al., 2010; McNeill et al., 2012)."

> Line 21, Page 24096 - The authors state that "There is a lack of knowledge concerning the aqueous phase contribution to the atmospheric chemistry," and cite a review article from 1997. While it is fair to say that, compared to the gas phase, the role of the aqueous phase is less well-known, a great many scientific advances made on this topic since 1997, and a multitude of research and review articles published (including some that are cited later in this manuscript). In particular organic chemistry in the aqueous

phase has received a great deal of attention in the last ten years. Please cite some more recent papers and give a more accurate picture of the state of the field.

See our answer to Reviewer #1 on the same topic. We reworded that sentence and additional details about current advances in atmospheric aqueous phase organic chemistry are given in the introduction.

> Line 6, page 24098 – It is generally false to state that the rate constants of aqueous phase oxidation reactions are faster than the equivalent reaction taking place in the gas phase. In the gas phase the reactions are limited by diffusion of the reactants through the aqueous phase and this is reflected in the rate constant. There may be some scenarios in which the rate, not the rate constant, is faster due to relatively high concentrations of reactants - is this what the authors mean to say? Again, this segment doesn't do justice to the advances in aqueous organic chemistry that have been made in the last ten years – try citing some of the more recent review articles.

We agree the sentence is ambiguous and misleading. It has been modified as follows: "Resulting products are similar to those observed in the gas phase, but branching ratios substantially differ from the gas phase (e.g. Herrmann, 2003; Poulain et al., 2010)."

> Lines 15-25, Page 24098 - This discussion of aqueous-phase modeling efforts is missing the Rutgers model (Lim et al, ES&T 2005 and others) and GAMMA (McNeill et al., ES&T 2012) Section 2.1, 2.2

Lim et al., 2005 model is now mentioned. This paragraph mentions clouds chemistry, whereas McNeill et al., 2012 model focuses on aerosol chemistry. McNeill et al., 2012 has been cited in the conclusions of the paper.

> Line 7, Page 24100 - While the formation of gas-phase isoprene-derived epoxides and tetrol products has been considered in this study, other aqueous-phase reactions involving these species have been studied (Surratt 2007) Given that partitioning into the aerosol phase is expected to be relatively high (Chan 2010), their behavior and

reactivity should be considered if these epoxide species are expected to be generated through usage of this model. Furthermore, these reactions have been shown to be highly dependent on the acidity of the aerosol (Eddingsaas 2010). Given the formation of highly oxidized products in your predictions, do you expect aerosol-phase H+ activity to vary significantly over the course of this simulation in conditions with lower values of L? Does the author expect any deviations from the expected acid/base equilibria of carboxylic acids mentioned in section 2.2?

The formation of epoxides in the isoprene oxidation scheme was considered in this study as part of the necessary updating of the GECKO-A protocol. We assume here that the main evolution of these epoxides is a simple hydration to form diols (and possibly tetrols). As stated above, aqueous phase reactivity is beyond the scope of this particular study. However, the reviewer comment is very interesting and we will keep it in mind for our following studies about aqueous phase organic reactivity.

As is stated in the reply to the first reviewer, pH was set to a constant value in our simulations.

> Pages 24101-24102 - Please provide the accommodation coefficients, Henry's Law constants, and hydration constants, and any other pertinent information regarding aqueous-phase processes represented in the model, perhaps as Supplementary Information. Glyoxal has been seen to have lower observed values for its accommodation coefïňĄcient than the 0.05 proposed by the author. (Ip 2009). Furthermore, for cloud droplets, accommodation coefficients are usually seen to be closer to 0.01 (Schwartz, 1986). As the subsequent uptake to aqueous aerosol is highly dependent on this value, it is possible that signiïňĄcantly different levels of aerosol-phase SOA may be observed when changed.

The number of species considered in the aqueous phase exceed 2×10^5 species for the a-pinene oxidation scheme (see table 1, page 24120). Providing the properties of each species cannot be easily managed in a publication. As mentioned in text (page 24101 & 24102), the Henry's law coefficients and hydration constants were either estimated using the GROMHE group contribution method or taken in the database from Raventos-Duran et al. (2010).

Concerning mass accommodation coefficient, we refer to our answer to Reviewer #1 on the same topic.

> Lines 23-25, Page 24102 - It is unclear what is meant by ". . .the only sink for the dissolved organic matter is caused by the gas phase chemical pump that shifts the water/gas equilibrium."

There are no direct sinks for dissolved species in our model configuration, apart from offgasing. When phase equilibrium is achieved, oxidation of the species in the gas phase supersaturates the aqueous phase, ultimately leading to a net offgasing rate to sustain equilibrium. When gas phase compounds are oxidized, dissolution equilibriums are therefore shifted toward the offgasing of dissolved compounds. This chemical pump is a sink for dissolved organic compounds.

> Line 14, Page 24103 - If the solar zenith angle being used is representing mid-latitude conditions, why is the temperature fixed to 278K? This value doesn't seem consistent with the temperate conditions of FAME08, where other values are being drawn from. Is this a typo?

