Manuscript entitled "Organic photolysis reactions in tropospheric aerosols: effect on secondary organic aerosol formation and lifetime"
by Hodzic et al.

Reviewer #1 (Comments to Author):

R1.1) This is -as far as I can tell, not being a chemist– an excellent work on a difficult subject. The manuscript shows the importance of photolysis reactions (both gas-phase and in-particle) on the formation rate and lifetime of secondary organic aerosols. The manuscript combines nicely some box model calculations with a global chemistry model simulation. I think however that the authors need to improve the presentation and language if they want to be understood by non-chemist aerosol scientists. Below is a list of comments:

Response R1.1) We thank the reviewer for recognizing the importance and merits of our work, and we have done our best to respond to reviewer's specific comments below.

R1.2) The conversion of lifetimes from permanent daylight conditions to equivalent summer or winter conditions is a little unclear (although I understand what the authors mean).

Response R1.2) The concept of the photolysis age in JNO2 equivalent summertime or wintertime days is already defined in the manuscript:
"We define the Photolysis Age in JNO2 equivalent days (Table 1) as the JNO2 exposure of the simulated SOA during our simulations normalized to a 1 day average summer (or winter) JNO2 exposure: Photolysis Age=(JNO2× time)/JNO2_average, where time is the duration of the simulation in days. Photolysis Age values are reported in Table 1 for our experiments. Typically, our 1 week simulations performed under constant lights at mid-latitudes and a solar zenith angle of 45° (JNO2 = 8.1×10^{-3} s^{-1}) are equivalent to about 2 equivalent weeks of exposure in the atmosphere at mid-latitudes during summer, or to about 38 equivalent days during winter."

We have also simplified Table 1 as discussed in R1.14.

R1.3) There is no reason to mix 45 SZA and mid-latitude conditions as it is done in a number of places (eg line 10 in the abstract, line 7 on page 8120, or in caption of figure 1). Likewise on line 25 on page 8120, why mention the 45 SZA here? A solar zenith angle of 45 is a solar zenith angle of 45 and can occur at many latitudes. So I would simply say that the effects of JNO2 for a SZA of 45 under permanent light conditions corresponds to (roughly) twice the effects of a varying JNO2 in summer mid-latitude conditions. Or maybe the "mid-latitude conditions" correspond to something else than the SZA but that's not clear in the manuscript. It is required also to say how the equivalence was done (or in what sense it is an equivalence) and what the uncertainty on this equivalence is.

Response R1.3) The reason for specifying both the solar zenith angle and the latitude in the paper is that the overhead ozone column changes at different locations which impacts the photolysis calculations. See Table 1 for the corresponding ozone overhead column values. This is now clarified in the manuscript:

"Typical ozone overhead values are used at different locations based on the Total Ozone Mapping Spectrometer data (http://disc.sci.gsfc.nasa.gov/acdisc/TOMS)."

R1.4) Some chemical terms and notations would benefit from being explicited. In particular the notation on line 21 page 8122 (and also in Fig 2) is not clear to me. Sorry if I sound stupid, but what does the H add to a K functional group that already has two R groups?

Response R1.4) H, K, N, O, etc. refer to various functional groups that may be present in a particular molecule, as detailed in lines 17-19 on that same page 8122. For example, HHKKK refers to a molecule that contains two hydroperoxide and three ketone groups. This is now more clearly explained in the manuscript:

"Ketone (K) and alcohol (O) moieties are present in a majority of the molecules, while hydroperoxides (H) are seen mainly at low NOx and nitrates (N) mainly at high NOx. Gas-phase photolysis leads to a decrease in most species, which seems to be particularly important for highly functionalized compounds containing multiple carbonyl and nitrate groups (e.g. HKKKK, HHKK, HHKKK, HKKK, NNKK, NNKO where e.g. HHKK refers to a molecule that contains two hydroperoxide and two ketone groups)."

R1.5) What is an activation value (line 10, page 8123)? Is this a dimensionless quantity?

Response R1.5) We have changed the term "activation value" to "activation factor" which is defined in the manuscript on page 8118:

"Kinetic data for OH / hydroperoxide reactions are sparse in the literature, and previous versions of GECKO-A assumed an activation factor (i.e. an enhancement of the rate constant due to the presence of the functional group) of 14 on the basis of data for the OH/CH3OOH reaction."

R1.6) It would be interesting to show what actinic wavelengths are involved. Can the effects of the photolysis (calculated here at pretty low concentrations) saturate with the amount of organics present in the atmosphere? or be amplified in the presence of aerosols and clouds? I would think that a figure showing the distribution and strengths of absorbed wavelengths would be useful to the reader.

Response R1.6) We interpret this question as saying: Can absorption by organics (gas or particle phase) affect the radiation field itself, and therefore provide a negative (saturating) feedback on the photochemistry? Typical aerosol optical depths (scattering + absorption) rarely exceed 2 even in highly polluted urban settings, and only a fraction (1 minus the single scattering albedo) is absorbed. Taking a very polluted conditions with total AOD = 2 and SSA = 0.9 gives an absorption optical depth of 0.2, corresponding to about 20% reduction in radiation (Beer-Lambert, $F(z,\lambda)/F_{TOA}(\lambda)=\exp(-AOD(z, \lambda))$ for overhead sun). This is a significant but not overwhelming reduction, so that even under these highly polluted conditions the photochemistry is expected to proceed vigorously. Regional and global effects are expected to be smaller.

This is now explained in the manuscript:

"We note that the absorption by organic gases and/or particles is not expected to substantially affect the radiation field itself. Even in highly polluted conditions, aerosol optical depth (AOD) rarely exceeds 2, and only a fraction (1 minus the single scattering albedo (SSA)) is absorbed e.g. AOD=2 and SSA=0.9 gives an absorption optical depth of 0.2, corresponding to about 20% reduction in radiation. This is a significant but not overwhelming reduction, so that even under these highly polluted conditions the photochemistry is expected to proceed vigorously. Regional and global effects are expected to be smaller."

R1.7) In section 3.1 the whole discussion is in terms of formation rate, why not discuss the effects on concentrations as well?

Response R1.7) In section 3.1, we choose to discuss the effect of photolysis on SOA formation yields as typically done in chamber experiments because we are using idealized box model simulations to quantify the effect of a given process on SOA formation. Talking about concentrations is not appropriate in this case as concentrations depend on e.g. dilution, boundary layer mixing and deposition which are not included in these idealized box model simulations.

R1.8) In section 3.2 for the first approach, it seems to me that there is another assumption which is that radiation at actinic wavelengths penetrates through the particle and can induce photolysis in the whole volume of the particle. I think this is a different thing than the "caging" effects mentioned by the authors. This may not be a bad assumption for small accumulation mode particles, but may not be correct for the larger particles and the smaller wavelengths. I must say I am not sure of this though but it would be good to discuss it!

Response R1.8) We interpret this question as asking whether it is realistic to assume that light can penetrate the whole volume of the particle without being attenuated by the absorbers. This could be a problem for species having a large MAC >> 1 m^2/g such as soot but it is a reasonable assumption for organic species and for MAC values considered in our calculations.

For instance, in the manuscript we consider a typical organic particle with MAC = 0.1 m^2/g and 200 nm diameter particles, density 1.5 g/cm^3. Its optical cross section is MAC x mass of particle = 0.1 x 6.3e-15 m^2, whereas its geometric cross section is (pi)R^2 = 3.1 e-14 m^2. So the ratio between optical/geometric cross section ~ 0.02. This is a rough calculation and should be done fully with Mie theory if the opt/geom ratio were closer to unity, but when it is so small it is just not necessary. For comparison, for soot MAC = 10 m^2/g and the ratio optical/geometric = 2, suggesting that the attenuation is expected to occur within the particle.

The following sentence was added to the manuscript:

"We note that for the chosen MAC value the light can penetrate the whole volume of the particle without being significantly attenuated by the absorbers (light attenuation was estimated to be less than 2-3%, see discussion SI Annex IV)."

And the following Supplementary Information was included:

Annex IV: Estimate of the light attenuation by an absorbing particle

<u>1) Method 1:</u>

The light attenuation can be roughly estimated as a ratio between the absorption cross section of the particle and its physical cross section. Here we assume a typical organic particle with MAC = 0.1 m^2/g, 200 nm diameter and 1.5 g/cm^3 density. Its optical cross section is MAC x mass of particle = 0.1 x 6.3 x 10^{-15} m^2, whereas its geometric cross section is πr^2 = 3.1 x 10^{-14} m^2. Thus, the ratio between optical and geometric cross section is ~ 0.02, meaning that about 2% of photons are absorbed by the particle, and that the rest will go through the particle. A more accurate estimate could be derived from the Mie theory, but the corrections due to the full theory are typically within a factor of 2 (Ray and Bhanti, 1997; Mayer and Madronich, 2004), and thus that is not required in this case. For comparison, for soot MAC = 10 m^2/g and the ratio optical/geometric = 2, suggesting that substantial attenuation is expected to occur within the particle.

Ray A.K., and Bhanti D.D., Effect of optical resonances on photochemical reactions in microdroplets. Applied Optics, Vol. 36, No. 12, 1997.

Mayer B., and Madronich, S. Actinic flux and photolysis in water droplets: Mie calculations and geometrical optics limit. Atmos. Chem. Phys. 4, 2241–2250, 2004.

2) Method 2:

According to the Beer Lamber's law the transmitted light can be written as:

$$I/I_0 = exp(-MAC \times \rho \times L) \quad (1)$$

Where MAC represents the mass absorption coefficient ($m^2\ kg^{-1}$), ρ density of the particle ($g\ cm^{-3}$), and L the particle diameter (m). If we consider a particle with MAC = 0.1 m^2/g, ρ = 1.5 $g\ cm^{-3}$, and L = $2x10^{-5}$ cm, we can calculate I/I_0 = 0.9704, which means that ~97% of the initial signal was transmitted.

The attenuation by the particle is ~3%. In other words, the optical depth of the considered particle is 0.03, which suggests that the attenuation of light (in the continuous model) is small.

R1.9) line 25, page 8124: do the authors mean "urban scale" or "urban conditions" here? Or is it the time the air mass passes over an urban area that is relevant?

Response R1.9) Urban scale is the correct wording here as we refer to the lifetime of SOA with regards to photolysis compared to its typical lifetime with respect to other removal processes and transport/mixing timescales.

R1.10) A mass absorption coefficient of 10 m2/g is not credible for SOA, and even less so if all the absorption occurs between the 300–400 nm wavelength range. Values of 10m2/g are typical for black carbon with absorption throughout the solar spectrum.

Response R1.10) In this study we use the value of 0.1 m^2/g for SOA. However, according to ambient measurements reported by Barnard et al., 2008, values as high as 10.5 m^2/g were observed at 300nm in Mexico City which is dominated by organic aerosols. They estimated that the light absorption by the "brown" (organic) carbonaceous aerosol can add about 40% to the light absorption of black carbon in Mexico City. We note that absorption coefficients are wavelength specific, and do not need to apply to the whole solar spectral range.

This study is referenced in the manuscript: *"Recently measured MAC values range from 0.03 to 0.5 m^2g^{-1} for laboratory data (Lambe et al., 2013) or from 0.1 to 10 m^2g^{-1} for ambient urban measurements (e.g. Barnard et al., 2008) in the 300-400 nm wavelength interval."*

R1.11) I am not sure Eqn. 1 and 2 are consistent, the first one depends on JNO2, the second not. Or is one of the JNO2 for normalized conditions in Eqn 1 but not the other one? What is the unit of the 0.4 value in Eqn 2?

Response R1.11) Eqs 1 and 2 are consistent, and are written as:

$$J\_SOA= [AF/J\_NO2] \times [mc] \times J\_NO2 \times [MAC] \times [QY] \qquad (1)$$

$$J\_SOA= 0.4 \times J\_NO2 \times [MAC] \times [QY] \qquad (2)$$

where AF is the actinic flux (photons m^{-2} s^{-1}), MAC is the SOA mass absorption coefficient (m^2 g^{-1}), mc is the mass of one carbon atom (g) and QY is the quantum yield. Using the photolysis model TUV we estimated estimate AF/jNO2 = 2e22 photons m^{-2} over 280-400 nm at 1 km altitude and overhead sun, which combined with mc gives: (2e22 photons m^{-2})(12 g mol^{-1})/(6e23 mol^{-1})= 0.4 photons g m^{-2}.

