

## Response to Reviewer # 1

We thank the reviewer for his detailed comments and appreciate the opportunity to clarify some sections of our manuscript. We combined the reviewer's first comment in this response (Jan 26) with the other one that was uploaded on Feb 8. The reviewer's comments address Section 4 of our paper, i.e. the applicability of the box model. Our main changes regarding these comments are:

- We discuss more carefully now the caveats and uncertainties of the box model and its input data. We explain differences to the previously used multiphase mechanism by Ervens et al. (2004).
- We highlight more clearly the motivation that we want to contrast two cases in terms of main aldehyde precursors (aromatics vs isoprene) and multiphase scenarios (fog vs clouds). Thus, our exploratory box model studies are guided by these two cases and results should be considered in a relative sense rather than as absolute values. In addition to absolute predicted aldehyde concentrations, we added figure parts showing aldehyde ratios (Figure 5d, e, i, j)
- While revising the manuscript, we noticed that our previous simulations were for  $T = 298$  K which is much higher than compared to the observations. In the revision, we redid the simulations for more appropriate temperatures, namely  $T = 10^{\circ}\text{C}$  in Whistler and  $T = 7^{\circ}\text{C}$  in Davis. Reduced temperature increases the Henry's law constants for the aldehydes (and all other compounds). Accordingly we replaced Figures 5 and 6. Figure 5 shows now better agreement with measured aldehyde concentration ranges and their ratios.

Detailed responses to the specific reviewer comments are given below. The original reviewer comments are italicized and blue; our responses are in regular font.

*First comment (Jan 26): This is a quite interesting study combining box model calculations with actual aerosol and cloud field measurements. As my initial comment I would like to ask for a more complete description of the aqueous phase chemical mechanism.*

*The authors should clearly describe the mechanism used which is a derivative of CAPRAM 2.4. (2004). As it could be critical what reactions have been carried forward and which one have been omitted (reasons ?), I feel that this should be documented. The current box model description is very unclear in this regard. Of course, referencing to other CAPRAM derivatives can be used. Maybe the changes undertaken can be summarized in a Table which could be integrated into the supplement*

In the Section 2.3 (Box model description) (now: 2.3.1: Chemical mechanism), we refer to a model study by Ervens, Feingold, Frost and Kreidenweis, JGR, 2004. We would like to point the reviewer to Table 2 in this publication as it provides the complete aqueous phase mechanism as used in the current study. In addition, this reference also includes discussion on the differences

between CAPRAM 2.4.(MODAC mechanism) (Ervens et al., 2003a) and the mechanism used here. Given that this mechanism is included in the peer-reviewed literature, we do not include a similar table in the current manuscript but only extended the mechanism description in Section 2.3: E.g., we added a few sentences in the revised version of the manuscript addressing possible biases in reaction rates of organics by neglecting reactions such as OH(aq) sources and – at the same time – OH(aq) sinks, and the information that we only use aromatics and isoprene as aldehyde precursors (as opposed to the earlier study that also included ethylene and cyclohexene).

*General: A reasonable study comparing model result with sophisticated field measurement result. I would like to recommend several changes and additions to make the comparison between model and measurements more clear. Of course there are ways to determine cloud interaction times and the manuscript should be strengthened in this regard. All of this corresponds to a major revision.*

We improved the estimates discussion of constraining cloud interaction times. Specifically, we point out that

- Air masses in Whistler were characterized by intercepted cumulus/stratocumulus clouds that also exhibited some orographic component. We agree that the transport time of air masses through an orographic (e.g. hill-capped) cloud can be well characterized by tracer experiments (e.g. (Colvile et al., 1996; Bower et al., 1997; Heinold et al., 2005), but the situation is more complex for de-/entraining convective clouds where air parcels might cycle multiple times throughout the cloud. Thus, a simplified estimate of the ratio of cloud length and wind velocity is not sufficient in such complex cloud situations.  
The situation is different for radiation fogs where droplet lifetimes are controlled by the settling time of droplets throughout the fog layer. We added some more detailed estimates of drop lifetime and particle processing time for both situations, i.e. the combination of different cloud types and radiation fog (Section 2.3.2).
- Aldehydes are volatile and might evaporate together with water during drop evaporation. However, recent studies show that aldehyde concentrations in deliquesced (haze) particles ( $RH < 100\%$ ) exceed those predicted by Henry's law constants ( $K_H$ ) by several orders of magnitude (Baboukas et al., 2000; Kroll et al., 2005; Matsunaga et al., 2005; Healy et al., 2009). Since the reasons for this deviation from  $K_H$  are not clear but likely depend on the nature and concentrations of other condensed phase species (including water), we cannot assess if and the extent to which aldehydes accumulate over multiple cloud cycles. – Thus, bounding processing time by the lifetime of a single droplet as a lower limit and the multiple of that for several cloud cycles seems a reasonable estimate.
- In short-lived droplets (i.e. on the order of a few minutes), very soluble gases (e.g.,  $HO_2$ , and our three target aldehydes) might not reach thermodynamic equilibrium before they evaporate together with water. Thus the impact of the aqueous phase on the gas phase

concentrations might be less significant in shorter-lived, and/or larger droplets. The lifetime of individual droplets will strongly depend on the cloud/fog dynamics and cannot be easily determined by observations, in particular in as complex terrain as e.g. at Whistler and might only be possibly accessible by detailed cloud models.

