

Report 2: We thank Referee n°2 for his suggestions and comments which helped improving the manuscript. The major point raised by the reviewer was totally justified since a mistake was still present in the calculation of dependency with temperature of the Henry's law constant. This correction improves the confidence in the partitioning ratio values. Also, many references have been added in the revised manuscript to meet the concern of the reviewer to put results into context with other works.

At last, answers to all criticisms are detailed point by point below.

**Major points:** One of the objectives of this paper is to show how trace gases are partitioned between gas and aqueous phases. This is described by the partitioning coefficient,  $q$ , which is the ratio of the aqueous phase concentration to what would be expected by Henry's Law equilibrium. First, this kind of ratio dates back to Chameides (1984) and Lelieveld and Crutzen (1991) who introduced the phase ratio (and should be cited). [...] If  $q = 1$ , then the trace gas should be in Henry's Law equilibrium. Based on Figure 7 in the paper, there are no trace gases in Henry's Law equilibrium, including the low solubility gases NO and NO<sub>2</sub>. Why are NO and NO<sub>2</sub> partitioned more in the aqueous phase than expected by Henry's Law equilibrium? This must be explained. I have thought of possible reasons and wonder if the liquid water content  $q_{cw}$  in the equation includes both cloud water and rain. Are there substantial amounts of rain (or large drops) being produced? If NO and NO<sub>2</sub> are transferred to the larger rain drops via microphysical processes, do they become supersaturated in the rain? The conclusions of the paper rely upon the partitioning coefficient illustrated in Figures 7 and 8. It is important to be confident that the values of  $q$  make sense.

**Reply:** Calculations for the partitioning coefficient were performed with model outputs, using the formula recalled by the reviewer. We checked the calculations and there was a mistake in the Henry's constant with a wrong dependency with temperature ( $1/T_0 - 1/T$ ) instead of  $-(1/T_0 - 1/T)$ . The error has been corrected and provides obviously much more reasonable results. Figures 7 and 8 have been redrawn and the text has been rewritten with the new data. In this version of the model, rain is not activated and in the cloud, low solubility gases NO and NO<sub>2</sub> have to be partitioned according to Henry's Law equilibrium. Our data are compared with the data provided in a recent review from Ervens (2015) that summarizes most of the previous evaluations of the partitioning coefficient in the literature.

We also checked with previous data from Lelieveld and Crutzen (1991) who calculated the phase ratio which depends on the temperature, the liquid water content, the effective Henry's law constant (so the pH) and found similar orders of magnitude for the phase ratio for the species that were described in that paper.

However, we feel that the  $q$  partitioning coefficient is more relevant to describe the deviation from Henry's law equilibrium, so this formulation has been kept in the paper and the discussion has been revised with the new calculations.

### **Specific comments**

**Comment 1:** Page 7, Line 12. It would be good to cite a reference (e.g. Hegg et al., 1984, *J. Geophys. Res.*; Chaumerliac et al., 1987, *J. Geophys. Res.*) to support the proportionality method for transferring trace gases and aerosols via microphysical processes.

**Reply 1:** The suggested references were added.

**Comment 2:** Page 7, Lines 17-22. Does the model include processes like rain collecting aerosols via impaction scavenging or Brownian diffusion?

**Reply 2:** No, the only process involving aerosol particles is their activation into cloud droplets and related effect on cloud chemistry through nucleation scavenging. It is now clearly stated in the introduction: “The development of such a coupled model first offers the opportunity to investigate the contribution of the particles serving as cloud condensation nuclei (CCN) to aqueous concentrations of given species by nucleation scavenging, which control the pH of the droplets and further affect oxidation processes (Leriche et al., 2007; Hegg, 2001)”. Also, in order to avoid any confusion between the contributions of particle originating compounds and mass transfer to aqueous concentrations, the terminology used in the manuscript has been completely modified. The expression “particle to cloud transfer” is not used anymore, and has been explicitly replaced by “nucleation scavenging”. Then, since the simulated cloud is non precipitating, the impaction scavenging is of minor importance compared to nucleation scavenging as shown for instance in Flossmann (1991).

Flossmann, A. I.: The scavenging of two different types of marine aerosol particles using a two-dimensional detailed cloud model, *Tellus B*, 43, 301-321, 1991.

**Comment 3:** Page 9, Lines 11-16. What are the definitions of “Marine” and “Highly Marine” airmasses? This is important to know for the analysis later in the paper.

**Reply 3:** It is true that the analysis reported in this paper would benefit from a short description of the cases highlighted in the manuscript, namely “Marine” and “Highly marine” cloud events. Such a description was added in the revised version of the paper at the end of Section 3.1, based on previous work by Deguillaume et al. (2014): “Cloud events in the westerly and northerly/northwesterly air masses were the most frequent, representing 72% of the air masses sampled at the PUY station, the majority of which were categorized as “Marine” or “Highly marine”. These two categories of cloud events displayed high pH values compared to other types, namely “Polluted” and “Continental” (mean pH 5.7, 6.2, 4.0 and 4.9 in “Marine”, “Highly marine”, “Polluted” and “Continental” clouds, respectively). In addition, “Highly marine” cases were characterized by high concentrations of Na<sup>+</sup> and Cl<sup>-</sup> (means of 311 and 232 μM, respectively), which were in contrast one order of magnitude lower in “Marine” cases (means of 32 and 30 μM, respectively). The clouds sampled in the westerly/southwesterly air masses were also frequently characterized by a strong marine signature (64%). Since the aerosol particles spectrum to be activated was measured in such an air mass, the model results will be compared to the “Marine” and “Highly marine” cases classified by Deguillaume et al. (2014).”

