Understanding the Volatility of Primary Organic Aerosol Emitted from Light-Duty Vehicles

University of California at Davis
Michael Kleeman, Toshihiro Kuwayama, Christopher Cappa,
Sonya Collier, Isabel Faria, Sara Forestieri, Qi Zhang

University of California at San Diego
Timothy Bertram, James Brady

CARB Seminar
March 20, 2014

Acknowledgement

- California Air Resources Board Grant Project # 10-313

- California Air Resources Board (CARB)
  - Nehzat Motallebi (Project Manager)
  - Mang Zhang (Project Engineer)
  - Sulekha Chattopadhyay (Air Pollution Specialist)
  - Shiyan Chen, Tuyen Dinh, Paul Moon, additional staff at CARB HSL

- UC Davis
  - Peter Green

- UC Davis
  - Chris Jakober (UCD graduate, Ph.D.)

Publications

1. S.D. Forestieri, S. Collier, T. Kuwayama, Q. Zhang, M.J. Kleeman, and C.D. Cappa. Real-time black carbon emission factor measurements from light duty vehicles. Environmental Science and Technology. 47(22), pp13104-13112 (2013), DOI: 10.1021/es401415a

2. S. Collier and Q. Zhang. Gas-phase CO2 subtraction for improved measurements of organic aerosol mass concentrations and oxidation degree by Aerosol Mass Spectrometer. Environmental Science and Technology. 47(24), pp 14324-14331 (2013).

3. S. Collier,T. Kuwayama, S. Forestieri, M.J. Kleeman, C.D. Cappa, J. Brady, T. Bertram, M. Zhang, Q. Zhang. Characterizing Organic PM Emissions from Vehicles: Dynamometer Tests Using a High-Resolution Aerosol Mass Spectrometer. In preparation.

4. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

5. T. Kuwayama, I. Faria, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Effect of Atmospheric Conditions on Organic Aerosol Emissions from Gasoline Fueled Motor Vehicles. In preparation.

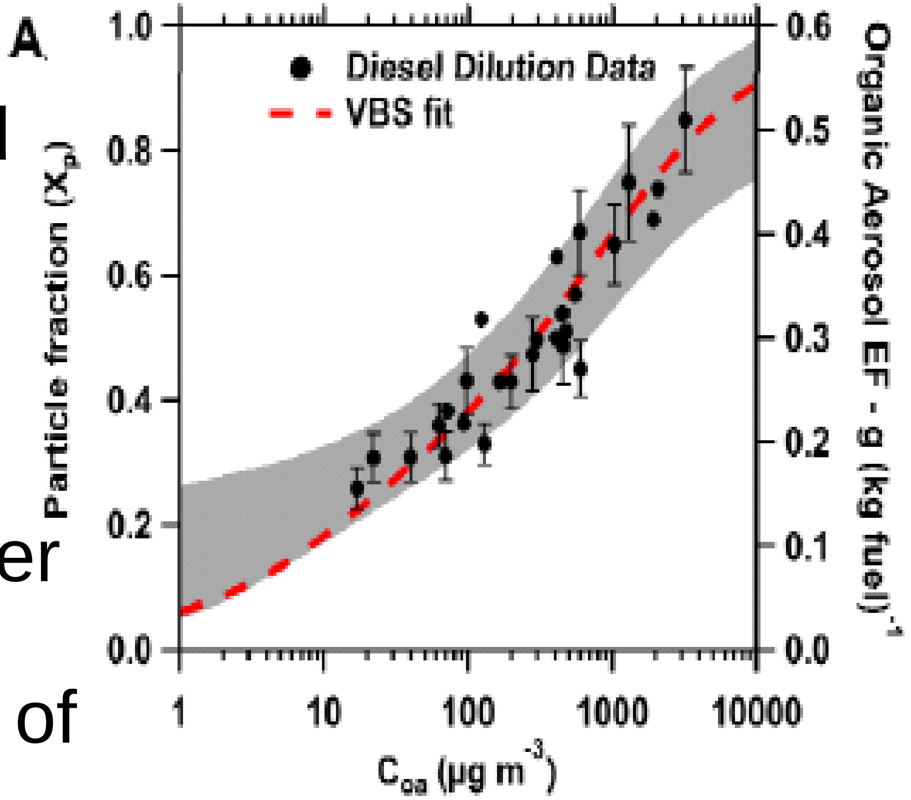
6. T. Kuwayama, I. Faria, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Gas-particle partitioning of carbonyl compounds in the exhaust of light duty gasoline vehicles as a function of humidity and elemental carbon concentrations. In preparation.

7. T.A. Crisp, J.M. Brady, C.D. Cappa, S. Collier, S.D. Forestieri, M.J. Kleeman, T. Kuwayama, B.M. Lerner, E.J. Williams, Q. Zhang, and T.H. Bertram. On the primary emission of formic acid from light duty gasoline vehicles and ocean-going vessels. In preparation.

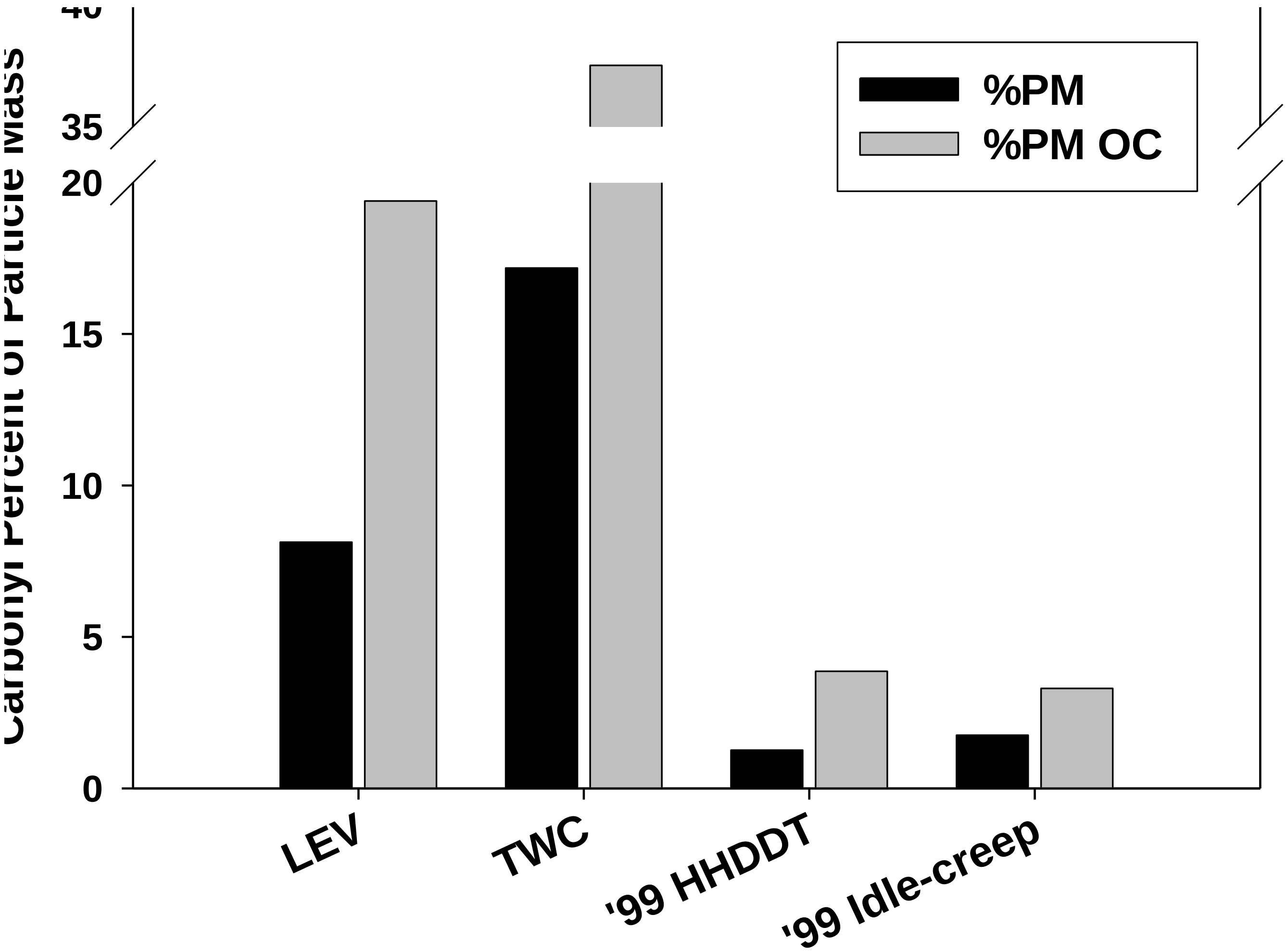
8. J.M. Brady, T.A. Crisp, S. Collier, T. Kuwayama, S.D. Forestieri, Q. Zhang, M.J. Kleeman, C.D. Cappa, and T.R. Bertram. Real-time emission factor measurements of isocyanic acid from light duty gasoline vehicles. Environmental Science and Technology, in review, 2014.

Motivation - is POA Semi-Volatile?

- POA appears semi-volatile under controlled laboratory conditions (POA>> 30 µg/m^3)
- Understanding POA emissions and gas-particle partitioning under real-world conditions is critical to proper design of emissions control programs

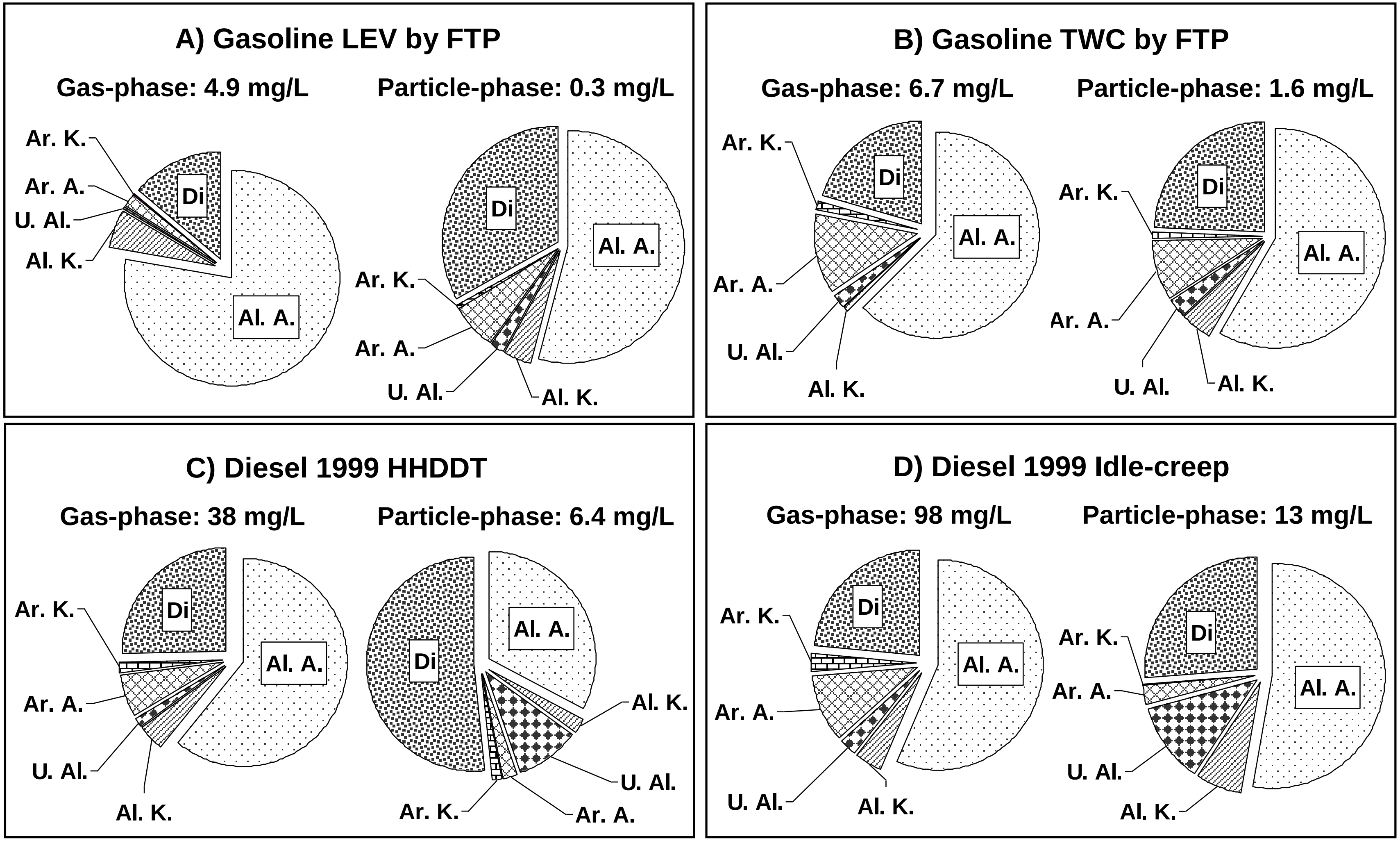


Large Fraction of LDV Organic Carbon Speciated as Carbonyls



Source: 2008 Jakober, C.A., M.A. Robert, S.G. Riddle, H. Destaillats, M.J. Charles, P.G. Green, and M.J. Kleeman. Carbonyl Emissions From Gasoline and Diesel Motor Vehicles. Environmental Science and Technology, 42, pp4697-4703

General Speciation of Carbonyls


A) Gasoline LEV by FTP

Gas-phase: 4.9 mg/L Particle-phase: 0.3 mg/L

B) Gasoline TWC by FTP

Gas-phase: 6.7 mg/L Particle-phase: 1.6 mg/L

C) Diesel 1999 HHDDT

Gas-phase: 38 mg/L Particle-phase: 6.4 mg/L

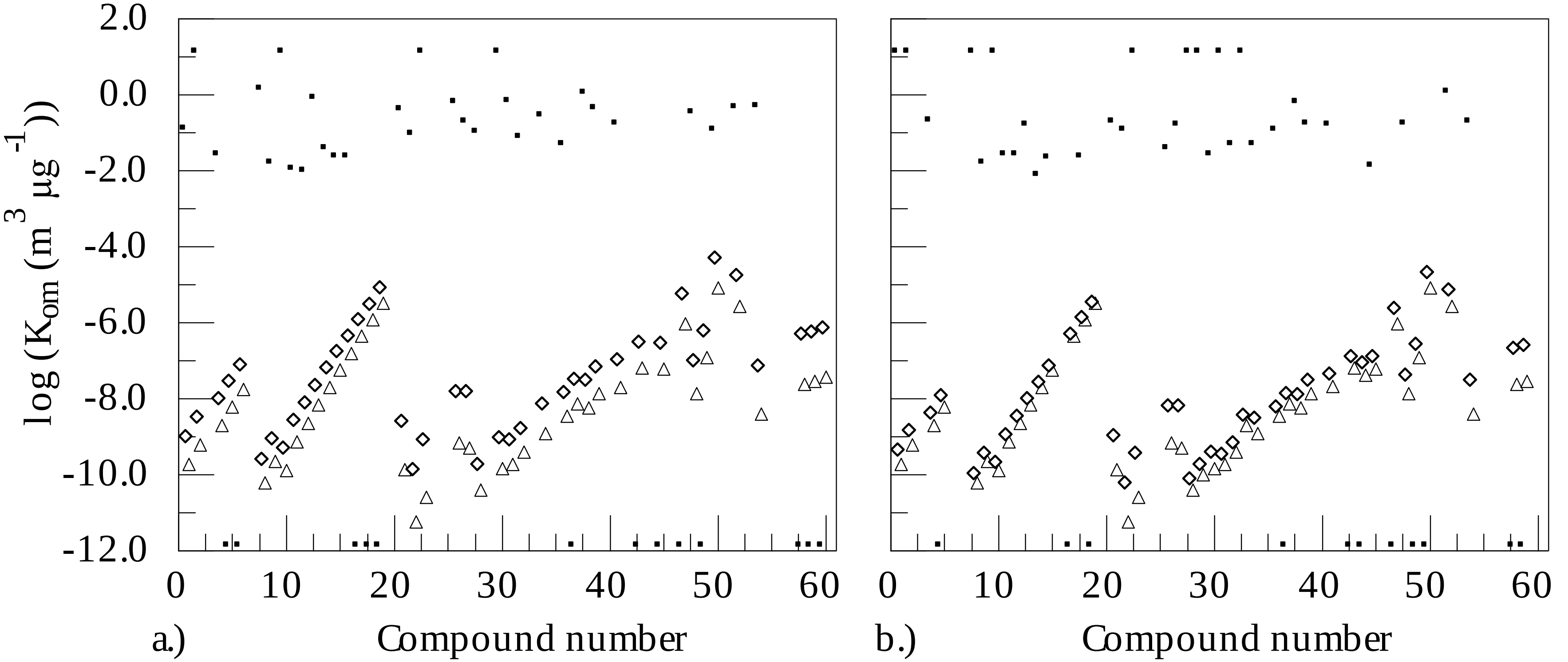
D) Diesel 1999 Idle-creep

Gas-phase: 98 mg/L Particle-phase: 13 mg/L

Al. A. = Aliphatic Aldehydes Al. K. = Aliphatic Ketones U. Al. = Unsaturated Aliphatics
Ar. A. = Aromatic Aldehydes Ar. K. = Aromatic Ketones Di = Dicarbonyls

Source: 2008 Jakober, C.A., M.A. Robert, S.G. Riddle, H. Destaillats, M.J. Charles, P.G. Green, and M.J. Kleeman. Carbonyl Emissions From Gasoline and Diesel Motor Vehicles. Environmental Science and Technology, 42, pp4697-4703

30% of Light Duty Vehicle POA Diluted to Realistic Concentrations Doesn't Obey Absorption Theory



Source:2010 Chen, J., C. Jakober, S. Clegg, and M.J. Kleeman. Theoretical vs. Observed Gas-Particle Partitioning of Carbonyl Emissions from Motor Vehicles. Journal of the Air and Waste Management Assocication, 60, 1237-1244.

