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Effects of SO_2 on optical properties of secondary organic aerosol generated from photooxidation of toluene under different relative humidity conditions

Wenyu Zhang et al.

Correspondence to: Weigang Wang (wangwg@iccas.ac.cn) and Maofa Ge (gemaofa@iccas.ac.cn)

S1. Calculation of mass absorption cross section

Mass absorption cross section (MAC, square meters per gram), is a convenient proxy for the relationship between radiative transfer and mass (Bond and Bergstrom, 2006). For small particles (e.g., particles smaller than 200nm), MAC is defined as

$$\mathrm{MAC} = \frac{6\pi}{\rho\lambda}\mathrm{Im}[\frac{m^2-1}{m^2+2}] \quad (1)$$

where ρ is the density of the particles, and m is complex refractive index (Bohren and Huffman, 1983).

S2. Calculation of simple forcing efficiency

Simple forcing efficiency (SFE) parameterization proposed by Bond and Bergstrom are used for investigating the direct radiative forcing at the Earth's surface (Chýlek et al., 1995;Bond and Bergstrom, 2006)

$$\mathrm{SFE} = \frac{S_0}{4}\tau_{atm}^2(1-F_c)[2(1-a_s)^2\frac{Q_{bs}\cdot C}{M} - 4a_s\frac{Q_a\cdot C}{M}] \quad (2)$$

where SFE is in units of watts per gram, S_0 is the solar irradiance (1370W/m^2), τ_{atm} is the atmospheric albedo (0.79), Fc is the cloud fraction (approximately 0.6), a_s is the surface albedo (average 0.19), M is aerosol mass, C is the cross section, Q_{bs} and Q_a are the aerosol backscattering efficiency and the absorption efficiency, respectively. On the basis that SOA are spherical, the SFE could simplified to equation (6):

$$\begin{aligned}\mathrm{SFE} &= \frac{S_0}{4}\tau_{atm}^2(1-F_c)\left[2(1-a_s)^2\frac{Q_{bs}\cdot\frac{1}{4}\pi D^2}{\rho\cdot\frac{1}{6}\pi D^3} - 4a_s\frac{Q_a\cdot\frac{1}{4}\pi D^2}{\rho\cdot\frac{1}{6}\pi D^3}\right] \\ &= \frac{S_0}{4}\tau_{atm}^2(1-F_c)\frac{3}{2\rho D}[2(1-a_s)^2Q_{bs} - 4a_sQ_a]\end{aligned} \quad (3)$$

At 532 nm, the SOA generated by toluene in all conditions showed no absorption, so Q_a could be set to zero and the ratio of SFE could be simplified to equation (7)

$$\mathrm{SFE} = \frac{3S_0}{4}\tau_{atm}^2(1-F_c)\frac{1}{\rho D}(1-a_s)^2Q_{bs} \quad (4)$$

Table S1. Reaction conditions, instruments, mass concentrations and refractive indexes of SOA derived from toluene.

Reaction conditions				SOA properties			Wavelength (λ/nm)	Reference
Toluene (ppm)	NO (ppm)	NO*x* (ppm)	Oxidation (ppm)	Mass (μg/m^3)	Refractive index			
					RI(n)	RI(k)		
~10	\	\	O_3, ~10	\	1.49-1.50	\	532	Redmond and Thompson et al., 2011
0.063-0.168	\	0.03-0.12	O_3, ~10	\	SSA, 0.95		355	Ma et al., 2012
1	\	\	O_3, ~20	592	1.45	0.024	405	Feng et al., 2019
1.7-3.7	0.6-3.1	0.6-3.1	propene	74-680	1.35-1.61	\	532	Kim and Paulson et al., 2010 Kim et al., 2011
4.0	\	0.5	CH_3ONO, ~0.01	127-216	1.632	0.047	355	Nayakama et al., 2010
					1.483	0.007	532	
4.0	0.1-0.6	0.1-0.6	CH_3ONO, ~0.01	30-160	1.449-1.567	0.0018-0.0072	405	Nayakama et al., 2013
					1.431-1.498	0.0000-0.0010	532	
					1.389-1.452	0.0000	781	
0.2	\	\	H_2O_2, 5	\	1.45	\	532	Li et al.,2014
0.34	\	\	H_2O_2, ~16; 30%RH	\	\	0.0005	365	Liu et al., 2016
0.34	1.8	1.8	H_2O_2, ~16; 30%RH		\	0.019	365	
0.4	1.8	1.8	H_2O_2, ~16; <5%RH		\		\	
0.3	1.8	1.8	H_2O_2, ~16; 50%RH					
0.34	1.8	1.8	H_2O_2, ~16; 80%RH					
0.2	\	0.07	None seed	47	\	0.02	350	Zhong and Jang, 2011
			AS	38-44		0.06		
			Acid	31-35		0.045		
4.0	0.04	0.4	\	\	1.464	0.000	532	Li et al.,2014

