SOURCE APPORTIONMENT OF AMBIENT ULTRAFINE AIRBORNE PARTICULATE MATTER

ARB Project # 01-306
CRC Project # E-55/59 – 1.5a

Michael J. Kleeman[1], Sarah G. Riddle[2], Michael A. Robert[1], Chris A. Jakober[3], James J. Schauer[4], and Michael P. Hannigan[5]

[1]UC Davis Civil and Environmental Engineering

[2]UC Davis Chemistry

[3]UC Davis Environmental Toxicology

[4]UW Madison Civil and Environmental Engineering

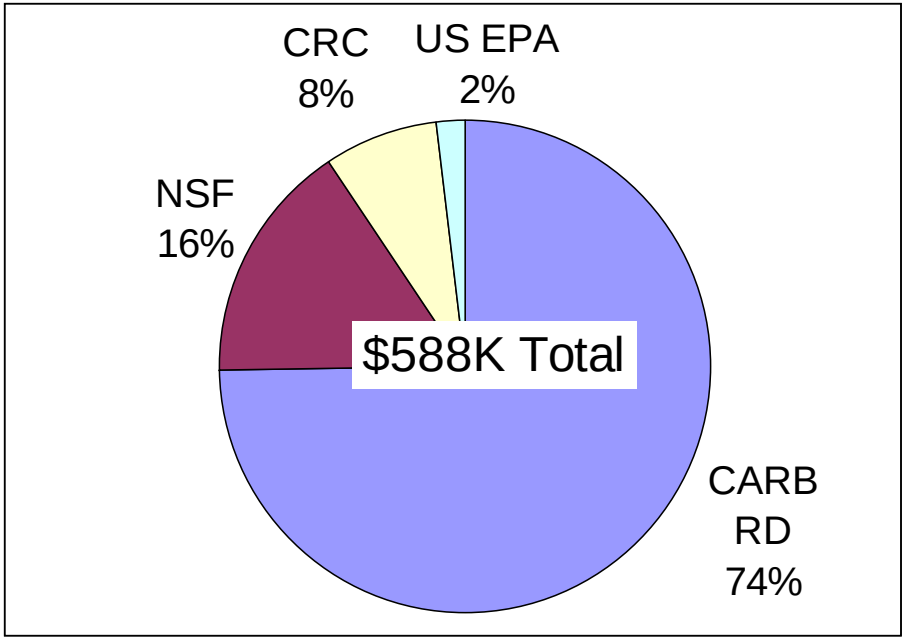
[5]U Colorado Boulder Mechanical Engineering

Acknowledgements - People

- Nehzat Motallebi (CARB)
- Judith Charles, Peter Green (UCD)
- Jorn Herner, Dan Chang (UCD)

Acknowledgements - Funding

- California Air Resources Board $440K
- National Science Foundation IGERT $92K
- Coordinating Research Council $45K
- United States Environmental Protection Agency UCD-SAHERC $11K



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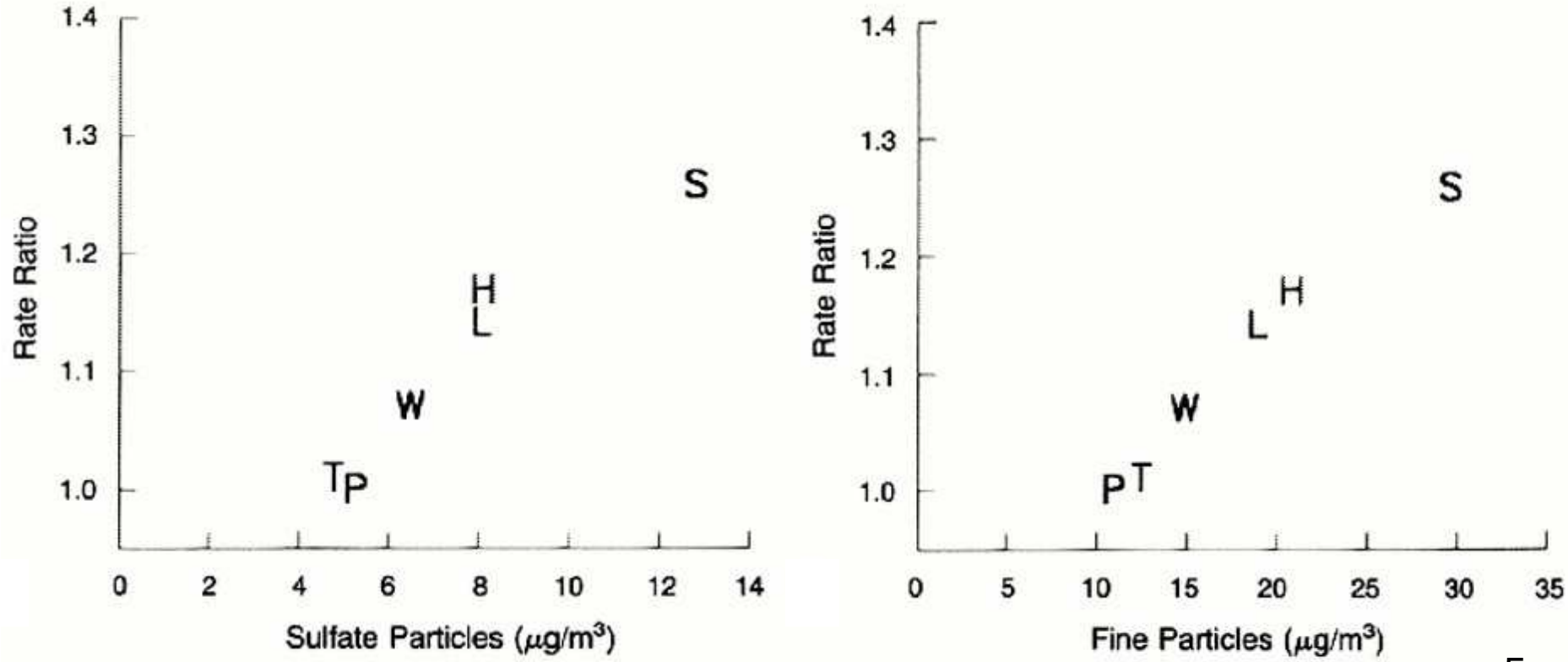
Motivation: Health Effects of PM2.5

- Epidemiological studies have identified an association between PM2.5 and human health effects, but the mechanisms of injury are still unknown



Source: DOCKERY DW, POPE CA, XU XP, et al. “AN ASSOCIATION BETWEEN AIR-POLLUTION AND MORTALITY IN 6 UNITED-STATES CITIES”, NEW ENGLAND JOURNAL OF MEDICINE 329 (24): 1753-1759 DEC 9 1993.

One Possible Hypothesis:

- UltraFine Particulate Matter (Dp < 100nm) (PM0.1) is partially responsible for the health effects detected by epidemiology
  - UFPM can move across cell membranes
  - UFPM is a more potent source of ROS than larger particle size fractions

- Very little is known about the sources of ultrafine PM0.1 in the atmosphere

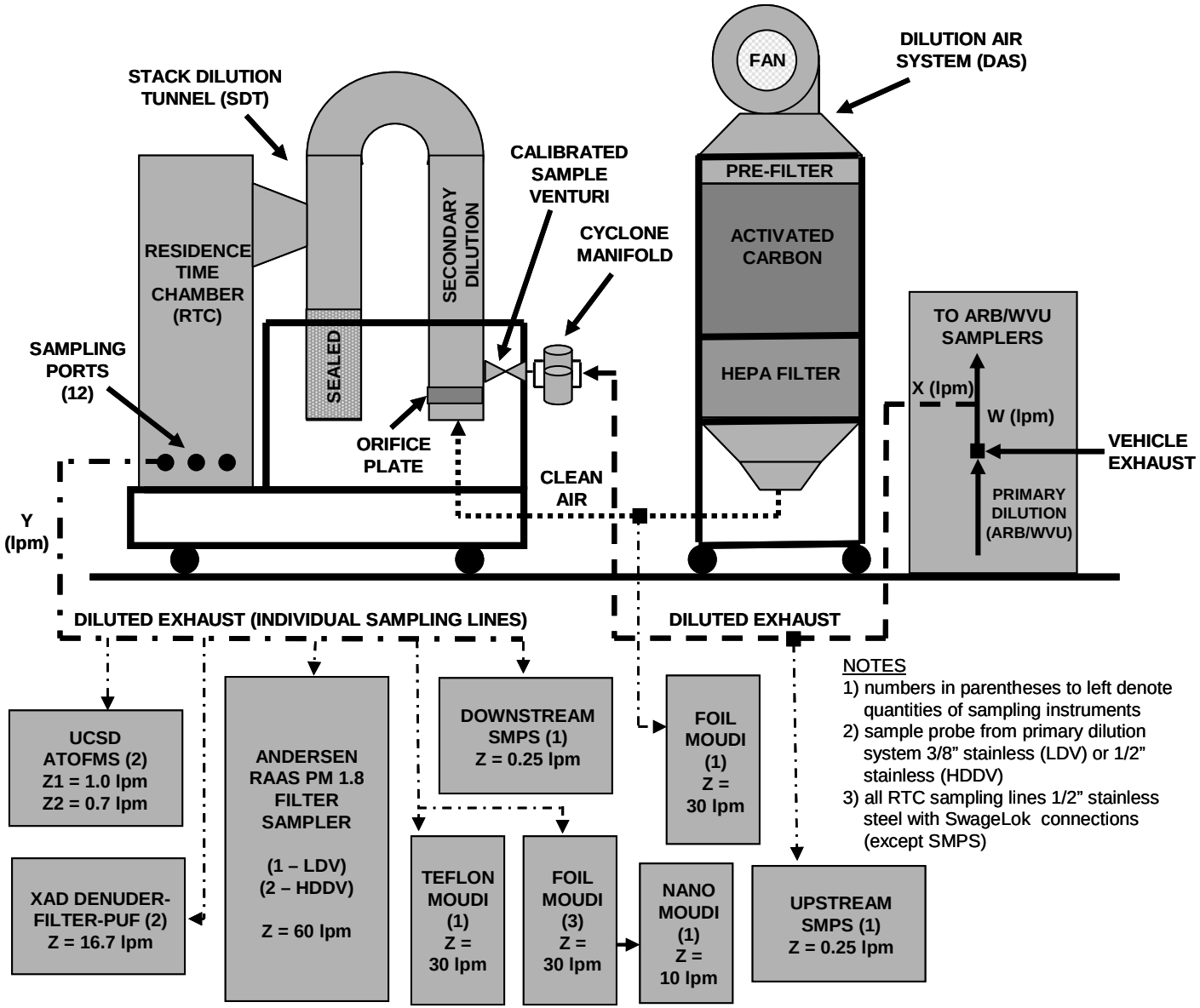
Problem: How Do We Calculate Source Contributions to PM0.1?

- PM0.1 CMB Analysis
  - Source profiles are not available for particles smaller than 100 nm
- PM0.1 PMF Analysis
  - Long time series of measurements are not available for particles smaller than 100 nm

Approach: New PM0.1 CMB Study

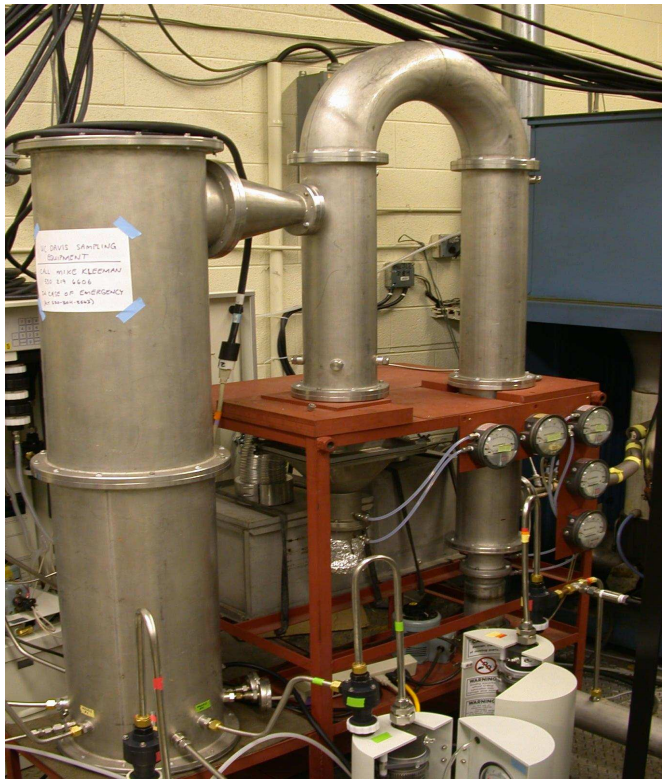
- Measure PM0.1 Source Profiles
  - Heavy Duty Diesel-powered motor vehicles (4 vehicles; Idle+creep and HHDDT cycles; 56K and 66K weight)
  - Light Duty Gasoline-powered motor vehicles (30 vehicles; FTP, UC, and CC cycles)
  - Wood combustion (4 species)
  - Rice Straw combustion (1 test)
  - Food cooking (1 test)
- Ambient PM0.1 sampling in California during winter stagnation events
  - Sacramento, Modesto, Bakersfield, CA
- PM0.1 Solvent extraction and GC-MS analysis

Approach: Dilution Sampling System

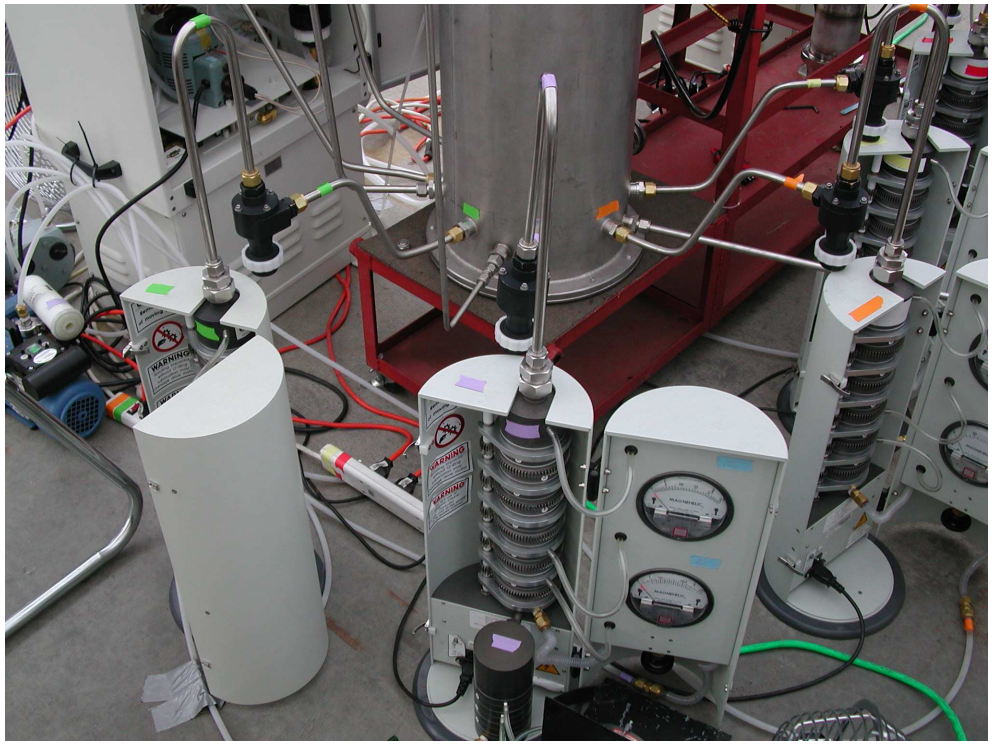


Source: 2007 Robert, M.A., C.A. Jakober, S. VanBergen, and M.J. Kleeman, Size and Composition Distribution of Particulate Matter 1. Light-duty Gasoline Vehicles. Journal of the Air and Waste Management Association, 57, pp1414-1428.

Methods: Dilution Source Sampling

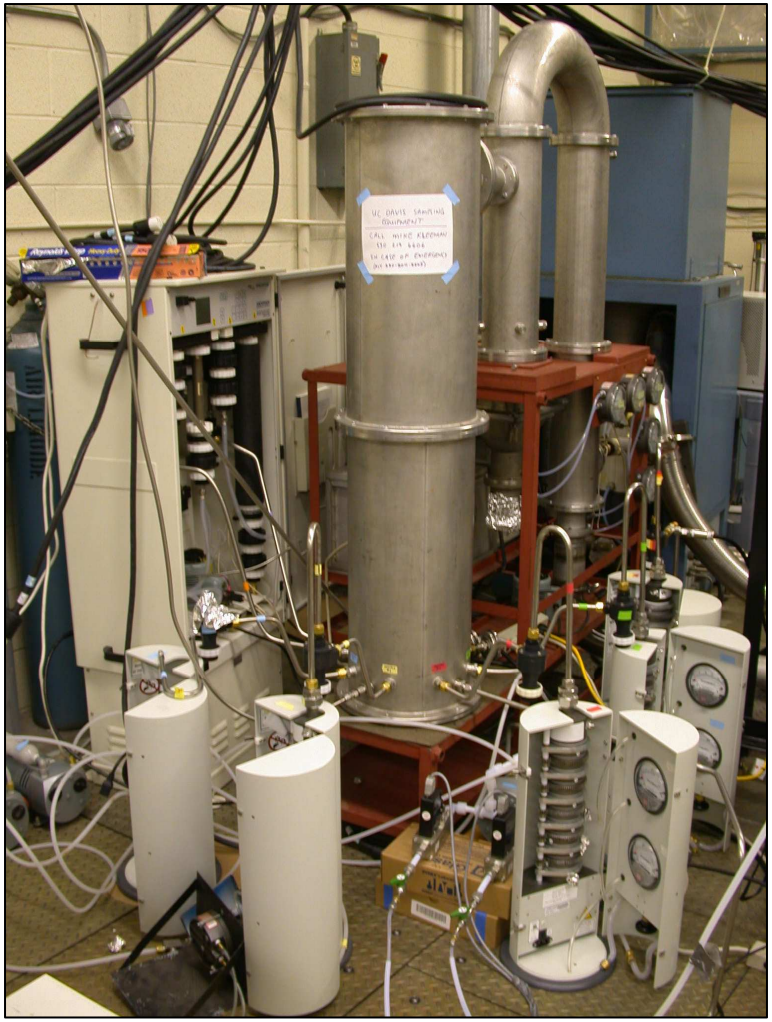


Stack Dilution Tunnel & Residence Time Chamber



PM0.1 Collection By Micro Orifice Uniform Deposit Impactors (MOUDIs)

Typical Sampling Configuration



Light Duty Gasoline Vehicle Test Matrix

Table 1. LDGVs tested.

