

First of all, I would like to thank the reviewer for the comments, which helped to significantly improve the paper. Detailed answers are given below. The reviewer's comments are quoted in bold.

Major comments:

**1. One thing that is missing from this study is a way for model results to be easily compared with aircraft observations. I suggest that the authors include vertical profiles of the trace gas species in the convectively perturbed and unperturbed regions of the model.**

A new Figure has been added for the COPT case showing the vertical profiles of formaldehyde in the inflow and outflow regions of the squall line and the unperturbed UT profile. The Figure has been commented including a comparison of aircraft observations by Borbon et al. (2011). See the answer to specific comment 11 for more details.

For the STERAO case, we think that the figure showing the vertical profiles of HCHO is not really helpful because the difference between the unperturbed UT and the convective outflow for the simulation with retention in ice is quite small. This Figure is shown in answer to specific comment 14 below.

**2. While the authors discussed in the text the contribution of different processes to the trace gas concentration, it would assist the reader to show these contributions graphically. For example, vertical profiles of the different processes (e.g. the rate of transfer from cloud water to graupel, and photochemical production) would be useful.**

We agree that additional vertical profiles of the dominant processes would help to understand the signature of clouds on the soluble species. We regret that we are unable to proceed with these graphics in the present state of the model. Extra developments are needed to extract these informations which are not yet coded.

Specific comments:

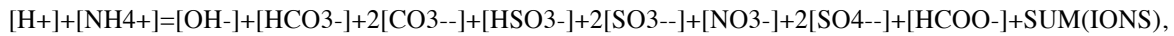
**1. Section 2: How are photolysis rate coefficients calculated? Are they modified for cloud scattering? Are aqueous-phase photolysis reactions modified for increased path length?**

Photolysis rate coefficients are calculated using the Tropospheric Ultraviolet & Visible Radiation Model (TUV, version 5), which takes into account cloud scattering effect. Moreover, the aqueous phase photolysis reactions are modified to increase the path length by a factor of 1.6 as recommended in Leriche et al. (2000). A sentence has been added page 965, line 5 to clarify this point:

“Photolysis rate coefficients are calculated using the Tropospheric Ultraviolet & Visible Radiation Model (TUV, Madronich and Flocke, 1999), which takes into account the cloud scattering. Moreover, the aqueous phase photolysis reactions are modified for increased path length, a factor of 1.6 is used as in Leriche et al. (2000).”

**2. Page 969, line 3. It would be good to show the actual polynomial equation that is solved to determine the pH of the drops.**

The pH value is obtained by solving the electro-neutrality equation:



with strong acid dissociation equilibrium. Here brackets represent ionic concentrations and  $\text{pH} = \log_{10}[H^+]$ .

The coefficients of the polynomial development of the pH equation are given by cumbersome expressions. Several lines of code are needed to write them down. The ion balance equation leads to  $H^+$  concentration after elimination of all anion concentrations using the dissociation equilibrium constants. A fairly simple case is given in Seinfeld and Pandis (1998) pp 345-348, for the carbon dioxide/water equilibrium showing a resulting sum of rational functions and its conversion in a polynomial form. Facing with the difficulty of accurately handling lengthy mathematical expressions, a computer algebra tool was used and a final check was made to verify the calculations, sum of rational functions versus polynomial development.

**3. Page 969, line 27. What effect does omitting gas trapping in growing ice hydrometeors have on the results? Does the Long et al. (2010) study quantify the contribution of retention via riming versus gas trapping (e.g., is gas trapping <10% contribution?)?**

Omitting gas trapping means less gas buried in ice crystals so more reactant in the gas phase. This is a limiting case corresponding to a zero burial coefficient. Long et al. (2010) found that gas trapping in ice hydrometeors is negligible with, for gas phase, rate about 1000 times lower than rate due to degassing through retention.

**4. Page 970, line 8. While the authors do say later (Section 3.3) that using one ice-phase concentration gives results of the same magnitude as those found by Barth et al. (2007), it would be nice to see a quantitative value describing differences between the method used in this study and a method predicting the trace species concentration in each cloud hydrometeor reservoir. Differences should arise because the fallspeed of snow and graupel are different and are even more different if hail is represented. Because this study uses the lower fallspeeds of graupel, it may be that representing the trace gas in ice with one prognostic variable is sufficient. This may not be true if hail is represented.**

The single ice phase chemistry is based on the hypothesis that trapped reactants in the ice phase are distributed in proportion of the mixing ratio of the hosting precipitating ice species. This is realistic partially because the sedimentation process of the precipitating ice particles leads to a natural stratification to ease the partition inside the clouds, i.e. a peak value of snow/aggregates above a layer where graupel dominates. As a result, ice phase chemistry is concerned by cloud regions where snow/aggregates and/or graupel particles are present. Hail is not considered explicitly in the ice chemical scheme for several reasons. Even if a specific "hail" category can be selected in the microphysical scheme of MesoNH (distinct from the "graupel" category), the formation of hail remains rather local and infrequent in clouds. Furthermore and because hail particles are coated by a film of liquid water it is difficult to assess for a true aqueous chemistry scheme in this case.