Problem

- Behavior of the partitioning mechanism under atmospherically relevant conditions (<30 μg/m^3 OC) is difficult to study
  - Detection limit challenges
  - Representative vehicle fleet and driving cycle

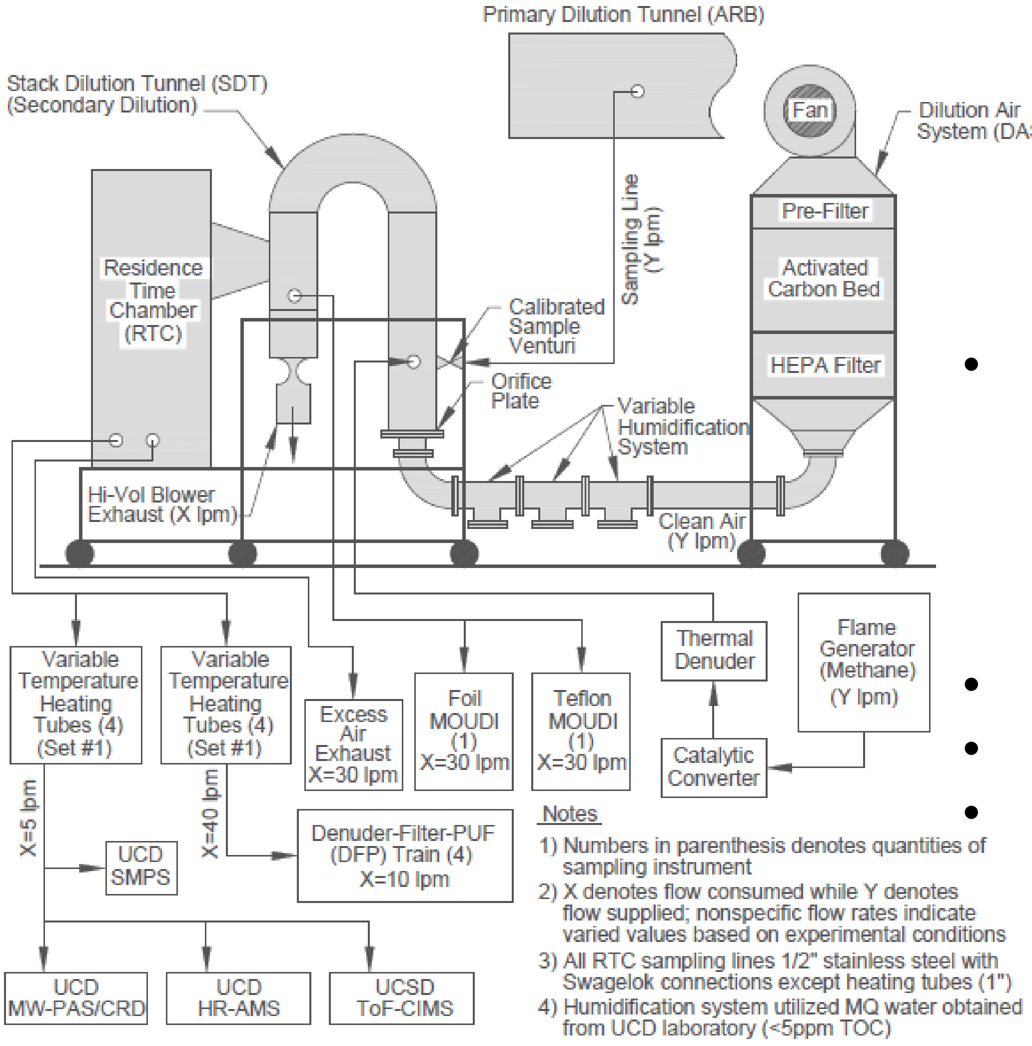
- What mechanism controls the partitioning?
- What are the right conditions to vary to test different theories about dominant mechanisms?

Approach

- Sample representative on-road vehicle fleet emissions after adjustments: dilution, RH, background EC, and temperature

Test Condition Matrix	
Base Condition RH = 55% Background EC = 0 µg/m3	Adjusted RH RH = 85% Background EC = 0 µg/m3
Adjusted EC RH = 55% Background EC = 20 µg/m3	Adjusted EC+RH RH = 85% Background EC = 20 µg/m3

Methodology



Notes

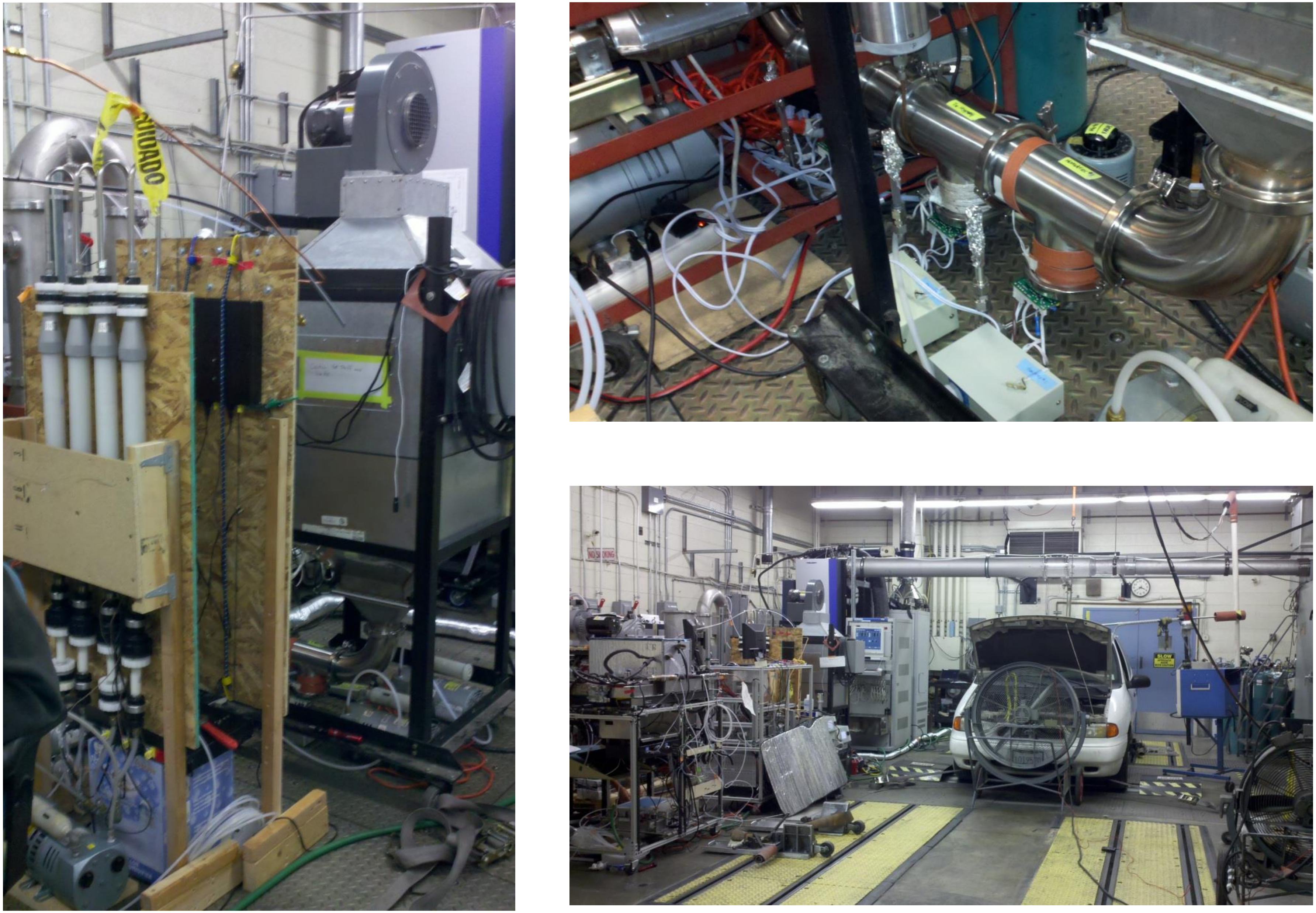
1) Numbers in parenthesis denotes quantities of sampling instrument
2) X denotes flow consumed while Y denotes flow supplied; nonspecific flow rates indicate varied values based on experimental conditions
3) All RTC sampling lines 1/2" stainless steel with Swagelok connections except heating tubes (1")
4) Humidification system utilized MQ water obtained from UCD laboratory (<5ppm TOC)

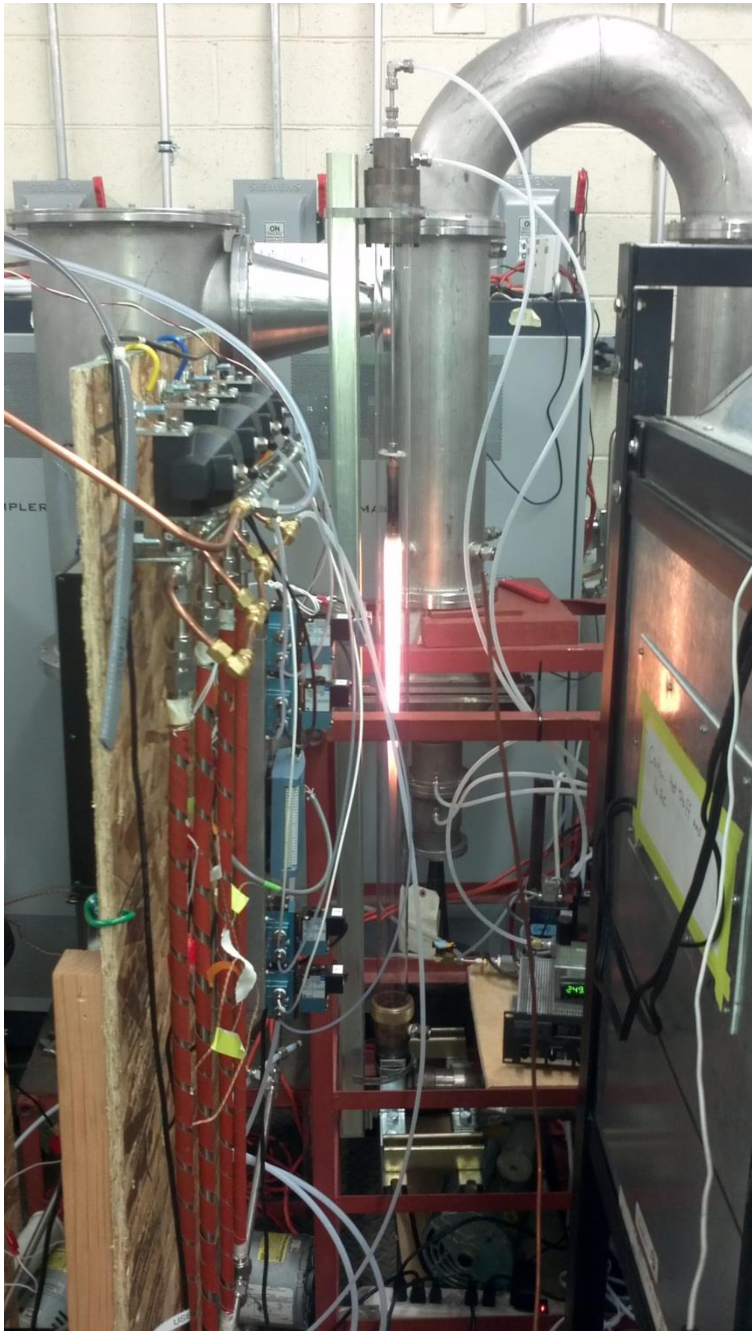
Primary Dilution System Adjustment to Exhaust

- Primary Dilution Ratio = 12.72

Secondary Dilution System Adjustments to Air Stream

- Secondary Dilution Ratio = 4.8
- RH adjustment = 55-85%
- EC adjustment = 0-20 μg/m^3


CUIDADO
NO SMOKING
SLOW



Vehicle Fleet Comparison

2002

Category	Year	Make	Model	Mileage	Engine Information
LEV PC	1996	Honda	Civic	77,703	4 cylinder
LEV PC	1998	Honda	Accord	97,811	4 cylinder
LEV PC	1999	Toyota	Camry LE	43,160	6 cylinder
LEV PC	1999	Nissan	Sentra GXE	52,630	4 cylinder
LEV PC	2002	Chevrolet	Monte Carlo	20,230	6 cylinder
LEV LDT/SUV	1998	Ford	Explorer	82,513	8 cylinder
LEV LDT/SUV	2000	Jeep	Grand Cherokee	31,751	6 cylinder
LEV LDT/SUV	2000	Toyota	Tacoma	51,554	6 cylinder
LEV LDT/SUV	2002	Nissan	Pathfinder	8,169	6 cylinder
LEV LDT/SUV	2003	Chevrolet	Silverado	1,264	8 cylinder

2011

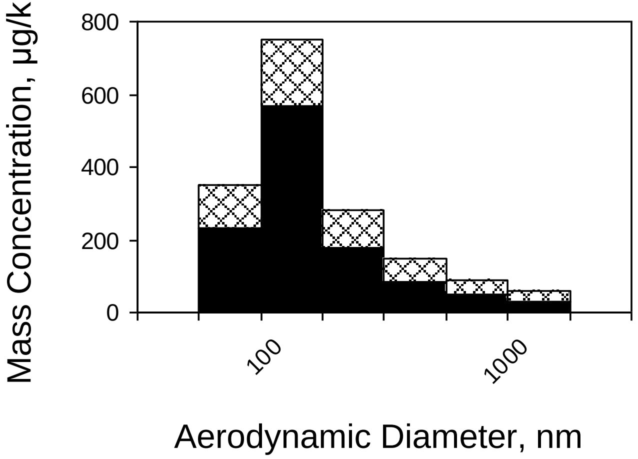
Category	Year	Make	Model	Mileage	Engine Information
LEV PC	1997	Ford	Taurus	130,092	6 cylinder
LEV PC	1998	Ford	Windstar	90,519	6 cylinder
LEV PC	2001	Chevrolet	Cavalier	52,666	4 cylinder
LEV PC	2003	Toyota	Camry Solara	97,304	6 cylinder
LEV LDT/SUV	2002	Chevrolet	S10 Pickup	57,690	4 cylinder
LEV LDT/SUV	2002	Chrysler	Grand Cherokee	83,200	8 cylinder
LEV LDT/SUV	2003	Toyota	Tacoma	100,535	4 cylinder
LEV LDT/SUV	2003	Nissan	Pathfinder	110,055	6 cylinder

Analytical Methods

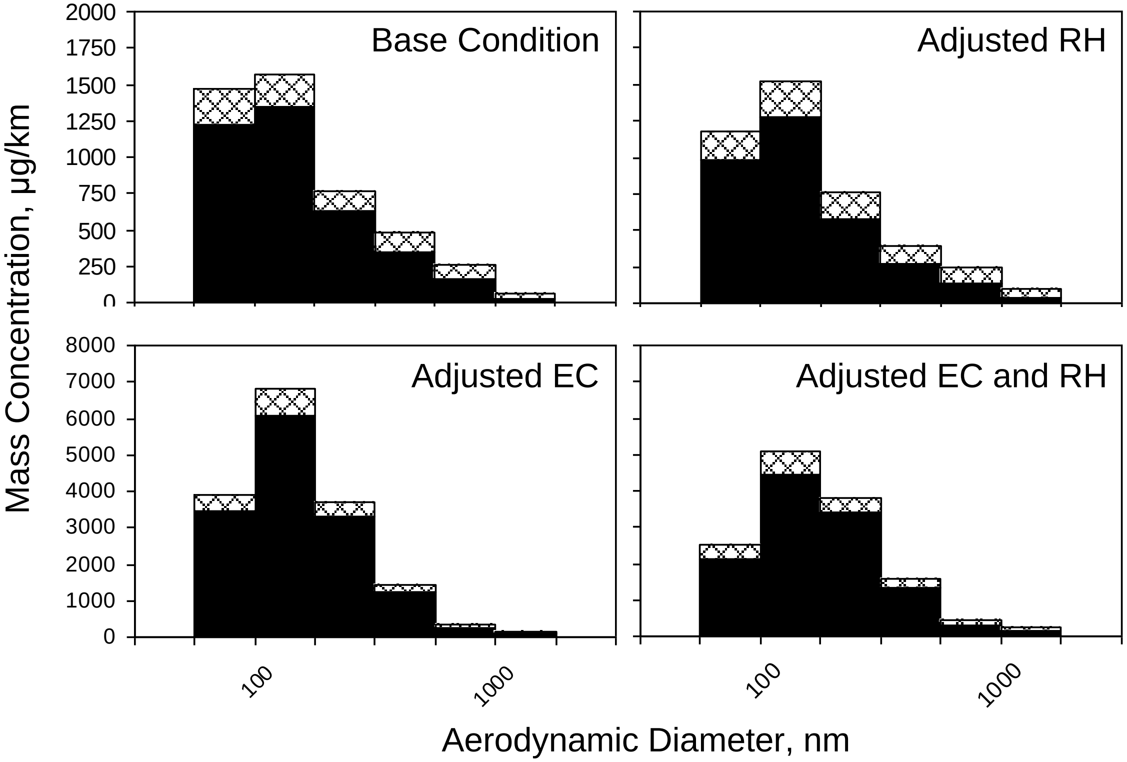
- OC/EC Aerosol Analyzer
  - NIOSH temperature protocol
- GC-MS
  - DFP train (Annular denuders coated in XAD, Quartz filter, and PUF) extracted in separate methanol and hexane DCM solutions
  - Samples derivatized using O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) (Jakober et al. 2008)
  - Sample recovery determined using 2-F-benzaldehyde for C<7 and 8-F-1-benzosuberone for C>7 (with backup recovery standards 4-F-benzophenone and 5-F-1-Indanone) (Jakober et al. 2008)
- HR-AMS
- CRD-PAS – EC
- ToF-CIMS

