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Interactive comment on "Organic photolysis reactions in tropospheric aerosols: effect on secondary organic aerosol formation and lifetime" *by* A. Hodzic et al.

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The manuscript by Hodzic et al. describes a modeling study of the impact of photolysis on gaseous and aerosol-phase organic compounds, and their impact on the formation of secondary organic aerosols (SOA). It uses an automated explicit gas-phase mechanism generator, GECKO-A, and uses its results to simulate idealized box model studies, chamber experiments, and global model simulations with GEOS-Chem. Although the results are very interesting, since the effect of photolysis is not included in model studies, although it apparently happens, the manuscript in its present form requires some major changes to be accepted for publication to ACP, as outlined below. In short, I recommend removing the part of the aerosol phase photolysis (section

3.2) and only keep the gas-phase, which has much less uncertainty. Then, repeat the global model simulations presented in section 3.3 for the gas-phase photolysis alone.

A number of important processes are missing from the aerosol-phase photolysis part, which, although partly mentioned by the authors, can lead to significant changes in their results, by most likely reducing the importance of aerosol-phase photolysis. These include oligomerization and aqueous-phase SOA formation, both of which are expected to increase the total SOA formation in model simulations. Both are largely unconstrained, especially oligomerization, but they are recognized as potentially major sources of SOA. The results presented need to take into account the presence of those processes in the real atmosphere, and present the outcomes with estimates of uncertainty, to avoid overstating the importance of photolysis on the global scale.

In addition to these processes, a major assumption is made in the aerosol-phase photolysis experiments, which is both questionable and misleading. Based on the modeling framework, any radical products generated by photolysis in the aerosol phase are immediately transferred in the gas-phase, due to lack of aerosol-phase chemistry. This leads to a number of problems: a) artificial evaporation of aerosol-phase products; b) strong modification of the gas-phase chemistry, probably already evidenced by the stiffness of the Jmolec simulation for a-pinene; c) neglection of known aerosol-phase chemistry initiated by the presence of those radicals, which can lead to either further functionalization or oligomerization, both of which would not lead to SOA loss.

Another problem with the aerosol-phase photolysis is the implementation in the global model. The experimental design implicitly assumes that all of SOA contains chromophores, thus it is brown carbon (BrC), and all of those compounds can bleach. This is a major assumption which is not supported by measurements. For example, very fast photobleaching has indeed been reported by Woo et al., 2015 (Faraday Discuss., 2013, 165, 357), but this was for compounds that were produced by aerosol chemistry mechanisms, which were not included in this study. A large fraction of BrC, formed primarily by combustion (which is primary organic aerosol, not SOA) but also from

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gaseous compounds from combustion, does not bleach so fast (e.g. Zhong and Jang, 2014; doi:10.5194/acp-14-1517-2014), which means that the photolysis happens at much lower rates for different types of precursors. Using a mean value for such a process is probably not the right way to go.

The box model description in Section 2 needs a better explanation and justification of the conditions used. A pre-existing OA concentration of 10 ug/m3 is very high, especially when putting this value into perspective for the global model. An OH concentration of 8e6 is also probably on the high end. In addition, simulations at 45 degrees north were mentioned, and with a constant daylight one would expect a constant J_NO2, which is not obvious neither at the end of Section 2, nor at the beginning of Section 3.1 where Boulder (40 N, and high altitude) is mentioned. I also find the link from x number of days to 2*x atmospheric equivalent an oversimplification; chemistry is highly non-linear and the product distribution changes during the night, e.g. due to organonitrates formation at high NOx conditions from NO3 radical initiated reactions. This assumption is used throughout the manuscript, and its validity (or not) can be easily demonstrated by a box model simulation with a true diurnal variability of the photolysis rates.

As a last comment, it was surprising to see global model results only for the lower portions of the atmosphere, while the longer SOA residence times above clouds might matter more. This is particularly true at the last sentence of Section 3.3, where the authors state “This photolytic loss pathway is expected to play a particularly important role in regions where wet deposition is not very efficient such as the upper troposphere and lower stratosphere”; the model presumably already contains this important result, why not show it here and only focus on the lower atmosphere?

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