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Dr Nadine Chaumerliac & Dr. Laurent Deguillaume
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To whom it may concern,
Atmospheric Chemistry and Physics (ACP)
Copernicus Publications

Dear Sir, Madam,

Please find enclosed our corrected article submitted to Atmospheric Chemistry and Physics (ACPD). The article is entitled: *Modeling the partitioning of organic chemical species in cloud phases with CLEPS (1.1), authored by C. Rose, N. Chaumerliac, L. Deguillaume, H. Perroux, C. Mouchel-Vallon, M. Leriche, L. Patryl, and P. Armand.*

This article proposes an advanced coupling between the cloud chemistry model CLEPS 1.0 (Mouchel-Vallon et al., 2017) including mass transfer from the gas phase and in-cloud aqueous chemical reactivity and warm microphysics describing the activation of aerosol particles into cloud droplets. The aim of the present study was more particularly to investigate the effect of particle scavenging on cloud chemistry. Several simulations were performed to assess the influence of various parameters on model predictions and to interpret long-term measurements conducted at the top of the puy de Dôme (PUY, France) in marine air masses. Specific attention was paid to carboxylic acids, whose predicted concentrations are on average in the range of the observations.

Major comments and minor corrections have been considered and we provide detailed replies point by point. Here, we like to stress two important aspects considered in the revised manuscript. First, the manuscript was originally addressed to GMDD justifying the technical aspects of the introduction. Following the reviewer's comment, the introduction has been rewritten and many references have been added in the revised manuscript to put results into context with other works and to better highlight the scientific significance of our work. Then, the major point raised by reviewer 2 was totally justified and revised estimations of the partitioning ratio might improve the confidence in the partitioning process among gas and aqueous phases.

All the changes in the revised version of the manuscript are indicated in blue for more clarity. We hope that the revised version of the manuscript will be accepted for publication in ACP.

Sincerely,

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Report 1: We thank Referee n°1 for his suggestions and comments which helped improving the manuscript. Comments are addressed point by point below. The manuscript was originally dedicated to GMDD, but got reoriented to ACPD by the editor.

Comment 1: My main concern is that the scientific significance of this study has not really been put into context. The section Introduction focuses on explaining the choices for the methods applied in the model framework. It would be more important to explain in Introduction: what are the scientific questions of this study and what is the significance of this topic?

Reply 1: As mentioned above, our manuscript was originally addressed to GMDD as it mainly describes the coupling between the chemical mechanism CLEPS 1.0 and a warm cloud microphysical scheme. This explains the technical aspects of the introduction. Following the reviewer's comment, the introduction has been rewritten in order to better highlight the scientific significance of our work:

- The most technical points related to the developments we performed were moved to Sections 2.1 and 2.2;
- Processes related to in-cloud aqueous chemistry are now mentioned, including a more explicit description of those contributing to aqueous concentrations, i.e. nucleation scavenging of particles, exchange of gases between air and droplets through mass transfer and aqueous reactivity. In addition, the use of "transfer" for both particle ("particle-to-cloud transfer") and gas phase ("mass transfer") related processes might be confusing. We have thus changed the terminology throughout the manuscript. The contribution of the particulate phase is now referred to "particle (nucleation) scavenging", while, following the common practice, the exchange between the gas phase and the droplet is still referred to as "mass transfer".
- The importance of aqueous cloud chemistry with respect to global atmospheric chemistry and climate was highlighted.
- The strength of the model regarding its capacity to estimate to contribution of the aforementioned sources to the simulated aqueous concentrations was further stressed, as this information is highly valuable since it cannot be obtained from measurements as stated by Leriche et al. (2007).

Comment 2: Page 2, Lines 1-2: "As a first step, CLEPS 1.0 has been integrated in a box model that takes into account neither aerosol particles nor microphysical processes, and thus only allows for the simulation of idealized cloud events" I don't understand what this sentence means? If the box model does not take into account the aerosol particles or microphysical processes, how does it differ from a standalone version of the chemistry model? Has this first step been a part of the work for this manuscript or is there a citation missing?