0.2	0.2	0.9	\		1.518	0.000		
5	0-10	0-10	\	770-2000	1.567-1.597	0.011-0.033	320	Liu et al., 2015
					1.546-1.571	0.002-0.015	405	
0.18	0.24	0.35	RH<5%	\	1.45	0.000	375	this work
					1.412	0.000	532	
0.19	0.28	0.43	SO_2=30ppb, <5%RH		1.37	0.014	375	
					1.348	0.000	532	
0.17	0.24	0.36	>80%RH		1.566	0.022	375	
					1.504	0.000	532	
0.18	0.23	0.26	SO_2=40 ppb, >80%RH		1.51	0.12	375	
					1.468	0.000	532	

Table S2. The identified MS peaks, molecular weights, formulas and calculated RI(n) values of main products of toluene-derived SOA in positive mode.

Molecular formula	M + H	M + Na	D	DS	W	WS	Calculated RI
$C_3H_9NO_3$	107.97	130.16		√			1.3727
$C_4H_{10}O_6$		113.10		√			1.3595
$C_4H_9NO_2$		126.05	√	√		√	1.4013
$C_4H_8O_5$	137.06		√				1.4073
$C_4H_8O_4$		142.94	√				1.4070
$C_5H_8O_5$	149.02	170.96	√	√	√	√	1.4413
$C_4H_6O_5$		157.08	√	√		√	1.4238
$C_7H_{15}NO_3$	162.04		√				1.4072
$C_5H_8O_6$	164.92		√	√	√	√	1.4451
$C_7H_9NO_4$	172.09				√	√	1.5110
$C_7H_{17}NO_6$		174.95		√		√	1.3787
$C_7H_{14}O_6$	195.12		√	√	√	√	1.4091
$C_6H_{15}NO_6$	198.11			√			1.3776
$C_8H_{10}O_6$	203.05					√	1.4793
$C_{11}H_{24}O_3$	205.07			√		√	1.3874
$C_7H_{10}O_7$	206.97					√	1.4715
$C_7H_{15}NO_6$	210.11		√	√	√		1.4112
$C_7H_{16}O_7$	212.15			√			1.3800
$C_{11}H_{22}O_4$	218.92		√				1.4173
$C_7H_{15}NO_7$	226.14		√				1.4124
$C_{11}H_{23}NO_4$	234.20	256.56	√	√	√	√	1.4190
$C_{14}H_{28}O_4$	261.23		√				1.4265
$C_{13}H_{27}NO_4$	262.23		√	√	√	√	1.4275
$C_9H_{20}O_9$	273.16		√	√			1.3894
$C_{13}H_{27}NO_5$	278.24		√	√	√	√	1.4268
$C_{13}H_{26}O_6$	279.16		√	√		√	1.4247
$C_{13}H_{29}NO_5$	280.26		√	√			1.3945
$C_{12}H_{27}NO_6$	282.27		√	√	√	√	1.3950
$C_{15}H_{31}NO_7$	290.27		√	√	√	√	1.4268
$C_{10}H_{20}O_{10}$	301.14		√	√	√	√	1.4204
$C_9H_{19}NO_{10}$	302.24		√	√	√		1.4231
$C_8H_{17}NO_{11}$	304.26		√	√	√	√	1.4293
$C_9H_{20}O_{11}$	305.25			√			1.3893
$C_{10}H_{18}O_{11}$	315.16					√	1.4529
$C_{14}H_{27}NO_7$	318.24				√		1.5227
$C_9H_{21}NO_{11}$	320.25		√	√	√	√	1.3934
$C_{16}H_{27}NO_7$	346.33				√		1.5258
$C_{11}H_{22}O_{12}$	347.22		√	√	√	√	1.4266
$C_{16}H_{33}NO_7$	352.24		√				1.4303
$C_{12}H_{25}NO_{11}$	360.31		√				1.4268
$C_{16}H_{28}O_9$	365.11					√	1.4947
$C_{14}H_{31}NO_{10}$	374.36		√	√	√		1.3991

