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Dr Laurent Deguillaume  
Dr. Camille Mouchel-Vallon  
February 24, 2017

To whom it may concern,  
Geoscientific Model Development  
Copernicus Publications

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Dear Sir, Madam,

Please find enclosed our corrected article submitted to Geoscientific Model Development (GMD). The article is entitled: *CLEPS: 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.

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This article describes in detail a protocol defining rules to write explicit organic oxidation chemical mechanisms for cloud chemistry. It is based on an extensive literature review and relies on the latest developments in empirical structure-activity relationships. Based on this protocol a new cloud chemistry model is proposed with an explicit aqueous chemical mechanism (CLEPS) coupled to the Leeds Master Chemical Mechanism.

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Following the second report of the reviewer, we proceed with the specific corrections and we provide detailed replies point by point to the comments. The points raised by the reviewer have significantly improve the paper. A new section has been completely rewritten to highlight the specificities of the CLEPS mechanism which can sometimes differ from CAPRAM (Ervens et al., 2003; Hermann et al., 2005) and to answer some of the reviewer comments dedicated to this particular comparison. Similarities and discrepancies between the two schemes are discussed and examples are provided for justifying choices in CLEPS when it is possible. Also, this new section allows avoiding repetitions and globally reduces the length of the paper as required by the reviewer. All the changes are indicated in a marked-up manuscript version for more clarity. We hope that the new revised version of the manuscript will be accepted for publication in GMD.

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Sincerely,



Laurent Deguillaume

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## Response to the reviewer:

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The manuscript has improved and the authors did a better job in explaining similarities to previous work. However, I still have several comments before the manuscript may be accepted for publication. The line numbers  
5 in my comments below refer to the marked-up manuscript that was attached to the response to the reviewers.

**First, we would like to thank the reviewer for his/her valuable comments. We are aware that some parts of the paper still needed more clarity. To improve this, a new section dedicated to the comparison of our mechanism CLEPS with CAPRAM has been added (section N° 5) in the manuscript. We also justify our chemical assumptions to better represent the oxidation processes of organic compounds in the aqueous  
10 phase.**

1) The abstract is rather lengthy, in particular in comparison to the introduction. I suggest shortening the abstract.  
**Yes, we agree with this comment. The abstract has been shortened.**

15 2) In general, the paper is very long and tedious to read. I suggest trying to shorten it where possible. I point out some repetitive paragraphs below.

**We can understand the reviewer's feeling. We believe that the revisions discussed here have shortened it and that the addition of a new section helps removing repetitive paragraphs.**

20 3) While discussing the commonalities of CAPRAM and CLEPS, the authors make it sound as if there is only one set of rate constants for inorganic and many organic reactions. A look at the NIST data base 'Solution Kinetics' shows that for many reactions there are multiple values with sometimes great discrepancies. CAPRAM 2.4 was built and revised and includes recommended values. This should be noted here.

**CLEPS is also built upon a set of recommended data from the older versions of the mechanism (M2C2, see  
25 Leriche et al., 2000, 2003, 2007 ; Deguillaume et al., 2004; Long et al., 2013). It started on the basis of the Jacob (1986) mechanism and was progressively extended and updated to increase details about inorganic chemistry, to add C1, C2, TMI chemistry as well as oxalic-iron complexes formation and photo-oxidation. In the new Section 5, the following was added to clarify this point: "These two mechanism are built upon their own set of recommended data (e.g., Ervens et al., 2004 for CAPRAM; Leriche et al., 2000, 2003, 2007;  
30 Deguillaume et al., 2004 for CLEPS)."**

4) In some parts, it still seems to me that important previous work was not considered. In a detailed analysis, it has been shown that the role of radicals other than OH for oxidation of organics in the aqueous phase is minor [Ervens et al., 2003a]. This should be at least mentioned and the addition of these radicals to the current  
35 mechanism justified. Has an analysis be done that shows that any reaction rates with other radicals that exceed those of OH?

**As mentioned in Section 3.1.4, NO<sub>3</sub>' is the main night-time oxidant in the gas phase. In the low-NO<sub>x</sub> conditions used in our test-case simulation, its role is minor in both phases. However, Herrmann et al. (2010) mention NO<sub>3</sub>' among the radicals that need to be considered for organic aqueous phase chemistry.**

For instance, future studies may identify conditions for which  $\text{NO}_3^-$  chemistry is important (*e.g.*, night time oxidation).

This question is already discussed in Section 3.1.4. We added a reference (Ervens et al., 2003a).

5 5) Doussin and Monod were by far not the first ones who published SARs for OH reactions with organics. Many of the data in their SAR were taken from the data set that was used earlier for similar SARs [Ervens et al., 2003b; Herrmann, 2003].

As mentioned in Section 3.1.3.3, Monod et al. (2005), Monod and Doussin (2008) and Doussin and Monod (2013) and simultaneously Minakata et al. (2009) are the first to publish SARs that allow estimating partial  
10 H-abstraction rate constants. Moreover estimating branching ratios by means of these SARs is also possible, contrarily to the methods exposed in Ervens et al. (2003b) and Herrmann (2003).

6) There are several SARs available for  $\text{NO}_3$  and  $\text{SO}_4^-$  reactions. They should be referred to and discussed in 3.4.2, *etc.* [Herrmann, 2003]. These SARs should be used instead of omitting reactions for  $\text{SO}_4^-$  and  $\text{NO}_3$  since  
15 this leads to a bias in the treatment of organic sinks.

The  $\text{NO}_3^-$  and  $\text{SO}_4^-$  rate constants estimation methods presented in Herrmann (2003) or Hoffmann et al. (2009) rely on using measured Bond Dissociation Energies (BDEs), or on estimating them when they are not available. Since we estimate  $\text{NO}_3^-$  reaction rates for all stable organic species in the CLEPS mechanism, the bias discussed by the reviewer can only be shown for  $\text{SO}_4^-$  reactions.

20 BDEs are most of the time not available for aqueous solutions. Therefore gas phase values are used, and Bensen's incremental method for the gas phase is applied when needed (Ervens et al., 2003b ; Hoffmann et al., 2009). These correlations have not been used in the CLEPS mechanism because i) BDEs estimations are often accompanied by high uncertainties, and ii) the assumption behind the use of gas phase data to  
25 treat aqueous phase data is that the solvent effect on both reactants and products is energetically identical for all reactions proceeding by H abstraction, which may be somewhat questionable in the case of acid (such as  $\text{HNO}_3$  and  $\text{HSO}_4^-$ ) formation in water.

In the new section 5, we also give an example to demonstrate that CLEPS is more likely to take into account the variety of possible oxidation products that are measured in the lab: "For instance, in Table 2 the hydrated glycolaldehyde final reactivity in CLEPS is equally distributed between three  $\text{HO}^\bullet$  attack  
30 sites and yields 33% glyoxylic acid, 28% glyoxal, 39% formic acid and formaldehyde. This result can be compared with the mechanism in CAPRAM 2.4 (Ervens et al., 2004) which leads to 100% glyoxylic acid since it only considers the aldehydic hydrogen abstraction."

7) Now the authors point out at several places that the cloud period of 12 hours is not realistic. Based on these  
35 statements, the 'test' of the model (p. 1, l. 40) should be better justified. Why not using shorter cloud periods of one hour or less as it has been done in previous model studies? Such tests do not require any sophisticated microphysics since it can be handled just like the performed model run by switching on the cloud for a realistic time after some initialization period. Given that the cloud is unrealistic, the comparisons to ambient measurements (p. 17, l. 34) does not seem very meaningful.

This paper aimed at looking at aqueous phase chemistry and for this we used an idealized cloud scenario that have been used in many others studies (Jacob et al., 1986; Herrmann et al., 2000; 2005,...). The coupling of the CLEPS model with a full microphysical model is the next step and at first will complexify the evaluation of the aqueous phase reactivity.

5 The new version of the paper now mentions the first hour of the cloud period, since this is indeed the period of time that can be meaningfully compared to ambient measurements: “In the first hours of the simulation, acetic and formic acids simulated concentrations are in the range of *in situ* measurements (Deguillaume et al., 2014).”

10 *Herrmann, H., Ervens, B., Jacobi, H. W., Wolke, R., Nowacki, P., and Zellner, R.: CAPRAM2.3: A chemical aqueous phase radical mechanism for tropospheric chemistry, J. Atmos. Chem., 36, 231-284, 10.1023/a:1006318622743, 2000.*

*Herrmann, H., Tilgner, A., Barzagli, P., Majdik, Z., Gligorovski, S., Poulain, L. and Monod, A.: Towards a more detailed description of tropospheric aqueous phase organic chemistry: CAPRAM 3.0, Atmos. Environ., 39(23-24), 4351–4363, doi:10.1016/j.atmosenv.2005.02.016, 2005.*

15 *Jacob, D. J.: Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate, J. Geophys. Res., 91(D9), 9807–9826, 1986.*

8) Some more details on the O/C calculation (end of Section 6.3) should be given. The end result largely depends on the initial O/C ratio. It has been shown previously that the O/C ratio of background aerosol can be enhanced due to cloud processing. This is not a new finding. Given the unrealistic cloud here, the resulting value is less important than the trend which has been shown by [Schrödner et al., 2014]. I do not agree with the authors that this reference is not relevant in this context. Also the statement in the conclusion about O/C ratio (p. 19, l. 8) should be discussed in the context of previous studies that have shown the same trends [Daumit et al., 2013; Ervens et al., 2014].

25 **The following sentence was added in Section 6.3 to clarify how O/C ratios are calculated and mention the modeled O/C ratios in Schrödner et al. (2014): “O/C is the ratio between the number of organic oxygen atoms and the organic carbon atoms in gas and cloud phases. The O/C ratios and  $n_C$  are a measure of the extent to which long-chain organic species are oxidized and are therefore indicators of their functionalization and/or fragmentation. One hour after the start of aqueous phase chemistry, O/C in the aqueous phase has remained around 1.0 and  $n_C$  has decreased to 2.8 after a sharp initial increase to 2.9, thus showing that fragmentation is a major process. This result is in good agreement with other aqueous phase studies (Bregonzio-Rozier et al., 2016; Epstein and Nizkorodov, 2012; Epstein et al., 2013) and other models (Schrödner et al., 2014), but are in disagreement with field studies, probably due to a lack of descriptions of high molecular weight substances, and of their reactivity, as well as oligomerization processes. The higher O/C ratios obtained by Schrödner et al. (2014) after cloud event (1.8 for their rural case) can be due to important oxalic acid concentrations dissolved into the aqueous phase in their model, when the cloud is being formed.”**

To our opinion, it is difficult to go into further comparisons with measured O/C ratios since most of the time the ratio relates to organic aerosol particles as in the study of Daumit et al. (2013) whereas in our

study the O/C in gas phase and in the cloud phase are discussed. In our study, the interest only lies in the fact that aqueous phase reactivity causes an increase in the O/C ratio in the gas phase especially when HO<sub>2</sub> is efficient (without DOC).