Category	Year	Make	Model	Mileage	Engine Information	Fuel Delivery Technology
LEV PC	1996	Honda	Civic	77,703	4 cylinder	SFI
LEV PC	1998	Honda	Accord	97,811	4 cylinder	SFI
LEV PC	1999	Toyota	Camry LE	43,160	6 cylinder	SFI
LEV PC	1999	Nissan	Sentra GXE	52,630	4 cylinder	SFI
LEV PC	2002	Chevrolet	Monte Carlo	20,230	6 cylinder	FI
LEV LDT/SUV	1998	Ford	Explorer	82,513	8 cylinder/302	SFI
LEV LDT/SUV	2000	Jeep	Grand Cherokee	31,751	6 cylinder	SFI
LEV LDT/SUV	2000	Toyota	Tacoma	51,554	6 cylinder	SFI
LEV LDT/SUV	2002	Nissan	Pathfinder	8,169	6 cylinder	SFI
LEV LDT/SUV	2003	Chevrolet	Silverado	1,264	8 cylinder/292	SFI
TWC PC	1988	Chrysler	Plymouth Horizon	32,097	4 cylinder	EPFI
TWC PC	1988	Honda	Civic DX	174,163	4 cylinder	EPFI
TWC PC	1991	Toyota	Camry	95,532	4 cylinder	MPFI
TWC PC	1991	Ford	Taurus	136,983	6 cylinder	MPFI
TWC PC	1994	Honda	Acura	104,441	4 cylinder	SFI
TWC PC	1998	Ford	Mustang	10,697	6 cylinder	SFI
TWC PC	1999	Cadillac	Sedan DeVille	35,320	8 cylinder/280	FI
TWC LDT/SUV	1987	Suzuki	Samurai	57,124	4 cylinder	Carbureted-2 BBL
TWC LDT/SUV	1989	Toyota	SR5 Pick up	59,231	6 cylinder	FI
TWC LDT/SUV	1989	Chrysler	Caravan LE	207,104	6 cylinder	EPFI
TWC LDT/SUV	1995	Chevrolet	Suburban	91,618	8 cylinder/350	TBFI
TWC LDT/SUV	1996	Nissan	Frontier Pick-up	55,940	4 cylinder	SFI
TWC LDT/SUV	1997	Ford	Expedition XLT	78,173	8 cylinder/280	SFI
OCAT PC	1977	Mercedes	280 E	118,119	6 cylinder	FI
OCAT PC	1979	Toyota	Corolla	8,661	4 cylinder	Carbureted-2 BBL
OCAT PC	1980	Honda	Accord	88,642	4 cylinder	Carbureted-3 BBL
NCAT PC	1953	Chevrolet	Bel-Air	96,176	6 cylinder	Carbureted-1BBL
NCAT PC	1965	Ford	Mustang	55,280	8 cylinder/289	Carbureted-4 BBL
SMOKER	1968	Ford	Cougar	63,622	8 cylinder/302	Carbureted-4 BBL
SMOKER	1993	Chevrolet	S-10 Blazer	162,750	6 cylinder	FI

Notes: FI = fuel injected; MPFI = multi-port fuel injected; EPFI = electronic port fuel injection; TBFI = throttle body injected; SFI = sequential fuel injected; BBL = barrel.

Source: 2007 Robert, M.A., C.A. Jakober, S. VanBergen, and M.J. Kleeman, Size and Composition Distribution of Particulate Matter 1. Light-duty Gasoline Vehicles. Journal of the Air and Waste Management Association, 57, pp1414-1428.

Driving Cycle Summary

Table 2. Driving cycle summary.

Driving Cycle	Phase/Mode	Average Speed (kph)	Maximum Speed (kph)	Distance (km)	Time Per Mode (sec)
FTP	1[a]	41.2	91.2	5.78	505
FTP	2[b]	25.7	55.2	6.29	869
FTP	3	41.2	91.2	5.78	505
UC	1[a]	22.8	66.1	1.45	300
UC	2[b]	43.9	108.1	14.32	1135
UC	3	22.8	66.1	1.45	300
CC	1	88.3	115.2	33.63	1370
CC	2	36.8	90.4	8.37	821

Notes: [a]Cold start; [b]phase/mode followed by 10 min with vehicle off.

FTP = Federal Test Procedure
UC = Unified Cycle
CC = Correction Cycle

Source: 2007 Robert, M.A., C.A. Jakober, S. VanBergen, and M.J. Kleeman, Size and Composition Distribution of Particulate Matter 1. Light-duty Gasoline Vehicles. Journal of the Air and Waste Management Association, 57, pp1414-1428.

Sample Aggregation With Dilution Factors

Table 3. Sample collection summary.

Sample ID	Vehicle Type	Driving Cycle	Number of Vehicles	Number of Cycles	Total Kilometers	Total Minutes	Dilution Ratio Information		
							Primary	Secondary	Total
LDGV-0	Pre-blank	n/a	n/a	n/a	n/a	175.0	1.0	8.9	8.9
LDGV-1	LEV PC/LDT/SUV	FTP	10	40	713.8	1252.7	16.9	7.5	127.3
LDGV-2	TWC PC	FTP	6	12	214.1	375.8	18.2	6.9	125.7
LDGV-3	TWC PC	UC	6[a]	6	103.3	173.5	14.5	3.9	55.8
LDGV-4	TWC HONDA	UC	1	2	34.4	57.8	20.5	3.7	75.1
LDGV-5	TWC LDT/SUV	Ucb	5	5	78.9	144.6	12.9	3.7	47.3
LDGV-6	TWC LDT/SUV	CC	5	5	210.1	182.6	10.1	3.8	37.9
LDGV-7	TWC LDT/SUV	FTP[b]	5	5	60.4	156.6	18.2	3.7	66.9
LDGV-8	OCAT PC	FTP	3	3	53.5	94.0	14.8	26.5	392.5
LDGV-9	NCAT PC	FTP	2	2	35.7	62.6	11.6	11.2	129.3
LDGV-10	SMOKERs	FTP	2	2	35.7	62.6	11.1	11.2	124.2
LDGV-11	Post-blank	n/a	n/a	n/a	n/a	178.0	1.0	12.4	12.4

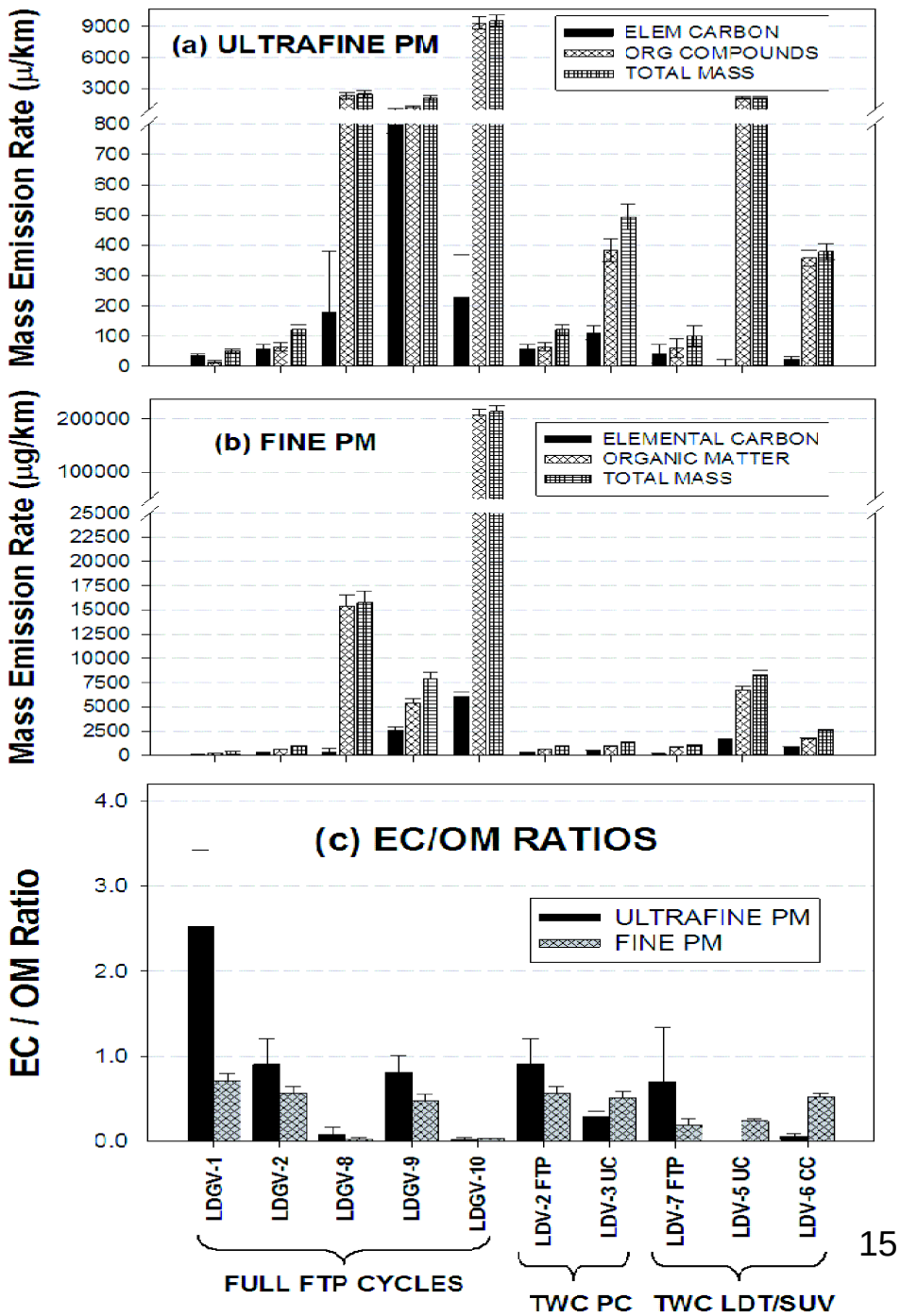
Notes: [a]TWC PC 1998 Honda Civic not included; [b]first two phases of driving cycle only.

Source: 2007 Robert, M.A., C.A. Jakober, S. VanBergen, and M.J. Kleeman, Size and Composition Distribution of Particulate Matter 1. Light-duty Gasoline Vehicles. Journal of the Air and Waste Management Association, 57, pp1414-1428.

Tailpipe Emissions Rates

Similar Trends for PM0.1 and PM1.8

PM0.1 Emissions Rates
LEV-FTP = 51µg km^{-1}
TWC-FTP = 122 µg km^{-1}
OCAT-FTP = 2500 µg km^{-1}
NCAT-FTP = 2091 µg km^{-1}
SMKR-FTP PM = 9600 µg km^{-1}



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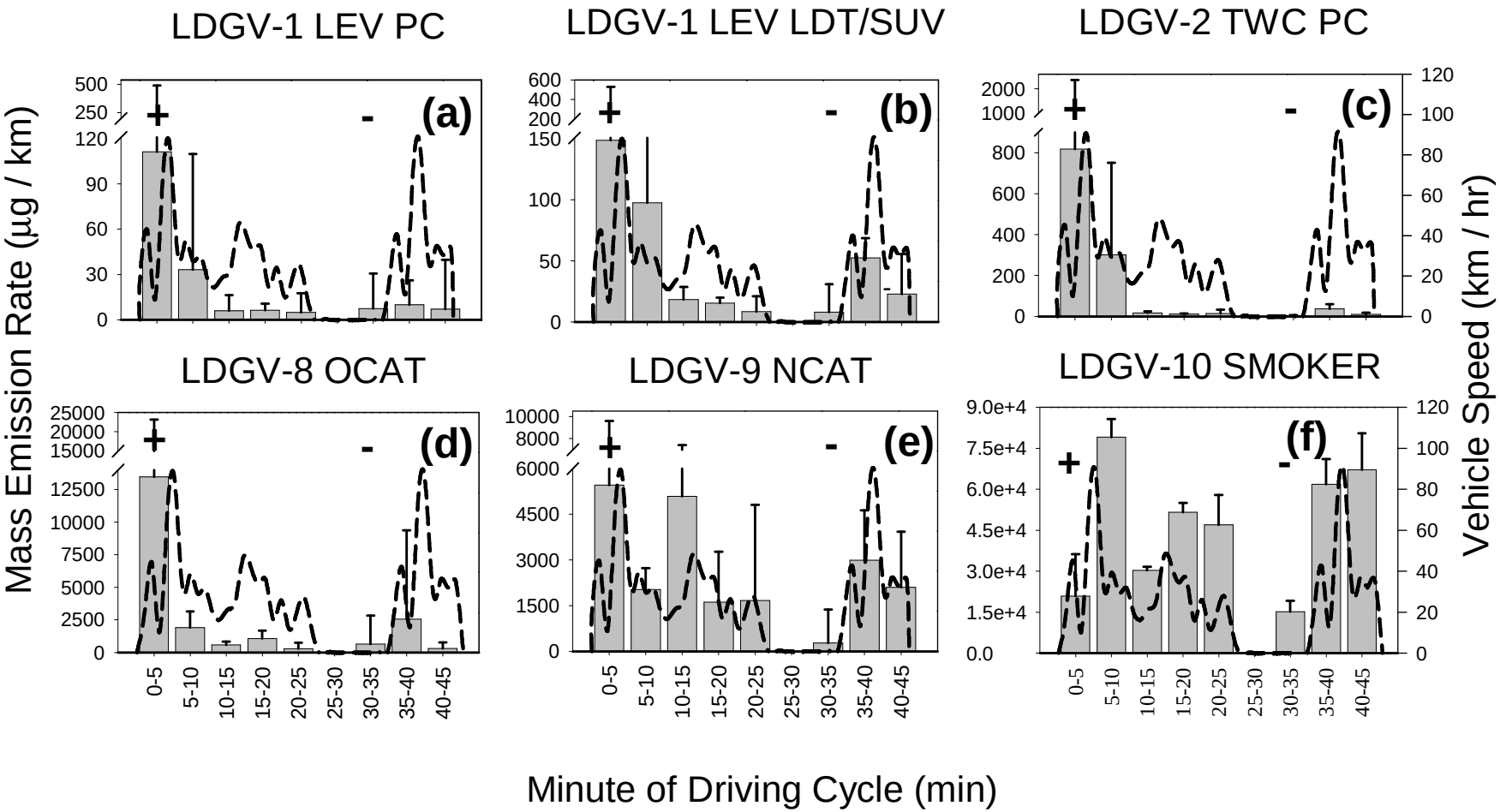
FTP PM0.1 Emissions Over Time



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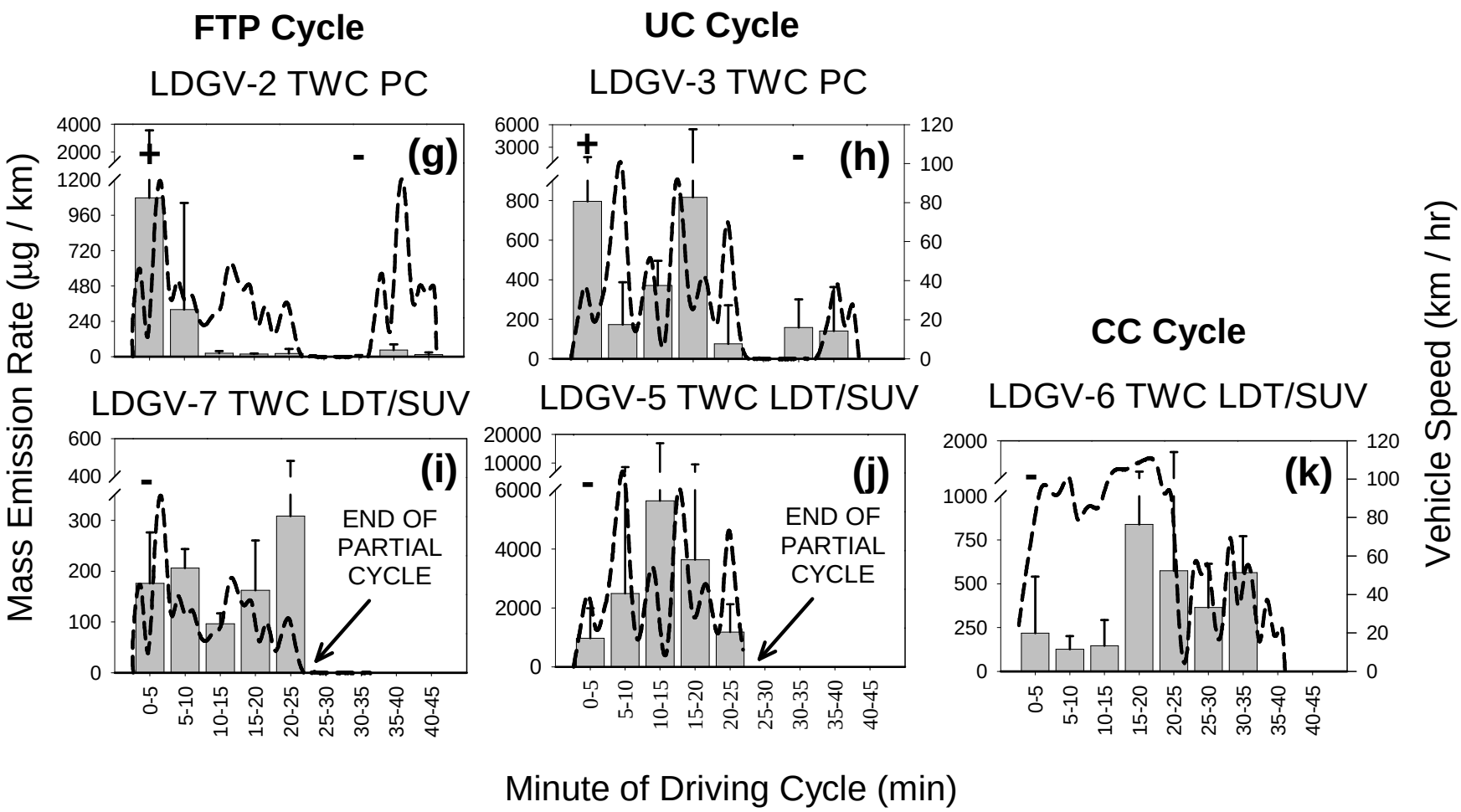
PM0.1 Driving Cycle Comparison



