

Dr. Camille Mouchel-Vallon

Dr Laurent Deguillaume

January 10, 2017

To whom it may concern,  
Geoscientific Model Development  
Copernicus Publications

Dear Sir, Madam,

You will find enclosed our revised version of the manuscript we submitted to Geoscientific Model Development. The article is entitled: *CLEPS 1.0: A New Protocol for Cloud Aqueous Phase Oxidation of VOC Mechanisms*, authored by C. Mouchel-Vallon, L. Deguillaume, A. Monod, H. Perroux, C. Rose, G. Ghigo, Y. Long, M. Leriche, B. Aumont, L. Patryl, P. Armand and N. Chaumerliac.

We provide a detailed point-by-point response to all referee comments and specify all changes in the revised manuscript. We hope our corrections on the manuscript will offer the possibility to publish our paper to GMD.

Sincerely,



Camille Mouchel-Vallon & Laurent Deguillaume



# Response to Anonymous Referee #1

We thank Anonymous Referee #1 for the interesting comments on our manuscript. All the individual comments are addressed below in bold.

## Main comments

### *1) Motivation of the current study*

*The intention of developing a ‘complete’ and ‘correct’ aqueous phase mechanism is clearly an ambitious and laudable project. However, it is clear that due to the lack of data many assumptions have to be made that should be better justified here. While such a mechanism can be used in a box model to assess chemical interactions in the multiphase system, it is impossible to track hundreds of species in a larger scale model. Therefore, I am missing a clearer direction on how this goal can be reached. For example, previous studies have suggested several strategies to reduce chemical mechanisms (Ervens et al., 2003; Ervens et al., 2008; Deguillaume et al., 2009; Woo and McNeill, 2015) for use in larger models. One way of reducing models is identifying the most important reactions and species. Such a discussion is missing here. – Instead as further directions it is suggested to include more species (succinic acid, tartronic acid).*

**Given that an almost complete MCM mechanism (4642 species and 13,566 reactions) has already been used in the CMAQ regional model (Ying and Li, 2011; Li et al., 2015), it is not technically impossible to implement the CLEPS mechanism coupled to MCM in a 3D model. However, the objective of this work is not to propose a chemical scheme for 3D models. Its goal is to provide a set of systematic rules to build nearly explicit mechanisms. In this scope, including more species is a way to test these rules and work toward their completeness. The matter of reducing chemical mechanisms to use them in large scale models is another (very complex) task. It is however not, in our opinion, in the scope of this paper.**

**The following was added to the conclusion to outline a use of CLEPS for developing reduced schemes:**

**“Several strategies can be used to build reduced multiphase mechanism. Explicit schemes like CLEPS can serve as a reference for the development of reduced chemical schemes like those proposed in Woo and McNeill (2015) or Deguillaume et al. (2009). Very few experimental data are available to validate reduced chemical scheme before implementation in 3D models, especially concerning cloud chemistry. Field measurements (van Pinxteren et al., 2015) and chamber experimental data (Bregonzio-Rozier et al., 2016) are available, but they do not cover the whole range of real atmospheric conditions that a large scale model can encounter. Using explicit modelling tools to serve as reference for a large set of environmental and chemical scenarios is therefore a possible solution to validate reduced multiphase chemical schemes for various environmental conditions. This is of course consistent only once the explicit mechanisms have been validated against the existing experimental data.”**

### *2) Similarities to CAPRAM*

*a) In the abstract and also later, it is claimed that ‘a new detailed aqueous phase mechanism . . . is proposed’. Given that all inorganic chemistry seems the same as other mechanisms (such as CAPRAM) and also all ‘overall’ rate constants are the same, I think this statement is highly exaggerated. I suggest marking in the reaction tables those processes and parameters that are new or different.*

**We don’t think it is highly exaggerated to claim that the mechanism is new. There are 207 inorganic reactions and 642 organic reactions. The inorganic reactions represent 24% of the full scheme. As the literature data is scarce on the subject, CLEPS and CAPRAM obviously share a lot of experimental data concerning inorganic chemistry and C<sub>1-2</sub> chemistry.**

**In our opinion, a detailed comparison of this mechanism with the CAPRAM mechanism is not in the scope of this paper. This work has been submitted to GMDD to present the new CLEPS mechanism and the associated detailed protocol rules. We are confident that having several detailed mechanisms available to the scientific community, based on different assumptions, can only be beneficial to better understand the processes governing aqueous phase chemistry. The confrontation between CLEPS and CAPRAM will be the subject of further studies to evaluate for instance the sensitivity of modelled cloud systems to the assumption used to build multiphase mechanisms.**

**The following have been added in different places in the paper to underline differences with CAPRAM:**

**Sect. 2: “This inorganic part of the mechanism is very similar to other available aqueous phase mechanisms. For example, the chemistry of transition metal ions includes Fe, Cu and Mn redox cycles also considered in the CAPRAM 2.4 mechanism (Ervens et al., 2003). Sulphur, nitrogen and H<sub>x</sub>O<sub>y</sub> systems are also relatively well documented (Herrmann et al., 2010). The CLEPS and CAPRAM mechanism generally consider similar reactivity for these chemical subsystems.”**

**Sect 3.1: “In this protocol, the hydration equilibria are differently considered from what is done in CAPRAM3.0 (Herrmann et al., 2005; Tilgner et al., 2013). In CAPRAM, hydration equilibria constants are documented as well as back and forward reactions rates when available. When no data are available, hydration constants from similar species are used.”**

**Sect. 3.2: “Our acidity constant estimates are similar to what is proposed in the other explicit aqueous phase chemistry mechanism such as CAPRAM. We systematized the procedure used in CAPRAM where unknown acidity constants are estimated from similar species.”**

**Sect. 3.3.3: “The SAR from Doussin and Monod (2013) was recently published. Therefore, Herrmann et al. (2005) and Tilgner et al. (2013) could not use this method to estimate rate constants and branching ratios. Instead, they rely on similarities when data are not available: for instance, they assume that the HO<sup>•</sup> addition rate constant on 2,3-dihydroxy-4-oxobutanoic acid is the same as maleic acid. In most cases, they assume that the reaction will proceed through the identified most probable pathway. In some cases, like for 2,4-butanedione, they attribute branching ratios from the equivalent measured gas phase reaction.”**

**Sect. 3.4.3: “Our approach for reactions with nitrate radicals is different than what has been proposed in previous aqueous phase mechanism, especially for estimating the branching ratios. We use similarity criteria to estimate the reaction rates whereas Herrmann et al. (2005) estimate these values using their own SAR (Herrmann and Zellner, 1998). They assume that the H-**

abstraction only occurs at the weakest C-H bond, which is determined from bond dissociation energies empirical estimates.”

Sect. 4.1: “In the CAPRAM mechanism (Ervens et al., 2003; Herrmann et al., 2005; Tilgner et al., 2013), the O<sub>2</sub>-addition step is explicitly introduced. This allows the direct treatment of the alkyl+alkyl vs. alkyl+O<sub>2</sub> competition that may occur in deliquesced particles. This is not in the objective of the present work and this consideration will also lead to the implementation in the mechanism of a lot of intermediate chemical species with short lifetime. It could be considered for future versions of the CLEPS mechanism.”

Sect. 4.5: “This treatment of peroxy and alkoxy radicals is an attempt at systematizing the approach that is also used in CAPRAM 3.0 (Herrmann et al., 2005; Tilgner et al., 2013). They also consider peroxy radicals recombination reactions using experimental data from Zegota et al. (1986), Schuchmann et al. (1985) and Poulain et al. (2010). Similarly to our mechanism, the possible cross-reactions are not considered. In the CAPRAM mechanism, alkoxy radicals can only be fragmented, with a very fast reaction rate following an analogy with gas phase values.”

Sect. 5.2: “The mass transcription description in this protocol differs from the coupling between RACM (Stockwell et al., 1997) and CAPRAM 3.0 that is proposed in Herrmann et al. (2005) and Tilgner et al. (2013). Because RACM is a reduced chemical scheme, gas phase species are lumped. Mass transfer therefore occurs between explicit aqueous phase species and fractions of lumped species. A delumping of RACM group compounds is included in the mechanism in the form of equilibrium reactions between the group compound and the standalone species. As an example, the “Ald” model species in RACM represents all gaseous aldehydes and is considered to be the source of dissolved acetaldehyde, propionaldehyde and butyraldehyde (Herrmann et al., 2005).”

The kinetic parameterization in our cloud chemistry model has been used for a long time (Jacob, 1986). The other cloud chemistry models almost always use experimentally measured Henry’s law constants. Ervens et al. (2003) proposed to estimate accommodation coefficient based on using a SAR to empirically estimate  $\Delta G_{\text{obs}}$ . As underlined by Ervens et al. (2003), this method should be used very carefully because the data needed to validate this method are very scarce. Future works could focus on (i) the sensitivity of the system to  $\alpha$  estimates and (ii) refining the SAR according to the more recent data reported in Davidovits et al. (2011).”

*b) It seems to me that several simplifications that have been tested in CAPRAM (Ervens et al., 2003) are repeated here – without the previous detailed sensitivity studies. Such simplifications include skipping the formation of peroxy radicals as an individual step (p. 9, l. 1-5), the self-recombination of peroxy radicals (p. 9, l. 10) and skipping of the tetroxide (p. 9-10). The previous work should be properly referenced here.*

**This has been addressed in the previous answer, in the added sentences to sect. 4.1 and 4.2.**

*c) How does the analysis of OH(aq) sinks and sources (p. 15, top) compare to previous studies such as CAPRAM (Herrmann et al., 2000; Ervens et al., 2003; Deguillaume et al., 2009; Tilgner et al., 2013)?*

**In Tilgner et al. (2013), HO<sup>•</sup> sources in cloud for a remote scenario similar to our simulation are dominated by direct uptake from the gas phase, by the Fenton type reactions and by the**

photolysis of  $\text{H}_2\text{O}_2$  and  $\text{Fe(III)}$ . Sinks are dominated by reactions with organic compounds, especially formate, hydrated formaldehyde, glycolaldehyde and methylglyoxal.

The following was added in the corresponding paragraph:

“However, in the first hours of the cloud event, mass transfer is the major source of  $\text{HO}^\bullet$ , like it was predicted in a previous modeling study on a shorter cloud event considering a remote chemical scenario (Tilgner et al., 2013). Fenton type reactions and photolysis reaction are also significant sources of  $\text{HO}^\bullet$  in their simulation.” and “Tilgner et al. (2013) also show that  $\text{HO}^\bullet$  only aqueous sinks are reactions with organic matter, especially carbonyl compounds such as hydrated formaldehyde, glycolaldehyde and methylglyoxal.”

*d) How does the modeled evolution of the O/C ratio compare to the trends as shown by (Schrödner et al., 2014)? Can the differences be ascribed to the more complex formulation of the branching ratios of the organic reactions?*

The O/C trends shown in Schrödner et al. (2014) have been calculated for organic aerosol (figure 10 in the article). They have shown higher values than those modelled in our work for the O/C ratio in the aqueous phase. For instance in their simulated clouds, modelled O/C ratios reach 1.7 after 48h in the rural cases, while in our simulations O/C ratios reach 1.1 values after 12h. This difference might be ascribed to higher reactive organic mass and lower  $\text{HO}^\bullet$  concentrations considered in our model. For instance, our test case considering DOC reactivity increases the reactive organic mass from approx.  $5 \mu\text{g m}^{-3}$  to approx.  $20 \mu\text{g m}^{-3}$ . This has the effect of reducing  $\text{HO}^\bullet$  concentration and O/C ratios. In Schrödner et al. (2014) simulations, organic mass reaches  $3.1 \mu\text{g m}^{-3}$  in the lower cloud, which can be the reason why they model higher O/C ratios. This is highly hypothetical, as the modelling setup and studied scenarios in Schrödner et al. (2014) are strongly different from the model runs in this work. To our opinion, we don't believe that mentioning this comparison is pertinent in this paper.

### *3) Basis of assumptions*

#### *a) Assumptions on equilibria (hydration, dissociation, gas/aqueous partitioning)*

*In Sections 3.1, 3.2 and 5.2, it is explained how unknown equilibrium constants are estimated. While it is clearly necessary to estimate such parameters due to the lack of their availability, it should be shown (i) the validity of these assumptions, (ii) a comparison of the estimated parameters to (the few) known parameters and (iii) which assumptions have been made in other aqueous phase mechanisms and whether these assumptions are less appropriate.*

Hydration equilibrium constants estimated with the GROMHE method have been evaluated in Raventos-Duran et al. (2010). Our modification concerning carboxylate ions is already discussed in Sect. 3.1 and in Fig. 1. We acknowledge that our estimates of acidity constants are a simple first approach. Further work should look into the validity of our assumptions on this subject, for example considering the work of Perrin et al. (1981). For all these assumptions, sensitivity studies should be carried out to check if our approximations need to be refined or not. In our opinion, this work is not in the scope of this paper.

Please refer to our answer to comment 2a) for comparison to the assumptions made in the CAPRAM mechanism.

*b) I understand that a completely consistent coupling of MCM and the aqueous phase mechanism is difficult. However, the fact that numerous species do not have a gas or aqueous phase equivalent, respectively (p. 11, Section 5.1) introduces an unnecessary inconsistency. In my opinion, it would be more consistent to introduce a solubility threshold (Henry's law constant) that determines where a species should reside.*

**The following has been added to sect. 5.1 to clarify our proposed solution for this inconsistency.**

**“For each species with no equivalent in the other phase, we create an artificial equivalent in the other phase for which no reactivity is described. The mass transfer parameters are estimated as described below (section 5.2) to accurately determine in which phase the species should reside.”**

*c) How well do calculated Henry's law constants based on GROMHE SAR compare to measured values? Can you refer to some comparison in a previous study or show it here (possibly in supplemental information)?*

**The calculated Henry's law constants based on GROMHE SAR have been thoroughly evaluated in Raventos-Duran et al. (2010). The following sentences have been added in sect. 5.2 for more consistency:**

**“Comparing this SAR with other available methods (Meyland and Howard, 2000; Hilal et al., 2008) Raventos-Duran et al. (2010) have shown that GROMHE is the more reliable SAR in general, estimating Henry's law constants with a root mean square error of 0.38 log units (approx. a factor of two). It particularly shows better performances than the other tested methods for the more soluble species, i.e. highly oxygenated, multifunctional organic species.”**

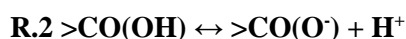
*4) Inconsistencies in the presented mechanism*

*a) Dissociation equilibria*

*- In Eq. 4, the resulting  $K_A$  constant should be dimensionless. In the Equilibria table in the supplemental information, data are given in M (according to literature). The unit is missing in this table and therefore it is very confusing and leads to a bias of a factor 18 (molecular weight of water) in all dissociation constants. How have the numbers in the table been used in the model?*

*- Later in the manuscript (p. 12, l. 28), it is stated that the equilibria are split into forward and back reaction. What values are used? How were they derived?*

**The units have been clarified in the tables:  $K_A$  values are in M and  $K_h$  values are dimensionless. Eq. 4 and R.2 have been rewritten to match the data.**



$$\text{Eq 4. } K_A = \frac{[>\text{CO}(\text{O}^-)][\text{H}^+]}{[>\text{CO}(\text{OH})]}$$

**In the model, equilibrium constants are used to derive back and forward reactions, based on the assumption that the equilibria are quasi-instantaneous. The forward rate constant  $k_f$  [ $\text{s}^{-1}$ ] is assumed to be very fast, with for instance:**

$$k_f = 10^6 \text{ s}^{-1}$$

**To reach equilibrium, the backward rate constant must then be:**

$$k_b = k_f/K_A$$

Because  $k_f$  is considered to be fast, implementing equilibria in this way yields the same results as implementing a total species approach which assume that equilibria are instantaneous. In this work, we provide equilibrium constants, and the implementation details should vary from a boxmodel to another. Future work should be carried out to study the sensitivity of the system to the chosen  $k_f$ . Known acid dissociation rate constants are in the range of  $10^6$ - $10^8$   $s^{-1}$  (see for example the constant listed in CAPRAM 2.4; Ervens et al., 2003). For such high rate constants, the choice of  $k_f$  shouldn't be sensitive. This is bigger issue for hydration which is known to be slower and pH dependent (see for instance the discussion in Doussin and Monod, 2013).

*b) Table 2 I do not understand the third example in Table 2. The 'global rate constant' is given as  $3.2e8$   $M^{-1} s^{-1}$ ; however, all rate constants for the various branching pathways exceed this number and yield a value that is an order of magnitude greater. Is this just a typo or were these (and possibly other?) rate constants used like this used in the model?*

**In the given example,  $k_1 = 8.1 \times 10^7$   $M^{-1} s^{-1}$ ,  $k_2 = 6.1 \times 10^7$   $M^{-1} s^{-1}$ ,  $k_3 = 8.5 \times 10^7$   $M^{-1} s^{-1}$ ,  $k_4 = 9.2 \times 10^7$   $M^{-1} s^{-1}$  :  $k_1 + k_2 + k_3 + k_4 = 3.2 \times 10^8$   $M^{-1} s^{-1}$ . Therefore, the  $3.2 \times 10^8$   $M^{-1} s^{-1}$  value is not a typo. However, there is a real typo in the table for the final estimated global reaction rate ( $3.2 \times 10^9$  instead of  $3.2 \times 10^8$ ) of the same species. We suppressed this mistake in the manuscript.**

#### *5) Discussion of results*

*a) Length of cloud In several previous model studies, it has been discussed in detail that cloud processing time is on a time scale on the order of a few minutes or at most an hour as it is restricted by the lifetime of a droplet (e.g., Feingold and Kreidenweis, 2002; Ervens et al., 2004; Tilgner et al., 2013). Therefore, the conclusions of the aqueous phase on the oxidation capacity of the atmosphere should be revised and related to more atmospherically relevant conditions.*

**We are aware that our simulation is performed using rough microphysical cloud properties (constant LWC and radius) over a long cloud period. Our simulation was performed without considering microphysical processes that are needed to conduct realistic cloud simulations. These processes are included in a module which is about to be completed and the results of more realistic cloud simulations should be submitted soon to GMDD. In this work we use a permanent cloud because our primary goal is to verify that our mechanisms have an effect on the air-water system. In this work, we are able to show that our mechanism effects are visible for long term simulations. Moreover, we have analysed the detailed budget (sinks and sources) of chemical species and we also clearly show that cloud chemical reactivity is highly variable over time and that chemical species concentrations can vary significantly over short time scale (few minutes).**

**This was added in Sect. 6.1 to clarify this point: "This is a permanent cloud simulation and no attempt is made to represent a specific documented cloudy situation. The objective is to test the multiphase mechanism over a long time scale to check that the mechanism is (i) working as intended and (ii) producing chemical effects in both phases. Testing the model over 12h is a first step to evaluate the impacts (or their absence) of detailed organic chemistry on multiphase cloud chemistry. Future studies will use variable environmental conditions that require the consideration of microphysical processes with our multiphase chemical module."**

**Following this general comment, the conclusion was modified with the following sentences: "These simulations were conducted for a long non-realistic permanent cloud. However, the**

mentioned results are atmospherically relevant, since the impact on O/C ratio and fragmentation can be observed in the first moments of the simulated cloud event.”