We have clarified this in the revised manuscript:

"We represent the photolytic SOA loss as a first order reaction, with effective reaction rate coefficient J_{SOA}:

$$J_{SOA} = [AF] \times [MAC] \times [mc] \times [QY] \qquad (1)$$

where AF is the actinic flux (photons m^{-2} s^{-1}), MAC is the SOA mass absorption coefficient (m^2 g^{-1}), mc is the mass of one carbon atom (g) and QY is the quantum yield or the probability that absorbed photons will lead to bond cleavage and the loss of some mass from the particle. We assume that if each absorbed photon leads to the loss of one C atom, the quantum yield is equal to one.

We scaled (1) to known NO_2 photolysis:

$$J_{SOA} = J_{NO2} \times [AF/J_{NO2}] \times [MAC] \times [mc] \times [QY] \qquad (2)$$

The photolysis model TUV (v5.1, (Madronich et al. 1993)) was used to estimate the UV actinic flux (= 2×10^{20} photons m^{-2} s^{-1}) and NO_2 photolysis (= 9.7×10^{-3} s^{-1}) over 280-400 nm at 1 km altitude and overhead sun, which combined with [mc] gives $[AF/J_{NO2}] \times [mc] = 0.4$ photons g m^{-2}."

R1.12) Line 13 on page 8127: 1.2 must be 1.2% or what?

Response R1.12) 1.2 is the average effective photolysis quantum yield that was reported by Wong et al., 2014 as 1.2 +/- 0.2 for a-pinene photolysis. Effective quantum yields can be larger than unity, depending on further reactions after the initial photodissociation. This is already explained in the manuscript:

"..whereas Wong et al. (2014) estimated an effective quantum yield of 1.2+/-0.2 for the loss of organics in the case of α-pinene SOA photolysis."

R1.13) Line 14 on page 8128: is the lifetime of 20 days a summer equivalent one? or for continuous daylight conditions?

Response R1.13) Those are equivalent days. This is now clarified in the manuscript:

"except for high-NOX toluene SOA with a lifetime of 20 equivalent summer days for which the effect of photolysis is likely underestimated in our simulations as discussed above."

R1.14) Table 1: the JNO2 exposure in 1 day is a complicated term accompanied by a complicated footnote to say that it is the same quantity as in the previous column but in unit of day -1 instead of s-1. Or am I missing something?

Response R1.14) We agree with the reviewer that this probably added more confusion than clarity. Thus we have removed the JNO2 exposure in 1 day columns from Table 1. This term wasn't used in the text and can be easily calculated from the JNO2 value itself as mentioned by the reviewer.

R1.15) Figure 2: the sums of the C atom ratios in each plot is far from 1. Where is the rest of the C mass? How many SOA constituents in total?

Response R1.15) On these plots we only show the fraction that has partitioned to the particle-phase, the rest of the C mass is in the gas-phase. The number of SOA constituents varies for various precursors e.g. 22,600 species for C12 n-alkane, 32,315 for C16 n-alkane, 126,587 for alpha-pinene, and 2,305 for toluene. We have added the following sentence to the caption of Figure 2 for clarity:

"The carbon atom ratio indicates the ratio of the carbon atoms in the condensed phase to the initial carbon load included in the parent backbone. The sum of the shown particle-phase constituents is lower than one as the rest of the carbon mass is in the gas-phase."

R1.16) Figure 4 is particularly unclear and the caption and the associated text calling Figure 4 did not help me at all. What is C*? Why is volatility expressed in mass concentrations of SOA?

Response R1.16) The volatility is expressed in terms of the effective saturation concentration (C*; which is the inverse of a Pankow-type partitioning coefficient, Donahue et al., 2006). The C* notation is very commonly used in the SOA literature at present. This was clarified in the caption of the figure:

"Distribution of products of OH oxidation of 1 ppt of α-pinene, toluene, C12 and C16 n-alkanes at low (0.01 ppb) and high (10 ppb) NOx levels according to their volatility. The volatility is expressed in terms of the effective saturation concentration (C*)."

R1.17) The caption of Figure 5 does not describe what is represented on the figure. The figure represents SOA concentration, not SOA formation, as a function of time, although I agree it tells something on SOA formation.

Response R1.17) We agree with the reviewer and have corrected the corresponding caption to read:

"Predicted effect of photolysis on SOA concentrations from the oxidation of 1 ppt of α-pinene, toluene, C12 and C16 n-alkanes at low (0.01 ppb) and high (10 ppb) NO_X levels."

R1.18) On Figure 7, bottom panels, it should be d[SOA]/[SOA] rather than just d[SOA]. The figures are far too small and I had to zoom many times to be able to read them. I also noted that figures are not called in order in the text.

Response R1.18) We thank the reviewer for catching this error, we have fixed the labels of the Figure 8 to read d[SOA]/[SOA]. We will make sure that the figures are big enough and easy to read on the ACP final pages during the proofreading stage.

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):

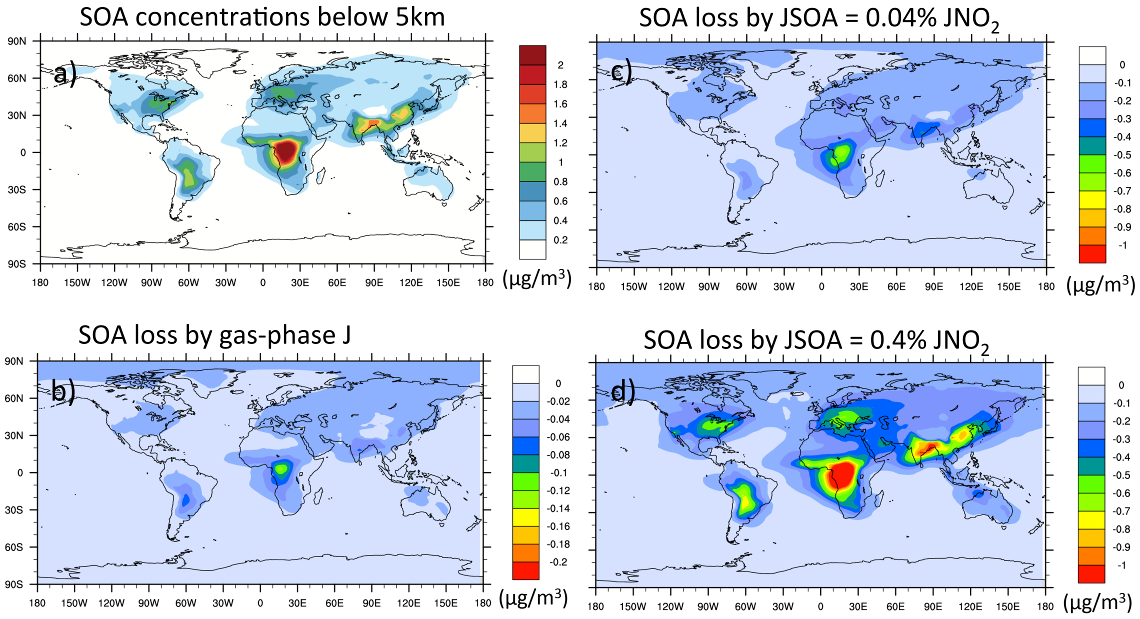

Figure 7: GEOS-Chem simulation for 2009 showing (a) the SOA concentrations within the lower troposphere (below 5km), and the absolute (µg m^{-3}) reductions in SOA concentrations due to gas-phase (b) and particle-phase (c, d) photolysis. Gas-phase photolysis is applied to semi-volatile organic compounds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

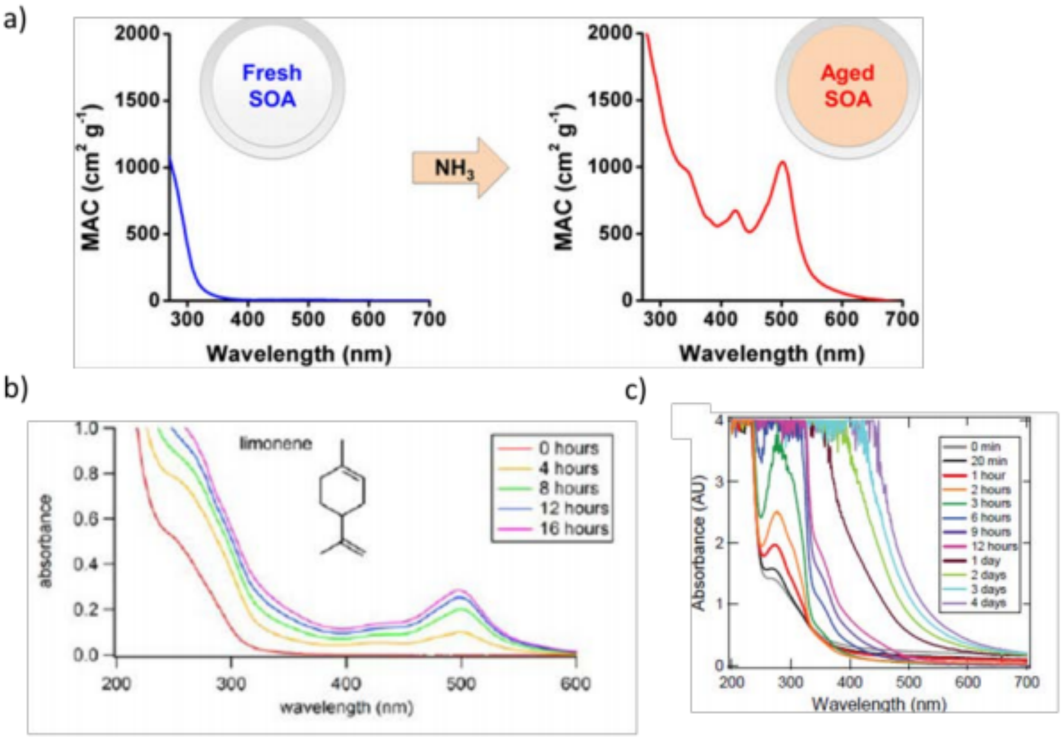

Figure: Representative absorption spectra for secondary BrC based on several literature studies including: a) enhanced absorbance in the visible spectrum associated with various carbonyl+NH_3 reactions (Updyke et al., 2012); b) enhanced absorption due to limonene SOA (carbonyl) + AS reactions (Bones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

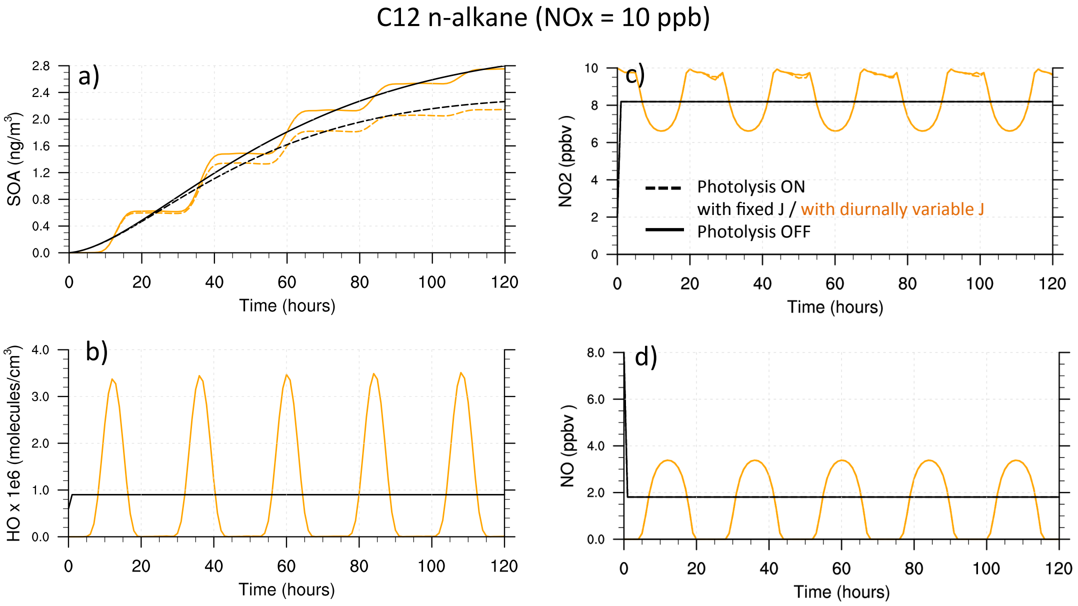

Figure SI-3: GECKO-A predicted SOA concentrations for the oxidation of C12 n-alkanes at high NOx). Two types of simulations are shown i.e. in orange, simulations with daily varying photolysis values predicted by GECKO-A for Boulder (June 21), and in black, simulations with fixed J rates using the daily 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:

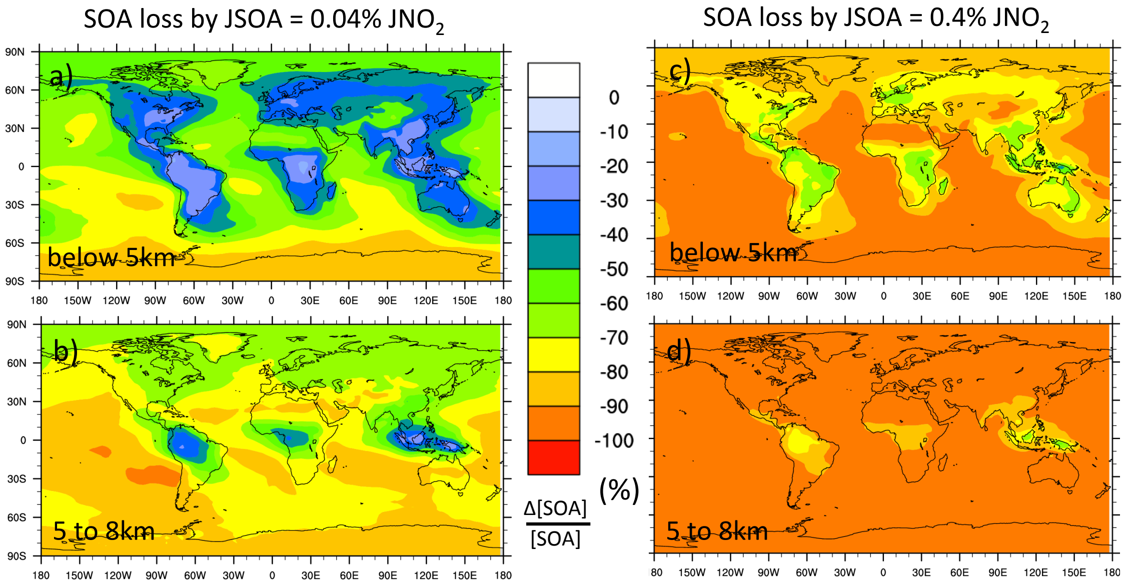

Figure 8: Relative reductions (%) in SOA concentrations due to particle-phase photolysis in the lower (a, c) and upper (b, d) troposphere. Two in-particle photolysis rates are considered i.e. J_{SOA} of 0.04% J_{NO2} (left side), and J_{SOA} of 0.4% J_{NO2} (right side).

"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)."

Organic photolysis reactions in tropospheric aerosols: Effect on secondary organic aerosol formation and lifetime

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Key words: secondary organic aerosol, photolysis rates, photo-fragmentation

Abstract

This study presents the first modeling estimates of the potential effect of gas- and particle-phase organic photolysis reactions on the formation and lifetime of secondary organic aerosols (SOA). Typically only photolysis of smaller organic molecules (e.g. formaldehyde) for which explicit data exist is included in chemistry-climate models. Here, we specifically examine the photolysis of larger molecules that actively partition between the gas and particle phases. The chemical mechanism generator GECKO-A is used to explicitly model SOA formation from α-pinene, toluene, and C_{12} and C_{16} n-alkane reactions with OH at low- and high-NOx. Simulations are conducted for typical mid-latitude conditions and a solar zenith angle of 45° (permanent daylight). The results show that after four days of chemical aging under those conditions (equivalent to eight days in the summer mid-latitudes), gas-phase photolysis leads to a moderate decrease in SOA yields i.e ~15% (low-NOx) to ~45% (high-NOx) for α-pinene, ~15% for toluene, ~25% for C_{12}-alkane, and ~10% for C_{16}-alkane. The small effect of gas phase photolysis on low volatility n-alkanes such as C_{16}-alkane is due to the rapid partitioning of early-generation products to the particle-phase where they are protected from gas-phase photolysis. Minor changes are found in the volatility distribution of organic products and in oxygen to carbon ratios. The decrease in SOA mass is increasingly more important after a day of chemical processing, suggesting that most laboratory experiments are likely too short to quantify the effect of gas-phase photolysis on SOA yields. Our results also suggest that many molecules containing chromophores are preferentially partitioned into the particle phase before they can be photolyzed in the gas-phase. Given the growing experimental evidence that these molecules can undergo in-particle photolysis, we performed sensitivity simulations using an empirically estimated SOA photolysis rate of $J_{SOA}=4\times10^{-4}\,J_{NO2}$. Modeling results indicate that this photolytic loss rate would decrease SOA mass by 40-60% for most species after ten days of equivalent atmospheric aging at mid-latitudes in the summer. It should be noted that in our simulations we do not consider in-particle or aqueous-phase reactions which could modify the chemical composition of the particle, and thus the amount of photolabile species. The atmospheric implications of our results are significant for both the SOA global distribution and lifetime. GEOS-Chem global model results suggest that particle-phase photolytic reactions could be an important loss process for SOA in the atmosphere, removing aerosols from the troposphere on timescales of less than 7 days that are comparable to wet deposition.

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1 Introduction

Secondary organic aerosols (SOA) are ubiquitous atmospheric constituents formed by photochemical oxidation of anthropogenic and biogenic hydrocarbons that can lead to adverse health effects (*Fann et al., 2012*) and radiative forcing of climate (*Boucher et al., 2013*). Their atmospheric burden and lifetime are highly uncertain due to our limited understanding of processes controlling their formation, aging and removal in the atmosphere. SOA yields and the volatility distribution of intermediate oxidation products greatly depend on the competitive chemistry of peroxy radicals (RO_2) formed from oxidation of parent hydrocarbons, which can react with nitrogen oxides (NO), hydroperoxy radicals (HO_2), or other RO_2 (*Ziemann and Atkinson, 2012*). The resulting oxygenated molecules contain carbonyl, peroxide or nitrate chromophores, and are potentially sensitive to photolysis during their lifetime in the atmosphere (*Finlayson-Pitts and Pitts, 2000*). Photolysis can occur in the gas-phase and in the condensed phase as particles containing photolabile compounds efficiently absorb light at actinic wavelengths (*e.g. Lambe et al., 2013; Wong et al., 2014*). Unlike OH reactions that mainly lead to addition of more functional groups, photolysis mainly fragments molecules into smaller and more volatile compounds thus significantly modifying SOA composition and properties during atmospheric aging.

Evidence that photolysis modulates SOA formation and lifetime in the atmosphere is supported by a growing number of laboratory experiments, which showed that exposure to UV lights can suppress SOA formation or even cause substantial loss of biogenic SOA. Presto et al. (*2005*) observed a 20-40% decrease in aerosol yields during α-pinene ozonolysis experiments conducted under UV lights. Zhang et al. (*2006*) found similar sensitivity to UV exposure for d-limonene ozonolysis SOA, with a mass yield decrease of 60% for compounds with saturation concentration of 1 $\mu g\ m^{-3}$. In both cases, the SOA decrease was attributed to the photolysis of gas-phase intermediates during the active growth phase and changes in their volatility distribution. Specific

SOA aging experiments were also performed to isolate the effect of photolysis from other processes (*e.g. Tritscher et al., 2011; Salo et al., 2011; Henry and Donahue, 2012; Donahue et al., 2012*). In those experiments, SOA was first formed from α-pinene ozonolysis in the dark, and then the products were irradiated (with UV lamps or solar lights), which allowed separation of the aging by OH-radical oxidation and photolysis from the initial condensation of primary products. Henry and Donahue (*2012*) reported a strong photolytic loss of 6×10^{-5} s^{-1} of the formed SOA mass upon UV 360nm black-light exposure with lower OH levels (~10^6 molecules cm^{-3}) via H_2O_2 photolysis. In additional experiments reported by Donahue et al. (*2012*), where OH was formed via HONO photolysis, an initial increase in SOA concentrations was first observed, followed by their strong decrease as OH concentrations dropped from 10^7 to 10^6 molecules cm^{-3}. The authors attributed this SOA loss to photolysis in the gas-phase followed by particle-to-gas re-equilibration, under the assumption that particle-phase quantum yields of photodissociation are small due to quenching and cage effects from neighboring molecules. However, recent studies that were able to decouple gas-phase and condensed-phase processes seem to suggest a rapid photolytic loss of SOA in the condensed phase. Epstein et al. (*2014*) irradiated α-pinene ozonolysis SOA denuded from gas-phase oxidants and organic vapors, and concluded that condensed-phase photolysis was responsible for a significant decrease in SOA mass caused by the photochemical loss of particle-bound peroxide species (a 50% loss over 1 equivalent week in the atmosphere). Wong et al. (*2014*) also reported a substantial photolytic loss of α-pinene SOA mass (generated by re-atomization after sampling into filters) under UVB lights with loss rates of 7.9×10^{-5} s^{-1} under dry conditions and a 2x faster loss (1.6×10^{-4} s^{-1}) under higher relative humidities.

During photochemical aging in the atmosphere, SOA can be both generated by oxidative functionalization with OH, and destroyed by photolysis. As these processes are occurring simultaneously and during the entire organic aerosol (OA) lifecycle in the atmosphere (typically a week), it is currently challenging to quantify separately the effect of photolysis on SOA yields and aging from laboratory experiments, and to describe their effect in the models. To our knowledge, photolysis of oxygenated organic molecules in the gas- or condensed-phase is ignored in most current chemistry-climate models, which could result in substantial errors in SOA predictions. In addition, the experimental quantification of SOA photolytic loss could be significantly biased due to SOA evaporation caused by heating inside the chamber upon UV light exposure (*Denjean et al., 2014*).

The objective of the present study is to examine the effect of both gas- and condensed-phase photolysis on SOA formation and lifetime using process and global modeling. 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, temperature, OH, NOx, O_3, and preexisting OA) to assess the maximum potential impact of photolysis on SOA formation. The mechanism generator GECKO-A is used to create explicit oxidation schemes for these precursors, which are then run within a box model to assess the effect of photolysis on SOA yields under a range of conditions. The effect of gas-phase photolysis is explicitly quantified in the box model, whereas the potential role of in-particle photolysis is empirically estimated and discussed based on sensitivity simulations. 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.

