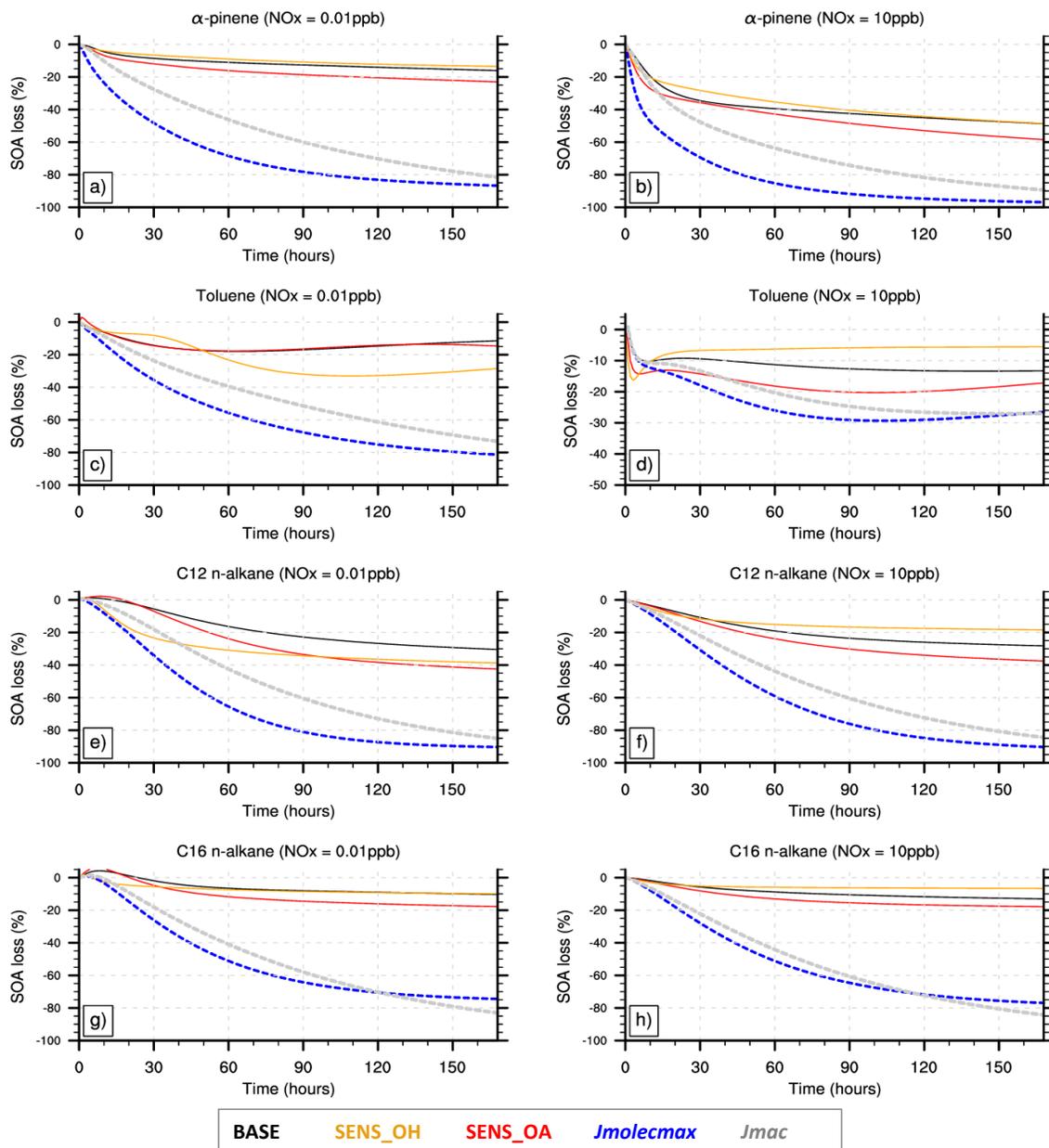


1 Supporting Information

2 Annex I: Percent change in SOA concentrations and composition

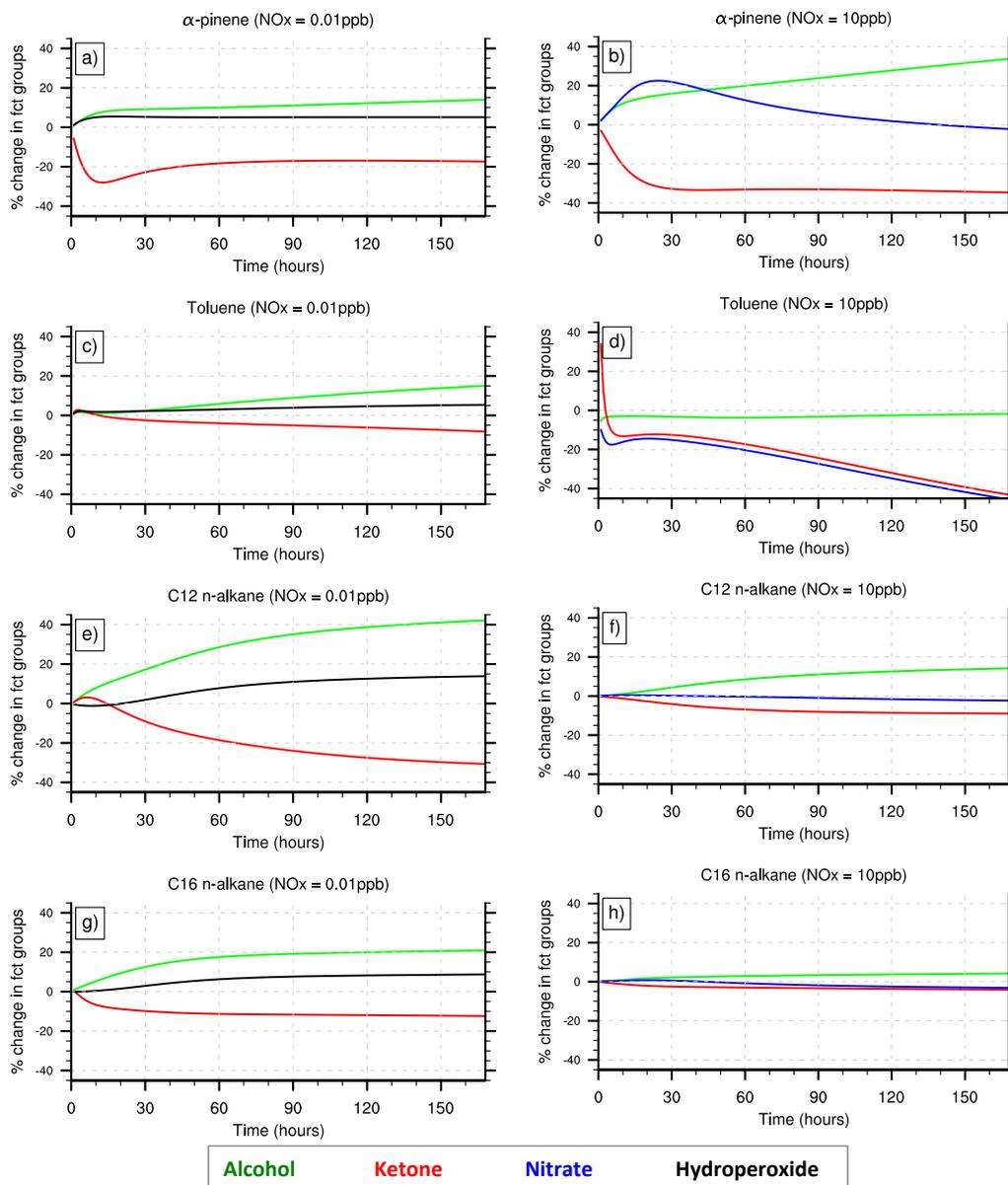


3

4 Figure S1: Percent change in SOA concentrations due to photolytic reactions in the gas phase
5 (BASE, SENS_OH and SENS_OA runs) and in the condensed phase ($J_{molecmax}$ and J_{mac} runs).