*b) OH profiles: Several previous studies have shown that the OH concentration in the gas phase is substantially reduced in the presence of clouds (Herrmann et al., 2000; Ervens et al., 2003; Tilgner et al., 2013). The current mechanism shows a doubling of OH(gas) during cloud. Admittedly, the initial conditions were slightly different than in the CAPRAM simulations. However, given the robustness of the previous results for various scenarios, the differences of the current study to previous ones should be discussed.*

**This is now added in the discussion of Fig. 3a&3b in Sect. 6.3:**

**“This trend in HO<sup>•</sup> mixing ratios contradicts previous modeling results (Herrmann et al., 2000; Barth et al., 2003; Ervens et al., 2003; Tilgner et al., 2013) which exhibit a decrease in HO<sup>•</sup> mixing ratios during cloud events. The chosen chemical scenario might be the reason for this difference. Even if the chemical scenario in our study is rather similar to the one in Ervens et al. (2003), we still differ in the amount of emitted organic compounds. In our test simulations, we mainly emit isoprene, with a small contribution of formaldehyde and acetaldehyde, whereas Ervens et al. (2003) emit a larger range of hydrocarbons of anthropogenic (alkanes, alkenes, aromatics) and biogenic origin (limonene,  $\alpha$ -pinene). As far as we understand the CAPRAM model setup, these hydrocarbons are not dissolved and it should be noted that they are highly reactive with HO<sup>•</sup>. This means that the large, and certainly major, sink of gaseous HO<sup>•</sup> caused by hydrocarbons reactivity is always present, even under cloud conditions. When the source of HO<sup>•</sup> radicals is reduced by the cloud event (e.g. due to HO<sub>2</sub> and NO separation), HO<sup>•</sup> radicals sinks are not significantly perturbed and HO<sup>•</sup> steady state mixing ratios decrease. Conversely, in our simulation the gaseous HO<sup>•</sup> sink is more significantly perturbed by the cloud event because most of the organic matter in our scenario is produced from isoprene oxidation and is readily soluble. In our case, it seems that the HO<sup>•</sup> gaseous source reduction is overcompensated by the reduction in HO<sup>•</sup> gaseous sinks. As a consequence, HO<sup>•</sup> steady state mixing ratios are higher during cloud events. This hypothesis especially highlights how the chosen chemical scenario and regime is important for simulation results and conclusions. Future work should therefore systematically explore cloud simulations under a large range of scenarios.”**

*c) How do the differences between the three scenarios in Fig. 3b compare to previous model studies? Can possible differences be ascribed to the new organic pathways?*

**The production of acids and destruction of carbonyl species in the gas phase *via* aqueous phase reactivity is similar to what has been shown in Tilgner et al. (2010) on smaller timescales. Differences in isoprene can be linked back to the reasons invoked in the previous answer.**

*6) Previous literature on aqueous phase chemistry*

*- p. 2, l. 12: In previous literature (Herrmann et al., 2015, and references therein) it is discussed that the presence of an aqueous phase (cloud) leads to the separation of the soluble HO<sub>2</sub> and the rather insoluble NO in the gas phase. Since their reaction is suppressed, less OH is formed. Therefore, it is not radical chemistry in the aqueous phase but different pathway strengths in the gas phase that lead to differences in OH during cloud.*

**This is noted and corrected.**



- p. 2, l. 3: *The statement that photolysis rates are 'highly enhanced in clouds' is not always true. While in thin clouds, photolysis rates are enhanced, in dense cloud they might be reduced (cf e.g. Fig. 2 in Ervens, 2015).*

**In this particular sentence, we are referring to photolysis inside cloud droplets and not inside interstitial air. It seems to us that the general consensus is that, depending on the position of a droplet in the cloud, the photolysis rates will be enhanced or reduced. However, theoretical calculations from Ruggaber et al. (1997) have shown that on average, actinic fluxes are indeed enhanced in cloud droplets.**

- p. 3, l. 5: *In the cited paper (Ervens et al., 2015) it is discussed that oligomerization of MACR and MVK is rather unimportant in the atmosphere because of the low solubility of these precursors.*

**We indeed overlooked the discussion about salting-out effects. The following sentence has been added: “Ervens et al. (2015) however argued in a modeling study that MVK and MACR solubility could be decreased by salting out effects, reducing their contributions to aqueous reactivity and SOA formation.”**

- p. 6, l. 30: *How well does the product distribution estimated here matches the detailed laboratory study (Perri et al., 2009)?*

**Perri et al. (2009) show that glyoxal, formic acid, glyoxylic acid, glycolic acid, oxalic acid, malonic acid and succinic acid could be formed from HO<sup>•</sup> oxidation of glycolaldehyde. In our mechanism, HO<sup>•</sup> oxidation of glycolaldehyde directly produces glyoxylic acid, glyoxal, formic acid and formaldehyde. Oxalic acid is not a first generation product of the oxidation of glycolaldehyde, but it can be formed indirectly from the oxidation of glyoxal and glyoxylic acid. Accretion reactions are not included in our protocol but could be responsible for the production of succinic and malonic acids. However, it should be noted that Perri et al. (2009) experiments were carried out at glycolaldehyde concentrations 1000 times higher than typical clouds levels, which could favour the formation of heavier weight species.**

- p. 8, Section 3.6: *Results of a recent key paper on aqueous photolysis should be discussed here (Epstein et al., 2013).*

**We added the following in Sect. 3.6:**

**“Epstein et al. (2013) have shown that aqueous photolysis quantum yields are highly dependent on the type of molecule. Using similarity criteria to estimate photolysis rates in the aqueous phase may be too error prone. Furthermore their estimates also show that photolysis would efficiently compete with HO<sup>•</sup> oxidation for very few of photolabile species. If more data and reliable SAR become available on this subject, a mechanism generated using the present protocol would be the ideal tool to expand on Epstein et al. (2013) study.”**

- p. 8, l. 34-36: *In the study by Ervens et al., 2015 it is stated “Unlike in laboratory experiments, atmospheric aqueous aerosol particles can be considered saturated with oxygen (~270 μM) due to their large surface–volume ratio. In all our model sensitivity studies with the multiphase model, the oxygen concentration reached saturation level after a few seconds.” – which is not clearly reflected in the text in the current manuscript.*

In the same paragraph, the sentence “In our mechanism, which is characterised by dilute conditions, dissolved oxygen is assumed to be always available (see Ervens et al., 2015) and alkyl radicals are too dilute to react with themselves.” has been replaced with:

**“In their bulk aqueous phase modeling study, Ervens et al. (2015) have shown that the aqueous phase under laboratory experiment conditions is not saturated with oxygen, leading to possible oligomerization. Their sensitivity studies however show that oxygen reached saturation in few seconds for atmospheric deliquescent particles, likely because of a large surface to volume ratio. We follow the same hypothesis for cloud droplets.”**

*- p. 14, l. 37ff: A lower OH concentration will not only lead to lower formation rates of these acids but also to lower destruction rates (Ervens et al., 2014). Therefore the role of OH for the total organic acid levels depends on the ratio of  $k(\text{formation})/k(\text{destruction})$ , which, in turn, might be a function of pH. This should be mentioned here.*

**This point is really interesting. However, our results show that pH doesn't change with added DOC. Therefore, differences in acids concentrations cannot be ascribed to asymmetrical reactivity between acids and corresponding bases. The only other possibility that we can think of are “fixed” sinks and sources not dependent on OH concentrations, *i.e.* photolysis and mass transfer.**

**This is now mentioned in Sect. 6.3.**

**“Because sinks and sources of acids due to HO<sup>•</sup> radicals should vary in equal proportions, the decrease in organic acids concentrations cannot be ascribed to reactivity with HO<sup>•</sup> radicals. We therefore has to consider fixed sinks that do not depend on HO<sup>•</sup> concentrations, *i.e.* photolysis and phase transfer. If we consider that acids reach pseudo steady state concentrations, we can assume that because photolysis and phase transfer are not modified by the additional DOC, some acids concentrations could decrease following their overall sources/sinks ratio.”.**

## Technical and minor comments

*p. 5, l. 21: ‘Rate constants’*

**Done.**

*p. 7, l. 24; p. 8, l. 14, and some other places in the manuscript: ‘Reaction rates’ are defined as the product of a rate constant and reactant concentration(s). It should be ‘rate constant’.*

**Done.**

*p. 10, l. 28: Give a reference for this concentration.*

**This concentration comes from our simulated peroxy radicals concentrations. The sentence has been replaced by the following: “In our simulation (see Section 6) the high range of concentrations for peroxy radicals is around  $10^{-10}$  M for the peroxy radical derived from glyoxal; tetroxide formation therefore occurs on a timescale of approximately 50 s.”**

*p. 15, l. 26: Which acids are included in ‘total acids’? Do they include formic and acetic acid?*

**‘Total acids’ include formic and acetic acids. It has been clarified in the text.**

*Table 1: The references below the table should be added to the main reference list and not listed here.*

**Done.**

*Table 4: What parameter does the footnote (b) refer to?*

**This footnote comes from a previous version of the paper. It is not used anymore and has been removed.**

*Figure 2, caption: ‘Relative’ should be replace by ‘related’*

**Done.**

*Fig. 3 and 4: Add in the caption that the red line is hidden by the blue one or even choose different line types (e.g., dotted vs solid)*

**Done.**

*Fig. 5: Clarify the caption: ‘10 most important species’ in terms of what?*

**This has been clarified. These species are the most important in terms of concentrations in the aqueous phase.**

## References

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## Response to Anonymous Referee #2

**We thank Anonymous Referee #2 for the interesting comments on our manuscript. All the individual comments are addressed below.**

*This paper introduces a new protocol for developing a detailed aqueous chemistry mechanism. It emphasizes oxidation by OH, NO<sub>3</sub>, and other oxidants in low NO<sub>x</sub> and dilute conditions, and does not include accretion processes. The detailed aqueous chemistry mechanism, coupled with the Master Chemical Mechanism (MCM v.3.3.1), is applied to an ideal cloud situation to examine the behavior of the chemistry.*

*This is an exciting, new advancement for our understanding of aqueous chemistry, especially for the oxidation of organic compounds dissolved in cloud water. The paper is fairly well written, although several spots need to be clarified. The paper can be improved by providing more information on the test case, giving more discussion on how the mechanism and results compare to previous studies (with and without detailed aqueous chemistry), and cleaning up the presentation of the paper. My suggestions of needed clarifications are given below.*

### Specific Comments

*1. Page 6, line 25 and Table 2. It is not completely clear to me what criteria are used to proceed with the reduction scheme. For example, why is a branch with a 19% contribution to the reaction removed? Is it simply because the other 3 pathways represent >75% of the global reaction rate? It seems that pathways that comprise 10% or less of the reaction rate can be ignored without much impact on the overall reaction scheme. What kind of impact occurs when the pathway contribution is larger, such as the 19% for the third example in Table 2?*

**The criteria used to reduce the size of the chemical mechanism have been chosen to consider the main chemical pathways and to avoid the consideration of negligible products. The example chosen to illustrate the reduction strategy in the paper is interesting because for 2-hydroxy, 3-oxobutanoate, the four available pathways are almost equiprobable. However, this is a really rare case. For most of the reactions described in the mechanism, we only neglect 10 to 15% of the total species reactivity (see footnotes in the mechanism tables - supplementary material). We believe that the impact of this reduction strategy can only be properly assessed with automatically generated chemical mechanisms (Aumont et al., 2005; Mouchel-Vallon et al., 2013).**

*2. Section 5. How does the CLEPS mechanism compare to previous aqueous chemistry studies (e.g. CAPRAM)?*

**This part of the paper deals with the coupling of CLEPS with a gas phase explicit mechanism. We refer the reviewer to our answer to Reviewer 1's comment 2a, specifically our amendments to part 5.2 discussing the difference in constructing the mass transfer coupling between our protocol and CAPRAM.**

*3. Page 13, line 10. While Rosenbrock solvers have become commonplace in chemistry transport models, other solver techniques also adequately solve the gas-aqueous chemistry mechanism (e.g., Ervens et al., 2003, JGR; Barth et al., 2003, JGR; McNeill et al., 2012, ES&T).*

**We agree with the reviewer's comment. We modified the sentence as follows: "Differential equations are solved with a Rosenbrock solver which has been shown to be a reliable numerical method for stiff ODE systems involved in modelling multiphase chemistry".**

*4. Page 13, line 12. Please restate the objective of section 6. The introduction says that "the box model is tested for an ideal cloud situation", which implies some kind of evaluation. However, there is no evaluation of the model results provided and there is only one instance of a comparison with previous modeling work (page 14, line 30).*

*As a follow up to the previous comment, please include more discussion in Section 6 of how the model results in this paper compare to previous ones, e.g. McNeill et al., 2012; Tilgner et al., 2013; Herrmann et al., 2005 – which can hopefully be directly compared due to their similarity of the test case conditions, and also Lelieveld and Crutzen, 1991; Jiang et al., 1997; Barth et al., 2003; Ervens et al., 2008, and Tilgner et al., 2010.*

**We understand the reviewer's concern about comparisons between CLEPS and previous mechanisms. Differences in chosen physical and chemical scenarios make this exercise particularly perilous. On this subject, see for instance our answer to Reviewer 1 comment 5b. We believe that specific inter-comparison studies should be run to properly evaluate and compare existing mechanisms. This will be done in the future. However, this is not the scope of this particular paper. This paper aims at describing and presenting a detailed systematic protocol for aqueous phase oxidation. Hence, the mechanism might be viewed as the “main result” of this work.**

**Nevertheless, qualitative comparisons with simulations from existing mechanism are addressed to some extent in our answers to Reviewer 1 comments 2b, 2c and in our new additions to Sect. 6.3., where some of our model outputs are compared to previous modelling studies using CAPRAM mechanism.**

*6. Section 6.1. More information about the case needs to be included. Specifically, the latitude, longitude, altitude, and size of the drops. Later in the discussion of the results, “sunset” is often used but what time is sunset?*

**This is noted and has been indicated in Sect. 6.1:**

**“The simulation is located at the sea level and the coordinates used to calculate actinic fluxes are 45.77°N 2.96°E.”**

**Sunset time (6:45pm) is now included in Sect. 6.1.**

*7. Section 6. I realize that the test case is an example. However, air parcels do not spend 12 hours in a cloud. Vertical motions maintain a cloud by moving air above its lifting condensation level. Thus, air parcels are constantly being transported into the cloud region (and out), and residence times are on the order of 10 minutes to 60 minutes. I suggest adding a statement commenting on this caveat. It is important because the results from this test case show that after a few hours aqueous chemistry controls the concentration of a dissolved trace gas, but in reality that air parcel is not in the cloud after a few hours.*

**Reviewer 1 raised the same issue. We hope to have addressed it in our answer to Reviewer 1 comment 5a) and in the related modifications to the conclusion and sect. 6.1.**

*8. Page 14, line 1. The isoprene diurnal profile is not realistic. It is explained by the gas-phase chemistry. Another factor is that the isoprene emissions are constant with time, while in reality they vary diurnally. Please discuss this factor in the paper.*

**This problem has been addressed in Sect. 6.2: “The resulting isoprene diurnal profile is not realistic, as in the atmosphere the isoprene diurnal profile is constrained by the diurnal variation of both its emissions and level of oxidants.”**

*9. Page 14, lines 9-12. I agree with the explanation of the H<sub>2</sub>O<sub>2</sub> time evolution. In addition, SO<sub>2</sub> concentrations must be depleted in order for H<sub>2</sub>O<sub>2</sub> concentrations to increase. Otherwise H<sub>2</sub>O<sub>2</sub> would continue to be consumed by SO<sub>2</sub>. Further, it is worth noting the time scales with respect to how long an air parcel actually spends inside a cloud.*

**In the simulations, sulphur is indeed quickly depleted. The end of the first paragraph of Sect. 6.3 has been modified as follows: “H<sub>2</sub>O<sub>2</sub> is a soluble species highly reactive with SO<sub>2</sub>, which explains the initial dip in its mixing ratio. After SO<sub>2</sub> is entirely depleted (not shown), the aqueous production of H<sub>2</sub>O<sub>2</sub> is responsible for its subsequent higher gaseous levels.”**

*10. Page 15, lines 16-19. How long does it take for aqueous-phase glyoxal concentrations to change from being controlled by mass transfer to being controlled by aqueous chemistry? Should we expect*

*to see this in observations of clouds in the atmosphere where the air parcel residence time in cloud may be shorter?*

Our detailed analysis of production/destruction fluxes of aqueous glyoxal (not shown) shows that dissolution of gaseous glyoxal dominates aqueous glyoxal production at the start of the cloud event. After approx. 10 minutes, aqueous phase chemistry becomes the main source of glyoxal. It is difficult to conclude if this could be observed under natural conditions. It depends on droplet lifetime and air parcel residence time. Sensitivity studies are needed to further address this issue.

*11. Page 15, lines 22-23. The comment about acetic and formic acid concentrations is interesting, but I did not see these values plotted. Could they be included in the figure (or at least report the concentrations)?*

We add in the text the reference to Deguillaume et al. (2014) that reports the mean concentrations of formic acid and acetic acid in cloud aqueous phase at the puy de Dôme station for the last ten years. In their classification for non-polluted conditions, the concentration of formic acid is on average equal to 6.3  $\mu\text{M}$  (range : 0.8-29  $\mu\text{M}$ ) in comparison to the 4  $\mu\text{M}$  of formic acid simulated by our model. The concentration of acetic acid is on average equal to 4.9  $\mu\text{M}$  (range : 0-23  $\mu\text{M}$ ) in comparison to the 1.5  $\mu\text{M}$  of acetic acid simulated by our model.

*12. Page 15-16. I did not completely understand the importance of dissolved organic carbon (DOC) and its role in the aqueous chemistry. Could more background information be provided?*

This importance of DOC as an  $\text{HO}^\bullet$  scavenger has been for instance discussed by Arakaki et al. (2013). It arises from the observation that cloud sampling field studies are able to identify only a few percent of the total Dissolved Organic Content (Deguillaume et al., 2014; Herckes et al., 2013). Most aqueous phase mechanisms, including CLEPS, only describe the reactivity of this known minor fraction. What is called DOC is the major constituent of dissolved organic matter, for which very little is known. Using experimental data, especially total  $\text{HO}^\bullet$  reactivity measurement, Arakaki et al. (2013) were able to propose an average  $\text{DOC} + \text{HO}^\bullet$  rate constant. We are able to reproduce a similar behaviour in our model. Because the reactivity of most species dissolved from MCM is not described in CLEPS, a large amount of the modeled dissolved organic content is not reacting toward  $\text{HO}^\bullet$  in the aqueous phase. The “with DOC” version of the simulations addresses this by assuming that the unreactive content of the aqueous phase reacts with  $\text{HO}^\bullet$  with an average  $\text{DOC} + \text{HO}^\bullet$  rate constant suggested by Arakaki et al. (2013).

*13. The supplementary material shows the pH values for the simulation. The pH seems to be quite low (3-3.5). Could the authors explain why such a low pH occurs? Are the results similar to previous simulations of this case?*

The simulated pH value is rather low but in the order of magnitude than was observed in other cloud chemistry model for remote conditions. For instance, Herrmann et al. (2005) and Deguillaume et al. (2004) for permanent cloud simulations showed values between 3 and 4. We are aware that this is not explained in the paper. This pH results from the balance between the production of strong inorganic acids (mainly sulfuric acid in our simulation) and the production of weak organic acids. Low pH values can therefore arise from (i) a lack of weak acids compared to other modelling results or (ii) an overestimation of acidity constants for organic acids.