## 5 Minor comments

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- p. 2, l. 14: 'phase partitioning' should be replaced by 'phase separation'

**Yes, we replaced "phase partitioning" by "phase separation".**

10 - p. 2, l. 28: It is not true that CAPRAM v.3 is the most cited aqueous phase mechanism. The earlier version 2.3 has about twice as many citations (Web of Science) [Herrmann et al., 2000].

**Yes, we agree with the reviewer. CAPRAM 2.3 is the most cited version of CAPRAM. To our opinion, CAPRAM 2.3 is more related to inorganic chemistry and describes the reactivity of organic compound up to 2 carbon atoms. CAPRAM 3.0 (Herrmann et al., 2005) incorporates the former version CAPRAM 2.4 (Ervens et al., 2003) and a new extended reaction mechanism for atmospherically important organic compounds containing more than two and up to six carbon atoms. This mechanism is therefore more complete and is comparable to what is described in CLEPS. We rewrote the text to avoid any confusion.**

- p. 35: Define 'dilute conditions'.

20 **"Dilute conditions" is used to describe cloud droplets conditions, in opposition to deliquescent particles. This has been replaced by "cloud droplets".**

- p. 3, l. 17: MVK and MACR have Henry's law constants of 6.5 M/atm and 41 M/atm. Under common fog or cloud conditions, their fraction in the aqueous phase is  $\ll 0.1\%$  - even without salting-out effects.

25 **This paragraph is effectively confusing and has been rewritten as following:**

**"In the present study, the CLEPS mechanism is extended to the oxidation of C1-4 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 (methylglyoxal-MGLY, glyoxal-GLY, acrolein-ACR, methacrolein-MACR, methylvinylketone-MVK) and are transferred into the aqueous phase depending on their solubility and reactivity in the aqueous phase."**

30 **Moreover, even MVK and MACR have low Henry's law constants, field measurements have reported aqueous concentrations 100 to 1000 times higher than the one estimated by the Henry's law constants (van Pinxteren et al., 2005).**

35 *van Pinxteren, D., Plewka, A., Hofmann, D., Müller, K., Kramberger, H., Svrčina, B., Bächmann, K., Jaeschke, W., Mertes, S., Collett Jr, J. L., and Herrmann, H.: Schmücke hill cap cloud and valley stations aerosol characterisation during FEBUKO (II): Organic compounds, Atmospheric Environment, 39, 4305-4320, 10.1016/j.atmosenv.2005.02.014, 2005.*

- p. 3, l. 31: I do not understand this. Even if all dissociated and hydrated forms are considered, I do not see how 87 chemical species yield 657 chemical forms. How can each species occur in about eight different forms (657 / 87).

5 **Yes, we agree with the comment, this is not explained in the text. For each organic species, we describe their hydration equilibria (mono, di and tri-hydrated forms) and their acid dissociation equilibria (mono and di-anion forms). The mechanism is available in the SI for more details. For example, for the organic compound 3-oxopyruvic acid  $\text{CO}(\text{OH})\text{COCHO}$  (see table-mechanism-C3.pdf in the SI, page 29), we consider its acid dissociation equilibria but also the mono and di-hydrated forms of the acid form and of the mono-anion. This lead to the consideration of 8 different forms of the species 3-oxopyruvic acid. This**  
10 **compound then lead by oxidation to the formation of one major  $\text{RO}_2$  (in this specific case) that is also in equilibrium with various chemical forms (8 forms). So for this compound, 16 different chemical forms have to be considered to describe its reactivity in CLEPS.**

15 **The text has been modified as follows: “This empirical reduction scheme helps to limit the number of species and reactions (657 different chemical forms (*i.e.*, hydrates, anions and derived radicals) representing 87 stable species reacting in 673 oxidation reactions).”**

- p. 6, l. 30; and p. 8, l. 32: Using Bond Dissociation Energies (BDEs) does not rely on estimates, These Energies have been measured and are tabulated [Benson et al., 1968; Benson, 1976].

20 **Yes, we agree with this comment. The sentence p. 6 l. 30 is modified as following: “In previous mechanisms, the most labile H-atom was identified (e.g., using Bond Dissociation Energy measurements)”.** The sentence p. 8, l. 32 is now in section 5 when we describe the differences between CLEPS and CAPRAM: **“they assume that the reaction will proceed through the identified most probable pathway using the bond dissociation energy measurements”.**

25 - p. 13, l. 8-11: This new text should be rewritten: 1) The first part sounds odd. I suggest changing it to ‘We made sure that all species have an equivalent in the respective other phase, even if this species in that phase is not reactive.’ 2) The mass transfer coefficients do not determine ultimately where a species resides as they describe the kinetics of the uptake. Only the Henry’s law constant describes the thermodynamics and therefore where a species will reside.

30 **The text has been rewritten following the reviewer’s comments.**

- p. 14, l. 12: ‘Kinetic parameterization’ of mass transfer or including chemical processes?

**We agree, we write “The kinetic parameterization of mass transfer in our cloud chemistry model”.**

35 - p. 14, l. 30: The mass transfer is not represented by a rate constant as this implies a chemical transformation. I suggest using ‘The mass transfer coefficients...’

**We agree, the text has been modified according to the comment.**

- p. 14, l. 31: Not all Henry’s law constants are estimated.

**Yes we agree. We suppress the word “estimated” in the sentence.**

- p. 15, l. 9: Specify whether dry or wet deposition or both.

**We only consider dry deposition. This has been corrected.**

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- p. 15, l. 18: Microphysics is not necessarily needed in order to simulate a more realistic cloud. In past models, reasonable approaches were taken by just switching on/off a cloud that is then present with constant LWC, drop size etc. for a shorter period than 12 hours.

10 **We agree with this. The sentence has been modified as follows “Future studies will use variable environmental conditions that require the consideration of microphysical processes with our multiphase chemical module.”**

- p. 16, l. 9, and p. 18, l. 22: Replace ‘dry’ by ‘cloud-free’. Real dry conditions (RH = 0%) are barely encountered in the atmosphere. What is the RH (water vapor concentration) during the gas-phase only runs?

15 **We agree with this. This has been corrected. The RH (10 %) conditions were precised in the text.**

- p. 16, l. 30/31 and 34/35: These lines are repetitive and can be combined.

20 **We agree with the reviewer. We combine these lines in one sentence: “Glyoxal, glycolaldehyde, pyruvic acid, glyoxylic acid and glycolic acid are readily soluble species that react in the aqueous phase (Herrmann et al., 2015), explaining the sharp decrease of their gas phase mixing ratios”.**

- p. 16, l. 39: How is oxalic acid partitioning treated in the model? Oxalic acid has a fairly high vapor pressure. The only reason it remains in the aqueous/particle phase is the fact that it forms salts and stable complexes [Furukawa and Takahashi, 2011; Paris and Desboeufs, 2013].

25 **Oxalic acid partitioning is treated like other species in the model. A Henry’s law constant is documented (Saxena and Hildemann, 1996). The complexation of oxalate ions with iron is also included in the mechanism (see R349-354 in the mechanism), and explains why oxalic acid largely remains in the aqueous phase.**

30 *Saxena, P., and Hildemann, L. M.: Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, J. Atmos. Chem., 24, 57-109, 1996.*

- p. 16, l. 39: What is meant by ‘oxidation sink for all species’? A reduction in the oxidation rates because DOC is added and therefore OH is reduced? Clarify.

35 **We replaced the sentence “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 sink (e.g., glyoxal, glycolaldehyde) because the reduced aqueous HO<sup>•</sup> concentrations (see Figure 4) limit the impact of the aqueous sink.” with “The addition of the missing aqueous HO<sup>•</sup> sink due to reaction with all dissolved unreactive species (red lines in Figures 3a & 3b) leads to higher concentrations of species for**

which reactive uptake is an overall sink (*e.g.*, glyoxal, glycolaldehyde). In this additional HO<sup>•</sup> sink, the reduced aqueous HO<sup>•</sup> concentrations (see Figure 4) limit the impact of the aqueous sink.”

- p. 17, l. 1-12, and l. 26-29: These lines can be combined as they are repetitive.

5 To avoid the repetition, we replace: “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 C2 compounds contributing to 18%, and C4 compounds contributing to 12% of HO<sup>•</sup> destruction. C1 and C3 together are responsible for 5% of the HO<sup>•</sup> sink.” by “Organics are the most important HO<sup>•</sup> sinks, with DOC contributing to 64%, C2 compounds contributing to 18%, and C4 compounds contributing to 12% of HO<sup>•</sup> destruction. C1 and C3 together are responsible for 5% of the HO<sup>•</sup> sink.”

- p. 17, l. 17: What is meant by ‘pseudo steady state conditions’? Are they in thermodynamic equilibrium with their gas phase counterparts?

15 Steady state conditions refer to conditions where sources are equal to sinks. We can remove the “Pseudo” from this expression to remove unneeded complications. In that case, the concentration of a given species is  $C = \text{sources/sinks}$ . However the explanation in this part is erroneous. We replace the sentences:

“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. 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 have 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.” with the following:

25 “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 chemistry is slowed down and their rates of production are slower, giving lower maximum concentrations.”

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- p. 18, l. 18: This statement is not true. The solubility of small functionalized organics often exceeds that one of their larger homologues (*e.g.*  $K_H(\text{glyoxal}) = 10^5 \text{ M/atm}$  vs  $K_H(\text{methylglyoxal}) = 3000 \text{ M/atm}$ ).

The sentence “Large molecules with high functionalization are statistically more soluble than smaller molecules” has been rephrased: “Large molecules with high functionalization are statistically more soluble than smaller, less functionalized molecules”.

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- p. 18, l. 36: Earlier it is said that photolysis processes are largely omitted due to the lack of data.

Yes, we agree with the reviewer. We suppress “their reactivity by direct photolysis” from the sentence.



- p. 19, l. 14/15: This text is confusing since it reads as if glyoxal *etc* are considered high molecular weight compound precursors.

**This sentence was suppressed in the final version of the manuscript. Because, the text was confusing.**

5 - p. 19, l. 17-19: This is not a conclusion of the current study.

**Yes, we agree. These sentences have been deleted from our manuscript.**

- p. 19, l. 38: Why are the mechanisms more useful for longer experiments? If all reactions are implemented correctly the time period or the number of phases (multiphase vs bulk aqueous phase) should not matter.

