Reviewer #2 (Comments to Author):

R2.1) 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.

Response R2.1) We thank the reviewer for recognizing the originality of our work and his/her thoughtful suggestions on how to improve the manuscript.

The major issue raised by the reviewer pertains to the uncertainties associated with the mechanistic treatment of particle-phase photolysis. The reviewer recognizes our attempt to delineate these uncertainties, but nevertheless suggests removing the section on particle-phase photolysis. We largely agree with the reviewer in that there are several key uncertainties pertaining to the mechanistic modeling of in-particle photolysis rates. In this context, we have revised Section 3.2 significantly to de-emphasize the results using our simple mechanistic approach for calculating in-particle photolysis rates. We choose instead to emphasize the empirically-based approach (which, by definition, circumvents some the mechanistic uncertainties identified by the reviewer) to demonstrate the potential importance of in-particle photolysis rates. We also show (but do not discuss in great detail) the results from the Jmolecmax calculation (i.e. assuming in-particle photolysis rates are the same as gas-phase photolysis rates) to provide a point of comparison to the empirical calculations (the Jmac approach) to a likely upper-limit estimate of the effect of in-particle approach (the Jmolecmax approach). We have completely removed the Jmolec simulations.

We think that it is precisely because the particle-phase processes are highly uncertain that the question of the potential role of the photolysis needs to be brought upfront. In current models, the condensation of gases into particles provides a “complete photo-protection” for molecules that would otherwise be easily photolyzed in the gas phase. Our sensitivity study is challenging that assumption and is intended to open the discussion using some input numbers that we consider typical for MACs at UV wavelengths, and quantum yield values that are seen in laboratory experiments.

To reflect these changes, Figures 5 and SI-1 have been updated and the text on pages 8125 (line 11) - 8126 (line 15) has been removed and replaced by this new paragraph:

“For comparison, the effect of applying the gaseous photolysis rates for the corresponding species in the condensed phase is shown in Figure 5 (Jmolecmax). Similar to the simulations above based on MAC, the photolysis is here again considered as an irreversible loss of organic carbon. The comparison between Jmac and Jmolecmax shows a fairly similar (within 20%) reduction in SOA mass for most precursors. The Jmolecmax run considers that chromophores and quantum yields are similar in their gas and particle phase absorption, which is a crude assumption neglecting possible effects form oligomerization, caging and quenching. In the absence of particle-phase chemistry, Jmolecmax could be viewed as an upper limit to photolysis effects, but changes in absorption with particle aging complicate this simple interpretation as both enhancement and decrease in absorption were reported (e.g. Shapiro et al., 2009; Bones et al., 2010; Updyke et al., 2012; Zhong and Jang, 2014).”

As suggested by the reviewer, we have also included in the paper a new simulation showing the effect of the gas-phase photolysis only on global SOA. The effect is minor compared to particle-phase photolysis as shown on the new figures (Figure 7b):