## Technical Comments

*1. Page 1, line 20.  $\rightarrow$  multiphase*

**Done.**

*2. Page 1, line 34. “GROMHE” is not defined. Is it needed in the abstract?*

**It is now defined in the text.**

3. Page 1, line 38. → *The photolysis rates in both phases ....*

**Done.**

4. Page 1, line 39. *The word “evaluate” is not what is done in the paper.*

**We replace “evaluate” by “test”.**

5. Page 2, line 33. *Please quantify what is meant by “low-NO<sub>x</sub>” and “dilute”.*

**This has been clarified for low-NO<sub>x</sub> conditions. The “dilute” part is discussed in details in the revised version of Sect. 4.1.**

6. Section 2. *Please cite the supplementary material listing the chemical mechanism and chemical species. This supplementary material is a good resource for researchers.*

**Done.**

7. Page 3, Line 6. *Please quantify “significantly soluble and highly reactive”. For example, I would suggest saying that their Henry’s Law coefficient is greater than a specific value.*

**This formulation is indeed vague and not always true. For instance, MVK and MACR have low solubility ( $H_{\text{MVK}} \approx 1\text{e}^{-2} \text{ M atm}^{-1}$  and  $H_{\text{MACR}} \approx 1\text{e}^{-1} \text{ M atm}^{-1}$ ). They are however highly reactive in the aqueous phase due to their double bonds and abundant enough in the gas phase to constitute a significant source of oxygenated compounds in the aqueous phase, *via* dissolution and reactivity.**

**This sentence has been modified as follows: “For instance methylglyoxal (MGLY), glyoxal (GLY), acrolein (ACR), methacrolein (MACR) and methylvinylketone (MVK) are significantly soluble (Henry’s law constant  $> 10^3 \text{ M atm}^{-1}$ ) and/or highly reactive in the aqueous phase (Ervens and Volkamer, 2010; Lim et al., 2010, 2013; Liu et al., 2009, 2012).”**

8. Page 3, line 28. *Please add information on what kind of “data are available”. I assume that Henry’s Law coefficients and reaction rates are meant, but this needs to be clear.*

**Done.**

9. Page 3, line 31. *Define “GROMHE”.*

**Done.**

10. Page 5, line 23. *Could a couple of sentences be added to explain “global reaction rate constants”?*

**“global” reaction rate constants is used in opposition to partial reaction rate constants (*i.e.* site specific). This is a confusing formulation. The sentence has been replaced with: “When rate constants of organic compounds reactions with HO $\cdot$  are available (see the review from Herrmann et al., 2010), they are used in the mechanism.”**

11. Page 6, line 22. → *Such a large set of species*

**Done.**

12. Page 6, line 23. *It seems that this paragraph should be part of the previous paragraph.*

**Done.**

13. Page 8, line 14. → *Although these reaction rates*

**Done.**

14. Page 9, line 19. *Add that the process is explained below this paragraph.*

**Done.**

15. Page 11, line 20. → *The last reaction*

**Done.**



16. Page 12, line 13. *Lelieveld and Crutzen (1991) adopted an accommodation coefficient value of 0.05 for soluble gases in which the accommodation coefficient was not known. Perhaps this reference began this practice and should be cited.*

**We added the reference from Lelieveld and Crutzen (1991).**

17. Page 13, line 20. *→ simulation has been run for 31 days. What is the purpose of a 31-day gas chemistry spin up?*

**The purpose of a gas chemistry spin up is to obtain a diurnal steady state representative of the chose scenario. The duration of this spin up only has to be long enough to reach the pseudo steady state. It has been arbitrarily set to 31 days but it could have been shorter, as the steady state is reached after approx. 20 days.**

18. Page 14, line 2. *A sentence should be added to say something about the isoprene products diurnal profiles.*

**The following has been added at the end of Sect 6.2: “The first oxidation products from isoprene (MACR, MVK) follow the same time profile as isoprene. The mixing ratios of other oxidation products vary also temporally depending on their production/destruction rates. For example, MGLY, GLY and glycolaldehyde mixing ratios decrease initially due to their oxidation by HO<sup>•</sup> and then increase strongly due to their production by the oxidation of isoprene.”**

19. Page 14, line 16. *When is sunset?*

**In our simulation, the sunset corresponds to 6:45 PM. It has been added in the manuscript.**

20. Page 14, line 22. *→ is also responsible*

**Done.**

21. Page 14, lines 23-27. *I suggest discussing the “with DOC” results together with the last paragraph on the page. That is, organize the discussion of Figures 3 and 4 to present “without DOC” results first, and then discuss “with DOC” results presented in Figures 3 and 4.*

**We respectfully disagree with this suggestion. The behaviour described for the “without DOC” simulation can often be highlighted with comparison to the “with DOC” simulation. In our opinion, it makes more sense to discuss these two simulations together, rather than separately.**

22. Page 14, line 32. *When is nighttime?*

**Nighttime corresponds to the time period from 6:45 PM et 12:00 PM. This has been added in the text.**

23. Page 15, line 7. *→ in terms of concentrations*

**Done.**

24. Page 15, line 13. *In SM6, it would be helpful to either put names with the chemical formulas, or organize the list by groups (alkanes, alkenes, etc.) as is done on the MCM web page.*

**This is a difficult request to grant! We thought that the chemical formulas might be of some use to the potential reader. The list was automatically generated from our computer code. The order is arbitrary. Putting names and organising the list might not be worth the time needed to do it. We'll find a compromise for this problem for future versions of this mechanism.**

25. Page 15, line 25. *→ acids as main contributors*

**Done.**

26. Page 15, line 25. *Since this topic sentence has been known for a while, it would be good to cite the appropriate reference, for example Chameides (1984) JGR.*

**Done.**

27. Page 15, line 37. → 15 LT ... 14 LT (local time)  
**Done.**

28. Page 16, line 9. → protocol provides  
**Done.**

29. Page 16, line 12. → introducing, for example, the  
**Done.**

30. Page 16, line 13. Remove “compounds”  
**Done.**

31. Page 16, line 17, → to impact the O/C ratio  
**Done.**

32. Page 16, lines 33-37 may be better placed at line 21  
**We completed this paragraph following reviewer 1 comments. We prefer not to move this paragraph.**

33. Table 4. I did not see where the (b) footnote is cited. What does the “constant” refer to?  
**This footnote comes from a previous version of the paper. It is not used anymore and has been removed. We apologize for this.**

34. Figures: Could there be tick marks on every axis so that it is easy to locate where the time is for each concentration time evolution?  
**Figures have been made more readable.**

35. Figure 5: The legend connected with the bottom 2 panels is too small to read. It may not be needed if it is the same as the legend in the top 2 panels.  
**Fixed.**

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This new cloud chemistry model allows for the analysis of individual aqueous sub systems and can be used to analyze the results from cloud chamber experiments and field campaigns.

## 1 Introduction

Clouds favour chemical reactions that would not occur in the gas phase or at a rate much slower than in the aqueous phase (Epstein and Nizkorodov, 2012; Herrmann, 2003; Herrmann et al., 2015). Reactivity in clouds is due to (1) highly enhanced photochemical processes in cloud droplets; (2) faster aqueous phase reactions than in clear sky, some of which do not occur in the gas phase, especially those involving ions and hydration; (3) possible interactions between the aqueous phase and particulate phase. Clouds can also be responsible for secondary organic aerosol (SOA) formation and ageing. However, aqueous phase processes suffer from large uncertainties. Blando and Turpin (2000) first proposed clouds as a source of SOAs. Recent field measurements (Kaul et al., 2011; Lee et al., 2012, 2011), experimental work (Brégonzio-Rozier et al., 2016) and modelling studies (Ervens, 2015; Ervens et al., 2011) have shown that aqueous phase processes could lead to SOA formation on the same order of magnitude as gas phase processes. The contribution of cloud and fog processes to SOA formation is firstly indirect, through the effects of cloud chemistry on the oxidant budget. Gas phase reactivity of volatile organic compounds (VOC) is controlled by daytime HO<sup>•</sup> oxidation, and it has been shown that [phase partitioning of its precursors in clouds](#)~~radical chemistry in the aqueous phase~~ plays a significant role in the budget of this oxidant (Herrmann et al., 2015). Secondly, cloud and fog processes act directly on SOA sinks and sources. Dissolution and processing of organic vapour in the aqueous phase can lead to the formation and destruction of SOA precursors through accretion (*i.e.*, carbon-carbon bond formation) and oxidation processes. These processes may compete in the aqueous phase (Kirkland et al., 2013; Renard et al., 2015), simultaneously acting as the source (through oligomerization and functionalization reactions) and sink (through fragmentation reactions) of SOAs. To elucidate the contribution of accretion and oxidation to the budget of SOA precursors, most recent studies on the topic have focused on the modelling and measuring of accretion processes (Ervens et al., 2015). However, equivalent knowledge of aqueous oxidation is needed because oxidation processes may control the availability of organic compounds and radicals to form accretion products. In this work, we therefore focus on aqueous oxidation processes, especially the competition between fragmentation and functionalization.

Competition between fragmentation and functionalization processes has been identified as a major factor in the production of SOA in the gas phase (Donahue et al., 2012; Jimenez et al., 2009). To better represent these processes in clouds, detailed multiphase mechanisms are needed. Such mechanisms are available for gas phase chemistry (Aumont et al., 2005; Jenkin et al., 1997), whereas very few exist for the aqueous phase. Among the aqueous phase mechanisms, the most cited is Chemical Aqueous Phase Radical Mechanism version 3.0 (CAPRAM 3.0). CAPRAM 3.0 represents one oxidation pathway for each considered species (Herrmann et al., 2005; Tilgner and Herrmann, 2010; Whalley et al., 2015), even if simple organic molecules react at several distinct oxidation sites at comparable rates. As a consequence, there is a loss of information in such mechanism that does not accurately represent both fragmentation and functionalization. To fill this gap, a new protocol is proposed to create an explicit aqueous phase oxidation mechanism to accurately represent the various oxidation pathways of organic matter: the Cloud Explicit Physicochemical Scheme (CLEPS [1.0](#)).

This protocol is developed under low-NO<sub>x</sub> ([< 1 ppbv](#)) and dilute conditions and uses recently available laboratory data and empirical estimation methods. ~~This~~The mechanism is implemented in a box model including the gas phase chemistry and kinetic mass transfer of soluble species between the gas phase and cloud droplets. The box model is tested in an ideal cloud situation.

## 2 Overview

The aqueous phase oxidation mechanism originally relied on inorganic chemistry (see Deguillaume et al., 2004; Leriche et al., 2007) and the oxidation of several organic C<sub>1</sub> and C<sub>2</sub> species, including photooxidation of iron complexes with oxalic acid (Long et al., 2013). The inorganic processes taken into account in CLEPS are described in Deguillaume et al. (2004) and Long et al. (2013). This inorganic mechanism simulates the redox processes involved in the evolution of H<sub>x</sub>O<sub>y</sub>, sulphur, nitrogen, halogen (Leriche et al., 2000, 2003) and transition metal ions (TMIs; Deguillaume et al., 2004). A special emphasis is given to the latter, as the speciation of TMIs is believed to drive the evolution of aqueous phase oxidants (H<sub>2</sub>O<sub>2</sub>, HO<sup>•</sup>, HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup>; Deguillaume et al., 2005) (see R14 to R95 in the mechanism tables). [This inorganic part of the mechanism is very similar to other available aqueous phase mechanisms. For example, the chemistry of transition metal ions includes Fe, Cu and Mn redox cycles also considered in the CAPRAM 2.4 mechanism \(Ervens et al., 2003\). Sulphur, nitrogen and H<sub>x</sub>O<sub>y</sub> systems are also relatively well documented \(Herrmann et al., 2010\). The CLEPS and CAPRAM mechanism generally consider similar reactivity for these chemical subsystems.](#)

In the present study, the CLEPS mechanism is extended to the oxidation of C<sub>1-4</sub> precursors and follows the protocol described in detail in sections 3 and 4. Although isoprene is not significantly dissolved in the atmospheric aqueous phase, its oxidation products are considered. For instance methylglyoxal (MGLY), glyoxal (GLY), acrolein (ACR), methacrolein (MACR) and methylvinylketone (MVK) are significantly soluble ([Henry's law constant > 10<sup>3</sup> M atm<sup>-1</sup>](#)) and/or highly reactive in the aqueous phase (Ervens and Volkamer, 2010; Lim et al., 2010, 2013; Liu et al., 2009, 2012). [Ervens et al. \(2015\) however argued in a modeling study that MVK and MACR solubility could be decreased by salting out effects, reducing their contributions to aqueous reactivity and SOA formation.](#)

For each species and its oxidation products, the CLEPS mechanism describes the oxidation of HO<sup>•</sup> (section 3.3) and NO<sub>3</sub><sup>•</sup> (section 3.4) and the explicit evolution of the produced peroxy radicals (section 4). When [data-rate constants](#) are available, the reactivity of organic compounds with other oxidants (SO<sub>4</sub><sup>•-</sup>, Cl<sub>2</sub><sup>•-</sup>,...) is also addressed (section 3.5). Hydration (section 3.1) and dissociation (section 3.2) equilibria are, respectively, considered for carbonyl and carboxylic functions.

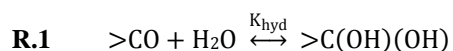
Moreover, recent developments in empirical estimates of kinetic and thermodynamic parameters (*e.g.*, [reaction-rates-rate constants](#), Henry's law constants) for aqueous phase chemistry (Doussin and Monod, 2013; Minakata et al., 2009; Monod and Doussin, 2008; Raventos-Duran et al., 2010) are included in the CLEPS mechanism. These structure activity relationships (SARs) are based on experimental data and rely on robust hypotheses about the [reaction-rates-rate constants](#) (section 3.3.2) and equilibrium constants (sections 3.1 and 3.2) of species that are not documented in the literature. For instance, SARs can provide estimations of the branching ratios between the different oxidation pathways with HO<sup>•</sup> radicals (Doussin and Monod, 2013; Minakata et al., 2009; section 3.3.3).

The mechanism currently includes 850 aqueous reactions and 465 equilibria. Inorganic reactivity is described for 67 chemical species (*e.g.*, TMIs, H<sub>x</sub>O<sub>y</sub>, sulphur species, nitrogen species and chlorine). For organic compounds, 87 chemical species are considered in the mechanism corresponding to 657 chemical forms (*e.g.*, hydrated forms, anionic forms). [The mechanism tables are available in the supplementary data.](#)

### 3 Stable organic species

#### 3.1 Hydration equilibria

Carbonyls, *i.e.*, aldehydes and less likely ketones, may undergo hydration leading to the formation of a gem-diol form:



$K_{\text{hyd}}$  [dimensionless] is the hydration constant and is defined as:

$$\text{Eq.1} \quad K_{\text{hyd}} = \frac{>\text{C}(\text{OH})(\text{OH})}{>\text{CO}}$$

There are 30 carbonyl species in the mechanism. Most of the C<sub>1-2</sub> species are well known and data are available in the literature. However, there is a lack of data for C<sub>3-4</sub> species, and empirical estimates must be performed.

To the best of our knowledge, there is only one SAR available to estimate hydration constants (Raventos-Duran et al., 2010); it is provided by the GROMHE ([GROUp contribution Method for Henry's law Estimate](#)) SAR for Henry's law constants.

This SAR is based on five descriptors and is optimized on a dataset comprising 61 species. Raventos-Duran et al. (2010) defined a global descriptor, *tdescriptor*, to represent functional group interactions with the sum of the so-called sigma Taft values ( $\sigma^*$ , e.g., Perrin et al., 1981). Similarly, *hdescriptor* is a global descriptor representing the inductive effect of functional groups attached to an aromatic ring through the sum of the meta-, para- and ortho-Hammett sigma values ( $\sigma_m$ ,  $\sigma_p$  and  $\sigma_o$ , respectively; e.g., Perrin et al., 1981; for more details see Raventos-Duran et al., 2010). It is applied for all stable carbonyl species when a measured value is not available. However, this method was originally developed only for stable non-ionic species.

In the present study, the SAR is extended to anionic species. The descriptors have been optimized to include the Taft and Hammett sigma values for the carboxylate moieties ( $\sigma^*(-CO(O^-)) = -1.06$ ,  $\sigma_m(-CO(O^-)) = 0.09$ ,  $\sigma_p(-CO(O^-)) = -0.05$  and  $\sigma_o(-CO(O^-)) = -0.91$ ; Perrin et al., 1981). The database from Raventos-Duran et al. (2010) has been extended to carboxylate species with measured values available in the literature (**Table 1**). Following the same method as Raventos-Duran et al. (2010), multiple linear regression optimization is performed by minimizing the sum of squared errors (SSE):

$$\text{Eq.2} \quad \text{SSE} = \sum_{i=1}^n (\log K_{\text{hyd,est}} - \log K_{\text{hyd,exp}})^2$$

where  $n$  is the number of experimental values in the database ( $n=65$ ), including both the values compiled and taken into account by Raventos-Duran et al. (2010) and the new carboxylate values. **Figure 1** shows both the previous and the updated values of the descriptors and the performance of the SAR. The new optimization for carboxylate compounds modifies the descriptors by at most 50% for the intercept. The other descriptors vary from 1% (*hdescriptor*) to 18% (*ketone flag*) of their initial values. There is greater uncertainty associated with this new optimization; the root mean square error (RMSE =  $\sqrt{\frac{1}{n} \sum_{i=1}^n (\log K_{\text{hyd,est}} - \log K_{\text{hyd,exp}})^2}$ ) is 0.61 log units, which is higher than the RMSE = 0.47 log units given in Raventos-Duran et al. (2010). However, the new optimization is still able to estimate  $K_{\text{hyd}}$  within a factor of 4 (3 in Raventos-Duran et al., 2010).

Hydration data are not available in the literature for the peroxy ( $RO_2^*$ ) and acylperoxy ( $RC(=O)(O_2^*)$ ) radicals. However, there is no reason to ignore the hydration of these radicals. As a first approach, when data are not available, we assign to a given  $RO_2^*$  the hydration constant of its parent species. For example, for the radicals derived from glycolaldehyde, we have:

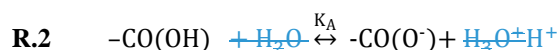
$$\text{Eq.3} \quad K_{\text{hyd}}(\text{CH}_2(\text{OH})\text{CO}(\text{OO}^*)) = K_{\text{hyd}}(\text{CH}(\text{OH})(\text{OO}^*)\text{CHO}) = K_{\text{hyd}}(\text{CH}_2(\text{OH})\text{CHO}) = 10$$

The lack of experimental data does not allow validation of this hypothesis and excludes further extension of the Raventos-Duran et al. (2010) SAR. This approximation is likely valid when there is no or weak interactions between the peroxy and carbonyl functions, i.e., when these functions are separated by several carbon atoms. This is also applied to short-chain hydrocarbons and acylperoxy radicals since it is the only way to counteract the lack of experimental data. When new data become available, they can be easily implemented to replace our hypothesis.

