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A study of volatility by composition, heating, and dilution measurements of secondary organic aerosol from 1,3,5-trimethylbenzene

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S1. Estimation of the saturation concentration of reaction products by PTR-MS

The mass spectrum of the products in the gaseous phase was obtained 4 h after the start of the reaction. The concentration of each mass number, X, in the gaseous phase (c_g) was calculated using Eq. (S1):

$$c_g = \frac{I_X}{S_X} \qquad @\ m/z = \mathrm{X} \tag{S1}$$

where I_X and S_X represent the ion intensity and the detection sensitivity at *m/z* of X, respectively.

For the aerosol analysis, the ion signal was summed when the filter was heated from room temperature (~25 °C) to 95 °C. The signal was observed within 120 min of the 180-min monitoring period. The concentration at each mass number, X, in the aerosols (c_a), which corresponds to the concentration when each compound in the aerosols is completely vaporized in the chamber, was calculated using Eq. (S2):

$$c_a = \frac{\frac{1}{t}\int_0^t (I_X - I_X(t=0))dt}{S_X} \cdot \frac{f \times t}{V} \ @\ m/z = \mathrm{X} \tag{S2}$$

where *f*, *t*, and *V* represent the flow rate during the analysis (0.2 slm), the analysis time (120 min), and the sampling volume (500 L = 16.7 L min^{-1} × 30 min), respectively. When estimating the ratio of c_a to c_g at each mass number, S_x is cancelled out since the same instrument (PTR-QMS 500, Ionicon Analytik) was used to obtain both c_a and c_g.

To estimate the saturation concentration of each product, the relationship between the absorption equilibrium constant ($K_{p,i}$) and the vapor pressure ($p_{L,i}^0$) of compound *i* in a unit of Torr (Odum et al., 1996) was used, as shown in Eq. (S3):

$$K_{p,i} / f_{om} = \frac{F_{i,om}}{A_i \cdot M_o} = \frac{760 \cdot R \cdot T}{MW_{om} \cdot 10^6 \cdot \zeta_i \cdot p_{L,i}^0} \tag{S3}$$

where f_{om} is the mass fraction of the total suspended particulate concentration (μg m^{-3}), A_i is the gas-phase concentration (ng m^{-3}), $F_{i,om}$ is the concentration of compound *i* in the absorbing organic material (om) phase (ng m^{-3}), *R* is the ideal gas constant (8.206 × 10^{-5} m^3 atm mol^{-1} K^{-1}), *T* is absolute temperature, MW_{om} is the mean MW of the om phase (g mol^{-1}), and ζ_i is the activity coefficient of compound *i* in the om phase. The activity coefficient was assumed as unity (Hellén et al., 2008). The c_a/c_g ratio corresponds to the $F_{i,om}/A_i$ ratio.

The ion signals of m/z 151–229 were only used for the evaluations of the saturation concentration. The signals of *m/z* < 151 were not used because there would be interference from fragment ions. The signals of *m/z* > 229 were not detected due to the low sensitivity of the quadruple mass spectrometer. We assumed that the ion signals at each mass number in both the gaseous and the aerosol phases could be attributed to the same compounds.

References

Hellén, H., Dommen, J., Metzger, A., Gascho, A., Duplissy, J., Tritscher, T., Prevot, A.S.H., Baltensperger, U.: Using proton transfer reaction mass spectrometry for online analysis of secondary organic aerosols. Environmental Science and Technology, 42, 7347–7353, 2008.

Odum, J.R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., Seinfeld, J. H.: Gas/particle partitioning and secondary organic aerosol yields. Environmental Science and Technology, 30, 2580–2585, 1996.

Table S1. Initial concentration condition, mass concentration of produced SOA, geometric mean size of produced SOA, and analytical methods employed in each experimental run.

Run	$[HC]_0$ ppm	$[NO]_0$ ppm	$[CH_3ONO]_0$ ppm	[SOA] [b] $\mu g\ m^{-3}$	Size nm	Measurements [c]	Comment
1	1.48	1.09	0.01	192	395	TD-AMS, LC-TOF-MS, PTR-MS	
2	1.48	1.19	0.01	228	558	TD-AMS, LC-TOF-MS, PTR-MS	Aging expt.[a]
3	1.50	1.21	0.01	203	364	TD-AMS, EDC (DR = 20)	
4	1.53	1.21	0.01	182	391	TD-AMS, EDC (DR = 40)	
5	1.52	1.20	0.01	184	391	TD-AMS, EDC (DR = 63)	
6	1.49	1.20	0.01	171	393	TD-AMS, EDC (DR = 86)	
7	1.51	1.18	0.01	254	408	flow diluter	

[a] SOA formed from the TMB photooxidation was exposed to OH radicals. [b] Calculated from the volume concentration by assuming particle density to 1.40 $g \cdot cm^{-3}$ (present study). [c] EDC is external dilution chamber, DR is dilution ratio.

Table S2. Measured mass-to-charge ratio (*m/z*), suggested ion formula, calculated molecular weight (MW), measured total intensities of extracted ion chromatogram (EIC) peaks, calculated O/C ratio, and predicted saturation concentrations for products existing in SOA from TMB.

