**Atmospheric
Chemistry
and Physics
Discussions**

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 reviewer 2 for his or her comments on our manuscript. Reviewer comments are italicized and are embedded within our responses.

This paper evaluates the relative importance of gas and aqueous phase photolysis and oxidation by OH for various volatile organic compounds (VOCs). The authors use a mathematical approach to guide researchers for further studies. For most of the compounds studied aqueous photolysis is not an important sink, except for glyceraldehyde and pyruvic acid.

The authors may want to include references for OH generation due to photolysis of

these VOCs on page 10017, line 20.

We have added the following references: (Zellner et al., 1990;Epstein et al., 2012;Faust and Allen, 1993;Faust, 1994;Chu and Anastasio, 2005;Monod et al., 2007)

Additionally, they may want to expand more (beyond methyl peroxide) on the discussion about the importance of this OH source and how it may affect their analysis.

We added the following sentences in the Introduction: "Direct photolysis and indirect photolysis (reaction with oxidants formed by photolytic reactions) are linked by the potential generation of OH in the photolysis of certain organic compounds. However, OH yields from direct photolysis of most organic compounds are uncertain and depend on the photolytic mechanism."

Page 10019, line 6: As the authors state, the assumption of gas and aqueous phase partitioning being in equilibrium is not necessarily always accurate. It would be interesting to see what happens if this is not the case and how the results may vary.

The y-axis of Figures 2-6 provides a straightforward visual sensitivity analysis of this equilibrium assumption. Departures from Henry's Law equilibrium will shift the values vertically along the y-axis. Previous researchers have quantified the departure from equilibrium as the ratio of the observed aqueous phase concentration of species "x" and the predicted aqueous phase concentration with Henry's Law. $R = C_x^{observed}/(kH_x*P_x^{observed})$ where kH_x is the Henry's law constant of species x in units of concentration*pressure^{-1} and $P_x^{observed}$ is the observed partial pressure of x. The kinetic effects due to local conditions govern departure from equilibrium. 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 ammo-

nia taken from several previous studies. While some researchers do find deviations from Henry's Law for specific situations, the range of R tends to center around unity, and therefore, this is where we base our analysis. For a specific situation where R is known, one could multiply the y-axis value by R to obtain a corrected Z or W parameter. Luckily, deviations from Henry's law would have to be significant to effect the order-of-magnitude estimations of the importance of aqueous phase processes.

We had several possible situations where Henry's Law may not hold in the manuscript and will add a few more in the revised version: 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 also introduced the parameter R, described how figures 2-6 provide a visual sensitivity analysis of the equilibrium assumption, and supported our decision to use Henry's law equilibrium as the basis of our analysis.

Page 10020, line 23: The authors should elaborate some more on this assumption about quantum yield.

We added two references to the statement that quantum yields are reduced in a condensed phase relative to the gas-phase. ((Bateman et al., 2011;Farkas and Hirshberg, 1937;Calvert and Pitts, 1966) Also, we modified the confusing wording on lines 23 and 24 to explain that because of the cage effect, the maximum aqueous quantum yield possible is equal to the corresponding gas phase quantum yield.

Page 10026, line 5: Instead of using the largest value for LWC, why don't the authors use a more average value. There are already a few assumptions they make that result in upper estimates, and in continuing to do so, they may fail to provide more realistic values.

Our initial intention was to use a relatively large value of LWC to 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.

Two references are missing from the list, Ervens et al. 2011 and Sander et al. 2011. Ervens 2010 is repeated twice.

We added the missing references to the list.

Page 10020, line 20: Add a reference for depression of quantum yield in solution.

We added the references: (Calvert and Pitts, 1966;Farkas and Hirshberg, 1937)

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C4143

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C4144