[In this protocol, the hydration equilibria are differently considered differently from what is done in CAPRAM3.0i \(Herrmann et al., 2005; Tilgner et al., 2013\). In CAPRAM, hydration equilibria constants are documented as well as back and forward reactions rates when available. When no data are available, hydration constants from similar species are used.](#)

### 3.2 Acid dissociation equilibria

To represent acid dissociation, the acidity constant  $K_A$  [dimensionlessM] is needed:



The acidity constant  $K_A$  is defined by:

$$\text{Eq.4} \quad K_A = \frac{[-\text{CO}(\text{O}^-)][\text{H}_3\text{O}^+\text{H}^+]}{[-\text{CO}(\text{OH})][\text{H}_2\text{O}]}$$

5 In general, the  $K_A$  values are well documented for short-chain organic compounds ( $\text{C}_{1-2}$ ). In the mechanism, each stable acid with one or two carbon atoms can be documented using acidity constant from the literature. This is not the case for  $\text{C}_3$  and  $\text{C}_4$  species, especially multifunctional species. In the whole mechanism, there are 38 organic acids, 7 of which have a documented  $K_A$  value (see Equilibria Tables in the mechanism tables). Like the hydration constants, the acidity constants must therefore be empirically estimated. To obtain the estimates, we use a similarity criterion: if there are no data available  
10 in the literature for a given species, the acidity constant from the closest documented species with the same organic function in the  $\alpha$  position from the carboxylic acid function is chosen. For example, the acidity constant for pyruvic acid (Lide and Frederikse, 1995) is attributed to 3-oxopyruvic acid because they both carry a ketone function next to the carboxylic acid function, *i.e.*:

$$\text{Eq.5} \quad K_A(\text{CHOC}(=\text{O})\text{CO}(\text{OH})) = K_A(\text{CH}_3\text{C}(=\text{O})\text{CO}(\text{OH})) = 10^{-2.4}$$

15 Perrin et al. (1981) showed that the  $\text{p}K_A$  values of aliphatic organic species are mostly influenced by the inductive effect of the organic function closest to the acidic function. Therefore, this first hypothesis should provide a good estimation of undetermined acidity constants.

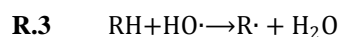
Following the hydration constant treatment, the acidity constants for peroxy radicals are initially taken from their parent species when experimental data are not documented. This assumption can be questioned but very few measurements suggest  
20 that peroxy radicals are more acidic than their parent species. Schuchmann et al. (1989) showed that the acetic acid peroxy radical ( $\text{CH}_2(\text{OO}^\bullet)\text{CO}(\text{OH})$ ) has a  $\text{p}K_a = 2.10$ , whereas acetic acid has a  $\text{p}K_a = 4.76$ , and they observed the same trend for the malonic acid peroxy radical, which has a second  $\text{p}K_a$  close to 3 compared to the malonic acid second  $\text{p}K_a = 5.7$ . Therefore, the hydration constants from Schuchmann et al. (1989) are used in the mechanism, and the estimated hydration constants can be directly substituted by laboratory data when the data become available.

25 [Our acidity constants estimates are similar to what is proposed in the other explicit aqueous phase chemistry mechanism such as CAPRAM. We systematized the procedure used in CAPRAM where unknown acidity constants are estimated from similar species.](#)

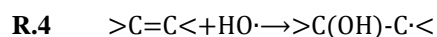
### 3.3 Reaction with $\text{HO}^\bullet$

#### 3.3.1 Mechanism

30 For aliphatic organic compounds,  $\text{HO}^\bullet$  reactivity proceeds by H-abstraction, yielding an alkyl radical following what can occur in the gas phase (Herrmann et al., 2010, 2015):

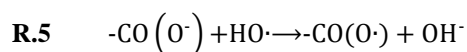


If the compound bears a  $\text{C}=\text{C}$  double bond, the addition is favoured:



35 In addition to the gas phase like pathways described above, it may be possible for  $\text{HO}^\bullet$  to undergo electron transfer in the presence of anions, especially carboxylate compounds (von Sonntag and Schuchmann, 1997):





### 3.3.2 Rates constants

[When rate constants of organic compounds reactions with HO<sup>•</sup> are available \(see the review from Herrmann et al., 2010\), they are used in the mechanism](#)

~~Based on the recent measurements of HO<sup>•</sup> rate constants for organic compounds reviewed in Herrmann et al. (2010), global reaction rate constants with HO<sup>•</sup> are used.~~ In the CLEPS mechanism, for a total of 343 reactions with HO<sup>•</sup>, only 43 kinetic constants are available in the literature. Empirical estimates are thus required in most cases. The estimates are obtained using the recent developments of SARs for the HO<sup>•</sup> rate. Doussin and Monod (2013) described the extension of a SAR previously published in Monod and Doussin (2008) and Monod et al. (2005). This SAR provides a way to estimate the H-abstraction rate constants for dissolved linear or cyclic alkanes, alcohols, carbonyls, carboxylic acids and carboxylates. This method includes descriptors that consider the effect of functional groups in the  $\alpha$ - and  $\beta$ -positions of the abstracted hydrogen atom. For each considered organic moiety, Doussin and Monod (2013) optimized the  $\alpha$ - and  $\beta$ -substitution factors. All estimates in the frame of the CLEPS mechanism are within the domain of validity of the Doussin and Monod (2013) SAR.

In the present study, the SAR was modified to account for the electron transfer on carboxylate compounds (R.5). The relevance of this process was discussed by Doussin and Monod (2013). They found an electron transfer rate constant for  $\alpha$ -carbonyl carboxylate anions of  $k(-\text{C}(=\text{O})\text{CO}(\text{O}^\cdot)) = 2.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , but it was not included in the original SAR due to the limited amount of experimental data. Their analysis was restricted to the  $\alpha$ -carbonyl bases (especially pyruvate and ketomalonate ions, for which electron transfer is dominant), due to the lack of abstractable H-atoms. However, other carboxylate ions could undergo this type of reaction, even if electron transfer is of minor importance because of the faster H-abstraction reactions. Therefore, in the present study, the SAR from Doussin and Monod (2013) has been modified to include the partial rate constant  $k(-\text{CO}(\text{O}^\cdot)) = 2.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for each possible electron transfer reaction. This partial rate constant is affected by the  $\alpha$ - and  $\beta$ -substitution factors in the same way as the original abstraction constants.

For all unsaturated species in the mechanism (*i.e.*, methylvinylketone - MVK, methacrolein - MACR, hydroxyl-methylvinylketone - MVKOH and hydroxyl-methacrolein - MACROH), the addition reactions rates have been evaluated following the literature and similarity criteria. For further developments involving unknown unsaturated compounds, the SAR from Minakata et al. (2009) should be used because it is the only method that can estimate partial addition rate constants on double bonds.

### 3.3.3 Branching ratios

Branching ratios are required to identify the most probable oxidation products. In previous mechanisms, the most labile H-atom was empirically identified (*e.g.*, using Bond Dissociation Energy estimations), and the reaction was assumed to proceed exclusively *via* this H-abstraction pathway (Ervens et al., 2003; Tilgner and Herrmann, 2010). This was the only hypothesis that could be considered because experimental data on the branching ratios in aqueous phase HO<sup>•</sup> reactions are extremely scarce. The recent introduction of group-contribution-based SAR (Doussin and Monod, 2013; Minakata et al., 2009) allows estimation of the contribution of each pathway to the global reactivity of each species. In our mechanism, for a given species the global reactivity rate is either provided by the literature or by SAR, but the branching ratios are always obtained from SAR estimates.

Furthermore, for simplicity, a reduction hypothesis was considered in the mechanism for each stable species because explicitly writing all possible reactions would yield a huge number of chemical species. For example, Aumont et al. (2005) showed that the number of species formed in the gas phase for such explicit schemes increases exponentially with the size of the carbon skeleton of the parent species. One can assume based on Aumont et al. (2005) that starting from a C<sub>4</sub> precursor in

the aqueous phase, the mechanism would require approximately  $10^3$  distinct species involved in approximately  $10^4$  reactions. Such a large set of species excludes the development of an aqueous phase oxidation mechanism by hand. A simple reduction scheme was therefore applied to mitigate this problem and an example is shown in **Table 2** for three selected species. Doussin and Monod (2013) SAR was applied to estimate the contribution of each possible pathway and to maintain at least 75% of the total reactivity. After the reduction is applied, the branching ratios are recalculated to maintain the global oxidation rate constant.

This empirical reduction scheme helps to limit the number of species and reactions (657 different chemical forms representing 87 species reacting in 673 oxidation reactions). This new aqueous phase mechanism then allows consideration of the most probable H-abstraction reaction. For example, in **Table 2** for the hydrated glycolaldehyde, the final reactivity in our mechanism is equally distributed between three HO $\cdot$  attack sites and yields 33% glyoxylic acid, 28% glyoxal, 39% formic acid and formaldehyde. This result can be compared with the mechanism of Ervens et al. (2004), which leads to 100% glyoxylic acid since it only considers the abstraction of the aldehydic hydrogen.

**Table 2** shows that the Doussin and Monod (2013) SAR estimates often lead to a significant abstraction of the hydrogen atom bonded to the oxygen atom in the hydroxyl moiety. This mechanism has never been addressed in an atmospheric chemical scheme. This reactivity of the alcohol function towards the HO $\cdot$  radical has been experimentally demonstrated by Asmus et al. (1973) for methanol, ethanol, tert-butanol and polyols. To determine whether this reactivity could be extended to all the considered alcohol functions in our mechanism, we investigated whether the process appears thermodynamically feasible by calculating the relative reaction free energies (Gibbs energies) using the Density Functional Theory (DFT, see details and references in the Supplementary Material **SM1**). The thermodynamic values for the reaction enthalpies and Gibbs energies are calculated for the H-abstraction by the HO $\cdot$  radical from C and O atoms in the following molecules: acetaldehyde, propionaldehyde, glycolaldehyde, glyoxal, methylglyoxal, L-lactic acid and L-lactate. H-abstraction from hydrated aldehydes is also included in this study. The results (see Supplementary Material **SM2**) show that H-abstraction is thermodynamically favourable: the reaction enthalpies range from -14 to -47 kcal mol $^{-1}$  and the corresponding free energies range from -13 to -47 kcal mol $^{-1}$ .

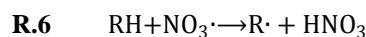
[The SAR from Doussin and Monod \(2013\) was recently published. Therefore, Herrmann et al. \(2005\) and Tilgner et al. \(2013\) could not use this method to estimate rate constants and branching ratios. Instead, they rely on similarities when data are not available: for instance, they assume that the HO \$\cdot\$  addition rate constant on 2,3-dihydroxy-4-oxobutanoic acid is the same as maleic acid. In most cases, they assume that the reaction will proceed through the identified most likely probable pathway. In some cases, like for 2,4-butanedione, they attribute branching ratios from the equivalent measured gas phase reaction.](#)

### 3.4 Reaction with NO $_3$ $\cdot$

NO $_3$  $\cdot$  is the main night-time oxidant in the gas phase. Although it plays a minor role under low-NO $_x$  conditions, NO $_3$  $\cdot$  chemistry has been taken into account in the protocol to make it versatile in the future. Previous modelling studies of aqueous-phase reactivity expect the same characteristics for dissolved NO $_3$  $\cdot$  radicals (Tilgner et al., 2010). For this reason, we represent NO $_3$  $\cdot$  oxidation for each stable species in the mechanism.

#### 3.4.1 Mechanisms

The mechanism of NO $_3$  $\cdot$  oxidation is similar to that of HO $\cdot$  oxidation: the reactivity mainly proceeds via H-abstraction of a labile hydrogen atom to form an alkyl radical and nitric acid:

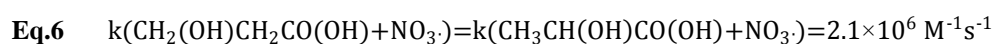


In this version of the mechanism, the addition of an NO<sub>3</sub><sup>•</sup> radical to the C=C double bond is not considered since insufficient data are available for these reactions and for the fate of the resulting organonitrate peroxy radicals. However, organonitrate compounds were recently identified in the ambient aerosol (Garnes and Allen, 2002; Lee et al., 2016; Rollins et al., 2012). In addition to local emission sources, organonitrate compounds originate from the gas phase chemistry of VOCs under high NO<sub>x</sub> conditions (Darer et al., 2011; Farmer et al., 2010; Heald et al., 2010; Paulot et al., 2009; Perring et al., 2013) followed by phase transfer and aqueous processing to the deliquescent aerosol and cloud aerosol phase (Nguyen et al., 2011) to form nitrates, alcohols or organosulphates, which contribute to SOA. In this study, we restricted the simulations to low-NO<sub>x</sub> conditions to reduce the potential importance of organonitrate chemistry, which requires further experimental and modelling developments.

### 3.4.2 ~~Reaction rates~~Rate constants

Data concerning NO<sub>3</sub><sup>•</sup> reactions rates are available in the literature, mostly for C<sub>1</sub> and C<sub>2</sub> species (Exner et al., 1994; Gaillard de Sémainville et al., 2007, 2010; Herrmann et al., 2010, 2015). Again, empirical estimates are required to describe the oxidation by NO<sub>3</sub><sup>•</sup> radicals when the data are unavailable.

For most C<sub>2-4</sub> species, we estimate the NO<sub>3</sub><sup>•</sup> ~~reaction rates~~rate constants using the similarity criteria. When an estimate is needed, we use the reaction rate of a similar documented species. The primary focus is on the nature, number, and relative position of the organic functions. For example, the reaction rate of 3-hydroxypropionic acid with NO<sub>3</sub><sup>•</sup> is estimated to be the same as the reaction rate of lactic acid because both are C<sub>3</sub> species with a carboxylic acid and a hydroxyl function:



(De Semainville et al., 2007)

### 3.4.3 Branching ratios

The branching ratios for NO<sub>3</sub><sup>•</sup> oxidation are not available in the literature. As a first approach, we use branching ratios for the NO<sub>3</sub><sup>•</sup> reactions that are identical to those estimated for HO<sup>•</sup> reactions because NO<sub>3</sub><sup>•</sup> H-abstraction proceeds following the same elementary mechanism as HO<sup>•</sup> H-abstraction. NO<sub>3</sub><sup>•</sup> radicals should be more sensitive to steric hindrance than HO<sup>•</sup> radicals. However, without experimental evidence supporting this assumption, in our mechanism, NO<sub>3</sub><sup>•</sup> radicals are unable to react *via* electron transfer and to abstract hydrogen atoms from -OH moieties. In these cases, electron transfer and -OH hydrogen abstraction are not included in the list of available NO<sub>3</sub><sup>•</sup> reactions, and the remaining pathways are rescaled to 100%. Therefore, for these types of reactions, the branching ratios for NO<sub>3</sub><sup>•</sup> oxidation may differ from those for oxidation by HO<sup>•</sup>.

Our approach for reactions with nitrate radicals is different than what has been proposed before in previous aqueous phase mechanism, especially for estimating the branching ratios. We use similarity criteria to estimate the reaction rates whereas Herrmann et al. (2005) estimate these values using their own SAR (Herrmann and Zellner, 1998). They assume that the H-abstraction only occurs at the weakest C-H bond, which is determined from bond dissociation energies empirical estimates.

### 3.5 Reaction with other oxidants

Reactions rates with radicals other than HO<sup>•</sup> or NO<sub>3</sub><sup>•</sup> are available in the literature (Herrmann et al., 2015; Zellner et al., 1995). They mainly concern reactions of C<sub>1-2</sub> species with Cl<sub>2</sub><sup>•-</sup>, CO<sub>3</sub><sup>•-</sup>, FeO<sup>2+</sup> and SO<sub>4</sub><sup>•-</sup>. These reactions are included in the mechanism, and the branching ratios are based on the HO<sup>•</sup> reaction branching ratios. However, reactions with these radicals are not included when information in the literature is unavailable, which would require further extension of the CLEPS

mechanism when applied to polluted (relatively rich in  $\text{SO}_4^{\cdot-}$  radicals) or marine (relatively rich in  $\text{Cl}_2^{\cdot-}$  and other halogenated radicals) environments.

Since our mechanism is developed for low- $\text{NO}_x$  conditions, the reactivity of selected oxygenated organic species with  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ , which was recently studied by Schöne and Herrmann (2014), is included in the mechanism (see reactions R586 and R590 in the mechanism tables). Although these reaction rates are in the range of  $10^{-1}$  to  $10^1 \text{ M}^{-1} \text{ s}^{-1}$ , their impact is non-negligible under specific conditions, especially under low- $\text{NO}_x$  conditions. Furthermore, reactions of  $\text{C}_{1-2}$  hydroperoxide compounds in Fenton-like reactions with  $\text{Fe}^{2+}$  have been studied by Chevallier et al. (2004) and are included in the mechanism (see reactions R238 and R330 in the mechanism tables).

### 3.6 Photolysis

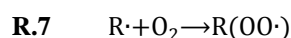
Most of the species considered in the mechanism are oxygenated and are likely to bear chromophore functional groups. To calculate the photolysis reaction rate, the polychromatic absorption cross-sections and quantum yields must be known. Again, the literature data concerning these subjects are scarce. Photolysis data are available for a few chromophore species:  $\text{H}_2\text{O}_2$  (Graedel and Weschler, 1981; Zellner et al., 1990), carboxylate-iron(III) complexes (Faust and Zepp, 1993; Long et al., 2013; Weller et al., 2013a, 2013b), and pyruvic acid (Reed Harris et al., 2014). Absorption cross-section and quantum yield data (preferably wavelength-dependent) are required to calculate photolysis frequencies. Pyruvic acid photolysis is not currently calculated in the model because only the photolysis frequencies are available in the literature.

Because the hydroperoxide (-OOH) moiety is expected to be photosensitive, we include photolysis reactions for species bearing this organic function, using the cross-sections and quantum yields measured for  $\text{H}_2\text{O}_2$  (as in Leriche et al., 2003). For further improvement, photolysis reactions will be extended to other compounds when experimental data are available to determine which aqueous phase oxygenated compounds are photosensitive. [Epstein et al. \(2013\) have shown that aqueous photolysis quantum yields are highly dependent on the type of molecule. Using similarity criteria to estimate photolysis rates in the aqueous phase may be too error prone. Furthermore their estimates also show that photolysis would efficiently compete with  \$\text{HO}\cdot\$  oxidation for very few of photolabile species. If more data and reliable SAR become available on this subject, a mechanism generated using the present protocol would be the ideal tool to expand on Epstein et al. \(2013\) study.](#)

## 4. Organic radicals

### 4.1 Alkyl radical $\text{O}_2$ addition

In dilute aqueous solution, alkyl radicals react with dissolved  $\text{O}_2$  to form peroxy radicals:



Recent studies suggest that under high organic radical concentrations, this addition competes with the self- or cross-reactions of alkyl radicals, yielding high molecular weight molecules, such as oligomers (see Ervens et al., 2015; Griffith et al., 2013; Lim et al., 2013; Renard et al., 2015). This competition can favour oligomerization if  $\text{O}_2$  is not readily available in the aqueous phase. [In their bulk aqueous phase modeling study, Ervens et al. \(2015\) have shown that the aqueous phase under laboratory experiment conditions is not saturated with oxygen, leading to possible oligomerization. Their sensitivity studies however show that oxygen reached saturation in few seconds for atmospheric deliquescent particles, likely because of a large surface to volume ratio. We follow the same hypothesis for cloud droplets.](#)~~In our mechanism, which is characterised by dilute conditions, dissolved oxygen is assumed to be always available (see Ervens et al., 2015) and alkyl radicals are too dilute to react with themselves.~~ The review by Alfassi (1997) showed that the kinetics of the great majority of  $\text{R} + \text{O}_2$  reactions are close to the diffusion limit, with rate constants of  $2.0\text{--}4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , and for non-carbon-centred radicals (such as nitrogen-centred radicals), significantly smaller rate constants are observed ( $10^7$  to  $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ). Hence, in our

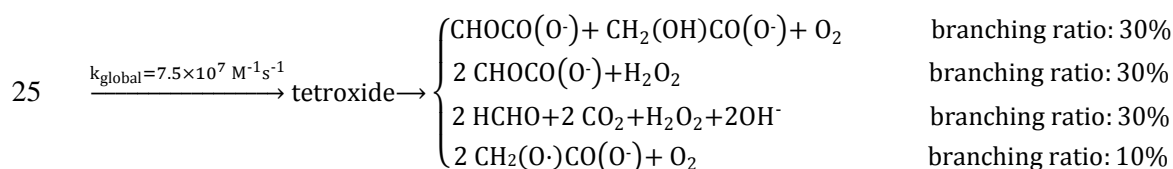
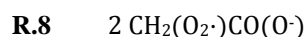
mechanism (which does not consider nitrogen-centred radicals), the H-abstraction and O<sub>2</sub>-addition steps are combined in a single step reaction due to the fast O<sub>2</sub>-addition reaction rate in the mechanism. [In the CAPRAM mechanism \(Ervens et al., 2003; Herrmann et al., 2005; Tilgner et al., 2013\), the O<sub>2</sub>-addition step is explicitly introduced. This allows the direct treatment of the alkyl+alkyl vs. alkyl+O<sub>2</sub> competition that may occur in deliquesced particles. This is not in the objective of the present work and this consideration will also lead to the implementation in the mechanism of a lot of intermediate chemical species with short lifetime. It could be considered for future versions of the CLEPS mechanism.](#)

## 4.2 Tetroxide formation and decomposition

In general, a peroxy radical reacts with itself or another peroxy radical to form a tetroxide, which quickly decomposes (von Sonntag and Schuchmann, 1997). These reactions could be introduced to the mechanism by having each peroxy radical react with every other peroxy radical. With 363 peroxy radicals in the mechanism, this would require more than 66,000 reactions to be written to account for these cross-reactions. As a first approach, we restrict the mechanism to self-reactions. There are available methods to simplify the description of cross-reactions (Madronich and Calvert, 1990). These methods could be adapted for future versions of the mechanism.