m/z	Ion formula	MW	Total int. of EIC peaks (normal, run 1) [a]	Total int. of EIC peaks (aging, run 2) [a]	O/C	$\log_{10} C^*$ (eq. adapted to TMB products)	$\log_{10} C^*$ (eq. by Li et al., 2016)
185.042	$C_6H_{10}O_5Na$	162.053	33,796	62,479	0.83	3.06	3.43
193.047	$C_8H_{10}O_4Na$	170.058	138,991	134,015	0.50	3.53	4.10
197.042	$C_7H_{10}O_5Na$	174.053	57,574	97,423	0.71	2.88	3.28
207.063	$C_9H_{12}O_4Na$	184.074	394,346	425,366	0.44	3.34	3.81
209.078	$C_9H_{14}O_4Na$	186.089	1,339,087	917,440	0.44	3.34	3.81
213.037	$C_7H_{10}O_6Na$	190.048	78,894	66,442	0.86	2.03	2.11
215.053	$C_7H_{12}O_6Na$	192.063	149,163	212,665	0.86	2.03	2.11
223.058	$C_9H_{12}O_5Na$	200.068	337,888	362,721	0.56	2.50	2.85
223.094	$C_{10}H_{16}O_4Na$	200.105	52,609	30,785	0.40	3.15	3.50
225.073	$C_9H_{14}O_5Na$	202.084	1,902,497	2,852,655	0.56	2.50	2.85
227.053	$C_8H_{12}O_6Na$	204.063	127,216	263,746	0.75	1.85	1.97
239.053	$C_9H_{12}O_6Na$	216.063	61,399	99,896	0.67	1.66	1.79
239.089	$C_{10}H_{16}O_5Na$	216.100	614,689	390,379	0.50	2.31	2.59
241.068	$C_9H_{14}O_6Na$	218.079	1,500,300	1,673,638	0.67	1.66	1.79
243.084	$C_9H_{16}O_6Na$	220.095	1,081,863	1,371,867	0.67	1.66	1.79
245.078	$C_{12}H_{14}O_4Na$	222.089	1,077,603	1,120,068	0.33	2.76	2.83
253.105	$C_{11}H_{18}O_5Na$	230.115	115,520	114,146	0.45	2.12	2.30
255.084	$C_{10}H_{16}O_6Na$	232.095	142,174	116,783	0.60	1.48	1.58
257.063	$C_9H_{14}O_7Na$	234.074	127,222	198,565	0.78	0.82	0.66
259.079	$C_9H_{16}O_7Na$	236.090	180,451	189,460	0.78	0.82	0.66
267.084	$C_{11}H_{16}O_6Na$	244.095	248,734	338,602	0.55	1.29	1.34
267.120	$C_{12}H_{20}O_5Na$	244.131	48,466	40,845	0.42	1.93	2.00
269.100	$C_{11}H_{18}O_6Na$	246.110	232,300	177,791	0.55	1.29	1.34
271.076	$C_{10}H_{16}O_7Na$	248.090	1,006,870	1,240,322	0.70	0.64	0.50
273.095	$C_{10}H_{18}O_7Na$	250.105	934,881	1,310,159	0.70	0.64	0.50
285.095	$C_{11}H_{18}O_7Na$	262.105	472,668	567,055	0.64	0.45	0.30
286.053	$C_9H_{13}NO_8Na$	263.064	1,116,433	2,098,323	0.89	1.68	-1.09
287.074	$C_{10}H_{16}O_8Na$	264.085	333,899	488,359	0.80	-0.21	-0.65
289.089	$C_{10}H_{18}O_8Na$	266.100	153,112	152,395	0.80	-0.21	-0.65
297.095	$C_{12}H_{18}O_7Na$	274.105	392,058	450,345	0.58	0.26	0.07
309.095	$C_{13}H_{18}O_7Na$	286.105	86,112	147,151	0.54	0.08	-0.17
319.115	$C_{15}H_{20}O_6Na$	296.126	655,649	411,098	0.40	0.52	0.17
335.110	$C_{15}H_{20}O_7Na$	312.121	776,371	557,866	0.47	-0.31	-0.72
337.105	$C_{18}H_{18}O_5Na$	314.115	996,703	1,045,977	0.28	0.76	-0.10

[a] We collected the same volume of air for each experimental filter.

Table S2. Measured mass-to-charge ratio (*m/z*), suggested ion formula, calculated molecular weight (MW), measured total intensities of extracted ion chromatogram (EIC) peaks, calculated O/C ratio, and predicted saturation concentrations for products existing in SOA from TMB (continued).

m/z	Ion formula	MW	Total int. of EIC peaks (normal, run 1) [a]	Total int. of EIC peaks (aging, run 2) [a]	O/C	$\log_{10} C^*$ (eq. adapted to TMB products)	$\log_{10} C^*$ (eq. by Li et al., 2016)
339.105	$C_{14}H_{20}O_8Na$	316.116	265,193	336,772	0.57	-0.95	-1.44
351.105	$C_{15}H_{20}O_8Na$	328.116	478,275	419,619	0.53	-1.14	-1.69
363.141	$C_{17}H_{24}O_7Na$	340.152	1,151,661	576,982	0.41	-0.69	-1.33
365.136	$C_{20}H_{22}O_5Na$	342.147	1,827,276	1,925,906	0.25	0.36	-0.86
367.100	$C_{15}H_{20}O_9Na$	344.111	535,723	258,279	0.60	-1.98	-2.71
369.116	$C_{15}H_{22}O_9Na$	346.126	405,546	425,047	0.60	-1.98	-2.71
377.136	$C_{21}H_{22}O_5Na$	354.147	226,718	163,024	0.24	0.17	-1.24
379.136	$C_{17}H_{24}O_8Na$	356.147	926,647	423,039	0.47	-1.52	-2.24
381.130	$C_{20}H_{22}O_6Na$	358.142	407,132	317,930	0.30	-0.45	-1.55
383.095	$C_{15}H_{20}O_{10}Na$	360.106	317,655	130,575	0.67	-2.82	-3.78
383.110	$C_{19}H_{20}O_7Na$	360.121	166,839	222,005	0.37	-1.08	-1.98
391.136	$C_{18}H_{24}O_8Na$	368.147	1,323,695	652,300	0.44	-1.71	-2.53
393.152	$C_{18}H_{26}O_8Na$	370.163	2,818,500	867,842	0.44	-1.71	-2.53
395.131	$C_{17}H_{24}O_9Na$	372.142	611,129	535,442	0.53	-2.35	-3.20
395.168	$C_{18}H_{28}O_8Na$	372.178	214,934	65,202	0.44	-1.71	-2.53
399.126	$C_{16}H_{24}O_{10}Na$	376.137	274,427	310,964	0.63	-3.00	-3.99
407.135	$C_{18}H_{24}O_9Na$	384.142	694,004	514,558	0.50	-2.54	-3.47
409.147	$C_{18}H_{26}O_9Na$	386.158	2,590,992	1,650,003	0.50	-2.54	-3.47
411.126	$C_{17}H_{24}O_{10}Na$	388.137	109,514	257,271	0.59	-3.19	-4.21
411.141	$C_{21}H_{24}O_7Na$	388.152	599,344	399,801	0.33	-1.47	-2.67
411.163	$C_{18}H_{28}O_9Na$	388.173	143,870	81,447	0.50	-2.54	-3.47
415.121	$C_{16}H_{24}O_{11}Na$	392.132	310,719	318,827	0.69	-3.85	-5.08
425.142	$C_{18}H_{26}O_{10}Na$	402.153	1,153,390	1,172,884	0.56	-3.38	-4.46
427.158	$C_{18}H_{28}O_{10}Na$	404.168	706,196	562,726	0.56	-3.38	-4.46
441.137	$C_{18}H_{26}O_{11}Na$	418.148	345,697	529,328	0.61	-4.22	-5.49
441.152	$C_{22}H_{26}O_8Na$	418.163	633,244	273,278	0.36	-2.48	-3.81
443.152	$C_{18}H_{28}O_{11}Na$	420.163	465,185	374,715	0.61	-4.22	-5.49
457.132	$C_{18}H_{26}O_{12}Na$	434.142	158,391	226,223	0.67	-5.06	-6.57
459.147	$C_{18}H_{28}O_{12}Na$	436.158	139,947	307,765	0.67	-5.06	-6.57
472.143	$C_{18}H_{27}NO_{12}Na$	449.153	1,616,158	1,140,221	0.67	-3.34	-7.02
475.142	$C_{18}H_{28}O_{13}Na$	452.153	371,298	395,561	0.72	-5.90	-7.68
488.138	$C_{18}H_{27}NO_{13}Na$	465.148	845,870	776,656	0.72	-4.19	-7.74
504.132	$C_{18}H_{27}NO_{14}Na$	481.143	271,311	426,529	0.78	-5.04	-8.46

