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

Authors: P. Massoli, A.T. Lambe, A.T. Ahern, L.R. Williams, M. Ehn, J. Mikkilä, M.R. Canagaratna, W.H. Brune, T.B. Onasch, J.T. Jayne, T. Petäjä, M. Kulmala, A. Laaksonen, C.E. Kolb, Paul Davidovits, D.R. Worsnop

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

P. Massoli, A. T. Lambe, A. T. Ahern, L. R. Williams, M. Ehn, J. Mikkilä,
M. R. Canagaratna, W. H. Brune, T. B. Onasch, J. T. Jayne, T. Petäjä, M. Kulmala,
A. Laaksonen, C. E. Kolb, P. Davidovits, and D. R. Worsnop

Citation: Massoli, P., et al. (2011), Correction to "Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles," *Geophys. Res. Lett.*, 38, L03805, doi:10.1029/2011GL046687.

[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]

---

[1]Auxiliary materials are available in the HTML. doi:10.1029/2011GL046687.

1 Auxiliary material to article: Relationship between aerosol oxidation level and

2 hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles

3

4

5 Massoli, P.[1], A.T. Lambe[1,2], A.T. Ahern[1,2], L. R. Williams[1], M. Ehn[3], J. Mikkilä[3], M. R.

6 Canagaratna[1], W. H. Brune[4], T. B. Onasch[1], J. T. Jayne[1], T. Petäjä[3], M. Kulmala[3], A.

7 Laaksonen[5], C. E. Kolb[1], P. Davidovits[2], and D. R. Worsnop[1,3,5]

8

9 [1] *Aerodyne Research Inc., Billerica, MA, USA*

10 [2] *Chemistry Department, Boston College, Chestnut Hill, MA, USA*

11 [3] *Division of Atmospheric Science, Department of Physics, University of Helsinki,*

12 *Helsinki, Finland*

13 [4] *Department of Meteorology, Pennsylvania State University, University Park, PA, USA*

14 [5] *Division of Physics, University of Eastern Finland, Kuopio, Finland*

15
16
17 **1. Experimental methods**
18
19 **1.1 Secondary organic aerosol (SOA) particles generation**
20
21 Secondary Organic Aerosol (SOA) particles were generated via OH oxidation of

22 precursor species followed by homogeneous nucleation in the Boston College Potential

23 Aerosol Mass (PAM) aerosol flow reactor, a 15L glass cylindrical chamber (46 cm length

24 and 22 cm diameter) developed at the Pennsylvania State University [*Kang et al.,* 2007].

25 In the PAM, OH radicals were produced at RH of $20 \pm 2\%$ by the reaction of excited

26 oxygen [$O(^1D)$] atoms with water vapor, which was introduced using a Nafion membrane

27 humidifier (Perma Pure LLC). $O(^1D)$ atoms were produced from *in situ* UV photolysis of

28 O_3 at $\lambda = 254$ nm using four mercury lamps (BHK Inc.), mounted in teflon-coated quartz

29 cylinders inside the chamber. The cylinders were continually purged with N_2 to prevent

30 O_3 formation and remove outgassing compounds. O_3 was generated by passing O_2

31 through a mercury lamp ($\lambda = 185$ nm) outside the reactor, and was measured with an O_3

32 monitor (2B Technologies); typical O_3 levels inside the reactor were 5-13 ppm. Both O_3

33 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) N_2 and 0.5 lpm O_2 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 N_2 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 μg 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

1   Table 1S: HR-ToF-AMS average SOA mass loadings ($\mu g/m^3$) generated in the PAM

2   reactor at the various experimental conditions described in the study.

3

4   **1.3 Size distribution measurements**

5   The size distributions of the generated SOA particles were routinely measured

6   with a dedicated TSI scanning mobility particle sizer (SMPS). For all SOA systems, the

7   peak of the generated size distribution was usually between 25 and 50 nm (mobility

8   diameter, Dm) at the highest and lowest OH exposure, respectively. This corresponded to

9   an AMS vacuum aerodynamic size, or D_{va}, [*Jayne et al.,* 2000; *DeCarlo et al.,* 2006] of

10 80 to 150 nm. Figure S1 shows two different HR-ToF-AMS mass size distributions

11 obtained in the particle time of flight (PToF) mode for α-pinene SOA generated at

12 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

13 as a proxy for changes in chemical composition of organic particles). Since the particle

14 composition remained constant across the AMS size distribution, we infer that all the

15 submicron polydisperse particles generated at a given OH exposure were chemically

16 similar, making the coupling of the chemical information (O:C) with the hygroscopic

17 properties (HGF$_{90\%}$, $\kappa_{ORG,CCN}$) meaningful.

18

19   Figure S1

20

21 Figure S1. PToF size distributions of α-pinene SOA particles generated at OH exposure

22 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

23 ratio across the AMS size distribution is reported as well.