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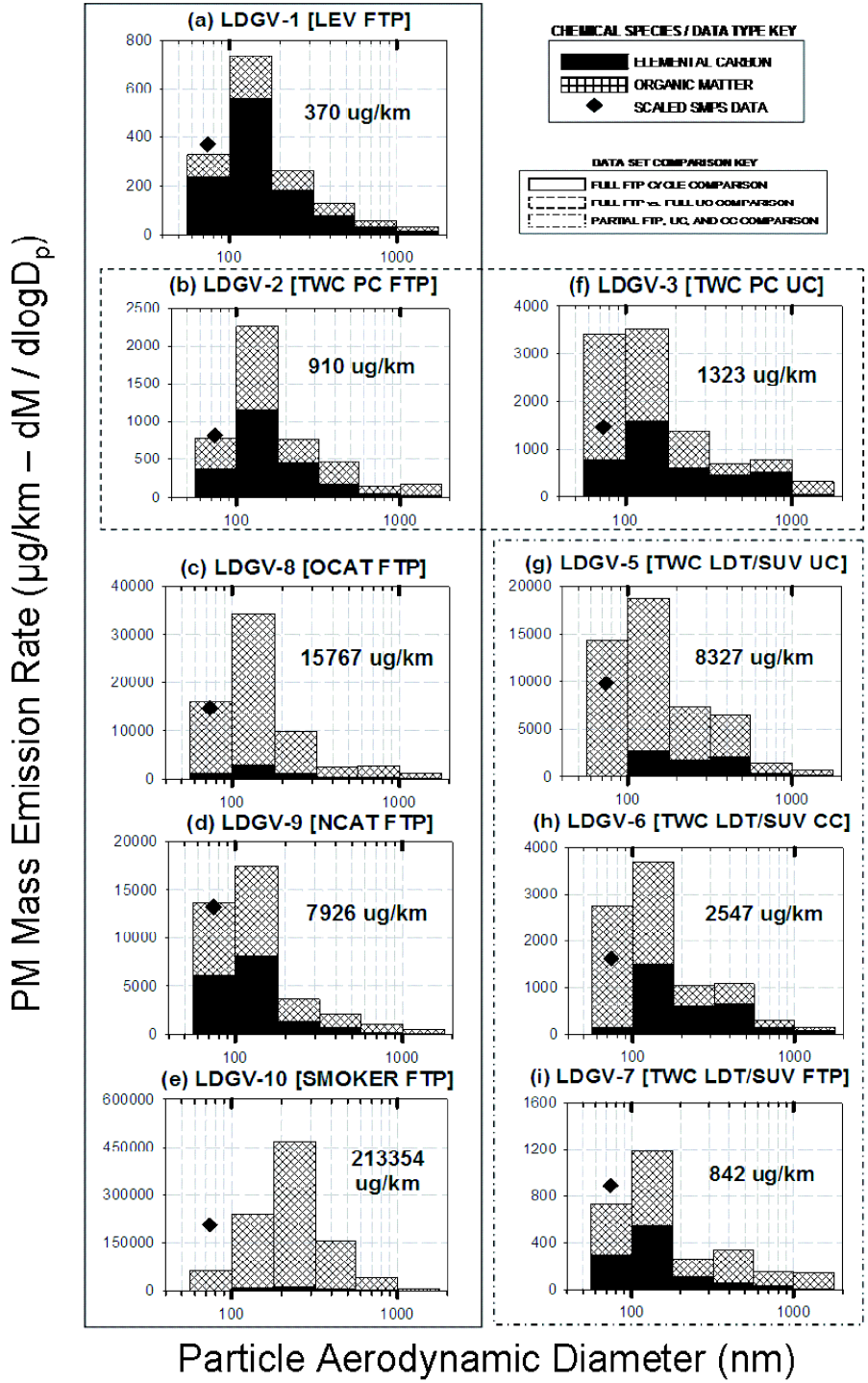
Light Duty Vehicle Particle Distributions

LEV = Low Emissions Vehicle
TWC = Three Way Catalyst
OCAT = Oxidation Catalyst
NCAT = Non Catalyst
SMOKER = smoking vehicle

FTP = Federal Test Procedure
UC = Unified Cycle
CC = Correction Cycle



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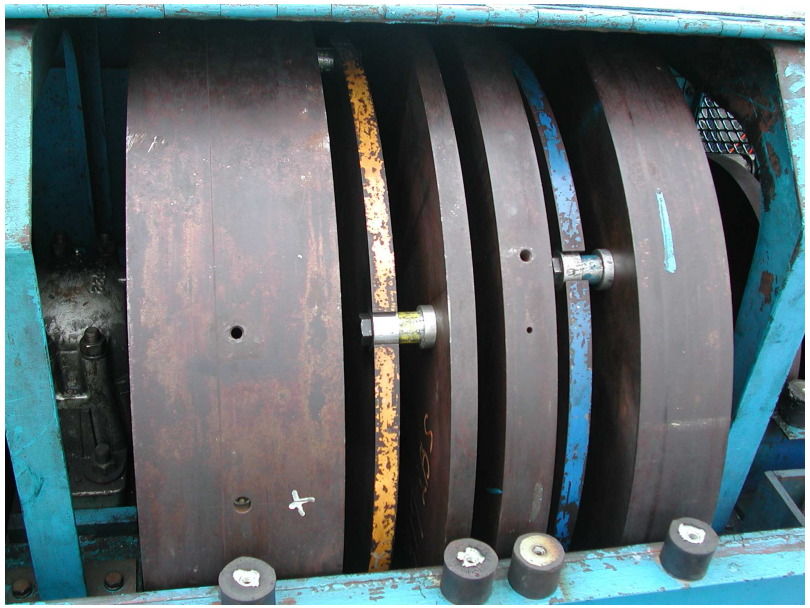
Typical HDV Sampling Configuration



Heavy Duty Diesel Vehicle Test Matrix

Table 1. HHDVs tested.

Model Year	Make	Mileage (miles)	Load Weight (lbs)	Engine Information				
				Type	Year	No. of Cylinders	Displacement (L)	Horse Power (bhp)
1999	Freightliner	138,553	56,000	Detroit Diesel Series 60	1998	6	12.7	500
1998	Kenworth	587,244	56,000 66,000	Cummins N14-460E+	1997	6	14.0	460
1992	Volvo	595,242	56,000	Caterpillar 3406B	1991	6	14.6	280
1985	Freightliner	988,726	56,000	Caterpillar 3406	1984	6	14.6	310

Source: 2007 Robert, M.A., C.A. Jakober, and M.J. Kleeman. Size and Composition Distribution of Particulate Matter 2. Heavy -duty Diesel Vehicles. Journal of the Air and Waste Management Association, 57, pp1429-1438.

Driving Cycle Summary

Table 2. HHDDT driving cycle summary.

Phase/Mode	Average Speed (mph)	Maximum Speed (mph)	Distance (mi)	Time per Mode (sec)
Idle[a]	0.0	0.0	0.00	1799
Creep[a]	1.8	8.2	0.50	1012
Transient[a]	15.3	47.5	2.60	687
Low-speed cruise[a]	39.9	59.3	23.00	2082
High-speed cruise	50.3	67.2	10.50	759

Notes: [a]Phase/mode followed by 10 min with vehicle off.

Source: 2007 Robert, M.A., C.A. Jakober, and M.J. Kleeman. Size and Composition Distribution of Particulate Matter 2. Heavy -duty Diesel Vehicles. Journal of the Air and Waste Management Association, 57, pp1429-1438.

Sample Aggregation With Dilution Factors

Table 3. Sample collection summary.

Sample ID	Vehicle Type	Driving Cycle	No. of Vehicles	No. of Cycles	Total Miles	Total Minutes	Dilution Ratio Information		
							Primary	Secondary	Total
HDDV-0	Pre-blank	n/a	n/a	n/a	n/a	187	1.0	10.0	10.0
HDDV-1	Freightliner (1999)	IDLE/CREEP	1	6	3.2	282	112.5	5.2	583.6
HDDV-2	Freightliner (1999)	56k 5-MODE	1	1	36.7	109	17.8	9.4	166.8
HDDV-3	Kenworth (1998)	56k 5-MODE	1	1	36.6	109	17.1	7.5	128.6
HDDV-4	Kenworth (1998)	66k 5-MODE	1	1	36.5	109	19.6	9.7	189.7
HDDV-5	Volvo (1992)	56k 5-MODE[a]	1	1	35.8	109	18.0	9.1	163.9
HDDV-6	Freightliner (1985)	56k 5-MODE	1	1	36.1	109	19.0	8.9	169.8
HDDV-7	Post-flank	n/a	n/a	n/a	n/a	152	1.0	10.0	10.0

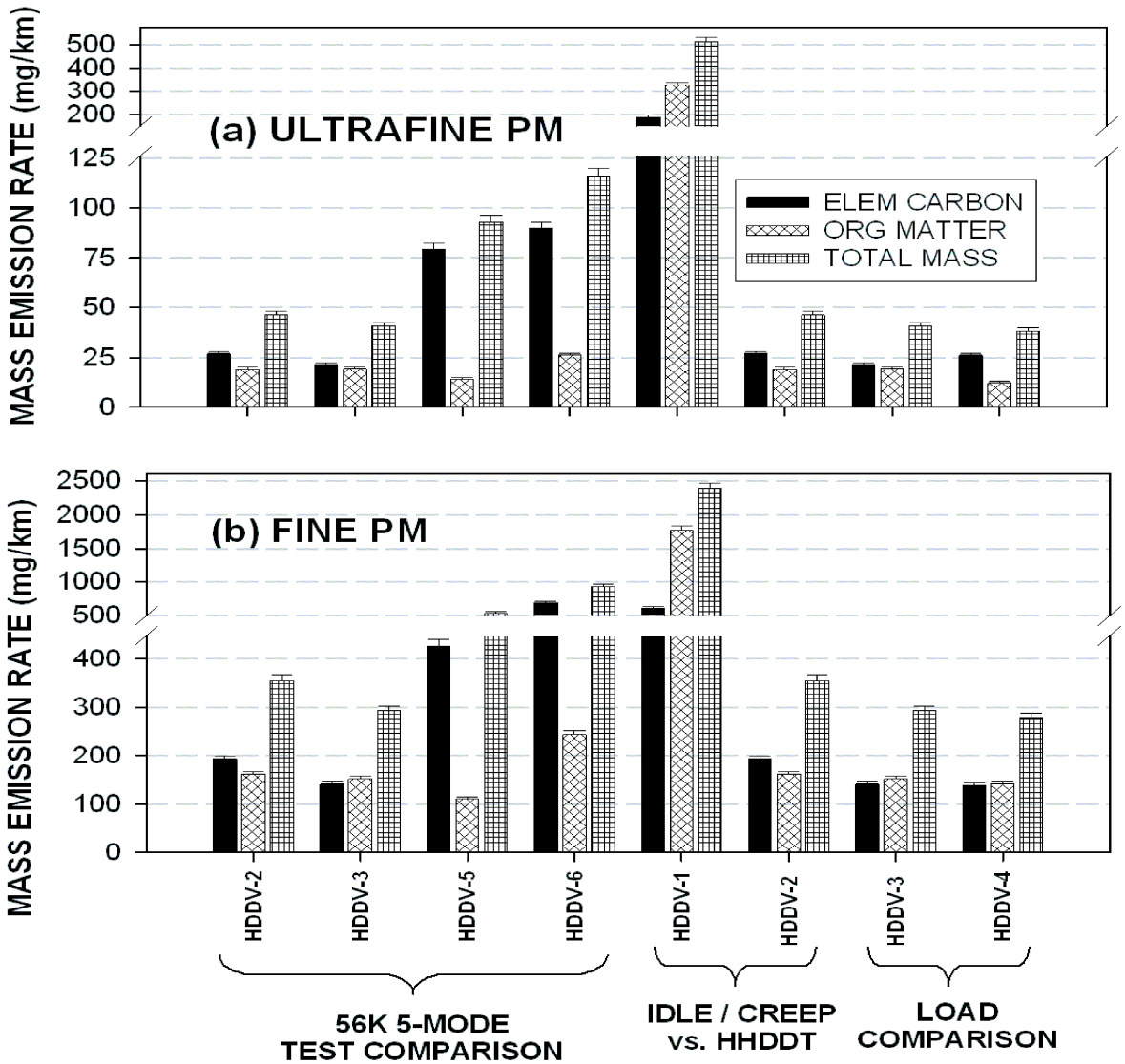
Notes: [a]Maximum Speed 56–60 mph due to engine governor.

Source: 2007 Robert, M.A., C.A. Jakober, and M.J. Kleeman. Size and Composition Distribution of Particulate Matter 2. Heavy -duty Diesel Vehicles. Journal of the Air and Waste Management Association, 57, pp1429-1438.

Tailpipe Emissions Rates

Similar Trends for PM0.1 and PM1.8 (older vehicles emit more mass)

PM0.1 Emissions Rates
56K 5-mode = 40 – 90 mg km^{-1}
56K idle-creep = 500 mg km^{-1}



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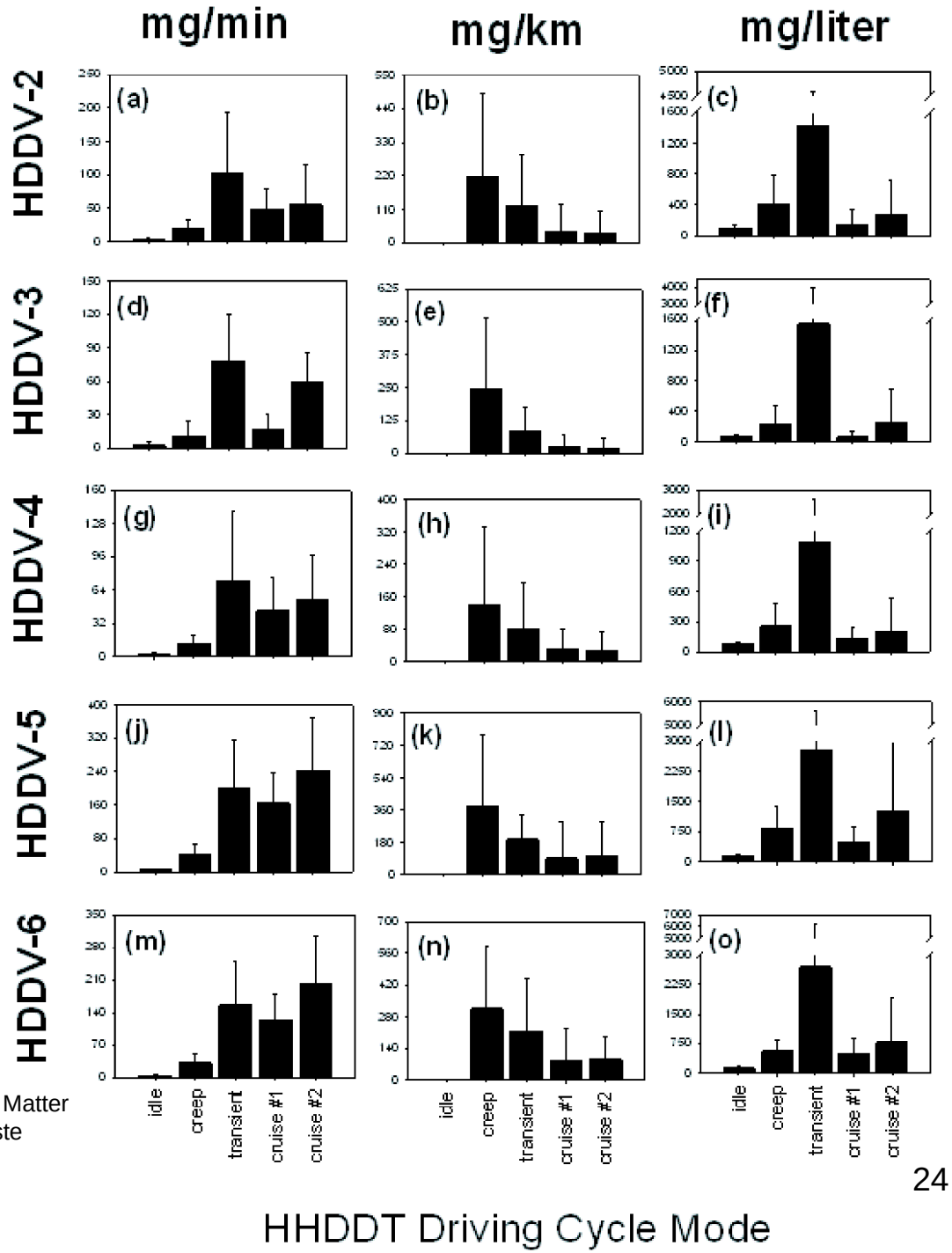
5-Mode PM0.1 Emissions Over Time



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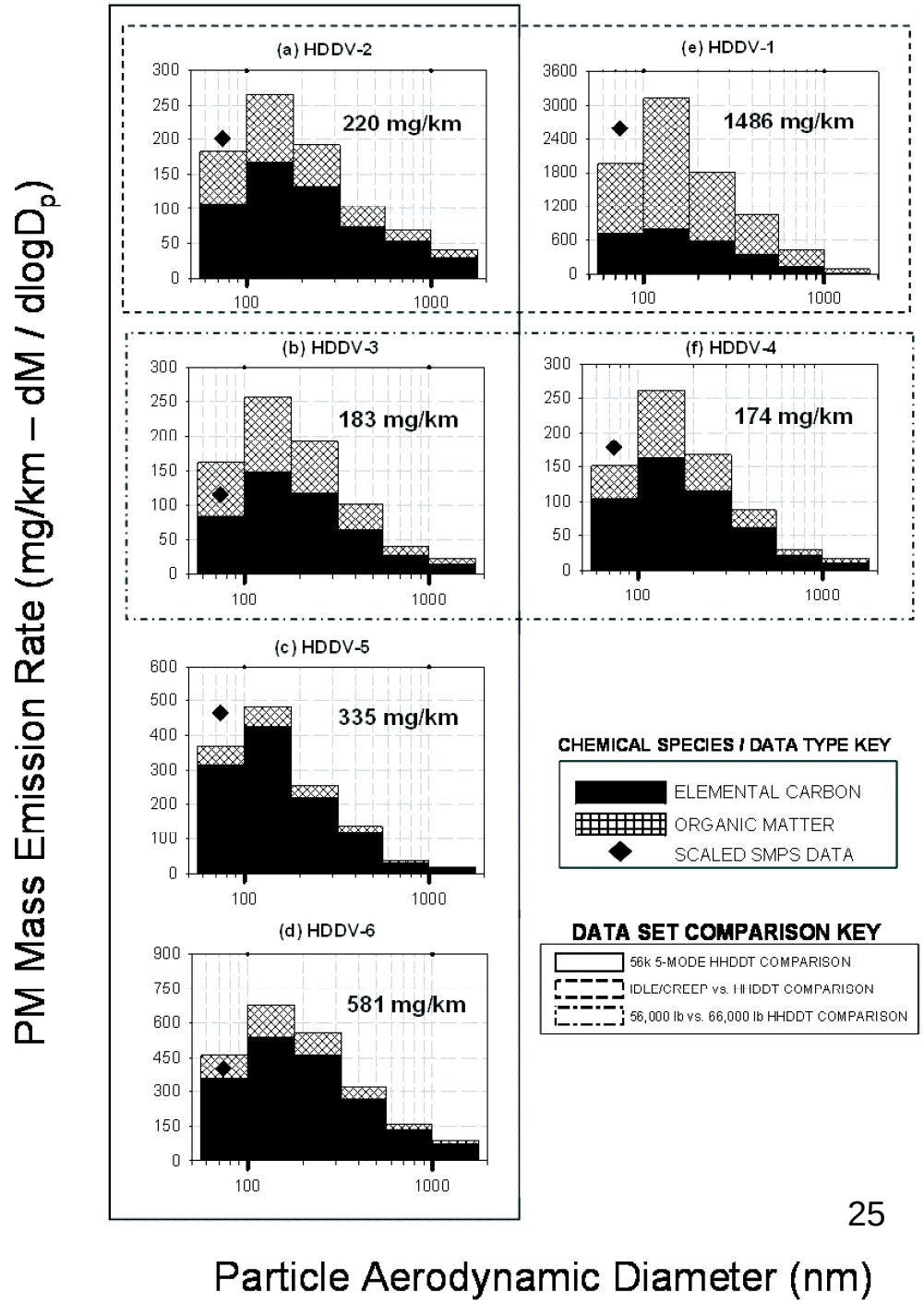
Heavy Duty Vehicle Particle Distributions