[a] We collected the same volume of air for each experimental filter.

Table S3. SMILES code, SPARC saturation concentration, and molecular weight of measured or suggested products formed from the photooxidation of TMB.

name	SMILES	log(C*/μg m^{-3})	MW	ref.
3,5-dimethylbenzaldehyde	O=CC1=CC(=CC(=C1)C)C	6.03	134.2	Smith et al., 1999
2,4,6-trimethylphenol	OC1=C(C=C(C=C1C)C)C	5.14	136.2	Smith et al., 1999
3,5-dimethyl-3(2H)-2-furanone	O=C1OC(=CC1C)C	6.32	112.1	Smith et al., 1999
3,5-dimethyl-5(2H)-2-furanone	O=C1OC(C=C1C)C	6.36	112.1	Smith et al., 1999
3-methyl-5-methylidiene-5(2H)-2-furanone	O=C1OC(=C)C=C1C	5.02	110.1	Smith et al., 1999
2-methyl-4-oxo-2-pentenal	O=CC(=CC(=O)C)C	5.78	112.1	Smith et al., 1999
citraconic anhydride	O=C(O1)C(C)=CC1=O	3.68	112.1	Smith et al., 1999
methylglyoxal	O=CC(=O)C	8.38	72.1	Smith et al., 1999
TM135OXMUC	O=CC1(OC1C(=CC(=O)C)C)C	5.31	168.2	MCM v3.3.1
C7M2CO5OOH	OOC(C(=O)C)C(=CC(=O)C)C	3.41	172.2	MCM v3.3.1
C7M3CO	CC(=O)C=C(C)C(=O)C(=O)C	4.47	154.2	MCM v3.3.1
CH3CO2H	CC(=O)O	7.68	60.1	MCM v3.3.1
CH3OOH	COO	7.83	48.0	MCM v3.3.1
HCHO	C=O	9.86	30.0	MCM v3.3.1
CH3OH	CO	8.41	32.0	MCM v3.3.1
CH3NO3	CON(=O)=O	8.42	77.0	MCM v3.3.1
CH3O2NO2	COON(=O)=O	8.17	93.0	MCM v3.3.1
CH3CO3H	CC(=O)OO	7.48	76.1	MCM v3.3.1
PAN	CC(=O)OON(=O)=O	6.84	121.0	MCM v3.3.1
MGLYOX	O=CC(=O)C	8.38	72.1	MCM v3.3.1
MMALANHY	O=C1C=C(C)C(=O)O1	3.68	112.1	MCM v3.3.1
MMALNHYOOH	CC1(OO)C(O)C(=O)OC1=O	-0.05	162.1	MCM v3.3.1
CO2H3CO3H	CC(=O)C(O)C(=O)OO	4.47	134.1	MCM v3.3.1
HCOCO3H	OOC(=O)C=O	6.35	90.0	MCM v3.3.1
HCOCO2H	O=CC(=O)O	8.55	74.0	MCM v3.3.1
C4PAN6	O=N(=O)OOC(=O)C(O)C(=O)C	3.20	179.1	MCM v3.3.1
MMALNHY2OH	O=C1OC(=O)C(C)(O)C1O	0.82	146.1	MCM v3.3.1
C5CODBCO3H	CC(=CC(=O)C)C(=O)OO	3.53	144.1	MCM v3.3.1
C4MCODBPAN	O=N(=O)OOC(=O)C(=CC(=O)C)C	3.62	189.1	MCM v3.3.1
C5CODBCO2H	CC(=O)C=C(C)C(=O)O	4.29	128.1	MCM v3.3.1
CH3COCO2H	OC(=O)C(=O)C	7.35	88.1	MCM v3.3.1
C5CO234	CC(=O)C(=O)C(=O)C	6.73	114.1	MCM v3.3.1
C5CO234OOH	CC(=O)C(=O)C(=O)COO	3.41	146.1	MCM v3.3.1
C5MDICARB	O=CC(=CC(=O)C)C	5.78	112.1	MCM v3.3.1
C6CO2OHOOH	OOC(C)(C=O)C(O)C(=O)C	3.26	162.1	MCM v3.3.1
C5CO243OH	CC(=O)C(O)C(=O)C	5.88	116.1	MCM v3.3.1
C6CO2M2OH	O=CC(C)(O)C(O)C(=O)C	3.78	146.1	MCM v3.3.1
C6CO3MOH	O=CC(C)(O)C(=O)C(=O)C	5.84	144.1	MCM v3.3.1
C5COHOCO3H	OOC(=O)C(C)(O)C(=O)C(=O)C	4.27	176.1	MCM v3.3.1
C4COMOHPAN	O=N(=O)OOC(=O)C(C)(O)C(=O)C(=O)C	3.19	221.1	MCM v3.3.1
CHOMOHCO3H	CC(O)(C=O)C(=O)OO	5.16	134.1	MCM v3.3.1
MXYFUONE	CC1OC(=O)C(=C1)C	6.36	112.1	MCM v3.3.1
NMXYFUOOH	OOC1(C)C(=O)OC(C)C1ON(=O)=O	2.34	207.1	MCM v3.3.1
C23O3MCHO	O=CC(C)OC(=O)C(=O)C	5.86	144.1	MCM v3.3.1
C23O3MCO2H	CC(OC(=O)C(=O)C)C(=O)O	3.17	160.1	MCM v3.3.1
C23O3MCOOH	CC(OC(=O)C(=O)C)OO	4.39	148.1	MCM v3.3.1
ACECOCOCH3	CC(=O)OC(=O)C(=O)C	5.43	130.1	MCM v3.3.1
ACCOCOMOOH	OOCC(=O)C(=O)OC(=O)C	2.48	162.1	MCM v3.3.1
CH3CHO	CC=O	8.98	44.1	MCM v3.3.1
HCOCH2OOH	OOCC=O	6.03	76.1	MCM v3.3.1
GLYOX	O=CC=O	8.61	58.0	MCM v3.3.1
HOCH2CHO	OCC=O	6.87	60.1	MCM v3.3.1
HOCH2CO2H	OCC(=O)O	5.17	76.1	MCM v3.3.1
HOCH2CO3H	OCC(=O)OO	5.93	92.1	MCM v3.3.1
C23O3MOH	CC(O)OC(=O)C(=O)C	5.53	132.1	MCM v3.3.1
C23O3MCO3H	OOC(=O)C(C)OC(=O)C(=O)C	4.04	176.1	MCM v3.3.1
C23O3MCPAN	O=N(=O)OOC(=O)C(C)OC(=O)C(=O)C	3.87	221.1	MCM v3.3.1
MXYFUOOH	CC1(OO)C(O)C(C)OC1=O	1.34	162.1	MCM v3.3.1
CO24C53OOH	OOC(C(=O)C)C(=O)C	5.06	132.1	MCM v3.3.1
C7M2CO5OH	CC(=O)C=C(C)C(O)C(=O)C	4.12	156.2	MCM v3.3.1