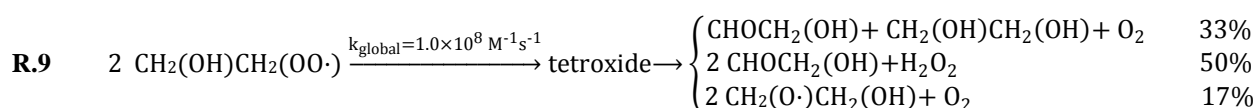
The decomposition of tetroxide follows different pathways, depending on the nature of the initial peroxy radical. Piesiak et al. (1984) proposed a mechanism for the evolution of the tetroxide formed after dimerization of β-hydroxyethylperoxy radicals. Zegota et al. (1986) studied the self-reaction of the acetylperoxy radical and Schuchmann et al. (1985) explored the fate of the acetate peroxy radical. The results of these studies have been extended in other experimental works for other peroxy radicals (Liu et al., 2009; Monod et al., 2007; Poulain et al., 2010; Schaefer et al., 2012; Schöne et al., 2014; Stemmler and von Gunten, 2000; Zhang et al., 2010). We therefore implement peroxy radical self-reactions following the similarity criteria [detailed below](#).

For β-peroxycarboxylic acids (>C(OO·)C(=O)(OH)) and their conjugated bases, we generalize the experimental results obtained by Schuchmann et al. (1985) for the acetate peroxy radical (CH<sub>3</sub>(OO·)C(=O)(O<sup>-</sup>)). For this radical, the tetroxide is degraded through four pathways (reaction R.8):



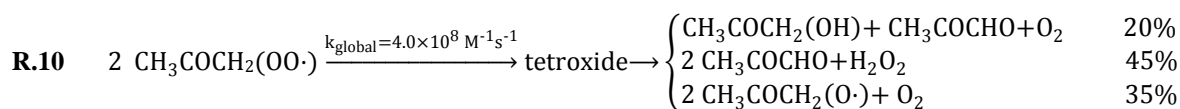
The four pathways retained in this work are the most important identified by Schuchmann et al. (1985). The sum of these pathways contributes to 87% of the tetroxide decomposition, and each individual contribution is scaled to reach 100% overall.

The evolution of β-hydroxyperoxy radicals (>C(OH)C(OO·)<) is represented by the experimental results obtained by Piesiak et al. (1984) for the β-hydroxyethylperoxy radical (CH<sub>2</sub>(OH)CH<sub>2</sub>(OO·)) (reaction R.9):

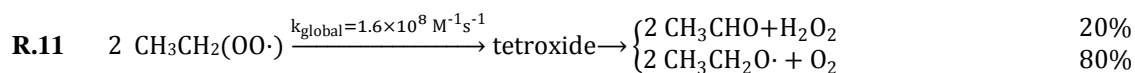


The three pathways are reported to contribute to 90% of the degradation of the tetroxide (Piesiak et al., 1984). The mechanism is restricted to these major pathways, and their individual contributions are scaled to reach 100% overall in our mechanism.

$\beta$ -oxoperoxy radicals ( $-\text{COC}(\text{OO}^\bullet)-$ ) are treated based on the studies of the acetonilperoxy radical by Poulain et al. (2010) and Zegota et al. (1986) (reaction R.10):



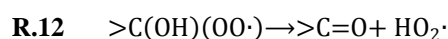
Except for the  $\alpha$ -hydroxyperoxy and acylperoxy radicals that are discussed in detail in the following subsections, peroxy radicals that are not included in the above categories are addressed using the estimates from Monod et al. (2007) for the ethylperoxy radical (reaction R.11):



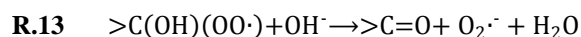
The rate constant was measured by Herrmann et al. (1999). Schuchmann and von Sonntag (1984) estimated that the first pathway (aldehyde pathway) contributes to 20% of the tetroxide decomposition. Studying the ethylperoxy radical derived from the photooxidation of ethylhydroperoxide, Monod et al. (2007) found that the second pathway (alkoxy pathway) is more likely than the aldehyde pathway, in agreement with previous studies (Henon et al., 1997; von Sonntag and Schuchmann, 1997). Therefore, we attributed the remaining degradation of the tetroxide to the alkoxy pathway.

### 4.3 $\alpha$ -hydroxyperoxy $\text{HO}_2^\bullet/\text{O}_2^\bullet$ elimination

When a hydroxyl moiety is in the alpha position of the peroxy function, the peroxy radical likely undergoes  $\text{HO}_2^\bullet$  elimination:



and an  $\text{O}_2^\bullet$  elimination following a basic catalysis (Zegota et al., 1986):



von Sonntag (1987) showed that the  $\text{HO}_2^\bullet$  elimination rate constant is dependent on the nature of the substituent attached to the carbon atom. Following this study, we generalized the  $\text{HO}_2^\bullet$  elimination rate constants for unknown species using available experimental values. The generalization rules are detailed in **Table 3**.

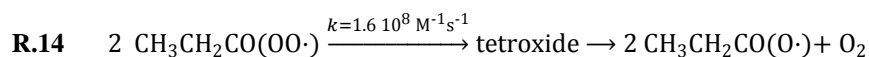
In the case of  $\alpha$ -dihydroxy-peroxy compounds ( $-\text{C}(\text{OH})(\text{OH})(\text{OO}^\bullet)-$ ), McElroy and Waygood (1991) showed that  $\text{HC}(\text{OH})(\text{OH})(\text{O}_2^\bullet)$  decays with a rate constant  $k > 10^6 \text{ s}^{-1}$ . Without additional estimates of  $\text{HO}_2^\bullet$  elimination, we apply the same elimination rate constant of  $k = 10^6 \text{ s}^{-1}$  for all  $\alpha$ -dihydroxy-peroxy compounds. Ilan et al. (1976) and Neta et al. (1990) provided an  $\text{O}_2^\bullet$  elimination reaction rate for the 2, $\alpha$ -hydroxypropylperoxy radical ( $k(\text{CH}_3\text{C}(\text{OH})(\text{OO}^\bullet)\text{CH}_3 + \text{OH}^-) = 5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and the  $\alpha$ -hydroxyethylperoxy radical ( $k(\text{CH}_3\text{CH}(\text{OH})(\text{OO}^\bullet) + \text{OH}^-) = 4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). Given the high concentrations of  $\text{OH}^-$  in water, these reactions are expected to be fast and should not be limiting steps. Therefore, an arbitrary rate constant  $k = 4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , close to the measured [reaction rates/rate constants](#), is assigned to each elimination reaction.

As shown in **Table 3**,  $\text{HO}_2^\bullet$  elimination is a fast process, with an associated lifetime ranging from  $1.5 \times 10^{-3} \text{ s}$  to  $0.1 \text{ s}$ . In our simulation (see Section 6) the high range of concentrations for peroxy radicals is around  $10^{-10} \text{ M}$  for the peroxy radical derived from glyoxal. At a concentration of a given peroxy radical of approximately  $10^{-10} \text{ M}$ , tetroxide formation therefore occurs on a timescale of approximately 50 s. Therefore, tetroxide formation and its subsequent decomposition are not considered for  $\alpha$ -hydroxyperoxy radicals, and only direct decomposition is included in the mechanism.

### 4.4 Acylperoxy decarboxylation



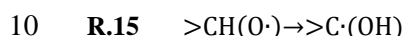
Acylperoxyl radicals (-CO(OO\*)) are treated like standard peroxyl radicals (see R.11) for which only the alkoxy formation pathway is considered due to the lack of an H-atom on the peroxyl radical. For the acylperoxyl derived from propionaldehyde, this gives:



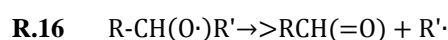
- 5 The acylalkoxy radical undergoes C-C bond scission and yields CO<sub>2</sub>, accounting for the expected decarboxylation of the acylperoxyl radical.

#### 4.5 Alkoxy radicals

Alkoxy radicals (RO\*) are formed after the decomposition of a tetroxide or after the H-abstraction from a -OH functional group. Their reactivity can proceed through two different pathways, 1-2 hydrogen shift (DeCosta and Pincock, 1989):



and C-C bond scission (Hilborn and Pincock, 1991):



- Both pathways are non-limiting steps that are in competition with each other. Schuchmann et al. (1985) studied the fate of acetate peroxyl radicals and showed that the produced alkoxy radical (CH<sub>2</sub>(O\*)C(=O)(O\*)) may be degraded following R.15 and R.16. However, they could not determine the relative contribution of both reaction pathways to the degradation of the alkoxy radical. In our mechanism, bond scission (R.16) is the only possible reaction when a neighbouring carbon atom is oxygenated. The scission leads to the formation of the most stable radicals, *i.e.*, the formation of secondary radicals is favoured over the formation of primary radicals. Alkoxy radicals evolve through a 1-2 hydrogen shift (R.15) when the neighbouring carbon atoms are not oxygenated.

- 20 Because of their very short lifetimes, alkoxy radicals are not explicitly considered in the mechanism. Instead, electron transfer and fragmentation products are directly included in the global reaction. For example, for the β-hydroxyethylperoxyl radical using the reaction rate and branching ratios from Piesiak et al. (1984) (see R.9):

Pathway 1: $2 \text{ CH}_2(\text{OH})\text{CH}_2(\text{OO}\cdot) \rightarrow 2 \text{ CHOCH}_2(\text{OH}) + \text{H}_2\text{O}_2$	$k = 5.0 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Piezak et al. (1984)
Pathway 2: $2 \text{ CH}_2(\text{OH})\text{CH}_2(\text{OO}\cdot) \rightarrow \text{CHOCH}_2(\text{OH}) + \text{CH}_2(\text{OH})\text{CH}_2(\text{OH}) + \text{O}_2$	$k = 3.3 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Piezak et al. (1984)
Pathway 3: $2 \text{ CH}_2(\text{OH})\text{CH}_2(\text{OO}\cdot) \rightarrow 2 \text{ CH}_2(\text{O}\cdot)\text{CH}_2(\text{OH}) + \text{O}_2$	$k = 1.7 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Piezak et al. (1984)
$\text{CH}_2(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow \text{C}'\text{H}_2(\text{OH}) + \text{CH}_2\text{O}$	Fast	
$\text{C}'\text{H}_2(\text{OH}) + \text{O}_2 \rightarrow \text{CH}_2(\text{OH})(\text{OO}\cdot)$	$k = 2.0 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$	
$2 \text{ CH}_2(\text{OH})\text{CH}_2(\text{OO}\cdot) \rightarrow 1.33 \text{ CHOCH}_2(\text{OH}) + 0.33 \text{ CH}_2(\text{OH})\text{CH}_2(\text{OH})$ $+ 0.34 \text{ CH}_2\text{O} + 0.34 \text{ CH}_2(\text{OH})(\text{OO}\cdot) + 0.50 \text{ H}_2\text{O}_2 + 0.16 \text{ O}_2 - 0.34 \text{ H}_2\text{O}$	$k = 1.0 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$	Piezak et al. (1984)

The ~~latter-last~~ reaction is the overall budget reaction, which is taken into account in the model.

- 25 [This treatment of peroxyl and alkoxy radicals is an attempt at systematizing the approach that is also used in CAPRAM 3.0 \(Herrmann et al., 2005; Tilgner et al., 2013\). They also consider peroxyl radicals recombination reactions using experimental data from Zegota et al. \(1986\), Schuchmann et al. \(1985\) and Poulain et al. \(2010\). Similarly to our mechanism, the possible cross-reactions are not considered. In the CAPRAM mechanism, alkoxy radicals can only be fragmented, with a very fast reaction rate following an analogy with gas phase values.](#)

## 5. Coupling CLEPS with MCM v3.3.1 mass transfer

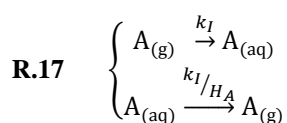
- 30 **5.1 Gas phase mechanism**

The CLEPS mechanism is coupled to the gas phase Master Chemical Mechanism, MCM v3.3.1 (Jenkin et al., 2015; Saunders et al., 2003) provided at: <http://mcm.leeds.ac.uk/MCM>. The new version 3.3.1 of MCM includes in particular the treatment of isoprene oxidation products such as epoxydiols, hydroxymethylmethyl- $\alpha$ -lactone (HMML) and methacrylic acid epoxide (MAE).

- 5 All gases are dissolved in CLEPS even if they are not further oxidized in the aqueous phase. Conversely, some aqueous species described in CLEPS can be outgassed even if there is no corresponding gas species in MCM. Among the 87 chemical species included in CLEPS, 33 do not have a counterpart in MCM. These are mostly highly oxygenated and highly soluble species. Conversely, 267 gas phase species from MCM have no corresponding aqueous species in CLEPS. [For each species with no equivalent in the other phase, we create an artificial equivalent in the other phase for which no reactivity is described. The mass transfer parameters are estimated as described below \(section 5.2\) to accurately determine in which phase the species should reside.](#)

## 5.2 Estimating mass transfer parameters

Mass transfer is described following the kinetic parameterization from Schwartz (1986). For a given species A:



- 15 where  $H_A$  [M atm<sup>-1</sup>] is the Henry's law constant for species A and  $k_I$  is the pseudo first order rate constant for mass transfer:

$$\text{R.18} \quad k_I = Lk_T = L \left( \frac{r^2}{3D_g} + \frac{4r}{3v\alpha} \right)^{-1}$$

where  $L$  [vol. water/vol. air] is the liquid water content of the cloud,  $r$  [cm] is the radius of the droplets,  $D_g$  [cm<sup>2</sup> s<sup>-1</sup>] is the gas diffusion coefficient,  $v$  [cm s<sup>-1</sup>] is the mean molecular speed and  $\alpha$  [dimensionless] is the mass accommodation coefficient. The parameters  $H_A$ ,  $D_g$ ,  $v$ , and  $\alpha$  are documented for each soluble species in order to fully describe mass transfer.

- 20 Estimates of unknown parameters are obtained following the approach of Mouchel-Vallon et al. (2013). The Henry's law coefficients are provided by the GROMHE SAR ([Raventos-Raventos-Duran et al., 2010](#)). [Comparing this SAR with other available methods \(Meyland and Howard, 2000; Hilal et al., 2008\) Raventos-Duran et al. \(2010\) have shown that GROMHE is the more reliable SAR in general, estimating Henry's law constants with a root mean square error of 0.38 log units \(approx. a factor of two\). It particularly shows better performances than the other tested methods for the more soluble species, i.e. highly oxygenated, multifunctional organic species.](#)

- 25 -When unavailable, the temperature dependencies (enthalpy of dissolution) are set to 50 kJ mol<sup>-1</sup>.  $D_g$  is calculated by scaling from a reference compound ( $\frac{D_{g,A}}{D_{g,H_2O}} = \sqrt{\frac{M_{H_2O}}{M_A}}$ ; where  $D_{g,H_2O} = 0.214/P$  cm<sup>2</sup> s<sup>-1</sup>,  $P$  [atm] is the atmospheric pressure and  $M_A$  is the molar mass [g mol<sup>-1</sup>]; Ivanov et al., 2007). The mean molecular speed is defined as  $\sqrt{\frac{8R'T}{\pi M_A}}$  with  $R'=8.3145 \cdot 10^7$  g cm<sup>2</sup> s<sup>-2</sup> K<sup>-1</sup> mol<sup>-1</sup>. The accommodation coefficients are set to a default value of  $\alpha = 0.05$  when no data are available ([Lelieveld and Crutzen, 1991](#); Davidovits et al., 2006, 2011). We add the temperature dependence of the mass accommodation coefficients based on the parameterization from Nathanson et al. (1996):

$$\text{R.19} \quad \frac{\alpha}{1-\alpha} = e^{-\frac{\Delta G_{\text{obs}}}{RT}}$$

$\Delta G_{\text{obs}} = \Delta H_{\text{obs}} - T\Delta S_{\text{obs}}$  [J mol<sup>-1</sup>] is interpreted as the free energy, where  $\Delta H_{\text{obs}}$  [J mol<sup>-1</sup>] and  $\Delta S_{\text{obs}}$  [J mol<sup>-1</sup> K<sup>-1</sup>] are thermodynamic solvation parameters (free enthalpy and entropy) derived by Nathanson et al. (1996) from experimental



works on the heterogeneous uptake coefficients performed at different temperatures. When  $\Delta H_{\text{obs}}$  and  $\Delta S_{\text{obs}}$  are experimentally available, they are used to estimate the temperature-dependent  $\alpha$ , and in other cases, if the value of  $\alpha$  is available in the literature, it is used without the temperature dependency.

The mass transcription description in this protocol differs from the coupling between RACM (Stockwell et al., 1997) and CAPRAM 3.0<sup>†</sup> that is proposed in Herrmann et al. (2005) and Tilgner et al. (2013). Because RACM is a reduced chemical scheme, gas phase species are lumped. Mass transfer therefore occurs between explicit aqueous phase species and fractions of lumped species. A delumping of RACM group compounds is included in the mechanism in the form of equilibrium reactions between the group compound and the standalone species. This means the mass transfer source follows exactly the same trends for all aqueous species derived from the same gas phase source. As an example, the “Ald” model species in RACM represents all gaseous aldehydes and is considered to be the source of dissolved acetaldehyde, propionaldehyde and butyraldehyde (Herrmann et al., 2005). <sup>†</sup>

The kinetic parameterization in our cloud chemistry model has been used for a long time (Jacob, 1986). The other cloud chemistry models almost always use experimentally measured Henry’s law constants. Ervens et al. (2003) proposed to estimate accommodation coefficient based on using a SAR to empirically estimate  $\Delta G_{\text{obs}}$ . As underlined by Ervens et al. (2003), this method should be used very carefully because the data needed to support validate this method are very scarce. Future works could focus on (i) the sensitivity of the system to  $\alpha$  estimates and (ii) refining the SAR according to the more recent data reported in Davidovits et al. (2011).

