

## Response to Reviewer # 2

We thank Reviewer #2 for his/her constructive comments and for pointing out several unclear sections in our manuscript. We address the comments in detail below and hope that our changes led to clarification. Reviewer comments are in italic and blue; our responses are in regular font.

During the revision of our manuscript we realized that our previous model simulations were for a (constant) temperature of  $T = 298$  K. Comparison to observed temperatures revealed that the temperatures were significantly lower ( $10^{\circ}\text{C}$  and  $7^{\circ}\text{C}$  in Whistler and Davis, respectively) and thus Henry's Law constants were higher by a factor of 2-3. We repeated our model simulations and replaced Figure 5 and 6. While numbers have slightly changed, none of our conclusions was affected.

*This paper reports measurements of aldehydes and dissolved organic carbon in cloud/fog water at Mount Whistler, BC Canada and Davis, California USA. These measurements, literature values and assumptions were used to estimate effective Henry's law constants for dissolved organic carbon. Larger values were associated with aged air masses, consistent with a greater degree of oxidation. Field measurements were used to initialize a box model that examined how the uptake of formaldehyde, glyoxal and methylglyoxal into cloud/fog water affected gas phase HO<sub>2</sub> concentrations. While the effects of aqueous formaldehyde uptake on HO<sub>2</sub> has been previously reported, similar work for other aldehydes has not been performed, to my knowledge. The authors found that aqueous aldehyde uptake reduced gas phase HO<sub>2</sub> concentrations by two orders of magnitude, and that this effect was predominantly caused by formaldehyde; glyoxal and methylglyoxal had little effect.*

*This paper should be published after minor revision. The revisions below are primarily structural, rather than scientific.*

*1. Uncertainties should be reported for key measurements. There is no mention of field blank measurements. How do we know measurements reflect ambient concentrations and not contaminants?*

We have detailed now in Section 2.2.2. the procedures for cleaning and blank measurements. We also provide TOC blank values and discuss that volatile species like formaldehyde will always be detected in this kind of blank just because they will partition into the samples, however concentrations are always low compared to actual fog and cloud concentrations. We also state uncertainties in terms of replicate measurements.

*2. The Box Model description needs a few more details. initial conditions for modeling (and a reference to Table 2) should be provided in section 2.3 not in results. In section 2.3, it says that "formation of formaldehyde is not explicitly simulated." But it does not say how formaldehyde is modeled. Briefly, the authors need to explain the chemistry included in the box model. What oxidants are included? Are the precursor VOCs continuously replenished or do they decrease*

*with time?*

We refer now already in Section 2.3.1 to the Table. By doing that, this Table is actually mentioned before the other one, and thus, numbering was switched.

We also extended the Table to include the full set of initial gases. HCHO is included in the list of initial gases and we do not assume any formation pathway. Thus, only its uptake to the aqueous phase and its sinks in both phases is considered. Since gas and aqueous concentrations are constrained by measurements (not necessarily during the same experiments as discussed here but at the same location), we think that this approach is appropriate within all other uncertainties associated with the application of a box model (cf also our responses to Reviewer #1). Thus, we use predicted formaldehyde concentrations as a ‘reference’ to compare the predicted glyoxal and methylglyoxal aqueous concentrations (cf also new Figures 5e) and j))

The oxidants in the gas phase are OH and O<sub>3</sub>; in the aqueous phase it is assumed that organics are only oxidized by OH. We added this information in the text and also refer specifically now to Tables 1-3 in Ervens et al. (2004) that include the full chemical mechanism used here. The precursors are assumed to be continuously replenished i.e. they are kept constant throughout the simulation, since measurements did not show any significant decreasing trend during cloud/fog events.

*3. DOC, OC, and TOOC concentrations are carbon concentration, e.g., DOC should be mg-C/liter, rather than mg/liter.*

The reviewer is right. We carefully went through the manuscript, including figures and tables and corrected the units accordingly where necessary.

*4. Page 10 line 23 "TOOC excludes methane and includes all other organic carbon that can be measured by standard techniques." this is very vague. One can measure total non-methane hydrocarbons as carbon.*

We refer here to the definition of TOOC by Heald et al. (2008). They discuss that total carbon closure is often not reached, with increasing amounts of ‘missing’ carbon (15-45%) with increasing photochemical age of air masses. The reason for this discrepancy is ascribed to the formation of semivolatile and multifunctional compounds that are predicted to comprise a large fraction of the oxidation products and are not captured by current measurement techniques.

We rephrased this explanation by Heald et al. and added it briefly to the manuscript.

*5. Page 11 line 22. More explanation is needed as to how F(OCaq) is calculated and what it is. The fraction of what, dissolved in cloudwater, is 1-46%?*

F(OCaq) is the fraction of organic carbon that is in the aqueous phase related to the total organic carbon. We clarified this in the text and added an equation (now Eq-3) that gives the definition of F(OCaq). We assume in these calculations that OC only partitions between the gas and aqueous phases, i.e. we imply that (i) cloud/fog droplets represent the only condensed phase, (ii) all

particles are scavenged by the aqueous phase, and (iii) organic mass is fully dissolved and thus contributes to DOC. While the assumption of full dissolution of all organic particle mass might overestimate DOC, it is likely a good approximation since most of organic mass is usually water-soluble. While also a significant *number* of particles might not be activated into droplets (because of too small sizes), these small particles only represent a minor fraction of *mass*.

