

“On the implications of aerosol liquid water and phase separation for organic aerosol mass”
by Havalala O. T. Pye et al.

Response to reviewer #1

We thank reviewer #1 for their comments and overall recommendation for publication. Our responses are in blue with new text added to the manuscript underlined.

This study investigated aerosol water interactions with semi-volatile SOA species and uptake of water onto OA with a focus on simulating conditions during the SOAS campaign. They have developed a method to take into account effects of non-ideality and phase separation on SOA formation and partitioning. They found that inclusion of water in an organic phase led to increased SOA concentrations, particularly at night. Aerosol properties, such as the OM/OC and hygroscopicity parameter were captured well, but additional improvements in daytime organic aerosol are needed to close the model measurement gap. I found this modeling study is conducted very well making use of comprehensive measurements conducted in the SOAS campaign. The authors made great efforts in implementing state-of-the-art knowledge of aerosol water and phase separation into the regional model. I appreciate this study very much and recommend for publication in ACP after the following comments are addressed.

- P4, L10: Have you actually implemented eq(1) into the model? Terpene and toluene SOA have higher viscosity and lower bulk diffusivity compared to isoprene SOA (e.g., Renbaum-Wolff et al., 2013; Song et al., ACP, 2016). Were SOA particles in SOAS totally dominated by isoprene SOA and only little influence by terpene or anthropogenic emissions? Please clarify and justify.

Equation (1) for the diffusivity of IEPOX in aerosol was implemented in the model. This diffusivity is used in the calculation of the uptake coefficient for IEPOX following Pye et al. (2013) and allows for a surface-based process or bulk reaction depending on the timescale for diffusion relative to reaction (captured by the parameter q):

$$\gamma = \left(\frac{1}{\alpha} + \frac{v}{4HRT\sqrt{D_a k_{particle}} f(q)} \frac{1}{f(q)} \right)^{-1}$$

$$f(q) = \coth(q) - 1/q$$

$$q = r_p \sqrt{\frac{k_{particle}}{D_a}}$$

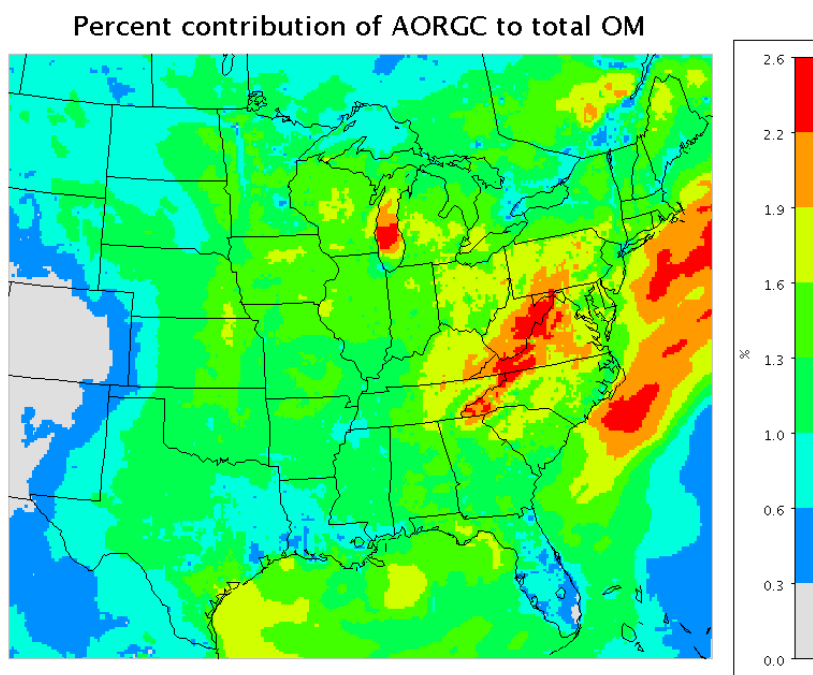
As the reviewer points out, the diffusivity of species in the aerosol phase is influenced by both composition and RH and we have only captured the RH dependence. SOAS was not dominated by isoprene SOA. Xu et al. 2015 and Hu et al. 2015 both report that low NO isoprene SOA (IEPOX-SOA) accounted for approximately 18% of total OA. Monoterpenes were also major contributors (Xu et al., 2015). Urban POA and SOA is estimated to contribute ~28% of the OA, which is consistent with the fossil carbon fraction (Kim et al., 2015), and there were also smaller contributions from biomass burning and other sources. The most relevant aerosol diffusivity for IEPOX uptake would be that of IEPOX in a