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2 Modeling framework

The mechanism self-generator GECKO-A (Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere) was used in this study to create the detailed gas-phase oxidation mechanisms for individual SOA precursors including α-pinene, toluene, and C_{12} and C_{16} n-alkanes. The chemical mechanisms are created using a prescribed set of rules determining reaction pathways and rate coefficients, based on laboratory kinetic data, and structure-activity relationships as described by Aumont et al. (*2005*). The protocol currently implemented in GECKO-A allows the generation of chemical mechanisms for aliphatic species only. For aromatic species (i.e toluene in this study), the mechanism is taken from the Master Chemical Mechanism (MCM) (*Jenkin et al., 2003*) up to the formation of ring opening products, where mechanism generation by GECKO-A is next used. Rate coefficients for reaction of OH with organics are based on structure-reactivity rules of Kwok and Atkinson (*1995*) and subsequent updates. In this study, we have updated the rate constants for H-atom abstraction from carbon atoms containing a hydroperoxide functionality (e.g., RC-H(OOH)R). Kinetic data for OH / hydroperoxide reactions are sparse in the literature, and previous versions of GECKO-A assumed an activation factor (i.e. an enhancement of the rate constant due to the presence of the functional group) of 14 on the basis of data for the OH/CH_3OOH reaction. That is, the presence of the –OOH group was assumed to increase the reactivity of the adjacent C-H bond(s) by this factor. We have changed this factor to 3.5 similar to that for –OH (Atkinson R. personal communication), and discuss its effect on our results in section 3.1. The choice of a lower activation factor is supported by measurements of gas-phase dodecyl hydroperoxides in the work of Yee et al. (*2012*), who found that the loss of these peroxides was much too fast when using the MCM value based on a large value of F(-OOH). For the gas-particle partitioning, instantaneous equilibrium is assumed, and the Nannoolal et al. (*2008*) approach is used to estimate the saturation vapor pressure for non-radical species. The fraction that is partitioned to the particle phase can be determined as $F_{aerosol,i} = \left(\frac{C_{OA}}{C_{OA}+C_i^*}\right)$ where C_{OA} is the aerosol mass concentration (μg m^{-3}), and C_i^* is an effective saturation mass concentration (μg m^{-3}). The gas/particle equilibrium and the composition of SOA are constantly modified as the gas-phase oxidation progresses during the atmospheric aging. Condensed-phase reactions are not considered, nor are potential diffusion

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limitations to SOA partitioning. Gas-phase photolytic reactions are included for molecules containing carbonyl, hydroperoxide or nitrate chromophores. For species containing several functional groups, each chromophore is treated independently, except for conjugated carbonyls. The photolysis of nitroaromatic compounds is not included. To determine the associated photolysis rates, each molecular structure predicted by GECKO-A is assigned a reference compound with its associated cross sections and quantum yields as described by Aumont et al. (*2005*, see Table 4). SI-Table 1 summarizes the photolysis rates for chromophores and molecular structures that are considered in GECKO-A. Particle-phase photolysis is not explicitly calculated in the default model, and sensitivity simulations will be preformed in this study to quantify its effects as discussed in section 3.2.

In this study simulations are performed in a box model with the prescribed conditions representative of ambient air as in the study by Hodzic et al. (*2014*) to quantify the effect of photolysis on SOA formation and yields. In these runs, temperature is set to 298K, photolysis frequencies are calculated for mid-latitudes at a solar zenith angle of 45° (J_{NO2} = 8.1×10^{-3} s^{-1} which corresponds to a constant daylight), NO_X levels are held at 0.01 ppb for low and 10 ppb for high-NOx conditions, ozone is set at 40 ppb, and OH is kept constant at 2×10^{6} molecules cm^{-3}. The pre-existing OA concentration is 10 µg m^{-3}, typical of moderately polluted conditions. Sensitivity simulations with higher OH values (8×10^{6} molecules cm^{-3}) or lower pre-existing OA (1 µg m^{-3}) are also performed. The initial hydrocarbon mixing ratio is fixed to an arbitrary low value of 1 ppt, so that the amount of aerosol produced from the given precursor is negligible compared to preexisting OA prescribed in the study and will not impact the gas/particle partitioning, nor the overall photochemical reactivity. Under these conditions, SOA yields are independent of the amount of initial precursor as discussed by Hodzic et al. (*2014*). SOA yields and volatility distribution of intermediate products depend to a large extent on the relative rates of RO_2+HO_2 and RO_2+RO_2 (minor) versus RO_2+NO reactions. We calculated that 8% of RO_2

reactions proceed with NO under "low-NOx" vs. 99.9% under "high-NOx" conditions considered in this study.

We define the *Photolysis Age* in J_{NO2} equivalent days (Table 1) as the J_{NO2} exposure of the simulated SOA during our simulations normalized to a 1 day average summer (or winter) J_{NO2} exposure: $Photolysis\ Age = \frac{(J_{NO2} \times time)}{J_{NO2\_average}}$ where *time* is the duration of the simulation in days. Photolysis Age values are reported in Table 1 for our experiments. Typically, our 1 week simulations performed under constant lights at mid-latitudes and a solar zenith angle of 45° ($J_{NO2} = 8.1\times10^{-3}\ s^{-1}$) are equivalent to about 2 equivalent weeks of exposure in the atmosphere at mid-latitudes during summer, or to about 38 equivalent days during winter.

3 Results and discussion

3.1 Importance of gas-phase photolysis of organics

To investigate the role of gas-phase photolysis on SOA formation and yields, we compared experiments with photolysis on and off for four typical SOA precursors including α-pinene, toluene, and C_{12} and C_{16} n-alkanes (Table 2). In the "photolysis off experiment" photolysis of all organic species (except for formaldehyde and methylhydroperoxide) is turned off, whereas all inorganic compounds (i.e. O_3, NO_2, NO_3, H_2O_2, HONO, HNO_3, HNO_4) still undergo photolysis. Figure 1 shows the results for two different levels of NO_X (0.01 ppb and 10 ppb), OH ($2x10^6$ and $8x10^6$ molecules cm^{-3}) and background OA (1 and 10 $\mu g\ m^{-3}$). BASE case simulations with and without photolysis of organics are shown in black. The results indicate that in a week of chemical aging with constant daylight or two weeks of equivalent atmospheric summertime exposure (representative of Boulder 40°N with the solar zenith angle of 45°) the gas-phase photolysis leads to a 10 to 45% decrease in SOA concentrations depending on the precursor. Most of the decrease occurs in the first 4 days of the simulation (8 equivalent atmospheric days). For a given species, the sensitivity to gas-phase photolysis is comparable under low- and high-NO_X conditions, except for α-pinene SOA, which seems to be more sensitive under high-NO_X. Our results also suggest that for most species the resulting loss of SOA due to gas-phase photolysis is increasingly more important as the chemical processing time is increased during the first week atmospheric exposure (Figure SI-1).

The largest effect on yields (Table 3) is predicted for α-pinene SOA, with a reduction of 16% under low-NOx and 47% under high-NOx during the entire experiment. The reduction is relatively small during the initial 10 hours, which is a typical duration of laboratory experiments, with a 2% decrease at low-NOx (10% high-NOx), and reaches ~5% (20%) after 1 day, or 12% (42%) after one week of equivalent atmospheric ageing. For toluene oxidation, the effect of photolysis is more limited, and does not exceed 15% for either low- or high-NOx conditions. We note however that the effect could be underestimated as the photolysis of nitroaromatic compounds, which are strong absorbers, is currently not represented in GECKO-A. For products of n-alkanes, the relative decrease in SOA yields is ~10% for C_{16} n-alkanes and ~25-30% for C_{12} n-alkane. The sensitivity to gas-phase photolysis is more important for C_{12} than C_{16} n-alkane, due to the fact that products of C_{16} n-alkane are partitioned to the particle-phase in a much greater fraction after one generation of chemistry where they are protected from gas-phase photolysis, whereas it takes several generations to produce substantial SOA from shorter chain n-alkanes (*Aumont et al., 2012*).

The efficiency of the gas-phase photolysis will depend on the residence time of organic vapors in the gas-phase, which can be significantly modified by the chemical environment. For instance, an increase in the OA mass available for the gas/particle partitioning is expected to enhance the partitioning of organics to the condensed phase where they will be protected from gas-phase photolysis. Similarly, a faster gas-phase oxidation rate (higher OH) is expected to lead to more rapid generation of the low volatility organic species which can condense into the particle-phase thus making them less vulnerable to the gas-phase photolysis. Sensitivity simulations with 4-

times higher OH concentrations (SENS_OH) and 10-times lower background OA (SENS_OA) are performed to evaluate these effects (Figure 1). As expected, SOA formation occurs more rapidly when a 4-fold increase in OH is considered. The decrease by an order of magnitude in the amount of the pre-existing OA (and thus reduced gas/particle partitioning) also affects the amount of SOA formed. A large (~75%) decrease in SOA production is observed for toluene because a significant fraction of the predicted oxidation products have effective saturation mass concentrations (C*) in the 1-10^3 μg m^{-3} range (Figure 4, see also Hodzic et al. (*2014*)). The effect is more limited for SOA produced from other precursors (up to 30%). 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. 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).

Figure 2 shows the major functional groups in SOA molecules from various precursors. Fifteen families of functional groups are considered and they account for 54% to 65% of the total SOA mass for α-pinene, 94% to 99% for toluene, and for 70% to 90% for C_{12} and C_{16} n-alkanes. Positional isomers are lumped into the same family of compounds. Ketone (K) and alcohol (O) moieties are present in a majority of the molecules, while hydroperoxides (H) are seen mainly at low NO_X and nitrates (N) mainly at high NO_X. Gas-phase photolysis leads to a decrease in most species, which seems to be particularly important for highly functionalized compounds containing multiple carbonyl and nitrate groups (e.g. HKKKK, HHKK, HHKKK, HKKK, NNKK, NNKO where e.g. HHKK refers to a molecule that contains two hydroperoxide and two ketone groups). These species are formed by several generations of chemistry and are mainly found in the particle-phase. Thus their decrease is more likely related to reductions in their precursor species due to photodegradation than to their direct loss by gas-phase photolysis. Some molecules containing alcohol groups (e.g. HHO, HKKO, HHKO) see an increase in their concentrations due to gas-phase photolysis (see also Figure SI-2). This increase can be explained by photolysis of hydroperoxides, which can lead to the formation of alkoxy radicals that can isomerize to form alcohols. Thus photolysis can both contribute to SOA loss and to a lesser extent to its formation. Typically, photolysis of carbonyl compounds (ketone and aldehydes) tends to break the α-carbon bond on either side of the C=O group, leading to smaller more volatile fragments, that are less likely to partition to the particle-phase. On the other hand, photolysis of hydroperoxides and nitrates leads to elimination of -OH or $-NO_2$, leading to alkoxy radicals, and potentially further functionalization of the carbon skeleton favoring formation of less volatile organic compounds, that can partition more readily to the particle.

One of the highly uncertain factors that can influence the composition of SOA at low- NO_X is the choice of the rate for abstracting the H atoms from the carbon atom that is adjacent to the hydroperoxide (-OOH) group. As discussed in Section 2, in this paper we have used a lower activation factor of 3.5 for estimating the rate constant of that process, instead of the GECKO-A default value of 14 (*Aumont et al., 2005*). As shown in Figure SI-4 this change doesn't affect the SOA production when the gas-phase photolysis of organics is turned off (~8 μg m^{-3} for C_{12} n-alkane). However, the composition of SOA formed from n-alkanes is significantly modified, as is the effect of gas-phase photolysis on SOA yields (~ 2x smaller when the value of 3.5 is considered). The main difference is found for HKKKK and HKKK molecules which are much more abundant when the value of 14 is used. These molecules originate typically from the successive OH reaction, leading to an hydroperoxide moieties under low-NO_X condition and their subsequent fast oxidation to a ketone moiety due to a the large activation factor used. Reducing this factor to 3.5 forces the OH to react away from the -OOH group. When the carbon backbone is sparsely functionalized, this increases the rate of production of multifunctional species, in

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particular multifunctional peroxydes (e.g. HHO et HHK). However, when the carbon backbone is highly functionalized, this leads to more fragmentation, because in most cases the OH attack is now next to other functional moieties (e.g. multifunctional ketones).

Figure 3 shows the effect of gas-phase photolysis on oxygen to carbon (O/C) ratios of particles for the BASE run. For all cases, changes in O/C ratios (<0.05) are minor. Slightly higher O/C ratios at low NO_X were found in the presence of gas-phase photolysis as photolyzed fragments are typically smaller and more volatile carbon chains that need to undergo further oxidation to condense into particles. Our results are consistent with chamber studies by Wong et al. (*2014*) that observed small changes in O/C with an increase in more oxidized compounds (high O/C) in α-pinene SOA due to fast photodegradation of less oxidized particulate organics such as carbonyls. Changes in SOA composition due to gas-phase photolysis can also affect the volatility distribution of oxidized organic compounds. Figure 4 doesn't show a clear shift in volatility due to gas-phase photolysis, but rather suggests that the SOA reduction is happening across a wide range of volatility bins.