MOUDI Size Distributions After Dilution to < 5 µg m^{-3}

Past Study: 2002

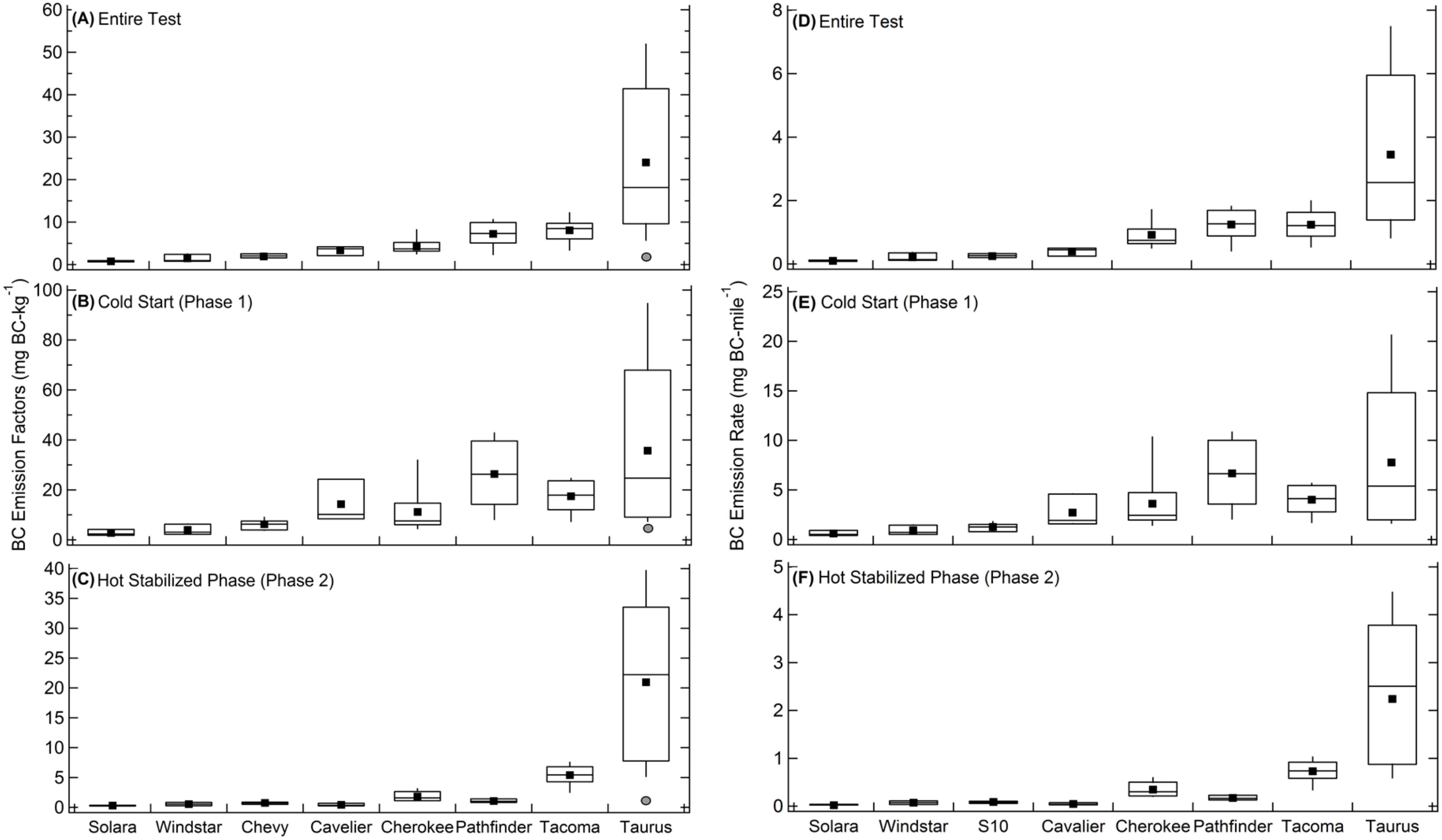


Present Study: 2011



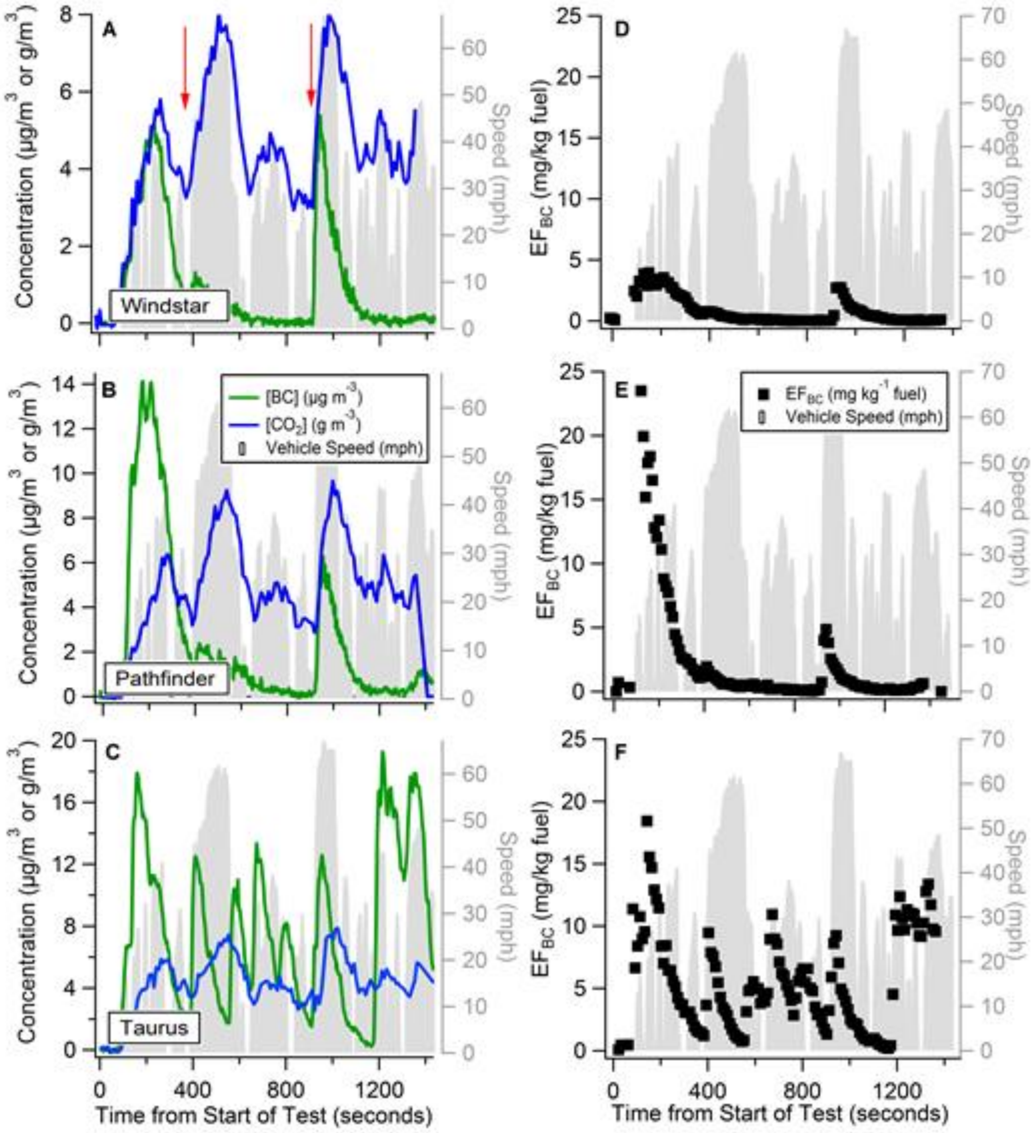
Note: MOUDI daily size distribution under variable experimental conditions in comparison to past source sampling study. Ratio of present to past OM and EC masses (D_A<100nm), 1.65 and 3.25 (25% and 15% mass uncertainties), respectively.

EC Emissions by Vehicle



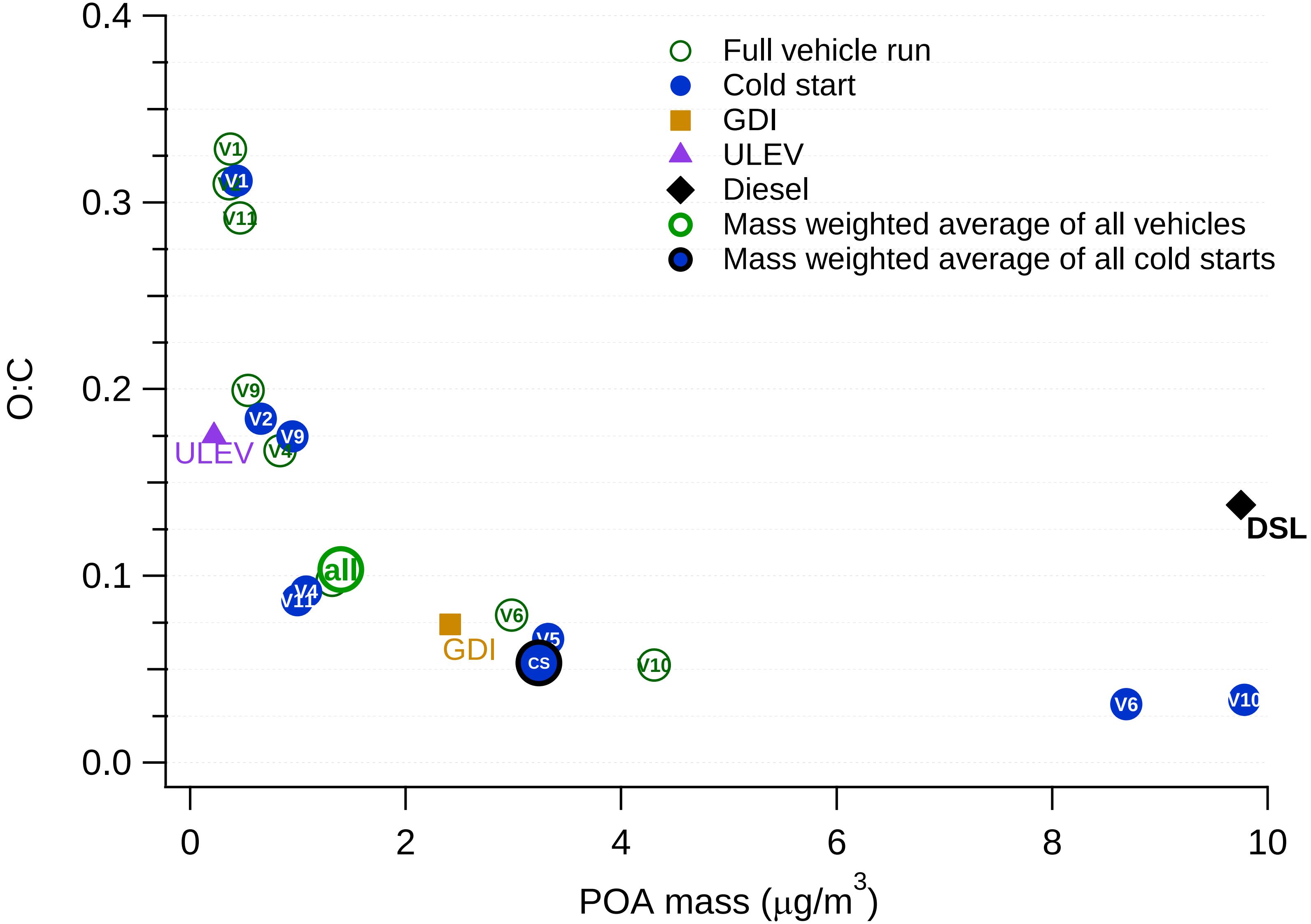
Source: S.D. Forestieri, S. Collier, T. Kuwayama, Q. Zhang, M.J. Kleeman, and C.D. Cappa. Real-time black carbon emission factor measurements from light duty vehicles. Environmental Science and Technology. 47(22), pp13104-13112 (2013), DOI: 10.1021/es401415a

EC Emissions Over Drive Cycle



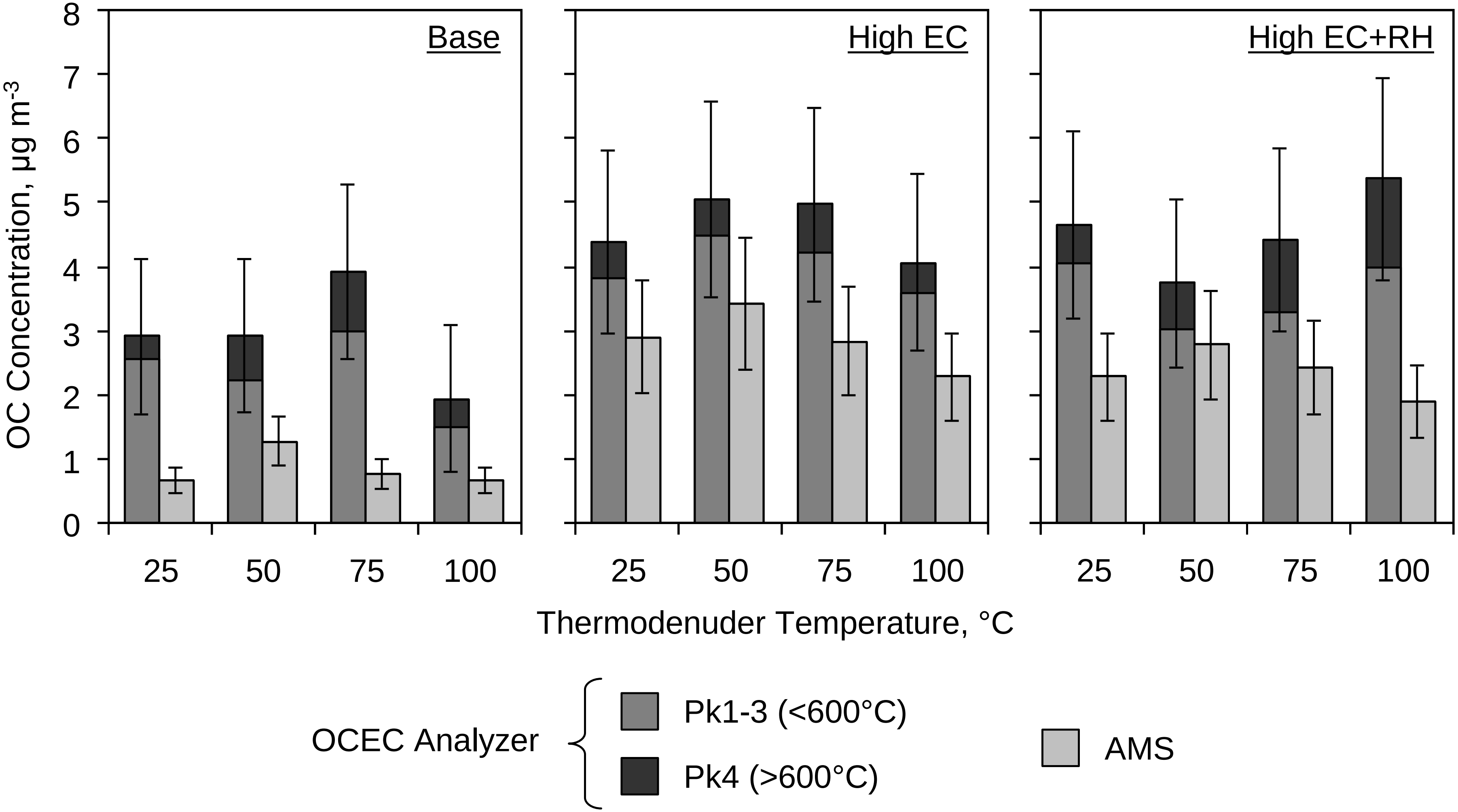
Source: S.D. Forestieri, S. Collier, T. Kuwayama, Q. Zhang, M.J. Kleeman, and C.D. Cappa. Real-time black carbon emission factor measurements from light duty vehicles. Environmental Science and Technology. 47(22), pp13104-13112 (2013), DOI: 10.1021/es401415a

AMS O:C Measurements



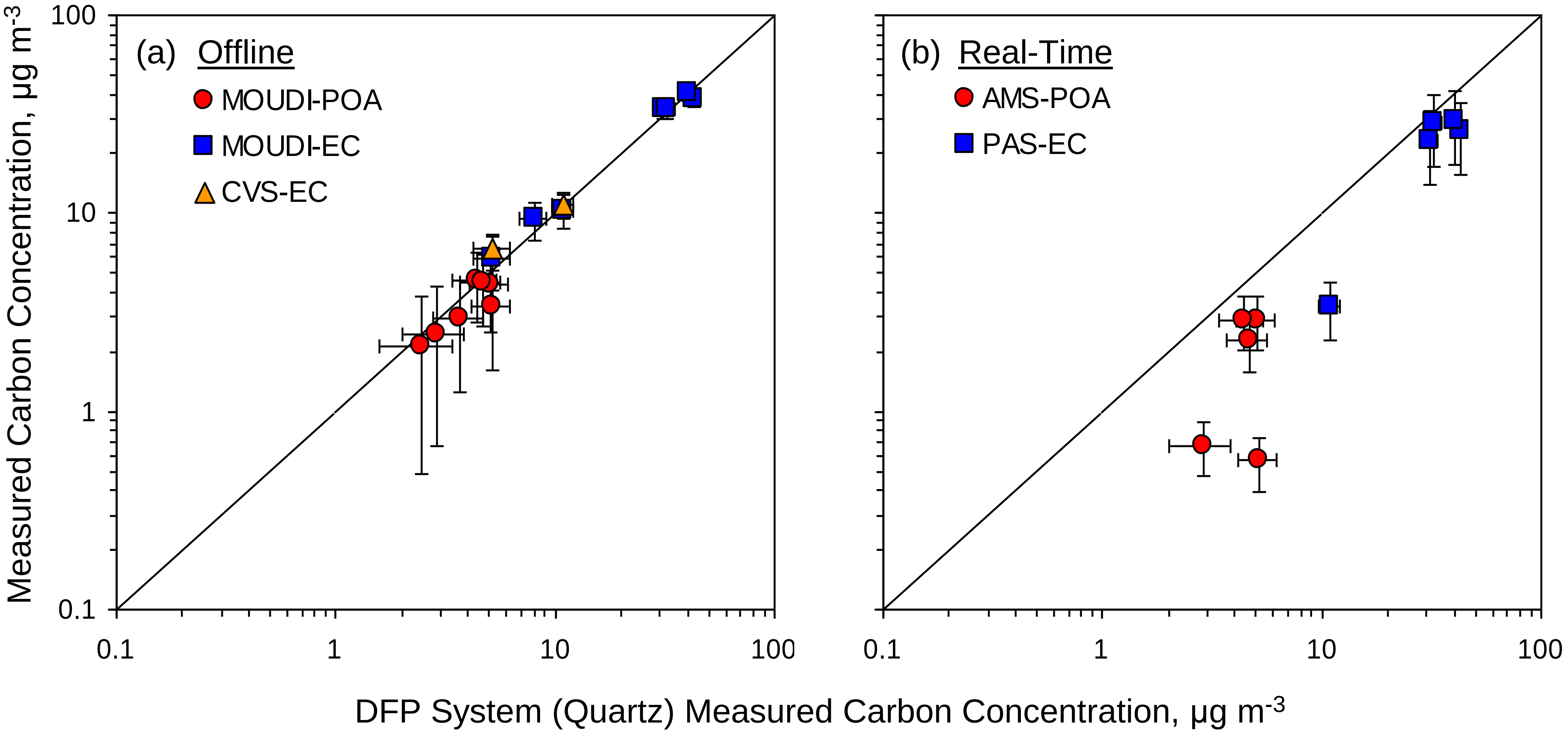
Source: S. Collier,T. Kuwayama, S. Forestieri, M.J. Kleeman, C.D. Cappa, J. Brady, T. Bertram, M. Zhang, Q. Zhang. Characterizing Organic PM Emissions from Vehicles: Dynamometer Tests Using a High-Resolution Aerosol Mass Spectrometer. In preparation.

