

1 Supplementary material for the manuscript:

2

3 **The link between organic aerosol mass loading and degree**
4 **of oxygenation: An α -pinene photooxidation study**

5

6 **L. Pfaffenberger, P. Barmet, J. G. Slowik, A. P. Praplan, J. Dommen, A. S. H.**
7 **Prévôt and U. Baltensperger**

8 Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen, Switzerland

9 Correspondence to: A. S. H. Prévôt (Andre.Prevot@psi.ch)

10

11

12 **Table S 1:** Overview of the HONO input into the smog chamber before switching on the
13 lights. The last column contains the ratio between HONO and α -pinene initial concentrations.

14

Expt. No.	initial HONO ppbv ($\pm 10\%$ instrument accuracy)	α -pinene ppbv	HONO / α -pinene
1	1.6	7	0.2
2	4.9	14	0.4
3	1.0	20	0.05
4	1.0	22	0.05
7	1.9	45	0.04
8	2.8	46	0.06
9	5.1	50	0.1

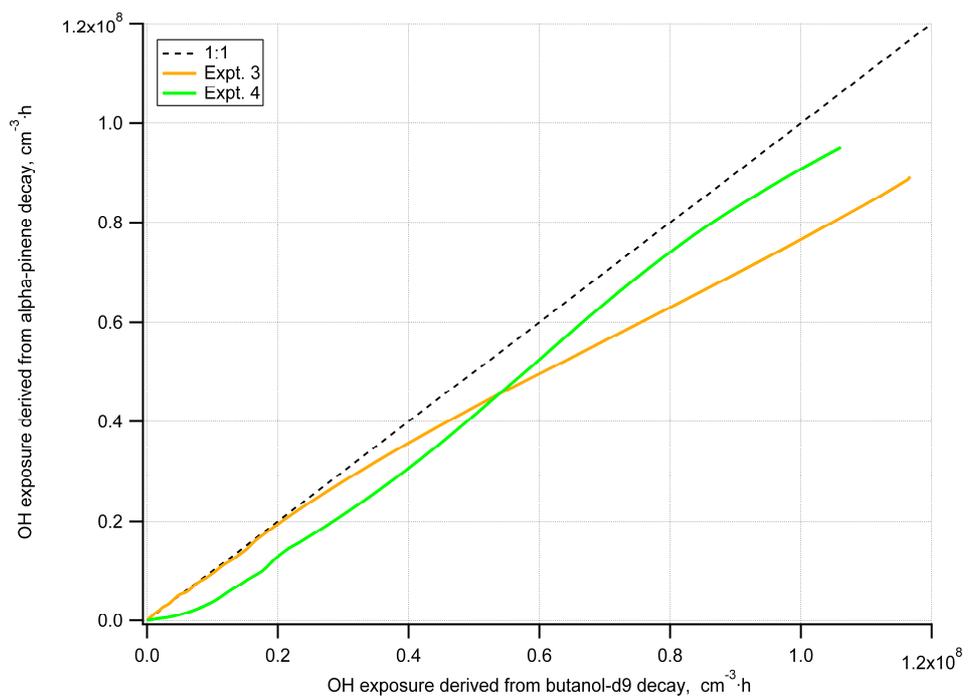
15

16

17 **Table S 2:** Slope of $\Delta f_{44}/\Delta(\text{OH exposure})$ for the period where aging dominates (see Fig. S6)
18 and the OH exposure needed to increase f_{44} by 1%.

Expt. No.	$\Delta f_{44}/\Delta(\text{OH exposure})$ $\cdot 10^{-8} \% \cdot \text{cm}^3 \cdot \text{h}^{-1}$	$\Delta \text{OH exposure}/\Delta f_{44}$ $\cdot 10^7 \cdot \text{cm}^{-3} \cdot \text{h} / \%$
8	2.0	5.1
3	2.1	4.7
2	3.3	3.1
4	3.5	2.8
9	3.7	2.7
1	3.9	2.6
6	5.5	1.8
7	5.7	1.8
5	8.6	1.2