24

25 **1.4 HTDMA measurements**

26   Particle growth in water was measured with the University of Helsinki

27 hygroscopic tandem differential mobility analyzer (HTDMA) described in detail in *Ehn*

28 *et al.* [2007]. The HTDMA measured hygroscopic growth factors HGF by size-selecting

29 a dry (~ 10%RH) particle diameter (D_d) with a Differential Mobility Analyzer (DMA,

30 *Winklmayr et al.*, [1991]), passing dry aerosols through dry air and water-humidified air

31 (conditioned to 90% RH in this case) into two DMAs operating in a voltage scanning

1   mode with a Condensation Particle Counter (CPC), and measuring the wet-to-dry particle

2   diameter ratio, e.g. $HGF_{90\%} = D_w/D_d$. The high RH value was determined by means of

3   accurate dewpoint measurement with a chilled mirror sensor. $HGF_{90\%}$ were measured for

4   D_d = 50 nm; such size was typically at or right after the peak of the SMPS size

5   distribution (c.f. paragraph 1.3), allowing to minimize the effect of doubly charged

6   particles. Each full HTDMA scan (5 to 200 nm in Dm) was 3 minutes long. The $HGF_{90\%}$

7   data were obtained via inversion algorithm taking the full HTDMA transfer function into

8   account [*Gysel, et al.,* 2009]. Based on calibration results at < 10% RH, a dry size

9   correction to the $HGF_{90\%}$ data was applied. The $HGF_{90\%}$ values were not corrected for

10   Kelvin effect (a negligible adjustment compared to the dry size correction). The absolute

11   uncertainty in the RH measurement is estimated to ±2%, which roughly propagates to an

12   absolute uncertainty of ±5% in the HGF values [*Swietlicki et al.,* 2008]. We did not

13   perform scaling to a fixed 90% RH as the RH variation was only ±0.5%; measurement

14   precision in the HGF values was 2% or less.

15

16   **1.5 CCN activity measurements**

17   Cloud condensation nuclei (CCN) activities were measured with a Droplet

18   Measurement Technologies DMT CCN Counter [*Roberts and Nenes*, 2005]. The CCN

19   activity was expressed by the single parameter κ [*Petters and Kreidenweis,* 2007] as

20   defined in Equation 1

21

22
$$\kappa_{CCN} = \frac{4A^3}{27D_d^3 \ln^2 S_c}; \qquad A = \frac{4\sigma_w M_w}{RT\rho_w} \qquad\qquad [1]$$

23

24   where S_c is the critical supersaturation (supersaturation level where 50% of

25   particles are CCN-activated), D_d is the dry diameter in nm, and M_w, ρ_w and σ_w are the

26   molecular weight, density, and surface tension of water (σ_w = 0.072 J m^{-2}). A DMA

27   upstream of the CCN and CPC was used to select dry diameters D_d in the range 50-150

28   nm. The fraction of particles activating to form CCN was determined by measuring total

29   particle concentrations with a co-located CPC (TSI 3022A). At each OH exposure level,

30   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 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 Dm

References

Aiken, A. C., et al. (2008), O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, *Environ. Sci. Technol., 42*(12), 4478 - 4485, doi:10.1021/es703009q.

Allan, J.D., et al. (2003), Quantitative Sampling Using an Aerodyne Aerosol Mass Spectrometer. Part 1: Techniques of Data Interpretation and Error Analysis, *J. Geophys. Res.,*, 108, No. D3, 4090, doi:10.1029/2002JD002358.

DeCarlo, P. F., et al. (2006), Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer, *Anal. Chem., 78*(24): 8281-8289, doi:10.1021/ac061249n.

Ehn, M., et al. (2007), Non-volatile residuals of newly formed atmospheric particles in the boreal forest, *Atmos. Chem. Phys.,* 7, 677-684

Gysel, et al. (2009), Inversion of tandem differential mobility analyser (TDMA) measurements, *J. Aerosol. Sci.,* 40, 134 - 151.

Jayne, J.T., et al. (2000), Development of an Aerosol Mass Spectrometer for Size and Composition. Analysis of Submicron Particles, *Aerosol Sci. Technol.,* 33, 49-70

Kang, E., et al. (2007), Introducing the concept of Potential Aerosol Mass (PAM), *Atmos. Chem. Phys., 7,* 6131-6144.

Lambe, A.T., et al. (2010), Characterization of Aerosol Photooxidation Flow Reactors: Heterogeneous Oxidation, Secondary Organic Aerosol Formation, and Cloud Condensation Nuclei Activity Measurements, *Atmos. Meas. Techn. Disc.,* in press

Petters, M. D., and S. M. Kreidenweis (2007), A single parameter representation of hygroscopicity growth and cloud condensation nucleus activity, *Atmos. Chem. Phys., 7,* 1961– 1971.

Roberts, G. C., and A. Nenes (2005), A continuous-flow streamwise thermal-gradient CCN chamber for atmospheric measurements, *Aerosol Sci. Technol.,* 39:206–221.

Rose, D., et al. (2008), Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment, *Atmos. Chem. Phys.,* 8, 1153-1179.

1   Swietlicki, E., et al. (2009), Hygroscopic properties of submicrometer atmospheric

2   aerosol particles measured with H-TDMA instruments in various environments – a

3   review, *Tellus B.,* 60, 432-469.

4

5   Winklmayr, W., et al. (1991), A new electromobility spectrometer for the measurement

6   of aerosol size distributions in the size range from 1 to 1000 nm, *J. Aerosol Sci.,* 22, 289–

7   296