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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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

¹Auxiliary materials are available in the HTML. doi:10.1029/2011GL046687.
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 ± 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 O3 at λ = 254 nm using four mercury lamps (BHK Inc.), mounted in teflon-coated quartz cylinders inside the chamber. The cylinders were continually purged with N2 to prevent O3 formation and remove outgassing compounds. O3 was generated by passing O2 through a mercury lamp (λ = 185 nm) outside the reactor, and was measured with an O3 monitor (2B Technologies); typical O3 levels inside the reactor were 5-13 ppm. Both O3 and OH will oxidize organic species; however, OH was always the principal oxidant.
Prior to an experiment, the reactor was conditioned with OH radicals until a near-zero particle background was attained. Carrier gas flows of approximately 8.5 liters per minute (lpm) N₂ and 0.5 lpm O₂ were used, with 8.5 lpm of flow pulled through the PAM and 0.5 lpm of excess flow removed prior to the reactor. At these flow conditions, the residence time was 110 s. Wall effects were reduced by diverting 15% of the flow at the exit through an internal perforated ring that samples air near the PAM reactor walls [Lambe et al., 2010]. Mixtures of α-pinene, m-xylene, and 1,3,5-trimethylbenzene (TMB) in N₂ were synthesized in compressed cylinders and introduced to the reactor at controlled rates using a mass-flow controller (MKS Instruments). An annular diffusion dryer loaded with silica gel desiccant was placed downstream of the reactor to reduce the RH to < 15% prior to measurements. Routine checks ensured that all the flow systems 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 μg 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 (µg/m³) 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 $\alpha$-pinene SOA generated at 4.3x$10^{11}$ and 1.1x$10^{12}$ 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 ($HGF_{90\%}$, $\kappa_{ORG,CCN}$) meaningful.

![Figure S1](image-url)

Figure S1. PToF size distributions of $\alpha$-pinene SOA particles generated at OH exposure of 4.3x$10^{11}$ (left) and 1.1x$10^{12}$ (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 (~ 10%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. $\text{HGF}_{90\%} = \frac{D_w}{D_d}$. 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 $\kappa$ [Petters and Kreidenweis, 2007] as
defined in Equation 1

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

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 $M_w$, $\rho_w$ and $\sigma_w$ 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 $Dc$, 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 $\kappa$ value) was obtained for each $D_d$. As there was no evident correlation between $\kappa$ and $D_d$, the $\kappa$ value reported for each SOA system is the average of the $\kappa$ 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 $\kappa_{CCN}$ 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 $\alpha$-pinene particles generated in the PAM flow reactor. The critical supersaturation $Sc$ (50% of the particles activated) decreases for larger selected $D_m$

References


