Interactive comment on “A comparison of the chemical sinks of atmospheric organics in the gas and aqueous phase” by S. A. Epstein and S. A. Nizkorodov

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We would like to thank Prof. Herrmann for his review of our manuscript. His comments are italicized and are embedded within our responses.

General: An interesting contribution investigating aqueous phase sink strength due to OH reaction and photolysis.

Unfortunately there are a few methodic failures in the approach the authors take: Aqueous phase effective quantum yields are far from being equal to the gas phase quantum yields (page 10020, line 20ff) and so the derived aqueous phase photolysis frequencies are all too high. While the authors state that through this approach upper limits are derived, the danger is that the resulting photolysis rates are so unrealistically high that the whole treatment does not lead to reliable data to judge whether solution phase processes are comparable to gas phase processes with regard to their efficiency. I find this approach too simplistic and the authors should at least use reasonable estimates of the effective solution phase quantum yields in question rather than applying the current crude approximation. Please search literature for solution phase quantum yields, conceptual treatments and estimations for effective quantum yields.

Our manuscript is designed to address the dearth of aqueous photolysis quantum yields in the literature by identifying compounds whose photolysis in cloud and fog droplets may be a significant sink. We do not aim to predict the actual aqueous removal rates. Our calculations are a guide for experimentalists in picking the most promising compounds for laboratory studies. In the text, we stress that this is not a modeling study and that our goal is to help guide researchers in the selection of potentially important molecules.

The authors are unaware of any estimation procedures for obtaining the solution phase quantum yields and we believe that this is because the experimental data that would be needed to guide these estimation procedures are too limited. There are a few studies of aqueous photolysis quantum yields for pesticides (Vione et al., 2006; Wan et al., 1994), substituted benzyl derivatives (Zimmerman and Sandel, 1963), four small aldehydes without correction for hydration (Hirshberg and Farkas, 1937), hydrogen peroxide (Chu and Anastasio, 2005), and methyl peroxyde (Epstein et al., 2012). This data set is too meager for the development of a conceptual treatment or even an educated estimation for the atmospherically relevant compounds we investigate. The best we can do under these circumstances is bound the direct aqueous photolysis yields at a maximum of the gas phase photolysis yield to identify potentially important compounds. As mentioned in the manuscript, solvent effects depress the aqueous quantum yield and therefore we do not expect it to be larger than the gas phase quantum yield. We are not suggesting that the aqueous and gas phase quantum yields are equal. Luckily, at this upper bound,
we identify only a few compounds that could potentially be important and recommend them for laboratory studies to quantitatively determine their significance. We have enhanced our discussion of this in the revised manuscript.

Second, the used LWC (page 10026, line 5) is absolutely unrealistic. 3 g/l is way too high. This has also to be corrected. See literature on cloud LWC for this.

Our initial intention was to use a relatively large value of LWC (LWC = 3 g/m$^3$, not 3 g/L as the reviewer accidentally indicates) so that the maximal possible contribution of the aqueous processes can be estimated (note that we also included results for a much lower LWC=0.05 g/m$^3$ in the ACPD paper). However, we agree with the reviewer that it would be better to use a more realistic upper bound for the LWC value. While researchers report maximum values in excess of 3 g/m$^3$ in the atmosphere, measurements this high are rare. We decided to use a more reasonable 0.5 g/m$^3$ for our analysis. LWC of 0.5 g/m$^3$ is approximately the largest value that is frequently measured in the atmosphere based on measurements of stratus and cumulus clouds contained in Hobbs, 1993. [See also the probability histogram for various LWC values in Seinfeld and Pandis, 1998 P. 340]. We made this correction in the text and figures. This revised value does not change any of our conclusions as it scales the magnitude of the aqueous phase processes by only a factor of 1/6th. This factor is a small contribution to our order of magnitude estimates. We added section in the text to illustrate the sensitivity of our analysis to LWC. Figure 10 was re-plotted in the revised version with a LWC of 0.05 g/m$^3$ and 0.5 g/m$^3$, which covers a significant fraction of the observed LWC values in clouds.

Thirdly, an estimate of reaching aqueous concentration according to Henry equilibrium is not realistic, again. The severe deviations from this have been treated in multiphase modelling.

Henry’s law equilibrium only holds under certain conditions, which are not guaranteed in the atmosphere. We highlight some of those conditions in the manuscript. For predictive models, mass transfer between phases is described in more accurate kinetic formulation that can take local conditions into consideration. However, as the goal of this work is not to model the exact details of the partitioning of organic compounds of interest between gas and aqueous phase but to identify compounds for which aqueous photolysis processes might be important, specifying specific atmospheric conditions necessary for predictive kinetic models would actually limit the usefulness of our results. Winiwarter et al., 1994 describes the performance of Henry’s law for weak acids and bases in cloud droplets taken from field measurements. They find that the assumption of Henry’s law for formic acid, acetic acid, and ammonia predicts aqueous phase concentrations that are between a factor of 0.001 and 10 of the true concentrations depending on the pH of the droplets. Leriche et al., 2000 shows a table illustrating the deviations from Henry’s Law as a function of pH for formic acid, hydrochloric acid, nitric acid, SIV, and ammonia taken from several previous studies. While some researchers do find deviations from Henry’s Law, the range of the ratio of the actual aqueous concentration and the predicted aqueous concentration tends to center around unity.

With several types of models, Chaumerliac et al., 2000 shows deviations from Henry’s law for hydrogen peroxide in simulated air parcels under different conditions. When gas phase chemistry, aqueous phase chemistry, and mass transfer are considered in the absence of SO$_2$ chemistry, Henry’s law does reasonably well in tracking aqueous concentrations in a simulation where 10 $\mu$m and 100 $\mu$m cloud droplets are formed and then dissipate. Moreover, since we treat each species individually in an air parcel with constant liquid water content, Henry’s law should be sufficient to make order of magnitude estimates of the potential significance of direct aqueous photolysis to guide future experimental work.

We added the text describing additional situations where Henry’s law equilibrium may not hold: irreversible chemical reactions that are so fast as to prevent the establishment of equilibrium (Finlayson-Pitts and Pitts, 2000), droplets that are not well mixed (Finlayson-Pitts and Pitts, 2000), clouds that have been recently formed (Chaumerliac
et al., 2000), or droplets that are not sufficiently dilute (Seinfeld and Pandis, 1998). We emphasize that for our simplified approach, we use Henry's law, but deviations from equilibrium are likely in more complex realistic situations. We also removed the sentence in the results section that describes Henry's law as an upper bound of the aqueous phase concentration because both over- and under-estimations are possible. We have also introduced the parameter \( R = \frac{C_{x,\text{observed}}}{(k_{H,x} P_{x,\text{observed}})} \) where \( k_{H,x} \) is the Henry's law constant of species \( x \) in units of \( \text{concentration} \times \text{pressure}^{-1} \), \( C_{x,\text{observed}} \) is the aqueous concentration of species \( x \) and \( P_{x,\text{observed}} \) is the observed partial pressure of \( x \). We discuss this parameter and show how the y-axis of Figures 2-6 allow for a straightforward sensitivity analysis of the Henry's Law equilibrium assumption.

I do suggest major revision of this study in view of the above. Details: Page 10018, line 15: There is no Ervens et al. (2011) in the references

We inadvertently referenced Ervens et al. (2010) twice in the references list. We replaced the second entry with Ervens et al. (2011).

References


