

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.

Main comments:

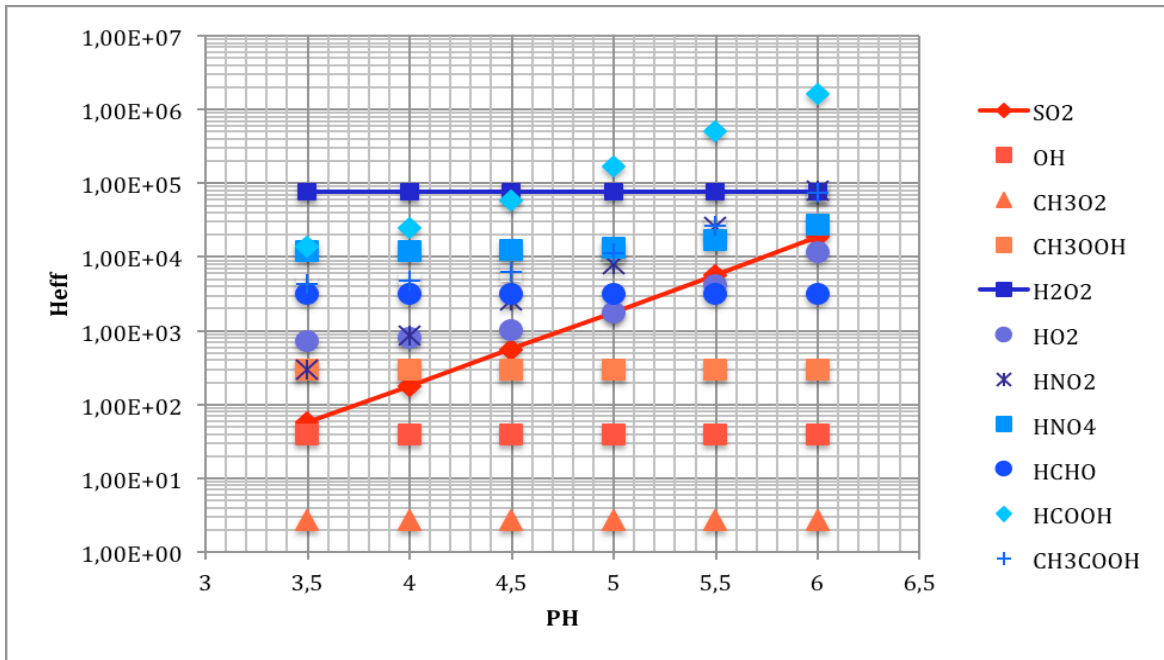
1) Most of the retention coefficients are estimates and are chosen based on the species' solubilities. Since you show that retention is an important effect that either acts as a reservoir or as a means to transport species, I wonder how sensitive your findings to these values are. In case of high sensitivity, one conclusion of your study should be that more measurements of retention coefficients are needed in order to better constrain the partitioning of species between all phases.

The sensitivity studies on the retention coefficient performed for the two convective cases COPT81 and STERAO clearly showed the impact of the retention mechanism on the signature of the cloud for soluble species. In this study, we have performed sensitivity studies following an "all or nothing" approach (RET=0 or RET=values given in Table 4 of the paper). We fully agree that refine studies are needed to estimate the degree of accuracy needed for the retention coefficients. A strategy could be to perform ensemble simulations for a large number of retention coefficients. This is well beyond the scope of this paper however.

The following paragraph was added in the conclusion page 988 after line 16 following the reviewer's recommendation:

“Simulations of mixed phase clouds show an important effect of retention that either acts as a reservoir (STERAO case) or as a sink through wet deposition (COPT case) for soluble species. Additional 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).”

2) Related to my first comments, it seems that the grouping of species in Table 4 is somewhat arbitrary. In particular the solubility of the acids will depend strongly on pH, and thus, some of the acids (HNO₂, HNO₄) might be only as soluble as CH₃OOH etc. At the very least, I think, you should add some comment to the Table that the different solubility categories are based on the assumption of a certain pH in order to avoid usage of these values in future studies for very different scenarios.



I agree with the reviewer. The figure above shows the effective Henry's law constant values calculated as function of the pH. The assumption made for the unknown values of retention coefficients in our model becomes problematic for pH values larger than 5. However, beyond pH = 5, the difference between the effective Henry's law constants of H₂O₂ and SO₂ becomes more and more reduced. Our assumption seems reasonable for the pH values in our simulations and the following comment has been added to the Table to avoid usage of these values in future studies with different scenarios: "This grouping of species is valid for pH values between 3 and 5". Also, a sentence has been added in section 2.5 page 971 line 22: "The grouping of species in Table 4 is valid for pH values between 3 and 5."