19



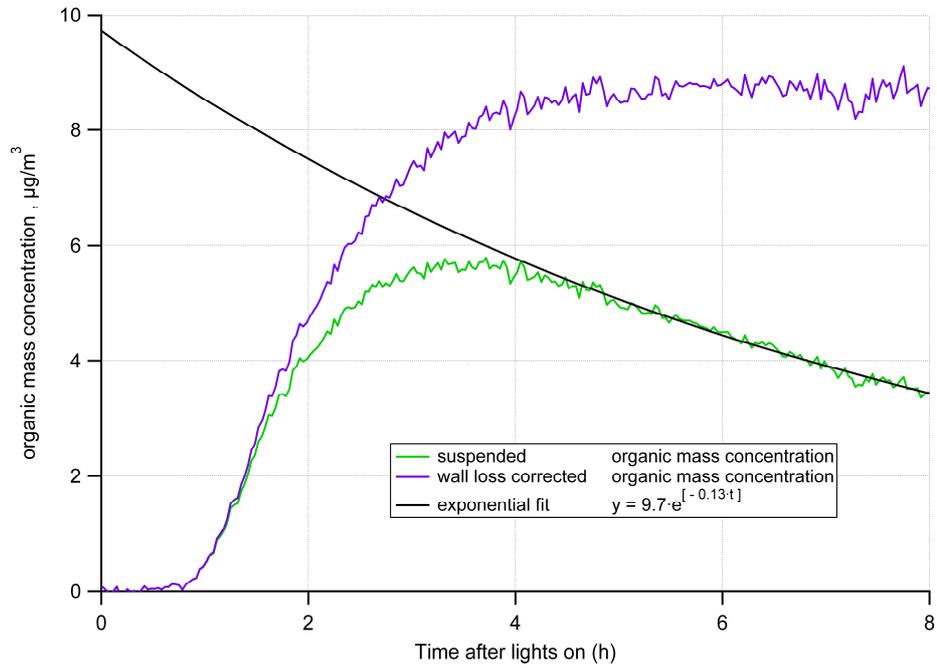
20

21

22 **Fig. S 1:** Comparison of OH exposures derived from α -pinene decay and butanol-d9 decay
23 for experiments where butanol-d9 was above detection limit throughout the entire
24 experiment. The dashed line represents the 1:1 line.

