Response to Anonymous Referee #2

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

This paper introduces a new protocol for developing a detailed aqueous chemistry mechanism. It emphasizes oxidation by OH, NO₃, and other oxidants in low NO_x and dilute conditions, and does not include accretion processes. The detailed aqueous chemistry mechanism, coupled with the Master Chemical Mechanism (MCM v.3.3.1), is applied to an ideal cloud situation to examine the behavior of the chemistry.
This is an exciting, new advancement for our understanding of aqueous chemistry, especially for the oxidation of organic compounds dissolved in cloud water. The paper is fairly well written, although several spots need to be clarified. The paper can be improved by providing more information on the test case, giving more discussion on how the mechanism and results compare to previous studies (with and without detailed aqueous chemistry), and cleaning up the presentation of the paper. My suggestions of needed clarifications are given below.

Specific Comments

1. Page 6, line 25 and Table 2. It is not completely clear to me what criteria are used to proceed with the reduction scheme. For example, why is a branch with a 19% contribution to the reaction removed? Is it simply because the other 3 pathways represent >75% of the global reaction rate? It seems that pathways that comprise 10% or less of the reaction rate can be ignored without much impact on the overall reaction scheme. What kind of impact occurs when the pathway contribution is larger, such as the 19% for the third example in Table 2?
The criteria used to reduce the size of the chemical mechanism have been chosen to consider the main chemical pathways and to avoid the consideration of negligible products. The example chosen to illustrate the reduction strategy in the paper is interesting because for 2-hydroxy, 3-oxobutanoate, the four available pathways are almost equiprobable. However, this is a really rare case. For most of the reactions described in the mechanism, we only neglect 10 to 15% of the total species reactivity (see footnotes in the mechanism tables - supplementary material). We believe that the impact of this reduction strategy can only be properly assessed with automatically generated chemical mechanisms (Aumont et al., 2005; Mouchel-Vallon et al., 2013).

2. Section 5. How does the CLEPS mechanism compare to previous aqueous chemistry studies (e.g. CAPRAM)?
This part of the paper deals with the coupling of CLEPS with a gas phase explicit mechanism. We refer the reviewer to our answer to Reviewer 1's comment 2a, specifically our amendments to part 5.2 discussing the difference in constructing the mass transfer coupling between our protocol and CAPRAM.

3. Page 13, line 10. While Rosenbrock solvers have become commonplace in chemistry transport models, other solver techniques also adequately solve the gas-aqueous chemistry mechanism (e.g., Ervens et al., 2003, JGR; Barth et al., 2003, JGR; McNeill et al., 2012, ES&T).
We agree with the reviewer's comment. We modified the sentence as follows: "Differential equations are solved with a Rosenbrock solver which has been shown to be a̲ reliable numerical method for stiff ODE systems involved in modelling multiphase chemistry".

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

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

We understand the reviewer's concern about comparisons between CLEPS and previous mechanisms. Differences in chosen physical and chemical scenarios make this exercise particularly perilous. On this subject, see for instance our answer to Reviewer 1 comment 5b. We believe that specific inter-comparison studies should be run to properly evaluate and compare existing mechanisms. This will be done in the future. However, this is not the scope of this particular paper. This paper aims at describing and presenting a detailed systematic protocol for aqueous phase oxidation. Hence, the mechanism might be viewed as the "main result" of this work. Nevertheless, qualitative comparisons with simulations from existing mechanism are addressed to some extent in our answers to Reviewer 1 comments 2b, 2c and in our new additions to Sect. 6.3., where some of our model outputs are compared to previous modelling studies using CAPRAM mechanism.

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

This is noted and has been indicated in Sect. 6.1:
"The simulation is located at the sea level and the coordinates used to calculate actinic fluxes are 45.77°N 2.96°E."
Sunset time (6:45pm) is now included in Sect. 6.1.

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

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

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

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

9. Page 14, lines 9-12. I agree with the explanation of the H_2O_2 time evolution. In addition, SO_2 concentrations must be depleted in order for H_2O_2 concentrations to increase. Otherwise H_2O_2 would continue to be consumed by SO_2. Further, it is worth noting the time scales with respect to how long an air parcel actually spends inside a cloud.

In the simulations, sulphur is indeed quickly depleted. The end of the first paragraph of Sect. 6.3 has been modified as follows: "H_2O_2 is a soluble species highly reactive with SO_2, which explains the initial dip in its mixing ratio. After SO_2 is entirely depleted (not shown), the aqueous production of H_2O_2 is responsible for its subsequent higher gaseous levels."

10. Page 15, lines 16-19. How long does it take for aqueous-phase glyoxal concentrations to change from being controlled by mass transfer to being controlled by aqueous chemistry? Should we expect to see this in observations of clouds in the atmosphere where the air parcel residence time in cloud may be shorter?

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

11. Page 15, lines 22-23. The comment about acetic and formic acid concentrations is interesting, but I did not see these values plotted. Could they be included in the figure (or at least report the concentrations)?
We add in the text the reference to Deguillaume et al. (2014) that reports the mean concentrations of formic acid and acetic acid in cloud aqueous phase at the puy de Dôme station for the last ten years. In their classification for non-polluted conditions, the concentration of formic acid is on average equal to 6.3 μM (range : 0.8-29 μM) in comparison to the 4 μM of formic acid simulated by our model. The concentration of acetic acid is on average equal to 4.9 μM (range : 0-23 μM) in comparison to the 1.5 μM of acetic acid simulated by our model.