AMS OC is Lower than Traditional OC from Car Exhaust



Source 2014. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

QA/QC Checks For OC Measurements



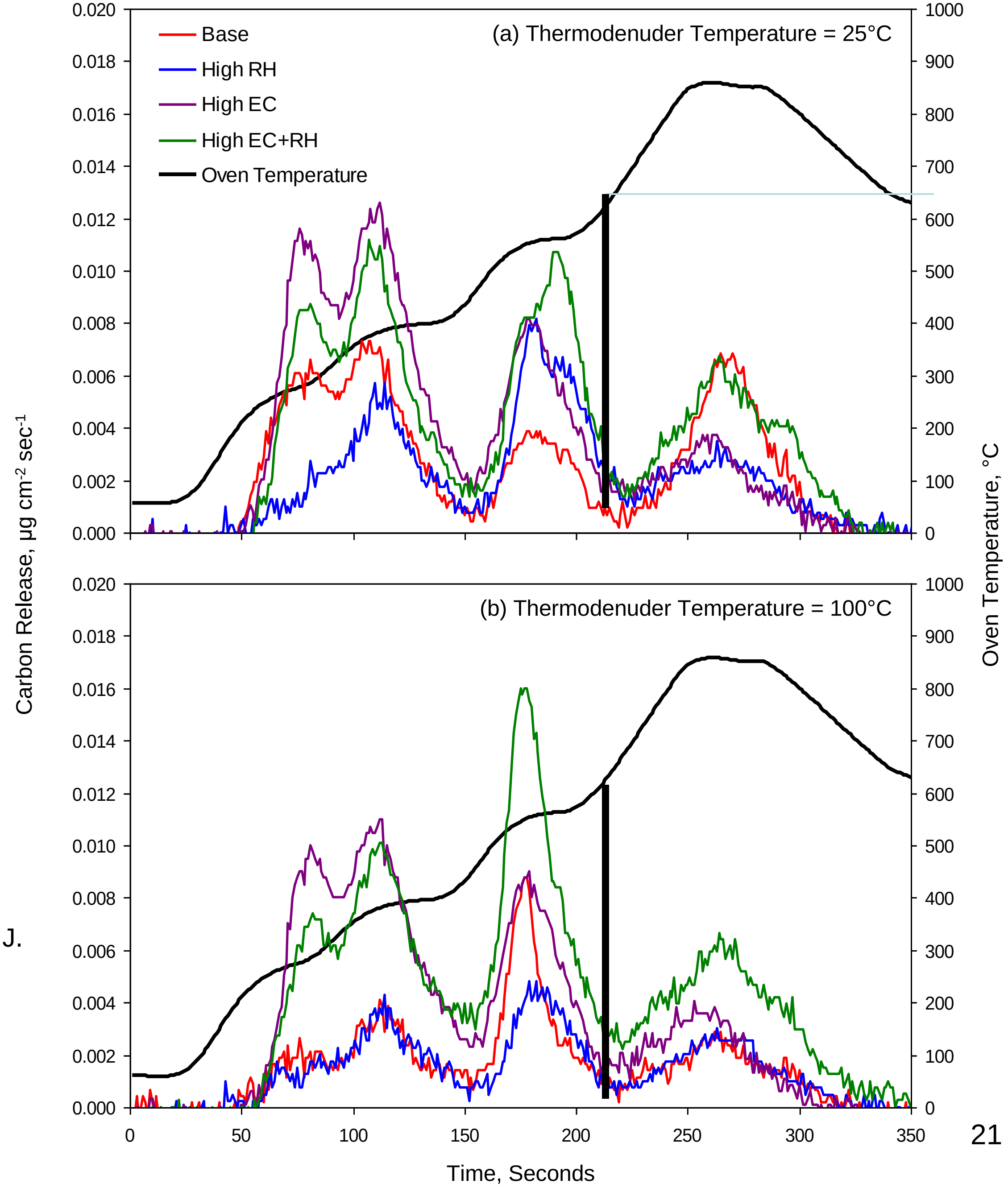
Source 2014. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

OC Thermograms

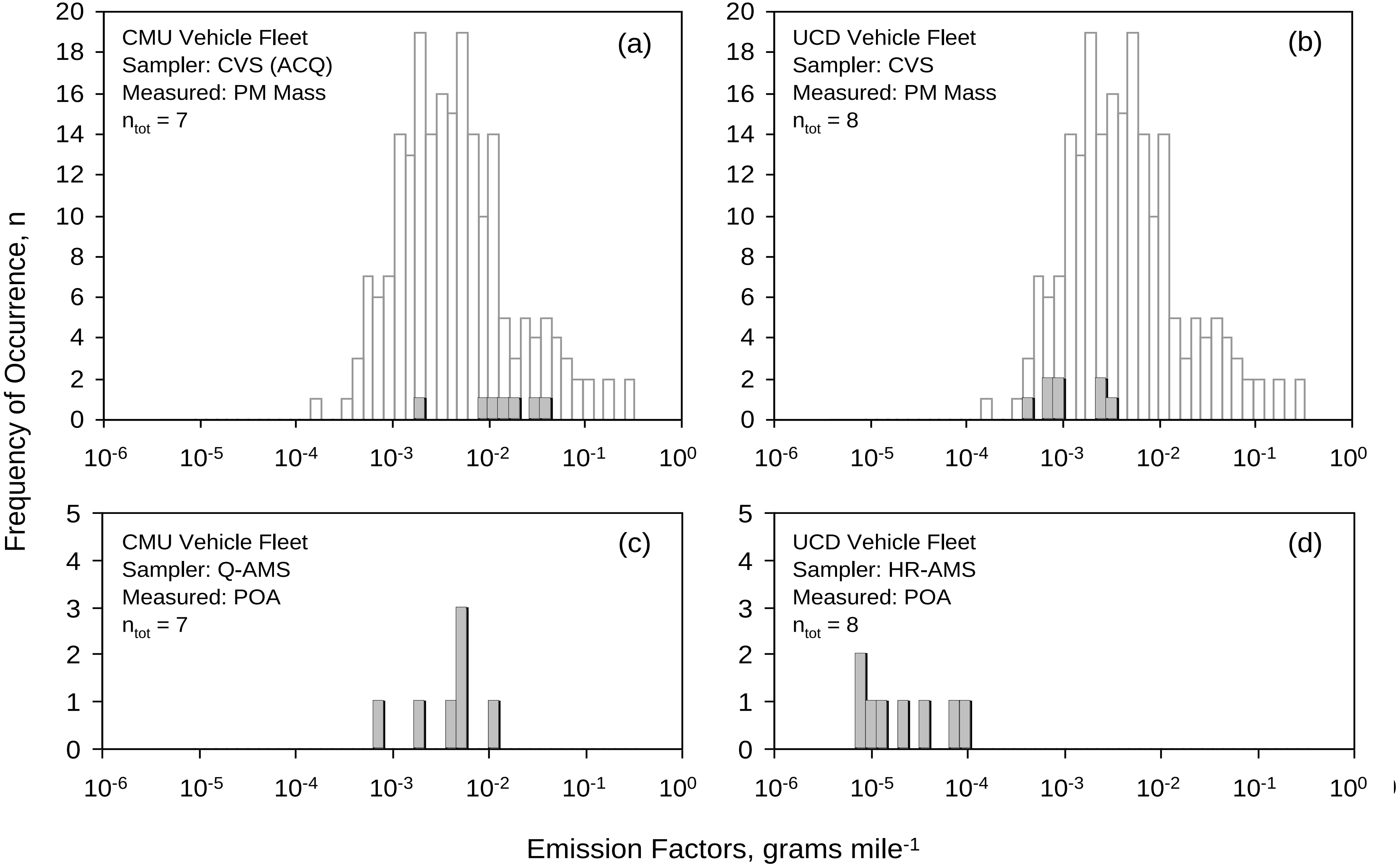
Significant OC evolves at T>600°C at atmospheric pressure.

How much of this material is “refractory” in the AMS at very low pressure?

Source 2014. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

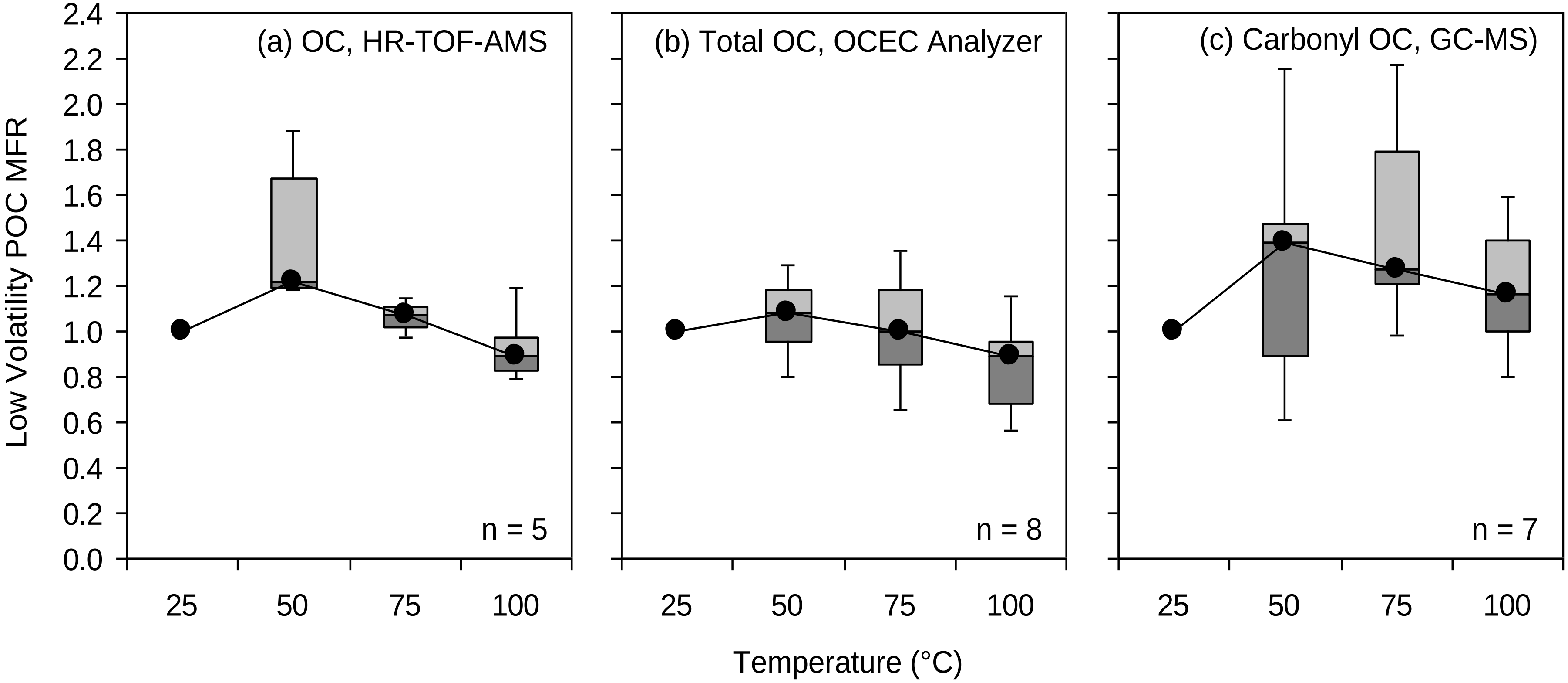


PM Emissions Factors



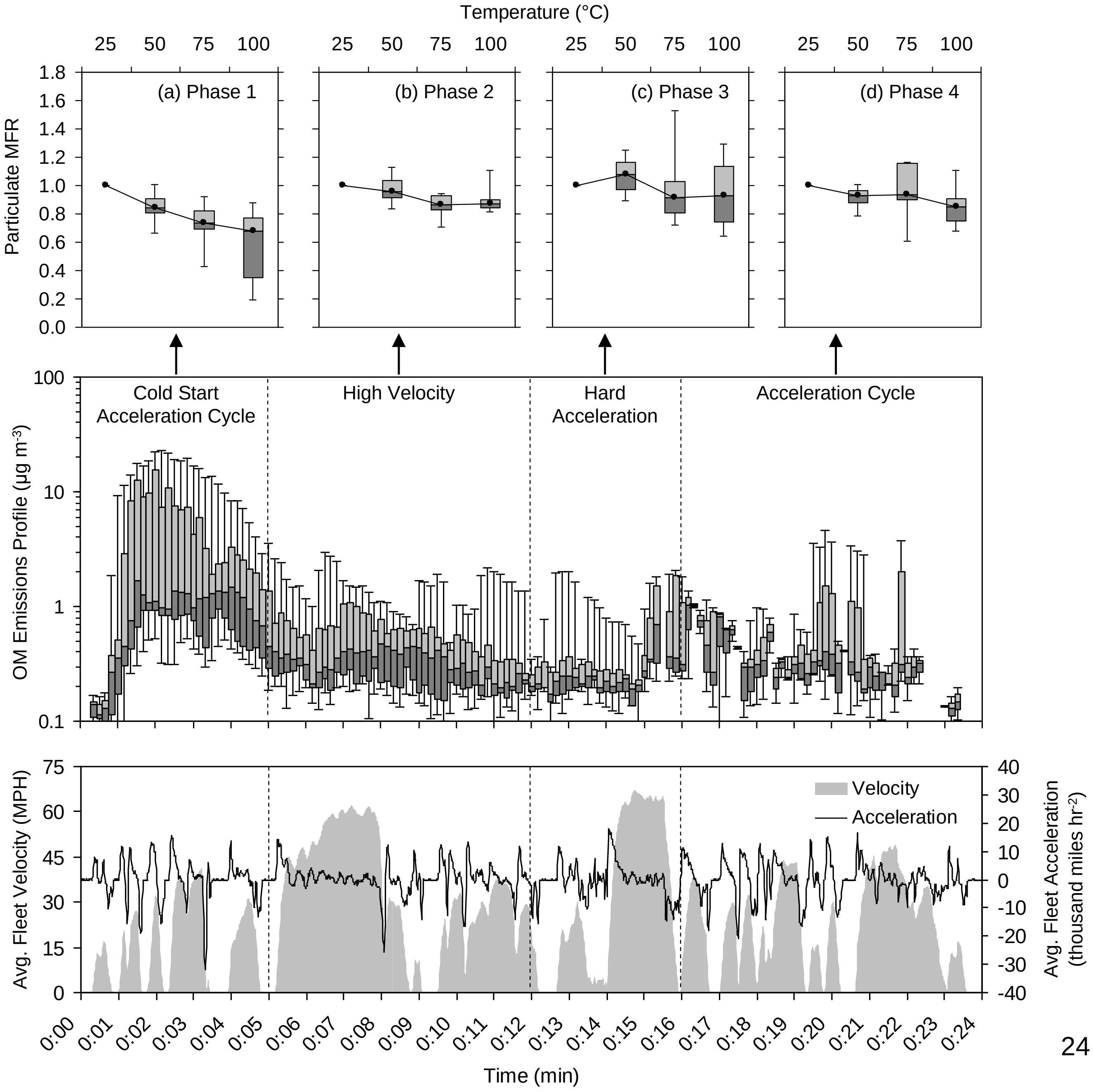
Source 2014. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

Mass Fraction Remaining of POA Averaged over UC Driving Cycle



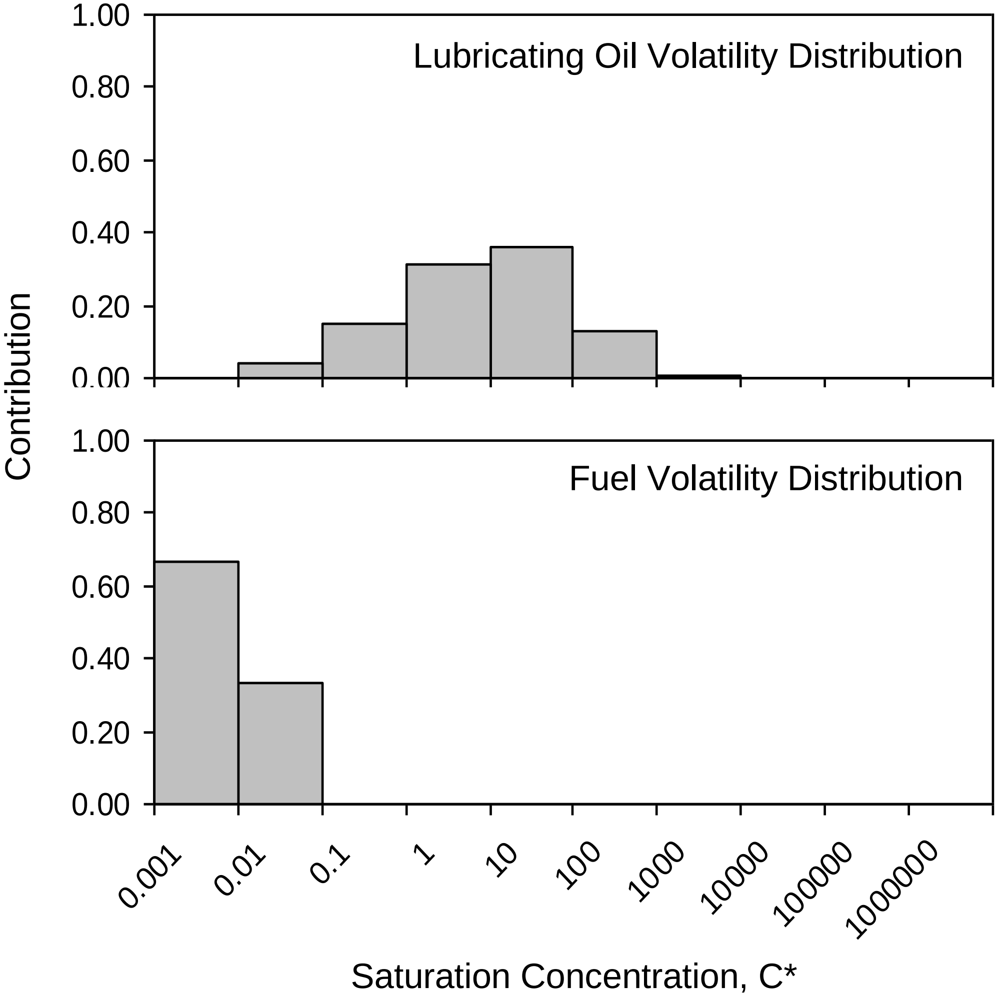
Source 2014. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

MFR as a Function of Time



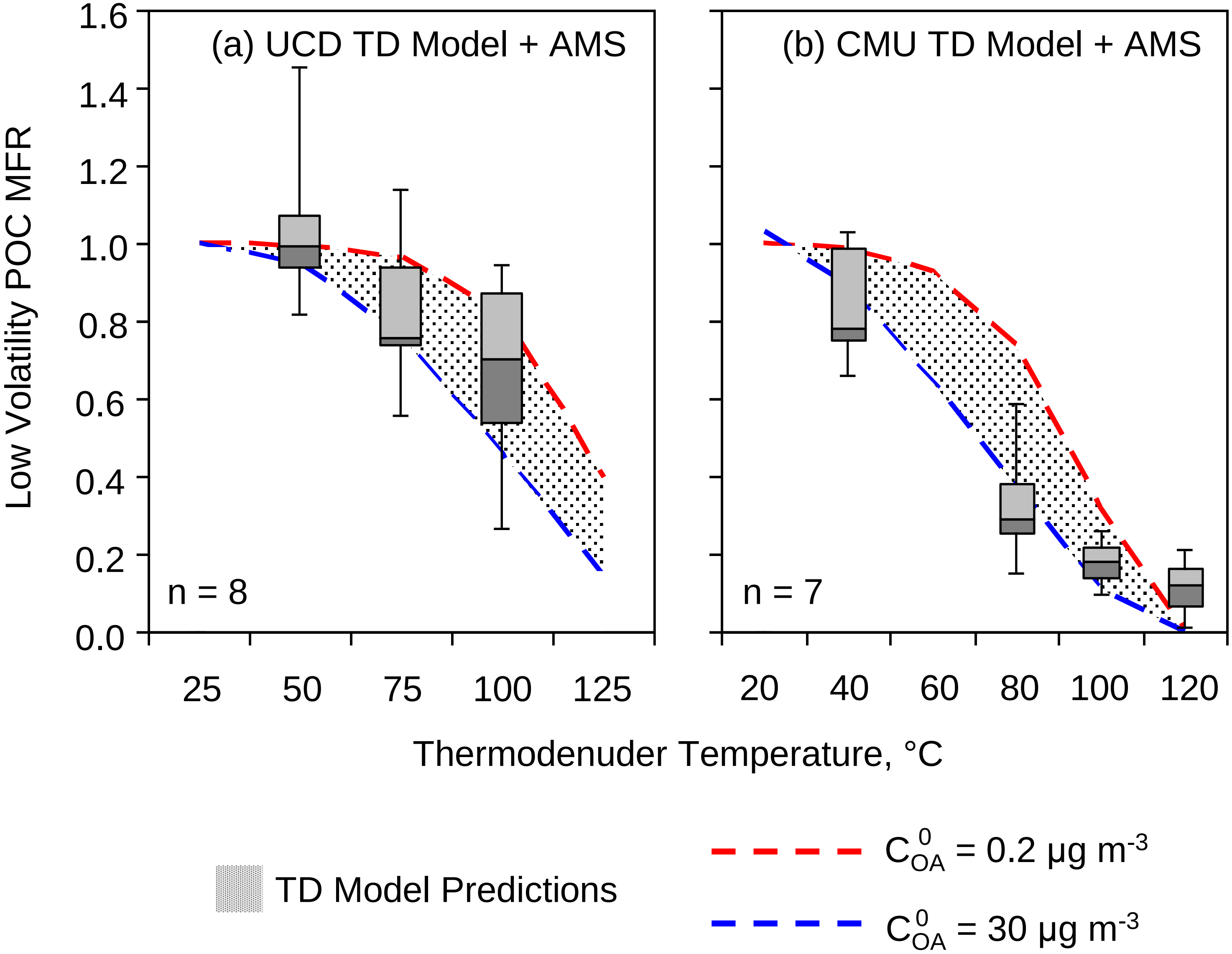
Source 2014. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

