



## Supplement of

## Particle size dependence of biogenic secondary organic aerosol molecular composition

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**Figure S1.** Size distributions of polydisperse SOA samples produced from the flow tube reactor (a, b, c) and atomizer (d) monitored with SMPS. Size distributions of monodisperse SOA obtained from polydisperse sample (a) are also shown. The mass concentration of polydisperse SOA sample (c) was multiplied by a factor of 20 to fit on this scale. The mass concentration of the 35 nm monodisperse sample in the inset was multiplied by a factor of 40.



**Figure S2.** Average NAMS spectrum of 60 nm monodisperse SOA (size and concentration listed in Table S1) over 150 single particle spectra collected.



**Figure S3.** Positive (+) and negative (-) ion mass spectra of high (blue; polydisperse sample a) and low (red; polydisperse sample c) mass loading SOA averaged over 5 replicate measurements.



**Figure S4.** Carbon oxidation state (OSc) vs. number of carbon atoms for assigned molecular formulas from the positive (+) and negative (-) ion mass spectra of low and high mass loading polydisperse SOA samples. Unique formulas in the low mass loading (5  $\mu$ g/m<sup>3</sup>) samples are shown in red. Unique formulas in the high mass loading (2300  $\mu$ g/m<sup>3</sup>) samples are shown in blue. Formulas common to both samples are shown in black

Sample Type	SOA Generation	Avg. Mode Diameter (nm)	Avg. Volume to Surface Ratio (nm)	Avg. Mass. Concentration (µg/m <sup>3</sup> )	Time Required for 10µg sample to be Collected (hr)
Polydisperse a		76	12.5	2300	0.07
35 nm		35	5.9	5	34
60 nm		59	10.0	66	2.5
85 nm	Flow Tube	85	14.3	87	1.9
110 nm	Reactor	113	20.0	48	3.5
Polydisperse b		43	7.1	240	0.69
Polydisperse c		23	3.8	5	33
Polydisperse d		240	N/A	510	0.33
35 nm	Atomizer	35	5.9	2	93
60 nm		62	10.0	23	7.3
110 nm		112	20.0	20	8.3

Table S1. SOA Samples Investigated in this Study

Sample Type	Ion Mode	Unique Molecular Formulas <sup>c</sup>	Common Molecular Formulas <sup>d</sup>	Avg. SI	Avg. RSD%	Avg. O/C
Polydisperse a	(+)	$1203\pm108$	998	5.8E+06	6.8	$0.28\pm0.01$
	(-)	$1035\pm89$	895	7.9E+06	3.3	$0.41\pm0.004$
35 nm <sup>a</sup>	(+)	$897\pm82$	791	3.6E+06	5.1	$0.36\pm0.01$
	(-)	$459\pm78$	305	3.1E+06	9.8	$0.51\pm0.01$
60 nm <sup>a</sup>	(+)	$1179 \pm 111$	935	8.3E+06	6.0	$0.32\pm0.02$
	(-)	$405\pm52$	341	8.5E+06	13	$0.48\pm0.01$
85 nm <sup>a</sup>	(+)	$1097 \pm 152$	897	8.9E+06	7.8	$0.31\pm0.02$
	(-)	$420\pm38$	312	5.0E+06	13	$0.46\pm0.01$
110 nm <sup>a</sup>	(+)	$1644 \pm 191$	1344	5.2E+06	7.1	$0.23 \pm 0.01$
	(-)	$587\pm54$	492	6.0E+06	9.8	$0.44\pm0.01$
Polydisperse b	(+)	$1115 \pm 156$	902	3.4E+06	7.5	$0.31 \pm 0.02$
	(-)	$847\pm45$	745	6.5E+06	4.2	$0.42\pm0.01$
Polydisperse c	(+)	$1047\pm103$	877	2.5E+06	11	$0.34\pm0.01$
	(-)	$743\pm55$	628	8.3E+06	5.6	$0.47\pm0.02$
Polydisperse d	(+)	$1029\pm83$	901	5.9E+06	3.8	$0.31\pm0.02$
	(-)	$896\pm77$	771	7.8E+06	10	$0.51\pm0.01$
35 nm <sup>b</sup>	(+)	$430\pm33$	335	1.9E+06	6.7	$0.37\pm0.01$
	(-)	$226\pm28$	178	8.6E+06	2.7	$0.47\pm0.01$
85 nm <sup>b</sup>	(+)	$914 \pm 86$	805	7.1E+05	5.4	$0.35\pm0.01$
	(-)	$552 \pm 46$	468	3.9E+05	2.8	$0.45\pm0.01$
110 nm <sup>b</sup>	(+)	$873 \pm 51$	769	6.3E+05	2.6	$0.36\pm0.01$
	(-)	$439\pm25$	390	4.3E+05	7.7	$0.45\pm0.01$

Table S2. Summary of Off-Line Composition Measurements with HR-MS

<sup>a</sup>Monodisperse samples were classified from polydisperse SOA sample (a).

<sup>b</sup>Monodisperse samples were classified from polydisperse SOA sample (d).

<sup>c</sup>These formulas represent the average and standard deviation from five replicate samples.

<sup>d</sup>These formulas represent the common ones observed in all five replicates for a given sample type.

Table S3. Summary of On-Line Measurements with NAMS							
Sample Type	Poly/Mono	Avg. O/C	Std. dev <sub>O/C</sub>				
Poly SOA a	poly	0.35	9.8E-03				
Poly SOA b	poly	0.40	1.5E-02				
Poly SOA (atomizer)	poly	0.45	8.6E-03				
60 nm	Mono	0.42	1.4E-02				
85 nm	Mono	0.35	1.3E-02				
110 nm	Mono	0.33	5.5E-03				
85 nm (atomizer)	Mono	0.45	1.9E-03				
110nm (atomizer)	Mono	0.46	3.6E-03				

Table S3. Summary of On-Line Measurements with NAMS