### 5.3 Model description

The mechanism resulting from the coupling of CLEPS with MCM v3.3.1 is integrated in a model based on the Dynamically Simple Model for Atmospheric Chemical Complexity (DSMACC; Emmerson and Evans, 2009) using the Kinetic PreProcessor (KPP: see Damian et al., 2002), which has been modified to account for an aqueous phase, as described in the following. The changes are summarized in blue on **Figure 2**.

Aqueous phase reactions are implemented as a new reaction type. Rate constants in units of  $\text{M}^{-n} \text{s}^{-1}$  are converted to  $\text{molec}^{-n} \text{cm}^{-3n} \text{s}^{-1}$ , depending on the constrained liquid water content. Aqueous phase equilibria are decomposed as forward and backward reactions. This alternative to the total species approach used in other models (Leriche et al., 2000) has the drawback of making the ODE (Ordinary Differential Equations) system stiffer. However, in our simulation, the model handles the stiffness without noticeable numerical issues. Moreover, this approach has the advantage of allowing the explicit treatment of cross-equilibria. The pH therefore evolves dynamically as  $\text{H}^+$  is explicitly produced and consumed in the equilibrium reactions.

Mass transfer is also implemented as a new reaction type. The ~~reaction rates~~ rate constants are calculated following Schwartz (1986) and depend on the estimated Henry’s law constants, gas diffusion coefficients, mean molecular speeds and accommodation coefficients (see section 5.2).

In DSMACC, TUV 4.5 (Madronich and Flocke, 1997) is used to calculate the photolysis rates in the gas phase (Emmerson and Evans, 2009). The TUV version included in DSMACC was modified to include aqueous phase photolysis reactions (**Figure 2**). To calculate the photolysis coefficients inside the droplets, the clear sky actinic flux values are multiplied by a factor 1.6 (Ruggaber et al., 1997), and the cross-sections and quantum yields are provided from available experimental data (Deguillaume et al., 2004; Long et al., 2013).

Differential equations are solved with a Rosenbrock solver which has been shown to be ~~the most~~ reliable numerical method for stiff ODE systems involved in modelling multiphase chemistry (Djouad et al., 2002, 2003).

## 6. Simulation of a test case

### 6.1 Initial conditions

The model is run with the initial and environmental conditions adapted from the low-NO<sub>x</sub> situation described by McNeill et al. (2012). Information about the emissions, deposition and initial concentrations of chemical species are provided in **Table 4**. The situation corresponds to summertime conditions, with the simulation starting on the 21<sup>st</sup> of June. The simulation is located at the sea level and the coordinates used to calculate actinic fluxes are 45.77°N 2.96°E. The main difference with the situation described in McNeill et al. (2012) is that isoprene is the only emitted primary organic compound. To compensate for the decrease in total emitted organic mass, the isoprene emission is increased from  $1.5 \times 10^6$  in McNeill et al. (2012) to  $7.5 \times 10^6$  molec cm<sup>-3</sup> s<sup>-1</sup> in our work. Furthermore, deposition is added for the major oxidation products of isoprene to prevent the accumulation of secondary organic species. The temperature is held constant (290K) during the whole simulation. Under these chemical conditions, the gas chemistry simulation is been run for 31 days (see Supplementary Material **SM3**).

At noon on the 31<sup>st</sup> day of the simulation ~~-(On that day, sunset happens at 6:45 pm),~~ a cloud event is simulated with a constant liquid water content of  $3 \times 10^{-7}$  vol. water/vol. air lasting until midnight with a fixed droplet radius of 10 μm. On that day, sunset happens at 6:45 pm (i.e. the actinic flux becomes null). This is a permanent cloud simulation and no attempt is made to represent a specific documented cloudy situation. The objective is to test the multiphase mechanism over a long time scale to check that the mechanism is (i) working as intended and (ii) producing chemical effects in both phases. Testing the model over 12h is a first step to evaluate the impacts (or their absence) of detailed organic chemistry on multiphase cloud chemistry. Future studies will use variable environmental conditions that require the consideration of microphysical processes with our multiphase chemical module.

The cloud event is initialized with 1 μM of iron, which is typical concentrations in continental cloud water (Deguillaume et al., 2014), to enable recycling of oxidants by redox cycles involving iron. The initial pH is set to 4 and is free to evolve. The pH quickly reaches 3.2 (see Supplementary Material **SM4**). An additional simulation is performed to consider the aqueous reactivity of dissolved organic species from the gas phase mechanism, and the reactivity of which is not represented in our aqueous phase mechanism. Each of these dissolved organic species reacts with the HO<sup>•</sup> radicals with a reaction rate of  $k = 3.8 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>. This value is taken from the work of Arakaki et al. (2013), which estimated the sink for aqueous HO<sup>•</sup> by dissolved organic carbon (DOC). This additional sensitivity test (called “with DOC”) is performed to improve the estimate of the HO<sup>•</sup> concentrations in the atmospheric drops. To account for the conversion of radicals, we assume that each of these reactions produces an HO<sub>2</sub><sup>•</sup> radical in the aqueous phase.

### 6.2 Gas chemical reactivity

**Figures 3a & 3b** show the time evolution of the targeted gases during the 31<sup>st</sup> day of the gas phase simulation (dashed lines). The NO<sub>x</sub> and O<sub>3</sub> mixing ratios (**Figure 3a**) are 0.54 ppbv and 87 ppbv, respectively, at noon while the HO<sup>•</sup> mixing ratio reaches a maximum of 0.12 pptv. The simulated mixing ratio of isoprene (**Figure 3b**) exhibits a 1.5 ppbv peak in the morning and a minimum of 0.9 ppbv in the afternoon. Because the simulated emission of isoprene is constant during the day ~~in the simulation~~ (and is turned off at night), its time evolution is constrained by the daytime evolution of its oxidants HO<sup>•</sup> and O<sub>3</sub>. In this case, the HO<sup>•</sup> radical is the main oxidants of isoprene ( $k_{\text{HO}+\text{isoprene}} \times \text{CHO} \approx 10 \times k_{\text{O}_3+\text{isoprene}} \times \text{CO}_3$ ). Therefore, simulated isoprene exhibits a minimum at noon when HO<sup>•</sup> reaches its maximum. The resulting isoprene diurnal profile is not realistic, as in the atmosphere the isoprene diurnal profile is constrained by the diurnal variation of both its emissions and level of oxidants. The oxidation of isoprene leads to the production of secondary organic species. The time evolutions of the most important secondary species are depicted in **Figure 3b**. The first oxidation products from isoprene (MACR, MVK) follow the same time profile as isoprene. The mixing ratios of other oxidation products vary also temporally depending on

their production/destruction rates. For example, MGLY, GLY and glycolaldehyde mixing ratios decrease initially due to their oxidation by HO<sup>•</sup> and then increase strongly due to their production by the oxidation of isoprene.

### 6.3 Impact of aqueous phase reactivity

**Figures 3a & 3b** show the time evolution of targeted gases during the cloud event (full lines) compared to the gas phase scenario (dashed lines). Previous modelling studies have shown that gas phase HO<sub>x</sub> chemistry is modified by the aqueous HO<sub>2</sub><sup>•</sup> chemistry (Jacob, 1986; Monod and Carlier, 1999). Recent experimental results from Whalley et al. (2015) confirmed that uptake and reactivity in clouds can have a significant impact on the HO<sub>2</sub><sup>•</sup> and HO<sup>•</sup> concentrations in the gas phase. In the simulation, at the onset of the cloud event, the HO<sub>2</sub><sup>•</sup> mixing ratio is reduced by 17%, and the HO<sup>•</sup> mixing ratios increases by 75%. After an initial sharp decrease, the H<sub>2</sub>O<sub>2</sub> mixing ratio exhibits a 50% increase after 4 hours compared to the dry situation. The increase of the HO<sup>•</sup> mixing ratios is caused by the important dissolution of organic matter, leading to reduced HO<sup>•</sup> sinks in the gas phase. H<sub>2</sub>O<sub>2</sub> is a soluble species highly reactive with SO<sub>2</sub>, which explains the initial dip in its mixing ratio. After SO<sub>2</sub> is entirely depleted (not shown), the ~~The~~ aqueous production of H<sub>2</sub>O<sub>2</sub> is responsible for its subsequent higher gaseous levels.

This trend in HO<sup>•</sup> mixing ratios contradicts previous modeling results (Herrmann et al., 2000; Barth et al., 2003; Ervens et al., 2003; Tilgner et al., 2013) which exhibit a decrease in HO<sup>•</sup> mixing ratios during cloud events. The chosen chemical scenario might be the reason for this difference. Even if the chemical scenario in our study is rather similar to the one in Ervens et al. (2003), we still differ in the amount of emitted organic compounds. In our test simulations, we mainly emit isoprene, with a small contribution of formaldehyde and acetaldehyde, whereas Ervens et al. (2003) emit a larger range of hydrocarbons of anthropogenic (alkanes, alkenes, aromatics) and biogenic origin (limonene,  $\alpha$ -pinene). As far as we understand the CAPRAM model setup, these hydrocarbons are not dissolved and it should be noted that they are highly reactive with HO<sup>•</sup>. This means that the large, and certainly major, sink of gaseous HO<sup>•</sup> caused by hydrocarbons reactivity is always present, even under cloud conditions. When the source of HO<sup>•</sup> radicals is reduced by the cloud event (e.g. due to HO<sub>2</sub> and NO separation), HO<sup>•</sup> radicals sinks are not significantly perturbed and HO<sup>•</sup> steady state mixing ratios decrease. Conversely, in our simulation the gaseous HO<sup>•</sup> sink is more significantly perturbed by the cloud event because most of the organic matter in our scenario is produced from isoprene oxidation and is readily soluble. In our case, it seems that the HO<sup>•</sup> gaseous source reduction is overcompensated by the reduction in HO<sup>•</sup> gaseous sinks. As a consequence, HO<sup>•</sup> steady state mixing ratios are higher during cloud events. This hypothesis especially highlights how the chosen chemical scenario and regime is important for simulation results and conclusions. Future work should therefore systematically explore cloud simulations under a large range of scenarios.

Glyoxal, glycolaldehyde, pyruvic acid, glyoxylic acid and glycolic acid are readily soluble species that react in the aqueous phase (Herrmann et al., 2015). Cloud dissolution and oxidation act as significant sinks for these species. For instance, the glyoxal mixing ratios is reduced by 67% at the start of the cloud event, and the glycolaldehyde mixing ratio is significantly reduced until sunset ~~(6:00 PM)~~ (6:0045 PM). For all secondary organic species, daytime gas phase oxidation is increased due to the higher HO<sup>•</sup> mixing ratios. The addition of aqueous dissolution and aqueous reactive sinks for soluble species explains the sharp decrease in the gas phase mixing ratios for glyoxal, glycolaldehyde, pyruvic acid, glyoxylic acid and glycolic acid. However, the aqueous phase is also a source of secondary organic species. For species that are universal intermediates or end products, the aqueous phase production can be outgassed and contribute to maintaining dry conditions mixing ratios (methylglyoxal, formaldehyde) or significantly increase the mixing ratios compared to dry conditions (acetic and formic acids). Aqueous phase production is also ~~be~~ responsible for introducing an infinitesimal amount of oxalic acid (< 10<sup>-9</sup> ppbv) into the gas phase, as there is no oxalic acid formation pathway in the gas phase. The addition of the missing aqueous oxidation sink for all dissolved species (red lines in **Figures 3a & 3b**) leads to higher concentrations of species for which

reactive uptake is an overall sinks (*e.g.*, glyoxal, glycolaldehyde) because the reduced aqueous HO<sup>•</sup> concentrations (see **Figure 4**) limit the impact of the aqueous sink. In contrast, lower aqueous HO<sup>•</sup> concentrations reduce the gas phase mixing ratios of species for which the aqueous phase reactivity is an important source (*e.g.*, formic, acetic and glycolic acids).

**Figure 4** shows the time evolution of the main organic aqueous species together with the H<sub>x</sub>O<sub>y</sub> compounds during the cloud event. The dissolved HO<sup>•</sup> concentration reaches a peak at 8.5×10<sup>-14</sup> M, which is similar to dissolved the HO<sup>•</sup> concentrations simulated by Tilgner et al. (2013) for non-permanent clouds in remote conditions and compiled by Arakaki et al. (2013). The oxalic acid concentration is low during the day (approximately 2×10<sup>-8</sup> M) because it is present in the form of iron-oxalate complexes, which are readily photolysed. Therefore, during the night (from 6:0045 PM to 12:00 PM), the oxalic acid concentration increases significantly to 10<sup>-7</sup> M.

The sensitivity test including the additional DOC sink shows that the reduced concentration of HO<sup>•</sup> radicals (from 8.5 to 3×10<sup>-14</sup> M maximum concentration) decreases the sinks of aqueous species from the gas phase (glycolaldehyde, methylglyoxal and 3,4-dihydroxybutanone), leading to higher aqueous phase concentrations. Conversely, the organic species, which are mostly produced in the aqueous phase (formic, pyruvic, glyoxylic, and oxalic acid) have reduced sources and sinks when HO<sup>•</sup> radicals are scavenged by the added DOC. Their concentrations are therefore lower in these conditions Because sinks and sources of acids due to HO<sup>•</sup> radicals should vary in equal proportions, the decrease in organic acids concentrations cannot be ascribed to reactivity with HO<sup>•</sup> radicals. We therefore has to consider fixed sinks that do not depend on HO<sup>•</sup> concentrations, *i.e.* photolysis and phase transfer. If we consider that acids reach pseudo steady state concentrations, we can assume that because photolysis and phase transfer are not modified by the additional DOC, some acids concentrations could decrease following their overall sources/sinks ratio. MACR and MVK are also less sensitive to the DOC addition. Their main source in water is their mass transfer after gas phase production. This is consistent with their behaviour in the gas phase during the cloud event and could explain why they are less sensitive to the HO<sup>•</sup> concentrations.

A detailed budget of aqueous HO<sup>•</sup> sinks and sources during the cloud period for the simulation with added DOC (see Supplementary Material **SM5**) shows that H<sub>2</sub>O<sub>2</sub> is the main source of HO<sup>•</sup> *via* the Fenton reaction and its photolysis. However, in the first hours of the cloud event, mass transfer is the major source of HO<sup>•</sup>, like it was predicted in a previous modeling study on a shorter cloud event considering a remote chemical scenario (Tilgner et al., 2013). Fenton type reactions and photolysis reaction are also significant sources of HO<sup>•</sup> in their simulation. The most important overall sink of HO<sup>•</sup> radicals in the aqueous phase is the reaction with the added DOC (64%), which results in a slight decrease in the simulated aqueous HO<sup>•</sup> concentrations in **Figure 4**. Besides DOC, simulated reactive organics are the most important HO<sup>•</sup> sinks, with C<sub>2</sub> compounds contributing to 18%, and C<sub>4</sub> compounds contributing to 12% of HO<sup>•</sup> destruction. C<sub>1</sub> and C<sub>3</sub> together are responsible for 5% of the HO<sup>•</sup> sink. Tilgner et al. (2013) also show that HO<sup>•</sup> only aqueous sinks are reactions with organic matter, especially carbonyl compounds such as hydrated formaldehyde, glycolaldehyde and methylglyoxal.

**Figure 5** depicts the contributions in terms of concentrations of the major species in the aqueous phase. The total concentration of organic matter (continuous line) reaches a maximum of 0.76 mM after 12 hours of cloud simulation, which corresponds to approximately 30 mgC L<sup>-1</sup>. This value is high but on the order of magnitude of the DOC measurements (Deguillaume et al., 2014; Giulianelli et al., 2014; Herckes et al., 2013, 2015; van Pinxteren et al., 2015). However, species whose reactivity is represented in the CLEPS aqueous mechanism (dashed line in **Figure 5**) constitute only 16% of the total concentration of dissolved species. Not all species dissolved from the MCM undergo a reactive sink in the aqueous phase (see list in Supplementary Material **SM6**). The 10 most abundant species in the aqueous phase contribute to 91% of the concentration of reactive species (126 vs. 138 μM) and 15% of the dissolved species. Among these 10 species, glyoxal, hydroxybutanedione, glycolaldehyde, 3,4-dihydroxybutanone and glyoxylic and glycolic acids are the most important contributors. A detailed time-resolved flux analysis of the sources and sinks of these species shows that their initial concentration increase is the result of their mass transfer from the gas phase. Then, balance between aqueous sources and

sinks defines the time evolution of their concentrations. For instance, the glyoxal concentration continues increasing because of the important source of the aqueous oxidation of glycolaldehyde. The main sink of glycolaldehyde through reaction with HO<sup>•</sup> is strong enough to make its concentration decrease over time. The two most important acids, glycolic and glyoxylic acids, have initial contributions from gas phase mass transfer and are then produced in the aqueous phase from the oxidation of glyoxal and glycolaldehyde. Acetic and formic acids present simulated concentrations that are in the range of *in situ* measurements (Deguillaume et al., 2014). Glycolic and glyoxylic acids present high concentrations in comparison to *in situ* measurements that should indicate that sources or sinks are therefore likely to be misrepresented in our mechanism.

The presence of acids ~~in the~~as main contributors to the aqueous phase organic composition shows the potential for cloud reactivity to be a source of acids (Chameides, 1984). The total amount of organic acids (including formic and acetic acids) in both phases is almost doubled in less than an hour by the aqueous phase sources, from approximately 0.48 ppbv of gaseous organic acids before the cloud event to a total of 0.98 ppbv of organic acids in both phases (see Supplementary Material SM7).

Figure 6 depicts the time evolution of the mean O/C ratio and the mean number of carbon atoms ( $n_C$ ) in the reactive organic compounds present in the aqueous phase (excluding CO<sub>2</sub> and iron-organic complexes) and in the gas phase (excluding CO and CH<sub>4</sub>), with and without the cloud event. The O/C ratios and  $n_C$  are a measure of the extent to which long-chain organic species are oxidized and can therefore be a proxy for their functionalization. The reactive aqueous phase is composed of species with an average carbon skeleton of approximately 2.7 carbon atoms and an O/C ratio of 1.1 at the end of the simulation. Large molecules with high functionalization are statistically more soluble than smaller molecules (Mouchel-Vallon et al., 2013; Raventos-Duran et al., 2010). Therefore, at the onset of the cloud event, the larger and more oxygenated species are dissolved, explaining the sharp increase in aqueous  $n_C$  at the beginning of the cloud event. In the gas phase, the O/C ratio and  $n_C$  follow a marked parabolic curve, reaching a maximum O/C = 0.8 at 15 hLT and a minimum  $n_C$  = 2.3 at 14 hLT. The O/C ratio and  $n_C$  then return to the dry-condition levels at sunset. During the day, cloud reactivity is responsible for the increasing O/C ratios and decreasing  $n_C$ . A higher O/C ratio indicates that the number of oxygenated functions per carbon atom has increased. A lower  $n_C$  means that, on average, the organic species have a shorter carbon skeleton as a result of cloud reactivity. This suggests that our aqueous mechanism simulates an efficient fragmentation and functionalization of organic compounds.

