

Response to Anonymous Referee #1

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

Main comments

1) Motivation of the current study

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

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

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

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

2) Similarities to CAPRAM

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

We don’t think it is highly exaggerated to claim that the mechanism is new. There are 207 inorganic reactions and 642 organic reactions. The inorganic reactions represent 24% of the full scheme. As the literature data is scarce on the subject, CLEPS and CAPRAM obviously share a lot of experimental data concerning inorganic chemistry and C₁₋₂ chemistry.

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

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

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

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

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

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

Sect. 3.4.3: “Our approach for reactions with nitrate radicals is different than what has been proposed in previous aqueous phase mechanism, especially for estimating the branching ratios.

We use similarity criteria to estimate the reaction rates whereas Herrmann et al. (2005) estimate these values using their own SAR (Herrmann and Zellner, 1998). They assume that the H-abstraction only occurs at the weakest C-H bond, which is determined from bond dissociation energies empirical estimates.”

Sect. 4.1: “In the CAPRAM mechanism (Ervens et al., 2003; Herrmann et al., 2005; Tilgner et al., 2013), the O₂-addition step is explicitly introduced. This allows the direct treatment of the alkyl+alkyl vs. alkyl+O₂ competition that may occur in deliquesced particles. This is not in the objective of the present work and this consideration will also lead to the implementation in the mechanism of a lot of intermediate chemical species with short lifetime. It could be considered for future versions of the CLEPS mechanism.”

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

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

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

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

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

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

In Tilgner et al. (2013), HO[•] sources in cloud for a remote scenario similar to our simulation are dominated by direct uptake from the gas phase, by the Fenton type reactions and by the photolysis of H₂O₂ and Fe(III). Sinks are dominated by reactions with organic compounds, especially formate, hydrated formaldehyde, glycolaldehyde and methylglyoxal.

The following was added in the corresponding paragraph:

“However, in the first hours of the cloud event, mass transfer is the major source of HO[•], 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[•] in their simulation.” and “Tilgner et al. (2013) also show that HO[•] only aqueous sinks are reactions with organic matter, especially carbonyl compounds such as hydrated formaldehyde, glycolaldehyde and methylglyoxal.”

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

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

3) Basis of assumptions

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

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

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

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

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

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

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

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

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

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

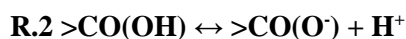
4) Inconsistencies in the presented mechanism

a) Dissociation equilibria

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

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

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



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

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

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

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

$$k_b = k_f/K_A$$

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

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

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

5) Discussion of results

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

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

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

Following this general comment, the conclusion was modified with the following sentences: “These simulations were conducted for a long non-realistic permanent cloud. However, the mentioned results are atmospherically relevant, since the impact on O/C ratio and fragmentation can be observed in the first moments of the simulated cloud event.”

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

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

“This trend in HO[•] 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[•] mixing ratios during cloud events. The chosen chemical scenario might be the reason for this difference. Even if the chemical scenario in our study is rather similar to the one in Ervens et al. (2003), we still differ in the amount of emitted organic compounds. In our test simulations, we mainly emit isoprene, with a small contribution of formaldehyde and acetaldehyde, whereas Ervens et al. (2003) emit a larger range of hydrocarbons of anthropogenic (alkanes, alkenes, aromatics) and biogenic origin (limonene, α -pinene). As far as we understand the CAPRAM model setup, these hydrocarbons are not dissolved and it should be noted that they are highly reactive with HO[•]. This means that the large, and certainly major, sink of gaseous HO[•] caused by hydrocarbons reactivity is always present, even under cloud conditions. When the source of HO[•] radicals is reduced by the cloud event (e.g. due to HO₂ and NO separation), HO[•] radicals sinks are not significantly perturbed and HO[•] steady state mixing ratios decrease. Conversely, in our simulation the gaseous HO[•] 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[•] gaseous source reduction is overcompensated by the reduction in HO[•] gaseous sinks. As a consequence, HO[•] steady state mixing ratios are higher during cloud events. This hypothesis especially highlights how the chosen chemical scenario and regime is important for simulation results and conclusions. Future work should therefore systematically explore cloud simulations under a large range of scenarios.”

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

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

6) Previous literature on aqueous phase chemistry

- p. 2, l. 12: In previous literature (Herrmann et al., 2015, and references therein) it is discussed that the presence of an aqueous phase (cloud) leads to the separation of the soluble HO₂ and the rather insoluble NO in the gas phase. Since their reaction is suppressed, less OH is formed. Therefore, it is not radical chemistry in the aqueous phase but different pathway strengths in the gas phase that lead to differences in OH during cloud.

This is noted and corrected.

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

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

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

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

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

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

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

We added the following in Sect. 3.6:

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

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

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

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

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

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

This is now mentioned in Sect. 6.3.

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

Technical and minor comments

p. 5, l. 21: ‘Rate constants’

Done.

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

Done.

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

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

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

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

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

Done.

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

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

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

Done.

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

Done.

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

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

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