This is not a typo. The value of 278 K is arbitrary, as explained above in the reply to Reviewer #1. Note that we are not studying a ground level air parcel in particular. Using a ground level of 288 K (U.S. standard atmosphere), and using the usual adiabatic cooling rate in the troposphere $\beta = -6.5\text{Kkm}^{-1}$, we obtain $T \approx 278K$ for an altitude of about 1.5 km, i.e. about the typical boundary layer height. This is of course a rough estimate but not inconsistent with warm cloud physical conditions.

> Line 18, Page 24103 - What is the justification for "adding a constant OH source of 1e7 radicals/cm3/s"?

See the reply to Referee #1 about initial conditions.

> The author mentions that the value of L used here is one typical of deliquesced atmospheric aerosol but does not explicitly mention if or what these particles have any inorganic material acting as a seed that could deliquesce. Depending on their composition, the presence of inorganic species in these aerosols will have a profound effect on particle composition and subsequently its net pH and activity, potentially changing some of the equilibrium/uptake values being considered. Furthermore, at such low values of L this value, this value can reflect total water volume fraction or total liquid aerosol fraction, which will lead to different relative concentrations at lower RH's.

In our model configuration, we don't take into account the influence of organic compounds on deliquescence, pH or activity and L is a prescribed parameter. It should be noted that most of the results presented in the paper are about simulations ran for L = 3e-7. In this case, solution can be considered as dilute and the impact of activity on equilibria is weak. We are fully aware that the aqueous phase of an aerosol should not be considered as a dilute solution or an ideal mixture. As already mentioned in a previous answer, we clarify the limitations of our approach for deliquescent aerosols as follows:

"The simulated organic content for aqueous aerosol conditions remains small for the three parent compounds considered in this study. However, we emphasize that the same uptake parameters are here applied for clouds and aerosols. Recent studies have shown that when aerosol water is not considered as a dilute solution and is modeled accordingly, SOA yields are higher than SOA yields from in-cloud oxidation (e.g. Ervens et al. 2011). This can arise from the effect of dissolved ions on equilibrium and uptake values (e.g. Ip et al., 2009) and from the effects of higher concentrations which allow the formation of higher molecular weight species (e.g. Ervens et al., 2011 and references therein). As the composition of the inorganic material on which the liquid phase deliquesces is not simulated in the model, the effect of dissolved ions such as sulfate or chloride on uptake parameters cannot be represented. Our results show that under conditions typical of a deliquescent aerosol, SOA formation cannot be explained only by phase partitioning and aqueous phase processes have to be taken into account. Nevertheless, under cloud like conditions, the three precursors yield substantial amounts of condensed organic matter even if aqueous phase processes are ignored."

> Line 15, Page 24104 - It is not clear what τ means, as written. By lifetime of the parent hydrocarbon, does this term refer to the duration of time for C0 to reach some arbitrarily low value? The amount of time that the hydrocarbon spends in gas phase before uptake/reaction? It would be helpful to explain this term more explicitly.

Yes, τ is defined as the time needed for C_0 to reach C_0/e. We also refer to the answer to Reviewer #1 on the same topic.

> Lines 20-25, Page 24105 – It is not accurate to say that oxidized products of aliphatic hydrocarbons are ignored in existing models. CMAQ covers this type of chemistry to an extent in both gas and aerosol phases (Carlton 2010).

See the answer to Reviewer #1 on the same topic.

> Typo at Line 12, Page 24104 – "number of lifetimes N_τ " instead of "number of lifetime N_τ "

It has been corrected in the manuscript.

>Line 26, Page 24112 – Line 5, Page 24113 - It has been observed and predicted that non-oxidative aqueous reactions such as the previously mentioned epoxide-based substitution chemistry can also contribute a significant amount to aerosol mass. (McNeill 2012, Tan 2010, Chan 2010.) Under lower NOx conditions, where these species can have comparable or higher amounts of SOA mass contributions than aqueous radical chemistry, these mechanisms should be taken into account to achieve accurate prediction of SOA formation.

Tan et al., 2010; McNeill et al., 2012 study the SOA formation potential of aqueous phase processing isoprene oxidation products like glyoxal, methylglyoxal and epoxide-

like species. These rather short chain species are currently widely studied and have been shown to be significant SOA contributors (e.g. Ervens et al., 2011). As stated above, condensed phase chemistry in beyond the scope of our study devoted to the phase partitioning of secondary organic produced in the gas phase. Our study shows that, in addition to these short chain species, a significant fraction of long chain organic species produced during the progressive oxidation of hydrocarbons may also partition to aqueous phase, especially under cloudy conditions. As for the short chain species, these organic species are likely processed in the aqueous phase and may ultimately represent significant contributors to the condensed organic matter. We conclude that further works should also focus on long chain hydrocarbons.

> Typo on chart title – "3×10^{-7}" instead of "3×10^{7}"

It has been corrected in the manuscript.

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