Here the main assumption is that at each time step, different ice particles contain a proportion of the total trapped trace gas in the ice phase, that depends on the local mixing ratio of the precipitating ice. It is necessary to do so because each fraction of trapped gas evolves according to the intrinsic evolution of the host ice particle in the cloud scheme. In particular the sedimentation rate of the trace gas in ice follows the sedimentation rate of the falling particle (Eq. 14 as an example).

In conclusion, we feel that the purpose of ice phase chemistry is to retain and to redistribute at cloud scale a fraction of dissolved gases in drops that freeze or rime but, at low computational cost since the process of gas retention in the ice phase is not well known. The idea we are developing here is that this gas-trapping affect can be accounted for but in a rather simple way which is commensurate to our knowledge of the processes.

**5. Page 971 and Table 4. The authors present the retention coefficients used for this study. Referee 1 commented that because of the importance of the retention process on the model results and the poorly constrained values of the retention coefficients, finding the sensitivity of the model results on the chosen retention coefficients would be useful to know. The referee also suggests making a recommendation for future studies based on the sensitivity analysis. I agree with the other referee that the sensitivity to the retention coefficient be analyzed. However, I would like to point out that there is not a consensus on the retention coefficients. Laboratory studies have been conducted finding a range of retention coefficients from 0.1 to 1.0 for a single species. As Stuart and Jacobson (2004) point out, there are several factors, e.g. Henry's law coefficient and how quickly the drop freezes, that contribute to whether a species is retained or not. Thus, I would recommend developing a physically-based method for assigning the retention coefficient (one that depended on these factors). Further, I would suggest that observations in real clouds continue to be made to help identify the retention coefficient, keeping in mind that drops that freeze quickly (possibly in severe thunderstorms) may have a different retention coefficient than clouds with drops that freeze more slowly (possibly in weak cold fronts).**

We agree with the referee analysis that physical arguments are in favour of retention coefficients related to corresponding Henry's law coefficients. A highly soluble trace gas should have a high retention coefficient to "extend" its affinity to water. However, as end user of theoretical atmospheric chemistry, this possible relationship linking retention and solubility must be established on a solid basis. This is beyond the scope of this work. The issue concerning the freezing time scale of the drops is difficult to introduce in models because particles are not followed individually and the freezing rates express mass transfer rates of a population of drops that feed the ice particle mixing ratio in a single model time step.

To underline the importance of the retention, the following sentences have been added in the conclusion page 988 line 17:

"Both simulations of mixed phase cloud show an important effect of retention that either acts as a reservoir (STERAO case) or as a sink through wet deposition (COPT case). More measurements of retention coefficients, both in real clouds and in laboratory are thus urgently needed in order to better constrain the partitioning of chemical species between all phases in mixed phase clouds. Ultimately, a physically-based method for assigning the retention coefficient has to be developed

taking into account all important factors identified by Start and Jacobson (2004).”

Model results are sensitive to the values of the retention coefficients chosen. So the case studies presented here are only illustrative of the capability of the module to simulate cloud chemistry. As the goal of our study was not to explore the sensitivity of the retention coefficients, we chose to not include in the paper a detailed sensitivity analysis on the retention coefficients values.

**6. Page 974, first paragraph. HARP case. While different initial profiles likely won't change the results of the study, I have a few questions and comments about the choice of initial profiles. Is the top of the boundary layer 1 km? Showing a profile of potential temperature would show the BL height and assure that the initial concentration profiles at 2 km altitude? Most of my experience shows O<sub>3</sub> profiles to be fairly constant from 0 to 10 km altitude and then increase above this level into the stratosphere. Is there an ozonesonde profile from Hawaii that shows a typical vertical profile? Hydrogen peroxide has a distinctive vertical profile as well, with peak values occurring near the top of the boundary layer and lower values at the surface because of dry deposition and lower values above where less water vapor is available for H<sub>2</sub>O<sub>2</sub> production. Have the authors done sensitivity simulations to explore the impact of the assumed vertical profile on the results of uptake and cloud chemistry?**

A quick look to the initial theta vertical profile for this marine case indeed shows a boundary layer height below 1km.