VBS Representation of Emissions



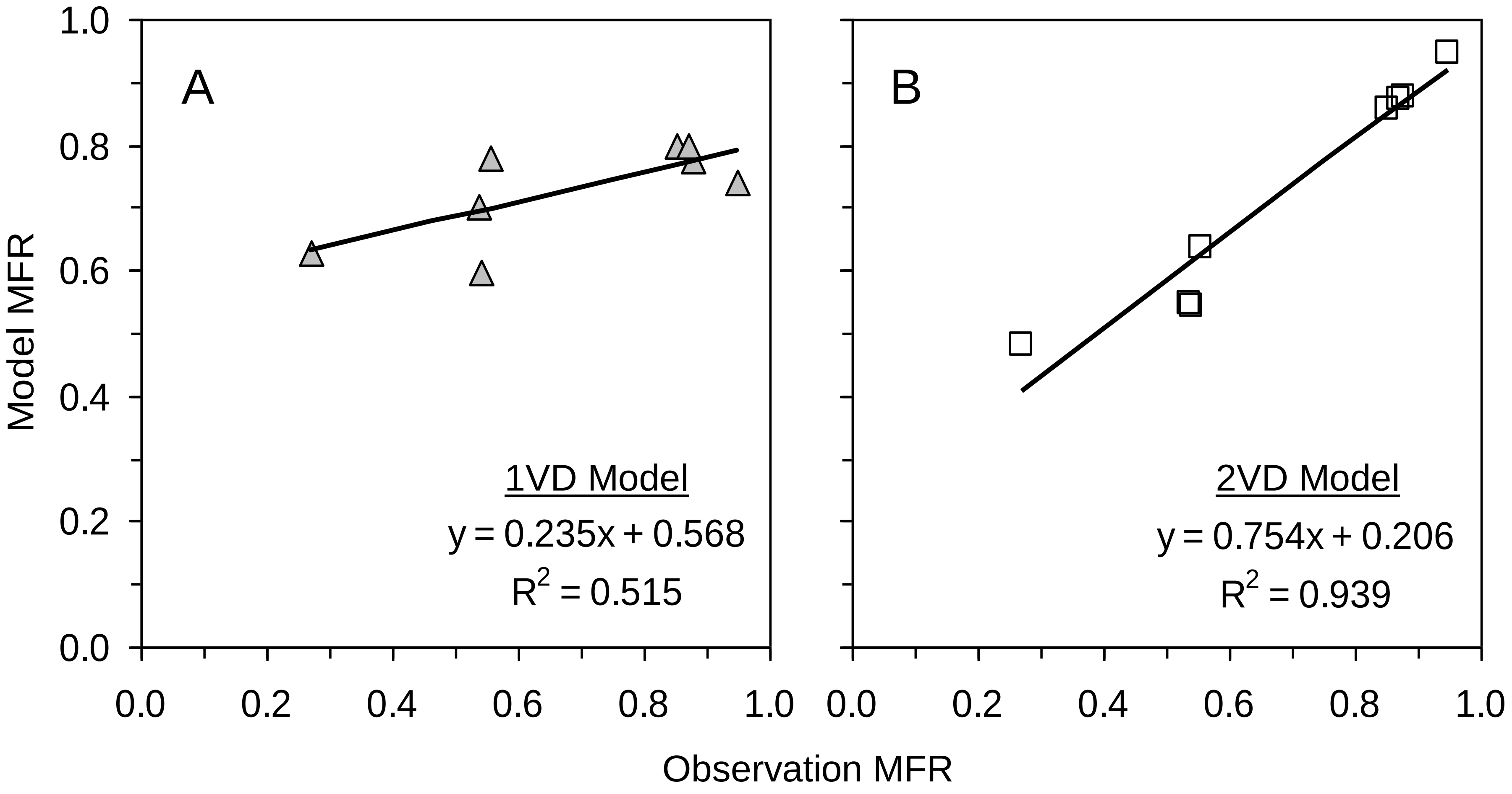
Source 2014. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

MFR Model Based on VBS



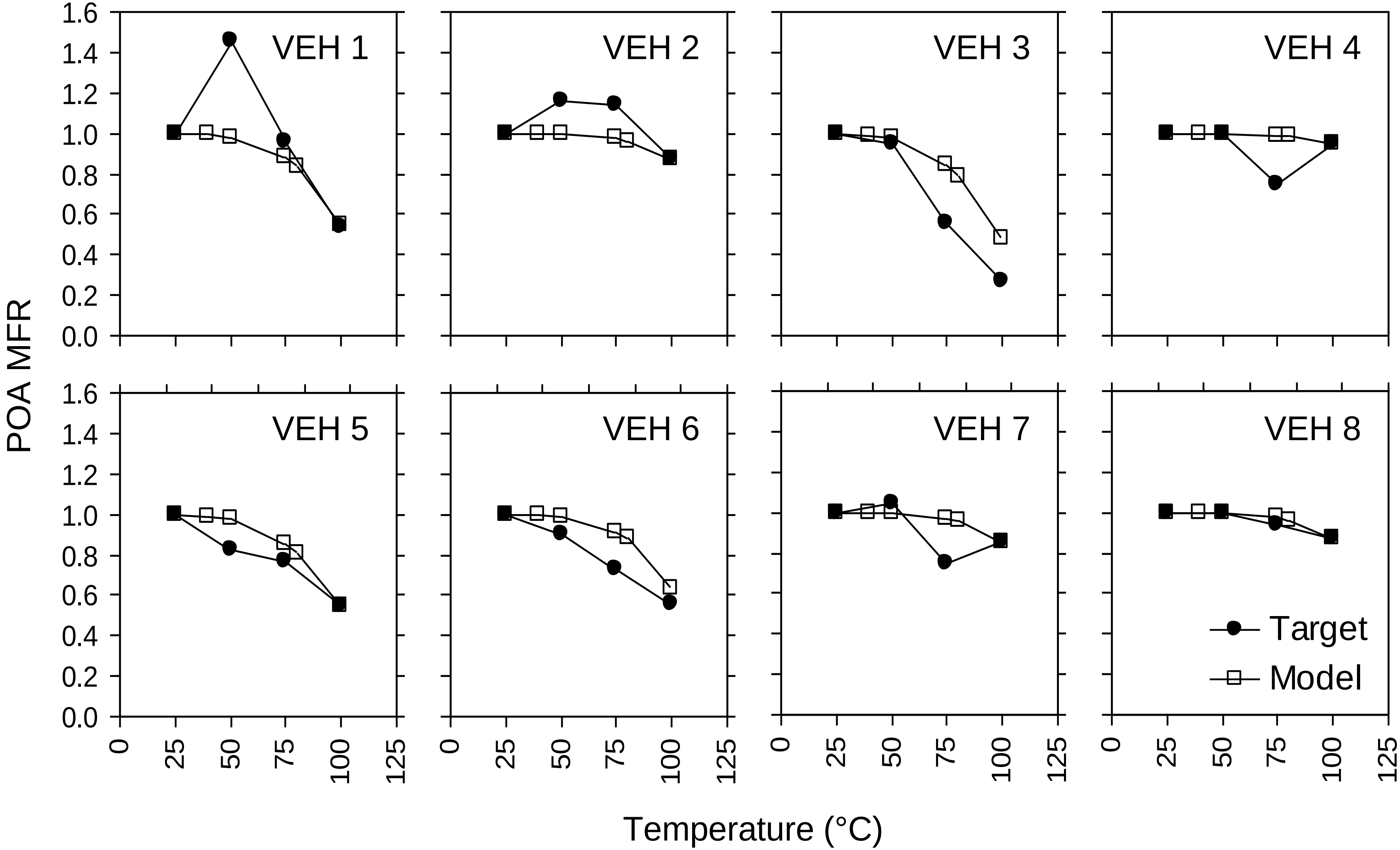
Source 2014. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

Residual Error in Mass Fraction Remaining Model



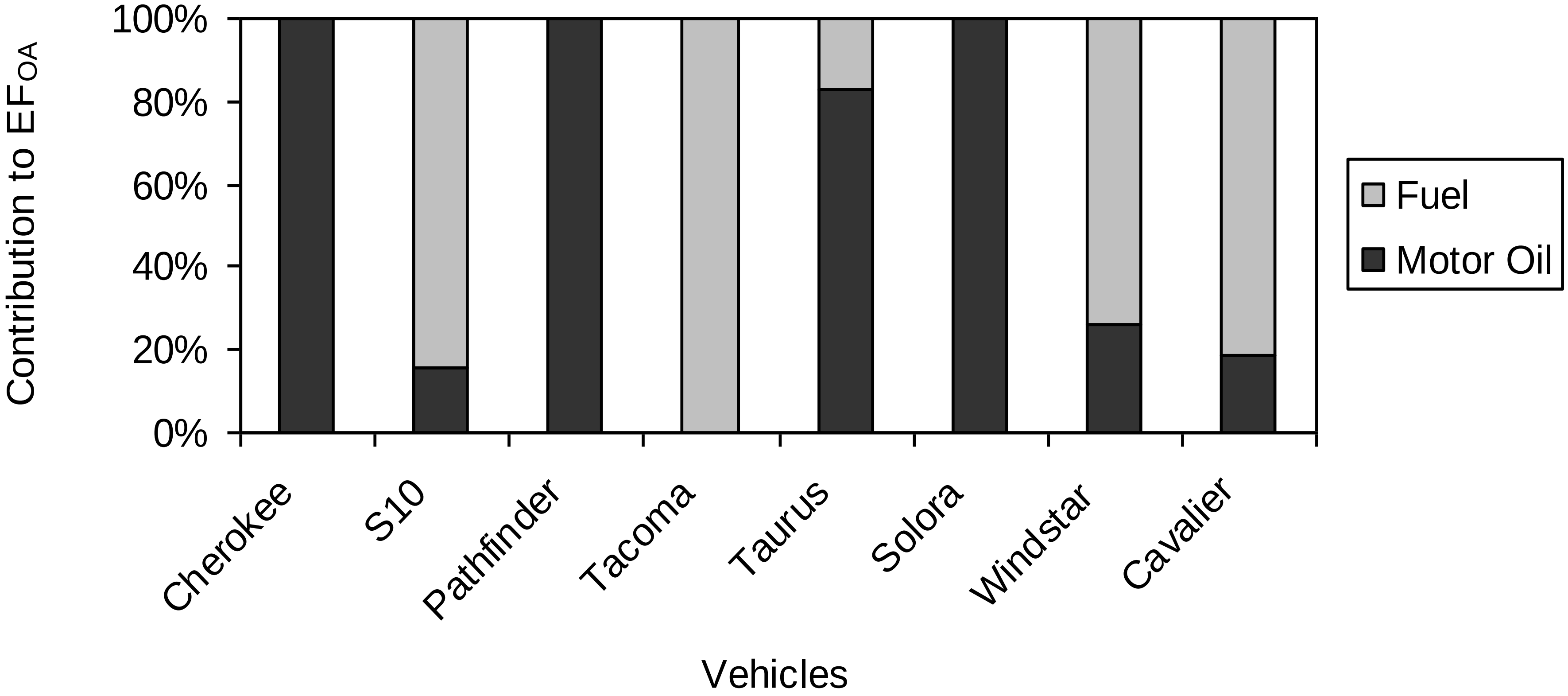
Source 2014. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

Individual Vehicle MFR Fits



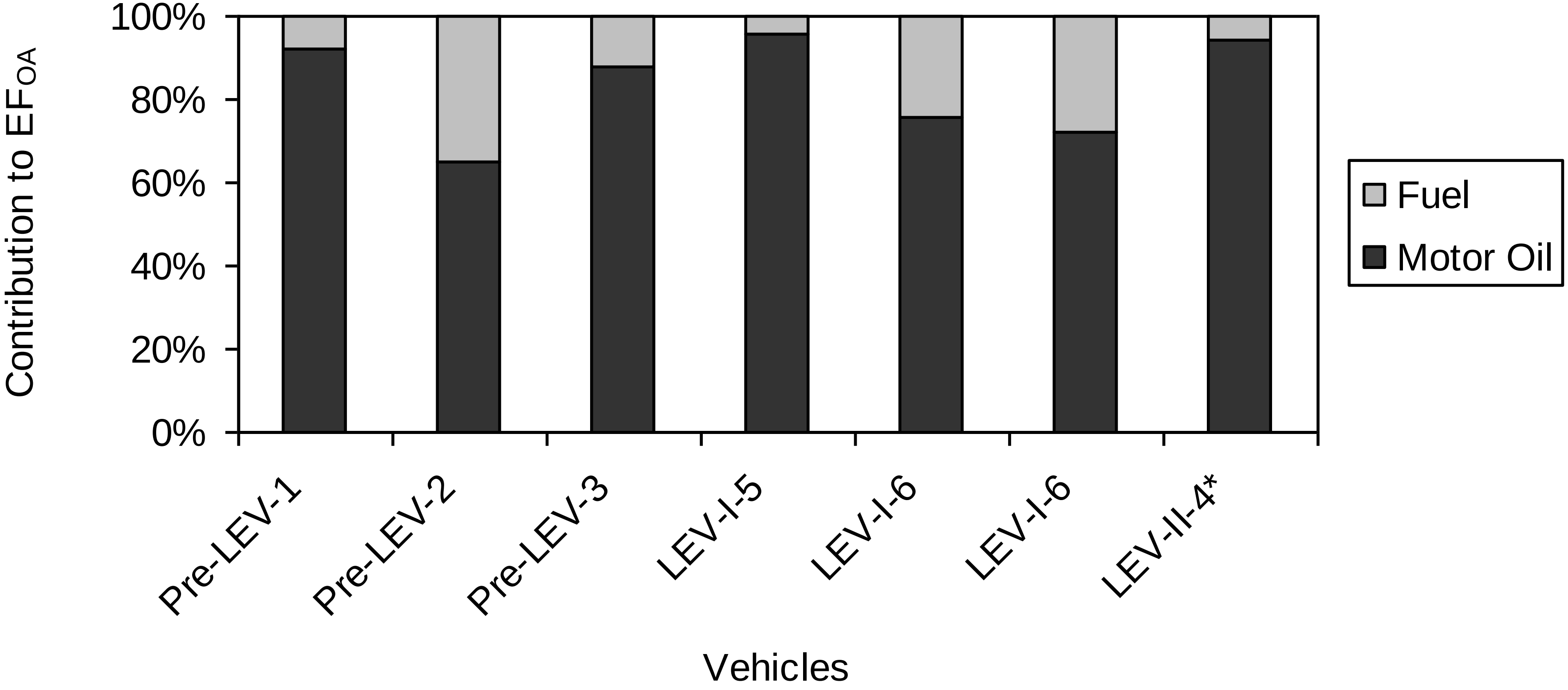
Source 2014. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

Motor Oil vs. Fuel POA Emissions (Present Study)



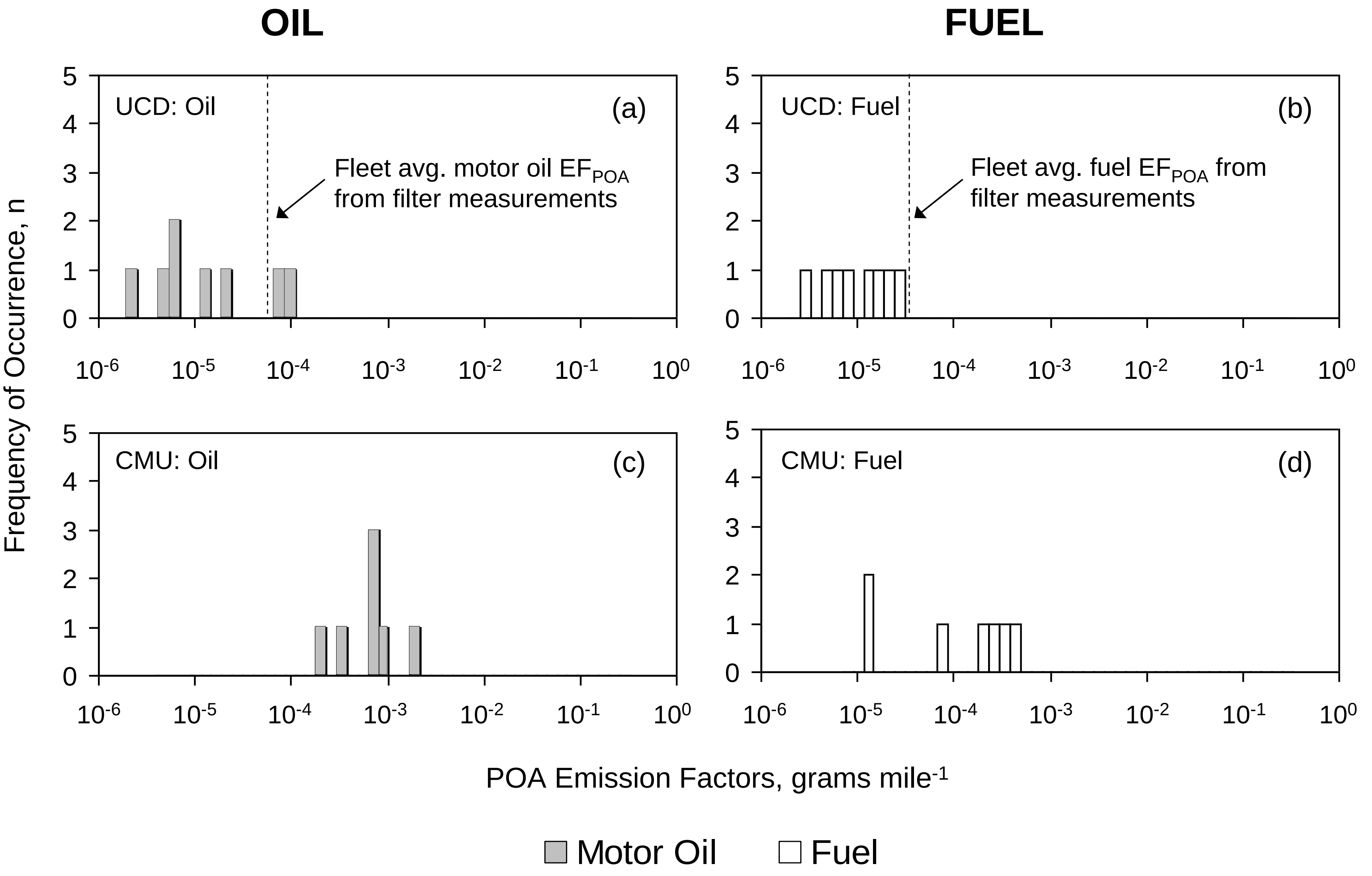
Source 2014. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

Motor Oil vs. Fuel POA Emissions (CMU Study)



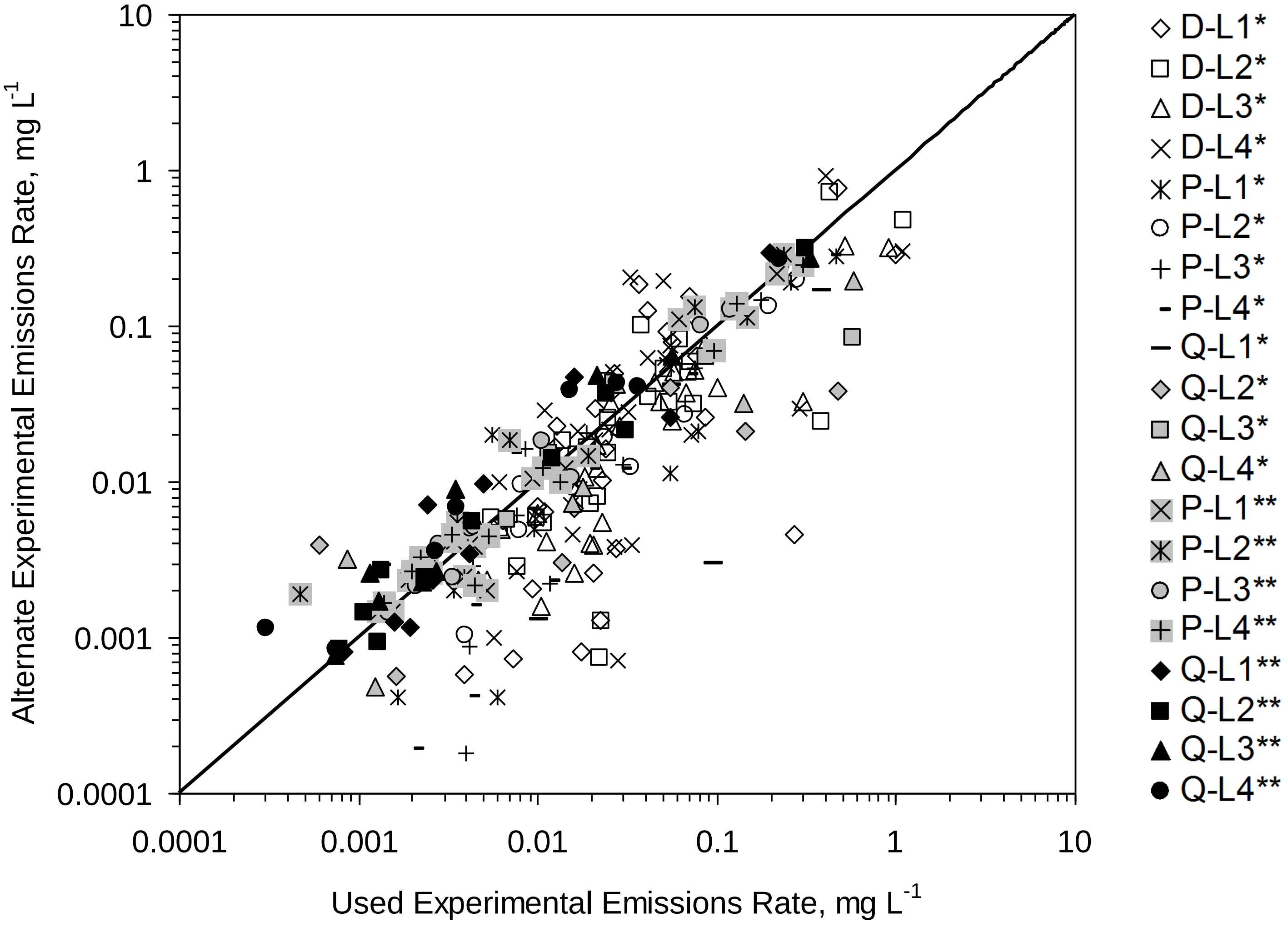
Source 2014. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

Motor Oil vs. Fuel Emissions – Fleet Characterization



Source 2014. T. Kuwayama, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Volatility of Primary Organic Aerosol Emitted from Light Duty Gasoline Vehicles. Environmental Science and Technology, submitted for publication.