10 **Yes, we agree. The sentence was rewritten as follows: “The mechanisms are more likely to be useful for experiments involving multi-phases such as in environmental cloud chambers (see for example Brégonzio-Rozier et al., 2016).”**

## Technical comments

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- p. 1, l. 27: hydrosoluble should be replaced by water-soluble as it is used like that later on

**Done.**

5 - p. 1, l. 39: 'is' --> 'are'

**Done.**

- p. 3, l. 21: charges missing on  $\text{SO}_4^-$  and  $\text{Cl}_2^-$

**Done.**

- p. 6, l. 3: replace 'from' by 'by'

10 **Done.**

- p. 6, l. 6: Add 'constant' ('rate constant').

**Done.**

- p. 8, l. 30; p. 9, l. 5: reaction rates --> rate constants

**Done.**

15 - p. 15, l. 5: 'The simulation is located...' sounds odd. Reword.

**Corrected.**

- p. 15, l. 35: 'oxidants' --> 'oxidant'

**Done.**

- p. 16, l. 17 and 19: 'They emit...' and 'We emit...' is very colloquial. Reword.

20 **The sentences have been rewritten.**

- p. 16, l. 21: hydrocarbons --> hydrocarbon

**Done.**

- p. 17, l. 1: 'sinks' --> 'sink'

**Done.**

25 - p. 17, l. 16: 'has' --> 'have'

**Done.**

- p. 17, l. 37: Add 'reaction' (reactive sink reaction)

**Done.**

## References

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# CLEPS 1.0: A new protocol for cloud aqueous phase oxidation of VOC mechanisms

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**Abstract.** A new detailed aqueous phase mechanism named the Cloud Explicit Physico-chemical Scheme (CLEPS 1.0) is proposed to describe the oxidation of water soluble organic compounds resulting from isoprene oxidation. It is based on Structure Activity Relationships (SARs) which provide global rate constants together with branching ratios for HO  abstraction and addition on atmospheric organic compounds. The GROMHE SAR allows the evaluation of Henry's law constants for undocumented organic compounds. This new aqueous phase mechanism is coupled with the MCM v3.3.1 gas phase mechanism through a mass transfer scheme between gas phase and aqueous phase. The resulting multiphase mechanism has been then implemented in a model based on the Dynamically Simple Model for Atmospheric Chemical Complexity (DSMACC) using the Kinetic PreProcessor (KPP) that can serve to analyze data from cloud chamber experiments and field campaigns.

The simulation of permanent cloud under low-NOx conditions describes the formation of oxidized mono- and diacids in the aqueous phase as well as a significant influence on the gas phase chemistry and composition and shows that the aqueous phase reactivity leads to an efficient fragmentation and functionalization of organic compounds.

## 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 (Br egonzio-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  oxidation, and it has been shown that phase partitioning-separation of its precursors in clouds 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 (Herrmann et al., 2005; Tilgner and Herrmann, 2010; Whalley et al., 2015) 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 A new protocol mechanism, the Cloud Explicit Physicochemical Scheme (CLEPS 1.0), is including organic compounds up to C4 has been developed under low-NO<sub>x</sub> (< 1 ppbv) and dilute cloudy conditions and uses recently available laboratory data and empirical estimation methods. The mechanism Then it 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. It will be described in details and finally compared with same kind of mechanisms such as CAPRAM (Herrmann et al., 2005; Tilgner and Herrmann, 2010; Whalley et al., 2015) to highlight new features that have been proposed to create an explicit aqueous phase oxidation mechanism to accurately represent the various oxidation pathways of organic matter. The box model is tested in an ideal cloud situation.~~

## **2 Overview of the CLEPS chemical mechanism**

The aqueous phase oxidation mechanism originally relied on inorganic chemistry (see Deguillaume et al., 2004; Leriche et al., 2007) and on the oxidation of several organic C<sub>1</sub> and C<sub>2</sub> species, including photo-oxidation of iron complexes with oxalic acid (Long et al., 2013). ~~The inorganic processes taken into account in CLEPS are described in ) and . This The inorganic mechanism simulates the redox processes involved in the evolution of H<sub>x</sub>O<sub>y</sub>, sulphur, nitrogen, halogens (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 (methylglyoxal-MGLY, glyoxal-GLY, acrolein-ACR, methacrolein-MACR, methylvinylketone-MVK) and are transferred into the aqueous phase ~~depending according to~~ on their solubility and reactivity in the aqueous phase. 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). 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 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.*, 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 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).

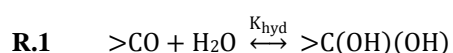
The mechanism currently includes 850 aqueous reactions and 465 equilibria. Inorganic reactivity is described for 67 chemical species (*e.g.*, TMI<sub>s</sub>, H<sub>x</sub>O<sub>y</sub>, sulphur species, nitrogen species and chlorine). For organic compounds, 87 chemical species are considered in the mechanism ~~corresponding leading to~~ 657 chemical forms (e.g., when considering their various products as hydrated forms, anionic forms, radicals forms). The mechanism tables are available in the supplementary data.

### 3 Development of the CLEPS aqueous phase mechanism

#### 3.1 Stable Non-radical organic species

##### 3.1.1 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 ( $\sigma^*(-\text{CO}(\text{O}^-)) = -1.06$ ,  $\sigma_m(-\text{CO}(\text{O}^-)) = 0.09$ ,  $\sigma_p(-\text{CO}(\text{O}^-)) = -0.05$  and  $\sigma_o(-\text{CO}(\text{O}^-)) = -0.91$ ; 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% (*hd*descriptor) to 18% (*ketone* flag) of their initial values. There is greater uncertainty associated with this new optimization; the root mean square error ( $\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^n (\log K_{\text{hyd,est}} - \log K_{\text{hyd,exp}})^2}$ ) is 0.61 log units, which is higher than the  $\text{RMSE} = 0.47$  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 ( $\text{RO}_2^{\cdot}$ ) and acylperoxy ( $\text{RC}(=\text{O})(\text{O}_2^{\cdot})$ ) 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  $\text{RO}_2^{\cdot}$  the hydration constant of its parent species. For example, for the radicals derived from glycolaldehyde, we have:

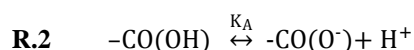
$$\text{Eq.3} \quad K_{\text{hyd}}(\text{CH}_2(\text{OH})\text{CO}(\text{OO}^{\cdot})) = K_{\text{hyd}}(\text{CH}(\text{OH})(\text{OO}^{\cdot})\text{CHO}) = K_{\text{hyd}}(\text{CH}_2(\text{OH})\text{CHO}) = 10$$

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 from what is done in CAPRAM 3.0 (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.~~

### 3.1.2 Acid dissociation equilibria

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



The acidity constant  $K_A$  is defined by:

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

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 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.*:

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

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.

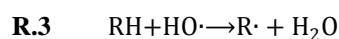
Following the hydration constant treatment, the acidity constants for peroxy radicals are initially taken from their parent species when experimental data are not documented. This assumption can be questioned but very few measurements suggest that peroxy radicals are more acidic than their parent species. Schuchmann et al. (1989) showed that the acetic acid peroxy radical ( $\text{CH}_2(\text{OO}^\bullet)\text{CO(OH)}$ ) 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.

~~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.~~

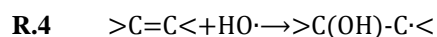
### 3.1.3 Reaction with $\text{HO}^\bullet$

#### 3.1.3.1 Mechanism

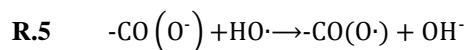
For aliphatic organic compounds,  $\text{HO}^\bullet$  reactivity proceeds by H-abstraction, yielding an alkyl radical following what can occur in the gas phase (Herrmann et al., 2010, 2015):



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



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):



#### 3.1.3.2 Rate constants

When rate constants of organic compounds reactions with  $\text{HO}^\bullet$  are available (see the review by Herrmann et al., 2010), they are used in the mechanism. In the CLEPS mechanism, for a total of 343 reactions with  $\text{HO}^\bullet$ , only 43 kinetic constants are available in the literature. Empirical estimates are thus required in most cases. The estimates are obtained using the ~~the a~~ recently developments of SARs ed SAR for the  $\text{HO}^\bullet$  rate constant. 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.

5 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  $k(-C(=O)CO(O^-)) = 2.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , 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  
10 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  $k(-CO(O^-)) = 2.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  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, hydroxy-  
15 methylvinylketone - MVKOH and hydroxy-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.

### 3.1.3.3 Branching ratios

20 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 $\cdot$  reactions are extremely  
25 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)  
30 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<sup>3</sup> distinct species involved in approximately 10<sup>4</sup> 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.  
35 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 (*i.e.*,  
40 [hydrates, anions and derived radicals](#)) representing 87 [stable](#) species reacting in 673 oxidation reactions). This new aqueous phase mechanism then allows consideration of the most probable H-abstraction reactions. ~~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· 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· 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<sup>-1</sup> and the corresponding free energies range from -13 to -47 kcal mol<sup>-1</sup>.

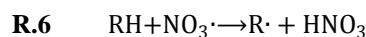
~~The SAR from Doussin and Monod (2013) was recently published. Therefore, Herrmann et al. (2005) and Tilgner et al. (2013) could not use this method to estimate rate constants and branching ratios. Instead, they rely on similarities when data are not available: for instance, they assume that the HO· 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.~~

### 3.1.4 Reaction with NO<sub>3</sub><sup>·</sup>

NO<sub>3</sub><sup>·</sup> is the main night-time oxidant in the gas phase. Although it plays a minor role under low-NO<sub>x</sub> conditions (Ervens et al., 2003), NO<sub>3</sub><sup>·</sup> 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<sub>3</sub><sup>·</sup> radicals (Tilgner and Herrmann et al., 2010). For this reason, we represent NO<sub>3</sub><sup>·</sup> oxidation for each stable species in the mechanism.

#### 3.1.4.1 Mechanisms

The mechanism of NO<sub>3</sub><sup>·</sup> oxidation is similar to that of HO· oxidation: the reactivity mainly proceeds via H-abstraction of a labile hydrogen atom to form an alkyl radical and nitric acid:

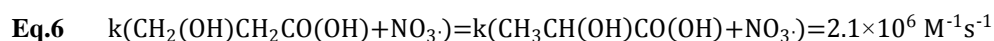


In this version of the mechanism, the addition of an NO<sub>3</sub><sup>·</sup> radical to the C=C double bond is not considered since insufficient data are available for these reactions and for the fate of the resulting organonitrate peroxy radicals. However, organonitrate compounds were recently identified 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.

