AMS CE for Chamber SOA

Ken Docherty et al.
Alion Science & Technology and NERL, EPA

[1] Alion Science and Technology, P.O. Box 12313, Research Triangle Park, NC 27713
[2] Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO 80309
[3] National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27713

Presented by J.L. Jimenez at the 2012 Aerodyne MS Users Meeting, Minneapolis, MN
Aerosol Science & Technology, submitted, 2012

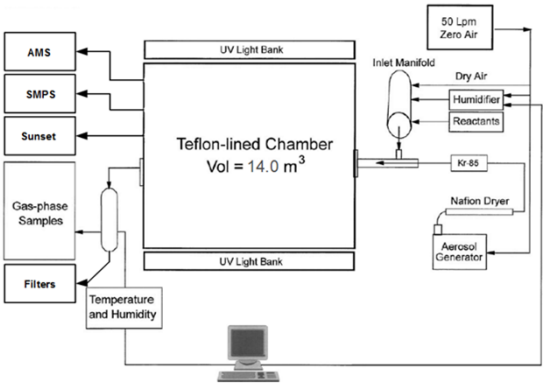
Introduction

- AMS collection efficiency (CE) is the product of several efficiency terms including lens transmission efficiency (E_L), beam broadening (E_S), and particle bounce (E_B) (Huffman et al., 2005)

$$CE(d_{va}) = E_L(d_{va}) * E_S(d_{va}) * E_B(d_{va})$$

- For ambient particles in urban areas, use of a CE=0.5 results in good agreement between AMS and collocated instrument measurements
- In both ambient and laboratory settings, CE < 1 is mainly due to solid particles bouncing from the vaporizer surface prior to volatilization
- CE of laboratory generated and ambient particles are influenced by:
  (1) relative humidity of sampling line (hence the dryer!)
  (2) acidity/neutralization of the sulfate fraction
  (3) mass fraction of NH_4NO_3
  (4) liquid organic content (Matthew et al., 2008; Middlebrook et al., 2012)
- CE of ambient particles appears to not be dependent on mass fraction of organic aerosol (OA, Middlebrook et al., 2012). More data needed, CE = 1 in some forests, BB?
- Existence and potential cause of variability in CE of laboratory-generated secondary OA is less well characterized and typically assumed to be unity

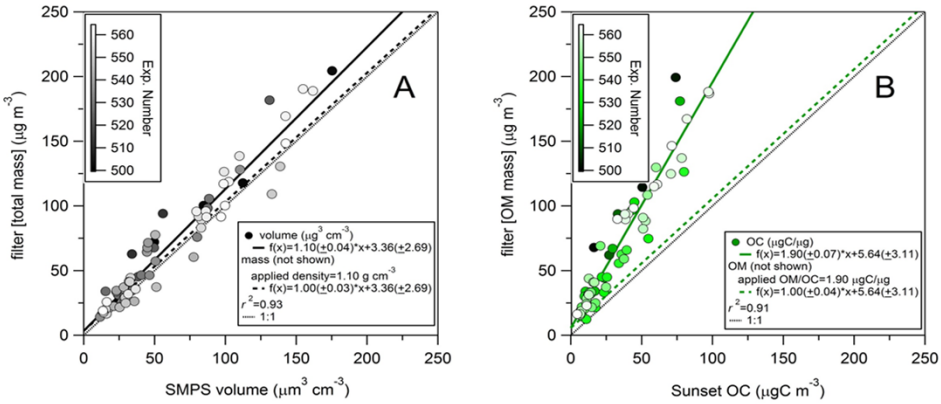
Experimental Setup



- Chamber operated as continuously-stirred tank reactor (CSTR)
- Production of SOA with stable concentration/composition over extended periods (days to weeks)
- Provides for the collection of large amounts of SOA for off-line characterization of SOA composition by pre-column derivatization GCMS (Jaoui et al., 2004)
- 4 hour residence time used for reactions included in this study
- Chamber-generated aerosol concentrations measured with Q-AMS, SMPS, Sunset EC/OC monitor, and gravimetric filter measurements