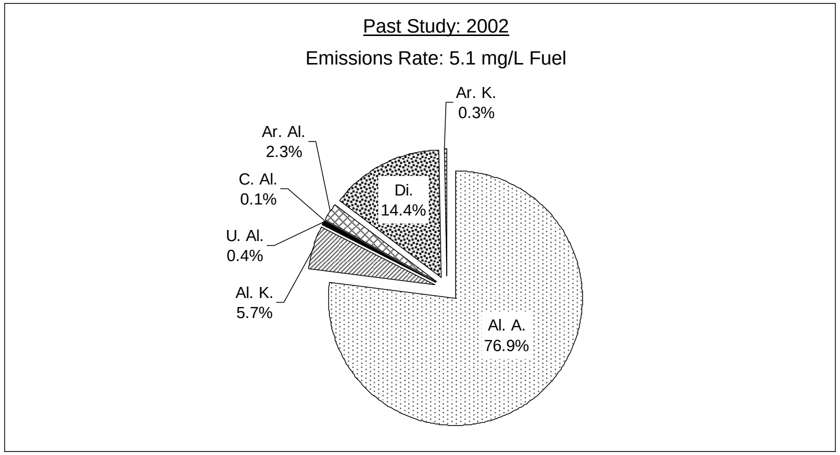
Carbonyl Measurement QA/QC

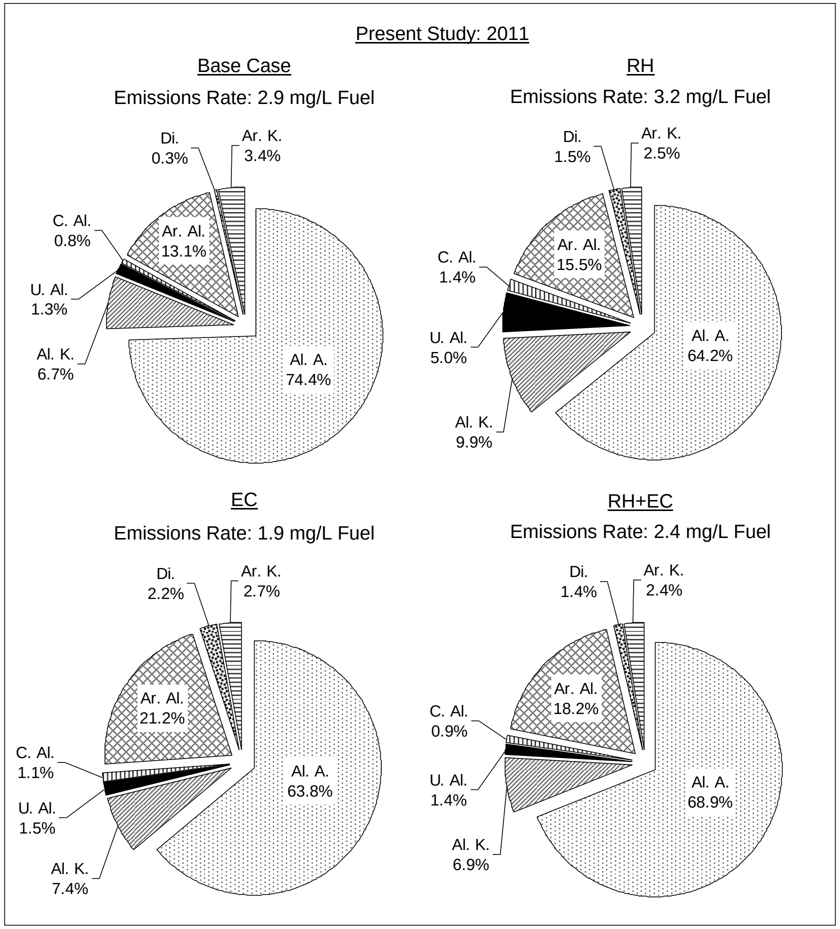


Source 2014. T. Kuwayama, I. Faria, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Effect of Atmospheric Conditions on Organic Aerosol Emissions from Gasoline Fueled Motor Vehicles. In preparation.

OM Speciation

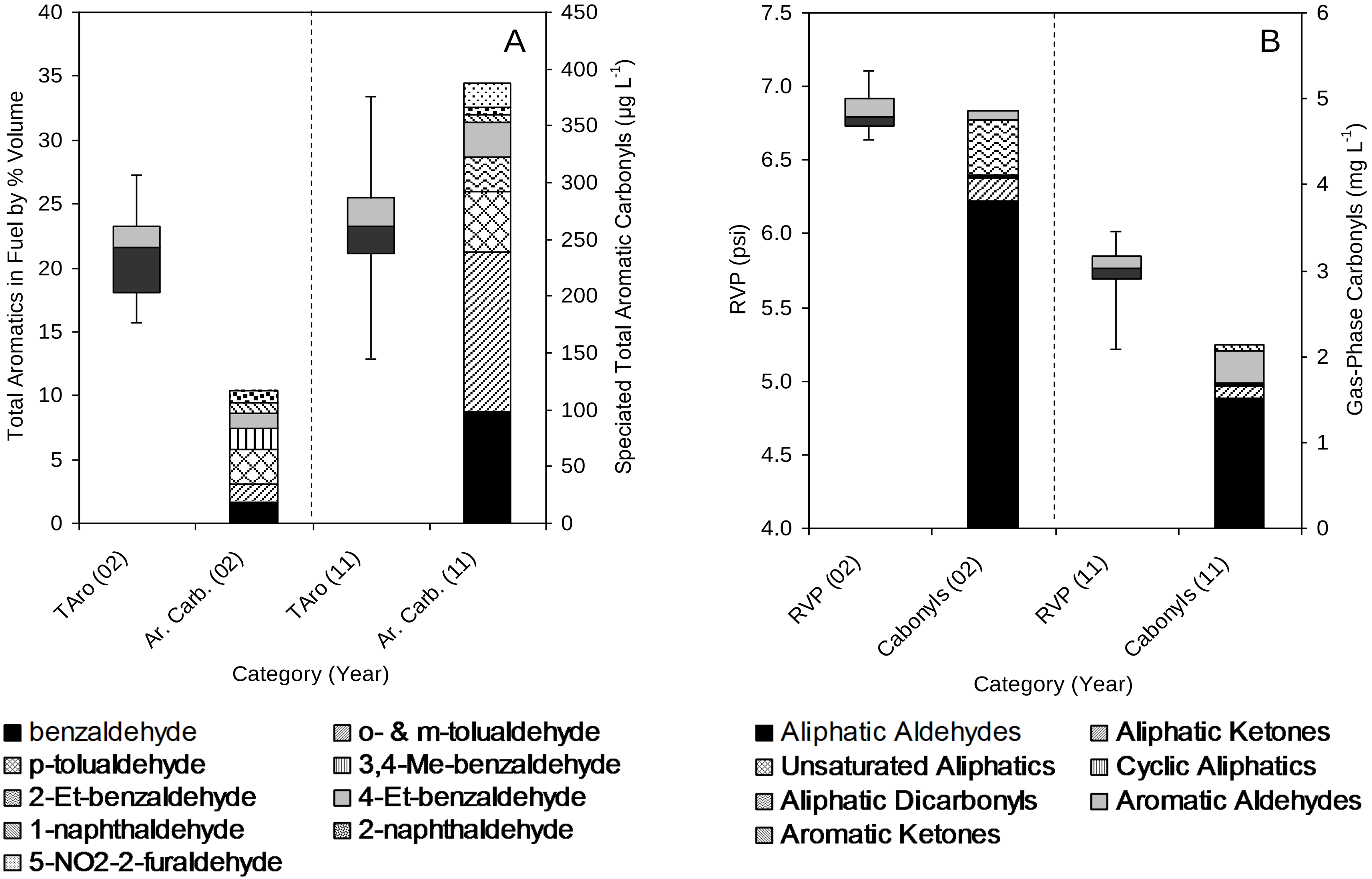
Light Aldehydes Account for 13-40% of POA





Source 2014. T. Kuwayama, I. Faria, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Effect of Atmospheric Conditions on Organic Aerosol Emissions from Gasoline Fueled Motor Vehicles. In preparation.

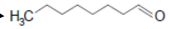
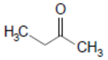
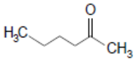
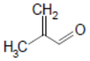
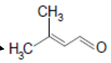
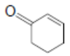
Gasoline Composition Trends vs. Carbonyl Trends

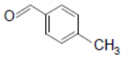
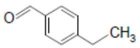
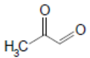
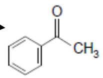
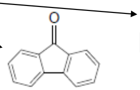


Source 2014. T. Kuwayama, I. Faria, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Effect of Atmospheric Conditions on Organic Aerosol Emissions from Gasoline Fueled Motor Vehicles. In preparation.

Carbonyl Species Concentrations

Emissions Rate (μg L^{-1}) for Measured Gas and Particle Phase Carbonyls

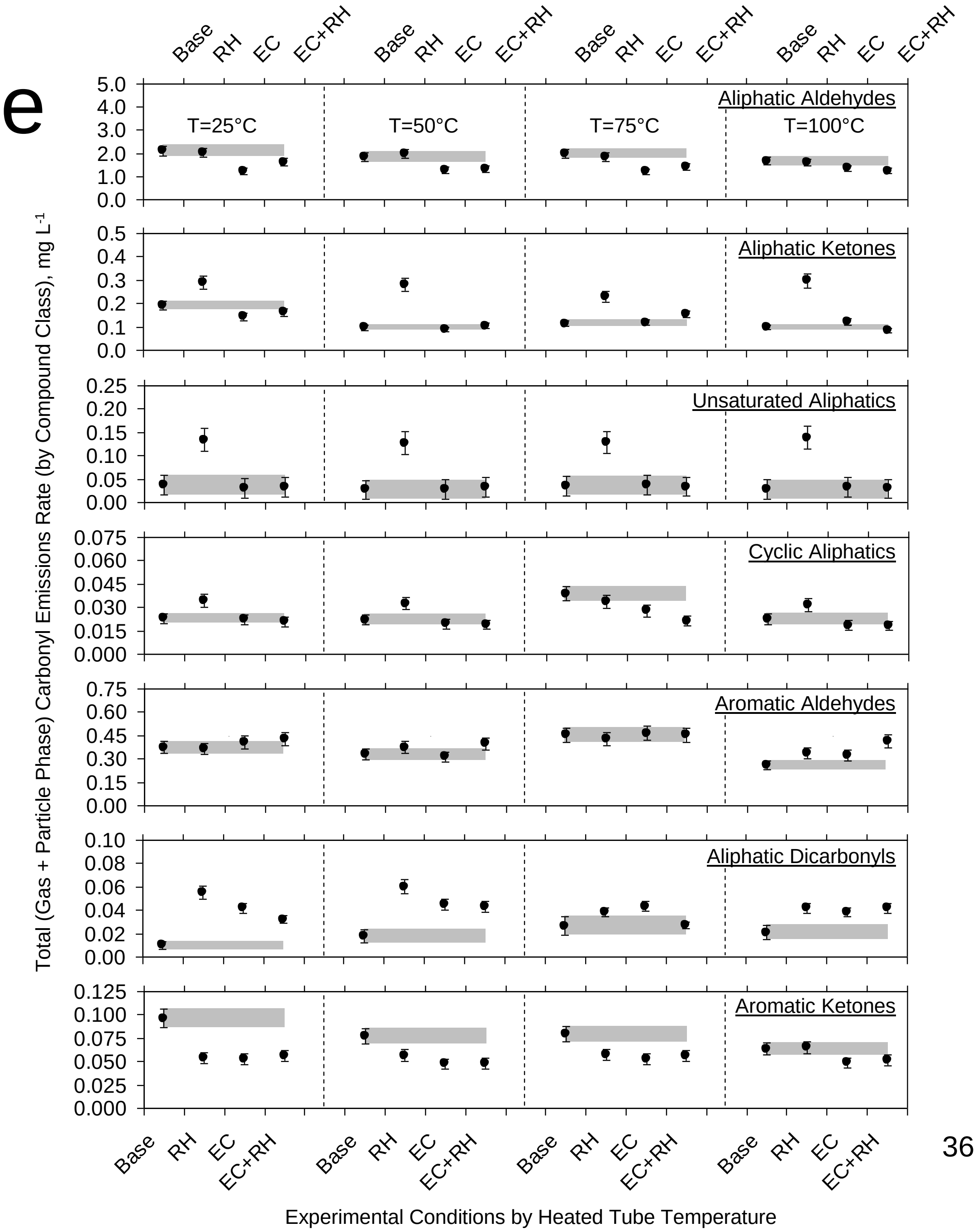








Compounds	T = 25°C				T = 50°C				T = 75°C				T = 100°C			
	Base Case	RH	EC	RH+EC	Base Case	RH	EC	RH+EC	Base Case	RH	EC	RH+EC	Base Case	RH	EC	RH+EC
Aliphatic Aldehydes																
propanal	525	677	230	117	416	703	197	145	411	510	158	153	250	545	261	148
butanal	79	236	6.7	41	105	228	6.3	12	81	152	22.4	47	36	181	50	27
pentanal	7.8		0.8	2.1			0.2	6.6	7.7				4.8			
hexanal	31	42	4.2	29	8.6	39	10	4.5	8.8	30	11	36	11	2.5	18	17
heptanal	15	25	17	14	10	21	10	8.7	15	28	24	21	3.6	5.9	12	11
octanal	91	107	82	101	81	97	78	84	105	113	109	116	76	74	91	97
nonanal	1267	837	771	1200	1150	774	897	980	1207	880	795	937	1197	697	818	847
decanal	62	53	74	69	48	54	37	33	83	63	43	57	46	43	63	51
undecanal	15	19	18	21	13	21	17	17	25	27	22	21	14	16	14	17
dodecanal	24	39	23	26	23	37	22	24	32	38	30	28	23	39	22	26
Aliphatic Ketones																
2-butanone	47	64	41	14	17	99	19	8.2	17	61	25	8.4	16	96	30	6.7
3-pentanone	det.	11	2.3			17	1.1		det.	12	3.8		det.	19	4.2	
2-pentanone		24	7.9	1.7		34	0.4			23	0.2	0.7		35		0.1
2-hexanone	130	167	71	132	70	140	57	91	80	104	71	127	72	112	74	75
2-heptanone	4.9	20	8.1	10	0.3	14	3.7	0.4	9.3	23	10	13		7.4	2.8	1.8
2-octanone	8.0	10	11	3.5	8.8	10	5.4	3.0	6.5	10	6.7	3.3	8.4	12	11	2.2
3-nonanone		12				6.5				6.0				9.3		
2-undecanone		7.5	1.5	1.9		6.6	1.5	1.6		7.2	1.6	2.2		9.4		
Unsaturated Aliphatics																
methacrolein		58	1.3	2.5		64	2.3	3.7		44	2.3	3.3		49	1.7	2.8
crotonaldehyde		5.4				4.7				6.2						
5-hexen-2-one	3.3	48	3.1	2.5	2.3	61	3.7	4.5	4.9	39	2.6	3.5	2.5	60	4.5	3.6
2,4-hexadienal									6.8		8.0					
4-hexen-3-one						2.2										
3-Me-2-butenal	20	42	17	28	15	50	16	24	15	35	16	27	18	47	17	23
trans-2-hexenal		4.4				4.0				5.3						
trans-4-decenal	14		9.5		10		6.0		8.3		8.1		7.4		9.3	
Cyclic Aliphatics																
2-Me-2-cyclopenten-1-one		3.6		0.1		3.1				4.5	0.9	0.7				
2-cyclohexen-1-one	0.3	3.3	5.5	4.5	0.2	2.9	3.9	4.9	0.5	4.1	6.6	4.3	det.		3.3	4.1
3-Me-2-cyclopenten-1-one	0.5	7.3	1.4	1.5	det.	4.0	1.0	0.6	1.0	6.4	2.0	1.8		6.4	0.8	0.5
3,5-Me-2-cyclohexen-1-one	2.2		2.2	2.6	1.6		2.4	2.5	2.3		2.3	2.3	2.4		2.4	2.5
pinonaldehyde	20	31	13	12	20	33	12	11	35	33	16	12	20	39	12	11
Aromatic Aldehydes																
benzaldehyde	97	94	131	136	61	93	77	109	125	127	150	128	31	66	60	107
o-tolualdehyde	60	60	60	52	68	63	46	55	51	70	69	61	34	59	49	65
m-tolualdehyde	80	112	92	94	74	110	79	97	109	126	106	117	65	101	87	100
p-tolualdehyde	53	82	46	56	47	82	43	51	63	98	55	62	48	83	49	57
4-Et-benzaldehyde	31	80	26	31	29	81	26	28	41	88	29	33	32	81	28	29
2-Et-benzaldehyde	31	38	29	36	31	38	27	33	40	42	33	36	30	47	30	33
5-NO2-2-furaldehyde	21	27	24	22	20	24	16	25	24	26	24	16	20	28	19	22
mesitaldehyde		16				16				16				23		
1-naphthaldehyde	5.8	9.2	4.4	4.4	5.8	9.3	4.0	4.5	6.9	9.1	5.1	3.9	5.9	14	4.0	4.1
2-naphthaldehyde	7.0	15	5.3	4.9	7.1	15	4.5	5.3	8.4	15	5.9	4.6	7.0	22	4.8	4.9
Aliphatic Dicarbonyls																
2,3-hexanedione			28	18			19	24			25	12			19	29
glyoxal		16				12			0.6	15	0.3			17	0.1	
methylglyoxal	9.9	30	14	14	18	28	26	19	26	17	18	15	21	20	19	13
Aromatic Ketones																
benzophenone	6.5	6.8	2.4	4.4	2.7	7.0	2.0	2.3	3.0	6.8	2.5	2.4	2.7	11	2.1	2.3
acetophenone	24	31	20	24	21	29	17	21	26	31	21	27	19	24	20	23
9-fluorenone	34		2.7	2.0	18		2.1	1.8	16		3.5	5.3	13		1.9	6.4
1-indanone	19	18	18	16	23	25	18	13	19	25	15	13	16	25	16	11