Our explicit modeling results suggest that gas-phase photolysis leads in some cases to moderate changes in SOA yields (<25% for most precursors; <45% for high-NO_X α-pinene), and small changes in volatility distribution and O/C ratios over 1 equivalent week of chemical aging in the mid-latitude atmosphere in summer or 2.5 weeks in winter. The implication in terms of SOA atmospheric lifetime is that gas-phase photolysis is a possible sink of intermediate organic vapors and thus SOA, although a smaller sink compared to dry deposition of these gaseous species (*Hodzic et al., 2014, Knote et al., 2014*). Indeed, the estimated summertime atmospheric lifetimes against photolysis of the SOA from the four precursors considered in our study range from about 10 days for α-pinene under high-NO_X conditions (unlikely case), to more than a month for α-pinene under low-NO_X conditions or for long chain n-alkane species. These lifetimes are considerably longer than values reported by laboratory studies (*e.g. Henry and Donahue, 2012*).

Current 3D models typically represent the oxidation products as lumped surrogate species based on their volatility that can further age by OH oxidation but cannot photolyze due to the undefined chemical structure of those intermediate species. Our results suggest that omitting their gas-phase photolysis will likely result in reasonably small biases in SOA predictions over urban scales. However, errors could be significant at the global scale in particular in the upper troposphere where models have the tendency to accumulate SOA due to a less efficient wet removal.

3.2 Importance of in-particle photolysis of organics

In the GECKO-A simulations described above, once the organic molecules are partitioned to SOA they are protected from gas-phase photolysis. However, these molecules still contain numerous chromophores (Figure 2) that absorb solar radiation, and could undergo photolysis inside the particle. Optical absorption is also likely to be modified by the heterogeneous formation of high molecular weight compounds inside the particle (*Graber and Rudich, 2006*). As GECKO-A does not include condensed-phase photochemical reactions (or heterogeneous chemistry), the effect of particle-phase photolysis on SOA cannot be calculated directly. In this section, we consider a simple alternative empirical approach to examine the potential effect of particle-phase photolysis within GECKO-A.

We base our estimates of condensed-phase photolysis on measured SOA mass absorption coefficient (*MAC*). Organic particles containing photolabile compounds have been shown to efficiently absorb light at actinic wavelengths. Recently measured *MAC* values range from 0.03 to 0.5 m^2g^{-1} for laboratory data (*Lambe et al.*, 2013) or from 0.1 to 10 m^2g^{-1} for ambient urban measurements (e.g. *Barnard et al., 2008*) in the 300-400 nm wavelength interval. We use those measurements to estimate the condensed-phase photolysis of SOA. We represent the photolytic SOA loss as a first order reaction, with effective reaction rate coefficient J_{SOA}:

$$J_{SOA} = [AF] \times [MAC] \times [mc] \times [QY] \qquad (1)$$

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$$J_{SOA} = J_{NO2} \times [AF/J_{NO2}] \times [MAC] \times [mc] \times [QY] \qquad (1)$$

$$J_{SOA} = J_{NO2} \times [AF/J_{NO2}] \times [MAC] \times [mc] \times [QY]$$

where *AF* is the actinic flux (photons m^{-2} s^{-1}), *MAC* is the SOA mass absorption coefficient (m^2 g^{-1}), *mc* is the mass of one carbon atom (g) and *QY* is the quantum yield or the probability that absorbed photons will lead to bond cleavage and the loss of some mass from the particle. We assume that if each absorbed photon leads to the loss of one C atom, the quantum yield is equal to one. We can scale (1) to known NO_2 photolysis:

$$J_{SOA} = J_{NO2} \times [AF/J_{NO2}] \times [MAC] \times [mc] \times [QY] \qquad (2)$$

The photolysis model TUV (v5.1, (*Madronich et al. 1993*)) was used to estimate the UV actinic flux (= 2×10^{20} photons m^{-2} s^{-1}) and NO_2 photolysis (= 9.7×10^{-3} s^{-1}) over 280-400 nm at 1 km altitude and overhead sun, which combined with [mc] gives $[AF/J_{NO2}] \times [mc] = 0.4$ photons g m^{-2}. Thus the resulting SOA photolysis rate can be written as:

$$J_{SOA} = 0.4 \times J_{NO2} \times [MAC] \times [QY] \qquad (3)$$

To estimate the plausible range of J_{SOA} values, we use the combinations of [MAC] x [QY] reported in the literature. Here we use *MAC* of 0.1 m^2g^{-1} as a lower limit for ambient aerosols. We note that for the chosen MAC value the light can penetrate the whole volume of the particle without being significantly attenuated by the absorbers (light attenuation was estimated to be less than 2-3%, see discussion SI Annex IV). *QY* has only been measured for a handful of species. Calvert and Pitts (*1966*) reported values of 0.01 (or 1%) for photolysis of aldehydes in the aqueous phase. Lignell et al. (*2013*) reported values of 0.5 for cis-pinonic acid, which is one of the constituents of α-pinene SOA, whereas Wong et al. (*2014*) estimated an effective quantum yield of 1.2±0.2 for the loss of organics in the case of α-pinene SOA photolysis. Given the range of values, here we use a conservative value of 0.01 (or 1%) for *QY*. Thus our best estimate for J_{SOA} is 0.04% of J_{NO2}. This value of J_{SOA} is applied as a first order removal rate for each photolabile species in the particle phase. The photo fragments are not longer considered and the condensed phase photolysis is here considered as an irreversible loss of one carbon atom. We

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note that this calculated value is 1-2 order of magnitude lower that those reported by Henry and Donahue (*2012*) who estimated the photolytic loss of SOA as 2% of J_{NO2} (total value of both particle and gas-phase photolysis and J_{NO2} of 3×10^{-3} s^{-1}). In their experiments, Henry and Donahue (*2012*) argued that photolysis is more efficient (higher QY) in the gas-phase than in the particle phase where quenching and caging are more likely to occur and could cause rapid recombination of fragments. Therefore a lower *QY* may be expected in the particles, although it is unclear whether similar molecules are involved in photolysis in the two phases. We also note that photolysis of SOA is assumed to not occur at visible wavelengths (i.e. QY = 0 for $\lambda > 400$ nm).

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Figure 5 shows that considering the above estimated condensed-phase photolytic loss of SOA ($J_{SOA} = 4\times10^{-4}\times J_{NO2} = 3.2\times10^{-6}$ s^{-1}; lifetime of 7 days at equivalent J_{NO2} atmospheric exposure, see Table 1) in GECKO-A simulations leads to a 40-60% decrease in SOA mass after ten days of equivalent atmospheric aging for most species (J_{mac} run, Figures 5 and SI-1). A more limited decrease (15%) is found for the high-NOx toluene SOA because the photolytic loss of nitroaromatic compounds, which are predicted to be the major SOA constituents (RVVO in Figure 2), is not included.

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For comparison, the effect of applying the gaseous photolysis rates for the corresponding species in the condensed phase is shown in Figure 5 ($J_{molecmax}$). Similar to the simulations above based on MAC, the photolysis is here again considered as an irreversible loss of organic carbon. The comparison between J_{mac} and $J_{molecmax}$ shows a fairly similar (within 20%) reduction in SOA mass for most precursors. The $J_{molecmax}$ 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, $J_{molecmax}$ 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*). In-particle reactions are likely to modify the chemical composition of the particle, and therefore change the amount of photolabile species. For example, the work of Yee et al. (*2012*) and Schilling-Fahnestock et al. (*2014*) indicate extensive formation of peroxyhemiacetals in the SOA from dodecane oxidation at low NO_X. However, the precursor molecules are third and fourth generation products, which contain additional, unfunctionalized ketone groups, which would still be susceptible to photolysis.

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The overall SOA loss rate due to the combined effect of gas- and particle-phase photolysis (and ongoing OH chemistry) in GECKO-A runs was estimated for the J_{mac} simulations (see Table 4). Values range between 3.1×10^{-6} and 5.6×10^{-6} s^{-1}, which translates to equivalent atmospheric SOA lifetimes of 4 to 8 days with regard to photolysis in the summer, except for high-NO_X toluene SOA with a lifetime of 20 equivalent summer days for which the effect of photolysis is likely underestimated in our simulations as discussed above. The estimated SOA lifetime with regard to photolysis is comparable or even shorter to the typical ~1 week aerosol atmospheric lifetime which suggests that photolysis may be an important removal mechanism for atmospheric SOA. Atmospheric implications of our findings are further investigated in section 3.3.

The above estimates for the α-pinene SOA photolytic loss rate cannot be directly compared with those of Henry and Donahue (*2012*) and Wong et al. (*2014*) due to several factors including: (i) the differences in the chemical composition of particles as the experiments typically use the SOA pre-generated by α-pinene ozonolysis for short (few hours) exposure, whereas in our simulations the SOA is generated mainly by OH oxidation, and over a much longer time period (> 1 week); (ii) the possible evaporation of SOA in the laboratory experiments due to chamber heating under the UV lamps, which was not quantified in those experiments and which does not occur in our model simulations; (iii) in-particle chemistry that could modify the composition and absorption properties of the SOA and which is not included in our model, and is generally not well understood.

For comparison with previous laboratory work, we ran the model under conditions similar to Henry and Donahue (*2012*), in which α-pinene was oxidized by ozone in the dark in the presence of hydrogen peroxide, and then the mixture was exposed to UV black lights as in Presto et al. (*2005*) and/or to OH oxidation. Figure 6 shows the sensitivity of the aerosol mass to assumed photolysis rates for these conditions. The experiment is performed for 5 hours at the constant J_{NO2} of 3×10^{-3} s^{-1} which corresponds to 4 hours of equivalent summertime atmospheric exposure (Table 1). Our results show that when exposed to only OH reactions (photolysis of organics was turned off), SOA concentrations increase by ~35% in 5 hours of aging. On the other hand, SOA exposed to only photolytic reactions (no OH) decrease by ~7% over the simulation period. The combined effect of both photolytic and OH reactions is therefore an overall increase in SOA concentrations by ~30%. As done previously we also performed a sensitivity simulation in which all molecules can photolyze in both gas- and particle-phases at the gas-phase rate. Figure 6 shows that with those reactions the SOA concentrations are decreased by ~50% ($J_{molecmax}$) in 5 hours. These results suggest that most of the photolabile molecules are partitioned to the particle phase where they are protected from gas-phase photolysis. The corresponding loss rate due to the combined effect of gas- and particle-phase photolysis and OH oxidation, is 3.4×10^{-5} s^{-1}, which is within a factor of 2-3 of the values reported by Henry and Donahue (*2012*) and Wong et al. (*2014*).

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3.3 Potential effect of photolysis on global SOA budget and lifetime

We implement the estimated SOA gas-phase and in-particle photolytic loss rates within the GEOS-Chem global chemistry model (*Bey et al., 2001*) to investigate the regional and global effect of photolytic reactions on SOA concentrations. The GEOS-Chem model configuration used in this study is described in detail by Jo et al. (*2013*). In particular, SOA is modeled using volatility basis set approach with aging in which oxygenated semi-volatile organic compounds (SVOC) formed by the gas-phase reaction of nine lumped hydrocarbon species (representing monoterpenes, sesquiterpenes, isoprene, and aromatic compounds) with OH, O_3, and NO_3 are partitioned between gas and particle phases using 4 volatility bins (with saturation vapor pressures ranging from 1-1000 $\mu g\ m^{-3}$ at 300K). Chemical aging of anthropogenic SVOC with OH (with a rate constant of $4x10^{-11}\ cm^3\ molecules^{-1}\ s^{-1}$) is assumed to reduce the vapor pressure of the products by one order of magnitude. It should be noted that, similar to previous studies, gas-phase photolysis of these intermediate species is not included. Model simulations are performed for year 2009.