Collection efficiency of the AMS for chamber-generated SOA

ρ_{avg} $\qquad$ OM/OC_{avg}

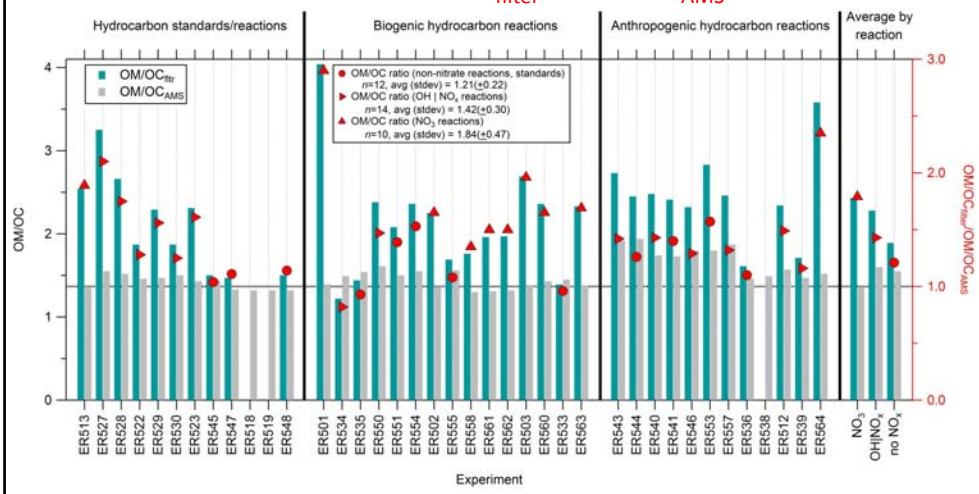


- Obtained through linear regression of filter mass, OM vs SMPS volume, Sunset OC
- Use of averages minimizes contribution of measurement variability to calculated CE
  - ρ_{avg} = 1.10(±0.04)
  - OM/OC_{avg} = 1.90(±0.07)
- Consistency and high correlation among filter, SMPS, and Sunset measurements
- No temporal trend apparent in scatter which would suggest an instrument performance issue

Collection efficiency of the AMS for chamber-generated SOA

OM/OC: Filter vs AMS

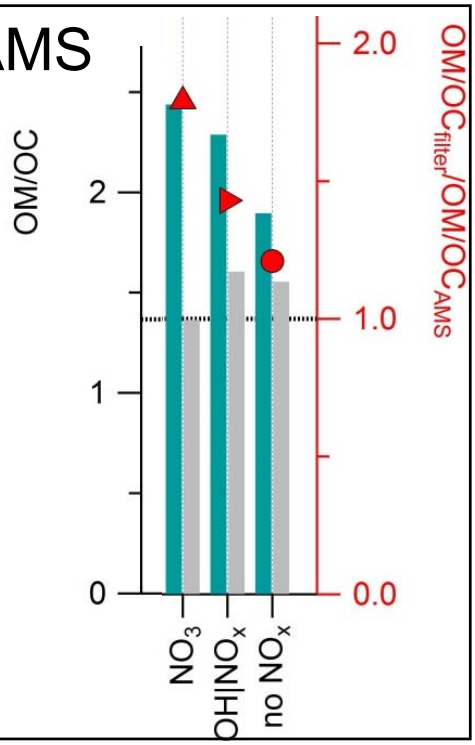
Red = $(OM/OC)_{filter}/(OM/OC)_{AMS}$

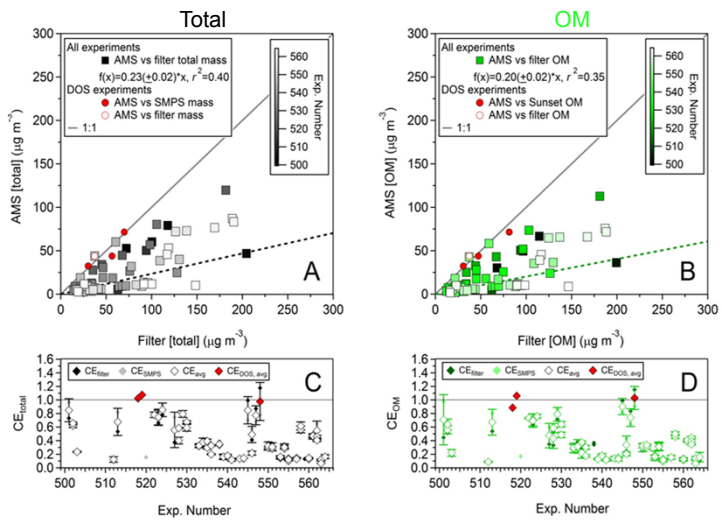


OM/OC: Filter vs AMS

Red = $(OM/OC)_{filter}/(OM/OC)_{AMS}$

- $(OM/OC)_{filter} > (OM/OC)_{AMS}$
- Part of the difference due to NO_2 of $RONO_2$ groups
  - Not accounted by standard AM processing (Farmer et al. 2012
  - Higher with NO_3 radical, then OH/NOx
- Still some ~20% higher fo reactions without $RONO_2$
  - H_2O^+? (Manjula)
  - Filter artifacts?

