

1 Supplementary material to article: Relationship between aerosol oxidation level and  
2 hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles  
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## 1 2 **1. Experimental methods**

### 3 4 **1.1 Secondary organic aerosol (SOA) particles generation**

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6 Secondary Organic Aerosol (SOA) particles were generated via OH oxidation of  
7 precursor species followed by homogeneous nucleation in the Boston College Potential  
8 Aerosol Mass (PAM) aerosol flow reactor, a 15L glass cylindrical chamber (46 cm length  
9 and 22 cm diameter) developed at the Pennsylvania State University [*Kang et al.*, 2007].  
10 In the PAM, OH radicals were produced at RH of  $20 \pm 2\%$  by the reaction of excited  
11 oxygen [ $O(^1D)$ ] atoms with water vapor, which was introduced using a Nafion membrane  
12 humidifier (Perma Pure LLC).  $O(^1D)$  atoms were produced from *in situ* UV photolysis of  
13  $O_3$  at  $\lambda = 254$  nm using four mercury lamps (BHK Inc.), mounted in teflon-coated quartz  
14 cylinders inside the chamber. The cylinders were continually purged with  $N_2$  to prevent  
15  $O_3$  formation and remove outgassing compounds.  $O_3$  was generated by passing  $O_2$   
16 through a mercury lamp ( $\lambda = 185$  nm) outside the reactor, and was measured with an  $O_3$   
17 monitor (2B Technologies); typical  $O_3$  levels inside the reactor were 5-13 ppm. Both  $O_3$   
18 and OH will oxidize organic species; however, OH was always the principal oxidant.  
19 Prior to an experiment, the reactor was conditioned with OH radicals until a near-zero  
20 particle background was attained. Carrier gas flows of approximately 8.5 liters per minute  
21 (lpm)  $N_2$  and 0.5 lpm  $O_2$  were used, with 8.5 lpm of flow pulled through the PAM and  
22 0.5 lpm of excess flow removed prior to the reactor. At these flow conditions, the  
23 residence time was 110 s. Wall effects were reduced by diverting 15 % of the flow at the  
24 exit through an internal perforated ring that samples air near the PAM reactor walls  
25 [*Lambe et al.*, 2010]. Mixtures of  $\alpha$ -pinene, m-xylene, and 1,3,5-trimethylbenzene  
26 (TMB) in  $N_2$  were synthesized in compressed cylinders and introduced to the reactor at  
27 controlled rates using a mass-flow controller (MKS Instruments). An annular diffusion  
28 dryer loaded with silica gel desiccant was placed downstream of the reactor to reduce the  
29 RH to  $< 15\%$  prior to measurements. Routine checks ensured that all the flow systems  
30 reaching the various instruments were balanced throughout the study.

## 1.2. Chemical composition measurements

The bulk submicron condensed-phase chemistry was probed with the Aerodyne Research, Inc., High Resolution Time of Flight Aerosols Mass Spectrometer (HR-ToF-AMS) [DeCarlo *et al.*, 2006, and references therein]. In addition to providing a quantitative measurements of the composition and mass size distributions of the SOA particles, atomic O:C and H:C ratios were obtained by means of elemental analysis [Aiken *et al.*, 2008] performed on the low resolution, higher sensitivity “V mode” data [DeCarlo *et al.*, 2006]. Descriptions of the AMS measurement principles and data analysis are available in other publications [Jayne *et al.*, 2000; Allan *et al.*, 2004].

Table 1S reports the average SOA mass loadings as measured by the HR-ToF-AMS for each of the experiments described in the article. We used organic precursor mixing ratios between 40 and 80 ppb resulting in SOA concentrations of 0.05 - 130  $\mu\text{g m}^{-3}$  depending on precursor species, concentration, and OH exposure. For the same OH exposure and precursor amount, the TMB SOA yielded the lowest mass loadings.

Table 1S

Table 1S: HR-ToF-AMS average SOA mass loadings ( $\mu\text{g/m}^3$ ) generated in the PAM reactor at the various experimental conditions described in the study.

## 1.3 Size distribution measurements

The size distributions of the generated SOA particles were routinely measured with a dedicated TSI scanning mobility particle sizer (SMPS). For all SOA systems, the peak of the generated size distribution was usually between 25 and 50 nm (mobility diameter,  $D_m$ ) at the highest and lowest OH exposure, respectively. This corresponded to an AMS vacuum aerodynamic size, or  $D_{va}$ , [Jayne *et al.*, 2000; DeCarlo *et al.*, 2006] of 80 to 150 nm. Figure 1S shows two different HR-ToF-AMS mass size distributions obtained in the particle time of flight (PToF) mode for  $\alpha$ -pinene SOA generated at  $4.3 \times 10^{11}$  and  $1.1 \times 10^{12}$  molec  $\text{cm}^{-3}$  s. Also shown are the m/z 44-to-m/z 43 ratios (chosen as a proxy for changes in chemical composition of organic particles). Since the particle composition remained constant across the AMS size distribution, we infer that all the

1 submicron polydisperse particles generated at a given OH exposure were chemically  
2 similar, making the coupling of the chemical information (O:C) with the hygroscopic  
3 properties ( $HGF_{90\%}$ ,  $\kappa_{ORG,CCN}$ ) meaningful.