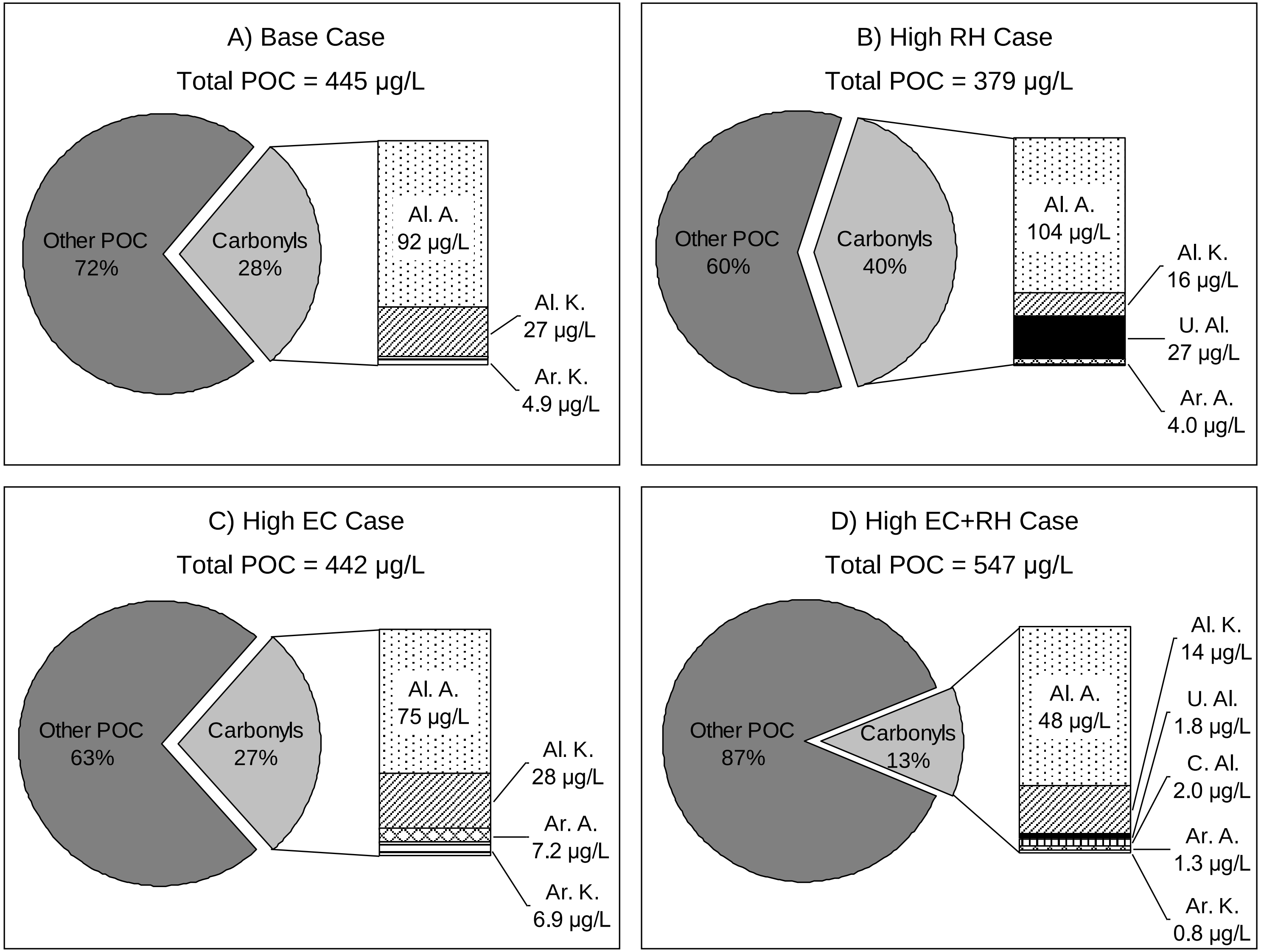
Source 2014. T. Kuwayama, I. Faria, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Effect of Atmospheric Conditions on Organic Aerosol Emissions from Gasoline Fueled Motor Vehicles. In preparation.

Humidity Affects the Total Carbonyls Concentration



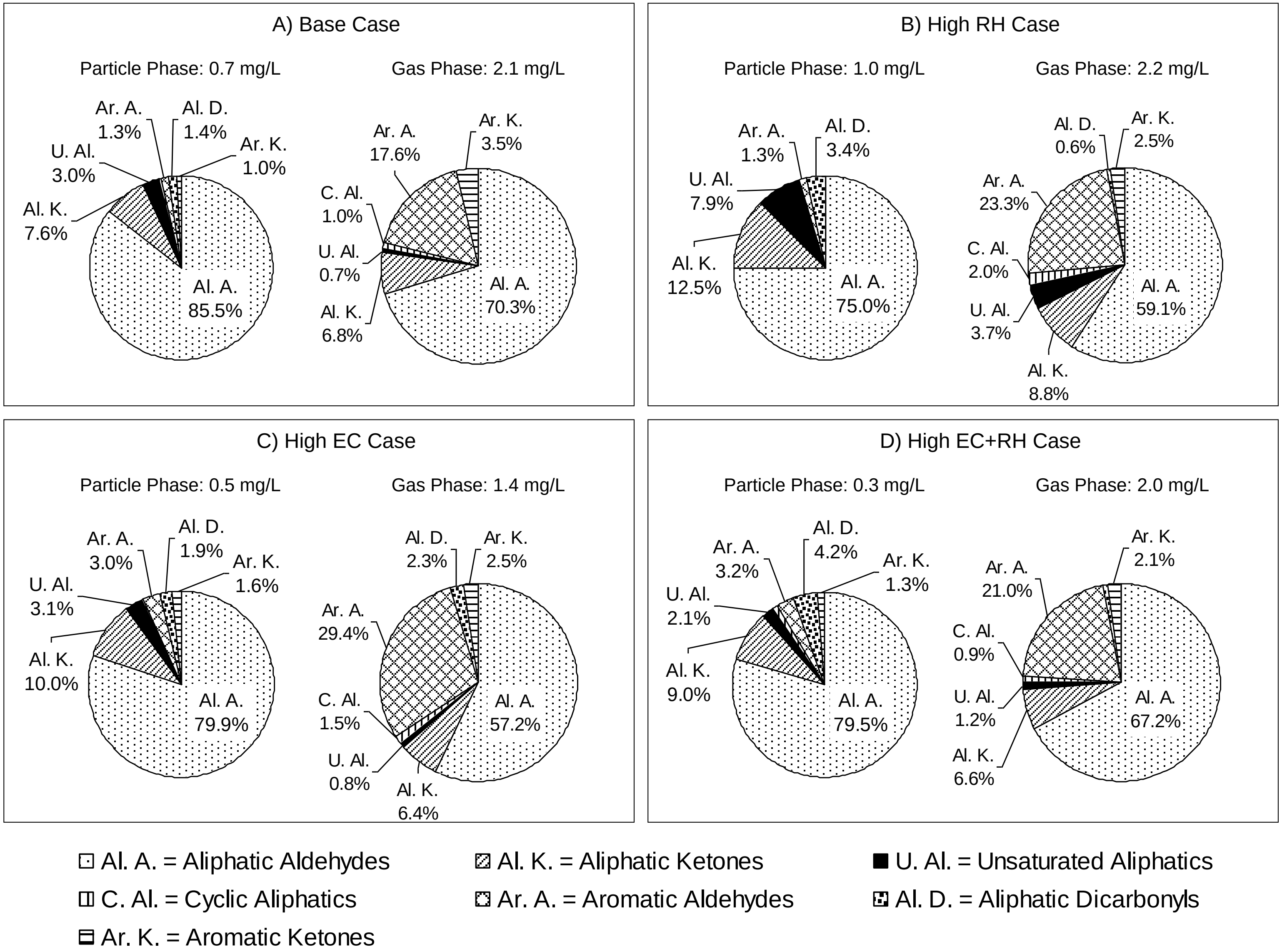
Source 2014. T. Kuwayama, I. Faria, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Effect of Atmospheric Conditions on Organic Aerosol Emissions from Gasoline Fueled Motor Vehicles. In preparation.

Humidity Affects Carbonyls in the POA



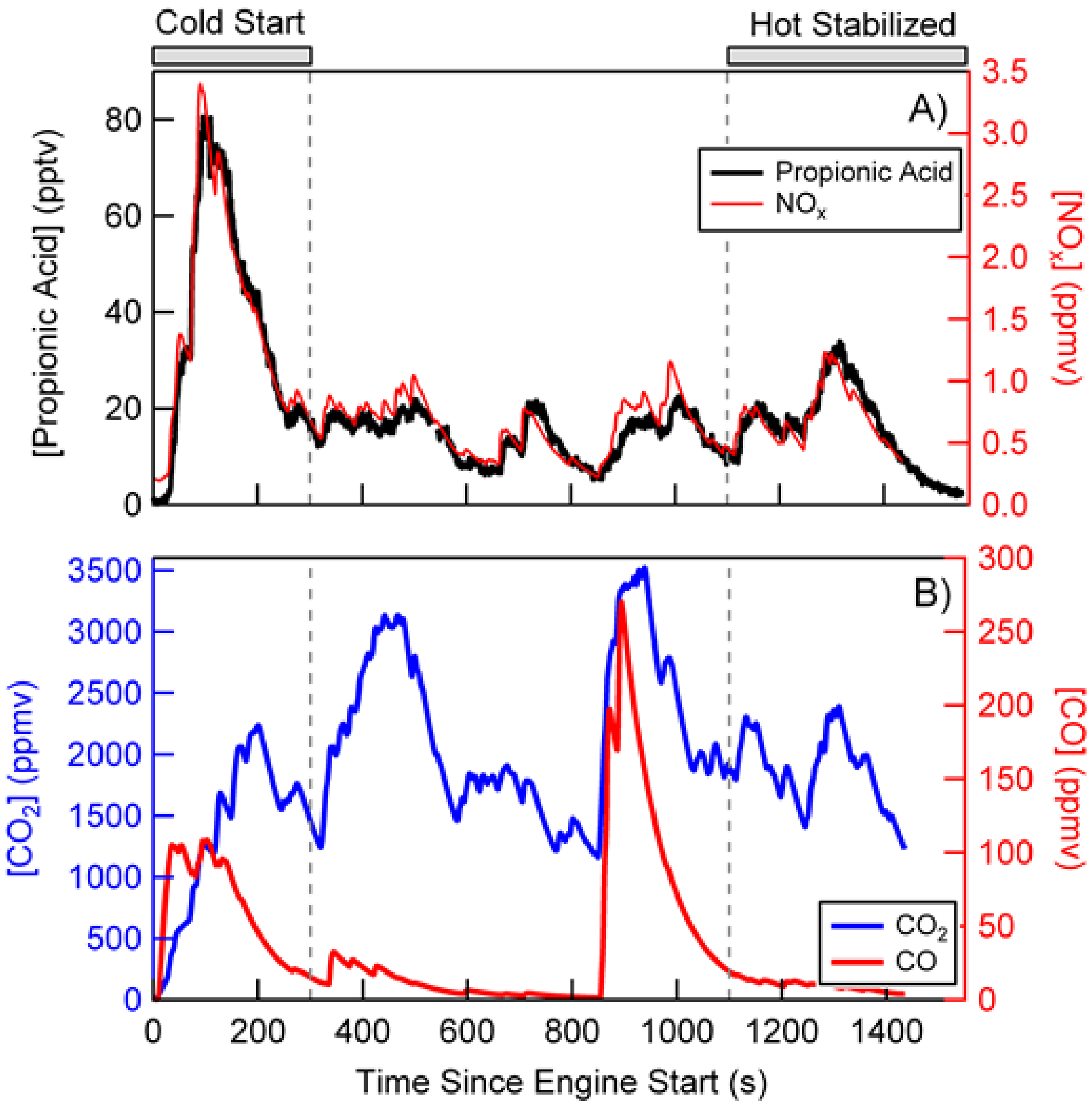
Source 2014. T. Kuwayama, I. Faria, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Effect of Atmospheric Conditions on Organic Aerosol Emissions from Gasoline Fueled Motor Vehicles. In preparation.

Carbonyl Speciation – Set 1

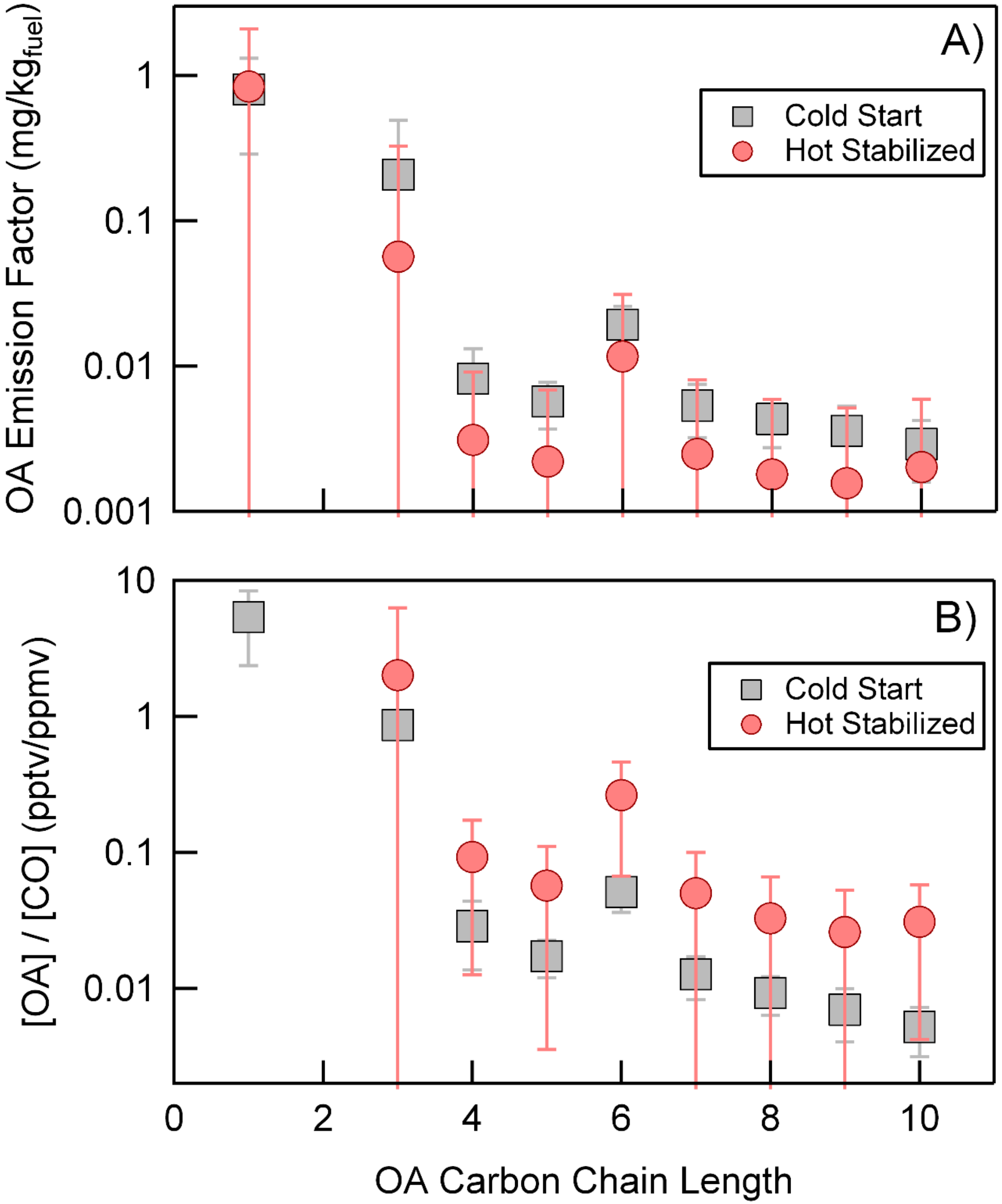


Source 2014. T. Kuwayama, I. Faria, S. Collier, S. Forestieri, J. M. Brady, T.H. Bertram, C.D. Cappa, Q. Zhang, and M.J. Kleeman. Effect of Atmospheric Conditions on Organic Aerosol Emissions from Gasoline Fueled Motor Vehicles. In preparation.