$C_{18}H_{32}O_{10}$	409.29					√	1.4974
$C_{15}H_{30}O_{13}$	419.31	441.30	√				1.4330
$C_{22}H_{46}O_{9}$	455.31			√			1.4085
$C_{17}H_{35}NO_{13}$	462.14		√	√		√	1.4366
$C_{15}H_{30}O_{16}$	467.10		√	√	√	√	1.4335
$C_{20}H_{42}O_{12}$	475.38			√			1.4066
$C_{23}H_{40}O_{12}$	509.25				√		1.5374
$C_{25}H_{47}NO_{10}$	522.60					√	1.5081
$C_{20}H_{41}NO_{15}$	536.16		√	√	√	√	1.4405
$C_{18}H_{36}O_{18}$	541.12		√	√	√		1.4380
$C_{27}H_{51}NO_{10}$	550.70					√	1.5109
$C_{22}H_{38}O_{16}$	559.50				√		1.5382
$C_{24}H_{50}O_{14}$	563.53		√	√	√		1.4127
$C_{26}H_{46}O_{14}$	583.51				√		1.5423
$C_{21}H_{44}O_{18}$	585.53		√	√	√		1.4110
$C_{24}H_{51}NO_{16}$	610.18		√	√	√		1.4147
$C_{26}H_{46}O_{16}$	615.15				√		1.5432
$C_{29}H_{52}O_{15}$	641.60				√		1.5465
$C_{28}H_{51}NO_{15}$	642.60				√		1.5461

Table S3. The identified mass spectra peaks, molecular weights, formulas and calculated RI(n) values of main products of toluene-derived SOA in negative mode.

Molecular formula	M - H	D	DS	W	WS	Calculated RI
$C_9H_{14}O_6$	217.04				√	1.4762
$C_{12}H_{16}O_4$	223.02			√		1.5459
$C_6H_{12}O_9$	227.21	√		√		1.4100
$C_{12}H_{26}O_4$	233.14		√			1.3918
$C_{10}H_{23}NO_5$	236.10		√		√	1.3908
$C_9H_{20}O_7$	238.88	√	√			1.3872
$C_7H_{14}O_9$	241.23	√				1.4173
$C_7H_{16}O_9$	243.13	√		√		1.3884
$C_{11}H_{25}NO_5$	250.13		√		√	1.3888
$C_9H_{18}O_8$	253.23	√				1.4166
$C_9H_{21}NO_7$	254.24		√			1.3911
$C_8H_{16}O_9$	255.22	√	√	√	√	1.4152
$C_{12}H_{22}O_6$	260.88	√		√	√	1.4523
$C_{11}H_{22}O_7$	265.13	√	√	√	√	1.4245
$C_9H_{18}O_9$	269.26	√				1.4175
$C_{14}H_{24}O_5$	271.09				√	1.4904
$C_{15}H_{30}O_4$	273.04	√				1.4264
$C_{13}H_{29}NO_5$	278.26	√	√	√	√	1.3945
$C_{10}H_{16}O_9$	279.04				√	1.4875
$C_{12}H_{27}NO_6$	280.25		√		√	1.3950
$C_{10}H_{20}O_9$	283.25	√	√	√	√	1.4196
$C_7H_{17}NO_{11}$	290.12		√		√	1.3925
$C_{15}H_{32}O_5$	291.14		√			1.3950
$C_{13}H_{26}O_7$	293.16	√	√	√	√	1.4267
$C_{11}H_{22}O_9$	297.14	√	√		√	1.4261
$C_{15}H_{26}O_6$	301.04				√	1.4918
$C_{13}H_{26}O_8$	309.18	√	√	√	√	1.4274
$C_{12}H_{24}O_9$	311.15	√	√	√	√	1.4235
$C_{15}H_{26}O_7$	317.06				√	1.4926
$C_{11}H_{16}O_{11}$	323.23			√		1.5230
$C_{13}H_{27}NO_8$	324.24	√	√	√	√	1.4256
$C_{13}H_{26}O_9$	325.17	√	√	√		1.4282
$C_{16}H_{28}O_7$	331.06				√	1.4941
$C_{15}H_{31}NO_7$	336.31	√	√	√		1.4287
$C_{16}H_{34}O_7$	337.19		√			1.3997
$C_{15}H_{32}O_8$	339.18	√	√	√	√	1.3984
$C_{11}H_{18}O_{12}$	341.09				√	1.4878
$C_{11}H_{22}O_{12}$	345.12	√		√		1.4266
$C_{11}H_{25}NO_{11}$	346.02		√			1.3972
$C_{16}H_{34}O_8$	353.18		√			1.4004
$C_{16}H_{32}O_9$	367.37	√				1.4318
$C_{17}H_{30}O_9$	377.06				√	1.4961