Reply 2: In its first version developed by Mouchel-Vallon et al. (2017), CLEPS 1.0 was limited to the simulation of cloud events with constant microphysics, i.e. constant droplet radius and liquid water content were considered throughout the simulation. In particular, the formation of the cloud through the activation of an aerosol spectrum was not simulated, nor the effect of these particles on cloud chemistry through nucleation scavenging, neither were the microphysical processes determining the evolution of the droplet spectrum. We agree with the reviewer that the abovementioned sentence was confusing, and we thus removed it in the revised version of the manuscript. Instead, we only focus on the strength of the new coupled model: "This paper describes the coupling between the chemistry model based on CLEPS 1.0 and a bulk two-moment warm cloud microphysical scheme allowing for the simulation of cloud events and comparison with long-term observations."

Comment 3: Page 2, Line 7: This phrase is very ambiguous "the impact of aerosol particles on the cloud chemistry (by nucleation scavenging)" and it should be clarified, what impact is actually meant.

Reply 3: As previously mentioned (Reply 1), the processes contributing to aqueous concentrations are now more explicitly described in the revised version of the introduction. For instance, the sentence mentioned by the reviewer was changed to: "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)."

Hegg, D. A.: The impact of clouds on aerosol populations, IGAC Activ. Newsl., 23, 3-6, 2001.

Comment 4: Page 2: It is said that the calculation of chemistry in a sectional cloud parcel model would be computationally too expensive. With current computing resources this sounds strange. What kind of CPU time does CLEPS require for the runs in this study?

Reply 4: According to Khain et al. (2000) and Flossmann and Wobrock (2010), several tens of bins are needed in a sectional cloud parcel approach to provide a satisfying description of the cloud. We agree with the reviewer that such an approach would still be fine in the current version of our 0D coupled-model, since the runs performed in the frame of this study on average require a CPU of 49 min (for 2 hours of simulation with a time step of 0.1 second). However, the final goal of our work is to implement our developments in a regional model, for which the sectional approach would definitely not be optimal. This is now clearly stated in the revised version of the manuscript: "They are however computationally too expensive to be used with detailed explicit aqueous-phase chemistry such as that described in CLEPS 1.0 as we aim in the future to include our developments in regional climate models."

Khain, A., Ovtchinnikov, M., Pinsky, M., Pokrovsky, A., and H. Krugliak.: Notes on the state-of-the-art numerical modeling of cloud microphysics, https://doi.org/10.1016/S0169-8095(00)00064-8, 2000.

Flossmann, A. I., Wobrock, W. :A review of our understanding of the aerosol-cloud interaction from the perspective of a bin resolved cloud scale modelling, Atmos. Res., 97, 4, 478-497, DOI 10.1016/j.atmosres.2010.05.008 (Elsevier), 2010.

Comment 5: Page 3, Line 34: Henry's law effective→effective Henry's law

Reply 5: Correction was made.

Comment 6: Section 2.2.1: The way the activation of droplets is calculated is unclear (even going back to papers Caro et al., (2004) and Leriche et al., (2007). Is it so that the activation of droplets is calculated on each time step, not only at the base of the cloud? The Abdul-Razzak Ghan parameterization calculates the number of activated droplets at the cloud base for an air parcel that is rising adiabatically. This means that the parameterization would not work for the droplet activation in-cloud because the already activated droplets would significantly affect the parcel supersaturation. This effect is not taken into account in the parameterization. What was the updraft speed used for the activation parameterization? Are there estimates for updrafts at puy de Dôme?

Reply 6: The number of activated droplets is calculated at each time step by:

$$N_{activated} = \left|N_{available\ for\ activation} - N_{already\ activated}\right|$$

However, activation is mainly efficient during the first time steps of the cloud occurrence.

The updraft at puy de Dôme is 0.4m/s, estimated as a mean value of the time profile described in Leriche et al. (2007), the air parcel rises adiabatically.

