

Erratum: Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles (Geophysical Research Letters (2010) 38 (L03805))

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Correction to “Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles”

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[1] In the paper “Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles” by P. Massoli et al. (*Geophysical Research Letters*, 37, L24801, doi:10.1029/2010GL045258, 2010) Text S1 is missing from the auxiliary material and now appears here.¹

Auxiliary material to article: Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles

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1. Experimental methods

1.1 Secondary organic aerosol (SOA) particles generation

Secondary Organic Aerosol (SOA) particles were generated via OH oxidation of precursor species followed by homogeneous nucleation in the Boston College Potential Aerosol Mass (PAM) aerosol flow reactor, a 15L glass cylindrical chamber (46 cm length and 22 cm diameter) developed at the Pennsylvania State University [Kang *et al.*, 2007]. In the PAM, OH radicals were produced at RH of $20 \pm 2\%$ by the reaction of excited oxygen [$O(^1D)$] atoms with water vapor, which was introduced using a Nafion membrane humidifier (Perma Pure LLC). $O(^1D)$ atoms were produced from *in situ* UV photolysis of O_3 at $\lambda = 254$ nm using four mercury lamps (BHK Inc.), mounted in teflon-coated quartz cylinders inside the chamber. The cylinders were continually purged with N_2 to prevent O_3 formation and remove outgassing compounds. O_3 was generated by passing O_2 through a mercury lamp ($\lambda = 185$ nm) outside the reactor, and was measured with an O_3 monitor (2B Technologies); typical O_3 levels inside the reactor were 5-13 ppm. Both O_3 and OH will oxidize organic species; however, OH was always the principal oxidant.

1 Prior to an experiment, the reactor was conditioned with OH radicals until a near-zero
2 particle background was attained. Carrier gas flows of approximately 8.5 liters per minute
3 (lpm) N₂ and 0.5 lpm O₂ were used, with 8.5 lpm of flow pulled through the PAM and
4 0.5 lpm of excess flow removed prior to the reactor. At these flow conditions, the
5 residence time was 110 s. Wall effects were reduced by diverting 15 % of the flow at the
6 exit through an internal perforated ring that samples air near the PAM reactor walls
7 [Lambe *et al.*, 2010]. Mixtures of α -pinene, m-xylene, and 1,3,5-trimethylbenzene
8 (TMB) in N₂ were synthesized in compressed cylinders and introduced to the reactor at
9 controlled rates using a mass-flow controller (MKS Instruments). An annular diffusion
10 dryer loaded with silica gel desiccant was placed downstream of the reactor to reduce the
11 RH to < 15% prior to measurements. Routine checks ensured that all the flow systems
12 reaching the various instruments were balanced throughout the study.

13 14 **1.2. Chemical composition measurements**

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

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

28
29 Table 1S
30

Table 1S: HR-ToF-AMS average SOA mass loadings ($\mu\text{g}/\text{m}^3$) 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 S1 shows two different HR-ToF-AMS mass size distributions obtained in the particle time of flight (PToF) mode for α -pinene SOA generated at 4.3×10^{11} and 1.1×10^{12} molec 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 submicron polydisperse particles generated at a given OH exposure were chemically similar, making the coupling of the chemical information (O:C) with the hygroscopic properties ($\text{HGF}_{90\%}$, $\kappa_{\text{ORG,CCN}}$) meaningful.

Figure S1

Figure S1. PToF size distributions of α -pinene SOA particles generated at OH exposure of 4.3×10^{11} (left) and 1.1×10^{12} (right) in the PAM flow reactor. The m/z 44-to-m/z 43 ratio across the AMS size distribution is reported as well.

1.4 HTDMA measurements

Particle growth in water was measured with the University of Helsinki hygroscopic tandem differential mobility analyzer (HTDMA) described in detail in Ehn *et al.* [2007]. The HTDMA measured hygroscopic growth factors HGF by size-selecting a dry ($\sim 10\% \text{RH}$) particle diameter (D_d) with a Differential Mobility Analyzer (DMA, Winklmayr *et al.*, [1991]), passing dry aerosols through dry air and water-humidified air (conditioned to 90% RH in this case) into two DMAs operating in a voltage scanning

mode with a Condensation Particle Counter (CPC), and measuring the wet-to-dry particle diameter ratio, e.g. $HGF_{90\%} = D_w/D_d$. The high RH value was determined by means of accurate dewpoint measurement with a chilled mirror sensor. $HGF_{90\%}$ were measured for $D_d = 50$ nm; such size was typically at or right after the peak of the SMPS size distribution (c.f. paragraph 1.3), allowing to minimize the effect of doubly charged particles. Each full HTDMA scan (5 to 200 nm in D_m) was 3 minutes long. The $HGF_{90\%}$ data were obtained via inversion algorithm taking the full HTDMA transfer function into account [Gysel, *et al.*, 2009]. Based on calibration results at $< 10\%$ RH, a dry size correction to the $HGF_{90\%}$ data was applied. The $HGF_{90\%}$ values were not corrected for Kelvin effect (a negligible adjustment compared to the dry size correction). The absolute uncertainty in the RH measurement is estimated to $\pm 2\%$, which roughly propagates to an absolute uncertainty of $\pm 5\%$ in the HGF values [Swietlicki *et al.*, 2008]. We did not perform scaling to a fixed 90% RH as the RH variation was only $\pm 0.5\%$; measurement precision in the HGF values was 2% or less.

1.5 CCN activity measurements

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

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

where S_c is the critical supersaturation (supersaturation level where 50% of particles are CCN-activated), D_d is the dry diameter in nm, and M_w , ρ_w and σ_w are the molecular weight, density, and surface tension of water ($\sigma_w = 0.072$ J m⁻²). A DMA upstream of the CCN and CPC was used to select dry diameters D_d in the range 50-150 nm. The fraction of particles activating to form CCN was determined by measuring total particle concentrations with a co-located CPC (TSI 3022A). At each OH exposure level, typically 3 or 4 different D_d were selected. Despite Rose *et al.* [2008] showed that small

doubly charged particles will not affect the accuracy in determining D_c , the effect of multiply-charged particles was minimized by selecting dry sizes at or after the peak of the SOA size distribution measured by the SMPS. For a given D_d , the CCN column supersaturation was systematically varied (stepping the column temperature, dT scanning mode) between 0.1-1.5% supersaturation in water or until 100% was reached, whichever occurred first. Data were acquired after the system had reached equilibrium after change in column temperature. A Sc value (and thereby a κ value) was obtained for each D_d . As there was no evident correlation between κ and D_d , the κ value reported for each SOA system is the average of the κ values estimated from multiple D_d .

The CCN instrument was routinely checked and calibrated with ammonium sulfate particles. Based on the precision in the Sc measurements, the error estimated for κ_{CCN} was 15%. Example CCN activation curves are shown in Figure S2.

Figure S2

Figure S2. CCN-activated fraction plotted as function of water supersaturation for 50, 75 and 100-nm α -pinene particles generated in the PAM flow reactor. The critical supersaturation Sc (50% of the particles activated) decreases for larger selected D_m

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