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Figure 7 shows the annual mean SOA concentrations predicted by the default GEOS-Chem run within the lower troposphere (below 5 km). The predicted continental background levels of SOA typically vary between 0.2 and 0.4 $\mu g\ m^{-3}$, and the highest concentrations (>1.5 $\mu g\ m^{-3}$) are found over tropical forest regions of Africa and South America. Industrialized and urban areas in China, Europe and the U.S. feature SOA values significantly larger (0.5-1.5 $\mu g\ m^{-3}$) than the background. These SOA values and spatial distribution are consistent with previous studies (*e.g. Spracklen et al., 2011; Jo et al., 2013*). Our results (Figure 7b) suggest that gas-phase photolysis of intermediate semi-volatile organic compounds leads to a very small (< 4%) reduction in SOA concentrations under ambient conditions. A much larger impact on SOA concentrations is predicted for in-particle photolysis. When the previously estimated photolytic loss of 0.04% J_{NO2} is applied within the GEOS-Chem model, the annual mean SOA concentrations in the lower troposphere are decreased by ~20-30% over source regions, and up to 60% over remote regions (Figure 8a). The absolute decrease is ~0.3 $\mu g\ m^{-3}$ over land and ~0.1 $\mu g\ m^{-3}$ over oceans, with the highest absolute decrease of 0.6 $\mu g\ m^{-3}$ coinciding with the maximum predicted SOA concentrations over Africa (Figure 7c). As the quantum yield of the particle-phase photolysis and mass absorption coefficients are highly uncertain, here we also consider an order of magnitude higher photolytic loss rate of 0.4% J_{NO2}. As shown in Figure 8c, this increase in J_{SOA} results in a larger reduction of SOA concentrations in the lower troposphere reaching 50-70% over land

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surfaces, and up to 70-90% over water surfaces. In both cases, a strong spatial gradient is found between land and water surfaces, with larger relative reductions in SOA concentrations over oceans. This gradient is due to the continuous photolytic losses, the effect of which accumulates further away from source regions. 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).

Our results suggest that photolysis of SOA, which is currently ignored in chemistry-climate and air quality models, could be an efficient removal process for organic particles. The diagnosed SOA tropospheric lifetime against photolytic removal (annual-average tropospheric mass burden divided by the annual tropospheric loss due to photolysis) ranges from 1 day for J_{SOA}=0.4% J_{NO2} to 7 days for J_{SOA}=0.04% J_{NO2}, and is comparable to the lifetime associated with the SOA wet deposition which ranges from 3.5 to 5.5 days in these model runs. 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.

4 Conclusions

In this study, we investigated the sensitivity of SOA formation and aging in the atmosphere to gas-phase and in-particle photolysis reactions of organic compounds that actively partition between gas and particle phases. We apply the explicit chemistry model GECKO-A to simulate SOA formation from OH oxidation of α-pinene, toluene, and C_{12} and C_{16} n-alkane precursors, and to explore the sensitivity of this formation to gas-phase photolysis explicitly calculated in the model. Our simulations are conducted for typical mid-latitude conditions (Boulder, CO) and a solar zenith angle of 45° under a week of permanent daylight. The results suggest that photolysis of intermediate organic compounds in the gas-phase leads to a moderate decrease in SOA yields i.e ~15% (low-NOx) to ~45% (high-NOx) for α-pinene, ~15% for toluene, ~25% for C_{12} n-alkane, and ~10% for C_{16} n-alkane during 8 days of equivalent atmospheric exposure in the summer or 3 weeks in winter. This decrease depends on the aerosol chemical composition under various NO_X levels, and the amount of photolabile molecules. SOA formed from precursors considered here contained substantial amount of photolabile molecules, many of which were partitioned to the particle-phase before they could undergo gas-phase photolysis.

We performed sensitivity studies to estimate the potential effect of condensed-phase photolysis on SOA formation by applying an empirical J_{SOA} rate of $4\times10^{-4}\times J_{NO2}$ s^{-1} to formed particles. Our results suggest that condensed-phase photolysis might have a substantial effect on SOA formation and subsequent aging, with a decrease of 40-60% in SOA yields over ten days of equivalent atmospheric aging at mid-latitudes in the summer.

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Explicit modeling of a typical α-pinene ozonolysis SOA aging experiment was also performed using GECKO-A. The results show a minor decrease (~7%) in SOA concentrations in 5 hours of the aging experiment due to gas-phase photolysis of organic vapors under black UV lights. The SOA decrease is much more pronounced (~50%) during the experiment when particle-phase photolysis was added using the gas-phase rates. The corresponding loss rate due to the combined effect of gas- and particle-phase photolysis is 3.4×10^{-5} s^{-1}, which is within a factor of 2-3 of the values reported by Henry and Donahue (*2012*) and Wong et al. (*2014*).

These photolysis processes were parameterized in a global chemistry model, and the results suggest that condensed-phase photolytic reactions of organic aerosols could be an important loss process in the atmosphere, removing SOA from the troposphere on timescales of ~7 days which is comparable to those for wet deposition. In comparison, the gas-phase photolysis of semi-volatile organic compounds had a much smaller effect on SOA concentrations. 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.

We note that the absorption by organic gases and/or particles is not expected to substantially affect the radiation field itself. Even in highly polluted conditions, aerosol optical depth (AOD) rarely exceeds 2, and only a fraction (1 minus the single scattering albedo (SSA)) is absorbed e.g. AOD=2 and SSA=0.9 gives an absorption optical depth of 0.2, corresponding to about 20% reduction in radiation. This is a significant but not overwhelming reduction, so that even under these highly polluted conditions the photochemistry is expected to proceed vigorously. Regional and global effects are expected to be smaller.

The implications of our results in terms of SOA modeling are twofold: (i) gas-phase photolysis of intermediate organic vapors which are currently ignored in most models, are likely to have a moderate impact on SOA yields over typical aerosol lifetimes in the atmosphere; (ii) in-particle photolysis could be a major sink for SOA if the quantum yields are substantial, and these need to be better constrained from measurements and included in 3D models. It is also worth noting that a substantial sink due to in-particle photolysis would imply that our current estimates of SOA formation rates would have to be revised upwards to be consistent with observed atmospheric SOA burdens. 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.

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Figures:

Figure 1: SOA formation from the oxidation by OH of 1 ppt of α-pinene, toluene, C_{12} and C_{16} n-alkanes at low (0.01 ppb) and high (10 ppb) NOx levels. Plots compare GECKO-A simulations with (dashed lines) and without (full lines) gas-phase photolysis of organics at the solar zenith angle of 45° (mid-latitudes) at constant daylight. To derive equivalent atmospheric summertime exposure of our experiment, the time axes should be multiplied by a factor of 2 (see Table 1). Reference simulation (BASE) is shown in black, and is compared to two sensitivity simulations testing for higher OH levels (SENS_OH in orange) and lower absorbing organic aerosol mass (SENS_OA in blue). See Table 2 for the description of various runs. 32

Figure 2: Particle-phase dominant functional groups in the top fifteen SOA constituents shown at the maximum of the SOA yield. The BASE case simulations with (red bars) and without (blue bars) photolysis of organic compounds are compared. The carbon atom ratio indicates the ratio of the carbon atoms in the condensed phase to the initial carbon load included in the parent backbone. The sum of the shown particle-phase constituents is lower than one as the rest of the carbon mass is in the gas-phase. 33

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Figure 6: GECKO-A simulation of a typical SOA aging experiment. SOA is first made in the dark in 2h from α-pinene ozonolysis in the conditions where the formation of hydroperoxides dominates (through RO_2+HO_2 reactions). After the 2nd hour the initial precursor has been consumed, and the SOA mixture is exposed to various conditions: (REF, black) UV black lights and OH of 10^6 molecules cm^{-3}; (J_{off}, red) only OH oxidation with OH=10^6 molecules cm^{-3} and photolysis are turned off for organic compounds; (OH_{off}, cyan blue) only UV black lights; ($J_{molecmax}$, orange) similar to the REF case, but the photolysis of organic

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molecules is performed also in the condensed phase. The UV lamp is that of Presto et al. (2005), with $J_{NO2}=3x10^{-3}\ s^{-1}$, NOx levels are kept at 0.01 ppb, and ozone levels are set at 50ppb during the aging simulations. SOA loss rates reported in the experiments are also shown in shaded purple areas with slopes corresponding to (1) Henry and Donahue (2012) ($6\times10^{-5}\ s^{-1}$), (2) Wong et al. (2014) for dry conditions ($7.9\times10^{-5}\ s^{-1}$) and (3) Wong et al. (2014) for humid conditions ($1.6\times10^{-4}\ s^{-1}$). 37

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). 39

Tables

Table 1: Photolysis rate coefficients and photolytic lifetimes for typical atmospheric conditions and for our simulations. Typical ozone overhead values are used at different locations based on the Total Ozone Mapping Spectrometer data (http://disc.sci.gsfc.nasa.gov/acdisc/TOMS).

Typical Conditions		**Average J_{NO2} (s^{-1})**	**Average J_{O1D}(s^{-1})**	**Average $J_{NO3\text{->}NO2+O}$ (s^{-1})**
Boulder CO, summer solstice	40°N, sea level, June 21, $O_{3col.}$=310DU, 10% ground albedo, no aerosols, no clouds	4.1×10^{-3}	1.0×10^{-5}	9.1×10^{-2}
Boulder CO, winter solstice	40°N, sea level, Dec 21, $O_{3col.}$=330DU, 10% ground albedo, no aerosols, no clouds	1.5×10^{-3}	1.2×10^{-6}	4.6×10^{-2}
Equator June 21	Sea level, $O_{3col.}$=260DU, 5% ground albedo, no aerosols, no clouds	3.3×10^{-3}	1.0×10^{-5}	7.3×10^{-2}
Equator March 21	Sea level, $O_{3col.}$=258DU, 5% ground albedo, no aerosols, no clouds	3.6×10^{-3}	1.3×10^{-5}	7.8×10^{-2}
Hyytiala, summer solstice	61°N, June 21, $O_{3col.}$=355DU, 5% ground albedo, no aerosols, no clouds	4.3×10^{-3}	6.2×10^{-6}	1.0×10^{-1}
Hyytiala, winter solstice	61°N, Dec. 21, $O_{3col.}$=355DU, 90% ground albedo, no aerosols, no clouds	2.6×10^{-4}	5.8×10^{-8}	1.0×10^{-2}

Model Simulation		**Average J_{NO2} (s^{-1})**	**Average J_{O1D}(s^{-1})**	**Average $J_{NO3\text{->}NO2+O}$ (s^{-1})**	**Photolysis Age in J_{NO2} equivalent days**	
					Boulder, CO summer solstice	**Boulder, CO winter solstice**
GECKO-A 1 week simulations (Table 2)	40°N, 45° solar zenith angle, 7 days	8.1×10^{-3}	2.1×10^{-5}	1.8×10^{-1}	14 eq. days	38 eq. days
GECKO-A α-pinene ozonolysis SOA (Figure 6)	Black lights, 5 hours	3.0×10^{-3}	1.2×10^{-5}	2.1×10^{-3}	0.15 eq. days (3.7 eq. hours)	0.42 eq. days (10 eq. hours)
Henry and Donahue (*2012*)	Black lights, 5 hours	3.0×10^{-3}	-	-	0.15 eq. days (3.7 eq. hours)	0.42 eq. days (10 eq. hours)

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Table 2: Description of GECKO-A simulations.

Experiments for SOA formed from α-pinene, toluene, C_{12},C_{16} n-alkane				
	Gas-phase photolysis of organics	Particle-phase photolysis	OH (molecules cm^{-3})	OA background ($\mu g\ m^{-3}$)
BASE	ON/OFF	OFF	$2x10^6$	10
SENS_OA	ON/OFF	OFF	$2x10^6$	1
SENS_OH	ON/OFF	OFF	$8x10^6$	1
$J_{molecmax}$(*)	ON	ON as gas-phase J	$2x10^6$	10
J_{mac}	ON	ON as 0.04% J_{NO2}	$2x10^6$	10

(*) Radical species that are produced by photolysis inside the particle are assumed to be permanently lost to the gas-phase.