25

26



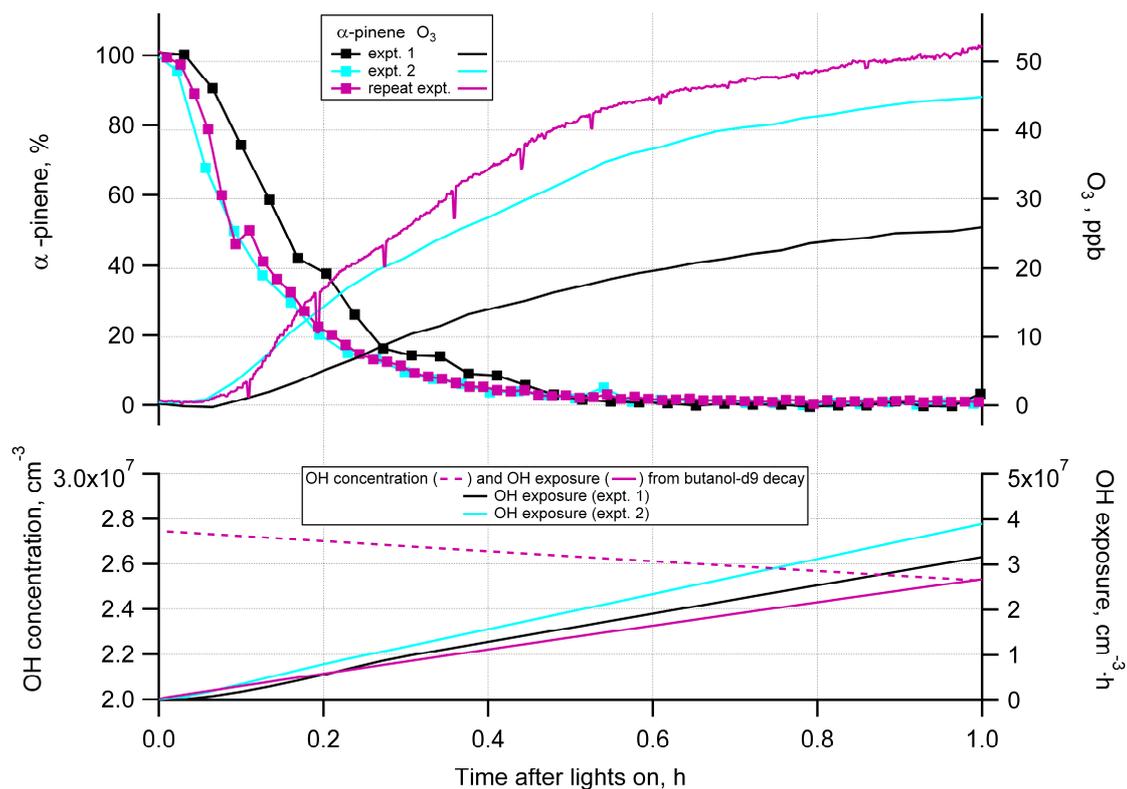
27

28

29 **Fig. S 2:** The measured organic mass concentration (green line) was fitted exponentially
30 (black line) for the last three hours of experiment 5 where wall loss dominates over organic
31 mass production. This procedure results into a lower limit of the wall loss corrected organic
32 mass concentration (purple line).

33 **Retrieval of the OH exposure of experiment 1 and 2 from a repeat experiment**

34 As the decay of α -pinene in the beginning of experiment 1 and 2 was very rapid, using the α -
35 pinene method including the extrapolation to the whole experiment time leads to a possibly
36 strong overestimation of the OH exposure. For this reason a repeat experiment was conducted
37 which showed the same characteristics in α -pinene decay, but with the OH tracer butanol-d9
38 present for the whole experiment time (See Fig. S 3). The repeat experiment resembles
39 strongly experiment 2, which has the same initial α -pinene concentration (14 ppbv). During
40 experiment 1 (with an initial α -pinene concentration of 7ppbv), the reactant decays within the
41 same time. This lower initial α -pinene concentration is also the reason for the lower O₃
42 production. The replaced OH exposures derived from the α -pinene decay for experiments 1
43 (black line) and 2 (turquoise line) are shown in the lower panel together with the OH
44 exposure of the repeat experiment (purple line).



46

47

48 **Fig. S 3:** The α -pinene and O_3 concentrations of experiment 1, 2 and the repeat experiment
 49 are shown as a function of light exposure time (upper panel). The lower panel shows the OH
 50 concentration and exposure retrieved from the decay of the tracer butanol-d9, present during
 51 the repeat experiment as well as the replaced OH exposures derived from the α -pinene
 52 method.