Table S3. SMILES code, SPARC saturation concentration, and molecular weight of measured or suggested products formed from the photooxidation of TMB (continued).

name	SMILES	log(C*/μg m^{-3})	MW	ref.
TM135MUO2H	CC(=O)C=C(C)C1OC1(C)C(=O)O	1.56	184.2	MCM v3.3.1
TM135MUO3H	OOC(=O)C1(C)OC1C(=CC(=O)C)C	3.51	200.2	MCM v3.3.1
TM135MUPAN	O=N(=O)OOC(=O)C1(C)OC1C(=CC(=O)C)C	3.32	245.2	MCM v3.3.1
EPXMALKT	O=CC1(C)OC1C(=O)C	6.39	128.1	MCM v3.3.1
EPXMKTCO2H	CC(=O)C1OC1(C)C(=O)O	3.10	144.1	MCM v3.3.1
EPXMKTCO3H	CC1(OC1C(=O)C)C(=O)OO	4.58	160.1	MCM v3.3.1
EPXMKTPAN	O=N(=O)OOC(=O)C1(C)OC1C(=O)C	4.41	205.1	MCM v3.3.1
C3MDIALOOH	OOC(C)(C=O)C=O	5.68	118.1	MCM v3.3.1
C3MDIALOH	O=CC(C)(O)C=O	6.74	102.1	MCM v3.3.1
TM135MUOOH	OOC(C)(C(O)C(=O)C)C1OC1(C)C=O	1.58	218.2	MCM v3.3.1
TM135MUNO3	O=CC1(C)OC1C(C)(ON(=O)=O)C(O)C(=O)C	2.47	247.2	MCM v3.3.1
TM135MUOH	O=CC1(C)OC1C(C)(O)C(O)C(=O)C	2.00	202.2	MCM v3.3.1
TMBOOH	OOCc1cc(C)cc(C)c1	4.18	152.2	MCM v3.3.1
TMBCHO	O=Cc1cc(C)cc(C)c1	6.03	134.2	MCM v3.3.1
DMPHOOH	OOc1cc(C)cc(C)c1	4.55	138.2	MCM v3.3.1
DMPHOHNO2	Cc1cc(C)c(N(=O)=O)c(O)c1	4.99	167.2	MCM v3.3.1
MXOHNO2OOH	OOC1(O)C(=CC2(C)OOC1(N(=O)=O)C2O)C	-1.59	249.2	MCM v3.3.1
TMBCO2H	Cc1cc(C)cc(c1)C(=O)O	3.52	150.2	MCM v3.3.1
TMBCO3H	OOC(=O)c1cc(C)cc(C)c1	4.53	166.2	MCM v3.3.1
TMBNO3	O=N(=O)OCc1cc(C)cc(C)c1	5.03	181.2	MCM v3.3.1
TMBOH	OCc1cc(C)cc(C)c1	4.67	136.2	MCM v3.3.1
TM135BPOOH	OOC1C(=CC2(C)OOC1(C)C2O)C	1.56	202.2	MCM v3.3.1
TM135OBPOH	CC1=CC2(C)OOC(C)(C1=O)C2O	4.99	184.2	MCM v3.3.1
TM135BPNO3	O=N(=O)OC1C(=CC2(C)OOC1(C)C2O)C	3.11	231.2	MCM v3.3.1
TM135BP2OH	CC1=CC2(C)OOC(C)(C1O)C2O	2.31	186.2	MCM v3.3.1
TM135BZOL	Cc1cc(C)c(O)c(C)c1	5.14	136.2	MCM v3.3.1
NTM135LOOH	OOC1(O)C(=CC2(C)OOC1(C)C2ON(=O)=O)C	0.99	263.2	MCM v3.3.1
NTM135OLOH	O=N(=O)OC1C2(C)OOC1(C)C(O)(O)C(=C2)C	1.20	247.2	MCM v3.3.1
TM135OLOOH	OOC1(O)C(=CC2(C)OOC1(C)C2O)C	0.05	218.2	MCM v3.3.1
TM135OLOH	OC1C2(C)OOC1(C)C(O)(O)C(=C2)C	-0.03	202.2	MCM v3.3.1
formic acid	O=CO	8.15	46.0	Fisseha et al., 2004
acetic acid	CC(O)=O	7.68	60.1	Fisseha et al., 2004
pyruvic acid	CC(C(O)=O)=O	7.35	88.1	Fisseha et al., 2004
lactic acid	CC(C(O)=O)O	5.51	90.1	Fisseha et al., 2004
oxalic acid	OC(C(O)=O)=O	5.58	90.0	Fisseha et al., 2004
malonic acid	OC(CC(O)=O)=O	1.83	104.1	Fisseha et al., 2004
succinic acid	OC(CCC(O)=O)=O	2.86	118.1	Fisseha et al., 2004
methyl maleic acid	O=C(C(C)=CC(O)=O)O	2.41	130.1	Fisseha et al., 2004
maleic acid	O=C(C=CC(O)=O)O	2.20	116.1	Fisseha et al., 2004
3,5-dimethylbenzoic acid	CC1=CC(C(O)=O)=CC(C)=C1	3.52	150.2	Fisseha et al., 2004
citric acid	OC(CC(O)=O)(C(O)=O)CC(O)=O	-4.29	192.1	Fisseha et al., 2004
MW88	CC(C(O)=O)=O	7.35	88.1	Sato et al., 2012
MW128	CC(C(O)=O)=CC(C)=O	4.29	128.1	Sato et al., 2012
MW162	CC(C(O)C(C)=O)(O)C(O)=O	1.00	162.1	Sato et al., 2012
MW170	CC(C(O)=O)=CC(C)=CC(O)=O	0.35	170.2	Sato et al., 2012
MW174	CC(C1C(C(O)=O)C)(O1)C(O)=O	-0.23	174.2	Sato et al., 2012
MW184	CC(C1C(C)=CC(C)=O)(O1)C(O)=O	1.56	184.2	Sato et al., 2012
MW186	CC(C1C(C)=CC(O)=O)(O1)C(O)=O	-1.04	186.2	Sato et al., 2012
MW190	CC(C(C(C(O)=O)C)=O)(O)C(O)=O	-3.75	190.2	Sato et al., 2012
MW192	CC(C(O)C(C(O)=O)C)(O)C(O)=O	-1.16	192.2	Sato et al., 2012
MW200	CC(C1C(C(C(C)=O)=O)C)(O1)C(O)=O	1.46	200.2	Sato et al., 2012
MW202	CC(C(O)C(C)=CC(C)=O)(O)C(O)=O	-0.28	202.2	Sato et al., 2012
MW204	CC(C1C(C(O)C(O)=O)(O)C)(O1)C(O)=O	-4.42	220.2	Sato et al., 2012
MW216	CC(C1C(C(C(C)=O)=O)(O)C)(O1)C(O)=O	-0.59	216.2	Sato et al., 2012
MW218	CC(C1C(C(O)C(C)=O)(O)C)(O1)C(O)=O	-1.49	218.2	Sato et al., 2012
MW232	CC(C(C(C(C(C)=O)=O)(O)C)=O)(O)C(O)=O	-0.82	232.2	Sato et al., 2012
MW234	CC(C(O)C(C(C(C)=O)=O)(O)C)(O)C(O)=O	-1.50	234.2	Sato et al., 2012
glycolic acid	OCC(O)=O	5.17	76.1	Plapran et al., 2014
butanoic acid	CCCC(O)=O	6.62	88.1	Plapran et al., 2014
glyoxal 2-mer	OC(C)(OC(C(C)=O)O1)C1O	2.05	162.1	Kalberer et al., 2004