- The uncertainties in terms of drop lifetime and size will clearly affect absolute aldehyde concentrations. Given that we only seek trends in concentration ratios in the two contrasted cases, in the framework of the bigger picture of our study - namely
  - (i) quantifying the contribution of aldehydes to DOC
  - (ii) comparing two new data sets of DOC and aldehydes to other locations
  - (iii) comparing impacts of aldehyde uptake on oxidant in different scenarios

we think that extensive sensitivity studies of these parameters exceed the scope of our study and would not significantly change our conclusions. Additions to the text along these lines were made in Section 2.3, new subsection 2.3.2. Gas/aqueous phase interaction.

*The main effect discussed, a decrease of gas phase HO<sub>2</sub> formation due to phase separation of aldehydes, turns out to be small.*

We do not claim that the effect of HO<sub>2</sub> formation due to phase separation is small. We state in the abstract, in the discussion of Figure 6, and in the conclusions that we predict a significant change in HO<sub>2</sub> levels (reduction in HO<sub>2</sub> by up to 91%, cf Figure 6a and b) – which is by no means small! To our knowledge, no previous study has compared (i) the potential impact of aldehyde phase separation for fog/cloud and biogenic/anthropogenic conditions and (ii) the potential impact of other aldehydes to that of formaldehyde. The marginal effect of larger aldehydes on HO<sub>2</sub> sources could not have been known *a priori*.

We emphasized it more now in the conclusions and hope that our minor wording changes in the respective sections clarify the reviewer's misconception.

*In the title "select aldehydes" could be changed to "selected aldehydes" or just "some aldehydes".*

We respectfully disagree with this suggestion. We chose 'select' according to its definition 'chosen from a number or group by preference' as opposed to 'selected' ('of a higher grade or quality than the ordinary') (cf <http://www.merriam-webster.com/dictionary>).

By using 'select', we express our preference of the three chosen species as they present proxies for different groups of aldehydes, namely (i) the most abundant one (HCHO) and (ii) multifunctional ones (CHOCHO, CH<sub>3</sub>COCHO) that are produced in different ratios depending on their source (anthropogenic vs biogenic).

*Details Page 33092, section 3.2: The box model description is insufficient and should be substantiated. I have mentioned this already as a separate first comment and hoped for a fast*

*(interactive) response by the authors. Please address this comment thoroughly. Please note that the mechanism cited here as Ervens et al. (2004) without naming it is generally addressed as CAPRAM 2.4 (MODAC mechanism) as it was developed in a multi-partner EC project named MODAC.*

We think that the reviewer might have confused two references here, namely Ervens et al. 2003a and Ervens et al., 2004. The former includes indeed the description of CAPRAM2.4(MODAC) whereas the latter is a subset of this mechanism that mostly focuses on the oxidation of organic compounds that leads to oxalate formation. As outlined in our response to the reviewer's first comment, we have added some details about the multiphase mechanism in Section 2.3.1. (Chemical Mechanism).

*Page 33088, line 10 ff: I think this should be formulated much more carefully, not all aldehydes are fully hydrated in aqueous solution. This should be mentioned and referenced. So, this particular difference will be largest for HCHO.*

The reviewer is right that not all aldehydes are completely hydrated in the aqueous phase. Given that HCHO is the most important aldehyde in terms of HO<sub>2</sub> sources in the gas phase, we reworded the sentence accordingly and only refer to formaldehyde here. In addition, we added a sentence about the low photolysis rates of (unhydrated) dissolved carbonyl compounds in general.

*Page 33104, section4: I have problems with application of the box model. Have there been tracer experiments being performed to come to cloud interaction times ?*

The clouds in Whistler were orographic or intercepted cumulus/stratocumulus clouds. The air flux through the orographic clouds was very slow; thus, they resembled fogs. However, due to the combination with more convective clouds, the air flux in the cloud events during which cloud water was sampled for analysis was not always in the same direction but air masses might have undergone significant vertical motion that could have caused recycling of air. Thus, tracer experiments as they have been done for previous experiments, e.g. in the case of strictly orographic hill-capped clouds could not be meaningfully performed.

In Davis, the situation was different during long-lasting fog events during which less air movement was occurring. In such situation of steady fog, drop lifetime is controlled by the settling velocity. Drop size distributions showed a maximum drop diameter at ~ 15 μm (Ervens et al., 2003). Based on this size, we estimated average drop lifetime (cf Section 2.3.2.).