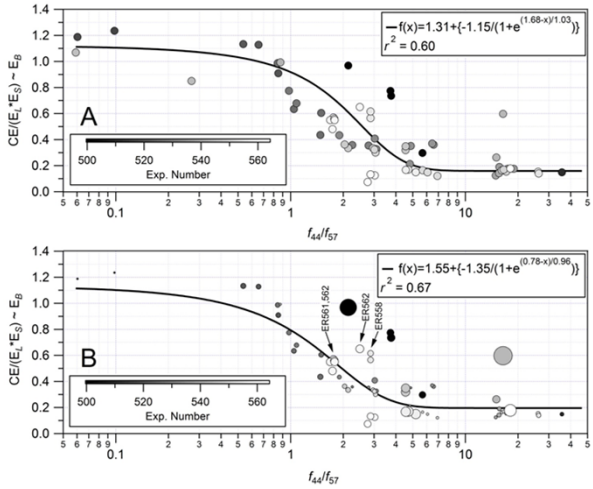




- Comparison of AMS total and OA measurements suggests highly variable CE
- Dioctyl sebacate standard (DOS, shown in red) aerosol sampled periodically to confirm instrument performance and calibrated IE
  - CE_{DOS} ~1.0 as expected
- Trends in CE similar between total and OM irrespective of which measurement (e.g., filter, SMPS, Sunset) is used

Collection efficiency of the AMS for chamber-generated SOA

E_B as a function of f_{44}/f_{57}



- Much stronger correlation of E_B with f_{44}/f_{57} with inversely proportional trend
- High CE for OA with low f_{44}/f_{57}, low CE for OA with high f_{44}/f_{57}
- Size of data points in lower plot reflects f_{NO3} which may have small secondary effect, but is less clear

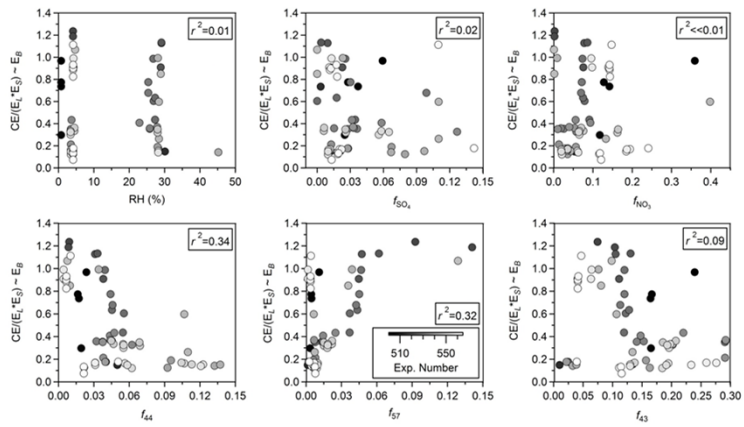
Collection efficiency of the AMS for chamber-generated SOA

Conclusions

- Assuming a CE=1 for chamber-generated SOA in all cases is not appropriate
- Large amount of variability in CE for different SOA types (range: ~0.20 – unity on average)
- Loss of particle mass in the lens system and due to beam broadening is minimal contributing 0-25% to overall CE values
- Bulk of CE appears to be due to bounce of particles from the vaporizer prior to volatilization indicating that not all SOA is liquid inside the AMS
- E_b of chamber-generated SOA apparently not influenced by relative humidity of the sampling line, bulk particle density, or OM/OC ratio
- Instead, E_b moderated by SOA composition and is most strongly correlated w/ f_{44}/f_{57}
- Relative contribution of organic nitrates may play a smaller secondary role in determining E_b of chamber-generated SOA, but is less clear
- Additional research is required to understand how the f_{44}/f_{57} ratio influences liquid organic content and phase of SOA as well as whether CE of ambient SOA is similarly impacted
  - Other users w/ chambers and flowtubes should see if they see the same or not
  - Does not apply directly to field data, but there could be some influence, Ken will follow up w/ another paper on that

Extra slides

Exploring potential causes of E_B



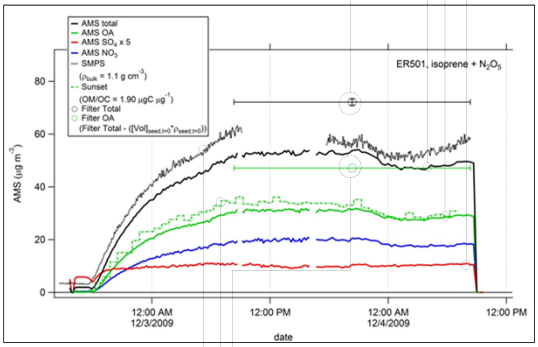
- No apparent relationship between particle bounce and previously identified factors (e.g., chamber relative humidity or relative contribution of inorganics including SO_4 and NO_3)
- Small amount of correction with f_{44} (CE decreases with increasing f_{44})
- Similar amount of correlation with f_{57} with opposite trend
- Also no relationship between E_B and density or OM/OC
- Typical metrics do not appear to explain or predict E_B