3) The Henry's law constant for HCHO listed in Table 1 is the effective Henry's law constant KH* and includes hydration Khydr, i.e. it is KH* = KH(1+Khydr) (cf Sander et al., 2006). Thus, including the hydration equilibrium in addition to KH*, will lead to an overestimate of the solubility of HCHO. Is it possible that this overestimate can explain the discrepancy to the conclusions regarding HCHO transport and sources for Case 2 (p.979, l. 19ff).

Indeed, it is the effective Henry's law value for HCHO in Table 1 as mentioned explicitly in the table. This is this value, which is used to compute the production and destruction terms through gas-liquid transfer in Eqs. (3) and (4). The hydration equilibrium constant is indicated in Table 2 because it is used to compute the total species concentration in the aqueous phase as it is explained page 965, lines 6-12. The hydration process is thus accounted only once in the simulation. To avoid any confusion, we have modified the sentence lines 8-9 as:

"Table 2 gives the aqueous phase equilibria, which are used to compute the effective Henry's law constant (except for the HCHO effective Henry's law value, given in Table 1) and the total species mixing ratio in the aqueous phase."

Minor comments:

p. 960, l. 12: This sentence seems out of place here and should rather be moved up to l. 2 where you talk about aqueous phase SOA formation.

We have moved up this sentence as suggested and the end of the previous paragraph has been rewritten as:

“In particular, new routes of SOA formation have been found through the condensation precursors having low volatility that are formed in cloud droplets or raindrops and released in the clear atmosphere when cloud or rain drops evaporate (Chen 15 et al., 2007; Lim et al., 2010; Ervens et al., 2011). However, the potential contribution of the aqueous phase reactivity is highly uncertain, as it is the case for the chemical nature of the aqueous phase products that are the precursors of the SOA (Hallquist et al., 2009; Ervens et al., 2011).”

p. 962, l. 10 f: Does ‘chemistry’ in these lines always mean the same, i.e. chemical reactions? Or does ‘aerosol chemistry’ refer to ‘aerosol chemical composition’?

Effectively, the term chemistry in “aerosol chemistry” refers to “aerosol chemical composition”. We have replaced “aerosol chemistry” by “aerosol chemical composition”.

p. 963, l. 9: How are low-volatility aerosol constituents treated, e.g. sulfate, nitrate, ..? Are they kept completely in the particle phase upon drop evaporation? What fraction of sulfur is in the form of the sulfur-containing ions that are lost?

Low volatility constituents are not transferred to the gas phase but are kept in the particle phase. However, as the aerosol module is not activated in the simulations, these concentrations are lost. Concerning the intermediate sulphur-containing ions that are lost (HOCH₂SO₃⁻, SO₃⁻, SO₄⁻, SO₅⁻ and HSO₅⁻), their mixing ratios are very low in comparison to mixing ratios of aqueous phase species from sulfur dioxide and from sulfuric acid.

p. 969, l. 20:L What is meant here by ‘ice reactivity’? Chemical reactions in ice? Or on the surface layer of ice?

Ice reactivity refers both to chemical reactions in ice and to chemical reactions on the surface layer of ice particles.

p. 974, l. 12 and 18: Refer here to Fig. 2a and 2b, respectively.

A proper reference to Fig. 2a and Fig. 2b has been added.

p. 974, l. 27ff: Does your discussion indeed only refer to sulfur dioxide or to total S(IV)?

For the aqueous phase, the discussion refers to sulphur dioxide as total species i.e. SO₂(aq) + HSO₃⁻ + SO₃²⁻. The term S(IV) is not used because it could be confused as this term includes HMSA. The following sentence has been added page 974, line 10:

“For aqueous phase, it is the total species mixing ratio, which is indicated e.g., for SO₂, it is the

sum of $\text{SO}_2(\text{aq}) + \text{HSO}_3^- + \text{SO}_3^{2-}$.”

p. 977, l. 14: Is here the reference to a figure missing? If you do not intend to refer to a figure here, ‘Results will be shown in the following’ might be better.