We agree that the initial profiles could be refined for each molecules according to this information. The idealized profiles used for this simulation are derived from climatological vertical profiles characteristics of a tropical marine atmosphere. We have not performed sensitivity studies on the initial profiles. Within the 3000 s simulation duration, we do not expect a major change in the compared impact on the soluble species between the two microphysical schemes.

**7. Page 974, line 26. Is there significant production of H<sub>2</sub>O<sub>2</sub> from aqueous-phase chemistry?**

The production of H<sub>2</sub>O<sub>2</sub> from aqueous-phase chemistry is insignificant in comparison to the source of H<sub>2</sub>O<sub>2</sub> in raindrops due to the transfer of H<sub>2</sub>O<sub>2</sub> from cloud droplets by collision/coalescence processes.

**8. Page 975, lines 2-3. Could the authors explain better why the lower solubility of SO<sub>2</sub> delays its scavenging by cloud water compared to H<sub>2</sub>O<sub>2</sub>?**

The pH value in cloud water is between 4 and 5.5, thus, the Henry's law effective coefficient for SO<sub>2</sub> is between  $1.8 \times 10^2$  and  $5.7 \times 10^3$  while the Henry's law effective coefficient for H<sub>2</sub>O<sub>2</sub> is  $7.73 \times 10^4$ . This difference explains why H<sub>2</sub>O<sub>2</sub> is scavenged with more efficiency in cloud water than SO<sub>2</sub>. To clarify this point, a sentence page 975 lines 3 has been added:

“Indeed, the effective Henry's law coefficient for sulphur dioxide is between  $1.8 \times 10^2$  and  $5.7 \times 10^3$  in cloud water (pH value between 4 and 5.5) while it is  $7.73 \times 10^4$  for hydrogen peroxide.”

**9. Page 975. Because trade-wind cumulus clouds grow and dissipate, it would be interesting to see what the redistribution of trace gases looks like after the cloud evaporates. Does the model simulation include this stage of the simulation and does it suggest interesting results e.g. a remnant cloud layer where formic acid exists, and SO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and HCHO are depleted?**

The HARP case is a 2D kinematical test case that simulates a shallow convection cloud in growing and mature stages. The case is highly idealized by purpose to focus on aqueous phase chemistry processes embedded in the microphysical evolution of the cloud. A realistic simulation of the full cloud cycle could be done in a 3D LES context for a population of trade-wind cumuli with some growing and other dissipating, but keeping the same chemical kinetics and microphysics. This is why the stage of the cloud evaporation is not simulated in our study.

**10. Page 978-979. The authors show HCHO mixing ratios for the COPT case and discuss processes that are important for those mixing ratios. These processes include sedimentation and melting of snow and graupel, and photochemical production of HCHO. It would help to show the contribution of these processes to HCHO using a figure. One way to do this is to produce vertical profiles of the horizontal sum of the different processes affecting soluble tracers.**

Again, we regret that we are not able in the present state of the model to extract this information.

**11. Pages 979-981. COPT case. Although it is not possible to compare these model results to aircraft measurements, it would be useful to plot the results in a way that could be interpreted for past and future aircraft studies. Often aircraft fly in the inflow region of the storm, get vertical profiles to the side of the storm, and fly in the outflow region of the storm. What would such a profile look like from these model results? I suggest showing vertical profiles that include typical inflow and outflow mixing ratios. Alongside this convectively-perturbed vertical profile, a vertical profile in the model domain that has not been affected by the convection would allow the reader to easily see the difference between convective outflow and background UT mixing ratios.**

The following Figure has been added in the manuscript:

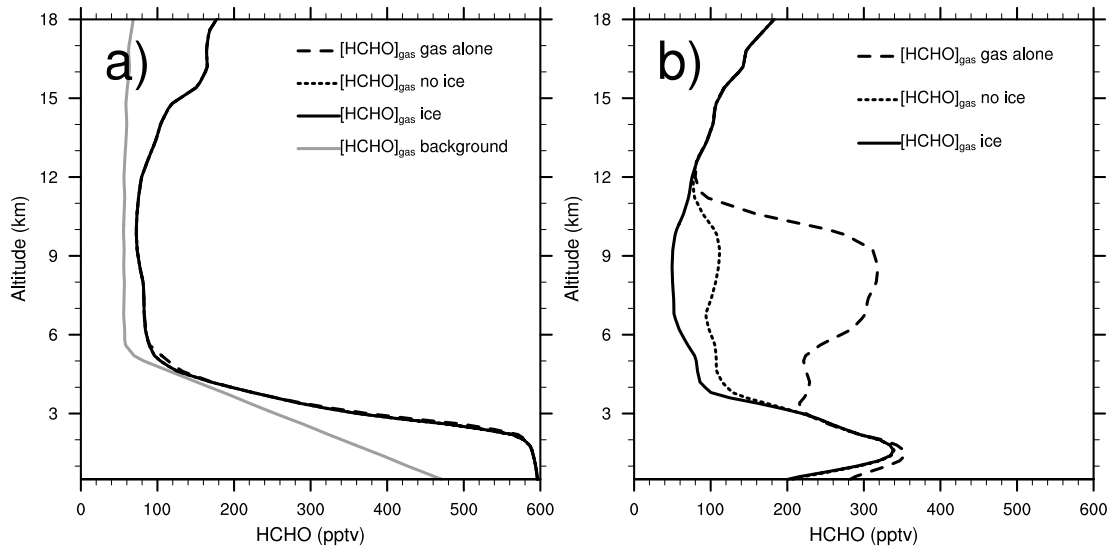


Fig. 8. Vertical profiles of gas phase mixing ratio of formaldehyde for the COPT81 case: (a) black lines are mixing ratio for GAS (dashed line), AQ-NOICE (dotted line) and AQ-ICE (solid line) simulations in the inflow region (20 km in horizontal distance) of the squall line during its mature stage and the solid grey line is the mixing ratio for the background troposphere, (b) black lines are mixing ratio for GAS (dashed line), AQ-NOICE (dotted line) and AQ-ICE (solid line) simulations in the outflow region (200 km in horizontal distance) of the squall line during its mature stage.

The following discussion on this new Figure has been included page 979 line 22 at the end of the paragraph:

“Figure 8 shows the vertical profiles of gas phase formaldehyde in the outflow and inflow regions and in the background troposphere. The comparison of the vertical profile in the inflow region and in the background troposphere shows the impact of the dynamic of the squall line in redistributing formaldehyde and its gas phase production in the boundary layer at the front of the squall line. In the outflow region, again the effect of the reduction of the vertical transport of HCHO by the convective updraft due to cloud chemistry is observed by comparing profiles of AQ-NOICE and AQ-ICE simulations with GAS simulation. In a same way, the enhancement of the scavenging of HCHO by the squall line through the retention in ice is visible comparing AQ-NOICE and AQ-ICE vertical profiles (Fig. 8b). In conclusion, the vertical profile of HCHO in the outflow region for the AQ-ICE simulation compares well with the vertical profile given in Figure 6 of Borbon et al. (2011) study.”

**12. Page 979. COPT case. Even though the model results cannot be evaluated directly with aircraft measurements, it would be useful to know how these results compare to measurements taken in tropical squall lines, e.g. compared to the Borbon et al. (2012) paper.**

This comparison is already discussed in the paper page 979 lines 15-22.

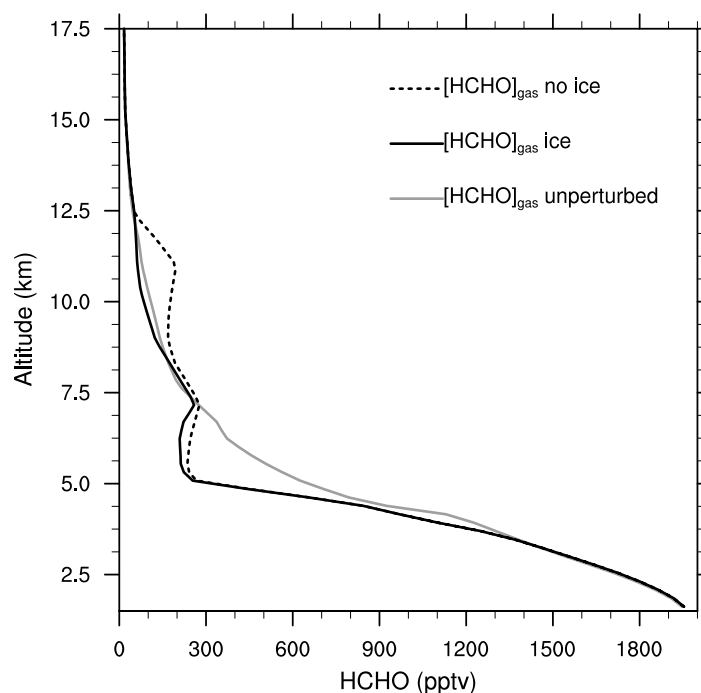
**13. Page 980. COPT case. How do the formic acid results compare to previous studies, e.g.**