53

54

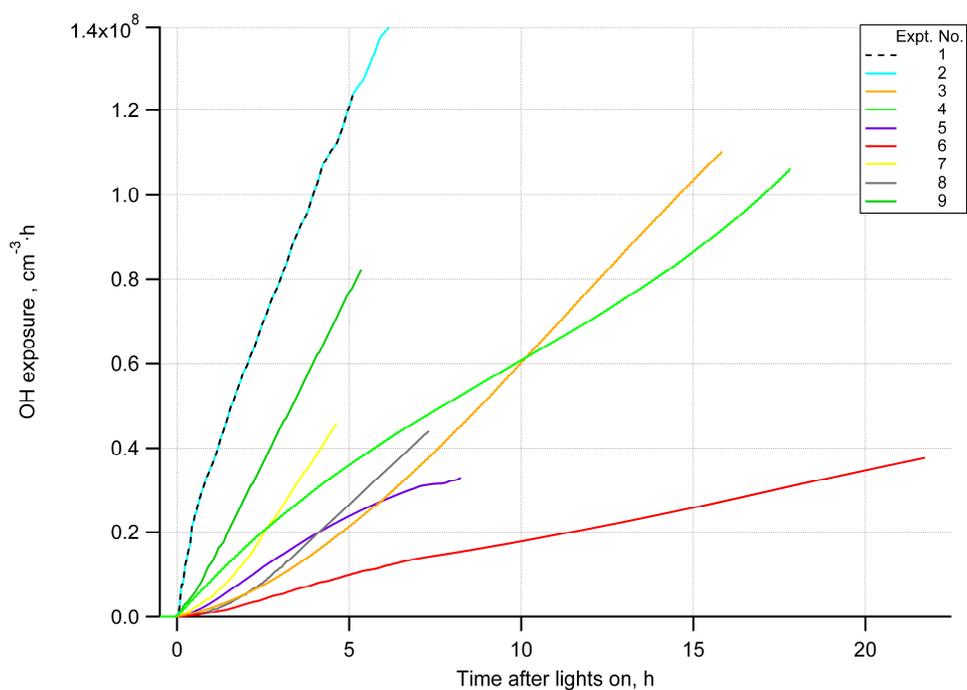
55

56

57

58

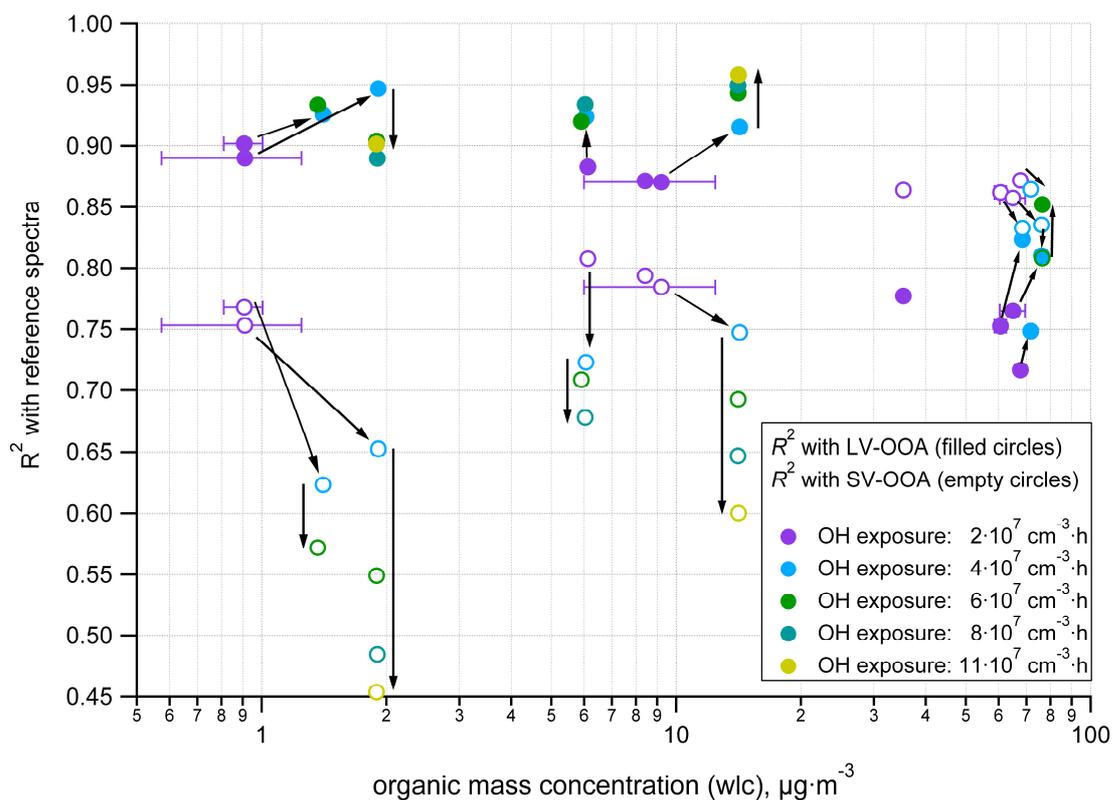
59



60

61

62 **Fig. S 4:** OH exposures for the nine different experiments (color code) derived from the
63 decay of α -pinene, butanol-d9 or a combination of both. The OH exposure of experiment 1
64 and 2 was derived from a repeat experiment.