#### 3.1.4.2 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.

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



(De Semainville et al., 2007)

### 10 3.1.4.3 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>.

20 ~~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 rate constants 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.~~

### 3.1.5 Reaction with other oxidants

25 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 SO<sub>4</sub><sup>•-</sup> radicals) or marine (relatively rich in Cl<sub>2</sub><sup>•-</sup> and other halogenated radicals) environments.~~

30 ~~Since our mechanism is developed for low NO<sub>x</sub> conditions, the~~ The reactivity of selected oxygenated organic species with H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>, which was recently studied by Schöne and Herrmann (2014), is [also](#) included in the mechanism (see reactions R586 and R590 in the mechanism tables). Although these **rate constants** are in the range of 10<sup>-1</sup> to 10<sup>1</sup> M<sup>-1</sup> s<sup>-1</sup>, their impact is non-negligible under specific conditions, especially under low-NO<sub>x</sub> conditions. Furthermore, reactions of C<sub>1-2</sub> hydroperoxide compounds in Fenton-like reactions with Fe<sup>2+</sup> have been studied by Chevallier et al. (2004) and are included in the mechanism (see reactions R238 and R330 in the mechanism tables).

### 3.1.6 Photolysis

Most of the species considered in the mechanism are oxygenated and are likely to bear chromophore functional groups. To calculate the photolysis rate, the polychromatic absorption cross-sections and quantum yields must be known. Again, the

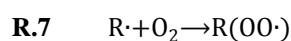
literature data concerning these subjects are scarce. Photolysis data are available for a few chromophore species: H<sub>2</sub>O<sub>2</sub> (Graedel and Weschler, 1981; Zellner et al., 1990), carboxylate-iron(III) complexes (Faust and Zepp, 1993; Long et al., 2013; Weller et al., 2013a, 2013b), and 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 H<sub>2</sub>O<sub>2</sub> (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 HO• 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.

## 3.2 Organic radicals

### 3.2.1 Alkyl radical O<sub>2</sub> addition

In dilute aqueous solution, alkyl radicals react with dissolved O<sub>2</sub> to form peroxy radicals:



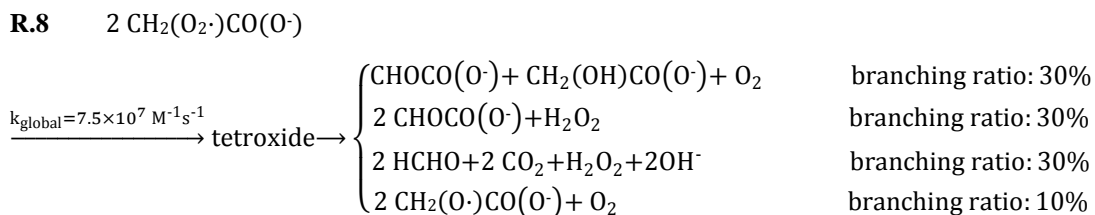
Recent studies suggest that under high organic radical concentrations, this addition competes with the self- or cross-reactions of alkyl radicals, yielding high molecular weight molecules, such as oligomers (see Ervens et al., 2015; Griffith et al., 2013; Lim et al., 2013; Renard et al., 2015). This competition can favour oligomerization if O<sub>2</sub> 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. The review by Alfassi (1997) showed that the kinetics of the great majority of R + O<sub>2</sub> reactions are close to the diffusion limit, with rate constants of 2.0–4.0×10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>, and for non-carbon-centred radicals (such as nitrogen-centred radicals), significantly smaller rate constants are observed (10<sup>7</sup> to 10<sup>8</sup> M<sup>-1</sup> s<sup>-1</sup>). Hence, in our mechanism (which does not consider nitrogen-centred radicals) 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, which are not presently considered in the CLEPS mechanism. 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.~~

### 3.2.2 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.

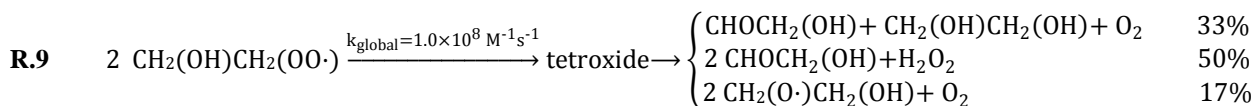
The decomposition of tetroxide follows different pathways, depending on the nature of the initial peroxy radical. Piesiak et al. (1984) proposed a mechanism for the evolution of the tetroxide formed after dimerization of  $\beta$ -hydroxyethylperoxy radicals. Zegota et al. (1986) studied the self-reaction 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  $\beta$ -peroxycarboxylic acids ( $>C(OO^\bullet)C(=O)(OH)$ ) and their conjugated bases, we generalize the experimental results obtained by Schuchmann et al. (1985) for the acetate peroxy radical ( $CH_2(OO^\bullet)C(=O)(O^-)$ ). For this radical, the tetroxide is degraded through four pathways (reaction R.8):



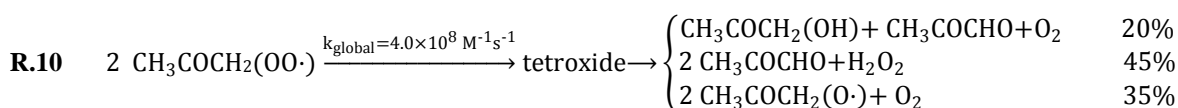
The four pathways retained in this work are the most important identified by Schuchmann et al. (1985). The sum of these pathways contributes to 87% of the tetroxide decomposition, and each individual contribution is scaled to reach 100% overall.

The evolution of  $\beta$ -hydroxyperoxy radicals ( $>C(OH)C(OO^\bullet)<$ ) is represented by the experimental results obtained by Piesiak et al. (1984) for the  $\beta$ -hydroxyethylperoxy radical ( $\text{CH}_2(\text{OH})\text{CH}_2(\text{OO}^\bullet)$ ) (reaction R.9):

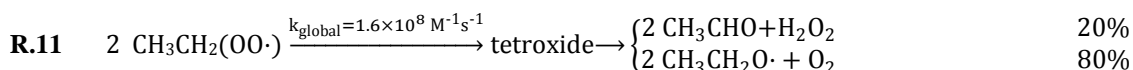


The three pathways are reported to contribute to 90% of the degradation of the tetroxide (Piesiak et al., 1984). The mechanism is restricted to these major pathways, and their individual contributions are scaled to reach 100% overall in our mechanism.

$\beta$ -oxoperoxy radicals ( $-\text{COC}(\text{OO}^\bullet)<$ ) are treated based on the studies of the acetylperoxy 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):

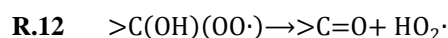


The rate constant was measured by Herrmann et al. (1999). Schuchmann and von Sonntag (1984) estimated that the first pathway (aldehyde pathway) contributes to 20% of the tetroxide decomposition. Studying the ethylperoxy radical derived from the photooxidation of ethylhydroperoxyde, Monod et al. (2007) found that the second pathway (alkoxyl pathway) is

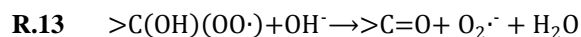
more likely than the aldehyde pathway, in agreement with previous studies (Henon et al., 1997; von Sonntag and Schuchmann, 1997). Therefore, we attributed the remaining degradation of the tetroxide to the alkoxy pathway.

### 3.2.3 $\alpha$ -hydroxyperoxyl $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ elimination

5 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):



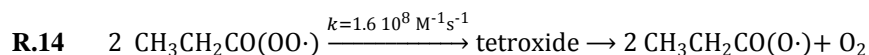
10 von Sonntag (1987) showed that the  $\text{HO}_2^\bullet$  elimination rate constant is dependent on the nature of the substituent attached to the carbon atom. Following this study, we generalized the  $\text{HO}_2^\bullet$  elimination rate constants for unknown species using available experimental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

In the case of  $\alpha$ -dihydroxy-peroxy compounds ( $-\text{C}(\text{OH})(\text{OH})(\text{OO}\cdot)$ ), 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 **rate constant** for the 2, $\alpha$ -hydroxypropylperoxy radical ( $k(\text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_3 + \text{OH}^-) = 5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and the  $\alpha$ -hydroxyethylperoxy radical ( $k(\text{CH}_3\text{CH}(\text{OH})(\text{OO}\cdot) + \text{OH}^-) = 4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). 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 rate constants, is assigned to each elimination reaction.

20 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; 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.

### 3.2.4 Acylperoxy decarboxylation

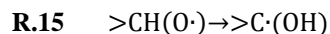
25 Acylperoxy radicals ( $-\text{CO}(\text{OO}\cdot)$ ) are treated like standard peroxy radicals (see R.11) for which only the alkoxy formation pathway is considered due to the lack of an H-atom on the peroxy radical. For the acylperoxy derived from propionaldehyde, this gives:



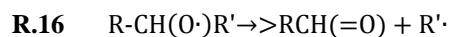
30 The acylalkoxy radical undergoes C-C bond scission and yields  $\text{CO}_2$ , accounting for the expected decarboxylation of the acylperoxy radical.

### 3.2.5 Alkoxy radicals

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



35 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 peroxy radicals and showed that the produced alkoxy radical ( $CH_2(O\cdot)C(=O)(O\cdot)$ ) 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.

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  $\beta$ -hydroxyethylperoxy radical using the **rate constant** and branching ratios from Piesiak et al. (1984) (see R.9):

Pathway 1: $2 CH_2(OH)CH_2(OO\cdot) \rightarrow 2 CHOCH_2(OH) + H_2O_2$	$k = 5.0 \cdot 10^7 M^{-1} s^{-1}$	Piesiak et al. (1984)
Pathway 2: $2 CH_2(OH)CH_2(OO\cdot) \rightarrow CHOCH_2(OH) + CH_2(OH)CH_2(OH) + O_2$	$k = 3.3 \cdot 10^7 M^{-1} s^{-1}$	Piesiak et al. (1984)
Pathway 3: $2 CH_2(OH)CH_2(OO\cdot) \rightarrow 2 CH_2(O\cdot)CH_2(OH) + O_2$	$k = 1.7 \cdot 10^7 M^{-1} s^{-1}$	Piesiak et al. (1984)
$CH_2(O\cdot)CH_2(OH) \rightarrow C\cdot H_2(OH) + CH_2O$	Fast	
$C\cdot H_2(OH) + O_2 \rightarrow CH_2(OH)(OO\cdot)$	$k = 2.0 \cdot 10^9 M^{-1} s^{-1}$	
<hr/>		
$2 CH_2(OH)CH_2(OO\cdot) \rightarrow 1.33 CHOCH_2(OH) + 0.33 CH_2(OH)CH_2(OH) + 0.34 CH_2O + 0.34 CH_2(OH)(OO\cdot) + 0.50 H_2O_2 + 0.16 O_2 - 0.34 H_2O$	$k = 1.0 \cdot 10^8 M^{-1} s^{-1}$	Piesiak et al. (1984)

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

~~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.~~

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

##### 4.1 Gas phase mechanism

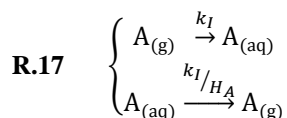
The CLEPS mechanism is coupled to the gas phase Master Chemical Mechanism, MCM v3.3.1 (Jenkin et al., 2015; Saunders et al., 2003) provided at: <http://mcm.leeds.ac.uk/MCM>. The new version 3.3.1 of MCM includes in particular the treatment of isoprene oxidation products such as epoxydiols, hydroxymethylmethyl-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

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. ~~We made sure that all species have an equivalent in the respective other phase, even if this species in that phase is not reactive. 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.~~

##### 4.2 Estimating mass transfer parameters



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



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:

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

5 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. 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-Duran et al., 2010). Comparing this SAR with other available  
10 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.