$C_{16}H_{28}O_{10}$	379.06				√	1.4954
$C_{18}H_{38}O_8$	381.21		√			1.4032
$C_{19}H_{32}O_8$	387.10			√	√	1.5313
$C_{18}H_{38}O_9$	397.20		√			1.4042
$C_{15}H_{31}NO_{11}$	400.20	√		√		1.4327
$C_{14}H_{28}O_{13}$	402.82	√		√	√	1.4295
$C_{17}H_{30}O_{11}$	409.08				√	1.4974
$C_{19}H_{41}NO_8$	410.16		√		√	1.4049
$C_{14}H_{24}O_{14}$	415.02				√	1.4945
$C_{17}H_{29}NO_{11}$	422.18			√		1.5313
$C_{15}H_{26}O_{14}$	429.03				√	1.4965
$C_{21}H_{44}O_9$	439.06				√	1.4072
$C_{23}H_{40}O_9$	459.28			√		1.5364
$C_{23}H_{42}O_9$	461.04				√	1.5036
$C_{19}H_{32}O_{13}$	467.04			√		1.5334
$C_{23}H_{46}O_{10}$	481.30	√	√	√	√	1.4422
$C_{20}H_{36}O_{13}$	483.04				√	1.5032
$C_{23}H_{49}NO_{11}$	514.36		√			1.4122
$C_{23}H_{40}O_{13}$	523.22			√		1.5380
$C_{24}H_{46}O_{12}$	525.24	√		√		1.4748
$C_{24}H_{50}O_{12}$	529.30		√		√	1.4120
$C_{22}H_{38}O_{15}$	541.05			√		1.5366
$C_{30}H_{59}NO_7$	544.71	√	√	√	√	1.4815
$C_{27}H_{50}O_{13}$	580.98				√	1.5126
$C_{27}H_{50}O_{14}$	597.21				√	1.5125