To clarify this point as suggested, we have replaced the sentence l. 14 by “Results will be shown in the following as averages....”.

p. 978, l. 19: Does ‘scavenging’ here also imply ‘loss by reaction’?

The term “scavenging” implies also “loss by reaction” inside the drops.

p. 979, l. 24: The sources for formic acid are not really clear [Khare et al., 1999; Paulot et al., 2011]. The fact that in other model studies small gas phase contributions were found might be an artifact of the chemical mechanism.

A small discussion about the remaining uncertainties of the source of formic acid based upon Paulot et al. (2011) has been added at the beginning of this paragraph as:

“Results from global model predict that formic acid originates primarily from the photooxidation of biogenic compounds. However, there is still a large uncertainty on the sources of formic acid. To reconcile simulated and observed formic acid mixing ratios, Paulot et al. (2011) reported evidence for a long-lived missing secondary source of carboxylic acids that may be associated with the aging of organic aerosols. In Barth et al. (2007b), formaldehyde is the major precursor of formic acid in the aqueous phase, which is a good tracer of cloud-processed air since its sources in the gas phase are low.”

p. 980, l. 9: do you mean /net production’ here?

The production term refers to net production, we have added the word “net” to avoid confusion as: “results actually show a very weak contribution of cloud reactivity in the net production of formic acid.”

p. 984, l. 22: Is there always sufficient SO_2 available to act as a significant loss for H_2O_2 ?

Yes, the initial mixing ratio of SO_2 in boundary layer is about half of the H_2O_2 mixing ratio and remains the main sink of H_2O_2 in aqueous phase all along the simulation.

p. 986, l. 8f: This sentence is not clear. Please, reword.

The sentence has been rewritten as:

“The aqueous phase chemical mechanism was developed to be consistent with the available gas phase chemical mechanism ReLACS, which is a reduced form of the RACM mechanism.”

p. 988, l. 11: It is true that a limited number of organics might lead to an underestimate of $\text{OH}(\text{aq})$ sinks; however, you also do not include several $\text{OH}(\text{aq})$ sources, such as Fenton reaction and nitrate photolysis. Overall, this omission might lead to partially cancelling

effects and an approximately correct OH(aq) concentration.

The nitrate photolysis is taken into account in the mechanism (cf. Tab. 3). We agree that, as the Fenton reaction is not included in the mechanism, there is a missing source of OH radical in aqueous phase in our mechanism. However, as suggested by the first measurements of OH concentrations in cloud droplets (about 10^{-16} M, personal communication Anne Monod), OH concentrations are overestimated by our model (about 10^{-13} M). Moreover, simulations including Fenton reactions and more complex VOC chemistry (Herrmann et al., 2005), are leading to smaller mixing ratios of OH radicals in droplets than our results show (about 10^{-14} M).

Figure 2: It might help to add to the figures (not only in caption) ‘gas’, ‘cloud’, and ‘rain’.

Mentions to ‘gas’, ‘cloud’ and ‘rain’ have been added to this Figure and to Figures 3 and 4.

Figure 3: Is this total S(IV) or SO₂? If the latter, I would think that total S(IV) might be more meaningful.

This is the total SO₂ mixing ratio in aqueous phase, see answer to comment below.

Figure 6b: Some of the lines are hard to distinguish. I cannot find the one for ‘SO₂ rain, C2R2’

This is because the mixing ratio of SO₂ in rain is close to zero, see Fig. 3. The following comment has been added, page 975, line 17:

“For the C2R2 case, the scavenging of gases below the cloud is inefficient (SO₂ mixing ratio in rain is close to zero and H₂O₂ mixing ratio in rain is very small, see Fig. 6) and the production of sulphuric acid in rainwater is negligible.”

Technical comments

p. 960, l. 5: better use ‘e.g., ‘ instead of ‘for instance’

Done

p. 961, l. 25: use consistently ‘mixed-phase’ or ‘mixed phase’

Done

p. 966, l. 10: equilibria

Done

p. 968, l. 3. Does the sentence continue with ‘e.g.’?

Yes, it is. This sentence has been corrected.

p. 979, l. 5: Better: ‘small contribution’ (the same at other places throughout the manuscript)

Done

p. 981, l. 11: low mixing ratio

Done

p. 985, l. 13: remove commas around 'in Meso-NH'

Done

p. 985, l. 23: half of those

Done

p. 985, l. 28: role of the ice phase

Done

Figure 6: 'Kessler' misspelled in Figures.

Done