Table S3. SMILES code, SPARC saturation concentration, and molecular weight of measured or suggested products formed from the photooxidation of TMB (Continued).

name	SMILES	log(C*/μg m^{-3})	MW	ref.
glyoxal 3-mer	CC1(OC(C(C)=O)O2)C2OC(C(C)=O)O1	4.56	216.2	Kalberer et al., 2004
glyoxal 4-mer	CC1(OC(C2(C)OC(O)C(C)(O)O2)O3)C3OC(C(C)=O)O1	-1.27	306.3	Kalberer et al., 2004
glyoxal 5-mer	CC1(OC(C2(C)OC(O)C(C)(O)O2)O3)C3OC(C4(C)OC(C)(O)C(O)O4)O1	-7.53	396.3	Kalberer et al., 2004
glyoxal 5-mer	CC1(OC(C2(C)OC(OC(C(C)=O)O3)C3(C)O2)O4)C4OC(C(C)=O)O1	1.55	360.3	Kalberer et al., 2004
glyoxal 6-mer	CC1(OC(C2(C)OC(OC(C(C)=O)O3)C3(C)O2)O4)C4OC(C5(C)OC(C)(O)C(O)O5)O1	-4.60	450.4	Kalberer et al., 2004
glyoxal 7-mer	CC1(OC(C2(C)OC(OC(C(C)=O)O3)C3(C)O2)O4)C4OC(C5(C)OC6(C)C(OC(C(C)=O)O6)O5)O1	-1.55	504.4	Kalberer et al., 2004
glyoxal 8-mer	CC1(OC(C2(C)OC(OC(C3(C)OC(O)C(C)(O)O3)O4)C4(C)O2)O5)C5OC(C6(C)OC7(C)C(OC(C(C)=O)O7)O6)O1	-7.91	594.5	Kalberer et al., 2004
glyoxal 2-mer + benzaldehyde	CC12C(OC(C(C)=O)O2)OC(C3=CC(C)=CC(C)=C3)O1	2.37	278.3	Kalberer et al., 2004
glyoxal 3-mer + benzaldehyde	CC12C(OC(C3(C)OC(O)C(C)(O)O3)O2)OC(C4=CC(C)=CC(C)=C4)O1	-2.86	368.4	Kalberer et al., 2004
glyoxal 4-mer + benzaldehyde	CC12C(OC(C3(C)OC4C(C)(OC(C(C)=O)O4)O3)O2)OC(C5=CC(C)=CC(C)=C5)O1	-0.97	422.4	Kalberer et al., 2004
glyoxal 5-mer + benzaldehyde	CC12C(OC(C3(C)OC4C(C)(OC(C5(OC(O)C(C)(O)O5)C)O4)O3)O2)OC(C6=CC(C)=CC(C)=C6)O1	-6.27	512.5	Kalberer et al., 2004
glyoxal 6-mer + benzaldehyde	CC12C(OC(C3(C)OC4C(C)(OC(C5(OC6C(C)(OC(C(C)=O)O6)O5)C)O4)O3)O2)OC(C7=CC(C)=CC(C)=C7)O1	-4.18	566.6	Kalberer et al., 2004
glyoxal 2-mer + pyrvic-acid	O=C(C1(OC(OC(C(C)=O)O2)C2(C)O1)C)O	0.81	232.2	Kalberer et al., 2004
glyoxal 3-mer + pyrvic-acid	O=C(C1(OC(OC(C2(C)OC(O)C(C)(O)O2)O3)C3(C)O1)C)O	-4.14	322.3	Kalberer et al., 2004
glyoxal 4-mer + pyrvic-acid	O=C(C1(OC(OC(C2(C)OC3C(C)(OC(C(C)=O)O3)O2)O4)C4(C)O1)C)O	-2.28	376.3	Kalberer et al., 2004
glyoxal 5-mer + pyrvic-acid	O=C(C1(OC(OC(C2(C)OC3C(C)(OC(C4(C)OC(O)C(C)(O)O4)O3)O2)O5)C5(C)O1)C)O	-7.99	466.4	Kalberer et al., 2004
glyoxal 6-mer + pyrvic-acid	O=C(C1(OC(OC(C2(C)OC3C(C)(OC(C4(C)OC5C(C)(OC(C(C)=O)O5)O4)O3)O2)O6)C6(C)O1)C)O	-5.52	520.4	Kalberer et al., 2004