## Barth et al. (2007)?

Barth et al. (2007) found a HCOOH production of about 100 pptv in the core of the storm where the cloud water is located, whereas, in the COPT case, this production is very low, a few pptv. Two main differences between Barth et al. (2007) and the COPT case in our study explain this discrepancy. First, in Barth et al. (2007), the initial mixing ratio of HCHO, the precursor of HCOOH in aqueous phase is about 2 ppbv at the surface whereas it is 500 pptv in the COPT case. Secondly, in the COPT case, the pH value in cloud water is high, between 6 and 6.5 whereas it is around 4.5 in the simulation of Barth et al. (2007). Thus, the destruction of formic acid is more efficient in our study because the formate ion pathway dominates at high pH value.

**14. Page 983, lines 26-29. STERAO case. It is not obvious in Fig. 11 that HCHO in the convective outflow is less than that in the unperturbed UT. Vertical profiles would help clarify the differences. In addition, the text simply says HCHO. Is it total HCHO mixing ratio or gas-phase mixing ratio?**

The text was referring to gas phase mixing ratio. The Figure below shows the vertical profiles of gas phase HCHO mixing ratio for the unperturbed troposphere and in the convective outflow (135 km in horizontal distance in reference to Fig. 11).



As mentioned in the text of the paper, this figure shows a small difference between the unperturbed UT and the convective outflow for the simulation with retention in ice with a low depletion of HCHO in the convective outflow. For the simulation without retention in ice, an enhancement of gas phase HCHO is observed in comparison to unperturbed profile in the convective outflow. However, we think that this figure is not really helpful because the difference between the unperturbed UT and the convective outflow for the simulation with retention in ice is quite small. The sentence page 983 lines 26-29 has been rewritten as:

“A relatively small depletion of gas phase HCHO in the convective outflow is found in comparison with unperturbed UT for the simulation with retention in ice. This effect is similar to the COPT81 case, and in agreement with Barth et al. (2007b).”

**15. Page 984. Same comment as above, but for the STERAO case. The authors show HCHO mixing ratios for the STERAO case and discuss processes that are important for those mixing ratios. It would be useful to show quantitatively the contribution of the processes via vertical profiles.**

The reviewer is right but we give here a similar response to comment 10 above.

**16. Page 984. A result that Barth et al. (2001) found for their simulations where  $RET = 0$  for all species is that soluble trace gases that degassed when freezing occurred subsequently went into the remaining cloud water at the top of the updraft. Do the authors find this process occurring in their simulations?**

This process is also found in our simulation and can be seen in Figures 11d and 12b in comparison to Figures 11c and 12a. A sentence has been added page 982 line 2 to underline this process:

“In the simulation without retention, HCHO degasses when freezing occurs, and is absorbed subsequently by the supercooled cloud water at the top of the updraft. This result was already found by Barth et al. (2001) in their simulation with no retention for all soluble trace gases.”

**17. Page 985, lines 10-12. What characteristics of the two microphysics schemes cause these differences? Different ice phase categories are mentioned, but I think the authors want to say that the higher density and fallspeeds of hail compared to graupel cause more dissolved species to transfer into graupel than hail. However, do the two microphysics schemes use different thresholds for when to create graupel or hail via a riming process?**

There are two ways for ice crystals like graupel to grow by riming process: the dry growth is when all the collected liquid water can freeze instantaneously and the wet growth is the opposite when the thermal balance equation of the graupel shows that the final temperature of the graupel stays above 0°C. The wet growth implies high amount of supercooled droplets. In the microphysical scheme of MesoNH, the two riming growths are integrated over the size distributions of the graupel and the lowest rate is retained (in other words, it is the limiting one). In MesoNH when 3 ice species are considered, a graupel particle growing by riming remains a graupel whatever the growth process is. In the case of 4 ice species with an additional “hail” category of particle, a graupel particle growing in wet mode is converted into a hail particle. Graupel and hail have different settings (for instance masse-size and fall speed-size relationships). The conversion of hail back to graupel is also possible in the model. This latest configuration with four ice species was not used in the present study.