When unavailable, the temperature dependencies (enthalpy of dissolution) are set to 50 kJ mol<sup>-1</sup>.  $D_g$  is calculated by scaling  
15 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  $\sqrt{\frac{8RT}{\pi M_A}}$  with  $R=8.3145$  10<sup>7</sup> 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):

$$20 \quad \mathbf{R.19} \quad \frac{\alpha}{1-\alpha} = e^{-\frac{\Delta G_{\text{obs}}}{RT}}$$

$\Delta G_{\text{obs}} = \Delta H_{\text{obs}} - T\Delta S_{\text{obs}}$  [J mol<sup>-1</sup>] is interpreted as a 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  
25 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 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 mass transfer parameterization in our cloud chemistry model has been used for a long time (Jacob, 1986). ~~The other~~ Most 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  
35



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).

#### 4.3 Model description

5 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**.

10 Aqueous phase reactions are implemented as a new reaction type. Rate constants in units of  $M^{-n} s^{-1}$  are converted to  $molec^{-n} cm^{-3n} s^{-1}$ , 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  $H^+$  is explicitly produced and consumed in the  
15 equilibrium reactions.

Mass transfer is also implemented as a new reaction type. The ~~rate constants~~ mass transfer coefficients are calculated following Schwartz (1986) and depend on the 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 (TUV 4.5, (Emmerson and Evans, 2009)) included in DSMACC to calculate the photolysis rates in the gas phase was has been 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).  
20

25 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 (Djouad et al., 2002, 2003).

#### 5. Comparison with existing cloud aqueous phase mechanism

The Cloud Explicit Physicochemical Scheme (CLEPS 1.0) has been developed in the most explicit way to take into account the most probable oxidation pathways of organic compounds. The protocol that is applied to develop CLEPS is in the same spirit as GECKO-A (Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere; Aumont et al., 2012; La et al., 2016; Mouchel Vallon et al., 2013) and as CAPRAM 3.0 (Chemical Aqueous Phase Radical Mechanism; Herrmann et al., 2005; Tilgner and Herrmann, 2010; Whalley et al., 2015). In this section, it is important to compare the main stages of the building of both aqueous phase mechanisms (CLEPS vs. CAPRAM) since GECKO-A is more dedicated to gas phase chemistry.  
30

CLEPS and CAPRAM present similarities. They are both developed on hypothesis in the choice of chemical pathways and rate constants that are carefully calibrated carefully against experimental data when available. For instance, inorganic chemistry, pH calculation, acidity constant estimates, photolysis rates calculations are similar in both aqueous mechanisms. These two mechanism were built upon their own set of recommended data (e.g., Ervens et al., 2004 for CAPRAM; Leriche et al., 2000, 2003, 2007; Deguillaume et al., 2004 for CLEPS). However, some differences exist and are listed below. Those  
35

differences are justified with the way both mechanisms will be applied for: coupling with a regional/global model, interpreting laboratory and/or observational data from field experiment, introducing biodegradation processes, *etc.*

First of all, the two mechanisms are ~~developed behind~~ coupled to two quite contrasted ~~different~~ gas phase mechanisms ~~quite contrasted~~ since CAPRAM is based upon RACM and CLEPS upon MCM, ~~respectively~~. The fact that RACM (Stockwell et al., 1997) includes lumped species while MCM is fully explicit ~~is going to leads~~ to different developments in the aqueous phase. In CAPRAM, the lumped gaseous species ~~is splitted~~ are split into several fractions that are then transferred to the corresponding species in the aqueous phase whereas in CLEPS, individual gas species are directly transferred to the corresponding aqueous phase species ~~individual gas species are transferred as a standalonewith direct matches to aqueous phase 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).

Secondly, CAPRAM only represents ~~only~~ one oxidation pathway for each non-radical aqueous species when usually in the laboratory several first generation oxidation products are detected (Perri et al., 2009). In CLEPS however, ~~considers the various possible oxidation pathways of organic compounds are considered and,~~ in this regard, ~~is~~ CLEPS more accurate to be compared with experimental data is more likely to take into account the variety of oxidation products. For example instance, in Table 2 for the hydrated glycolaldehyde, ~~the final reactivity in our mechanism~~ CLEPS is equally distributed between three HO<sup>•</sup> attack sites and yields 33% glyoxylic acid, 28% glyoxal, 39% formic acid and formaldehyde. This result can be compared with the mechanism ~~of~~ in CAPRAM 2.4 (Ervens et al., (2004), which leads to 100% glyoxylic acid since it only considers the aldehydic hydrogen abstraction ~~of the aldehydic hydrogen~~.

Then, an important difference between CLEPS and CAPRAM ~~is~~ lies in the hypotheses that are ~~done~~ made when ~~missing~~ rate constants, branching ratios, solubility and hydration constants are missing. In CLEPS, ~~we systematically apply the recent SAR from Doussin and Monod (2013) is systematically applied~~ to estimate rate constants and branching ratios for the HO<sup>•</sup> oxidation, ~~and the GROMHE SAR (Raventos Duran et al., 2010) for solubility and hydration constants~~. In CAPRAM, Herrmann et al. (2005) and Tilgner et al. (2013) may 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 using the bond dissociation energy measurements (Benson, 1976; Evans and M. Polanyi, 1938). In some other cases, like for 2,4-butanedione, they attribute branching ratios from the equivalent measured gas phase reaction. ~~The choice for SAR methods in CLEPS is motivated by a systematic approach that can fit with automated chemical scheme generation tools (as used in GECKO A).~~

There is one exception ~~for the oxidation of organic compounds by NO<sub>3</sub><sup>•</sup> for the estimation of the rate constant for the estimation of NO<sub>3</sub><sup>•</sup> reaction rates~~ since no SAR are available up to now. In CLEPS, similarity criteria are used for the rate constants and branching ratios are estimated in the same way ~~than~~ as for HO<sup>•</sup>. In CAPRAM, ~~they use the~~ Evans-Polanyi-type correlations are used to estimate the rate constants assuming that the H-abstraction only occurs at the weakest C-H bond (Herrmann and Zellner, 1998; Hoffmann et al., 2009).

In CLEPS, even solubility and hydration constants are estimated using SAR (GROMHE). In this way, all species identified in the gas phase mechanism MCM are dissolved in CLEPS whereas in CAPRAM only some organic compounds are transferred in the aqueous phase when their solubility is documented or ~~is~~ estimated based on similarity criteria.

Some attention should be paid when comparing the hypotheses made to develop CLEPS and CAPRAM since some of them are related ~~with~~ to deliquescent particles and/or cloud droplets. CAPRAM, contrary to CLEPS, explicitly treats the O<sub>2</sub>-addition step on the alkyl radicals. This allows the direct treatment of the alkyl+alkyl vs. alkyl+O<sub>2</sub> competition that may occur in deliquescent particles. In CLEPS, the fate of peroxy radicals is an attempt at systematizing the approach used in CAPRAM that also considers peroxy radicals recombination reactions using experimental data from Zegota et al. (1986).

Schuchmann et al. (1985) and Poulain et al. (2010). The possible cross-reactions are ~~not~~ considered in ~~both~~ neither of these aqueous phase mechanisms.

To summarize, CLEPS is based upon one of the most updated gas chemical mechanism (MCM) that uses very efficient preprocessor KPP and Rosenbrock solver. This is a good basis to develop explicit aqueous phase chemistry model that is suitable to interpret laboratory data and to describe the phase separation observed in long term measurement stations (from the WMO and/or ACTRIS networks).

## 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 (1000 hPa, 290.15 K, 10 % relative humidity). 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 1.5×10<sup>6</sup> in McNeill et al. (2012) to 7.5×10<sup>6</sup> molec cm<sup>-3</sup> s<sup>-1</sup> in our work. Furthermore, dry deposition is added for the major oxidation products of isoprene to prevent the accumulation of secondary organic species. The temperature is held constant (290.15 K) 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, relative humidity is increased to 100 % and a cloud event aqueous phase conditions are simulated activated with assuming a constant liquid water content of 3×10<sup>-7</sup> vol. water/vol. air lasting until midnight with a fixed droplet radius of 10 μm for twelve hours. On that day, sunset happens at 6:45 pm (i.e. the actinic flux becomes null). This is a permanent cloud simulation and no As a first attempt, the cloud is supposed to be permanent is made to represent a specific documented cloudy in order situation. The objective is to test the multiphase mechanism over a long time scale to 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 scenario 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 rate constant of  $k = 3.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . 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

5 morning and a minimum of 0.9 ppbv in the afternoon. Because the simulated emission of isoprene is constant during the day (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 oxidant of isoprene ( $k_{\text{HO}^*+\text{isoprene}} \times C_{\text{HO}^*} \approx 10 \times k_{\text{O}_3+\text{isoprene}} \times C_{\text{O}_3}$ ). 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

15 **Figures 3a & 3b** show the time evolution of targeted gases during the cloud ~~event-scenario~~ (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-cloud-free~~ 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 aqueous production of H<sub>2</sub>O<sub>2</sub> is responsible for its subsequent higher gaseous levels.

20 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, isoprene is the main emitted organic compound with a small contribution of formaldehyde and acetaldehyde, whereas a larger range of hydrocarbons of anthropogenic (alkanes, alkenes, aromatics) and biogenic origin (limonene, α-pinene) are emitted in Ervens et al. (2003). ~~As far as we understand~~ In 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 hydrocarbon 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.