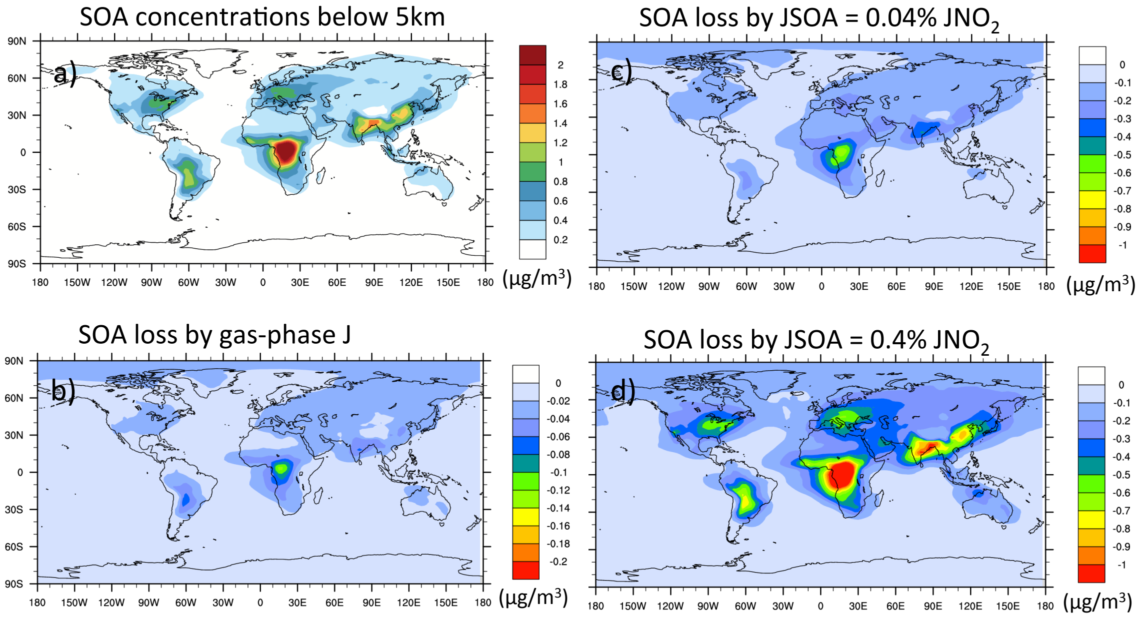

Figure 7: GEOS-Chem simulation for 2009 showing (a) the SOA concentrations within the lower troposphere (below 5km), and the absolute (µg m^{-3}) reductions in SOA concentrations due to gas-phase (b) and particle-phase (c, d) photolysis. Gas-phase photolysis is applied to semi-volatile organic compounds using the e-folding J lifetime of 20 days as estimated in

Table 3. Two particle-phase photolysis rates are considered i.e. JSOA of 0.04% JNO2 (c), and JSOA of 0.4% JNO2 (d).

The following text was also included: ***"Our results (Figure 7b) suggest that gas-phase photolysis of intermediate semi-volatile organic compounds leads to a small (< 4%) reduction in SOA concentrations."***

In the conclusion: ***"In comparison, the gas-phase photolysis of semi-volatile organic compounds had a much smaller effect on SOA concentrations."***

R2.2) 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.

Response 2.2) The potential formation processes mentioned by the reviewer such as oligomerization and aqueous phase chemistry are highly uncertain and not included in our box model. Their mechanistic representation is currently not well understood for most compounds and including them into GECKO-A is beyond the scope of this paper. As suggested by the reviewer we have explained that our box model calculations represent an upper limit, and that our calculations are based on an empirical approach (see R2.1) leading to the conclusions that photolysis is a competitive removal process to wet deposition.

We appropriately caveat the limitations of our study, particularly in regard to the possible effects of particle-phase processes that we have not included in our study. This is described in the manuscript: (pages 8132-8133):

"We recognize that processes occurring inside the particle-phase (e.g oligomerization), which were not included in our study, can modify the chemical composition and properties of those chromophores, thus enhancing or reducing their ability to absorb radiation and undergo photolysis. These reactions are still not well characterized (Atkinson and Ziemann, 2012) and are beyond the scope of this paper."

And we have added the following sentence to the conclusions to emphasize the uncertainties related to missing particle-phase chemistry:

"Finally, we note that a fuller understanding of ambient SOA formation rates will require a better understanding of SOA formation from other condensed-phase processes such as oligomerization and aqueous-phase chemistry."

R2.3) 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.

Response R2.3) We have clearly pointed out and further highlighted in this revision, the lack of aerosol chemistry is a limitation. As explained in R2.1 we have de-emphasized the 'mechanistic' approach for calculating the effect of in-particle photolysis, and have stressed that our results are likely an upper limit.

R2.4) 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 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.

Response R2.4) We agree with the reviewer that the laboratory measurements can show both an enhancement and a decrease in absorption depending on the chemical system. As shown on the figure below for various systems the absorption can be significantly increased. In addition, our MAC (0.1 m^2/g) is based on values reported for ambient mixtures rather than laboratory experiments.