#### Figure 1S

7 Figure 1S: PToF size distributions of  $\alpha$ -pinene SOA particles generated at OH exposure  
8 of  $4.3 \times 10^{11}$  (left) and  $1.1 \times 10^{12}$  (right) in the PAM flow reactor. The m/z 44-to-m/z 43  
9 ratio across the AMS size distribution is reported as well.

### 11 1.4 HTDMA measurements

12 Particle growth in water was measured with the University of Helsinki  
13 hygroscopic tandem differential mobility analyzer (HTDMA) described in detail in *Ehn*  
14 *et al.* [2007]. The HTDMA measured hygroscopic growth factors HGF by size-selecting  
15 a dry ( $\sim 10\%RH$ ) particle diameter ( $D_d$ ) with a Differential Mobility Analyzer (DMA,  
16 *Winklmayr et al.*, [1991]), passing dry aerosols through dry air and water-humidified air  
17 (conditioned to 90% RH in this case) into two DMAs operating in a voltage scanning  
18 mode with a Condensation Particle Counter (CPC), and measuring the wet-to-dry particle  
19 diameter ratio, e.g.  $HGF_{90\%} = D_w/D_d$ . The high RH value was determined by means of  
20 accurate dewpoint measurement with a chilled mirror sensor.  $HGF_{90\%}$  were measured for  
21  $D_d = 50$  nm; such size was typically at or right after the peak of the SMPS size  
22 distribution (c.f. paragraph 1.3), allowing to minimize the effect of doubly charged  
23 particles. Each full HTDMA scan (5 to 200 nm in  $D_m$ ) was 3 minutes long. The  $HGF_{90\%}$   
24 data were obtained via inversion algorithm taking the full HTDMA transfer function into  
25 account [*Gysel, et al.*, 2009]. Based on calibration results at  $< 10\% RH$ , a dry size  
26 correction to the  $HGF_{90\%}$  data was applied. The  $HGF_{90\%}$  values were not corrected for  
27 Kelvin effect (a negligible adjustment compared to the dry size correction). The absolute  
28 uncertainty in the RH measurement is estimated to  $\pm 2\%$ , which roughly propagates to an  
29 absolute uncertainty of  $\pm 5\%$  in the HGF values [*Swietlicki et al.*, 2008]. We did not  
30 perform scaling to a fixed 90% RH as the RH variation was only  $\pm 0.5\%$ ; measurement  
31 precision in the HGF values was 2% or less.

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## 2 1.5 CCN activity measurements

3 Cloud condensation nuclei (CCN) activities were measured with a Droplet  
4 Measurement Technologies DMT CCN Counter [Roberts and Nenes, 2005]. The CCN  
5 activity was expressed by the single parameter  $\kappa$  [Petters and Kreidenweis, 2007] as  
6 defined in Equation 1

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$$8 \quad \kappa_{CCN} = \frac{4A^3}{27D_d^3 \ln^2 S_c}; \quad A = \frac{4\sigma_w M_w}{RT\rho_w} \quad [1]$$

9

10 where  $S_c$  is the critical supersaturation (supersaturation level where 50% of  
11 particles are CCN-activated),  $D_d$  is the dry diameter in nm, and  $M_w$ ,  $\rho_w$  and  $\sigma_w$  are the  
12 molecular weight, density, and surface tension of water ( $\sigma_w = 0.072 \text{ J m}^{-2}$ ). A DMA  
13 upstream of the CCN and CPC was used to select dry diameters  $D_d$  in the range 50-150  
14 nm. The fraction of particles activating to form CCN was determined by measuring total  
15 particle concentrations with a co-located CPC (TSI 3022A). At each OH exposure level,  
16 typically 3 or 4 different  $D_d$  were selected. Despite *Rose et al.* [2008] showed that small  
17 doubly charged particles will not affect the accuracy in determining  $D_c$ , the effect of  
18 multiply-charged particles was minimized by selecting dry sizes at or after the peak of the  
19 SOA size distribution measured by the SMPS. For a given  $D_d$ , the CCN column  
20 supersaturation was systematically varied (stepping the column temperature,  $dT$  scanning  
21 mode) between 0.1-1.5% supersaturation in water or until 100% was reached, whichever  
22 occurred first. Data were acquired after the system had reached equilibrium after change  
23 in column temperature. A  $S_c$  value (and thereby a  $\kappa$  value) was obtained for each  $D_d$ . As  
24 there was no evident correlation between  $\kappa$  and  $D_d$ , the  $\kappa$  value reported for each SOA  
25 system is the average of the  $\kappa$  values estimated from multiple  $D_d$ .

26 The CCN instrument was routinely checked and calibrated with ammonium  
27 sulfate particles. Based on the precision in the  $S_c$  measurements, the error estimated for  
28  $\kappa_{CCN}$  was 15%. Example CCN activation curves are shown in Figure 2S.

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Figure 2S

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2 Figure 2S: CCN-activated fraction plotted as function of water supersaturation for 50, 75  
3 and 100-nm  $\alpha$ -pinene particles generated in the PAM flow reactor. The critical  
4 supersaturation  $S_c$  (50% of the particles activated) decreases for larger selected  $D_m$

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