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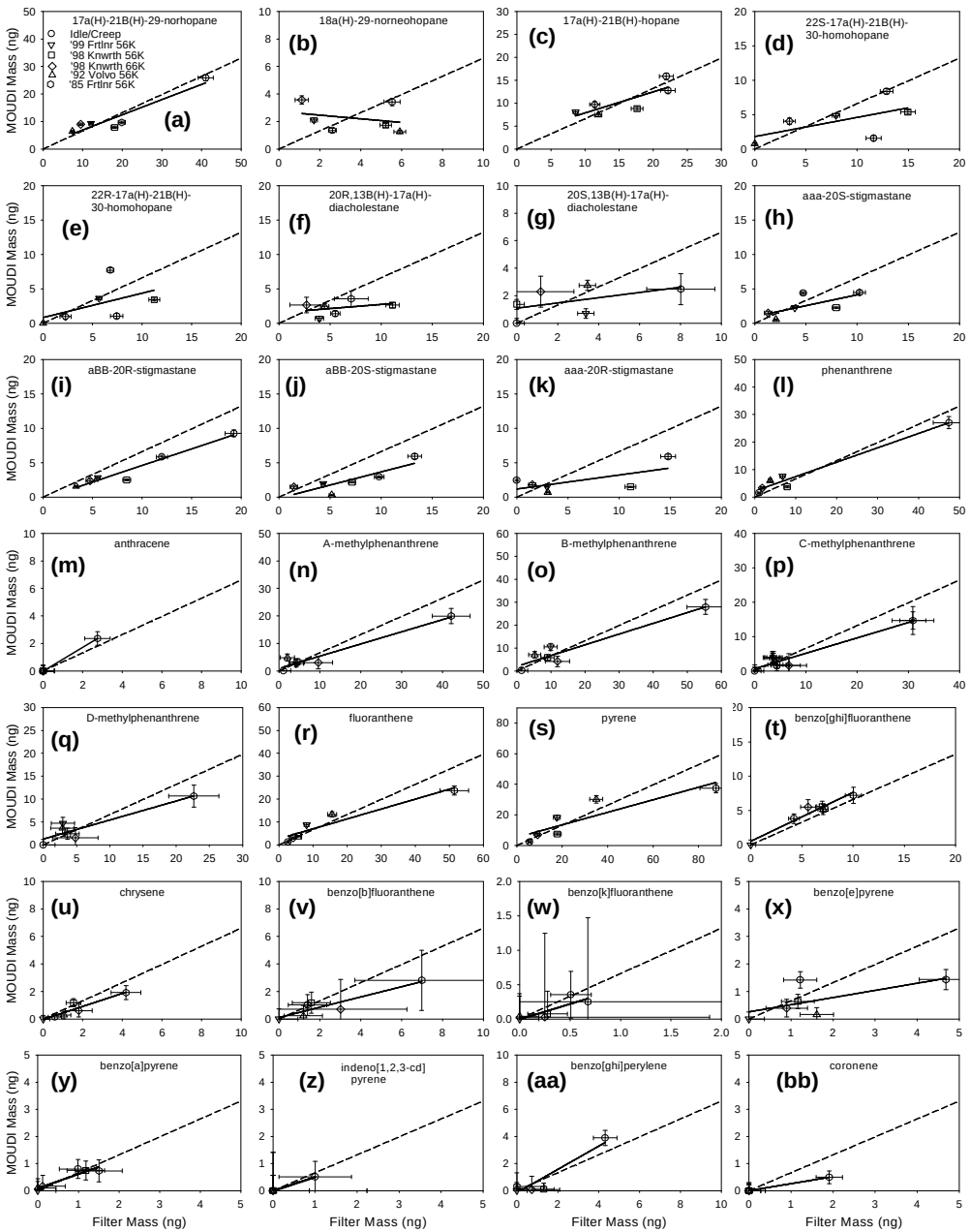
Methods: GC-MS Analysis

- Extraction for foil substrates and quartz filters
  - Spiked with deuterated internal standards
  - Extracted in 10-15 mL of dichloromethane (DCM)
- Diesel, gasoline, and meat smoke
  - Chromatography: Agilent DB-XLBMSD GC column
  - Mass Spectrometry: Varian 2000 ion trap MS
    - (both full scan and SIM)
- Wood smoke and rice straw analysis
  - Chromatography: Agilent 5MS GC column
  - Mass Spectrometry: Agilent 5973 MS (EI)

QA/QC Example: Heavy Duty Diesel Vehicles



QA/QC checks compare the ∑(MOUDI) vs. co-located filter.

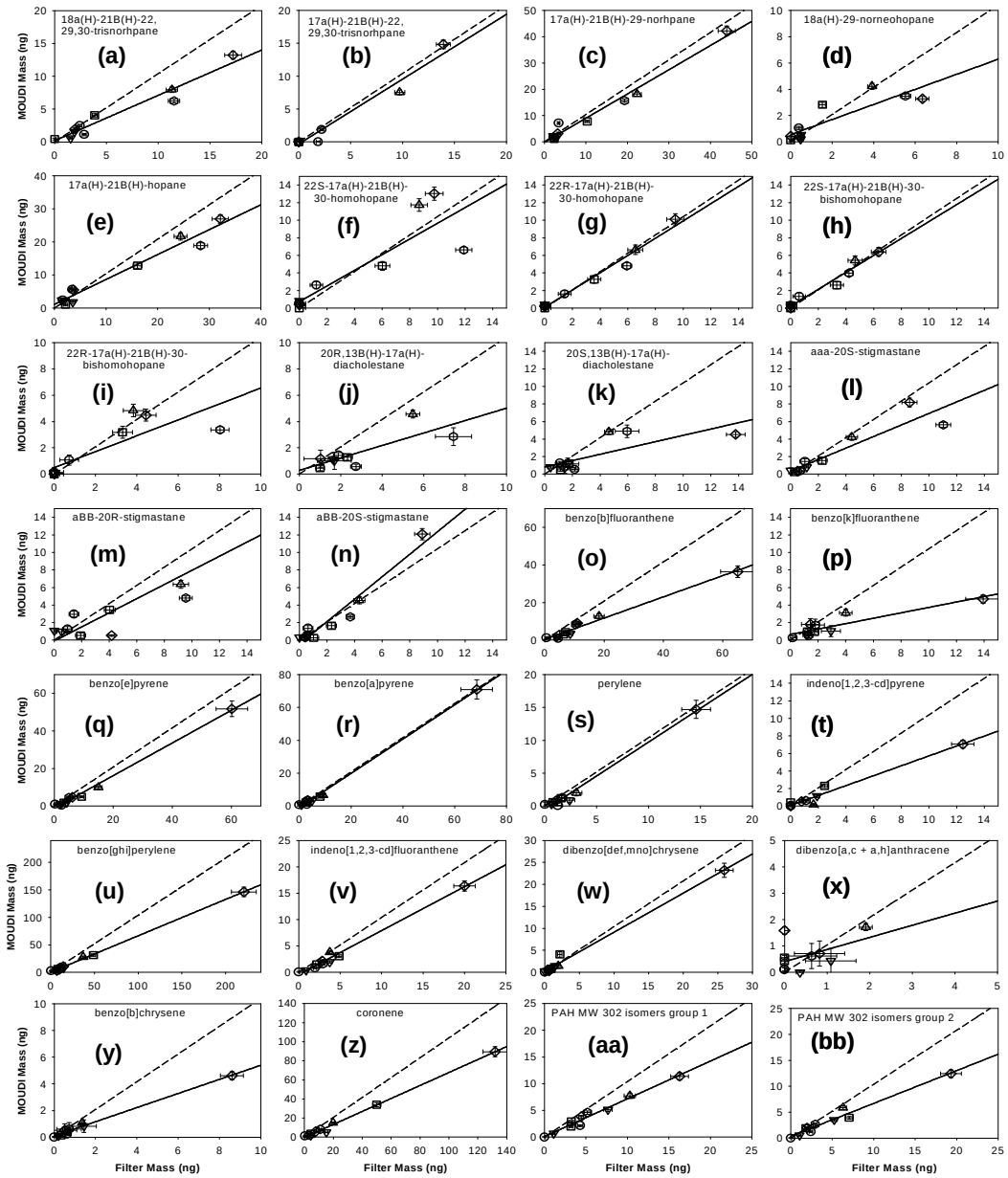
Consistent Hopanes:
17α(H)-21β(H)-29-norhopane
17α(H)-21β(H)-hopane

Consistent Steranes:
αββ-20R-stigmastane
αββ-20S-stigmastane

PAHs
Most PAHs above MDL behaved consistently

Source: 2007 Riddle SG, M.A. Robert, C.A. Jakober, M.P. Hannigan, M.J. Kleeman. Size distribution of trace organic species emitted from heavy-duty diesel vehicles. Environmental Science and Technology 41 pp 1962-1969.

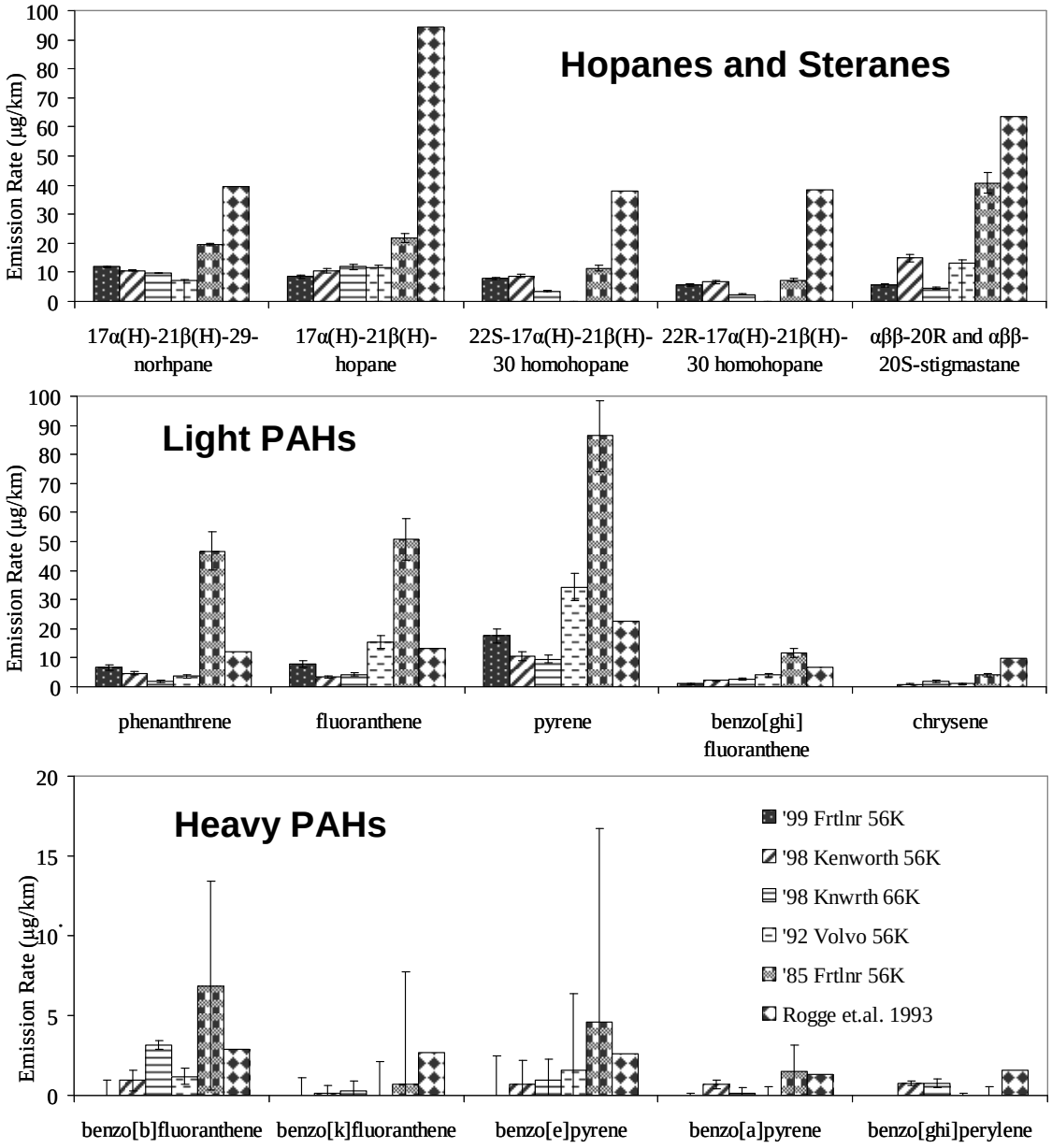
LDGV Co-located Comparison



- Filter samples and summed MOUDIs agree for
  - most PAHs
  - 17α(H)-21β(H)-29-norhopane
  - 17α(H)-21β(H)-hopane
  - αββ-20R-stigmastane,
  - αββ-20S-stigmastane

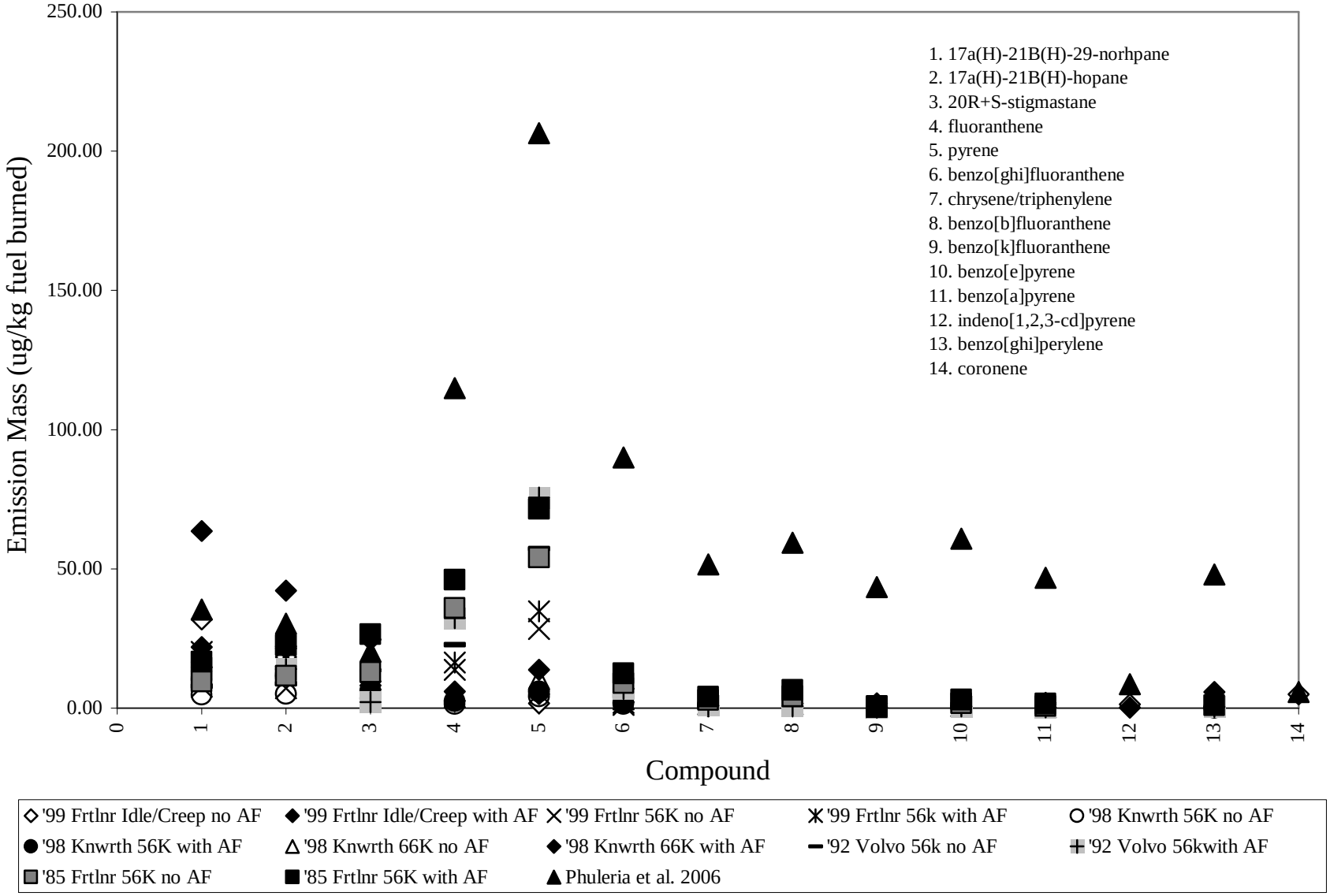
Source: 2007 Riddle SG, M.A. Robert, C.A. Jakober, M.P. Hannigan, M.J. Kleeman. Size distribution of trace organic species emitted from light duty gasoline vehicles. Environmental Science and Technology, 41, pp7464-7471.