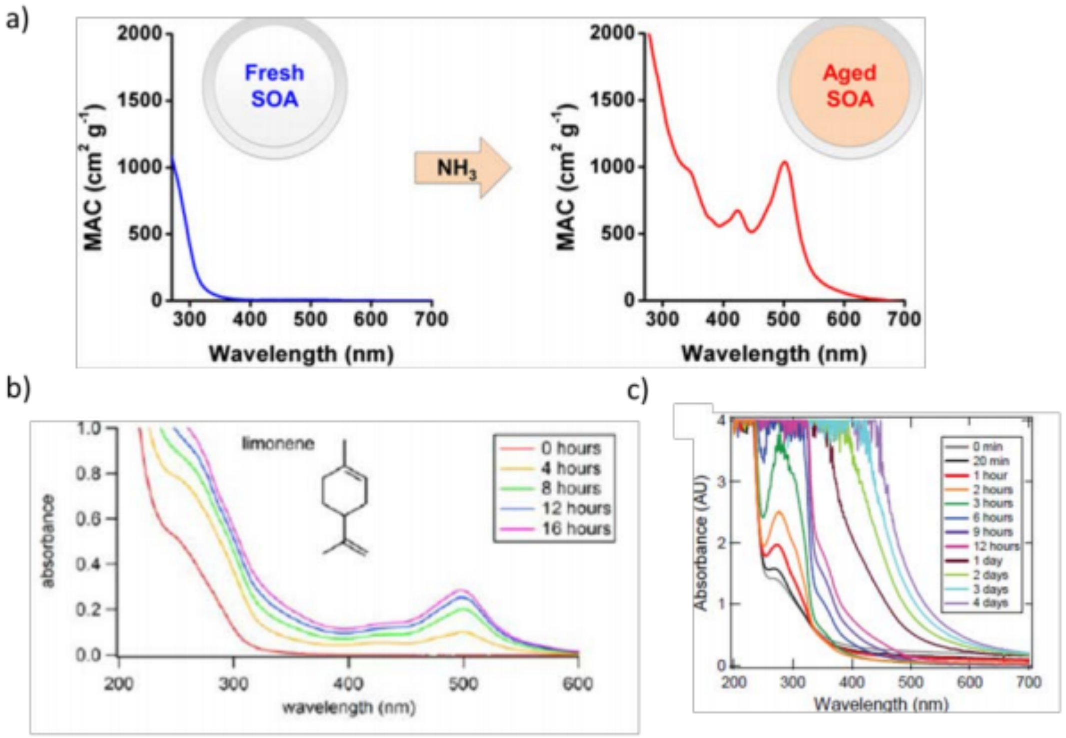

Figure: Representative absorption spectra for secondary BrC based on several literature studies including: a) enhanced absorbance in the visible spectrum associated with various carbonyl+NH_3 reactions (Updyke et al., 2012); b) enhanced absorption due to limonene SOA (carbonyl) + AS reactions (Bones et al., 2010); c) enhanced absorption due to glyoxal + AS/AN reactions (Shapiro et al., 2009).

This is now explained in the manuscript:

"In the absence of particle-phase chemistry, Jmolecmax could be viewed as an upper limit to photolysis effects, but changes in absorption with particle aging complicate this simple interpretation as both enhancement and decrease in absorption have been reported (e.g. Shapiro et al., 2009; Bones et al., 2010; Updyke et al., 2012; Zhong and Jang, 2014)."

R2.5) 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.

Response R2.5) As suggested by the reviewer we have more clearly defined the objectives and limitations of the box model study. The box model calculations are designed to obtain insights into the effect of photolysis in an idealized setting (similar to smog chamber studies). The 3D model simulations provide insights into the spatial and temporal effects of photolysis relative to other loss mechanisms (dry and wet deposition) while taking into account the full diurnal variability of the gas-phase chemistry, including the diurnal variability of the nitrate-radical initiated oxidation of monoterpenes and sesquiterpenes (Jo et al., 2013). This is now explained in the manuscript:

"First, we study the multi-day growth of SOA from four typical precursors (α-pinene, toluene, and semi-volatile and intermediate volatility n-alkanes) under idealized conditions (constant fixed daylight) to assess the maximum potential impact of photolysis on SOA formation. […] We then include a simplified parameterization of photolysis reactions within a global chemistry model to estimate the potential effect of photolysis on ambient SOA under realistic conditions involving spatial and temporal variability in SOA precursor emissions and chemistry, and in the presence of other competing SOA loss processes."