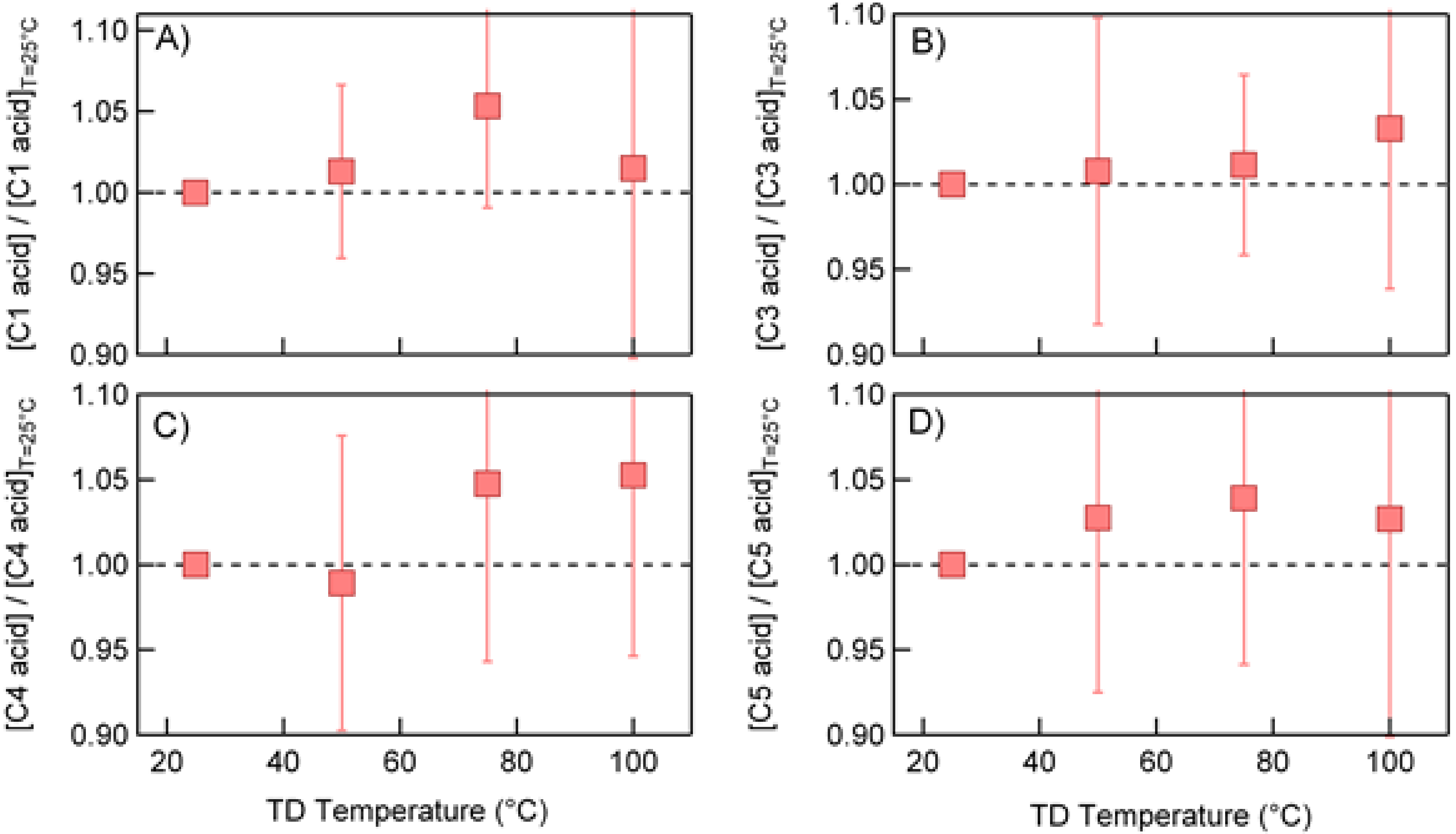
Emissions of Gas-Phase Organic Acids



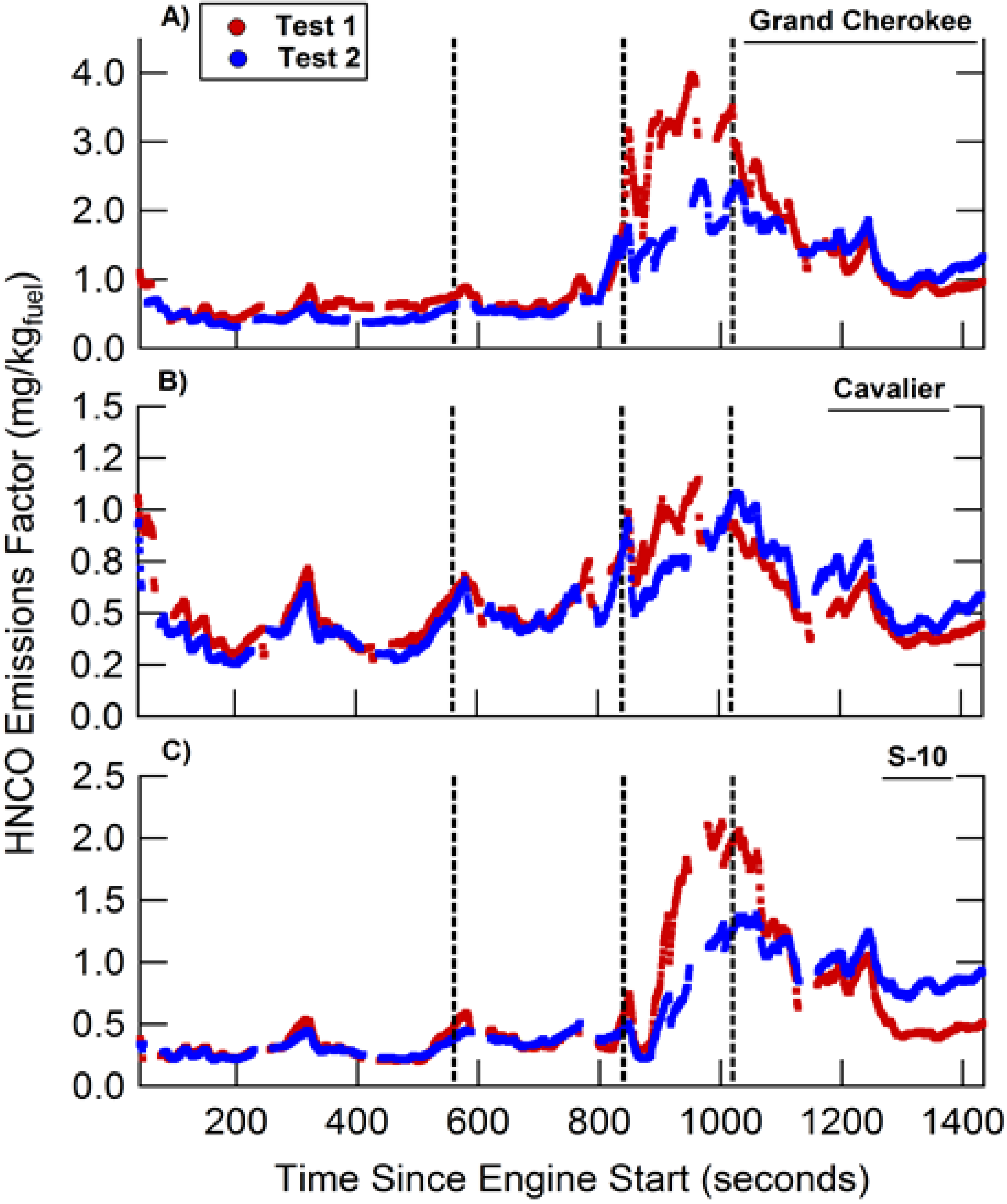
Organic Acid (OA) Emissions



Effect of Temperature on Organic Acid Partitioning



Isocyanic Acid (HNCO) Emissions



Source J.M. Brady, T.A. Crisp, S. Collier, T. Kuwayama, S.D. Forestieri, Q. Zhang, M.J. Kleeman, C.D. Cappa, and T.R. Bertram. Real-time emission factor measurements of isocyanic acid from light duty gasoline vehicles. Environmental Science and Technology, in review, 2014.

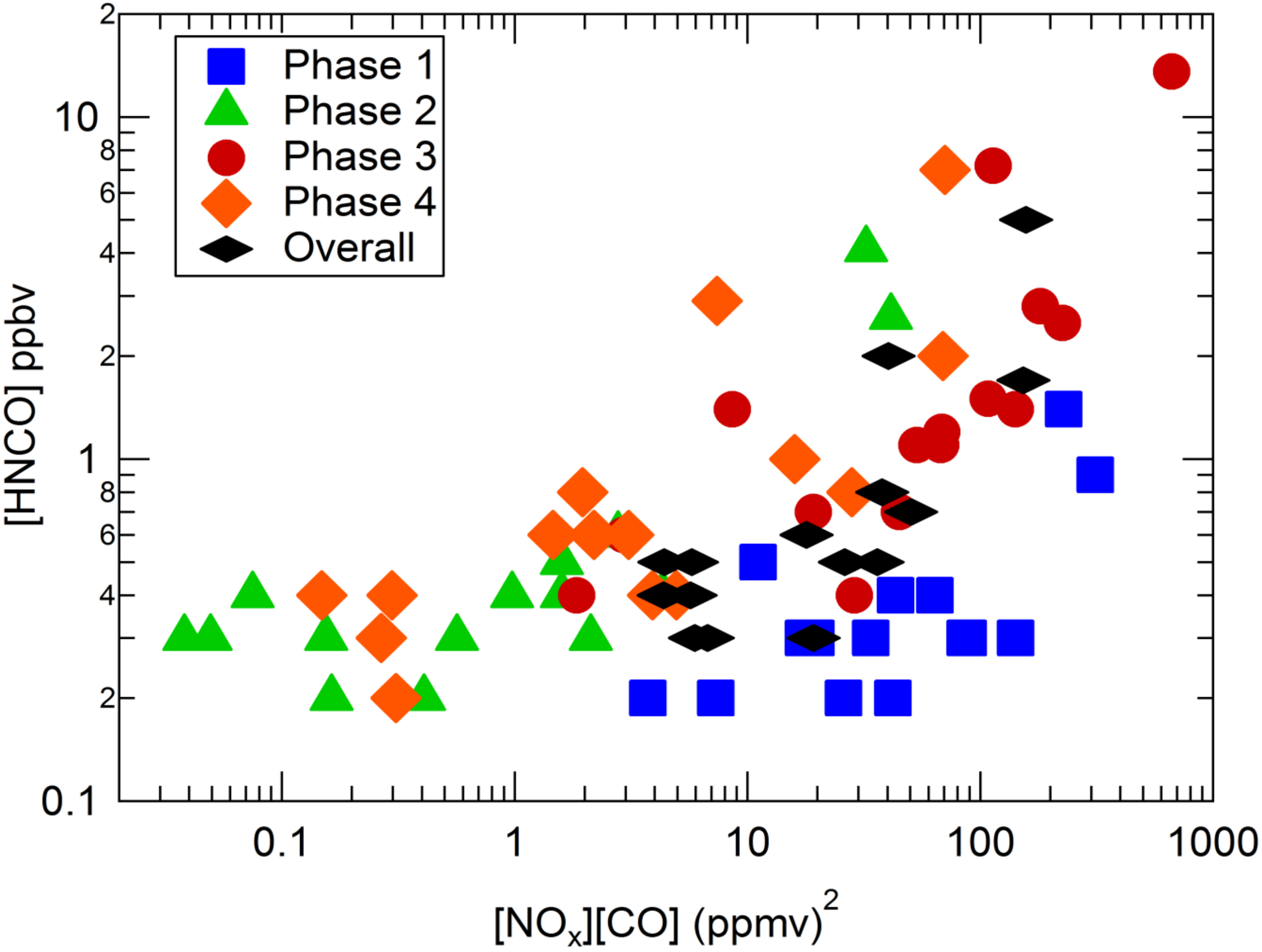
HNCO Formation Mechanism

- NO(g)<->*NO->*N + *O
- CO(g) <-> *CO
- *N + *CO <-> *NCO
- H_2(g) <-> 2*H
- NH_3(g) -> *NH_3 <-> *NH_2 + *H
  <-> *NH + 2*H<->*N + 3*H
- *H + *NCO -> HNCO(g)

- 2NO + NH_3 + 5CO -> 3HNCO + 2CO_2

Source J.M. Brady, T.A. Crisp, S. Collier, T. Kuwayama, S.D. Forestieri, Q. Zhang, M.J. Kleeman, C.D. Cappa, and T.R. Bertram. Real-time emission factor measurements of isocyanic acid from light duty gasoline vehicles. Environmental Science and Technology, in review, 2014.

Dependence of HNCO production rate on catalyst temperature, CO, and NO_X mixing ratios



Source J.M. Brady, T.A. Crisp, S. Collier, T. Kuwayama, S.D. Forestieri, Q. Zhang, M.J. Kleeman, C.D. Cappa, and T.R. Bertram. Real-time emission factor measurements of isocyanic acid from light duty gasoline vehicles. Environmental Science and Technology, in review, 2014.

Conclusion

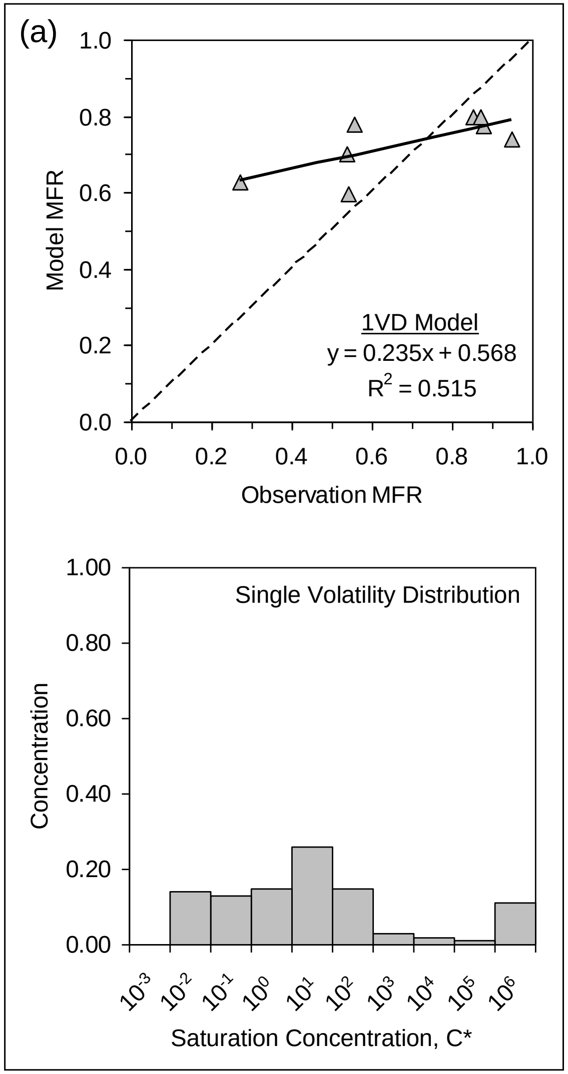
1) POA from light duty vehicles can be categorized as fuel products (non-volatile with T) or motor oil (volatile with T)

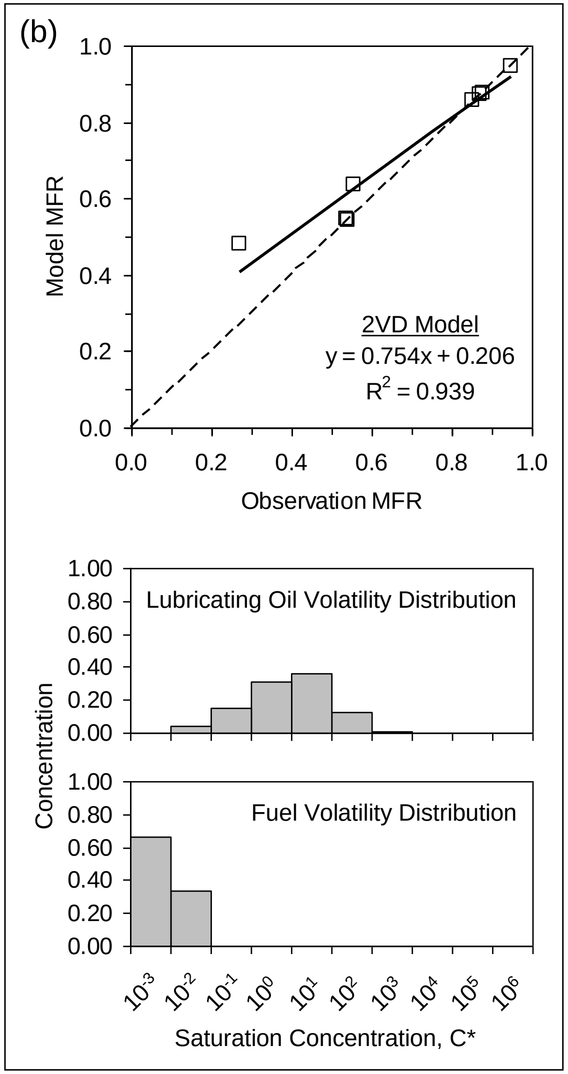
2) Vehicle emissions must be measured to build up a statistical distribution. Using the “average” volatility will give the wrong result.

3) Elevated RH in the dilution air enhances the production of carbonyl species that likely act as building blocks for the fuel product POA

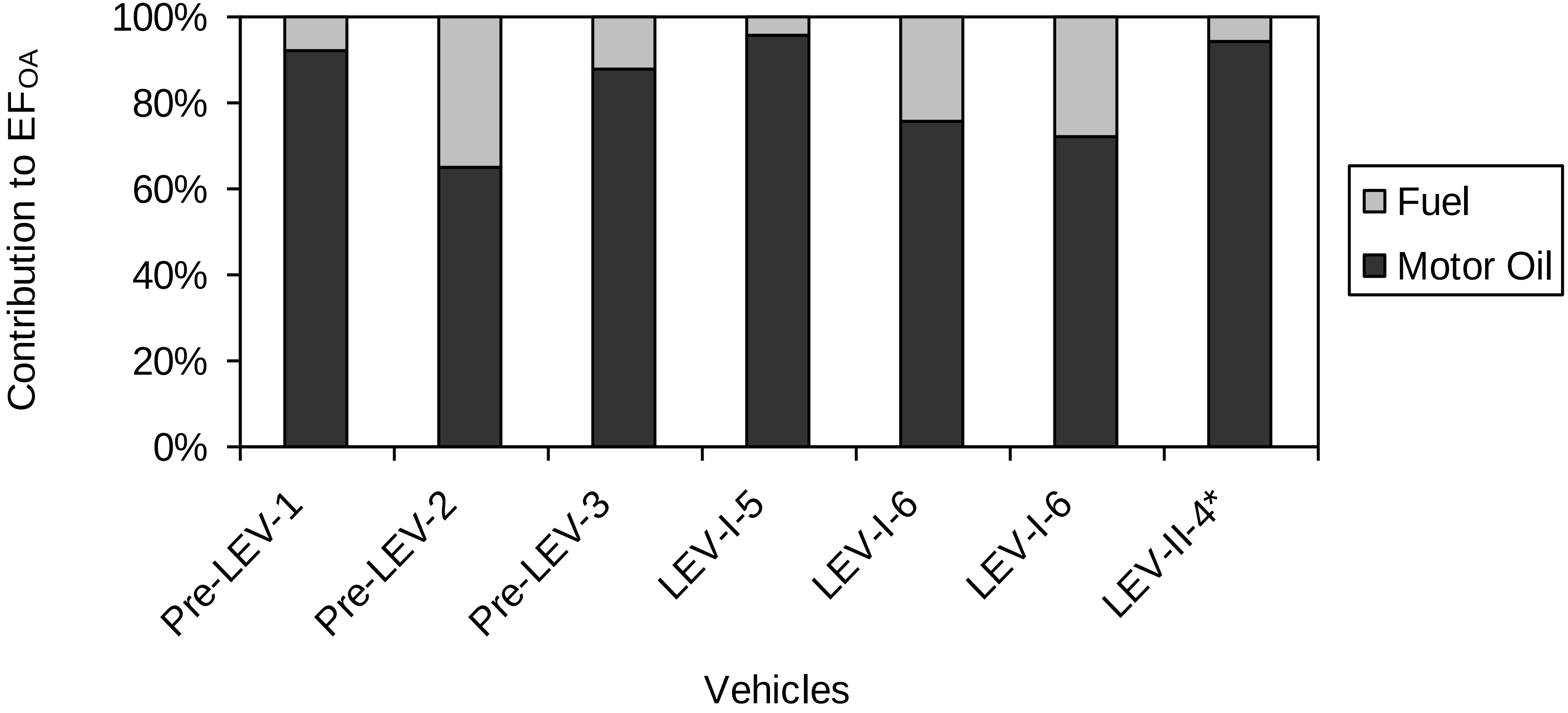
4) Increased adsorption surface (background EC) in the dilution air inhibits total production of carbonyl species

Implications: Regional Modeling of POA





Implications: SOA Formation From High Emitters



Recommendations

- Measurements of POA emissions attributable to motor oil and fuel combustion are needed for a larger and more representative fleet of light duty gasoline vehicles in California.
- Further measurements should be made to explore the mechanisms of fuel-derived POA using carbonyl building blocks.
- The ability of the AMS to measure POA from light duty gasoline vehicles should be studied further.
- A clearer understanding on this issue is needed to avoid misinterpretation of results in current and future studies.