Diesel PM 1.8 vs. PM2.5



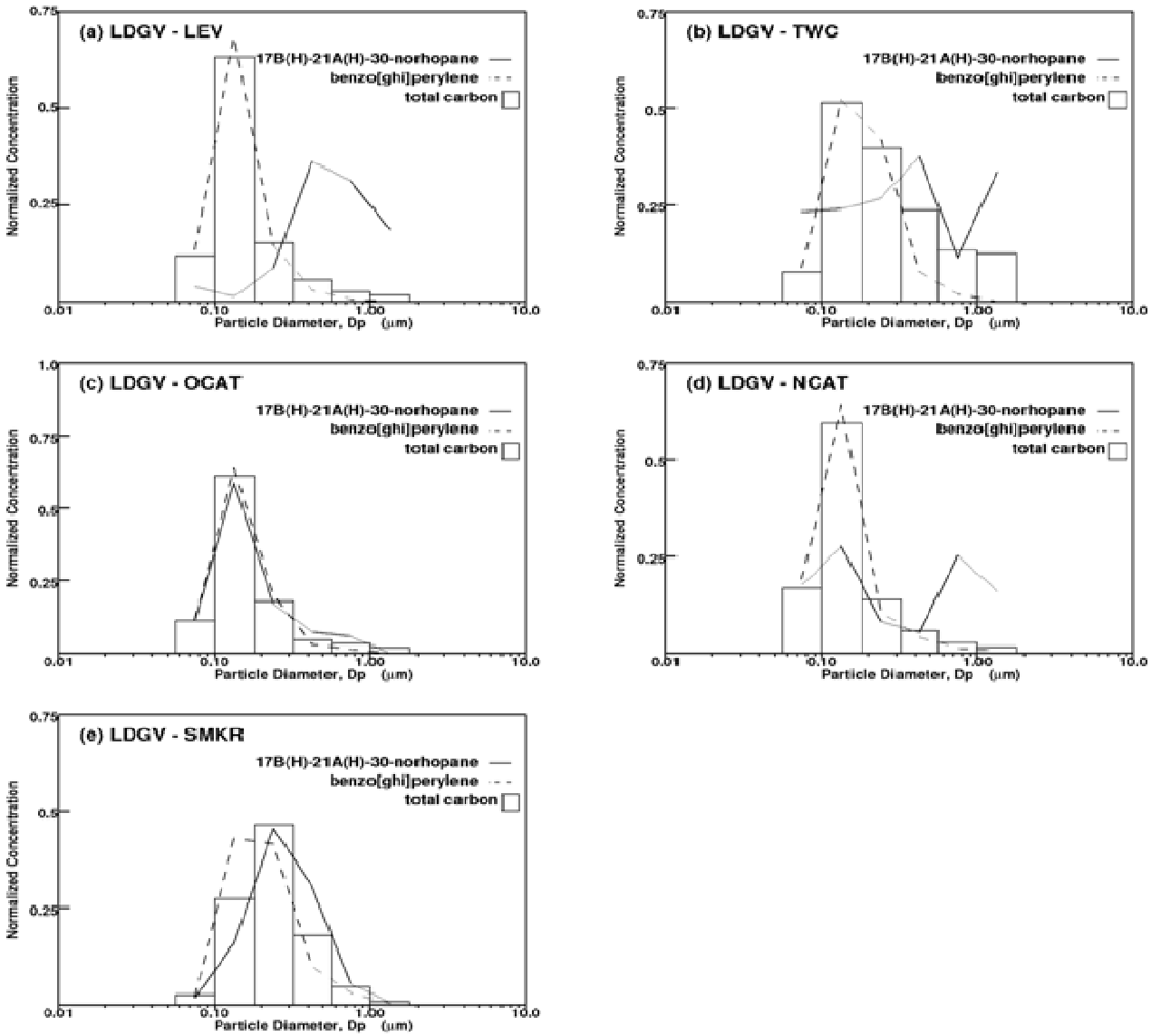
Source: 2007 Riddle SG, M.A. Robert, C.A. Jakober, M.P. Hannigan, M.J. Kleeman. Size distribution of trace organic species emitted from heavy-duty diesel vehicles. Environmental Science and Technology 41 pp 1962-1969.

Diesel PM0.18



Source: 2007 Riddle SG, M.A. Robert, C.A. Jakober, M.P. Hannigan, M.J. Kleeman. Size distribution of trace organic species emitted from heavy-duty diesel vehicles. Environmental Science and Technology 41 pp 1962-1969.

Light Duty Gasoline Vehicle Source Profiles



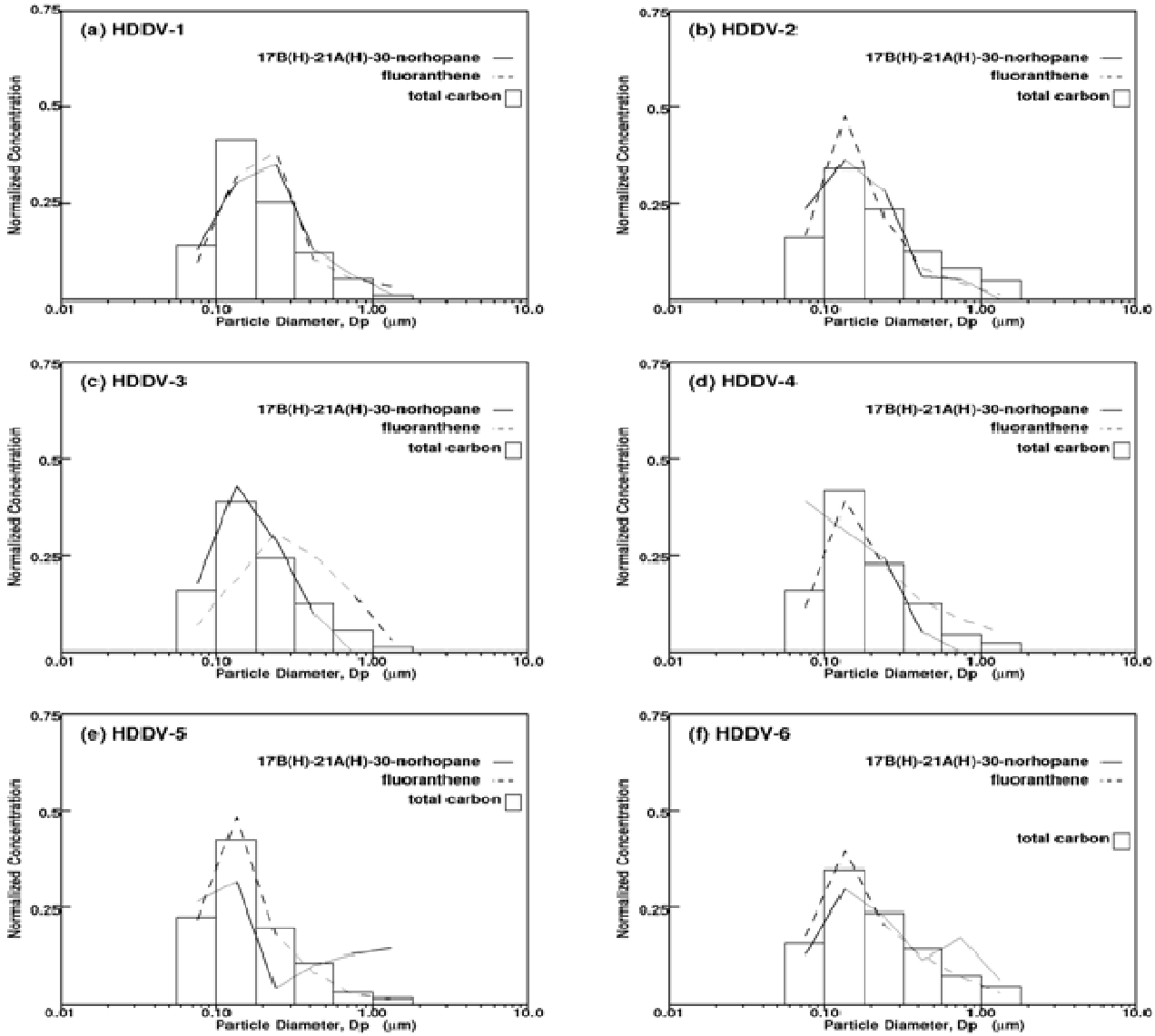
Obvious differences between hopane + sterane vs. PAH vs. TC size distributions

Vehicles without operating catalyst have greater fracton of hopanes + steranes in particles with Dp > 0.32 µm

Primary mode for SMOKER vehicles shifted to larger sizes

Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, and C.A. Jakober. Lubricating Oil and Fuel Contributions to Particulate Matter Emissions from Light Duty Gasoline and Heavy Duty Diesel Vehicles. Environmental Science and Technology, 42, pp235-242.

Heavy Duty Diesel Vehicle Source Profiles



Higher loads reduce the apparent particle density causing greater penetration to the PM0.1 size range

Higher loads can reduce the PM1.8 concentration but increase the PM0.1 concentration

Differences between hopane and PAH size distributions increase at higher loads

Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, and C.A. Jakober. Lubricating Oil and Fuel Contributions to Particulate Matter Emissions from Light Duty Gasoline and Heavy Duty Diesel Vehicles. Environmental Science and Technology, 42, pp235-242.

Regression Analysis Approach

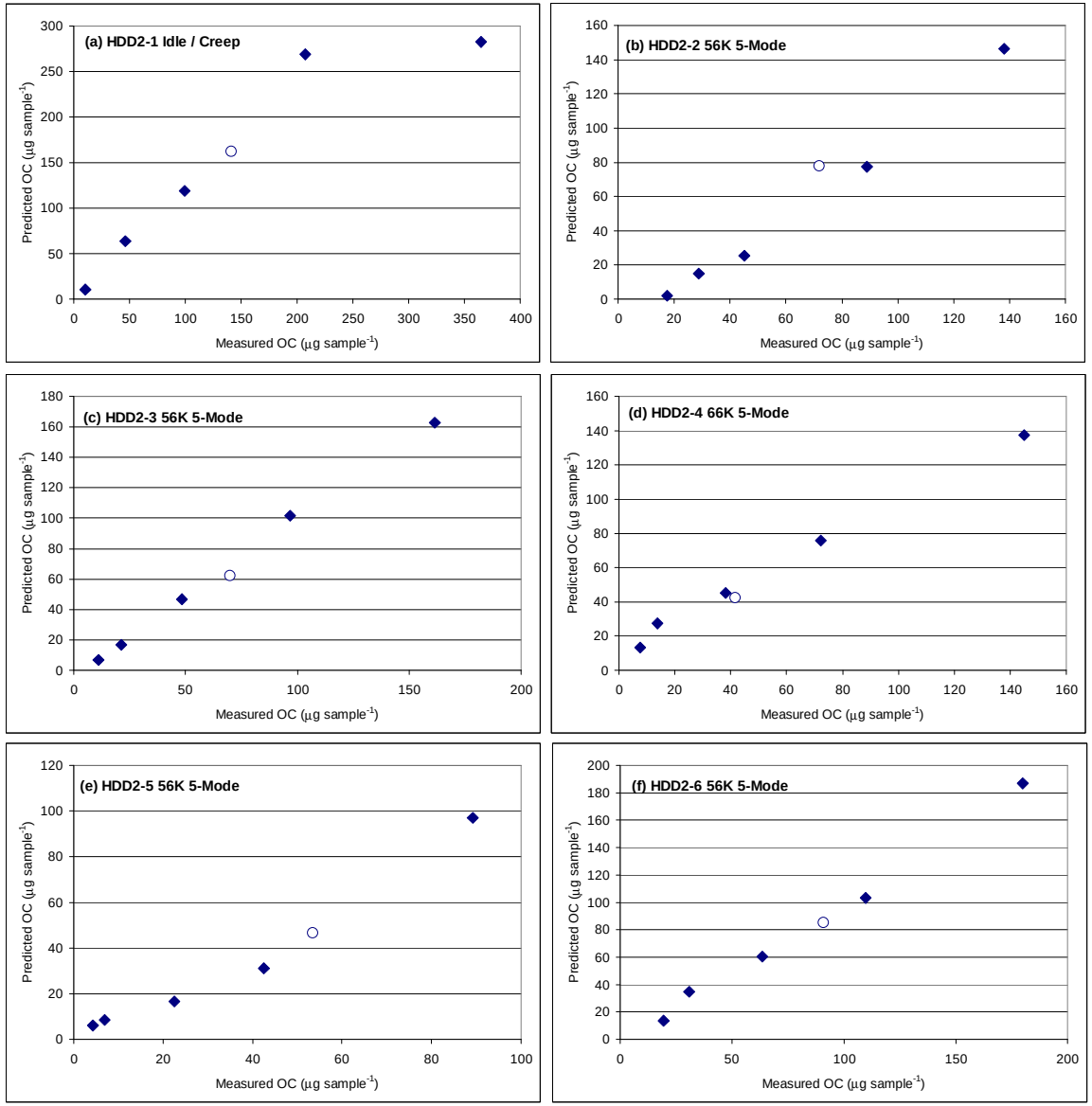
- Fuel and Lubricating Oil make separate contributions to EC and OC
- Tracer compounds
  - Lubricating oil - 17α(H)-21β(H)-29-norhopane
  - Gasoline - benzo[ghi]perylene
  - Diesel fuel – fluoranthene
- Y = A*X1 + B*X2
- Carbon = (μg C / ng oil tracer) * oil tracer
  + (μg C / ng fuel tracer) * fuel tracer

Separating Oil and Fuel Contributions With Multiple Regression

	Elemental Carbon (µg EC / ng tracer)			Organic Carbon (µg OC / ng tracer)		
	Oil tracer	**Diesel fuel tracer**	**R^2**	**Oil tracer**	**Diesel fuel tracer**	**R^2**
Diesel Vehicles						
HDD-1	2.6 ± 0.64	7.1 ± 9.8	0.97	5.6 ± 2.8	11.2 ± 42.1	0.94
HDD-2	5.6 ± 8.7	4.95 ± 4.92	0.93	4.6 ± 3.2	2.2 ± 1.8	0.97
HDD-3	8.7 ± 0.37	5.4 ± 0.62	1.00	7.9 ± 0.48	2.7 ± 0.81	0.99
HDD-4	0.24 ± 0.51	24.0 ± 1..5	0.99	0.0 ± 0.45	15 ± 1.4	0.99
HDD-5	2.2 ± 4.7	12.3 ± 1.6	0.96	0.71 ± 0.94	1.95 ± 0.31	0.98
HDD-6	9.8 ± 4.6	8.5 ± 1.6	0.97	0.045 ± 0.69	2.6 ± 0.23	0.99
Gasoline Vehicles	**Oil tracer**	**Gasoline fuel tracer**		**Oil tracer**	**Gasoline fuel tracer**	
LEV	0.82 ± 0.28	6.3 ± 0.11	1.00	1.0 ± 0.28	1.4 ± 0.11	0.99
TWC	1.1 ± 0.79	1.7 ± 0.13	0.99	1.50 ± 0.70	0.97 ± 0.12	0.99
OCAT	1.45 ± 0.39	0.036 ± 0.20	0.99	2.9 ± 1.3	4.0 ± 0.66	1.00
NCAT	1.1 ± 1.2	0.34 ± 0.026	0.99	3.5 ± 1.6	0.25 ± 0.034	0.98
SMKR	0.20 ± 0.055	0.047 ± 0.014	0.97	3.7 ± 0.46	0.91 ± 0.12	0.99

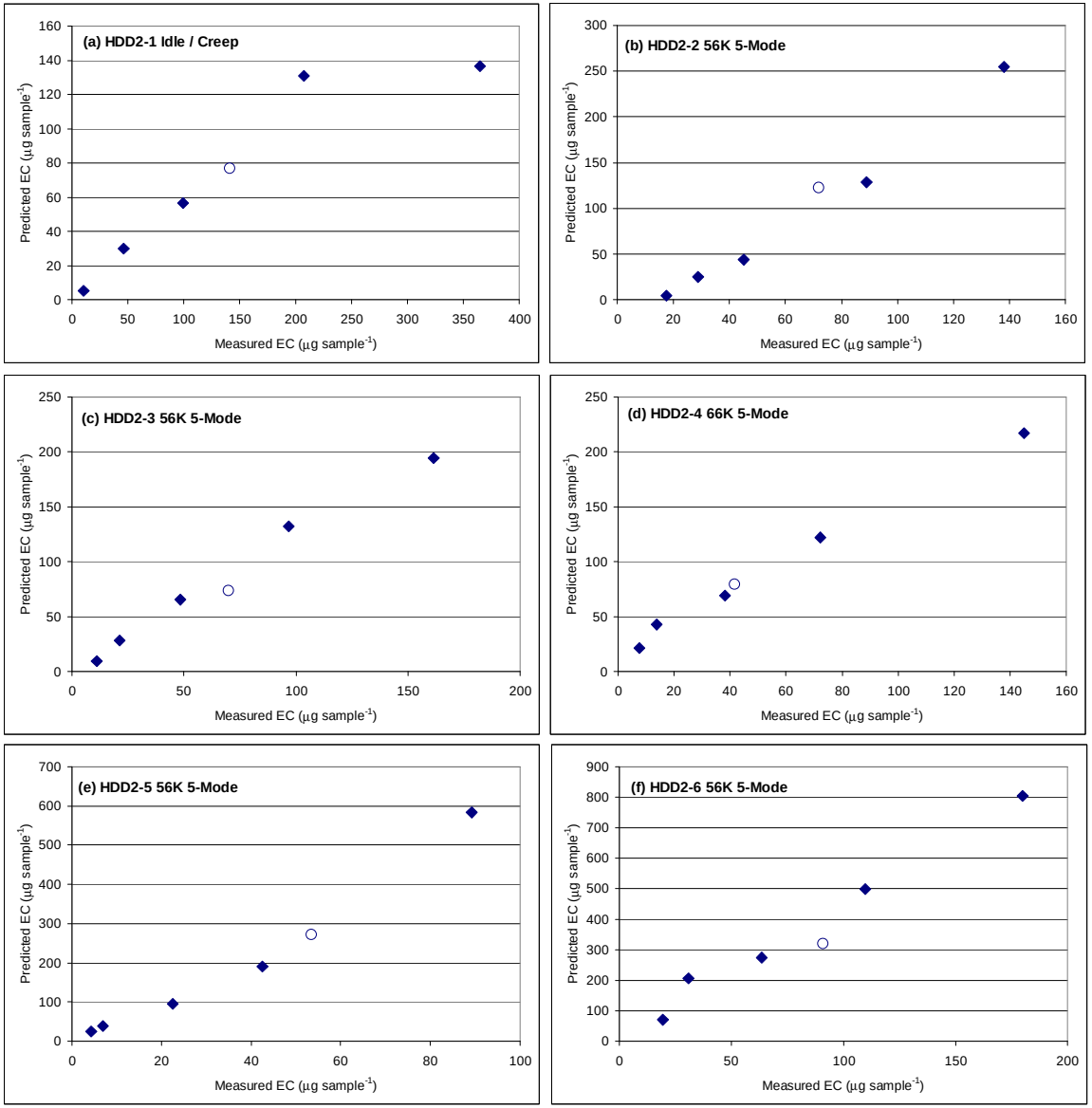
Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, and C.A. Jakober. Lubricating Oil and Fuel Contributions to Particulate Matter Emissions from Light Duty Gasoline and Heavy Duty Diesel Vehicles. Environmental Science and Technology, 42, pp235-242.