We have clarified in Section 2 that a constant daylight refers to a constant JNO2:

"In these runs, temperature is set to 298K, photolysis frequencies are calculated for mid-latitudes at a solar zenith angle of 45° ($JNO_2 = 8.1\times10^{-3}\ s^{-1}$ which corresponds to a constant daylight),.."

OH concentrations of 8e6 molecules/cm^3 are used only for sensitivity simulations (reference simulations use 2e6 molecules/cm^3). The background OA levels of 10 μg/m^3 are chosen as a default value and we test the sensitivity of our results to a lower value in the paper. The results suggest that although the absolute SOA concentrations change, the sensitivity to photolytic reactions remains qualitatively similar (within 10%) regardless of the OH or the organic aerosol background values used in this study. These sensitivity effects are already discussed in the manuscript in Section 3.1:

"For all precursor species, the sensitivity to photolytic reactions remains qualitatively similar (within 10%) regardless of the OH and OA background values (Figure SI-1). As expected, a decrease in background OA concentrations leads in most cases to an enhancement of the SOA photolytic loss, whereas an increase in OH levels tends to result in a reduced SOA photolytic removal."

R2.6) 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.

Response R2.6) As suggested by the reviewer we performed additional sensitivity simulations in order to verify whether the sensitivity to gas-phase photolysis

changes between simulations assuming a permanent daylight (fixed J values like in the manuscript) vs. simulation with a diurnal cycle in J values.
Two types of simulations are compared on the figure below:

- in orange: simulations with photolysis values predicted by the TUV model within GECKO-A for Boulder (June 21)
- in black: simulations with fixed J rates using the daily average J values from the previous run

In all simulations NOx was set to 10 ppb and O_3 to 40 ppb. In the diurnally varying simulations, OH was free running, whereas in the fixed J simulations OH was set to the diurnal average value of the previous run. As shown on the figure below, the response to gas-phase photolysis is very similar between the two sets of runs. The decrease in SOA concentrations is about 20% in simulations using both the fixed J values, and the diurnally variable J values. Therefore, our conversion from X number of days at constant light to 2*X atmospheric equivalent days is a reasonable assumption. This is now explained in the manuscript:

"We also note that the sensitivity to gas-phase photolysis is not significantly modified when diurnally variable photolysis rates are considered instead of fixed constant daylight conditions (see Figure SI-3)."

The following text has also been added to the supplementary material:

"Additional sensitivity simulations were performed to verify whether the sensitivity to gas-phase photolysis of the considered chemical systems changes between simulations assuming a permanent daylight (fixed J values like in the manuscript) vs. simulation considering a diurnal cycle for J values.
As shown on Figure SI-3, the response to gas-phase photolysis is very similar between the two sets of runs, with a decrease in SOA concentrations of about 20%."