Table 3: Predicted reduction in SOA yields due to gas-phase photolysis, and corresponding first order loss rates and lifetimes. The results are from the GECKO-A BASE case simulation, and yields values are taken at the maximum of the SOA formation from each precursor. The loss rate coefficients were estimated by numerically fitting the first order decay of SOA due to photolysis occurring over one week of processing at constant light (J_{NO2}=$8.1x10^{-3}$ s^{-1}). Low (0.01 ppb) and high (10 ppb) NOx simulations are shown.

Considered System	Reduction in SOA yields by gas-phase photolysis		Estimated loss rate (s^{-1})		Estimated lifetime (days, under simulation conditions*)	
	Low NOx	High NOx	Low NOx	High NOx	Low NOx	High NOx
α-pinene + OH	-16%	-47%	4.6×10^{-7}	2.1×10^{-6}	25.0	5.4
Toluene + OH	-11%	-13%	5.6×10^{-7}	4.3×10^{-7}	20.8	27.0
$C_{12}H_{26}$ + OH	-30%	-28%	1.2×10^{-6}	1.1×10^{-6}	9.3	10.4
$C_{16}H_{34}$ + OH	-10%	-13%	3.6×10^{-7}	3.7×10^{-7}	30.0	31.0

(*) To derive equivalent atmospheric loss rates (lifetimes) at mid-latitudes values should be divided (multiplied) by a factor of 2 in summer and 5.4 in winter which is the ratio between J_{NO2} used in our experiment and the typical atmospheric values.

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Table 4: Estimated loss rates and lifetimes due to gas-phase and in-particle phase photolysis as predicted by GECKO-A for the *Jmac* simulation over one week of aging at constant light (J_{NO2}=8.1x10^{-3} s^{-1}).

Considered System	Estimated loss rate (s^{-1})		Estimated lifetime (days, under simulation conditions*)	
	Low NOx	High NOx	Low NOx	High NOx
α-pinene + OH	3.7×10^{-6}	5.6×10^{-6}	3.1	2.1
Toluene + OH	3.1×10^{-6}	1.1×10^{-6}	3.7	10.5
$C_{12}H_{26}$ + OH	4.7×10^{-6}	4.4×10^{-6}	2.5	2.6
$C_{16}H_{34}$ + OH	3.7×10^{-6}	3.5×10^{-6}	3.1	3.3

(*) To derive equivalent atmospheric loss rates (lifetimes) at mid-latitudes values should be divided (multiplied) by a factor of 2 in summer and 5.4 in winter which is the ratio between J_{NO2} used in our experiment and the typical atmospheric values.

Figures

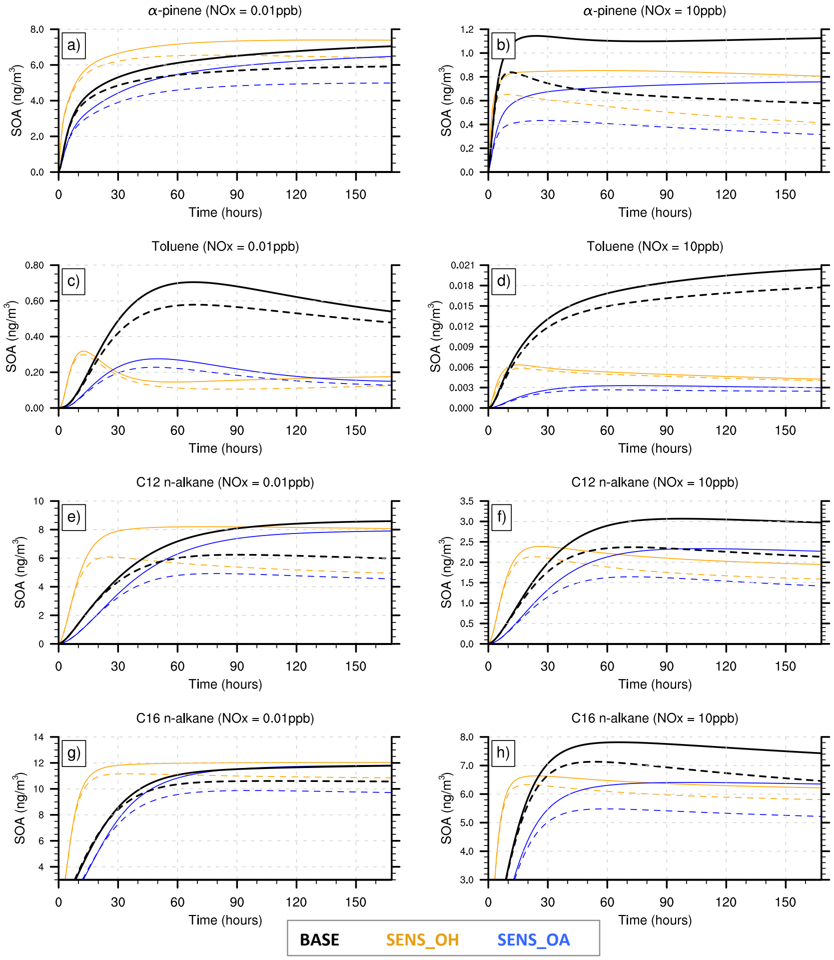
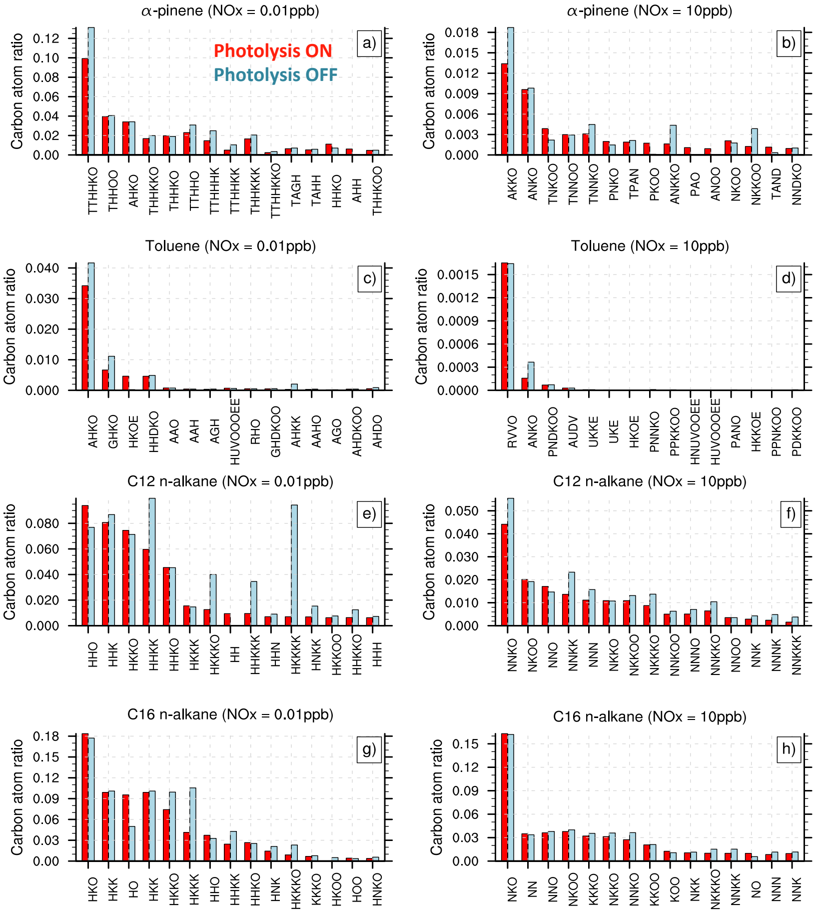


Figure 1: SOA formation from the oxidation by OH of 1 ppt of α-pinene, toluene, C_{12} and C_{16} n-alkanes at low (0.01 ppb) and high (10 ppb) NOx levels. Plots compare GECKO-A simulations with (dashed lines) and without (full lines) gas-phase photolysis of organics at the solar zenith angle of 45° (mid-latitudes) at constant daylight. To derive equivalent atmospheric summertime exposure of our experiment, the time axes should be multiplied by a factor of 2 (see Table 1). Reference simulation (BASE) is shown in black, and is compared to two sensitivity simulations testing for higher OH levels (SENS_OH in orange) and lower absorbing organic aerosol mass (SENS_OA in blue). See Table 2 for the description of various runs.



(A) Acid; (D) aldehyde; (H) hydroperoxide; (G) peracid; (K) ketone; (N) nitrate; (O) hydroxy; (P) PAN; (R) aromatic ring; (T) non-aromatic ring; (U) unsaturated; (V) = nitro

Figure 2: Particle-phase dominant functional groups in the top fifteen SOA constituents shown at the maximum of the SOA yield. The BASE case simulations with (red bars) and without (blue bars) photolysis of organic compounds are compared. The carbon atom ratio indicates the ratio of the carbon atoms in the condensed phase to the initial carbon load included in the parent backbone. The sum of the shown particle-phase constituents is lower than one as the rest of the carbon mass is in the gas-phase.

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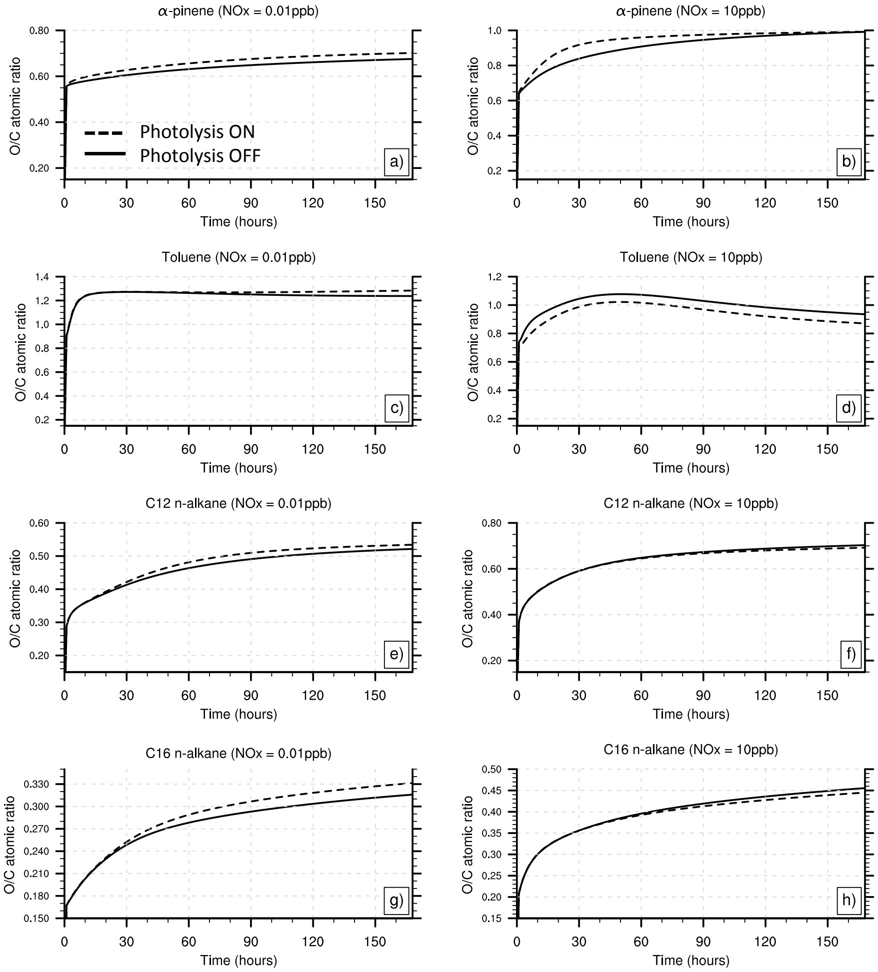
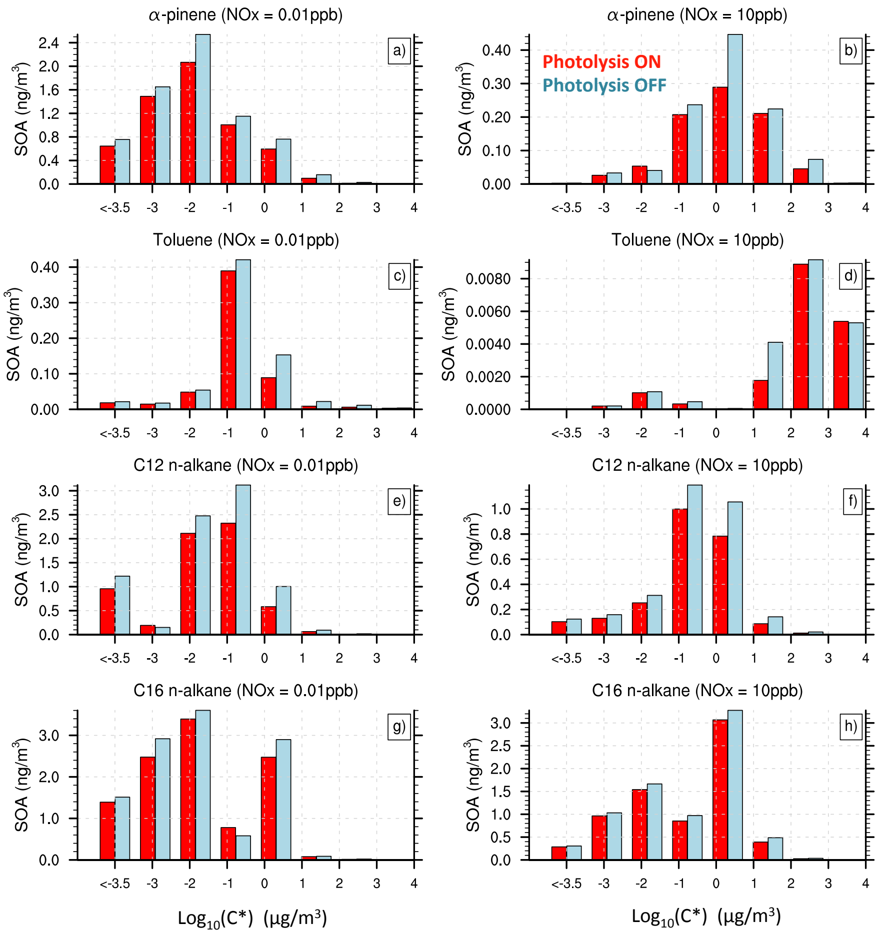