Predicted vs. Measured HDDV OC



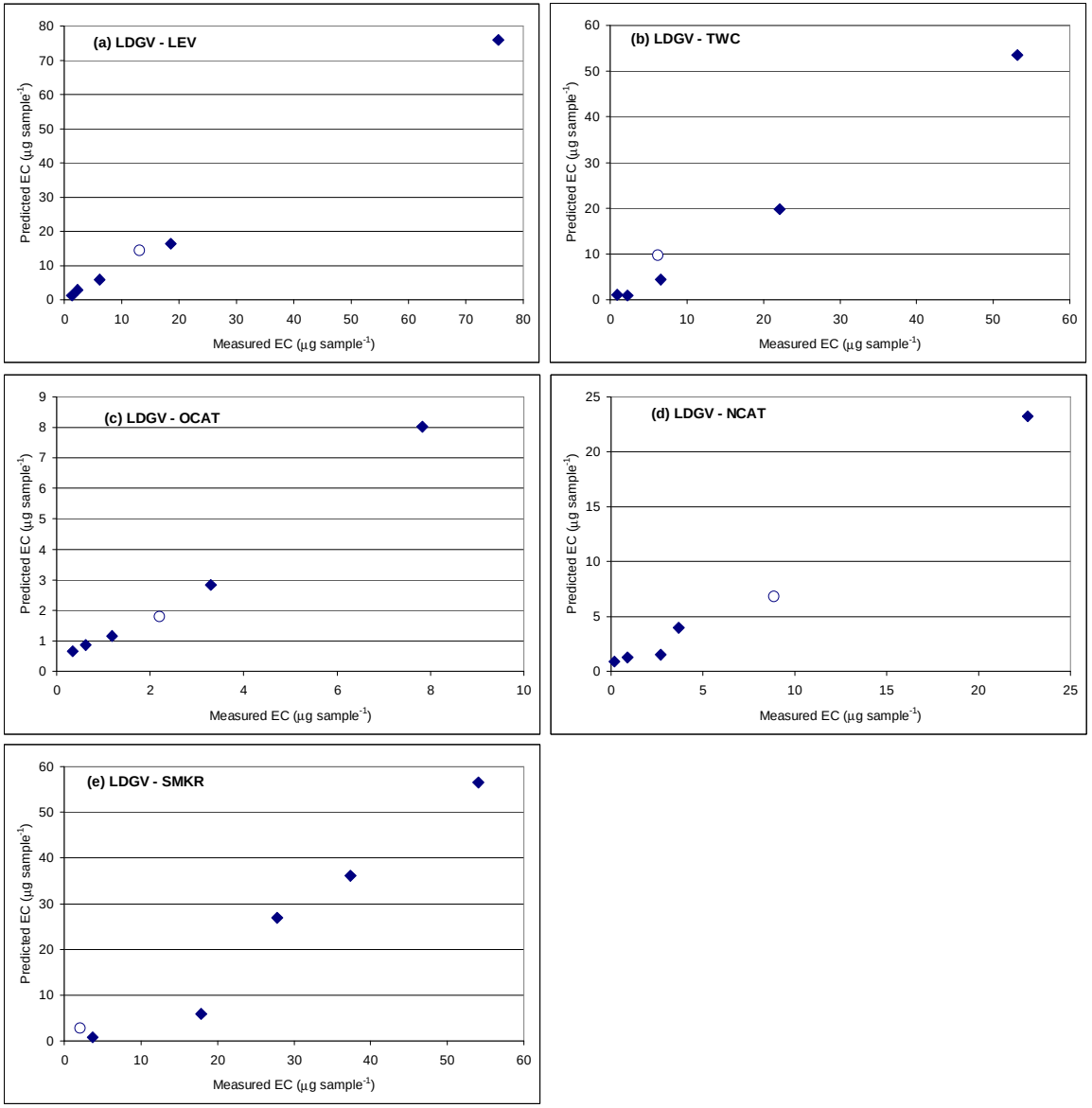
Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, and C.A. Jakober. Lubricating Oil and Fuel Contributions to Particulate Matter Emissions from Light Duty Gasoline and Heavy Duty Diesel Vehicles. Environmental Science and Technology, 42, pp235-242.

Predicted vs. Measured HDDV EC



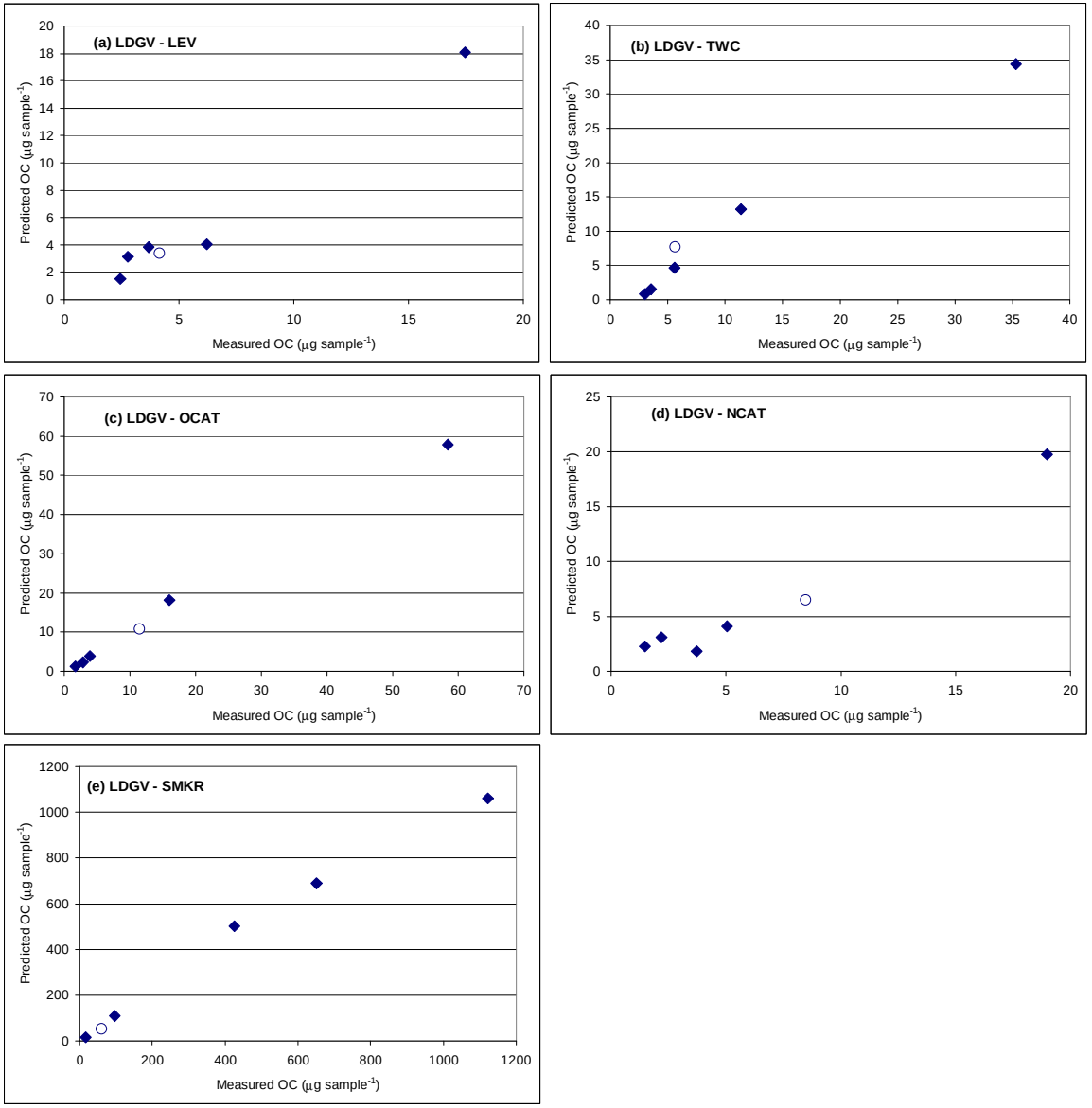
Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, and C.A. Jakober. Lubricating Oil and Fuel Contributions to Particulate Matter Emissions from Light Duty Gasoline and Heavy Duty Diesel Vehicles. Environmental Science and Technology, 42, pp235-242.

Predicted vs. Measured LDV EC



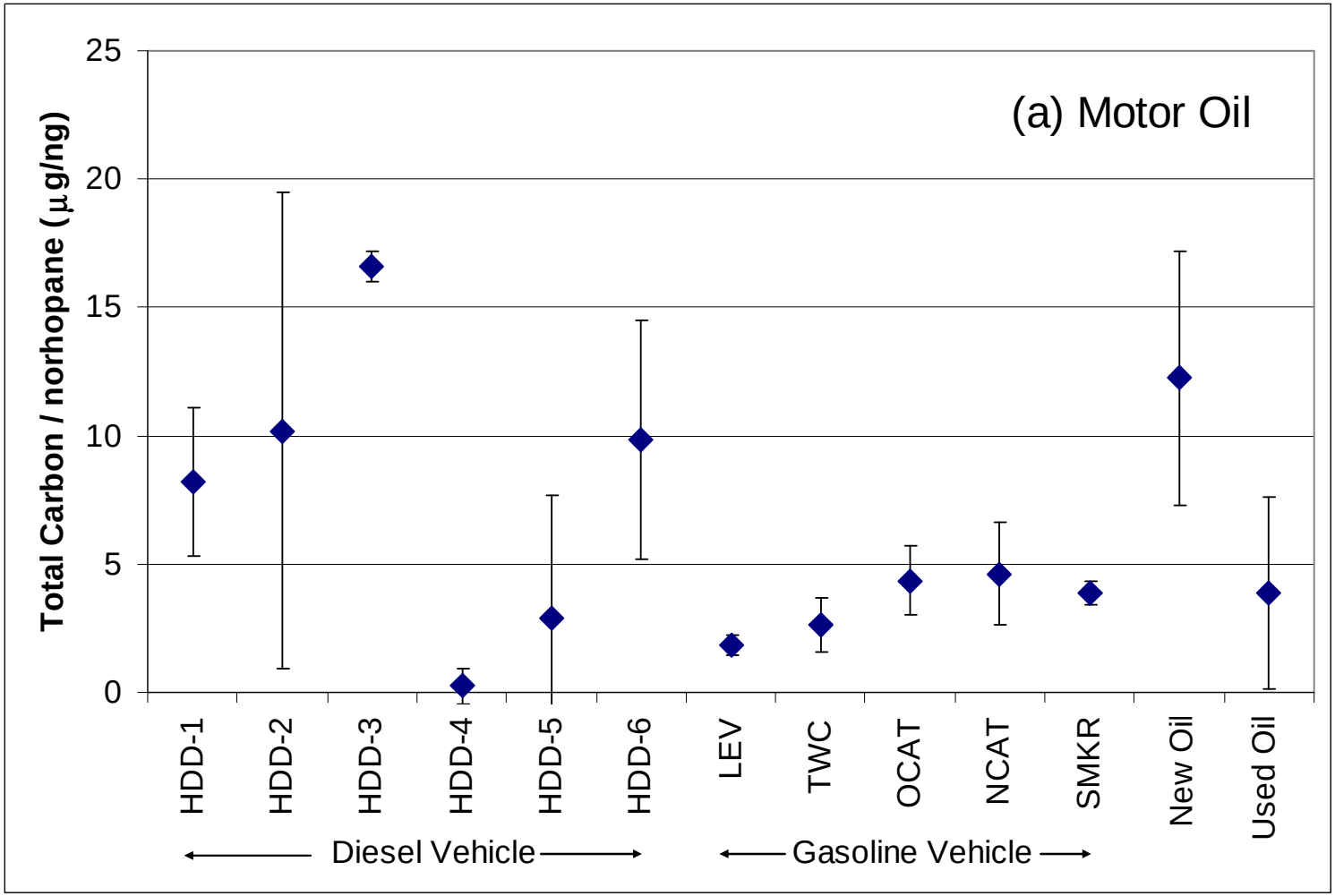
Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, and C.A. Jakober. Lubricating Oil and Fuel Contributions to Particulate Matter Emissions from Light Duty Gasoline and Heavy Duty Diesel Vehicles. Environmental Science and Technology, 42, pp235-242.

Predicted vs. Measured LDV OC



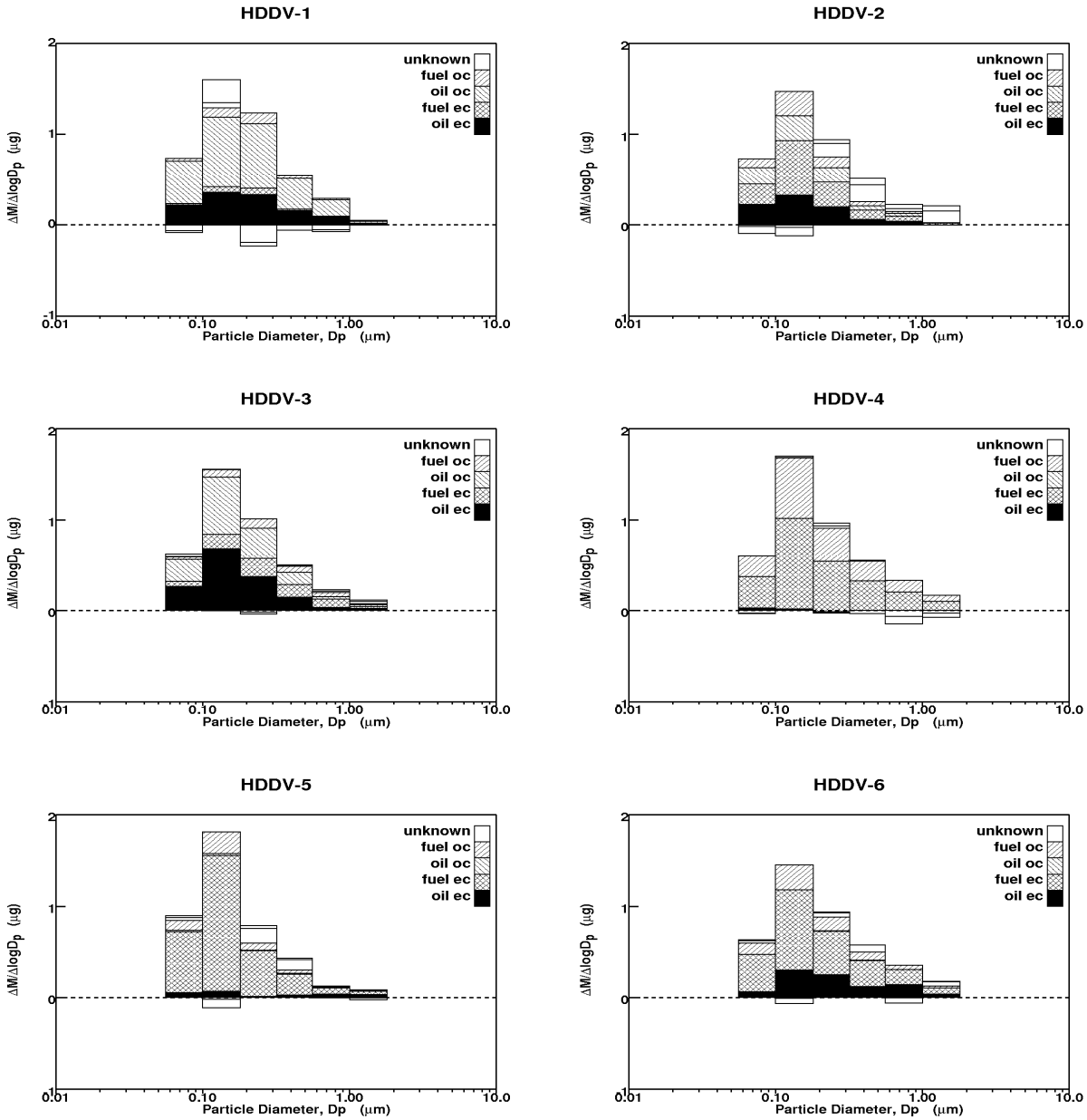
Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, and C.A. Jakober. Lubricating Oil and Fuel Contributions to Particulate Matter Emissions from Light Duty Gasoline and Heavy Duty Diesel Vehicles. Environmental Science and Technology, 42, pp235-242.

Total Carbon per unit of Norhopane



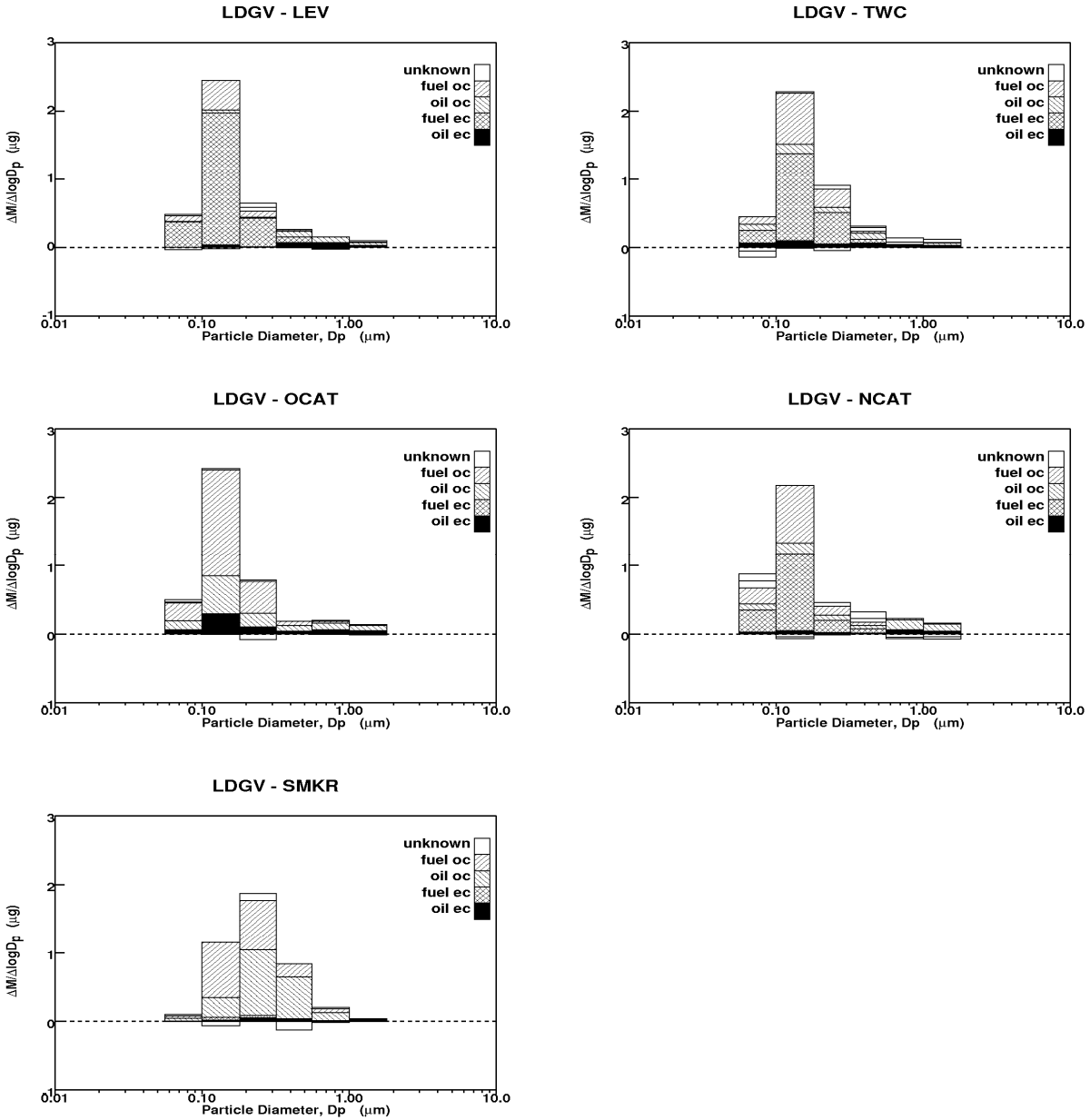
Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, and C.A. Jakober. Lubricating Oil and Fuel Contributions to Particulate Matter Emissions from Light Duty Gasoline and Heavy Duty Diesel Vehicles. Environmental Science and Technology, 42, pp235-242.