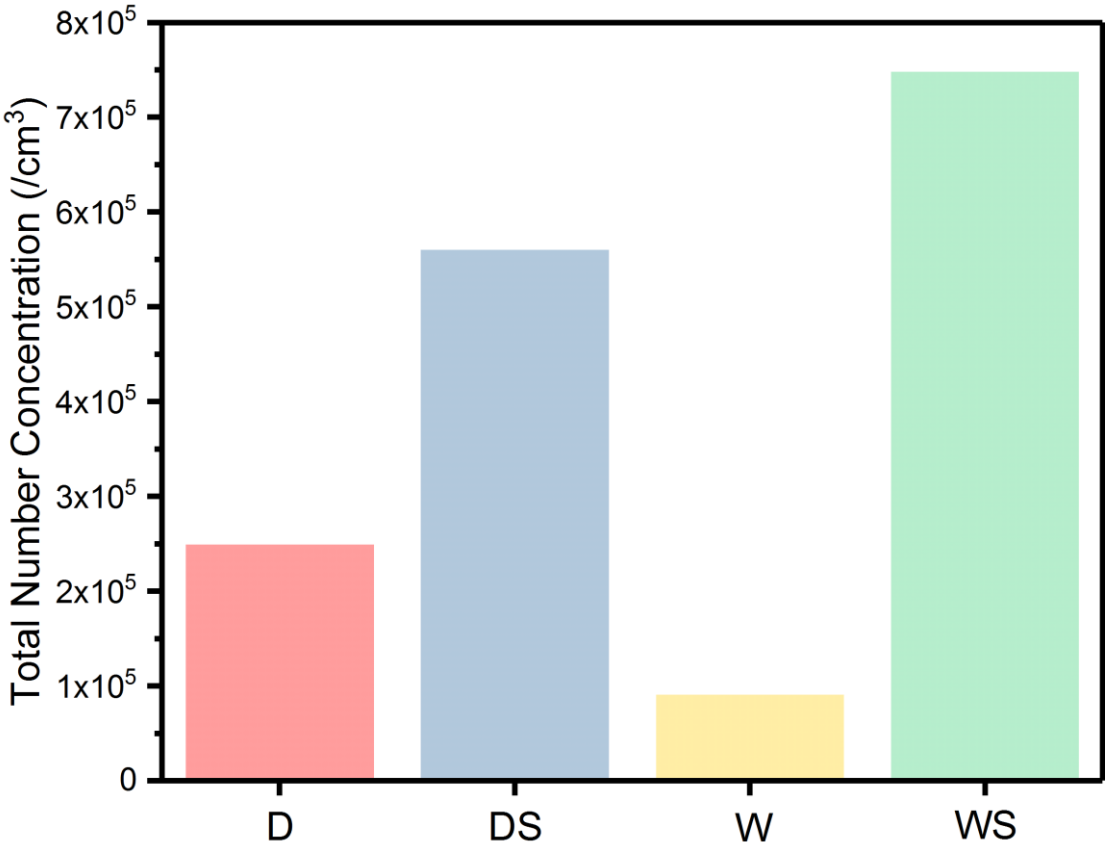

Figure S1. The maximum of total number concentrations of SOA derived from toluene under the D, DS, W and WS conditions.

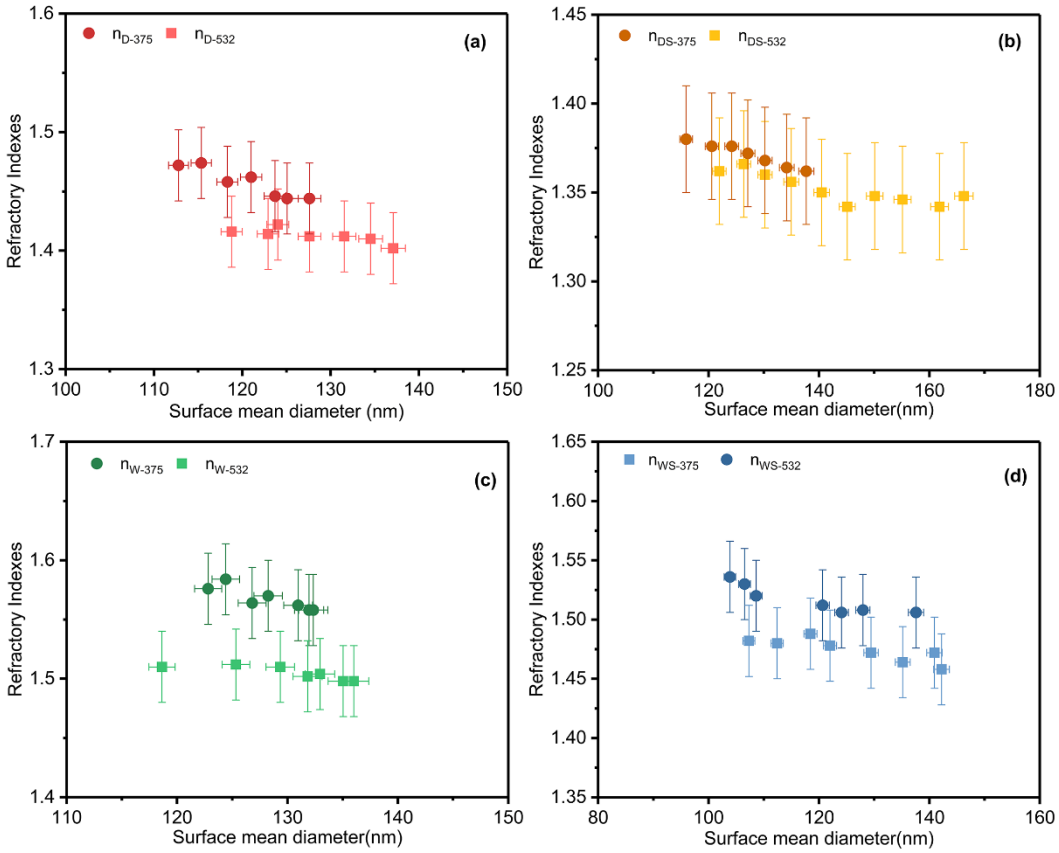

Figure S2. Variation tendency of the values of RI of toluene-derived SOAs under the four different conditions at (a) D1, (b) DS1, (c) W1 and (d) WS1.