Comment 7: Page 7, Line 2: What are the "inputs related to the dissolution of the particulate matter in the cloud droplet"?

Reply 7: The sentence was changed to: "The term T_{ap} has been introduced in Eq. (10) to take into account the contribution of the soluble fraction of particulate phase to aqueous concentration of species i via particle nucleation scavenging."

Comment 8: Page 10: The motivation for the simulation without dissolution is unclear to me. The result from this exercise is that there is less uptake when the particle dissolution is neglected. This seems to me quite obvious since the effective Henry's law constant is (by its definition) always higher than the Henry's law constant.

Reply 8: The expression "particle dissolution" was probably not appropriate and has been replaced by "particle scavenging" (by nucleation). The simulation without particle scavenging is of great interest as it clearly demonstrates the fact that accounting for nucleation scavenging is crucial to retrieve reliable concentrations of some species, including for instance nitrate as well as di-carboxylic acids (see Table 4). This last aspect is further illustrated in Fig. 9, which clearly shows that particle scavenging has to be taken into account as it is the main (or even unique) source for some of the chemical species described in the model, such as tartric, succinic and malic acids.

The use of "transfer" for both particle ("particle-to-cloud transfer") and gas phase ("mass transfer") contributions was confusing. The terminology has been thus changed throughout the manuscript to clarify the text. The contribution of the particulate phase is now referred to as "particle scavenging" and/or "nucleation scavenging", while the exchanges between the gas phase and the droplet is still referred to as "mass transfer", following Schwartz (1986).

Schwartz, S.: Mass-transport considerations pertinent to aqueous phase reactions of gases in liquid-water clouds, Chemistry of Multiphase Atmospheric Systems, NATO ASI Ser., vol. G6, Springer-Verlag, New York, 1986.

Comment 9: Page 10, Line 29: What would be considered a significant change in the cloud microphysical properties and which properties are meant here? The motivation for the comparison between mass transfer and particle dissolution is also unclear. If I am not mistaken, in Figure 9, it is actually the effective Henry's law coefficient that determines the ratio between "particle dissolution" and "mass transfer" (at least for compounds that are not produced by aqueous phase chemistry). This would mean that mass transfer has little to do with this ratio. Would Figure 9 change at all if, for example, the mass transfer coefficient was doubled?

Reply 9: Regarding the first comment the microphysical properties refer to cloud liquid water content and droplet radius, and should have been explicitly mentioned. Regarding the magnitude of this change, the use of the expression "not significant" was also not appropriate, as the difference observed between the two simulations (Run 1 = reference and Run 3 = increased organics loading in the particle phase) is negligible. In fact, concerning the liquid water content (LWC), it turns out that the average of the ratio $\frac{LWC(Run\ 3)-LWC(Run\ 1)}{LWC(Run\ 1)}$ is $\sim 3 \times 10^{-6}$. Applying similar reasoning to droplet radius leads to similar conclusions. The abovementioned sentence was thus changed to: "The increased amount of organic matter in the particulate phase did not affect the cloud microphysical properties, namely the cloud liquid water content and droplet radius, which were rather determined by the dominant inorganic fraction representative of marine aerosols."

The second part of the comment has already been addressed in Reply 8. The results shown in Fig. 9 clearly illustrate one of the major strengths of the model, which is capable of estimating the sources of the compounds that are found in the cloud droplet. Comparing mass transfer from gas phase to aqueous phase and particle scavenging by nucleation thus makes sense, as it indicates which one of these two processes is the major contributor to aqueous concentration of a given species.

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_2. Why are NO and NO_2 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 qcw in the equation includes both cloud water and rain. Are there substantial amounts of rain (or large drops) being produced? If NO and NO_2 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_2 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^+ and Cl^- (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_2O_2 from frozen samples?

Reply 6: The outgassing of H_2O_2 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_2O_2."

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 ($4\ 10^{-14}$ M) and Run 6 ($9\ 10^{-14}$ 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, tartric 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 $(dN/dt)_{NUC}$ Δt 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 Δt 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}.