40 Glyoxal, glycolaldehyde, pyruvic acid, glyoxylic acid and glycolic acid are readily soluble species that react in the aqueous phase (Herrmann et al., 2015), explaining the sharp decrease of their gas phase mixing ratios. 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 (6:45 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-cloud-free~~ conditions mixing ratios (methylglyoxal, formaldehyde) or significantly increase the mixing ratios compared to ~~dry-cloud-free~~ conditions (acetic and formic acids). Aqueous phase production is also 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 ~~HO<sup>•</sup>oxidation-sink for due to reaction with~~ all dissolved ~~unreactive~~ species (red lines in **Figures 3a & 3b**) leads to higher concentrations of species for which reactive uptake is an overall **sink** (e.g., glyoxal, glycolaldehyde). ~~because in this additional HO<sup>•</sup> sink, 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~~ scenario. 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 6:45 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 chemistry is slowed down and their rates of production are slower, giving lower maximum concentrations. 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 have 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 behavior 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. ~~Organics are the most important HO<sup>•</sup> sinks, with DOC contributing to 64%, 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. 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 **reaction** 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. ~~— In the first hours of the simulation, 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 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~~. ~~O/C is the ratio between the number of organic oxygen atoms and the organic carbon atoms in gas and cloud phases. O/C ratios are calculated by counting the number of organic oxygen atoms in a given gas and cloud phases, and by dividing it by the number of organic carbon atoms in the same phase. The O/C ratios and  $n_C$  are a measure of the extent to which long-chain organic species are oxidized and are therefore indicators of their functionalization and/or fragmentation. 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.~~ One hour after the start of aqueous phase chemistry beginning of the cloud, O/C in the aqueous phase has remained around 1.0 and  $n_C$  has decreased to 2.8 after a sharp initial increase to 2.9, thus showing that fragmentation is a major process. O/C in the gas phase has increased from 0.74 to 0.77 and  $n_C$  has decreased from 2.43 to 2.25. This result is in good agreement with other aqueous phase studies (Bregonzio-Rozier et al., 2016; Epstein and Nizkorodov, 2012; Epstein et al., 2013) and other models (Schrödner et al., 2014), but are in disagreement with field studies, probably due to a lack of descriptions of high molecular weight substances, and of their reactivity, as well as oligomerization processes. The higher O/C ratios obtained by Schrödner et al. (2014) after cloud event (1.8 for their rural case) can be due to important oxalic acid concentrations dissolved into the aqueous phase in their model, when the cloud is being formed. These values can be compared to the simulated O/C ratios in Schrödner et al.

(2014). They obtain much higher O/C ratios in clousoafter cloud event (1.8 for their rural case). The main reason that could explain this difference is the exclusion of the counting of CO<sub>2</sub> (O/C = 2) and of carbonate ions (O/C = 3) in our calculation. Also in Schrödner et al. (2014), the uptake of some soluble gas phase species (e.g. formic and acetic acid) can explain greater O/C ratio. It is difficult to ascribe this difference to a specific reason. This could be due to an organic content more dominated by formic acid (O/C = 2). As no detail is given in Schrodner et al. (2014) about the O/C calculation, it could also be that they count CO<sub>2</sub> (O/C = 2) and carbonate ions (O/C = 3) in their calculation, which mechanically increases the resulting value. At the end of our simulation, 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, less functionalized 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<sub>C</sub> at the beginning of the cloud-event. In the gas phase, the O/C ratio and n<sub>C</sub> follow a marked parabolic curve, reaching a maximum O/C = 0.8 at 15 LT and a minimum n<sub>C</sub> = 2.3 at 14 LT. The O/C ratio and n<sub>C</sub> then return to the drycloud-free-condition levels at sunset. During the day, cloud reactivity is responsible for the increasing O/C ratios and decreasing n<sub>C</sub>. These results suggest that our aqueous mechanism simulates an efficient fragmentation during the day, but again, our simulation does not take into account high molecular weight substances, their reactivity, as well as oligomerization processes that have been observed in filed studies. A higher O/C ratio indicates that the number of oxygenated functions per carbon atom has increased. A lower n<sub>C</sub> 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<sub>C</sub> 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<sub>C</sub> 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 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 cloud droplets conditions in cloud droplets 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. 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 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 cloud droplets 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, tarttronic 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 multi-phases (gas + water)~~ in environmental cloud chambers ([see for example](#) 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.

### 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](mailto:l.deguillaume@opgc.univ-bpclermont.fr).

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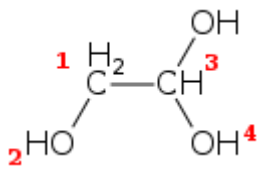
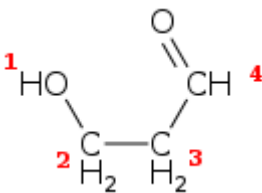
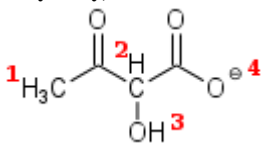


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**Table 1: Experimental hydration constants for carboxylate species.**

<b>Species</b>	<b>K<sub>hyd</sub></b>	<b>References</b>
<b>Glyoxylate</b>		
CH(=O)C(=O)(O <sup>-</sup> )	67	Tur'yan (1998)
<b>Monoethyl Oxaloacetate</b>		
CH <sub>3</sub> CH <sub>2</sub> -O-C(=O)C(=O)CH <sub>2</sub> C(=O)(O <sup>-</sup> )	3.125	Kozłowski and Zuman (1987)
<b>Pyruvate</b>		
CH <sub>3</sub> C(=O)C(=O)(O <sup>-</sup> )	0.0572	Pocker et al. (1969)
<b>α-ketobutyrate</b>		
CH <sub>3</sub> CH <sub>2</sub> C(=O)C(=O)(O <sup>-</sup> )	0.08	Cooper and Redfield (1975)
<b>α-ketoisovalerate</b>		
CH <sub>3</sub> C(CH <sub>3</sub> )C(=O)C(=O)(O <sup>-</sup> )	0.075	Cooper and Redfield (1975)
<b>β-fluoropyruvate</b>		
CH <sub>2</sub> (F)C(=O)C(=O)(O <sup>-</sup> )	19	Hurley et al. (1979)

**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) [ $M^{-1} s^{-1}$ ]	Contribution to the global reaction rate	Reactivity threshold considered	Retained pathways	Scaled Contribution	Final estimated rate constants [ $M^{-1} s^{-1}$ ]
<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 %	$C_2 : 90 \%$	Yes No Yes Yes	28 % - 33 % 39 %	$k_1 = 3.1 \times 10^8$ - $k_3 = 3.6 \times 10^8$ $k_4 = 4.3 \times 10^8$
	$k_{Global} = 1.1 \times 10^9$					$k_{Global} = 1.1 \times 10^9$
<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 %	$C_3 : 75 \%$	Yes No No Yes	38 % - - 62 %	$k_1 = 1.5 \times 10^9$ - - $k_4 = 2.6 \times 10^9$
	$k_{Global} = 4.1 \times 10^9$					$k_{Global} = 4.1 \times 10^9$
<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 %	$C_4 : 75 \%$	Yes No Yes Yes	31 % - 33 % 36 %	$k_4 = 1.0 \times 10^8$ - $k_3 = 1.1 \times 10^8$ $k_4 = 1.1 \times 10^8$
	$k_{Global} = 3.2 \times 10^8$					$k_{Global} = 3.2 \times 10^8$

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

**Table 3: Generalization of HO<sub>2</sub>' 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> ' 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> (a)	-
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>

(a) = 0 at nighttime concentration,

b)

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

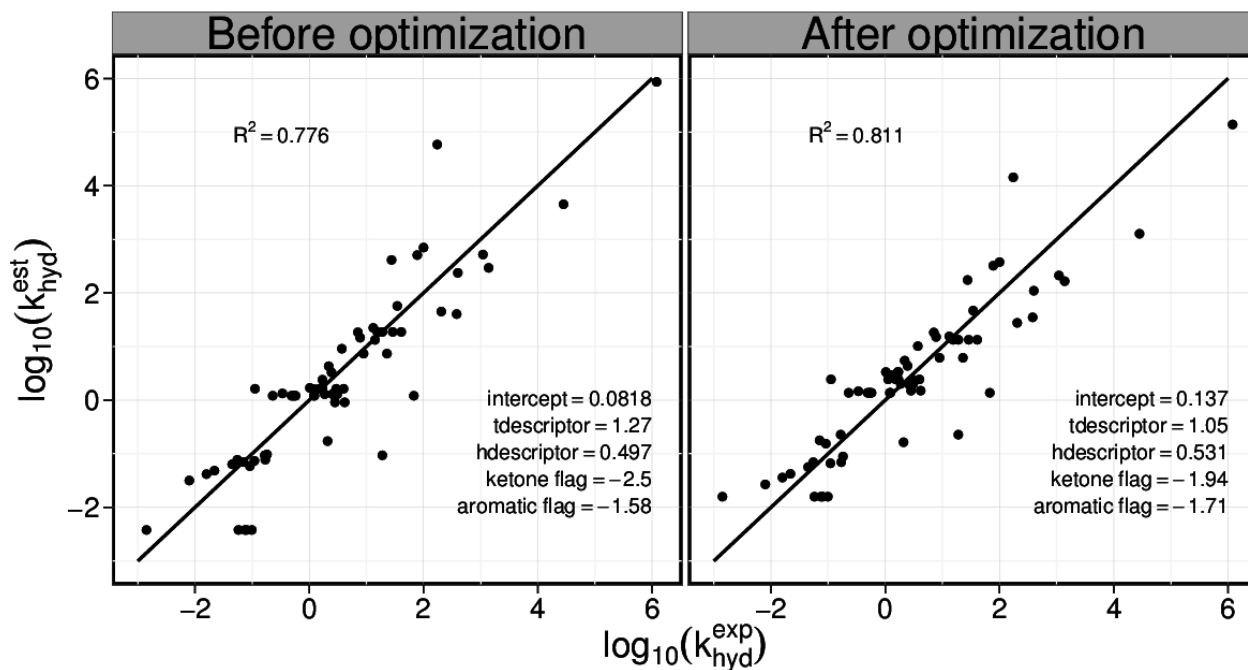


Figure 1: Scatterplots of the estimated  $\log(K_{\text{hyd}})$  using the SAR from Raventos-Duran et al. (2010) versus the experimental  $\log(K_{\text{hyd}})$ , before (left panel) and after (right panel) the optimization for carboxylates. Values for the optimized descriptors are shown on the bottom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