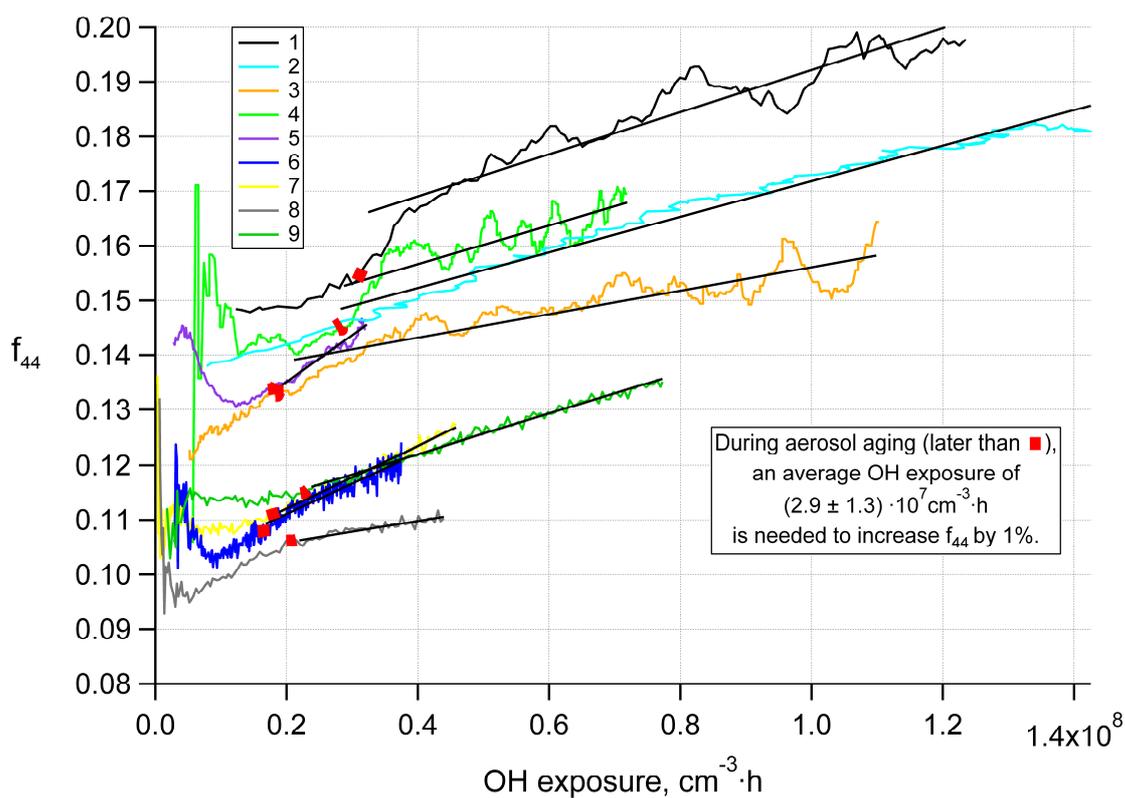


65

66

67 **Fig. S 5:** Squares of the Pearson correlation coefficients, R^2 , of measured mass spectra in
 68 comparison with LV-OOA (filled circles) and SV-OOA (empty circles) reference spectra (Ng
 69 et al., 2011) as a function of the organic mass concentration (wlc). The color code represents
 70 the OH exposure as a time stamp around which the averaging of the measured mass spectra
 71 was performed (± 15 min).

72



73

74

75 **Fig. S 6:** The organic mass fraction f_{44} as a function of OH exposure for the nine smog
 76 chamber experiments. The data was fitted with a line for the period when aging dominates,
 77 i.e. after the peak of suspended organic mass is reached. The slopes of $\Delta f_{44}/\Delta(\text{OH exposure})$
 78 are shown in Table S2. The average slope of the nine experiments results in a needed OH
 79 exposure of $2.9 \pm 1.3 \cdot 10^7 \text{ cm}^{-3} \cdot \text{h}$ to increase f_{44} by 1%.

80

81

82

83 **References**

84

85 Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H., and Worsnop,
86 D. R.: Changes in organic aerosol composition with aging inferred from aerosol mass
87 spectra, *Atmos. Chem. Phys.*, 11, 6465-6474, 2011.

88

89