At the beginning of the cloud event, many oxygenated and large compounds are dissolved leading to an increase in the O/C ratio and  $n_C$  in the gas phase. Then, the reactivity in the aqueous phase generates smaller and more oxygenated species that desorb back to the gas phase, and the increase in the O/C ratio is stronger than under clear sky conditions. The observed effects of aqueous reactivity are confirmed by the addition of DOC, which leads to a slower increase in the O/C ratio and a slower decrease in  $n_C$  in both phases because lower HO<sup>•</sup> radicals concentrations result in a weaker oxidation capacity of the aqueous phase.

## 7. Conclusions

In this paper we described a new protocol with an explicit chemical scheme for aqueous phase oxidation. This protocol ~~proposes-provides~~ an up-to-date method to describe the dissolution of soluble VOCs, their hydration and/or acid dissociation equilibria (as well as iron-oxalate complexation), their reactivity by direct photolysis and their reactivity with HO<sup>•</sup> or NO<sub>3</sub><sup>•</sup> radicals. It was developed for dilute conditions and low-NO<sub>x</sub> conditions and can be generalized to other, more polluted environments by introducing, for example, the multiphase reactivity of organonitrates. In this version, the mechanism includes alkanes, alcohols, carbonyls, carboxylic acids and hydroperoxides ~~compounds~~. The fate of the newly formed organic radicals is also addressed in detail. The protocol is applied to secondary organic species formed in the aqueous



phase. Finally, it is formulated in such a way that it could be implemented in automated chemical scheme generation tools, such as GECKO-A (Aumont et al., 2012; La et al., 2016; Mouchel-Vallon et al., 2013).

Under the simulated cloudy conditions, aqueous phase reactivity is shown to impact ~~on~~ the O/C ratio and the size of the secondary organic species, affecting the fragmentation and the functionalization processes resulting from atmospheric oxidation. Furthermore, the addition of a sink for dissolved organic matter shows that this impact on fragmentation and functionalization is sensitive to the aqueous phase oxidative capacity. These simulations were conducted for a long non-realistic permanent cloud. However, the mentioned results are atmospherically relevant, since the impact on O/C ratio and fragmentation can be observed in the first moments of the simulated cloud event.

As long as the mechanism is used to simulate organic chemistry under dilute conditions, such as in cloud droplets, the hypotheses it is built on remains valid. However, modifications should be performed before applying the model to less dilute atmospheric aqueous phases, such as deliquescent aerosols. First, the non-ideality of such aqueous solutions should be taken into account. Second, H-abstraction and O<sub>2</sub>-addition should be divided into two distinct steps, and accretion reactions should be considered (Renard et al., 2013). However, the first objective of this work is to thoroughly describe oxidation processes. Accretion processes will be accounted for in future versions of the mechanism. In our simulation, high molecular weight compound precursors, such as glyoxal, glycolaldehyde, and long-chain highly oxygenated species, were dissolved and preferentially formed in the aqueous phase. Models considering radical-initiated oligomer formation are not currently available, except in a few focused cases (Ervens et al., 2015; Woo and Mc Neil 2015). Recent modelling studies implemented newly identified accretion processes to evaluate their potential impacts on SOA formation. However, equivalent accurate knowledge of aqueous oxidation is required since oxidation processes may control the organic radical availability to form accretion products.

Our generated explicit mechanism is based on the Kinetic PreProcessor (KPP) which was built for implementation in chemistry transport 3D models, such as WRF-Chem (Grell et al., 2005) and GEOS-Chem (Eller et al., 2009). The CLEPS mechanism would require some reduction to be coupled with 3D transport models in a similar way to what exists for gas phase chemistry (Emmerson and Evans, 2009; Szopa et al., 2005; Watson et al., 2008) and aqueous phase oxidation (Deguillaume et al., 2009). Several strategies can be used to build reduced multiphase mechanism. Explicit schemes like CLEPS can serve as a reference for the development of reduced chemical schemes like those proposed in Woo and McNeill (2015) or Deguillaume et al. (2009). Very few experimental data are available to validate reduced chemical scheme before implementation in 3D models, especially concerning cloud chemistry. Field measurements (van Pinxteren et al., 2015) and chamber experimental data (Bregonzio-Rozier et al., 2016) are available, but they do not cover the whole range of real atmospheric conditions that a large scale model can encounter. Using explicit modelling tools to serve as reference for a large set of environmental and chemical scenarios is therefore a possible solution to validate reduced multiphase chemical schemes for various environmental conditions. This is of course consistent only once the explicit mechanisms have been validated against the existing experimental data.

This protocol is a powerful tool to explore and propose new reaction mechanisms as a basis to understand experimental studies of scarcely investigated compounds (succinic acid, tartronic acid). The mechanisms generated by our protocol can be used for different purposes in the study of atmospheric aqueous phase processes. They can be evaluated and adapted to laboratory experiments involving a small number of precursors that react only in the aqueous phase. The mechanisms are more likely to be useful for larger-scale experiments involving longer timescales and two phases (gas + water) in environmental cloud chambers (Brégonzio-Rozier et al., 2016). They are also of interest for the modelling studies of field campaigns such as HCCT (Whalley et al., 2015) or SOAS (Nguyen et al., 2014). The SOA and the cloud chemistry communities are currently interested in studying the respective contributions of oxidation and accretion processes to the transformations of organic matter in the aqueous phase and to the oxidative capacity of clouds. Most recent modelling

studies have focused on implementing newly identified accretion processes to evaluate their potential impacts on SOA formation (Ervens et al., 2015; McNeill, 2015; McNeill et al., 2012; Woo and McNeill, 2015). In this work, guidelines are developed to update oxidation mechanisms that will be compared in the future to descriptions of the formation of accretion products, such as oligomers, organonitrates and organosulphates.

## 5 Code availability

The mechanism used in this paper is available in KPP format upon request to l.deguillaume@opgc.univ-bpclermont.fr. Any suggestions and corrections to the mechanism (*e.g.*, new experimental rate constant we may have missed, typos) are also welcomed at the same address. The modified version of DSMACC (originally downloaded at <https://github.com/barronh/DSMACC>) that was used for the simulations is also available upon request to l.deguillaume@opgc.univ-bpclermont.fr.

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Table 1: Experimental hydration constants for carboxylate species.

Species	$K_{\text{hyd}}$	References
<b>Glyoxylate</b>		
$\text{CH(=O)C(=O)(O}^-)$	67	Tur'yan (1998)
<b>Monoethyl Oxaloacetate</b>		
$\text{CH}_3\text{CH}_2\text{-O-C(=O)C(=O)CH}_2\text{C(=O)(O}^-)$	3.125	Kozłowski and Zuman (1987)
<b>Pyruvate</b>		
$\text{CH}_3\text{C(=O)C(=O)(O}^-)$	0.0572	Pocker et al. (1969)
<b><math>\alpha</math>-ketobutyrate</b>		
$\text{CH}_3\text{CH}_2\text{C(=O)C(=O)(O}^-)$	0.08	Cooper and Redfield (1975)
<b><math>\alpha</math>-ketoisovalerate</b>		
$\text{CH}_3\text{C(CH}_3\text{)C(=O)C(=O)(O}^-)$	0.075	Cooper and Redfield (1975)
<b><math>\beta</math>-fluoropyruvate</b>		
$\text{CH}_2\text{(F)C(=O)C(=O)(O}^-)$	19	Hurley et al. (1969)

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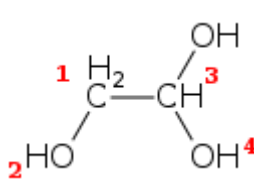
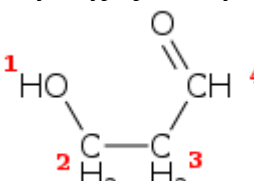
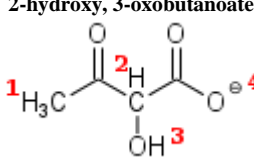
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**Table 2: Examples of the reduction scheme applied to estimate HO<sup>•</sup> reactions branching ratios.  $k_i$  values are the partial reaction rate corresponding to the labeled atoms  $i$  in the left column.**

Molecule	Estimated H-abstraction rates $k_i$ on atom labeled $i$ following Doussin and Monod (2013) [M <sup>-1</sup> s <sup>-1</sup> ]	Contribution to the global reaction rate	Reactivity threshold considered	Retained pathways	Scaled Contribution	Final estimated <a href="#">reaction rates/ constants</a> [M <sup>-1</sup> s <sup>-1</sup> ]
<b>Hydrated Glycolaldehyde</b> 	$k_1 = 2.9 \times 10^8$ $k_2 = 0.9 \times 10^8$ $k_3 = 3.4 \times 10^8$ $k_4 = 4.0 \times 10^8$	26 % 8 % 30 % 36 %	C <sub>2</sub> : 90 %	Yes No Yes Yes	28 % - 33 % 39 %	$k_1 = 3.1 \times 10^8$ - $k_3 = 3.6 \times 10^8$ $k_4 = 4.3 \times 10^8$
$k_{\text{Global}} = 1.1 \times 10^9$						$k_{\text{Global}} = 1.1 \times 10^9$
<b>3-hydroxypropionaldehyde</b> 	$k_1 = 1.5 \times 10^9$ $k_2 = 9 \times 10^7$ $k_3 = 7 \times 10^7$ $k_4 = 2.5 \times 10^9$	36 % 2 % 2 % 60 %	C <sub>3</sub> : 75 %	Yes No No Yes	38 % - - 62 %	$k_1 = 1.5 \times 10^9$ - - $k_4 = 2.6 \times 10^9$
$k_{\text{Global}} = 4.1 \times 10^9$						$k_{\text{Global}} = 4.1 \times 10^9$
<b>2-hydroxy, 3-oxobutanoate</b> 	$k_1 = 8.1 \times 10^7$ $k_2 = 6.1 \times 10^7$ $k_3 = 8.5 \times 10^7$ $k_4 = 9.2 \times 10^7$ <sup>(*)</sup>	25 % 19 % 27 % 29 %	C <sub>4</sub> : 75 %	Yes No Yes Yes	31 % - 33 % 36 %	$k_4 = 1.0 \times 10^8$ - $k_3 = 1.1 \times 10^8$ $k_4 = 1.1 \times 10^8$
$k_{\text{Global}} = 3.2 \times 10^8$						$k_{\text{Global}} = 3.2 \times 10^8$

<sup>(\*)</sup> electron transfer reaction



**Table 3: Generalization of HO<sub>2</sub><sup>•</sup> elimination rate constants for unknown species, following von Sonntag (1987).**

von Sonntag (1987)			
compilation			
1 <sup>st</sup> Substituent	2 <sup>nd</sup> Substituent	HO <sub>2</sub> <sup>•</sup> elimination rate constant k (s <sup>-1</sup> )	Generalization
H	H	<10	-
H	CH <sub>3</sub>	52	Primary peroxy radicals
H	CH <sub>2</sub> (OH)	190	β-hydroxyperoxy radicals
CH <sub>3</sub>	CH <sub>3</sub>	665	Secondary peroxy radicals

**Table 4: a) Chemical scenario used for the gas phase simulation of 31 days. b) Aqueous phase initial concentration.**

a)

Gas phase species	Initial mixing ratio [ppb]	Emission [molec cm <sup>-3</sup> s <sup>-1</sup> ]	Deposition [s <sup>-1</sup> ]
SO <sub>2</sub>	1	2.91×10 <sup>5</sup>	1×10 <sup>-5</sup>
NO	-	2.86×10 <sup>5</sup>	-
NO <sub>2</sub>	0.3	-	4×10 <sup>-6</sup>
N <sub>2</sub> O <sub>5</sub>	-	-	2×10 <sup>-5</sup>
HNO <sub>3</sub>	0.3	-	2×10 <sup>-5</sup>
O <sub>3</sub>	40	-	4×10 <sup>-6</sup>
H <sub>2</sub> O <sub>2</sub>	1	-	1×10 <sup>-4</sup>
CH <sub>4</sub>	1.7×10 <sup>3</sup>	-	-
CO <sub>2</sub>	3.57×10 <sup>5</sup>	-	-
CO	1.5×10 <sup>2</sup>	3.7×10 <sup>6</sup>	1×10 <sup>-6</sup>
Isoprene	1	7.50×10 <sup>6</sup> <sup>(a)</sup>	-
Dihydroxybutanone	-	-	5×10 <sup>-5</sup>
MACR	-	-	5×10 <sup>-5</sup>
MVK	-	-	5×10 <sup>-5</sup>
Glyoxal	0.1	-	5×10 <sup>-5</sup>
Methylglyoxal	0.1	-	5×10 <sup>-5</sup>
Glycolaldehyde	-	-	5×10 <sup>-5</sup>
Acetaldehyde	0.1	3.17×10 <sup>3</sup>	5×10 <sup>-5</sup>
Formaldehyde	0.5	3.03×10 <sup>3</sup>	5×10 <sup>-5</sup>
Acetone	0.1	8.92×10 <sup>3</sup>	5×10 <sup>-5</sup>
Pyruvic Acid	-	-	5×10 <sup>-5</sup>
Acetic Acid	1×10 <sup>-3</sup>	3.35×10 <sup>3</sup>	5×10 <sup>-5</sup>
Formic Acid	-	-	5×10 <sup>-5</sup>
Methanol	2	1.07×10 <sup>4</sup>	5×10 <sup>-5</sup>
Methylhydroperoxide	0.01	3.35×10 <sup>3</sup>	5×10 <sup>-6</sup>

<sup>(a)</sup> = 0 at nighttime, <sup>(b)</sup> constant

b)

Aqueous phase species	Initial concentrations [μM]
Fe <sup>2+</sup>	1

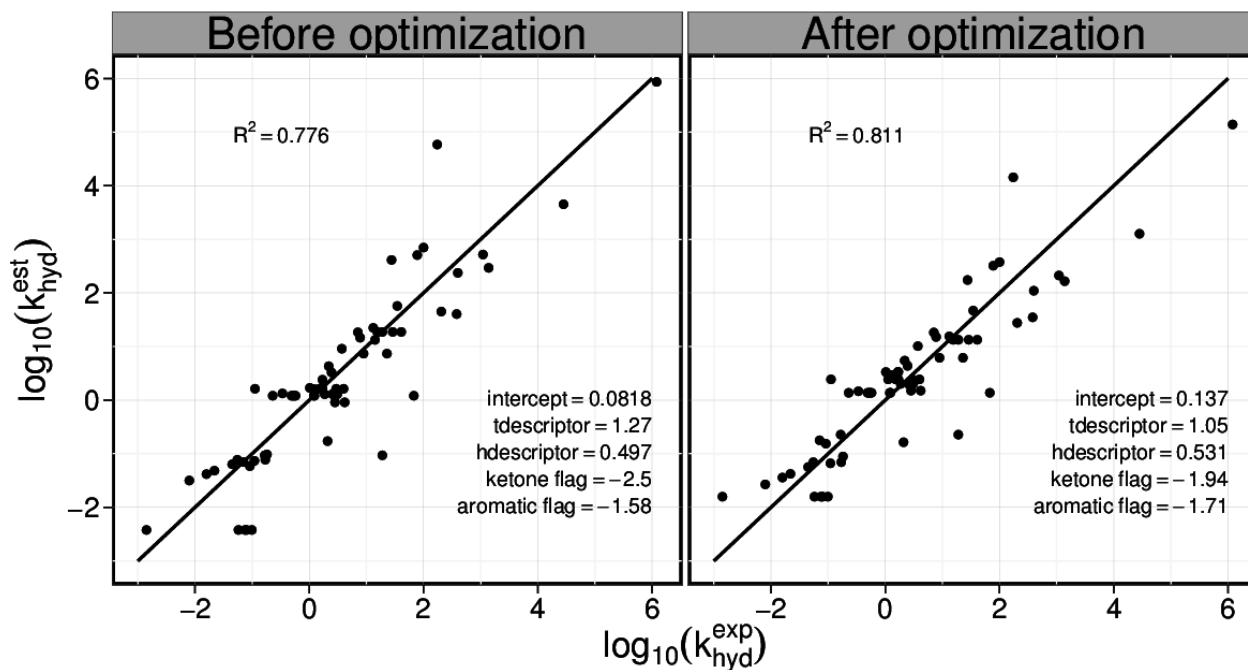


Figure 1: Scatterplots of the estimated  $\log(K_{\text{hyd}})$  using the SAR from Raventos-Duran et al. (2010) versus the experimental  $\log(K_{\text{hyd}})$ , before (left panel) and after (right panel) the optimization for carboxylates. Values for the optimized descriptors are shown on the bottom right of each panel. The values chosen before the optimization are taken from Raventos-Duran et al. (2010).