Collection efficiency of the AMS for chamber-generated SOA

Typical time profile for dynamic chamber reaction and critical measurements

Measured quantities:

Filter total (not shown)
AMS total SMPS volume
AMS OA Sunset OC
AMS SO_4



CE calculations:

CE total:
- $Total_{AMS}/Mass_{Filter}$
- $Total_{AMS}/Mass_{SMPS}$

CE OM:
- OM_{AMS}/OM_{Filter}
- OM_{AMS}/OM_{Sunset}

Calculated quantities:

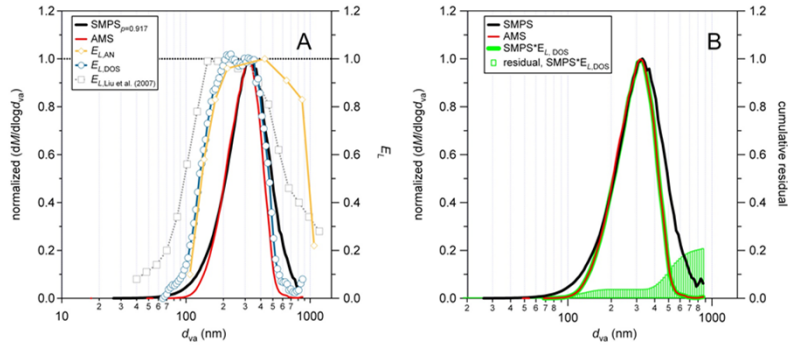
*Filter OM = Filter total – ($V_{seed,t=0}$ * ρ_{seed})*

*Sunset OM = Sunset OC * OM/OC_{avg}*

*SMPS mass = $volume_{SMPS}$ * ρ_{avg}*

Collection efficiency of the AMS for chamber-generated SOA

Estimating contribution of lens transmission efficiency (E_L) to overall CE

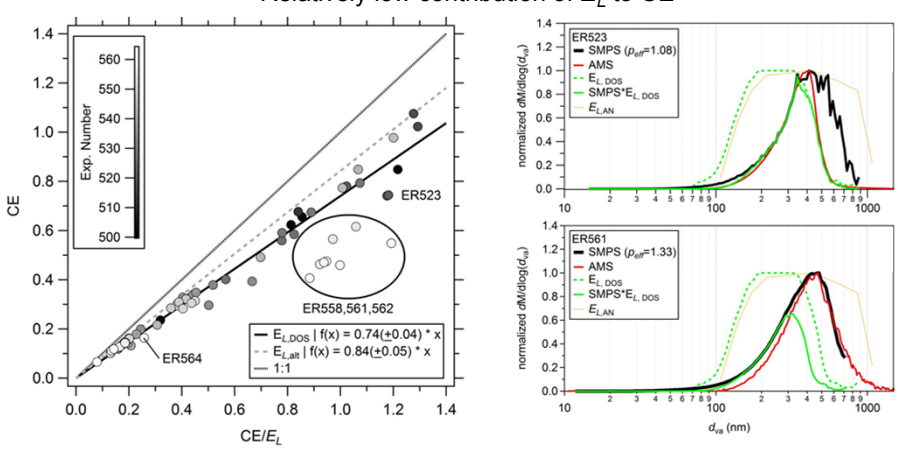


- Lens transmission as function of particle size evaluated with polydisperse DOS ($E_{L,DOS}$) and size-selected monodisperse NH_4NO_3 $E_{L,NH4NO3}$)
- Similar lens transmission limits at small particle diameters (E_L=0.5 at ~130 nm)
- Notably better performance at large particle diameters with $E_{L,NH4NO3}$
- Fractional mass loss due to lens transmission inefficiencies calculated as the cumulative residual between SMPS and $E_{L,DOS}$-adjusted SMPS distributions for each reaction

$$1\text{-}E_L = 1\text{-}(dM_{SMPS}{*}E_{L,DOS}/dM_{SMPS})$$

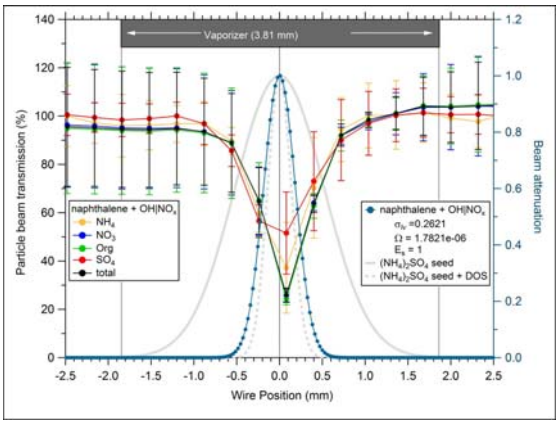
- CE/E_L reflects CE with the contribution of lens transmission efficiency removed