Reconstructed HDV Source Profile



Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, and C.A. Jakober. Lubricating Oil and Fuel Contributions to Particulate Matter Emissions from Light Duty Gasoline and Heavy Duty Diesel Vehicles. Environmental Science and Technology, 42, pp235-242.

Reconstructed LDV Source Profiles



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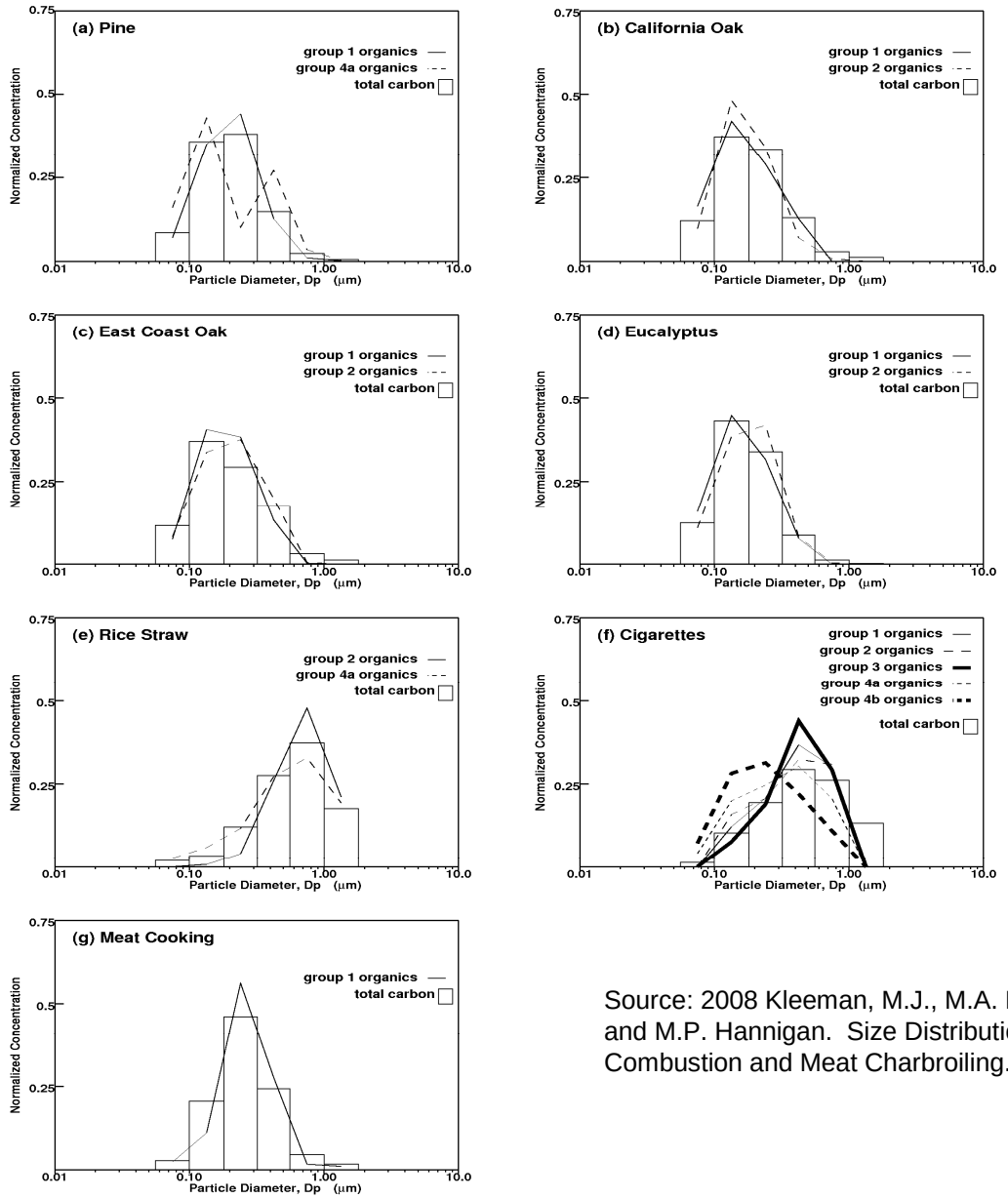
Biomass Combustion and Food Cooking



Levoglucosan size distribution is well correlated with total carbon in most cases

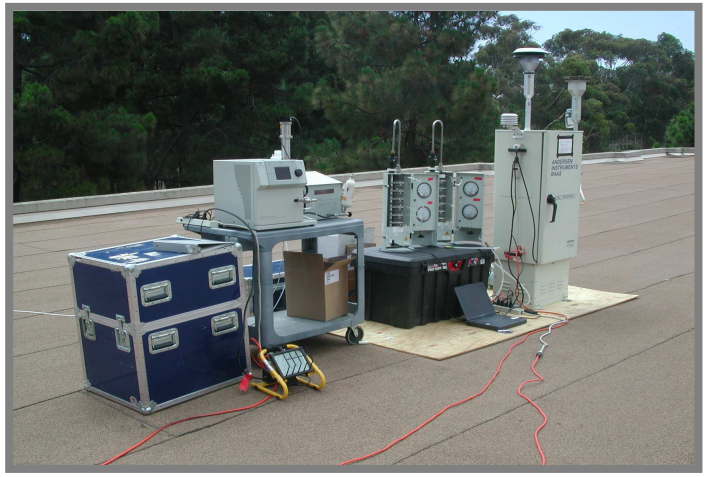
Cholesterol size distribution is well correlated with total carbon in most cases

PM2.5 estimates for source profiles can likely be used for PM0.1 as well

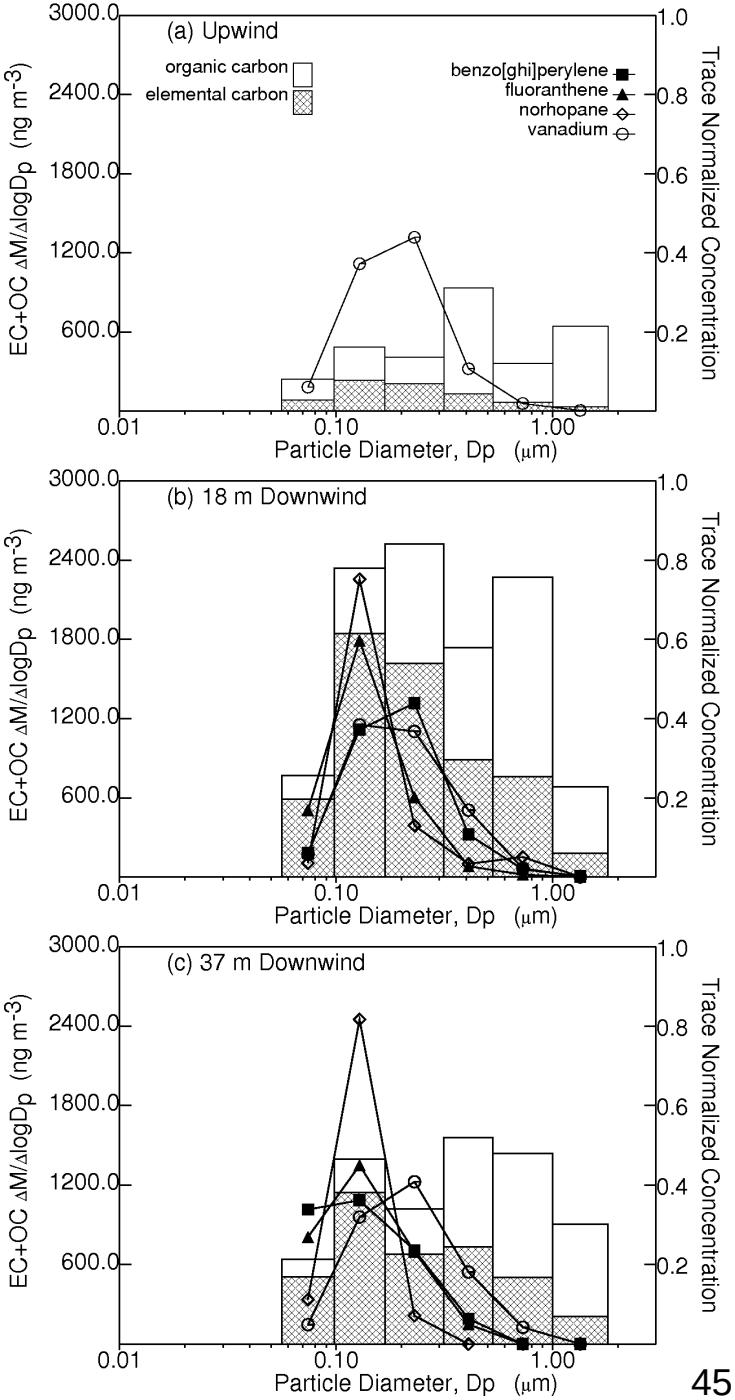
Source: 2008 Kleeman, M.J., M.A. Robert, S.G. Riddle, P.M. Fine, M.D. Hays, J.J. Schauer, and M.P. Hannigan. Size Distribution of Trace Organic Species Emitted From Biomass Combustion and Meat Charbroiling. Atmospheric Environment, 42 pp3059-3075.

Size-Resolved CMB Source Apportionment of Near-Roadway PM in San Diego, 2003

BACKGROUND AND I-5 SITES

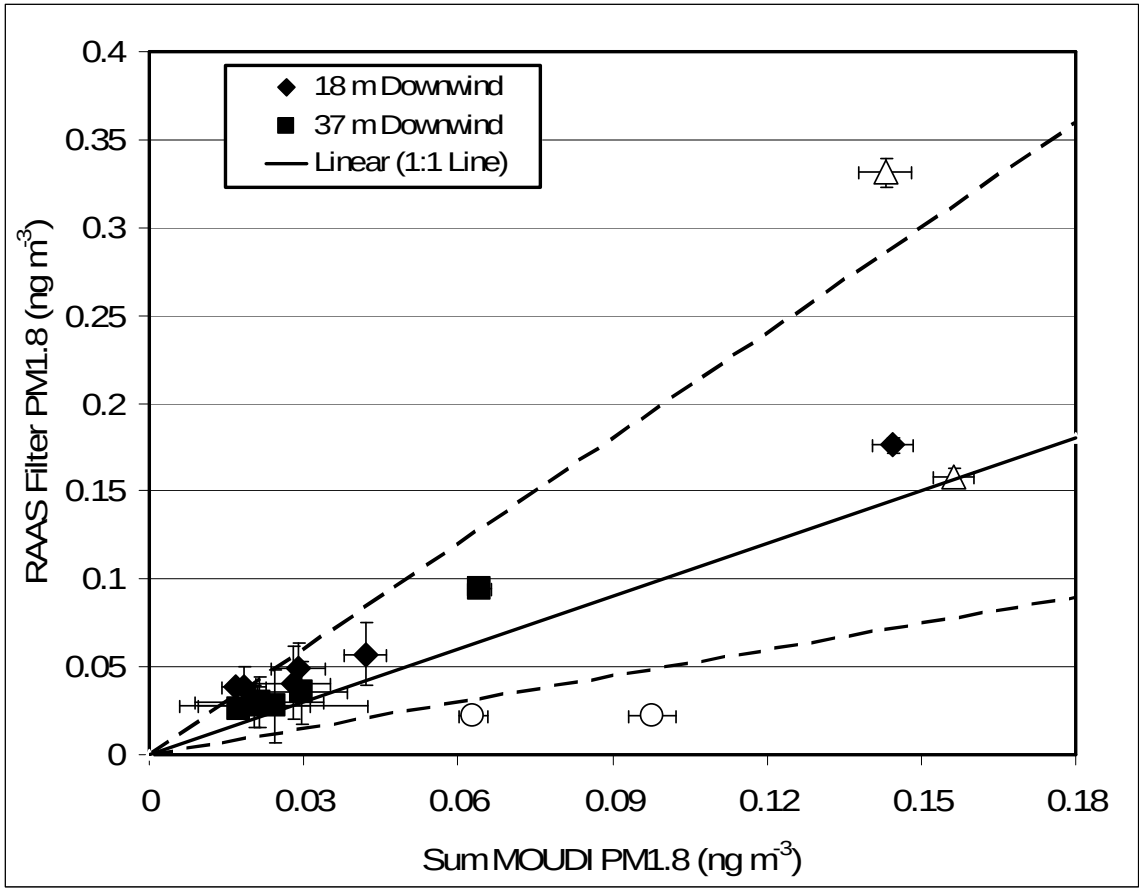


Molecular Marker Size Distributions



Source: 2008 Riddle, S., M.A. Robert, C.A. Jakober, M.P. Hannigan, and M.J. Kleeman. Size-resolved Source Apportionment of Airborne Particulate Matter in a Roadside Environment. Environmental Science and Technology, 42, pp6580-6586.

Co-Located Sample Agreement



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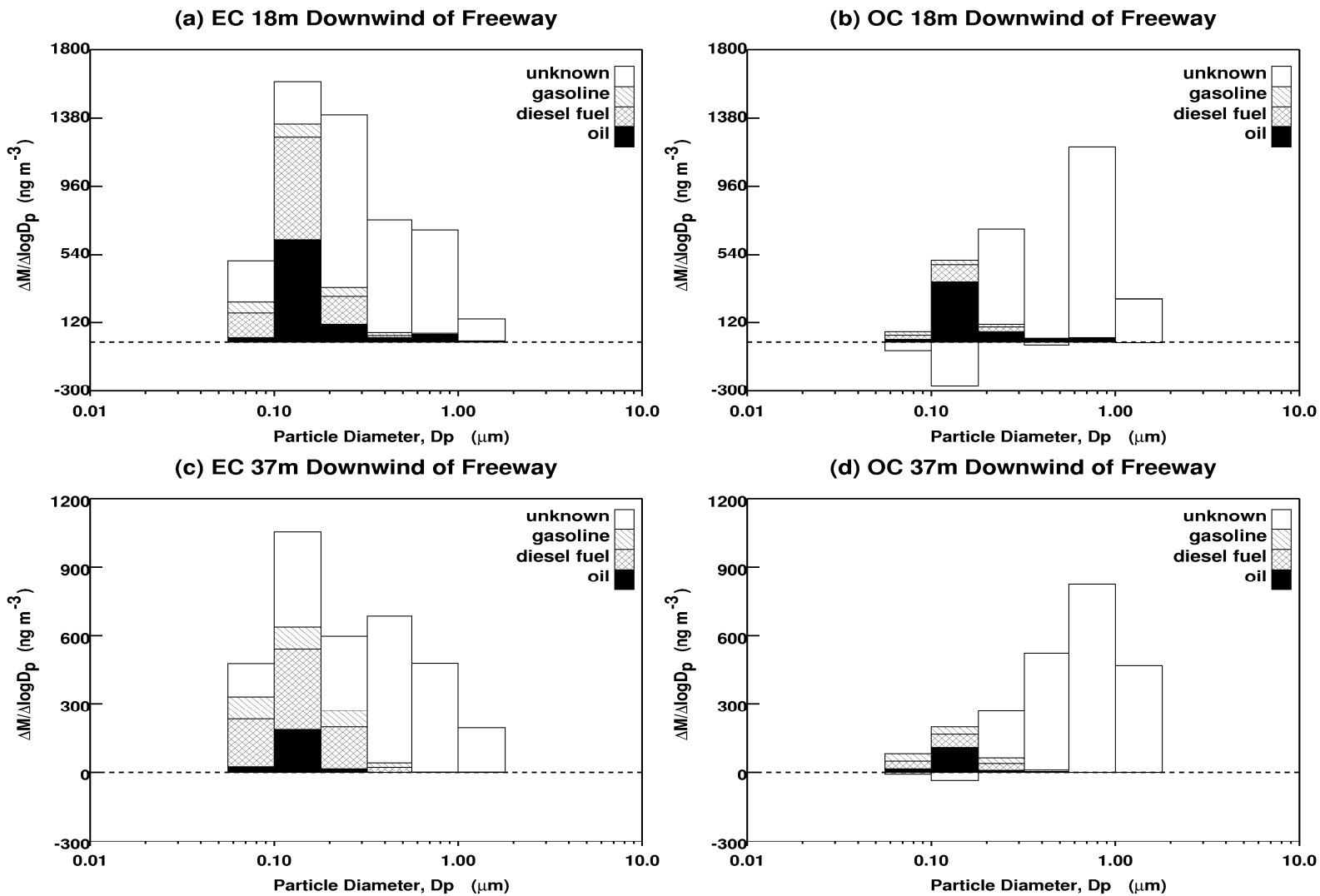
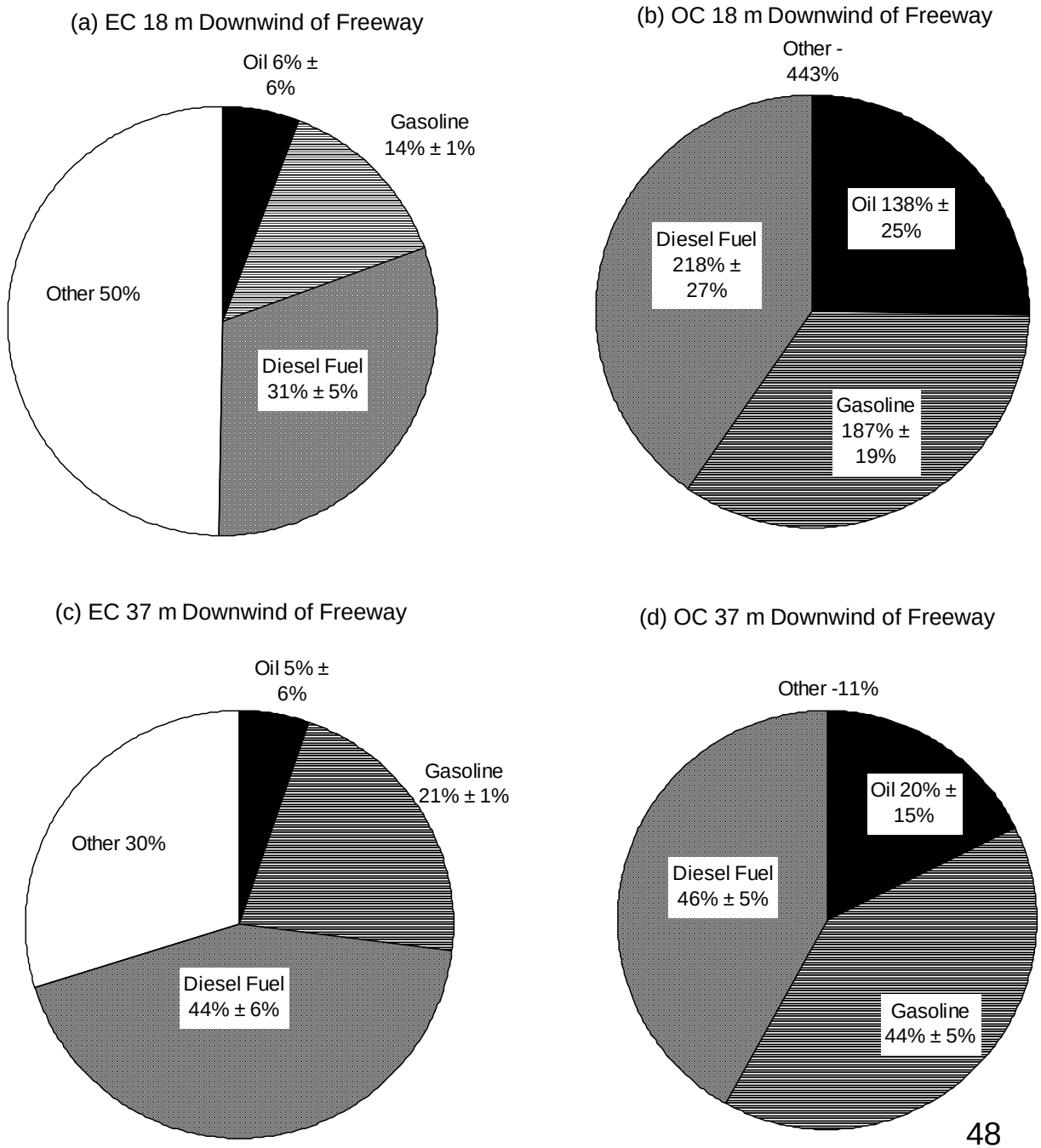
Size-Resolved Source Apportionment of Near Roadways