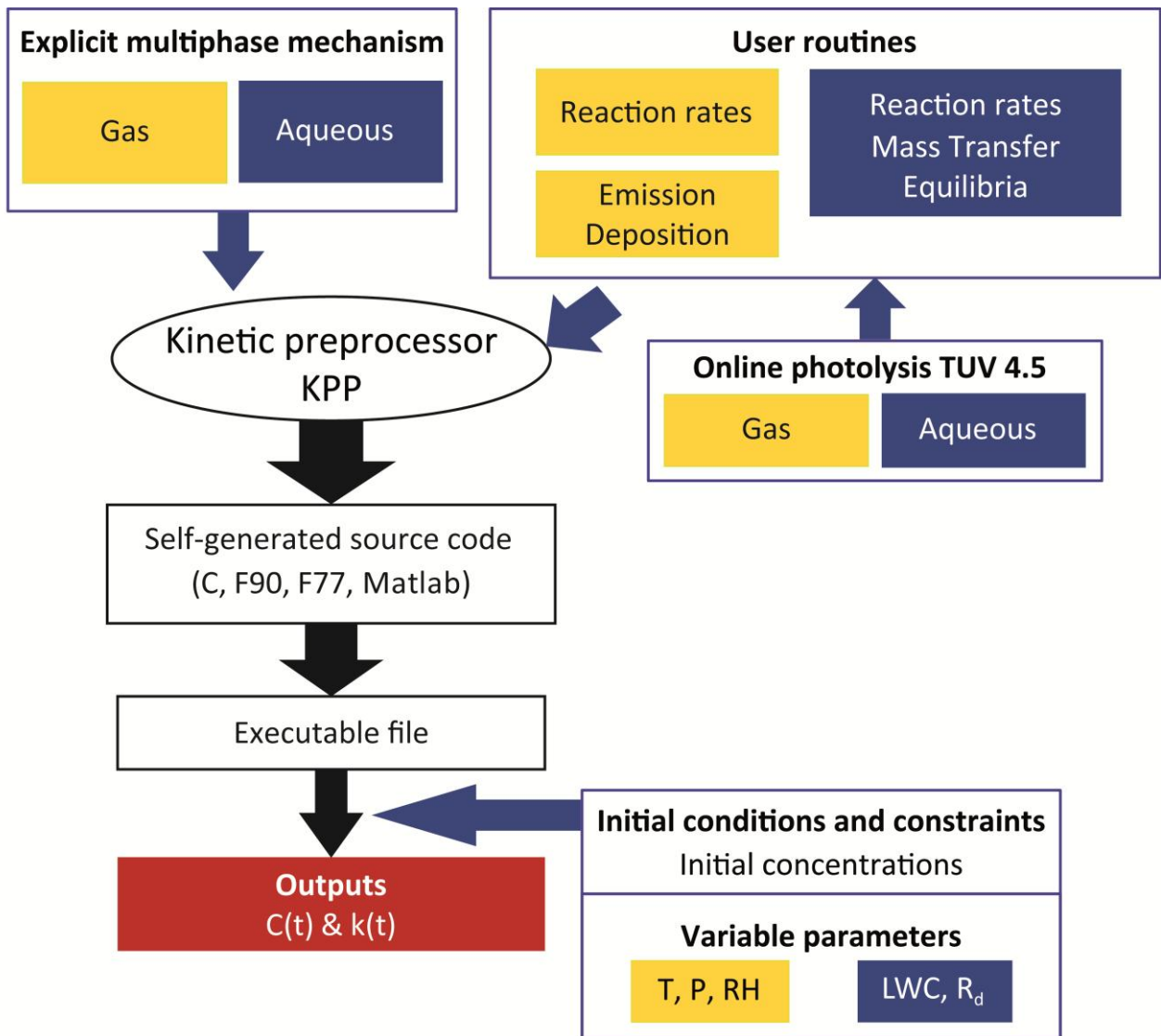
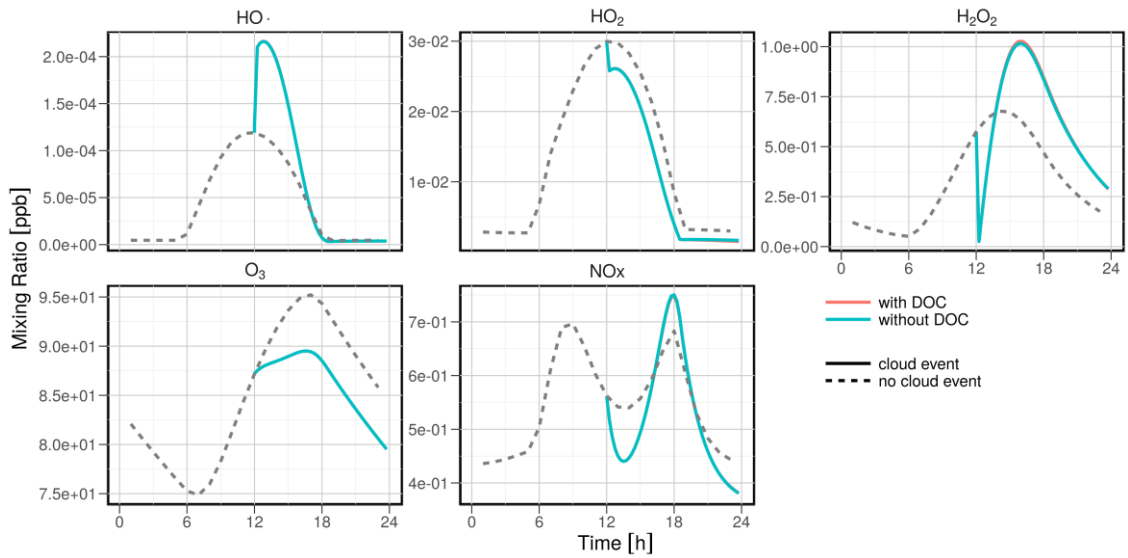
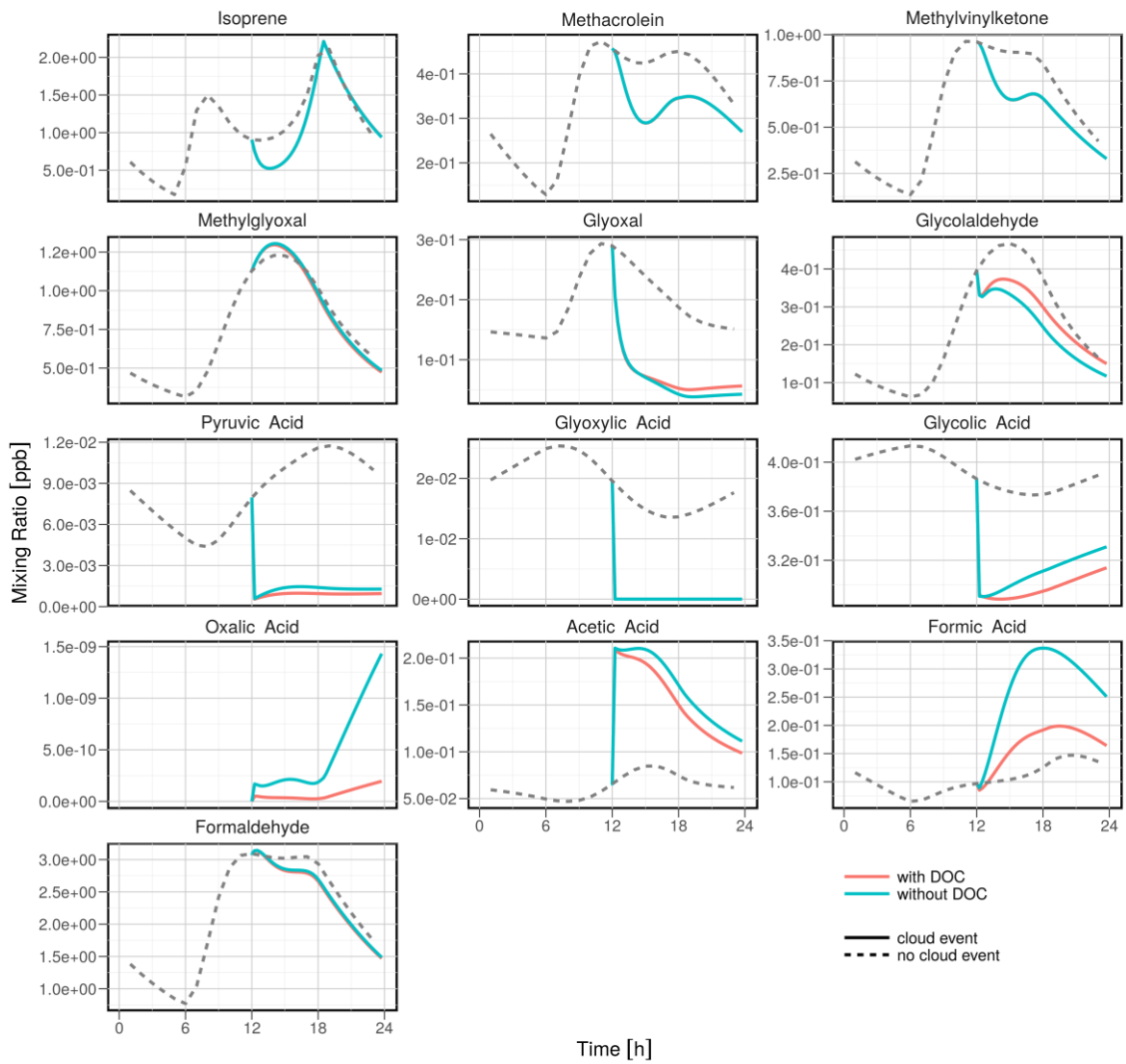


Figure 2: Schematic diagram of the DSMACC version of the Kinetic PreProcessor. The developments related to aqueous-phase reactivity are shown in blue.

a)