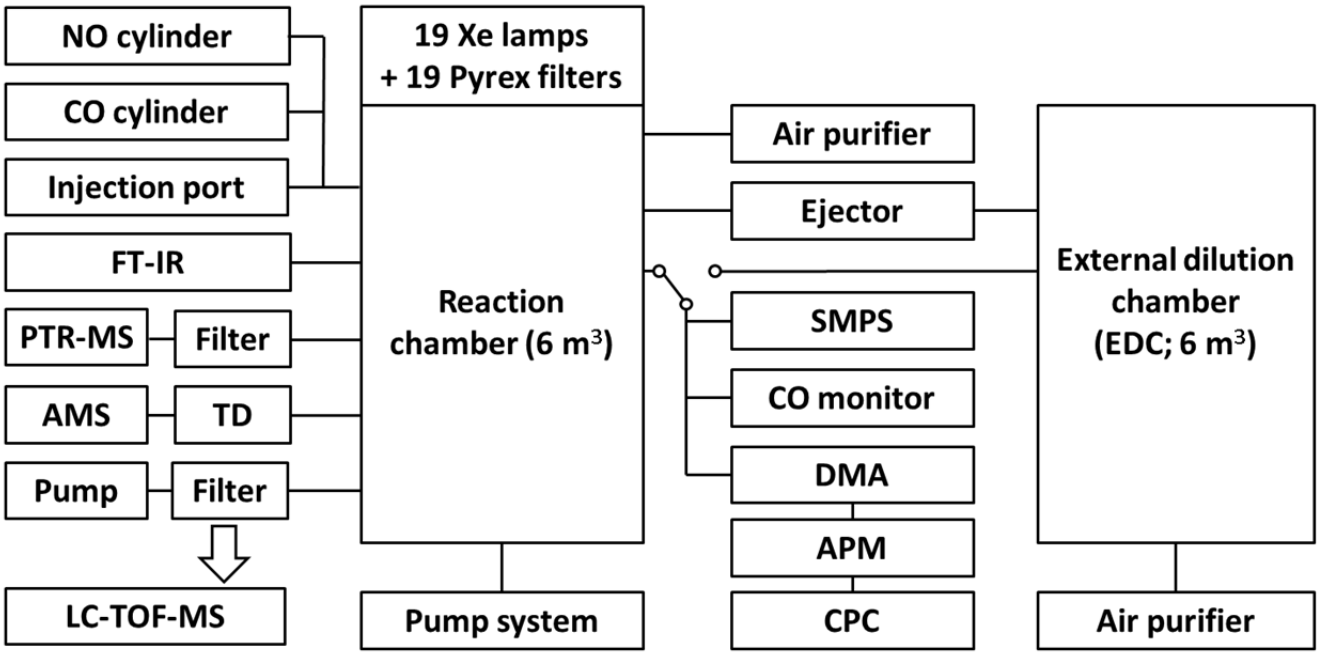

Figure S1. Schematic diagram of the chamber system and analytical instruments used in this study.