multicomponent aerosol particle, thus using the value for monoterpene SOA is not necessarily a better approach than what we have used at this time. We have clarified that the diffusivity is used for IEPOX.

The diffusivity of ~~isoprene products~~ IEPOX in the particle (D_a , cm^2s^{-1}) was predicted by fitting a line through the data in the work of Song et al. (2015) resulting in

- P4, L21: "SOA from cloud processing is relatively minor in terms of average SOA concentrations.": Please justify this sentence by adding some explanations or reference(s). Have you investigated this by modeling or is this implied by measurements? Was aqueous phase processing (particle-phase chemistry in deliquesced particles) also minor?

Aqueous phase processing in deliquesced particles was significant as it is the major route to IEPOX SOA in the model. Extensive vertical profiling from aircraft during SENEX and SEAC4RS concluded that SOA formation in clouds was small and not statistically significant (Wagner et al., 2015). Cloud processing is also predicted to be relatively minor in CMAQ (although additional work is needed on this topic). SOA from cloud processing accounted for less than 3% of the organic aerosol concentration in our base simulation:



SOA from cloud processing is predicted to result in less than 3% of total organic aerosol in CMAQ relatively minor in terms of average SOA concentrations.

- P5, L13: Just to draw your attention, the recent study (Li et al., 16, 3327, ACP, 2016) has extended eq(2) by including number of N and S per molecule to estimate volatility.

Thank you for the reference. At this time, we do not use equation 2 for sulfate or nitrate containing organic compounds.

- P5, eq(2): This should be C_0 , but not C^* . As you discuss in this manuscript, C^* (effective saturation mass concentration) includes the effect of non-ideality, but I believe eq(2) can be only used to estimate pure compounds saturation mass concentration.

Correct. We have revised the equation (and text) to reflect it is for pure compounds.

Donahue et al. (2011) developed a relationship between the saturation concentration of a pure species ($C^*_i = C^*_0,i$), number of carbons per molecule, and number of oxygens per molecule (nO) ignoring sulfate and nitrate for use with the 2-D volatility basis set (VBS)...

- Figure 4: I wonder why C^* of glyoxal is $1e02 \text{ ug m}^{-2}$. I believe C_0 of glyoxal is much higher based on eq(2). Is this because glyoxal is very water soluble so that C^* is lowered?

The point labeled "GLY" in Figure 4 corresponds to glyoxal aerosol produced from reaction with OH (Table 2). Since that aerosol is nonvolatile in the model, it is arbitrarily plotted at a C^* of 0.01 ug/m^3 (as already indicated in figure caption).

- Figure 4: It seems that high molar mass and low volatility compounds (i.e., particlephase products such as dimers, peroxyhemiacetals, oligomers, etc. that would locate close to the alkane line) were not considered in CMAQ. Do you have reason? Were such compounds not detected by measurements in SOAS?

Our model does contain oligomers (OLGB and DIM for example). To be close to the alkane line, that would imply they have little oxygen. The DIM species is a tetrol-tetrol dimer with an OM/OC of 2.07. OLGB (the generic biogenic oligomer) has an OM/OC of 2.1. Thus, the oligomers we have in the model are highly oxygenated and do not fall on the alkane line. Due to SOAS site being regionally representative and experiencing aged pollution, most compounds should be oxygenated to some degree.

- P13, L12, P14, L2: All IEPOX-derived species were assumed to be non-volatile and I suppose that the model also assumed that such product formation is irreversible. Have you evaluated this assumption by sensitivity simulations? Is it possible that such product formation is actually reversible and might evaporate under certain conditions?