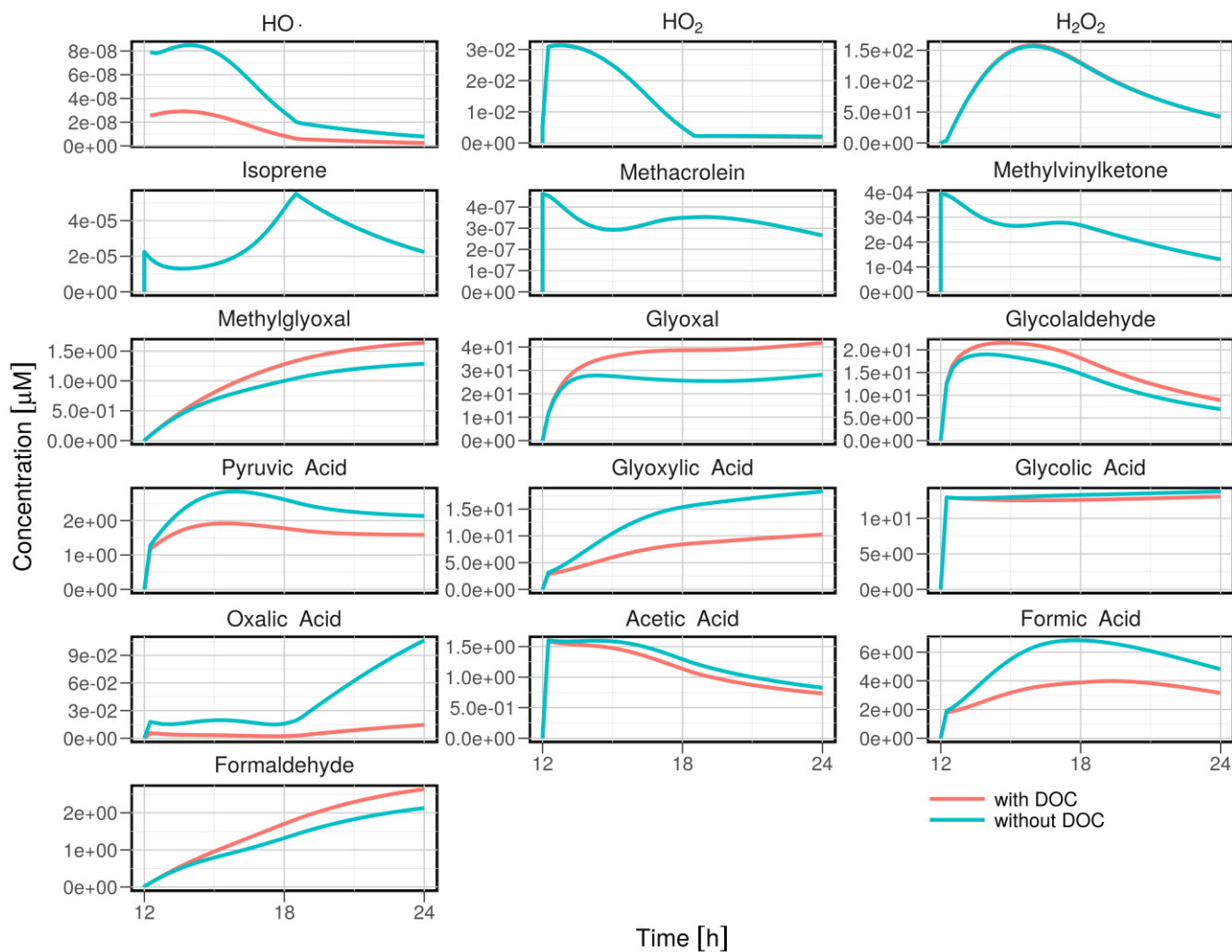


b)



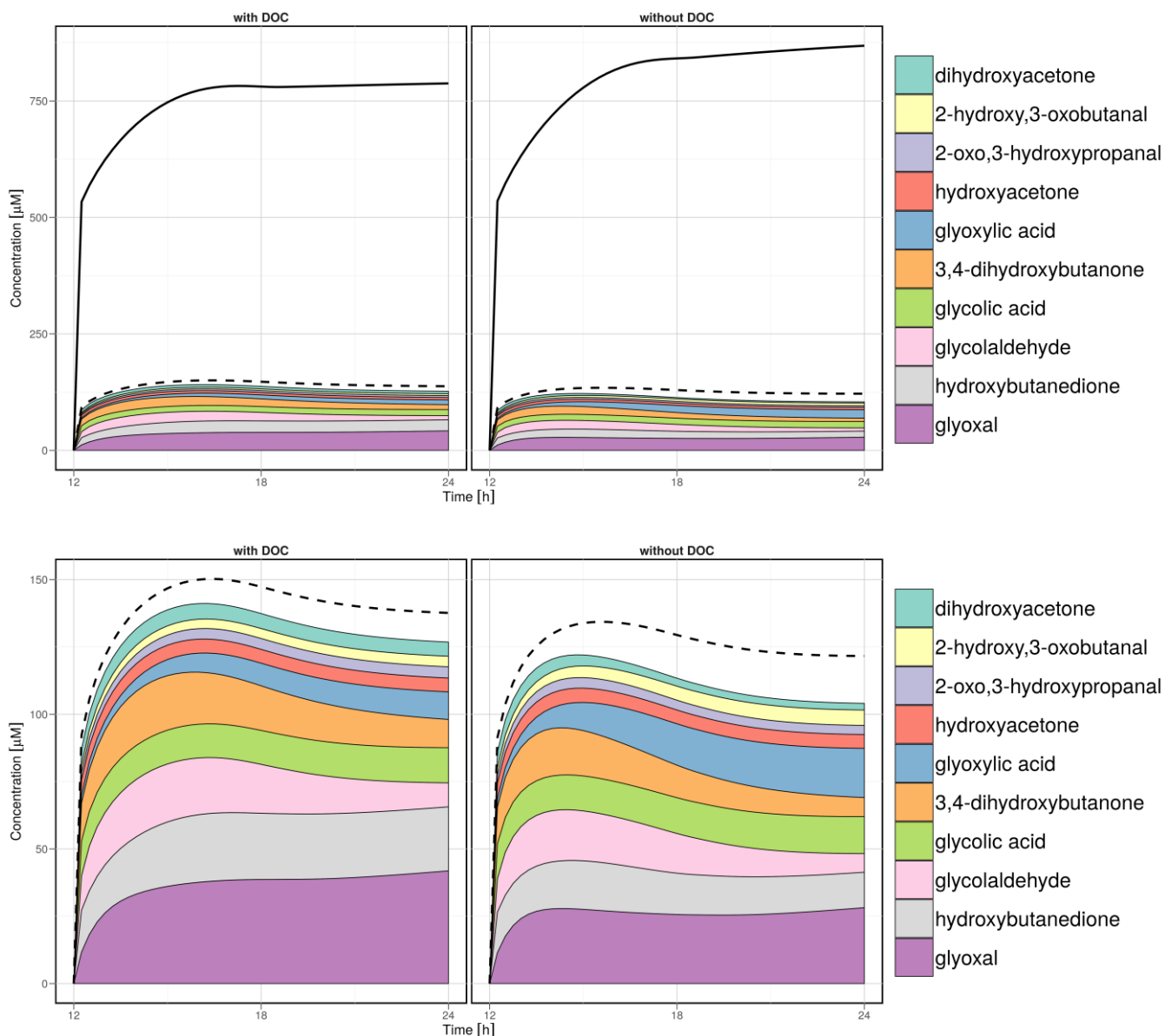
5 **Figures 3a & b:** Time evolution of the gas phase mixing ratios without the cloud event (dashed lines) and during the cloud event (continuous line). The cloud event simulations are depicted with (red lines) and without (blue lines) DOC. Please note that for most plots, the red line is hidden by the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





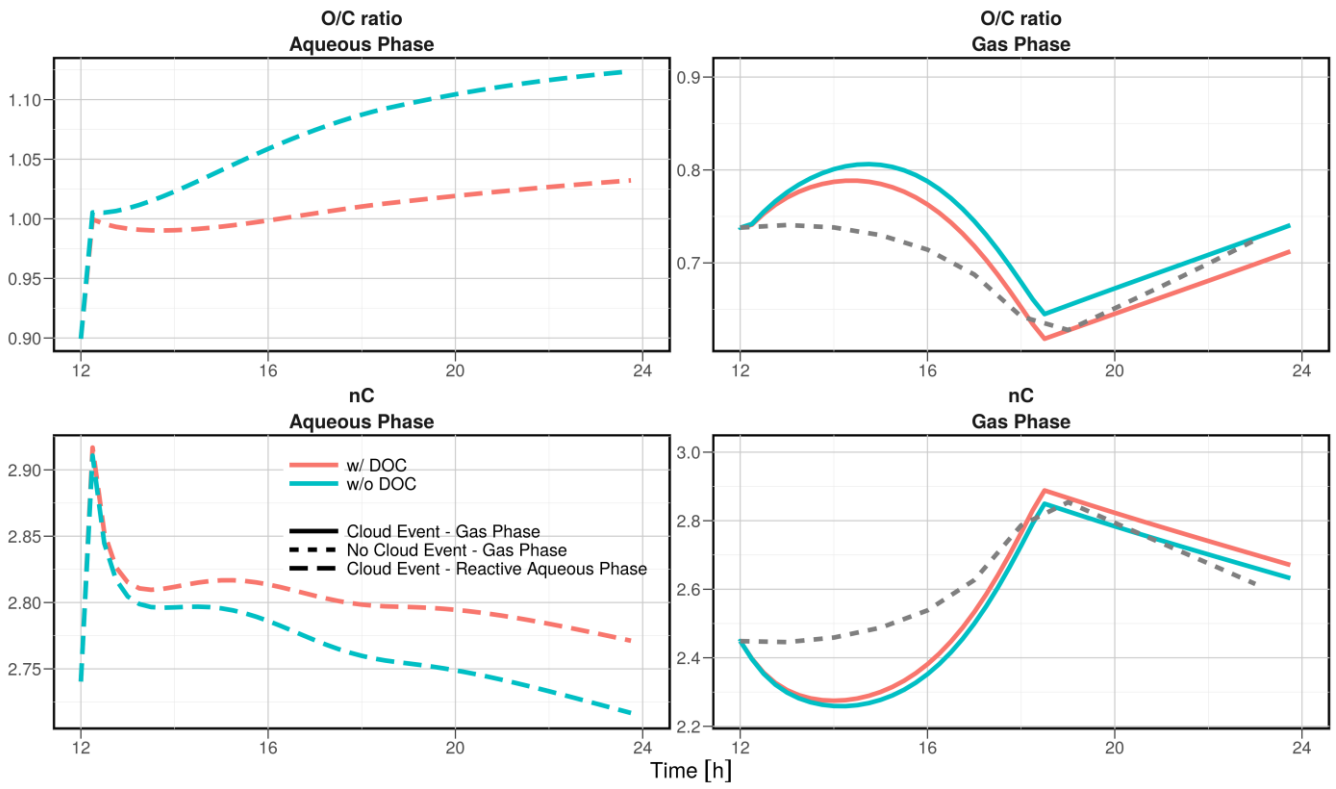
**Figure 4:** Time evolution of the dissolved species concentrations during the simulated cloud event—with (red lines) and without (blue lines) DOC. The vertical scale is in  $\mu\text{M}$ ; therefore, the  $\text{HO}\cdot$  radical concentrations are in the  $10^{-14}$  M range. Please note that for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

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**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.**

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**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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