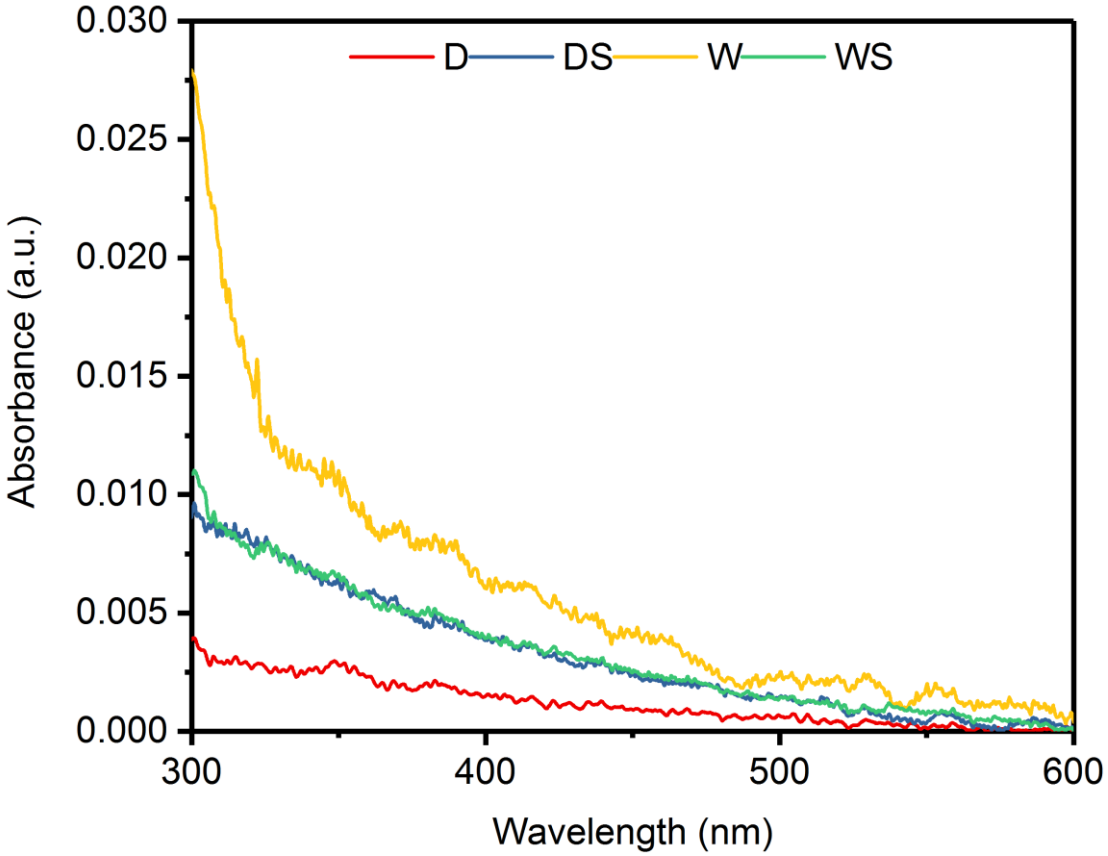

Figure S3. UV-Vis absorption spectrum of toluene SOA under the four different conditions.

