Review of "Modeling the partitioning of organic chemical species in cloud phases with CLEPS (1.1)" by Rose et al.

Summary

This article describes the coupling of a highly detailed gas and aqueous-phase chemistry module with a liquid-only cloud physics module. The coupled model is applied to a cloud event observed at Puy de Dome in France so that model-predicted concentrations of organic acids can be evaluated with measurements. The study shows that the organic acids originate from the gas or aerosol phase and that aqueous-phase chemistry plays a minor role in contributing to the production of these acids (except for possibly acetic and glyoxylic acids). The authors nicely explain through sensitivity simulations how different processes affect the organic acid concentrations.

The paper addresses its objectives (evaluating the coupled cloud physics-chemistry model) sufficiently. However, there is a lack of putting the study and its results into context with other work. This is a needed step in order to meet the journal's focus on the science learned from the study. Second, a major part of this study examined the partitioning of trace gases between gas and aqueous phases. However, the partitioning coefficient results did not completely make sense. Further discussion is below. I recommend addressing the following concerns before consideration of publication.

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). The phase ratio uses the Henry's Law equilibrium equation and adjusts the units to get a dimensionless quantity. The quantities $C_a$ and $C_g$ can be defined as the following.

$$C_a[\frac{molecules}{cm^3}] = X[\frac{mol\ X}{L\ H_2O}] * q_{cw}[\frac{L\ H_2O}{L\ air}] * Na[\frac{molecules}{mol}] * 0.001[\frac{L\ air}{cm^3\ air}]$$

$$C_g[\frac{molecules}{cm^3}] = P_X[atm\ X] * \frac{Na[\frac{molecules}{mol}]}{R[atm\ X\frac{L}{mol\ X\ \cdot K}] * T[K]} * 0.001[\frac{L\ air}{cm^3\ air}]$$

The Henry's Law equation is the following.

$$X[\frac{mol\ X}{L\ H_2O}] = K_{Heff}[\frac{mol\ X}{L\ H_2O\ \cdot\ atm\ X}]\ P_X[atm\ X]$$

Using the first two equations to substitute for X and $P_x$ and dropping the units give the following.

$$C_a * \frac{1000}{q_{cw}\,Na} = K_{Heff} * 1000 * \frac{R\,T}{Na} * C_g$$

This equation simplifies to the following.

$$\frac{C_a}{C_g} = K_{Heff} * R * T * q_{cw}$$

Thus, $q$ is simply monitoring whether the trace gas is in Henry's Law equilibrium as $q$ is just rearranging the above equation as,

$$q = \frac{C_a}{K_{Heff}\,R\,T q_{cw}\,C_g}$$

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 $q_{cw}$ in the equation includes both cloud water and rain. Are there substantial amounts of rain (or large drops) being produced? If NO and $NO_2$ 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.

<u>Specific Comments</u>

1. Page7, 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.
2. Page 7, lines 17-22. Does the model include processes like rain collecting aerosols via impaction scavenging or Brownian diffusion?
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.
4. Page 9, line 22. The modeled concentrations are average values of what? Are they averaged over space or time or both?
5. Page 9, line 25 or so. Are photolysis rates used for the chemistry appropriate for the February 28 to March 1 event?
6. Page 9, line 29. Is there a reference regarding the outgassing of $H_2O_2$ from frozen samples?

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.
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.
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?
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.

Technical Comments

P. 1, L35, to derive → to drive

P. 1, L36, add a comma after "conditions", or add "that is"

p. 6, L4, The number of nucleated particles would be equal to $(dN/dt)_{NUC} \Delta t$ and not just $(dN/dt)_{NUC}$.

P. 8, L10, → data were

P. 8, L16-20, cite Table 3 in this paragraph

P. 9, L 28, → the hydrogen peroxide

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.