**Comment 4:** Page 9, Line 22. The modeled concentrations are average values of what? Are they averaged over space or time or both?

**Reply 4:** The abovementioned modeled concentrations are averaged over the simulation apart from the cloud condensation and evaporation phases. The averaging period was chosen to only consider conditions representative of a “well-formed” cloud, similar to those observed during cloud sampling at the station. This averaging period roughly corresponds to the length of the plateau in Fig. 2, which represents the profiles of altitude and temperature used to describe the trajectory of the modeled air parcel throughout the simulation. This plateau corresponds to that of cloud liquid water content and droplet radius displayed on Fig. 3. Part of this information was added in the revised version of the manuscript: “The modeled concentrations are average values calculated throughout the simulation apart from the condensation and evaporation phases, to be close to the measuring conditions in a well-formed cloud (this period roughly corresponds to the plateau displayed on Fig. 2 and Fig. 3)”.

**Comment 5:** Page 9, Line 25 or so. Are photolysis rates used for the chemistry appropriate for the February 28 to March 1 event?

**Reply 5:** The calculation of photolysis rates in the TUV radiative transfer model does take into account the location of the site (latitude/longitude) as well as the day of year and time of day. The simulations discussed in this study were performed on March 1st.

**Comment 6:** Page 9, Line 29. Is there a reference regarding the outgassing of H<sub>2</sub>O<sub>2</sub> from frozen samples?

**Reply 6:** The outgassing of H<sub>2</sub>O<sub>2</sub> is discussed in Marinoni et al. (2011), cited earlier in the sentence. In order to make it more explicit, this sentence was slightly rephrased: “Additionally, during the wintertime, the hydrogen peroxide concentration is often derived from frozen samples (Marinoni et al., 2011; Snider et al., 1992), which, as demonstrated in the aforementioned studies, can lead to an underestimation of the actual in-cloud concentration because of the outgassing of H<sub>2</sub>O<sub>2</sub>.”

Snider, J.R., Montague, D.C. and Vali, G.: Hydrogen peroxide retention in rime ice, *J. Geophys. Res.*, 97, 7569-7578, 1992.

**Comment 7:** Page 11, Lines 14-23. It would be interesting to see the aqueous OH concentration in addition to the organic acids, because OH(aq) is the main oxidant of these acids.

**Reply 7:** The respective concentrations of OH(aq) in Run 1 (4 10<sup>-14</sup> M) and Run 6 (9 10<sup>-14</sup> M) have been added in the discussion on the organic acids.

**Comment 8:** Page 11, Lines 24-27. The change between Run 1 and Run 6 for succinic, tartaric and malic acids appears to be quite small. It does not seem to be significant enough to discuss.

**Reply 8:** We agree with this comment and the lines have been deleted.

**Comment 9:** Page 12, Lines 16-31. It is surprising that there is no aqueous-phase chemistry source for HCOOH shown in Figure 9. Why is that?

**Reply 9:** Actually there is an aqueous-phase chemistry source for HCOOH, which is barely noticeable on Fig. 9. This source is low because Fig. 9 only shows the average relative contribution of each source over the simulation. In fact, mass transfer of HCOOH from the gas phase to the droplet is very strong compared to other sources during the first steps of the simulation, and this has a significant effect on the calculation of the average contribution. If the analysis shown on Fig. 9 would have been performed at each time step, one would have observed a contribution of aqueous reactivity after a few time steps of simulation. Such detailed analysis is indeed possible with our model, but was however behind the scope of this paper and left for future investigations.

**Comment 10:** Page 13, Lines 13-17. This paragraph is not needed for the middle of the conclusions. It would be better suited in the Introduction.

**Reply 10:** As suggested, this paragraph was moved to the end of the introduction.

### **Technical comments**

P. 1, L35, to derive → to drive: What we want to say in this sentence is that the mechanism CLEPS 1.0 was “built” following the protocol developed by Mouchel-Vallon et al. (2017). Thus we replaced “derive” by “build”.

P. 1, L36, add a comma after “conditions”, or add “that is”: “that is” was included.

P. 6, L4, The number of nucleated particles would be equal to  $(dN/dt)_{NUC} \Delta t$  and not just  $(dN/dt)_{NUC}$ : the expression has been modified in the revised version of the manuscript: “At each time step, the number of newly nucleated droplets  $\left(\frac{\partial N_{cw}}{\partial t}\right)_{NUC} \times \Delta t$ , where  $\Delta t$  is the time step) and...”.

P. 8, L10, → data were: **Changed**

P. 8, L16-20, cite Table 3 in this paragraph: **Reference added**

P. 9, L 28, →the hydrogen peroxide: **Typo fixed**

Figure 7 is challenging to read because one’s eye is drawn to the diamonds connected by the line. On the other hand, Figure 8 is easy to read. I wonder if the triangle markers in Figure 7 could be larger or made into a box plot (like Fig. 8) and then overlay the  $H_{eff}$  markers and line:

**The figure has been reshaped as suggested, i.e. using bars for q factor and larger markers for  $H_{eff}$ .**