*The authors are now using the interaction time as a variable but it would be more interesting to see how the box model results behave when air-cloud interaction times are used which are realistic at the different station. I would like to suggest to get best guesses of these interaction times, draw them into Figure 5. The LWC is now just represented as a line , not a range. Better mark it as a range. Then, mark the best available interaction time interval also as a range. Discuss the model results in that area where both ranges cross and compare them with the*

*measurements. This would add much clarity to the discussion of the box model results.*

We realized that the text at the beginning on Section 4.1 might have been misleading. We clarified now that we did several simulations, each with a constant LWC but overall the set of simulations covered a range of LWCs. As stated already in the caption of the original Figure 5 ‘grey lines represent the LWC RANGE as observed in Whistler and Davis, respectively’. So, we are not sure why the reviewer had the impression that we only showed it as a single line.

We thank the reviewer for the suggestions how to make a connection stronger between our model studies and the observations in better constraining the processing time despite all caveats due to the simplicity of the box model. We added vertical lines to give approximate bounds of the air/cloud interaction time by (i) estimates of the lifetime of individual droplets as a lower limit, using reasonable ranges of cloud thickness (~ 600 m) and vertical air motion and (ii) the number of cloud cycles a particle might undergo (approximately three, derived based on the evolution of aerosol composition).

Whereas restricting the processing time to one cloud cycle (~ few minutes) implies that aldehydes evaporate completely during drop evaporation, the assumption of multiple cloud cycles represents the assumption that aldehydes do not evaporate and thus accumulate in particles. The true fraction of retained aldehydes is likely bounded by these assumptions but cannot be further constrained due to the lack of understanding of key parameters that determine aldehyde retention in haze particles.

In the revised Figure 5, we show that in the resulting square the predicted aldehyde concentrations are indeed within the right order of magnitude of measurements of all three aldehydes. However, as outlined above, we caution this estimate due to the uncertainty in drop lifetime that might affect aldehyde partitioning and processing.

*Other field measurement saw enormous enrichment of carbonyl compounds in the aqueous phase. At present, it cannot be judged from this manuscript if something similar happened here. Please discuss.*

Unfortunately, during the field experiments in Whistler and Davis, no gas phase aldehyde measurements were performed which prevents us from performing estimates on their gas/aqueous phase partitioning. Several studies have shown that the partitioning of formaldehyde, glyoxal and methylglyoxal in cloud/fog water can be approximately described based on thermodynamic equilibrium (Munger et al., 1995; van Pinxteren et al., 2005; Li et al., 2008). Calculating the corresponding equilibrium mixing ratios based on Henry’s law constants and the measured aqueous phase concentrations in Whistler and Davis results in mixing ratios of a few ppt for glyoxal and methylglyoxal which is in the same range as measurements at other locations (Fu et al., 2008).

In a detailed cloud study, deviations from aqueous phase concentrations as predicted based on Henry’s law constants by factors of ~0.7, ~2, and ~3 for formaldehyde, glyoxal and methylglyoxal, respectively, were found (van Pinxteren et al., 2005). Given the similar temperature dependencies of the Henry’s law constants for the three aldehydes, such deviations

can be explained by  $\Delta T < \pm 5$  K which is certainly within the variation of temperature between cloud events and/or by uncertainties of Henry's law constant measurements that originate from different experimental studies (cf e.g.  $3710 \text{ M atm}^{-1} < K_{\text{H}298}(\text{methylglyoxal}) < 32000 \text{ M atm}^{-1}$ , depending on ionic solutes (Berterton and Hoffmann, 1988; Zhou and Mopper, 1990)). We are not aware of any studies that show an 'enormous enrichment' of these species in dilute aqueous phase as represented by cloud and fog water.

We added some discussion that any apparent deviations could be also partially explained by uncertainties in the assumed (effective) Henry's Law constants since (i) reported values differ by up to an order of magnitude and (ii) all constants are highly sensitive to temperature.

*Page 33109 /110 Please check the conclusion section for consistency. On the last page it says the effect is small. The last sentence then states a "significant impact" suggested by "these studies" – which ones ? This is confusing.*

We quantified in the conclusion section the 'greatest impact on HO<sub>2</sub> levels by formaldehyde' and added the information that its dissolution and reaction into the aqueous phase might reduce HO<sub>2</sub> levels to up to 91%.

*The statement that the results of this work "...are robust" is axiomatic and needs substantiation.*

The reviewer is right that we overstated the accuracy of our box model studies by calling them 'robust'. We softened the language and state now more carefully that the purpose of our box model studies is to explore the predicted trends and ratios of aldehydes given the limitations and uncertainties of the box model in terms of the chemical and meteorological input data.

*The statement "...the box model simulations ...might not fully quantitative..." is not adequate - The status as described is different in my view: The authors need to prove that the model at all relates to the observations.*

We hope that our changes as outlined throughout this response and in the revised manuscript clarify that we are aware that such a simple model is likely not suited to perform such a task. Instead our box model simulations were used to contrast two different scenarios, guided by measurements in anthropogenically-impacted fog and more biogenically-impacted clouds.

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