We have not examined the volatility of IEPOX SOA in CMAQ. Recent studies have explored the semivolatile nature of IEPOX SOA through measurements. Lopez-Hilfiker et al. (already cited in manuscript) indicates IEPOX-OA is largely nonvolatile and measured 2-methyltetrols may contain decomposition products of oligomers. Hu et al. (2016) reached the same conclusion using a thermal denuder-AMS combination. While our paper was in review, Isaacman-VanWertz et al. (2016) was also published and indicates that measured 2-methyltetrols, while semivolatile, are more heavily partitioned to the particle phase than their volatility would suggest. We will add a citation to Isaacman-VanWertz et al. We are exploring the reversibility of IEPOX-OA partitioning as part of future work.

- P15, Figure 7: Model reproduced OC well, while overestimating POC and underestimating SOC. Is it possible actually this may suggest that measurements might have overestimated SOC? I suppose that SOC was assumed to be equivalent to OOA based

on AMS-PMF analysis (correct?). What are uncertainties of the measurements? I wonder this, as AMS measures chemical composition and estimate secondary formation processes by post numerical analysis, while the model simulates secondary processes directly.

Two methods were used to estimate the primary/secondary split. (1) For AMS data, PMF analysis provided a BBOA factor at CTR, but no primary factor at LRK. HOA was not resolved at LRK or CTR during SOAS. (2) Section 2.9 presents a modified OC/EC technique for estimating primary OC from routine monitoring networks such as SEARCH, IMPROVE, and CSN. The assumption is that the model POC/EC ratio can be used to estimate observed POC. Since POC is semivolatile, we estimate that a fraction of POC will volatilize in the atmosphere thus reducing the POC/EC ratio downwind of sources. This is uncertain and may be a lower bound on SOC if chemical transformation also converts POC to SOC. However, if emission inventories underestimate SVOC emissions, the POC/EC method may underestimate POC. The two methods are relatively consistent, but there is considerable uncertainty. For that reason, we indicate “Model predictions of OC, SOC, and POC were compared to network observations using the methods described in section 2.9 to determine how model errors in POA (specifically the nonvolatile assumption) could mask errors in SOA.”

- P21, L8: Could gas-phase ELVOC formation or particle-phase chemistry help to close the measurement-model gap?

Yes, and this is a topic of future work. Some particle-phase chemistry (acid-catalyzed reactions, oligomerization) is already considered.

References not in the ACPD version:

Gabriel Isaacman-VanWertz, Lindsay D. Yee, Nathan M. Kreisberg, Rebecca Wernis, Joshua A. Moss, Susanne V. Hering, Suzane S. de Sá, Scot T. Martin, M. Elizabeth Alexander, Brett B. Palm, Weiwei Hu, Pedro Campuzano-Jost, Douglas A. Day, Jose L. Jimenez, Matthieu Riva, Jason D. Surratt, Juarez Viegas, Antonio Manzi, Eric Edgerton, Karsten Baumann, Rodrigo Souza, Paulo Artaxo, and Allen H. Goldstein “Ambient Gas-Particle Partitioning of Tracers for Biogenic Oxidation”, *Environmental Science & Technology*, 50 (18), 9952-9962, doi: 10.1021/acs.est.6b01674, 2016.

Wagner, N. L., Brock, C. A., Angevine, W. M., Beyersdorf, A., Campuzano-Jost, P., Day, D., de Gouw, J. A., Diskin, G. S., Gordon, T. D., Graus, M. G., Holloway, J. S., Huey, G., Jimenez, J. L., Lack, D. A., Liao, J., Liu, X., Markovic, M. Z., Middlebrook, A. M., Mikoviny, T., Peischl, J., Perring, A. E., Richardson, M. S., Ryerson, T. B., Schwarz, J. P., Warneke, C., Welti, A., Wisthaler, A., Ziemba, L. D., and Murphy, D. M.: In situ vertical profiles of aerosol extinction, mass, and composition over the southeast United States during SENEX and SEAC4RS: observations of a modest aerosol enhancement aloft, *Atmos. Chem. Phys.*, 15, 7085-7102, doi:10.5194/acp-15-7085-2015, 2015.