6 These simulations are all compared to the reference BASE dark simulation.

7



8

9 Figure S2: Percent change in functional groups (# per carbon) found in the particle phase due to
 10 gas-phase photolytic reactions of organic compounds. Results are for the BASE run, and the
 11 percentage represents $(J_{ON} - J_{OFF}) / J_{OFF}$. Functional groups which absolute values are close to zero
 12 are not shown (e.g. nitrate at low NO_x, hydroperoxides at high NO_x, and aldehydes).

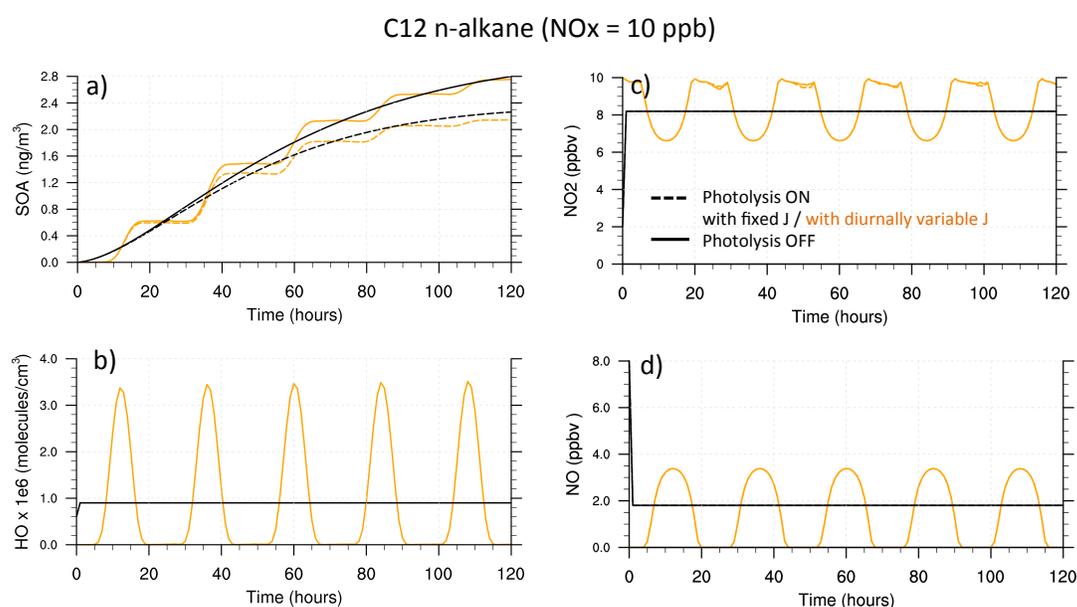
13

14 Annex II: Sensitivity to diurnal cycle in J values

15 Additional sensitivity simulations were performed to verify whether the sensitivity to
16 gas-phase photolysis of the considered chemical systems changes between simulations
17 assuming a permanent daylight (fixed J values like in the manuscript) vs. simulation
18 considering a diurnal cycle for J values.

19 As shown on Figure S3, the response to gas-phase photolysis is very similar between the
20 two sets of runs, with a decrease in SOA concentrations of about 20%.