Relatively low contribution of E_L to CE



- Overall, lens transmission efficiency contributes just over one quarter of mass discrepancy between SMPS and AMS
- Decreases slightly if discrepancy between SMPS and AMS at small particle sizes is attributed to measurement artifacts ($E_{L,ALT}$)
- Using $E_{L,DOS}$ nearly three-quarters of CE is due to E_S * E_B
- Number of outliers noted due to better than anticipated (via $E_{L,DOS}$) lens transmission efficiency (overestimates E_L contribution for these reactions)

Contribution of particle beam broadening (E_S) to overall CE

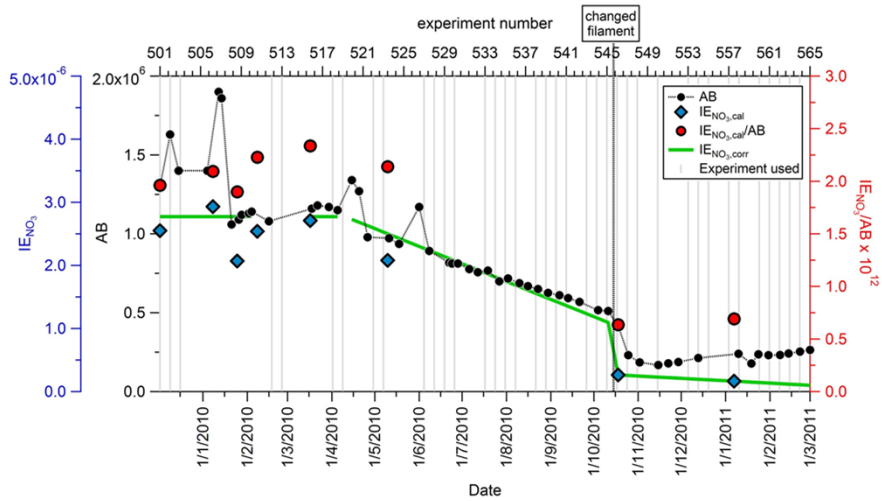


- Beam width probe (BWP) not available during main experiments
- Select reactions repeated with BWP to measure beam dimensions
- Displayed dimensions shown for napthalene photooxidation (lowest CE among all conducted reactions)
- Minimal beam broadening for this reaction
- E_S assumed to be unity for all reactions consistent with the literature (Huffman et al. 2005)
- Result: $CE/E_L{*}E_S \sim CE/E_L \sim 26\%$ indicating that bulk of overall CE is due to E_B

Acknowledgments

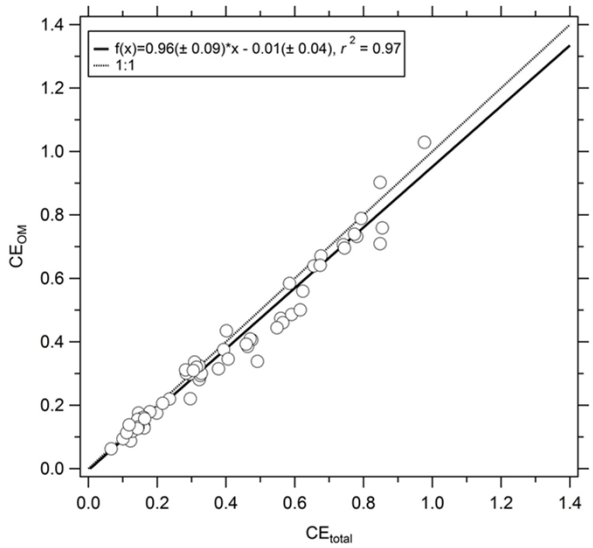
- Doug Worsnop and ARI for use of the beam width probe
- JLJ was supported by DOE (BER, ASR program) DE-SC0006035 and NASA NNX12AC03G