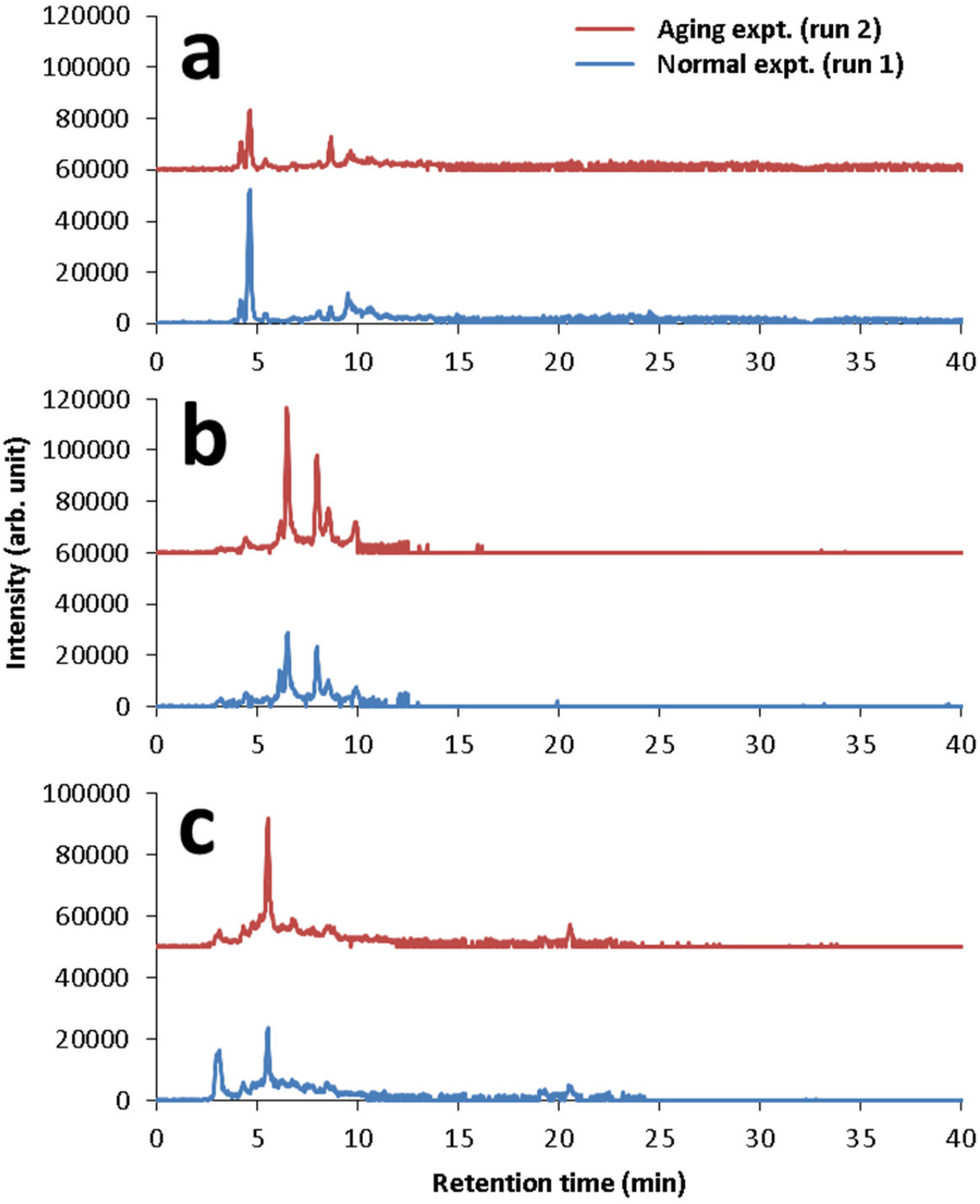

Figure S2. Extracted ion chromatograms observed for (a) $C_9H_{14}O_4Na^+$, (b) $C_9H_{14}O_5Na^+$, and (c) $C_9H_{14}O_6Na^+$ by positive-mode LC-TOF-MS.

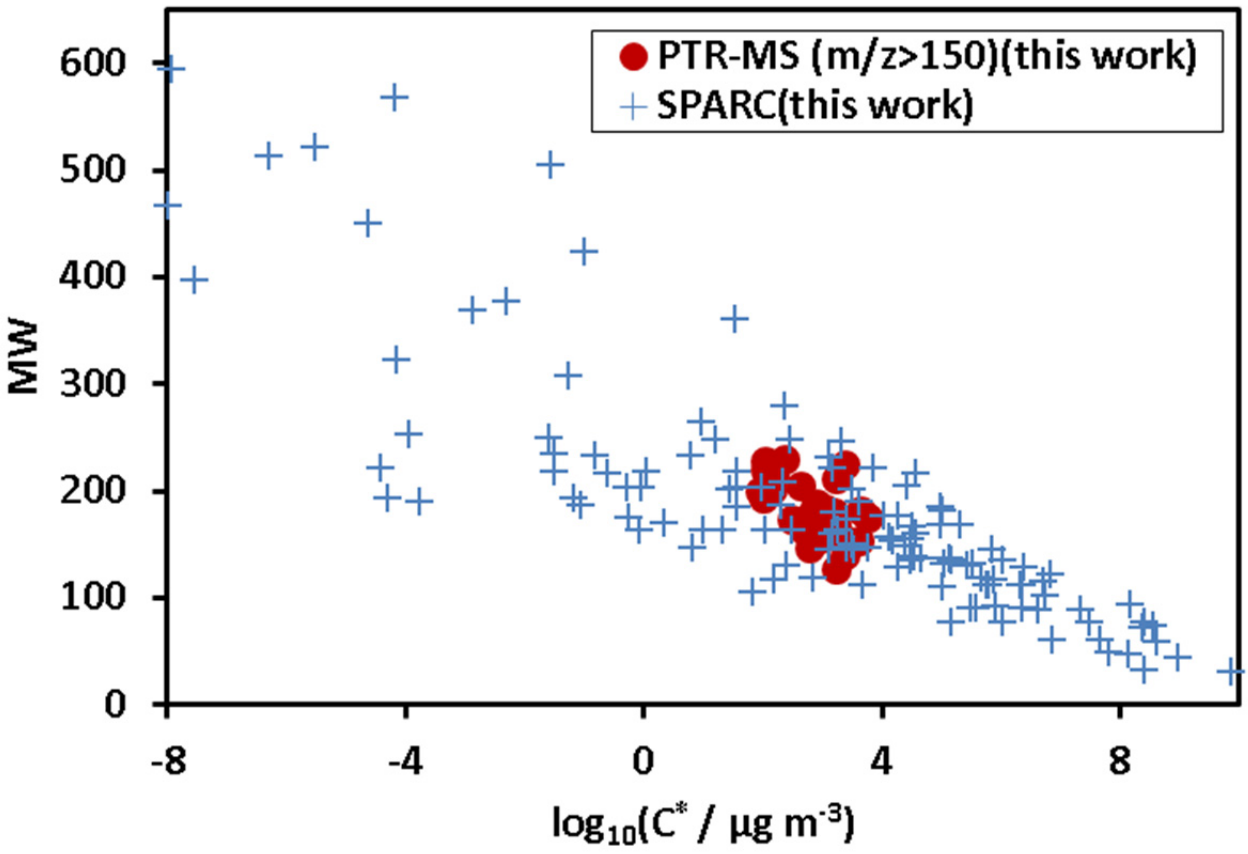

Figure S3. Molecular weight plotted as a function of saturation concentration for products formed from the photooxidation of TMB (molecular corridor).