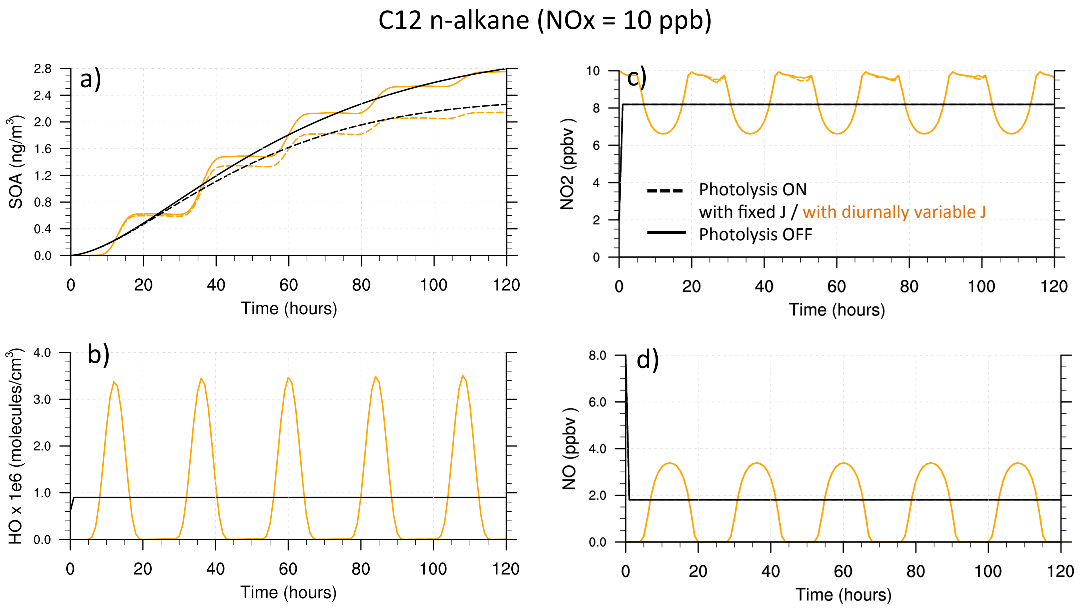

Figure SI-3: GECKO-A predicted SOA concentrations for the oxidation of C12 n-alkanes at high NOx). Two types of simulations are shown i.e. in orange, simulations with daily varying photolysis values predicted by GECKO-A for Boulder (June 21), and in black, simulations with fixed J rates using the daily average J values from the previous run. In all simulations NOx was set to 10 ppb, and O_3 to 40 ppb. In the diurnally varying simulations, OH was free running, whereas in the fixed J simulations OH was set to the diurnal average value of the previous run.

R2.7) 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?

Response R2.7) We thank the reviewer for pointing out this omission, and have added the corresponding plots in Figure 8 showing the reduction in SOA concentrations in the upper troposphere. The new figure and text are shown below:

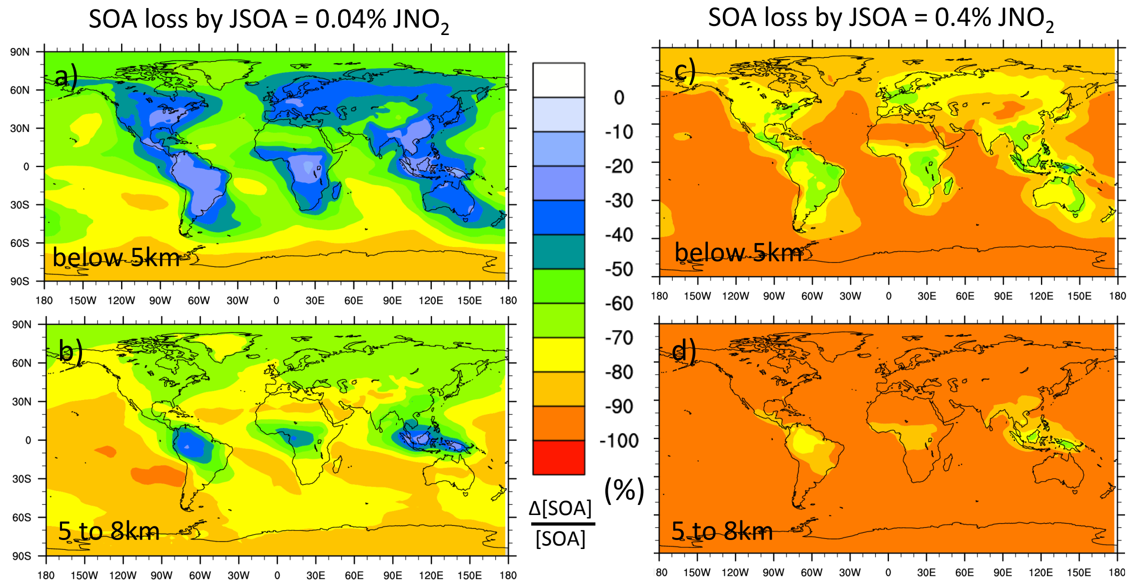

Figure 8: Relative reductions (%) in SOA concentrations due to particle-phase photolysis in the lower (a, c) and upper (b, d) troposphere. Two in-particle photolysis rates are considered i.e. J_{SOA} of 0.04% J_{NO2} (left side), and J_{SOA} of 0.4% J_{NO2} (right side).

"Model results show that the relative decrease in SOA concentrations is ~20-30% stronger in the upper troposphere compared to the lower troposphere (Figure 8b,d)."