IE Calibrations during this period



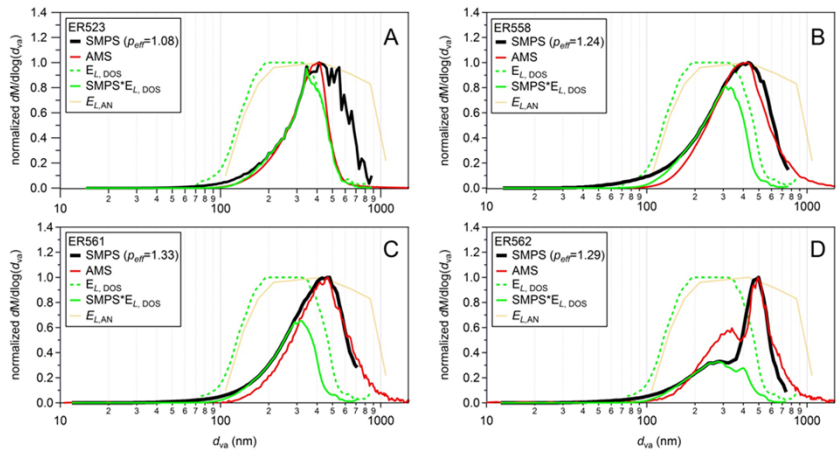
Collection efficiency of the AMS for chamber-generated SOA