Figure 3: Oxygen to carbon (O/C) ratios as predicted by the BASE case simulation with (dashed lines) and without (full lines) gas-phase photolysis of organics.



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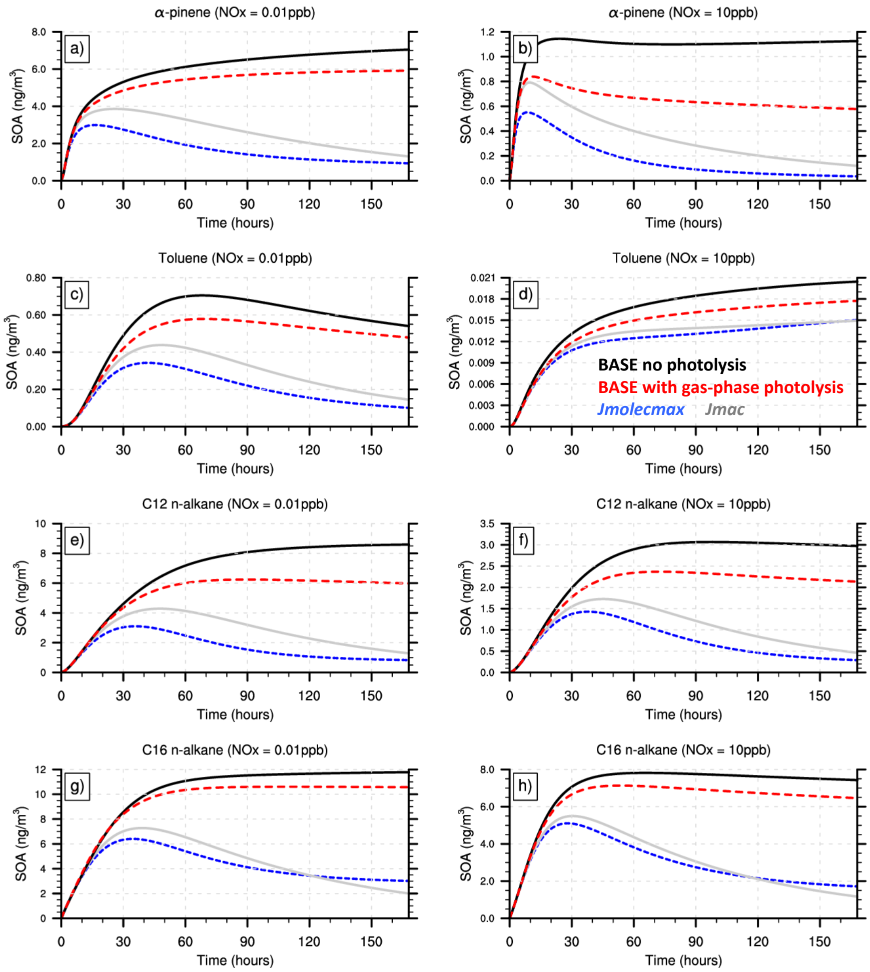

Figure 5: Predicted effect of photolysis on SOA concentrations from the oxidation of 1 ppt of α-pinene, toluene, C_{12} and C_{16} n-alkanes at low (0.01 ppb) and high (10 ppb) NO_X levels. Plots compare GECKO-A simulations for the BASE no photolysis run (black), BASE run with gas-phase photolysis (red), $J_{molecmax}$ (blue) and J_{mac} (gray). To derive equivalent atmospheric summertime exposure of our experiments, times should be multiplied by a factor of 2 (Table 1). See Table 2 for the description of various runs.

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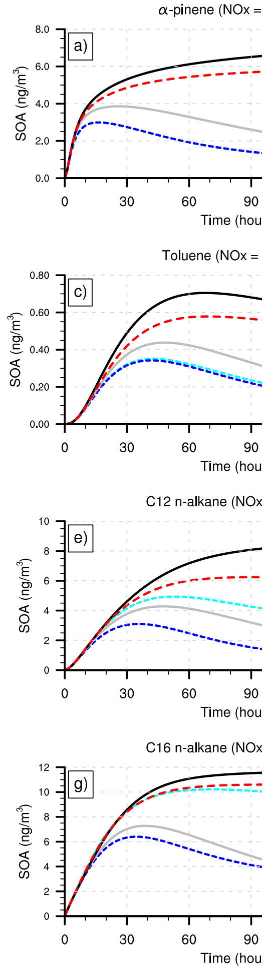

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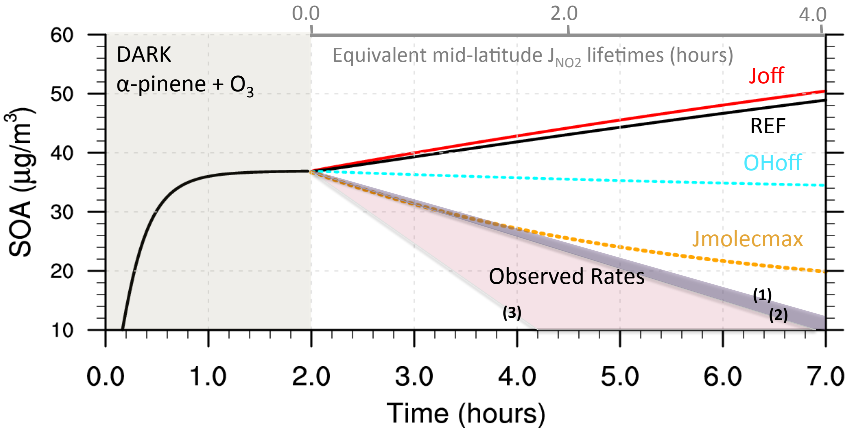

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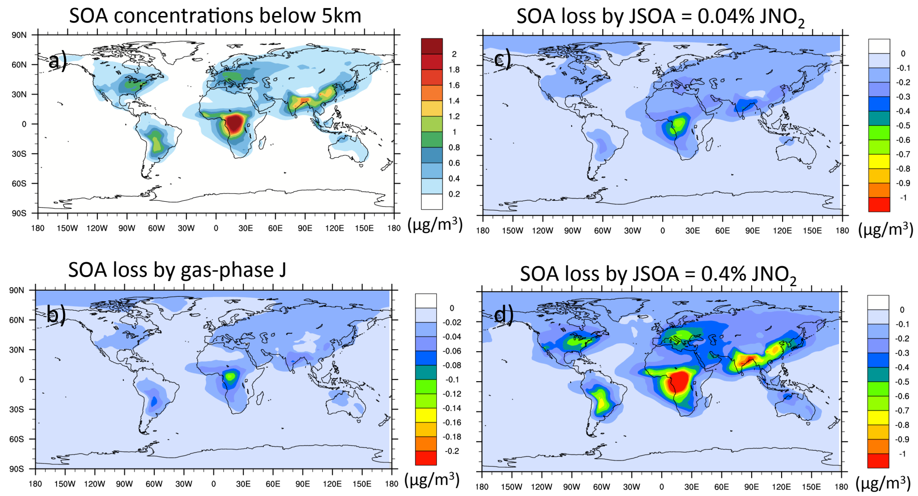

Figure 7: GEOS-Chem simulation for 2009 showing (a) the SOA concentrations within the lower troposphere (below 5km), and the absolute (µg m^{-3}) reductions in SOA concentrations due to gas-phase (b) and particle-phase (c, d) photolysis. Gas-phase photolysis is applied to semi-volatile organic compounds using the e-folding J lifetime of 20 days as estimated in Table 3. Two in-particle photolysis rates are considered i.e. J_{SOA} of 0.04% J_{NO2} (c), and J_{SOA} of 0.4% J_{NO2} (d).

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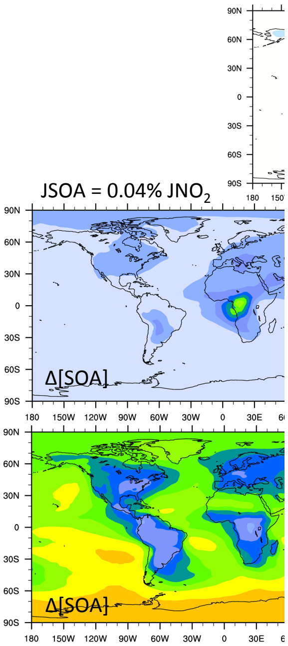

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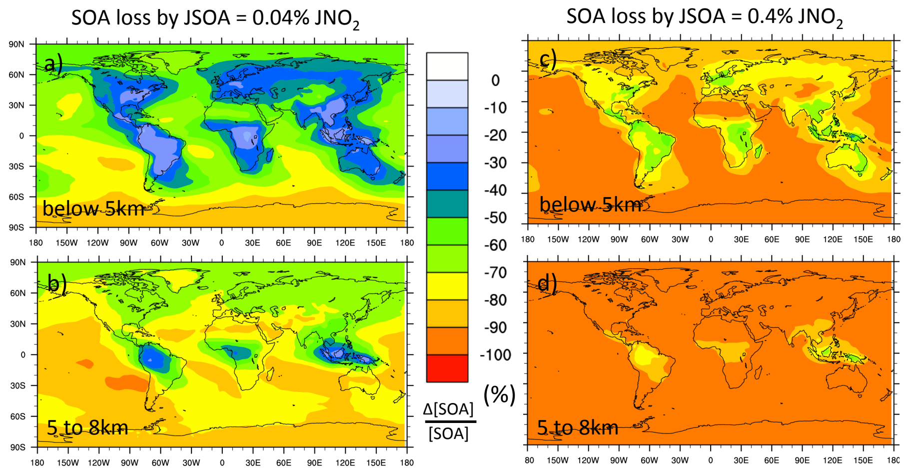

Figure 8: Relative reductions (%) in SOA concentrations due to particle-phase photolysis in the lower (a, c) and upper (b, d) troposphere. Two in-particle photolysis rates are considered i.e. J_{SOA} of 0.04% J_{NO2} (left side), and J_{SOA} of 0.4% J_{NO2} (right side).

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