21

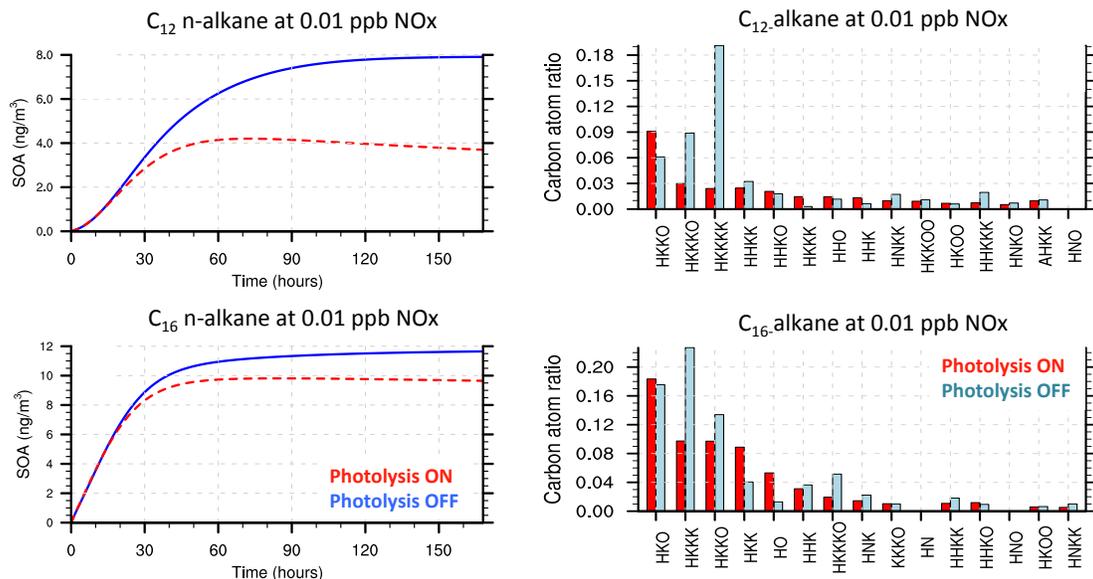


23 Figure S3: GECKO-A predicted SOA concentrations for the oxidation of C12 n-alkanes at high
24 NO_x). Two types of simulations are shown i.e. in orange, simulations with daily varying
25 photolysis values predicted by GECKO-A for Boulder (June 21), and in black, simulations with
26 fixed J rates using the daily average J values from the previous run. In all simulations NO_x was
27 set to 10 ppb, and O₃ to 40 ppb. In the diurnally varying simulations, OH was free running,
28 whereas in the fixed J simulations OH was set to the diurnal average value of the previous run.

29

30

31 **Annex III: Choice of hydroperoxide rate constant**



A = acid; H = hydroperoxide; K = ketone; N = nitrate; O = hydroxy

32

33 Figure S4: Sensitivity of the results to the choice of the hydroperoxide rate constant at low NO_x
 34 conditions for C₁₂ and C₁₆ n-alkane precursors. Sensitivity simulations are similar to the BASE
 35 case run, except that the rate for abstracting the H in -OOH in hydroperoxides was changed to 14
 36 (which was the default value used in GECKO-A up to now (Aumont *et al.*, 2005)). In the BASE
 37 case simulation (and throughout this paper) the used value is 3.5.

38

39

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

41

42 1) Method 1:

43

44 The light attenuation can be roughly estimated as a ratio between the absorption cross
45 section of the particle and its physical cross section. Here we assume a typical organic
46 particle with $MAC = 0.1 \text{ m}^2 \text{ g}^{-1}$, 200 nm diameter and 1.5 g/cm^3 density.

47

48 Its optical cross section is $MAC \times \text{mass of particle} = 0.1 \times 6.3 \times 10^{-15} \text{ m}^2$, whereas its
49 geometric cross section is $\pi r^2 = 3.1 \times 10^{-14} \text{ m}^2$. Thus, the ratio between optical and
50 geometric cross section is ~ 0.02 , meaning that about 2% of photons are absorbed by the
51 particle, and that the rest will go through the particle.

52

53 A more accurate estimate could be derived from the Mie theory, but the corrections due
54 to the full theory are typically within a factor of 2 (Ray and Bhanti, 1997; Mayer and
55 Madronich, 2004), and thus that is not required in this case.

56

57 For comparison, for soot $MAC = 10 \text{ m}^2 \text{ g}^{-1}$ and the ratio optical/geometric = 2, suggesting
58 that substantial attenuation is expected to occur within the particle.

59

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

62

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

65

66 2) Method 2:

67

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

69

$$70 \quad I/I_0 = \exp(-MAC \times \rho \times L) \quad (1)$$

71

72 Where MAC represents the mass absorption coefficient ($\text{m}^2 \text{ kg}^{-1}$), ρ density of the particle
73 (g cm^{-3}), and L the particle diameter (m).

74

75 If we consider a particle with $MAC = 0.1 \text{ m}^2 \text{ g}^{-1}$, $\rho = 1.5 \text{ g cm}^{-3}$, and $L = 2 \times 10^{-5} \text{ cm}$, we
76 can calculate $I/I_0 = 0.9704$, which means that $\sim 97\%$ of the initial signal was transmitted.

77

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

81

82