Comparison of CE_{total} vs CE_{OM}



Collection efficiency of the AMS for chamber-generated SOA

Size distributions of outlier data points in Figure 4



Collection efficiency of the AMS for chamber-generated SOA

Table S1. Experimental details

Reaction	Date	Hydrocarbon	Oxidant	Seed	$[Volume]_{seed}$ $\mu m^3\ m^{-3}$	$[Mass]_{seed}$ $\mu g\ m^{-3}$	$[Mass]_{total}$ $\mu g\ m^{-3}$	Vol. Frac. SOA (%)	Mass Frac. SOA (%)	CE (sdev*)	f_{44}/f_{57} (sdev*)
Hydrocarbon standards/reactions											
ER513	02/16/10	azaleic acid	n/a	n/a	n/a	n/a	94.08	n/a	n/a	0.73	2.13
ER527	05/11/10	decane	OH | NO_x	$(NH_4)_2SO_4$	1.33	2.38	33.96	95.37	92.46	0.60	1.50
ER528	05/18/10	undecane	OH | NO_x	$(NH_4)_2SO_4$	0.95	1.69	64.78	98.35	97.32	0.53 (0.14)	1.26 (0.31)
ER522	04/15/10	dodecane	OH | NO_x	$(NH_4)_2SO_4$	0.88	1.58	45.22	97.77	96.37	0.91	0.85
ER529	06/01/10	dodecane	OH | NO_x	$(NH_4)_2SO_4$	2.26	4.04	109.91	97.66	96.19	0.99	0.84
ER530	06/08/10	dodecane	OH | NO_x	$(NH_4)_2SO_4$	1.18	2.11	31.11	95.54	92.74	0.73 (0.07)	1.03 (0.07)
ER523	04/20/10	tridecane	OH | NO_x	$(NH_4)_2SO_4$	0.47	0.85	124.71	99.58	99.32	1.13 (0.01)	0.60 (0.08)
ER545	09/21/10	oleic acid	O_3	$(NH_4)_2SO_4$	1.78	3.18	43.36	95.14	92.09	0.99	0.87
ER547	10/25/10	oleic acid	O_3	$(NH_4)_2SO_4$	1.00	1.79	22.14	94.59	91.20	0.85	0.27
ER518	03/18/10	DOS	n/a	NaCl	0.14	0.31	57.60[a]	99.85[b]	n/a	1.24	0.10
ER519	03/22/10	DOS	n/a	NaCl	0.43	0.92	25.38[a]	98.47[b]	n/a	1.19	0.06
ER548	10/04/10	DOS	n/a	$(NH_4)_2SO_4$	0.10	0.18	37.25	99.70	99.52	1.07	0.06
Biogenic hydrocarbon reactions											
ER501	12/02/09	isoprene	NO_x	$(NH_4)_2SO_4$	3.01	5.39	72.13	95.03	91.92	0.97	2.14
ER534	07/06/10	isoprene	OH | NO_x	$(NH_4)_2SO_4$	1.49	2.66	22.64	91.81	86.67	0.41	3.03
ER535	07/12/10	isoprene	OH	$(NH_4)_2SO_4$	1.46	2.61	30.27	94.19	90.54	0.38 (0.07)	2.50 (0.85)
ER550	10/25/10	isoprene	OH | NO_x	$(NH_4)_2SO_4$	0.76	1.35	25.92	96.62	94.50	0.33 (0.02)	4.55 (0.01)
ER551	11/01/10	isoprene	OH	$(NH_4)_2SO_4$	0.83	1.49	113.42	99.18	98.67	0.35 (0.02)	2.08 (0.07)
ER554	11/17/10	isoprene	OH	$(NH_4)_2SO_4$	0.90	1.61	16.97	93.54	89.49	0.32 (0.02)	3.01 (0.05)
ER502	12/09/09	α-pinene	NO_x	$(NH_4)_2SO_4$	3.01	5.39	109.06	96.81	94.80	0.76 (0.03)	3.74 (0.02)
ER555	11/29/10	α-pinene	OH	$(NH_4)_2SO_4$	0.99	1.78	88.07	98.73	97.94	0.14 (0.02)	6.22 (0.63)
ER558	01/10/11	α-pinene	NO_x	$(NH_4)_2SO_4$	1.29	2.31	132.50	98.91	98.23	0.59 (0.04)	2.87 (0.01)
ER561	01/31/11	β-pinene	NO_x	$(NH_4)_2SO_4$	1.70	3.04	182.92	98.96	98.31	0.56 (0.01)	1.73 (0.05)
ER562	02/08/11	β-pinene	NO_x	$(NH_4)_2SO_4$	1.76	3.15	87.18	97.70	96.25	0.56 (0.08)	2.00 (0.42)
ER503	12/15/09	δ-limonene	NO_x	$(NH_4)_2SO_4$	4.23	7.58	204.45	97.63	96.15	0.30	5.68
ER560	01/24/11	δ-limonene	NO_x	$(NH_4)_2SO_4$	1.76	3.14	94.36	97.88	96.55	0.16 (0.01)	4.82 (0.33)
ER533	06/28/10	β-caryophylene	O_3	$(NH_4)_2SO_4$	1.23	2.19	55.15	97.46	95.86	0.36 (0.01)	2.52 (0.38)
ER563	02/14/11	β-caryophylene	NO_x	$(NH_4)_2SO_4$	1.61	2.88	113.41	98.40	97.39	0.11 (0.03)	2.88 (0.14)
Anthropogenic hydrocarbon reactions											
ER543	09/07/10	benzene	OH | NO_x	$(NH_4)_2SO_4$	1.16	2.08	20.46	93.05	88.69	0.14	15.68
ER544	09/13/10	benzene	OH	$(NH_4)_2SO_4$	2.18	3.90	23.54	87.81	80.16	0.15	13.60
ER540	08/16/10	toluene	OH | NO_x	$(NH_4)_2SO_4$	0.50	0.90	35.74	98.42	97.43	0.19	15.64
ER541	08/23/10	toluene	OH	$(NH_4)_2SO_4$	1.83	3.28	34.19	93.49	89.40	0.12	14.92
ER546	09/27/10	toluene	OH | NO_x	NH_4NO_3	0.11	0.20	62.02	99.80	99.68	0.43 (0.24)	15.72 (0.98)
ER553	11/15/10	toluene	OH	$(NH_4)_2SO_4$	0.43	0.77	42.43	98.86	98.15	0.16 (0.01)	16.61 (0.48)
ER557	12/06/10	toluene	OH | NO_x	$(NH_4)_2SO_4$	0.68	1.22	39.54	98.04	96.81	0.15 (0.01)	26.16 (0.11)
ER536	07/19/10	1,3,5-TMB	OH	$(NH_4)_2SO_4$	1.41	2.52	92.59	98.28	97.21	0.28 (0.10)	4.84 (0.04)
ER538	08/02/10	1,3,5-TMB	OH | NO_x	$(NH_4)_2SO_4$	0.94	1.68	27.08	95.94	93.39	0.37 (0.01)	6.52 (0.09)
ER512	02/08/10	naphthalene	OH | NO_x	$(NH_4)_2SO_4$	0.20	0.36	81.61	99.73	99.56	0.15	35.64
ER539	08/10/10	naphthalene	OH | NO_x	$(NH_4)_2SO_4$	1.23	2.20	67.91	97.95	96.66	0.18 (0.01)	18.17 (0.71)
ER564	02/22/11	napthalene	NO_x	$(NH_4)_2SO_4$	1.94	3.48	18.99	86.23	77.59	0.18	18.07

* Average CE values are reported along with the associated standard deviation for those reactions in which CE was calculated over several different filter sampling intervals.

[a] Calculated from SMPS volume density with ρ_{DOS}=0.917 g cm^{-3}

Table S2. Literature values for chamber-generated SOA

Reaction System	Metric	Average (Range)	St.Dev.	Reference
Isoprene | OH | NO_x	OM/OC	1.770		Aiken et al. (2008)
		(1.92 – 2.00)		Chhabra et al. (2009)
α-pinene | O_3	density	1.198	0.004	Zelenuk et al. (2008)
		1.213	0.003	Zelenuk et al. (2008)
		1.240	0.030	Malloy et al. (2009)
		1.190		Bahreini et al. (2005)
	OM/OC	1.500		Aiken et al. (2008)
		1.600		Chhabra et al. (2009)
α-pinene | OH | NO_x	density	1.300	0.100	Alfarra et al. (2006)
	OM/OC	1.670		Aiken et al. (2008)
β-caryophylene | O_3	density	1.300		Bahreini et al. (2005)
1,3,5,-TMB | OH | NO_x	density	1.370	0.020	Alfarra et al. (2006)
Toluene | OH | NO_x	OM/OC	1.720		Aiken et al. (2008)
		(2.10 – 2.15)		Chhabra et al. (2009)
m-xylene | OH | NO_x	OM/OC	(1.93 – 2.09)		Chhabra et al. (2009)

