**Atmospheric
Chemistry
and Physics
Discussions**

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Interactive comment on "Explicit modeling of volatile organic compounds partitioning in the atmospheric aqueous phase" *by* C. Mouchel-Vallon et al.
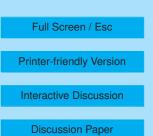
Anonymous Referee #2

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General Comments

In this paper, the authors analyze the output of the GECKO-A model in terms of the aqueous solubility of the products formed from the gas-phase oxidation of isoprene, octane, and a-pinene. A novel oxidation state vs. solubility 2-D diagram approach is employed for the analysis. Predictions of partitioning to the aqueous phase are made under aerosol and cloud water conditions. No aqueous-phase organic chemistry is considered. This is an interesting contribution and it may be suitable for publication in ACP after revision, but it has some weaknesses.

A primary concern is that the authors attempt to estimate SOA formation in the aqueous

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phase while neglecting aqueous-phase reactions. This simplification is particularly problematic in aerosol water. The results of this study are inconsistent with recent lab and modeling studies showing significant SOA formation in aerosol water, driven by aqueous phase processes that are either neglected or inadequately represented here (Volkamer 2007, Lim 2005, Tan 2010, Surratt 2010, Galloway 2009, McNeill 2012, etc.) Therefore, it is suggested that the authors tailor the language of the paper to highlight their analysis of VOC solubility, which is novel and interesting, and eliminate (or at least heavily qualify) the estimates of SOA formation as this model is incomplete in that regard.

Specific Comments/Questions:

Section 1:

- Line 21, Page 24096 - The authors state that "There is a lack of knowledge concerning the aqueous phase contribution to the atmospheric chemistry," and cite a review article from 1997. While it is fair to say that, compared to the gas phase, the role of the aqueous phase is less well-known, a great many scientific advances made on this topic since 1997, and a multitude of research and review articles published (including some that are cited later in this manuscript). In particular organic chemistry in the aqueous phase has received a great deal of attention in the last ten years. Please cite some more recent papers and give a more accurate picture of the state of the field.

- Line 6, page 24098 – It is generally false to state that the rate constants of aqueous-phase oxidation reactions are faster than the equivalent reaction taking place in the gas phase. In the gas phase the reactions are limited by diffusion of the reactants through the aqueous phase and this is reflected in the rate constant. There may be some scenarios in which the rate, not the rate constant, is faster due to relatively high concentrations of reactants - is this what the authors mean to say? Again, this segment doesn't do justice to the advances in aqueous organic chemistry that have been made in the last ten years – try citing some of the more recent review articles.

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- Lines 15-25, Page 24098 - This discussion of aqueous-phase modeling efforts is missing the Rutgers model (Lim et al, ES&T 2005 and others) and GAMMA (McNeill et al., ES&T 2012) Section 2.1, 2.2

- Line 7, Page 24100 - While the formation of gas-phase isoprene-derived epoxides and tetrol products has been considered in this study, other aqueous-phase reactions involving these species have been studied (Surratt 2007) Given that partitioning into the aerosol phase is expected to be relatively high (Chan 2010), their behavior and reactivity should be considered if these epoxide species are expected to be generated through usage of this model. Furthermore, these reactions have been shown to be highly dependent on the acidity of the aerosol (Eddingsaas 2010). Given the formation of highly oxidized products in your predictions, do you expect aerosol-phase $H+$ activity to vary significantly over the course of this simulation in conditions with lower values of L? Does the author expect any deviations from the expected acid/base equilibria of carboxylic acids mentioned in section 2.2?

Section 2.2

- Pages 24101-24102 - Please provide the accommodation coefficients, Henry's Law constants, and hydration constants, and any other pertinent information regarding aqueous-phase processes represented in the model, perhaps as Supplementary Information. Glyoxal has been seen to have lower observed values for its accommodation coefficient than the 0.05 proposed by the author. (Ip 2009). Furthermore, for cloud droplets, accommodation coefficients are usually seen to be closer to 0.01 (Schwartz 1986). As the subsequent uptake to aqueous aerosol is highly dependent on this value, it is possible that significantly different levels of aerosol-phase SOA may be observed when changed.

- Lines 23-25, Page 24102 - It is unclear what is meant by "...the only sink for the dissolved organic matter is caused by the gas phase chemical pump that shifts the water/gas equilibrium."

Section 2.3

- Line 14, Page 24103 - If the solar zenith angle being used is representing mid-latitude conditions, why is the temperature fixed to 278K? This value doesn't seem consistent with the temperate conditions of FAME08, where other values are being drawn from. Is this a typo?

- Line 18, Page 24103 - What is the justification for "adding a constant OH source of 1e7 radicals/cm3/s"?

Section 3.1

- The author mentions that the value of L used here is one typical of deliquesced atmospheric aerosol but does not explicitly mention if or what these particles have any inorganic material acting as a seed that could deliquesce. Depending on their composition, the presence of inorganic species in these aerosols will have a profound effect on particle composition and subsequently its net pH and activity, potentially changing some of the equilibrium/uptake values being considered. Furthermore, at such low values of L this value, this value can reflect total water volume fraction or total liquid aerosol fraction, which will lead to different relative concentrations at lower RH's.

- Line 15, Page 24104 - It is not clear what τ means, as written. By lifetime of the parent hydrocarbon, does this term refer to the duration of time for C0 to reach some arbitrarily low value? The amount of time that the hydrocarbon spends in gas phase before uptake/reaction? It would be helpful to explain this term more explicitly.

- Lines 20-25, Page 24105 – It is not accurate to say that oxidized products of aliphatic hydrocarbons are ignored in existing models. CMAQ covers this type of chemistry to an extent in both gas and aerosol phases (Carlton 2010).

- Typo at Line 12, Page 24104 – "number of lifetimes $N\tau$" instead of "number of lifetime $N\tau$"

Conclusions

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- Line 26, Page 24112 – Line 5, Page 24113 - It has been observed and predicted that non-oxidative aqueous reactions such as the previously mentioned epoxide-based substitution chemistry can also contribute a significant amount to aerosol mass. (McNeill 2012, Tan 2010, Chan 2010.) Under lower NOx conditions, where these species can have comparable or higher amounts of SOA mass contributions than aqueous radical chemistry, these mechanisms should be taken into account to achieve accurate prediction of SOA formation.

Figure 1

- Typo on chart title – "3x10-7" instead of "3x107"

Extra Sources

Volkamer, R.; San Martini, F.; Molina, L. T.; Salcedo, D.; Jimenez, J. L.; Molina, M. J. A missing sink for gas-phase glyoxal in Mexico City: Formation of secondary organic aerosol. Geophys. Res. Lett. 2007, 34, L19807, doi:10.1029/2007GL030752.

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Ip, H. S. S., X. H. H. Huang, and J. Z. Yu (2009), Effective Henry's law constants of glyoxal, glyoxylic acid, and glycolic acid, Geophys. Res. Lett., 36, L01802, doi:10.1029/2008GL036212.

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 24095, 2012.

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