12. Page 15-16. I did not completely understand the importance of dissolved organic carbon (DOC) and its role in the aqueous chemistry. Could more background information be provided?
This importance of DOC as an HO˙ scavenger has been for instance discussed by Arakaki et al. (2013). It arises from the observation that cloud sampling field studies are able to identify only a few percent of the total Dissolved Organic Content (Deguillaume et al., 2014; Herckes et al., 2013). Most aqueous phase mechanisms, including CLEPS, only describe the reactivity of this known minor fraction. What is called DOC is the major constituent of dissolved organic matter, for which very little is known. Using experimental data, especially total HO˙ reactivity measurement, Arakaki et al. (2013) were able to propose an average DOC + HO˙ rate constant.
We are able to reproduce a similar behaviour in our model. Because the reactivity of most species dissolved from MCM is not described in CLEPS, a large amount of the modeled dissolved organic content is not reacting toward HO˙ in the aqueous phase. The "with DOC" version of the simulations addresses this by assuming that the unreactive content of the aqueous phase reacts with HO˙ with an average DOC + HO˙ rate constant suggested by Arakaki et al. (2013).

13. The supplementary material shows the pH values for the simulation. The pH seems to be quite low (3-3.5). Could the authors explain why such a low pH occurs? Are the results similar to previous simulations of this case?
The simulated pH value is rather low but in the order of magnitude than was observed in other cloud chemistry model for remote conditions. For instance, Herrmann et al. (2005) and Deguillaume et al. (2004) for permanent cloud simulations showed values between 3 and 4. We are aware that this is not explained in the paper. This pH results from the balance between the production of strong inorganic acids (mainly sulfuric acid in our simulation) and the production of weak organic acids. Low pH values can therefore arise from (i) a lack of weak acids compared to other modelling results or (ii) an overestimation of acidity constants for organic acids.

Technical Comments

1. Page 1. line 20. → multiphase
Done.
2. Page 1, line 34. "GROMHE" is not defined. Is it needed in the abstract?
It is now defined in the text.

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

4. Page 1, line 39. The word "evaluate" is not what is done in the paper.
We replace "evaluate" by "test".

5. Page 2, line 33. Please quantify what is meant by "low-NOx" and "dilute".
This has been clarified for low-NO$_x$ conditions. The "dilute" part is discussed in details in the revised version of Sect. 4.1.
6. Section 2. Please cite the supplementary material listing the chemical mechanism and chemical species. This supplementary material is a good resource for researchers.
Done.

7. Page 3, Line 6. Please quantify "significantly soluble and highly reactive". For example, I would suggest saying that their Henry's Law coefficient is greater than a specific value.
This formulation is indeed vague and not always true. For instance, MVK and MACR have low solubility (H$_{MVK}$ ≈ 1e^{-2} M atm^{-1} and H$_{MACR}$ ≈ 1e^{-1} M atm^{-1}). They are however highly reactive in the aqueous phase due to their double bonds and abundant enough in the gas phase to constitute a significant source of oxygenated compounds in the aqueous phase, *via* dissolution and reactivity. This sentence has been modified as follows: "For instance methylglyoxal (MGLY), glyoxal (GLY), acrolein (ACR), methacrolein (MACR) and methylvinylketone (MVK) are significantly soluble (Henry's law constant > 10^3 M atm^{-1}) and/or highly reactive in the aqueous phase (Ervens and Volkamer, 2010; Lim et al., 2010, 2013; Liu et al., 2009, 2012)."

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

9. Page 3, line 31. Define "GROMHE".
Done.

10. Page 5, line 23. Could a couple of sentences be added to explain "global reaction rate constants"?
"global" reaction rate constants is used in opposition to partial reaction rate constants (*i.e.* site specific). This is a confusing formulation. The sentence has been replaced with: "When rate constants of organic compounds reactions with HO˙ are available (see the review from Herrmann et al., 2010), they are used in the mechanism."

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

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

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

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

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

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

17. Page 13, line 20. → simulation has been run for 31 days. What is the purpose of a 31-day gas chemistry spin up?
The purpose of a gas chemistry spin up is to obtain a diurnal steady state representative of the chose scenario. The duration of this spin up only has to be long enough to reach the pseudo steady

state. It has been arbitrarily set to 31 days but it could have been shorter, as the steady state is reached after approx. 20 days.

18. Page 14, line 2. A sentence should be added to say something about the isoprene products diurnal profiles.
The following has been added at the end of Sect 6.2: "The first oxidation products from isoprene (MACR, MVK) follow the same time profile as isoprene. The mixing ratios of other oxidation products vary also temporally depending on their production/destruction rates. For example, MGLY, GLY and glycolaldehyde mixing ratios decrease initially due to their oxidation by HO· and then increase strongly due to their production by the oxidation of isoprene."

19. Page 14, line 16. When is sunset?
In our simulation, the sunset corresponds to 6:45 PM. It has been added in the manuscript.

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

21. Page 14, lines 23-27. I suggest discussing the "with DOC" results together with the last paragraph on the page. That is, organize the discussion of Figures 3 and 4 to present "without DOC" results first, and then discuss "with DOC" results presented in Figures 3 and 4.
We respectfully disagree with this suggestion. The behaviour described for the "without DOC" simulation can often be highlighted with comparison to the "with DOC" simulation. In our opinion, it makes more sense to discuss these two simulations together, rather than separately.

22. Page 14, line 32. When is nighttime?
Nighttime corresponds to the time period from 6:45 PM et 12:00 PM. This has been added in the text.

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

24. Page 15, line 13. In SM6, it would be helpful to either put names with the chemical formulas, or organize the list by groups (alkanes, alkenes, etc.) as is done on the MCM web page.
This is a difficult request to grant! We thought that the chemical formulas might be of some use to the potential reader. The list was automatically generated from our computer code. The order is arbitrary. Putting names and organising the list might not be worth the time needed to do it. We'll find a compromise for this problem for future versions of this mechanism.

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

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

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

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

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

30. Page 16, line 13. Remove "compounds"

Done.

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

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

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

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

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

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