5 The line is the  $y = x$  line.

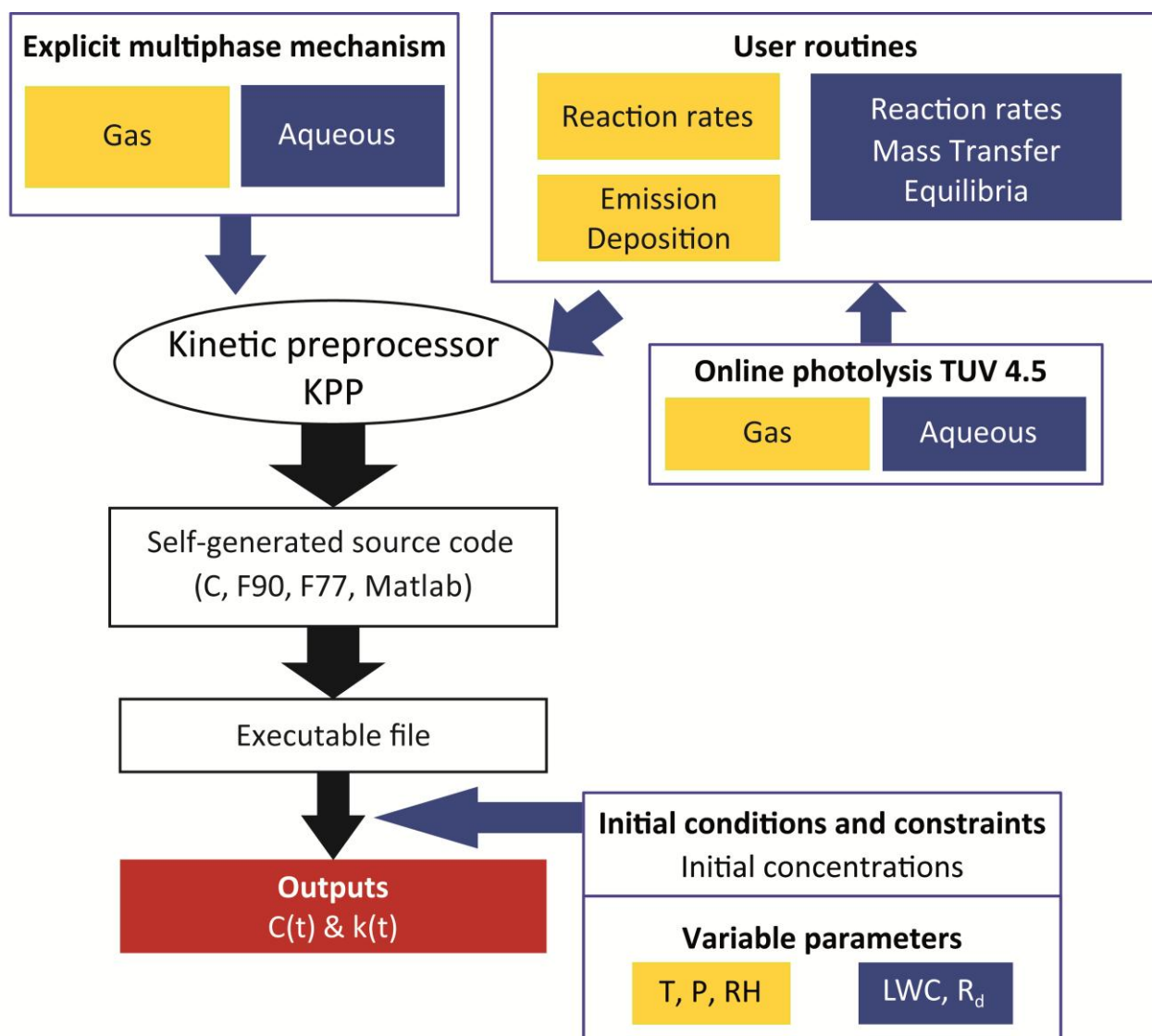
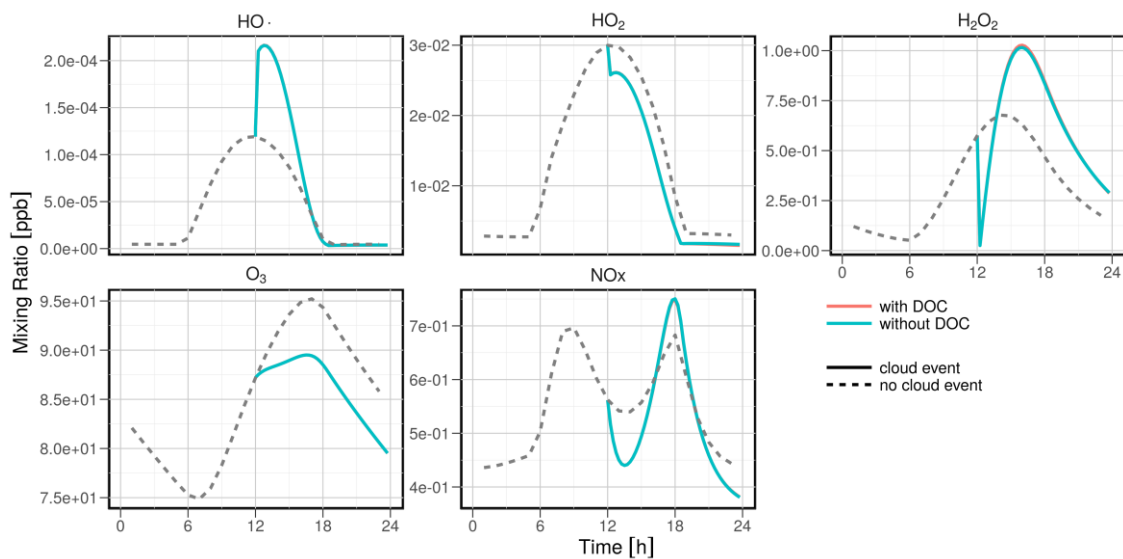
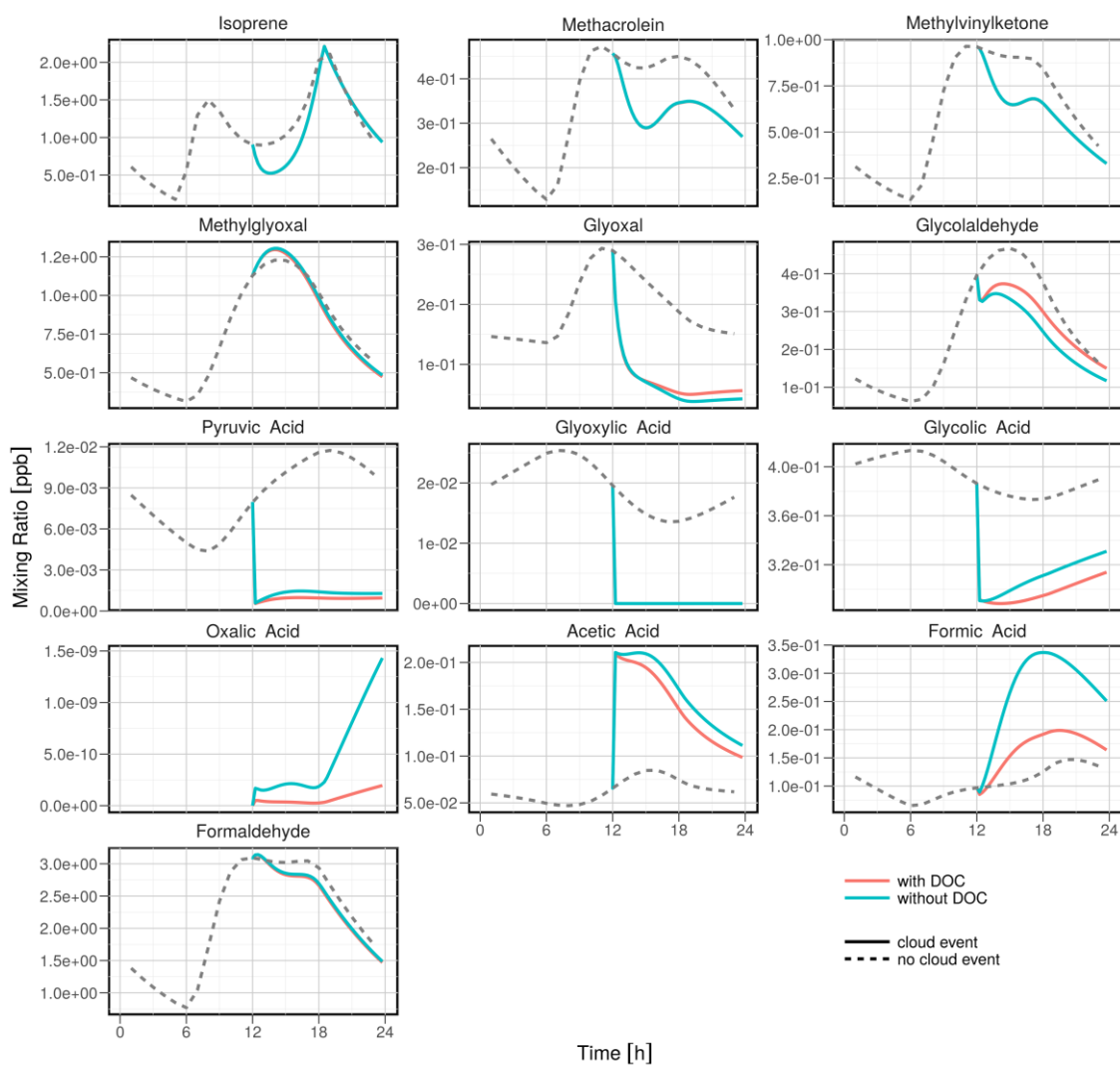


Figure 2: Schematic diagram of the DSMACC version of the Kinetic PreProcessor. The developments [relative-related](#) to aqueous-phase reactivity are shown in blue.

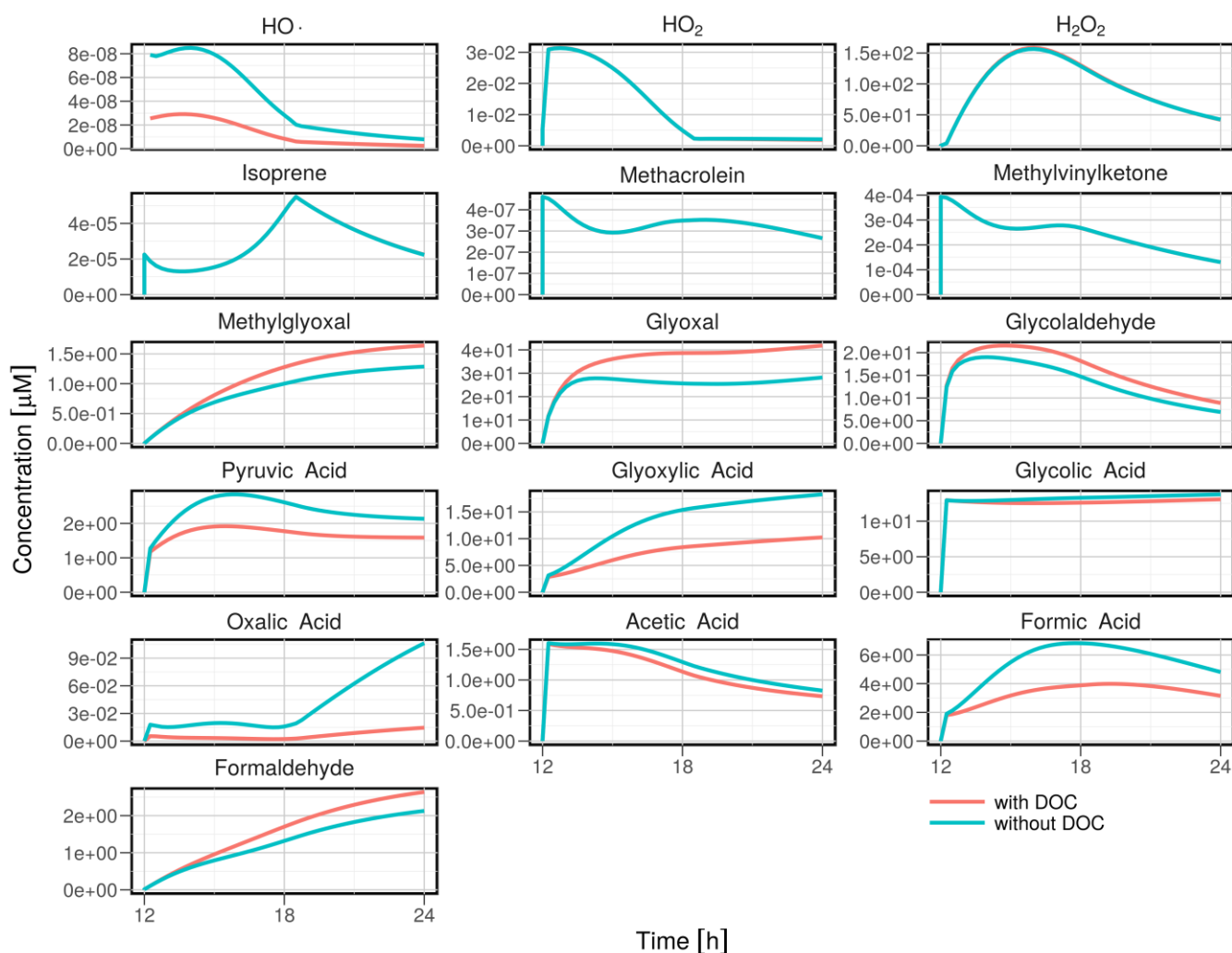
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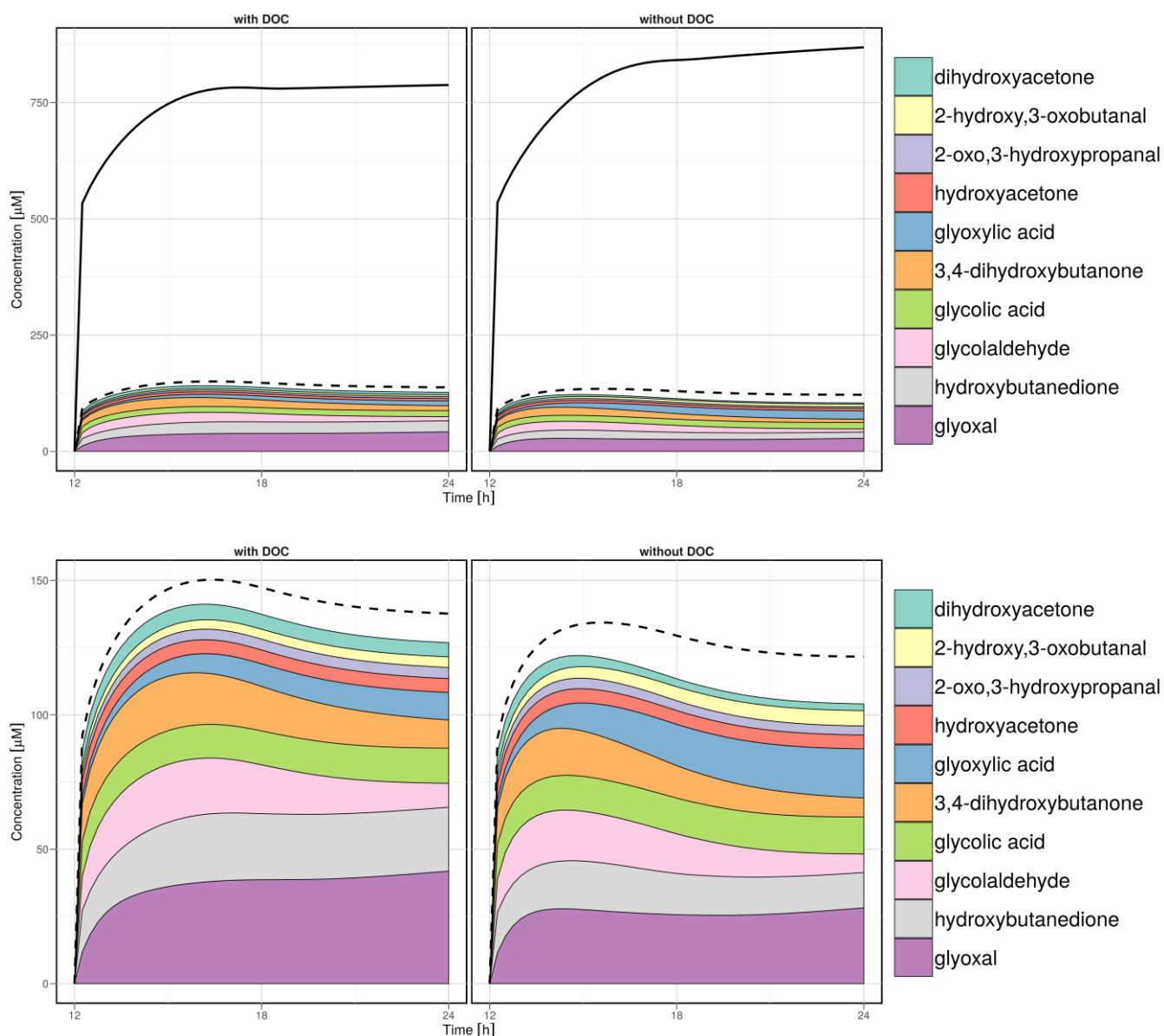
b)



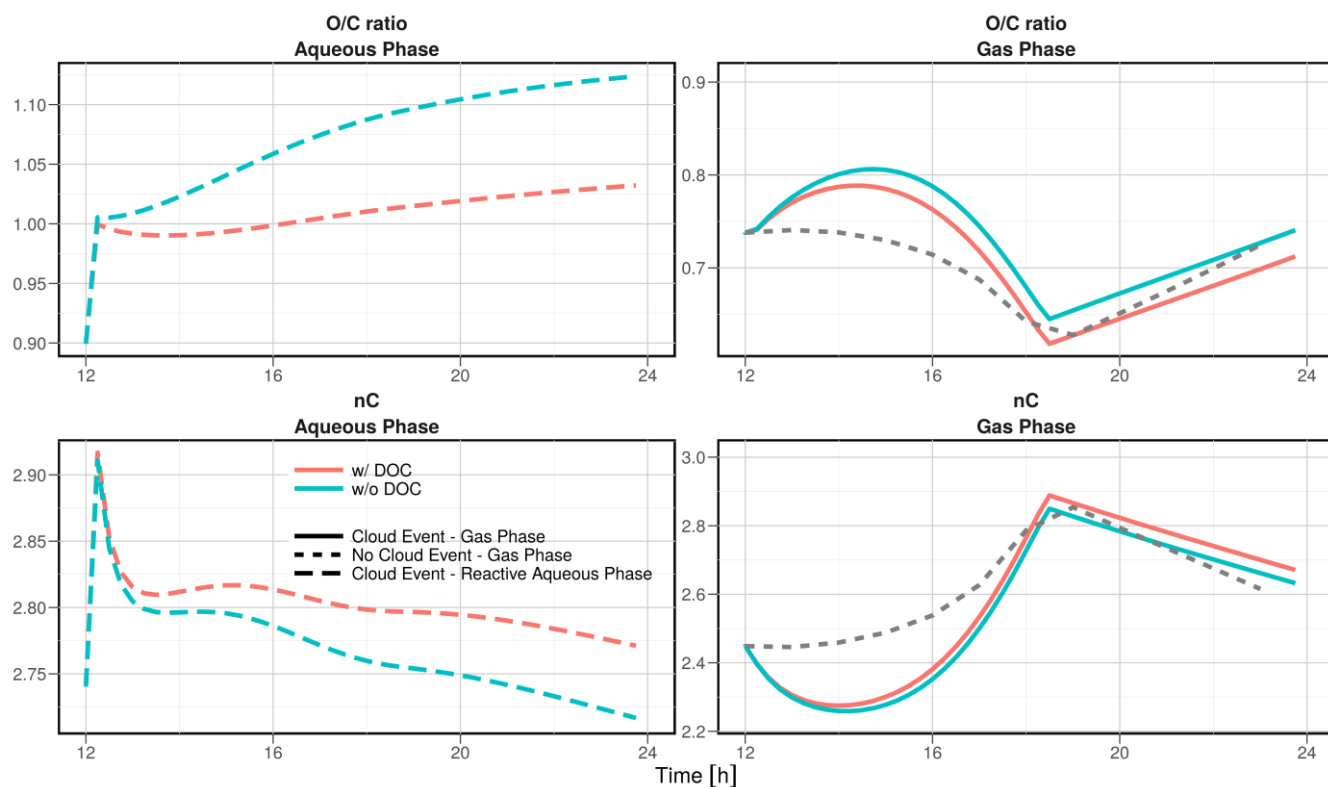
5 **Figures 3a & b: Time evolution of the gas phase mixing ratios without the cloud event (dashed lines) and during the cloud event (continuous line). The cloud event simulations are depicted with (red lines) and without (blue lines) DOC. [Please note that for most plots, the red line is hidden by the blue line.](#)**



**Figure 4:** Time evolution of the dissolved species concentrations during the simulated cloud event with (red lines) and without (blue lines) DOC. The vertical scale is in  $\mu\text{M}$ ; therefore, the HO· radical concentrations are in the  $10^{-14}$  M range. Please note that for some plots, the red line is hidden by the blue line.



**Figure 5:** Contribution of the 10 most important species (in terms of concentrations) in the aqueous phase (colours). The solid line depicts the total concentration of dissolved organic compounds. The dashed line depicts the total concentration of reactive dissolved species.



**Figure 6:** Time evolution of the mean O/C ratio for the reactive species (top; ratios are calculated on a number of atoms basis; CO, CO<sub>2</sub>, CH<sub>4</sub>, and iron-organic complexes are excluded from the calculation) and the mean number of carbon atoms  $n_C$  (bottom) in the aqueous phase (left) and in the gas phase (right) for the gas phase simulation (short dashed lines) and the cloud event simulation (continuous lines). Cloud event simulations are depicted with (red lines) and without (blue lines) DOC.

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