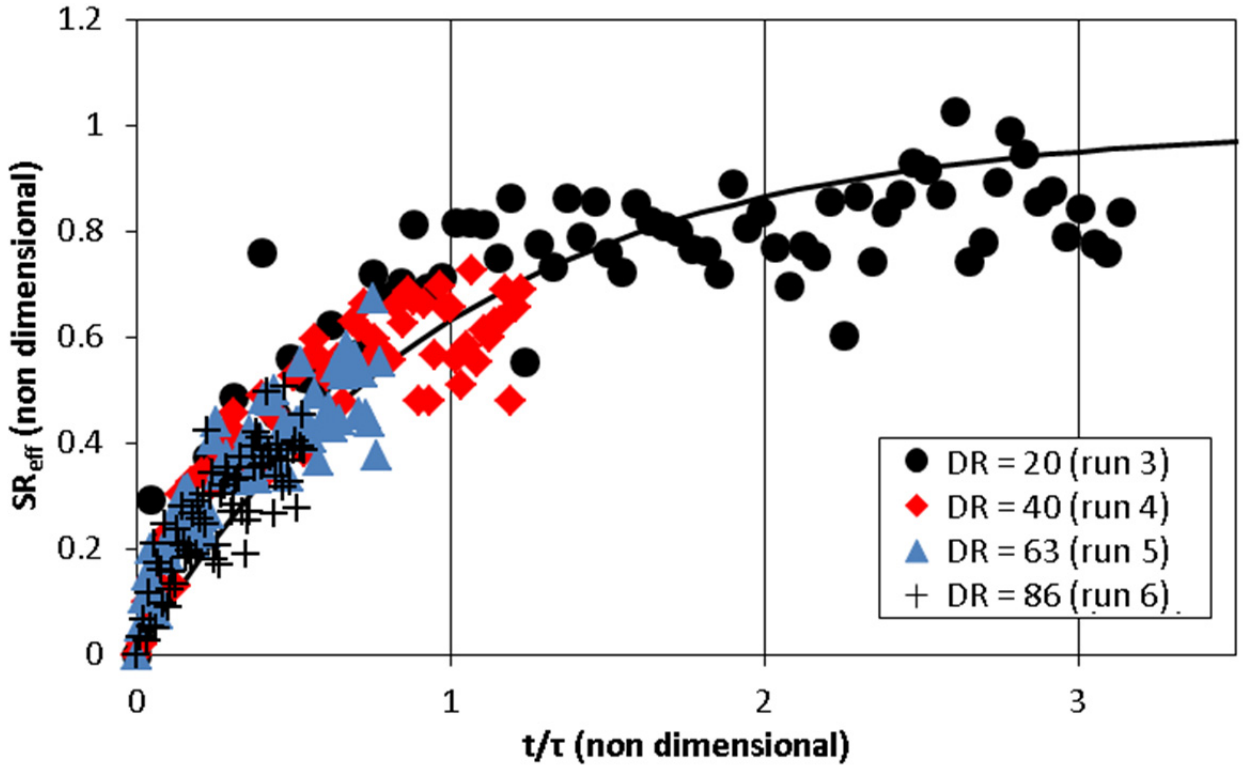

Figure S4. Effective saturation ratio (SR_{eff}) plotted as a function of the ratio of time (t) to equilibration timescale (τ).

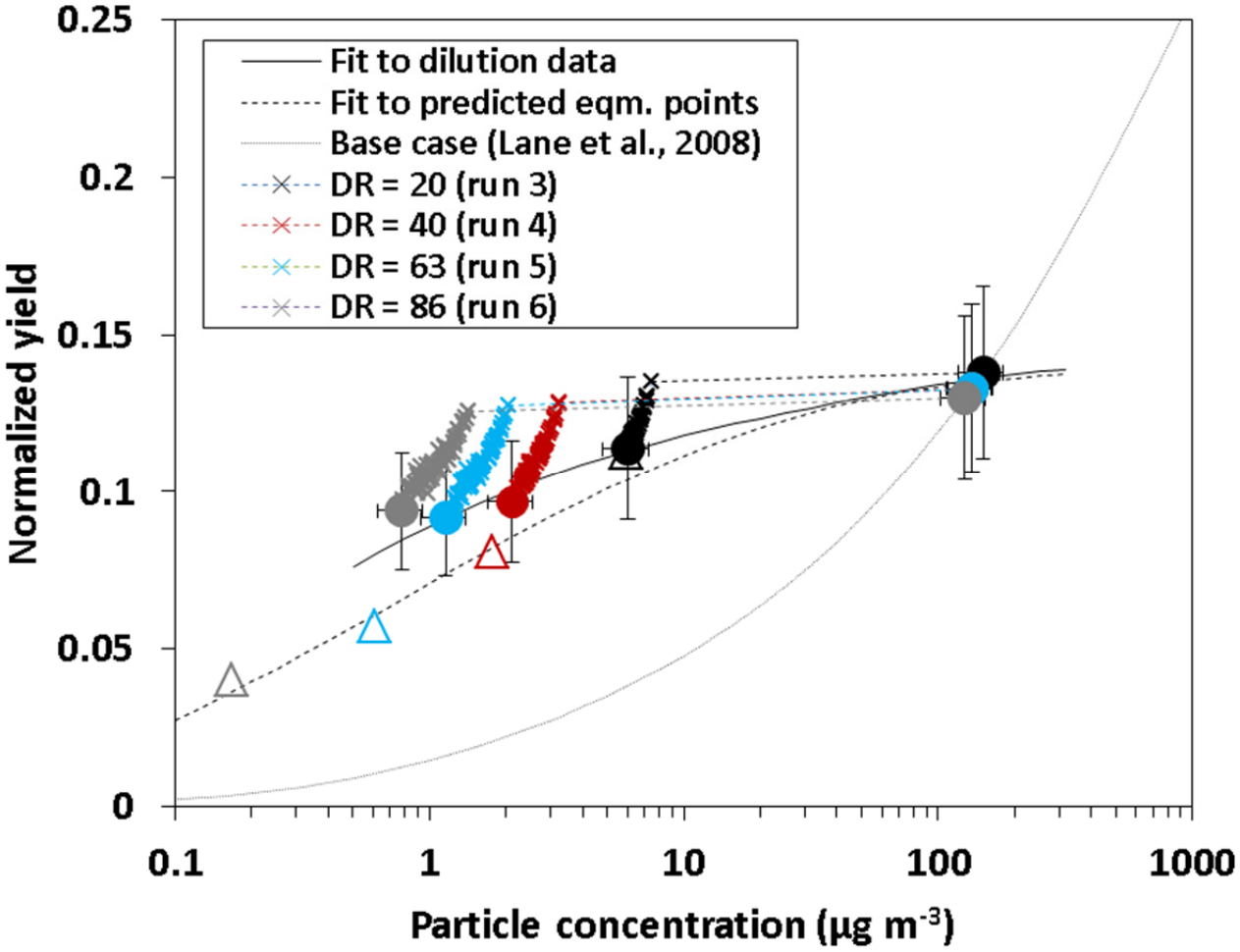

Figure S5. Normalized yield measured during dilution experiments as a function of particle concentration; circle symbols represent data observed before and after dilution; triangle symbols represent equilibrium points predicted based on results of equilibration timescale analysis.