Collection efficiency of the AMS for chamber-generated SOA

Table S3. Comparison of OM/OC values calculated from filter samples and AMS f_{44}

	Hydrocarbon	Oxidant	OM/OC_{fil}	f_{44} (%)	O/C_{AMS} [a]	OM/OC_{AMS} [b]	OM/OC ratio
Hydrocarbon standards/reactions							
ER513	azaleic acid	N/A	2.54	1.36	0.13	1.35	1.89
ER527	decane	OH | NO_x	3.25	5.55	0.29	1.55	2.10
ER528	undecane	OH | NO_x	2.66	5.00	0.27	1.52	1.75
ER522	dodecane	OH | NO_x	1.87	3.80	0.22	1.46	1.28
ER529	dodecane	OH | NO_x	2.29	3.94	0.23	1.47	1.56
ER530	dodecane	OH | NO_x	1.87	4.50	0.25	1.50	1.25
ER523	tridecane	OH | NO_x	2.31	3.21	0.20	1.43	1.61
ER545	oleic acid	O_3	1.50	3.41	0.21	1.44	1.04
ER547	oleic acid	O_3	1.47	0.97	0.12	1.33	1.11
ER518	DOS	N/A	N/A	0.91	0.11	1.32	N/A
ER519	DOS	N/A	N/A	0.85	0.11	1.32	N/A
ER548	DOS	N/A	1.50	0.76	0.11	1.32	1.14
Biogenic hydrocarbon reactions							
ER501	isoprene	NO_x	4.04	2.37	0.17	1.39	2.90
ER534	isoprene	OH | NO_x	1.22	4.36	0.25	1.49	0.82
ER535	isoprene	OH	1.44	5.48	0.29	1.54	0.93
ER550	isoprene	OH | NO_x	2.38	6.89	0.34	1.61	1.47
ER551	isoprene	OH	2.08	4.58	0.25	1.50	1.39
ER554	isoprene	OH	2.36	5.55	0.29	1.55	1.53
ER502	α-pinene	NO_x	2.25	1.69	0.14	1.36	1.65
ER555	α-pinene	OH	1.69	5.89	0.30	1.56	1.08
ER558	α-pinene	NO_x	1.76	0.43	0.10	1.30	1.35
ER561	β-pinene	NO_x	1.96	0.64	0.10	1.31	1.50
ER562	β-pinene	NO_x	1.97	0.78	0.11	1.32	1.50
ER503	δ-limonene	NO_x	2.69	1.93	0.15	1.37	1.96
ER560	δ-limonene	NO_x	2.36	3.11	0.20	1.43	1.65
ER533	β-caryophylene	O_3	1.39	3.48	0.21	1.45	0.96
ER563	β-caryophylene	NO_x	2.33	2.16	0.16	1.38	1.69
Anthropogenic hydrocarbon reactions							
ER543	benzene	OH | NO_x	2.73	13.24	0.59	1.92	1.42
ER544	benzene	OH	2.45	13.64	0.60	1.94	1.26
ER540	toluene	OH | NO_x	2.48	9.54	0.44	1.74	1.43
ER541	toluene	OH	2.41	9.25	0.43	1.73	1.40
ER546	toluene	OH | NO_x		10.82	0.49	1.80	N/A
ER553	toluene	OH	2.83	10.80	0.49	1.80	1.57
ER557	toluene	OH | NO_x	2.46	12.17	0.54	1.87	1.32
ER536	1,3,5-TMB	OH	1.61	3.78	0.22	1.46	1.10
ER538	1,3,5-TMB	OH | NO_x		4.47	0.25	1.49	N/A
ER512	naphthalene	OH | NO_x	2.34	5.98	0.31	1.57	1.49
ER539	naphthalene	OH | NO_x	1.71	3.99	0.23	1.47	1.16
ER564	napthalene	NO_x	3.58	5.06	0.27	1.52	2.35
						average ratio (stdev)	1.48 (±0.42)

[a] $O/C_{AMS} = 0.0382*f_{44}+0.0794$ (Aiken et al., 2008)

[b] $OM/OC_{AMS} = 1.260*O/C_{AMS} + 1.180$ (Aiken et al., 2008)