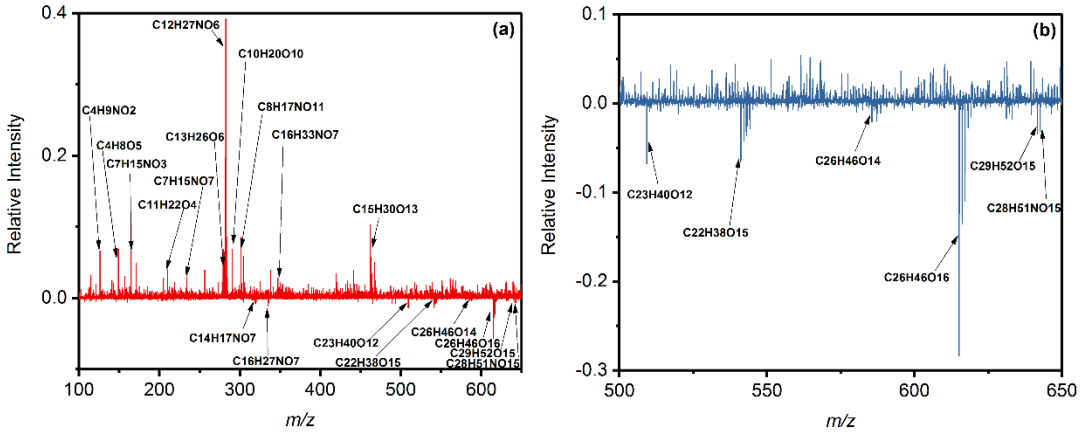

Figure S4. Results of mass spectra difference of toluene SOA under the D condition minus the W condition in (a) positive mode and (b) larger version of figure S4(a), oligomers above 500 Da were multiplied 5 times. The Y axis is the subtraction of relative intensity (indicated by the peak intensity relative to the strongest peak intensity) between condition D and W.

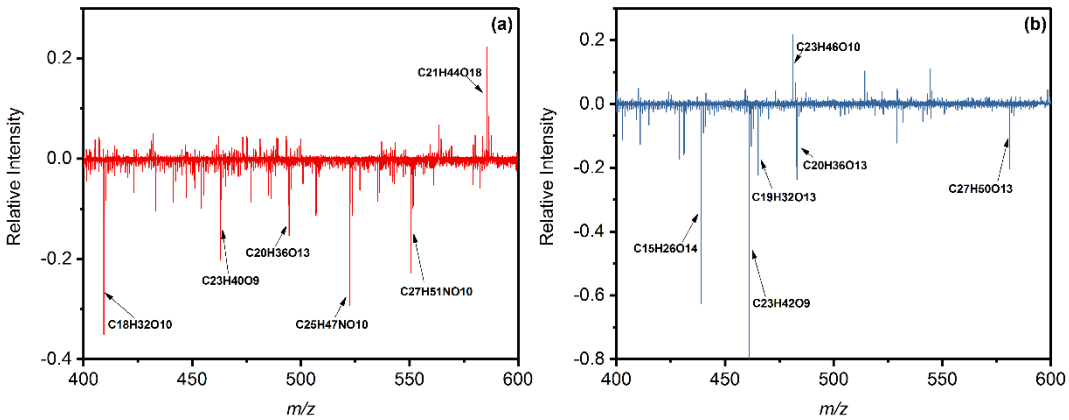

Figure S5. Larger version of results of *m/z* above 400 mass spectra difference of toluene SOA under the DS condition minus the WS condition in (a) positive mode and (b) negative mode (oligomers above 400 Da were multiplied 5 times). The Y axis is the subtraction of relative intensity (indicated by the peak intensity relative to the strongest peak intensity) between condition DS and WS.

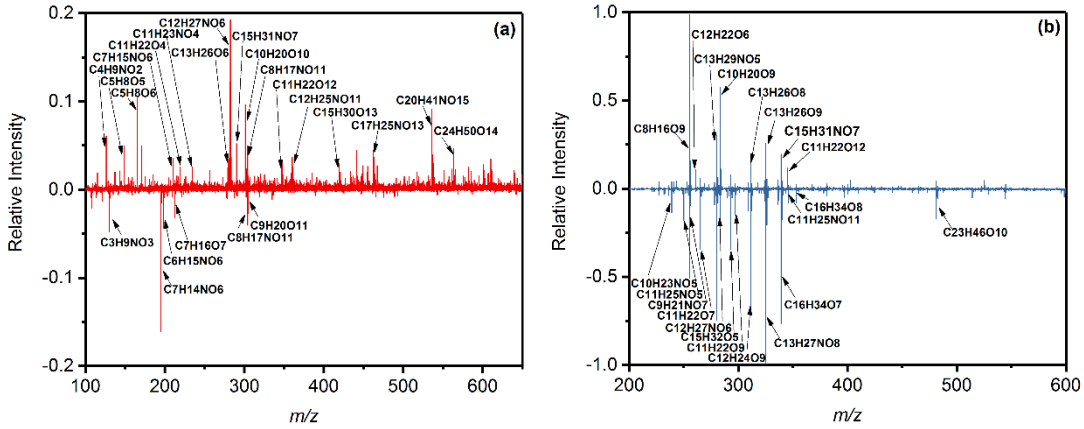

Figure S6. Results of mass spectra difference of toluene SOA under the D condition minus the DS condition in (a) positive and (b) negative mode. The Y axis is the subtraction of relative intensity (indicated by the peak intensity relative to the strongest peak intensity) between condition D and DS.