*6. Page 12 line 16-17 This sentence does not make any sense to me, and makes me wonder whether or not I understand what F(OCaq) is. The authors need to clarify.*

We hope that our response to the previous comment makes it clearer what we mean by F(OCaq). We also reworded the sentence Section 3.2.

Since F(OCaq) and F(OCp) are on the same order of magnitude and most of OCp as present in CCN will be dissolved in water within the cloud (fog) volume, we conclude that most of the dissolved organic carbon in cloud/fog water originates from dissolved particles rather than from soluble gases that are taken up into cloud/fog water.

*7. Sections on DOC and aldehyde measurements should be tightened.*

We removed the details on ion analysis as we do not make use of ion analysis in the final version of the manuscript. We shortened substantially the details of DOC and carbonyl analysis and refer to other studies and only detail the differences from the previous studies (e.g. mass spec analysis).

*8. Page 13, line 7 "whereas the inferred aging does not necessarily occur in the aqueous phase" The meaning of this phrase is not clear. Do the authors mean "as a result of gas (and maybe also aqueous) chemistry" ?*

Yes, the reviewer is right. We reworded this sentence accordingly and it reads now "Similar trends have been observed for the degree of oxygenation of organic aerosol particles that usually show enhanced amounts of highly oxidized material in aged air masses whereas the ageing *can occur either in the gas or aqueous phase.*"

*9. Page 13 line 11: Figure 3b should be deleted from this sentence. Page 13 line 24: Figure 3c should read Figure 3b*

We noticed this mistake during proof reading prior to publication in ACPD. In the published ACPD paper this had been corrected already.

*10. Page 17 line 22-29. This discussion is a little confusing. Do the authors mean to say that reaction times represent the aqueous chemistry happening in several cloud cycles?*

Yes, that is what we mean. We added extensive discussion on the consequences of different drop life times on the uptake and accumulation of soluble gases in Section 2.3.2. In addition, we discuss consequences and uncertainties regarding aldehyde partitioning and possible

accumulation in deliquesced particles and uncertainties associated with estimates of gas/aqueous interaction times (cf also response to comments by Reviewer #1 regarding our estimates of cloud interaction times).

*11. Page 18 Might the Lee et al 2012 experiments reflect longer reaction times or reactions in aerosol water?*

We thank the reviewer for this idea. Indeed given that fact that both organic and oxidant (OH) concentrations were higher than compared to typical cloud water concentrations, the experimental conditions by Lee et al. (2012) resembled levels as in aerosol water (e.g., (Tan et al., 2009; Ervens and Volkamer, 2010)). We added this information to the text.

*12. Table 1 needs a lot more explanation. Define terms used in the table, especially TOOC, so that the table will be understandable on its own. Why are there two columns under DOC? What are these concentrations? Is OC<sub>p</sub> carbon in the particle phase in clouds or in the aerosol? F(OC<sub>aq</sub>) is percentage of what? (gas+aqueous+particle??) Which of these columns are measurements?*

We improved the table by clearly marking what numbers are measurements and how the other values were derived. The information is now included in the table caption and column headers, respectively.

*13. Many figures need formatting. For example, larger (consistent sized) labels. No box surrounding the figure, no grid lines in Fig 1. Link references in the Figure captions to references.*

We improved all figures in order to have consistent labels, axes etc. Specifically:

- Figure 1: We removed the box and unified labels
- Figure 2: We improved the caption by connecting the numbered locations in the figure to references.
- Figure 3: We use the same font size in both figure parts. In addition, the numbers on the x-axis of part b) are now connected to the figure caption.
- Figure 4: In order to be consistent with other figures, we reduced the font size.
- Figure 5: We replaced the figure with a new one (new model results for simulations using temperature-dependent Henry's law constants). We also added four more panels that include aldehyde ratios (gly/mgly and (gly+mgly) / HCHO for both locations)
- Figure 6: We replaced this figure based on the new model results and made sure that the two figure parts have the same size and fonts.

*Indicate somewhere the time of year for the locations included.*

This information is now included in the caption of Figures 2 and 3 for all locations.

*Say what error bars represent.*

The error bars span the range between minimum and maximum observed concentrations. This information is now included in the caption of Figures 2c and 3.

References

- Ervens, B., and Volkamer, R.: Glyoxal processing by aerosol multiphase chemistry: towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles, *Atmos. Chem. Phys.*, 10,8219-8244, 2010.
- Lee, A. K. Y., Hayden, K. L., Herckes, P., Leaitch, W. R., Liggio, J., Macdonald, A. M., and Abbatt, J. P. D.: Characterization of aerosol and cloud water at a mountain site during WACS 2010: secondary organic aerosol formation through oxidative cloud processing, *Atmos. Chem. Phys.*, 12, 2,7103-7116, 10.5194/acp-12-7103-2012, 2012.
- Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Effects of Precursor Concentration and Acidic Sulfate in Aqueous Glyoxal-OH Radical Oxidation and Implications for Secondary Organic Aerosol, *Environ. Sci. Technol.*, 43, 21,8105-8112, 10.1021/es901742f, 2009.