**18. Because I am requesting additional plots (see major comments), I suggest removing Fig. 13 because it looks like Fig. 11. That is, H<sub>2</sub>O<sub>2</sub> behaves similarly to HCHO.**

As suggested by the reviewer, Fig. 13 has been removed and sentences page 984 line 20 and lines 23-25 have been changed accordingly:



“The same effect is observed for hydrogen peroxide (Figs. 12a and 12b).”

“A significant depletion is observed in the convective cores for hydrogen peroxide in gas phase for the simulation with retention in ice (Fig. 12c) underlying its capture in the ice phase (similar to HCHO, not shown).”

Technical comments:

**1. page 964, line 8. I think the authors mean to say “mean molecular speed” and not quadratic.**

This has been corrected.

**2. Page 966, equation 6 needs the “c” subscripted for rc.**

Done

**3. Page 967, line 24. I think the authors mean to say, “chemistry mechanism”.**

We would like to leave the name of “chemistry monitor”, as it is the part of the code calling the subroutines for microphysical transfers, for solving the set of differential of chemical species mixing ratio, for computing the pH, etc.

**4. Page 967, line 28. Please add explanation of what is meant by “by first ordering the gas-phase species”. Does that mean the gas-phase chemistry was calculated first? Or does it mean that cloud-free grid points are calculated first?**

In the model, there is a single chemical solver dealing with the gas phase (41 species) and with the aqueous phase (2x25 species) when cloud and/or precipitation are present. Because the gas phase is present everywhere, the gas species are ordered first, and then the aqueous species are added. As a result, the size of the chemical system to solve varies as 41x41 or 66x66 or 91x91 from gridpoint to gridpoint. Furthermore and because the KPP package of Sandu and Sander (2006) contains routines with low-storage sparse matrix algebra, it is computationally very efficient to regroup first thousands chemical systems of consecutive grid points, and then to call the chemical solver for a huge system such as we do.

The sentence has been rewritten as:

“In order to mix the treatment of cloud-free and aqueous phase chemistry, it is useful to order first the gas reactants and then to add the aqueous species.”

**5. Page 969, line 20. I think “generally” or “traditionally” is more appropriate than “classically”.**

“Classically” has been changed to “traditionally”.

**6. Page 970, line 1. Change to “pristine ice, which are newly formed”.**

Done

**7. Page 970, line 3. Change “concerned” to “included”.**

Done

**8. Page 972, lines 6-8 should be written more explicitly. There should be a sentence saying that because species with  $RET=0$  are not in ice, there is no need for a prognostic ice species equation. And line 6 could be written as “As shown in Table 4, 14 soluble chemical species and 5 intermediate ions have prognostic equations for the ice phase”. That is, clarifying early in the sentence what 14 and 5 refer to.**

The sentence, line 6-8, has been changed as suggested.

**9. Page 973, line 18-28. I assume that the authors are reporting the findings by Cohard and Pinty (2000) throughout the paragraph. If so, it would be better to attribute their work at the start of the paragraph. For example, “Cohard and Pinty (2000) found numerous differences between .... They found after 1200 s of model simulation ...”**

The paragraph has been rewritten accordingly.

**10. Page 975, line 14. Please explain how Figure 6 is produced. Are these mixing ratios for a particular point in the model domain, or an average value for the model domain?**

Figure 6 shows the time series of averaged mixing ratio in the centre of the cloud at 300 metres of altitude. This has been clarified in the text page 975, line 14:

“Figure 6, showing the time series in the centre of the cloud at 300 metres of altitude, summarizes these results:...”.

**11. Page 976. It would be good if lines 10-11 are moved to the top of the paragraph.**

The sentence, lines 10-11, has been moved to the top of the paragraph.

**12. Page 979, line 3. Spell out ETH and ALK for easier reading.**

The sentence has been changed into:

“Non-soluble precursors of HCHO, such as ETH and ALK ReLACS species (respectively ethane and alkanes others than methane and ethane together with alkynes, alcohols, esters and epoxides).

**13. Page 980, line 26. Is the maximum value of 280 pptv correct (Fig. 9 has maximum values of 2 pptv)?**

Yes, it is correct. The red colour represents values larger than 2 pptv.

**14. Fig. 5, pH cross sections. I suggest using contour levels of 0.2.**

Done.

**15. Fig. 6, Kessler is misspelled in the figure legend.**

Done.

**16. Fig. 10, The line segment in Fig. 10a is not placed correctly (it is too far to the left).**

Done.