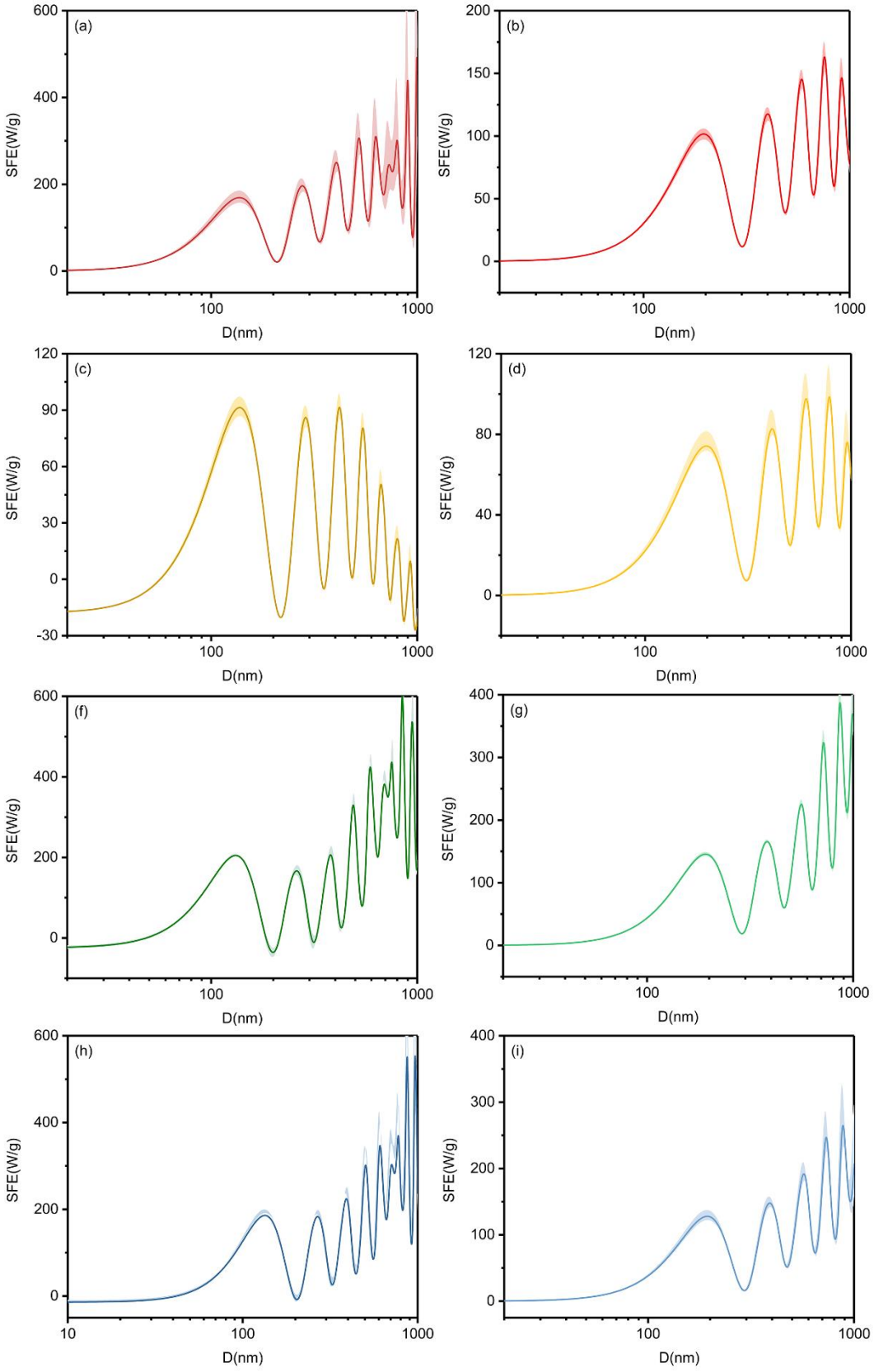

Figure S7. The simple forcing efficiency (SFE) of the toluene-derived aerosol under the D condition at (a) 375 nm and (b) 532 nm, the DS condition at (c) 375 nm and (d) 532 nm, the W condition at (e) 375 nm and (f) 532 nm and the WS condition at (g) 375 nm and (h) 532 nm. The lines are the average values, the shaded areas are uncertainties.