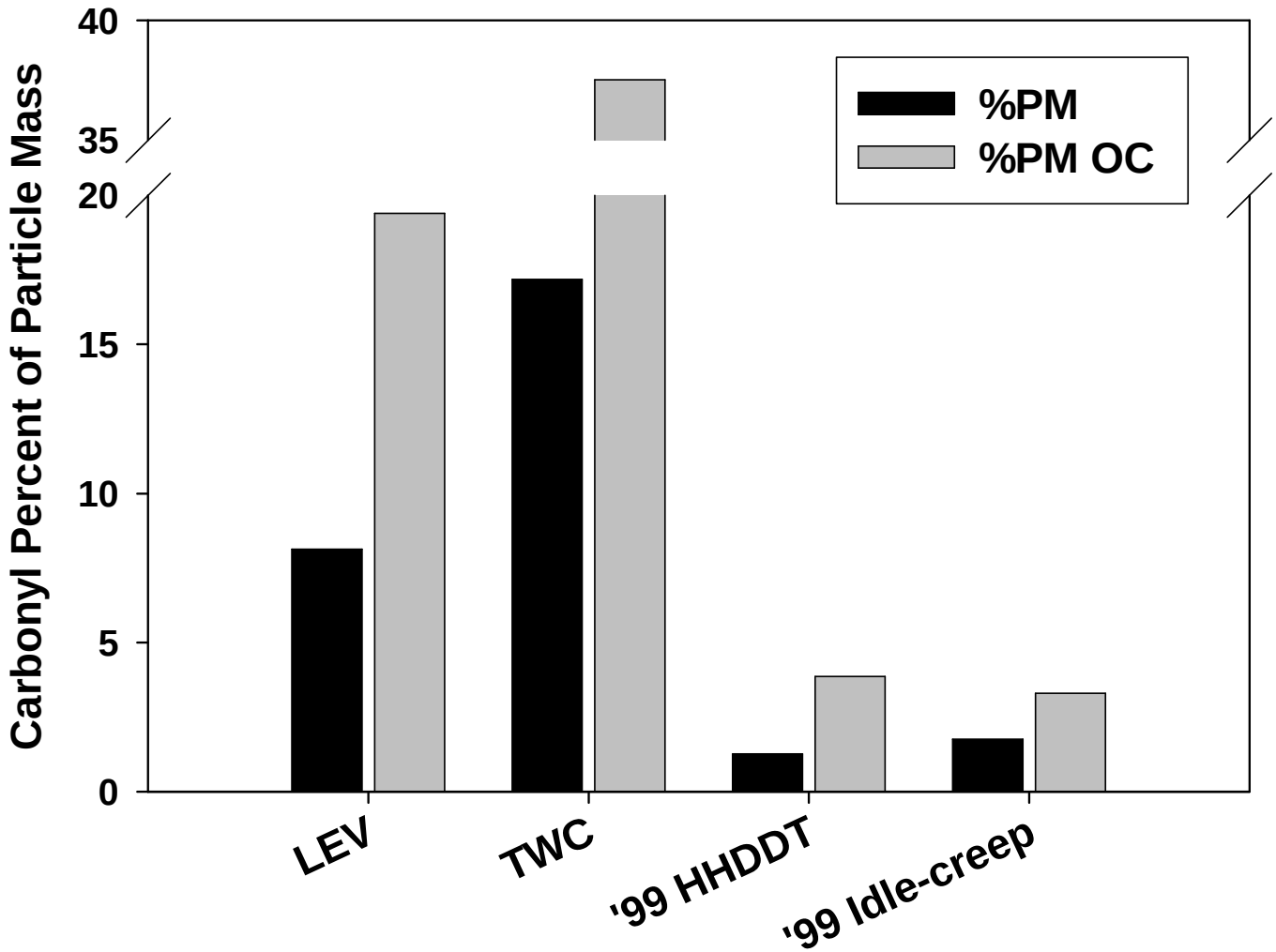
Source: 2008 Riddle, S., M.A. Robert, C.A. Jakober, M.P. Hannigan, and M.J. Kleeman. Size-resolved Source Apportionment of Airborne Particulate Matter in a Roadside Environment. Environmental Science and Technology, 42, pp6580-6586.

Source Apportionment of PM0.1 Near Roadways



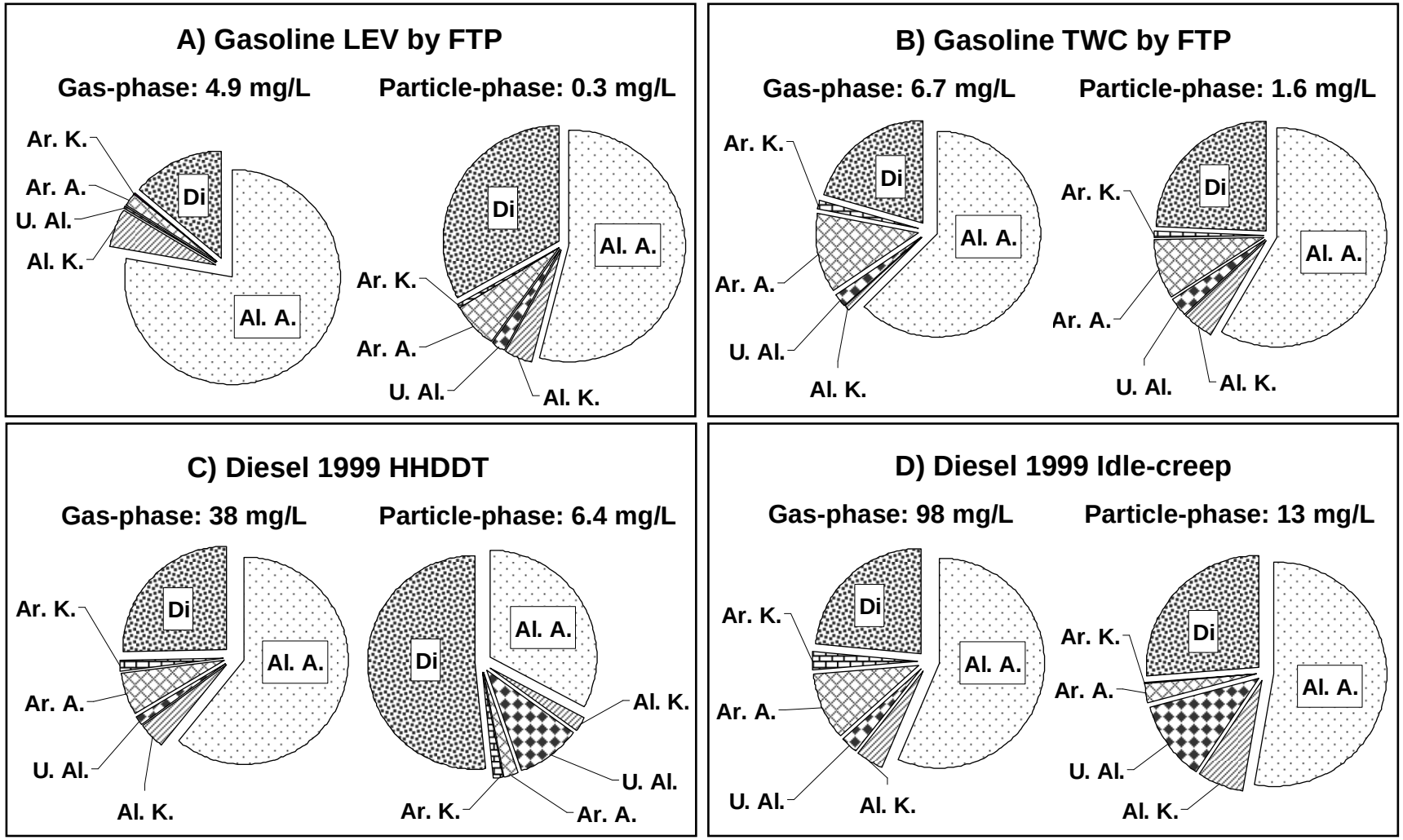
Source: 2008 Riddle, S., M.A. Robert, C.A. Jakober, M.P. Hannigan, and M.J. Kleeman. Size-resolved Source Apportionment of Airborne Particulate Matter in a Roadside Environment. Environmental Science and Technology, 42, pp6580-6586.

Fraction of Identified PM From Dynamometer Tests



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.

Dynamometer PM Speciation



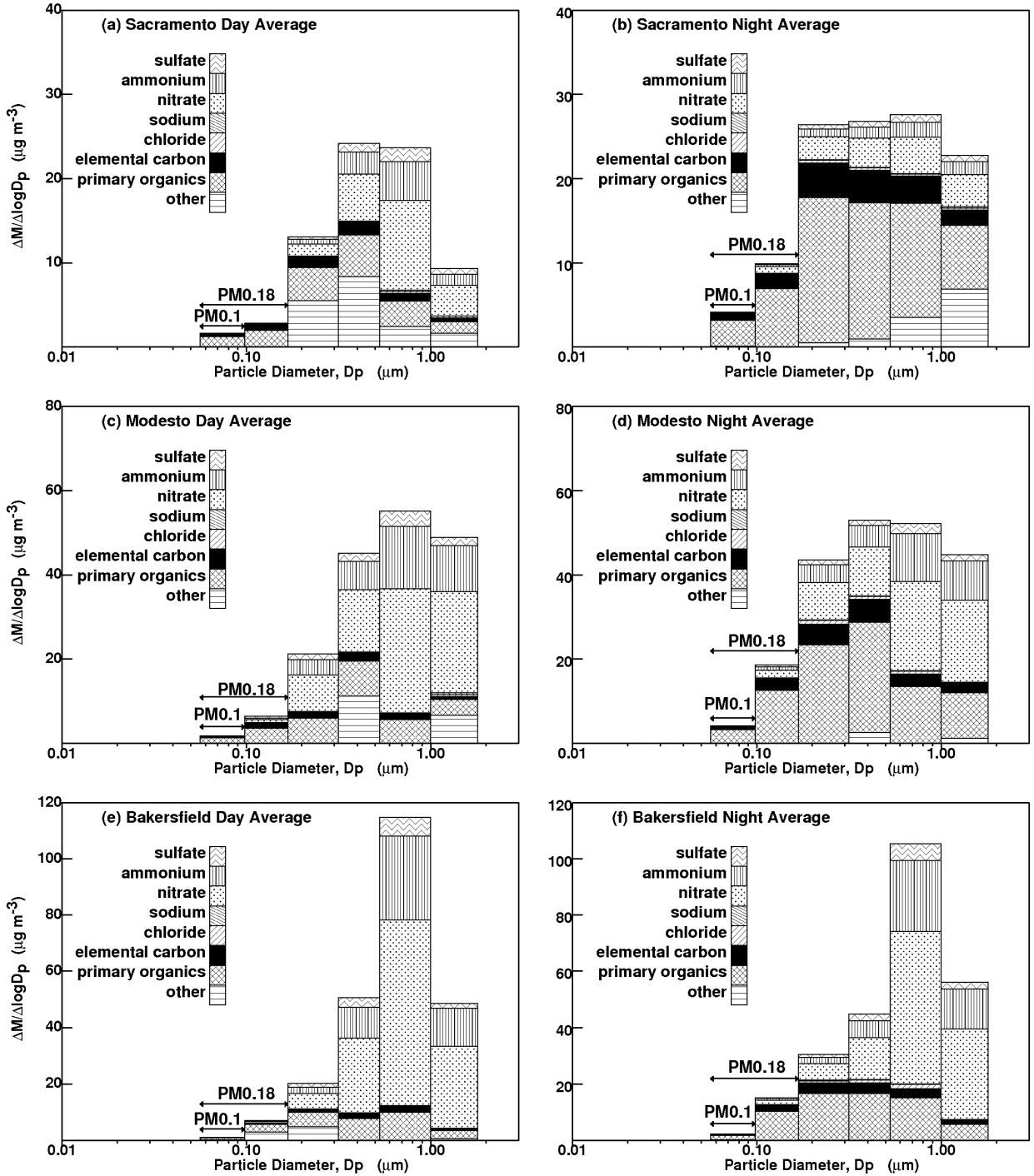
Al. A. = Aliphatic Aldehydes **Al. K. = Aliphatic Ketones** **U. Al. = Unsaturated Aliphatics**
Ar. A. = Aromatic Aldehydes **Ar. K. = Aromatic Ketones** **Di = Dicarbonyls**

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.

California Regional Particulate Air Quality Study (CRPAQS)

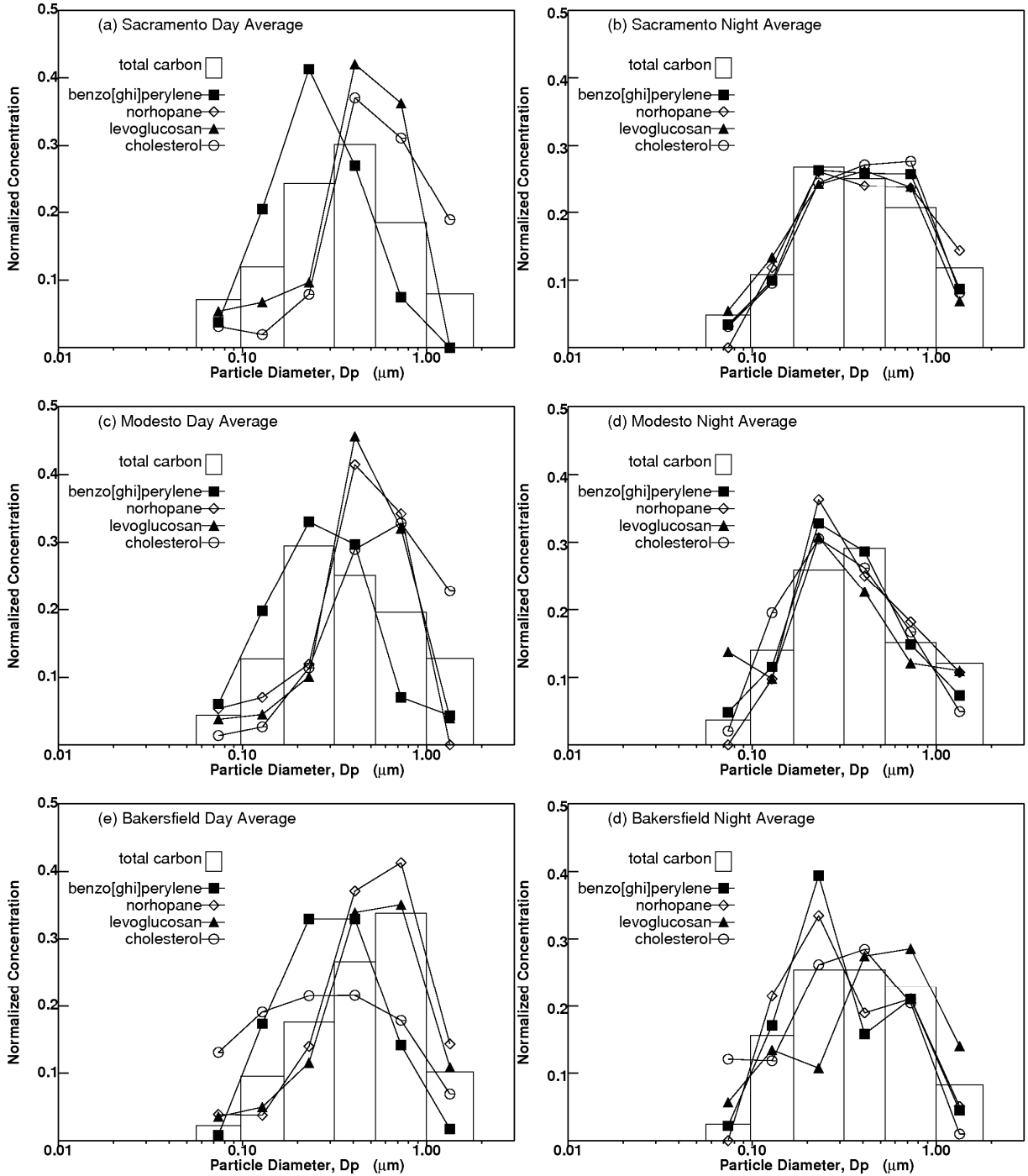
- Size-Resolved PM samples
  - Sacramento / Davis
  - Modesto
  - Bakersfield
- Extraction for foil substrates and quartz filters
  - Spiked with deuterated internal standards
  - Extracted in 10-15 mL of dichloromethane (DCM)
- GC-MS Analysis
  - Chromatography: Agilent DB-XLBMSD GC column
  - Mass Spectrometry: Varian 2000 ion trap MS
    - (both full scan and SIM)

CRPAQS Measured PM Size Distributions



Source: 2008 Kleeman, M.J., S.G. Riddle, and C.A. Jakober. Size Distribution of Particle-Phase Molecular Markers During a Severe Winter Pollution Episode. Environmental Science and Technology, 42, pp4697-4703.

CRPAQS Measured PM Molecular Marker Size Distributions



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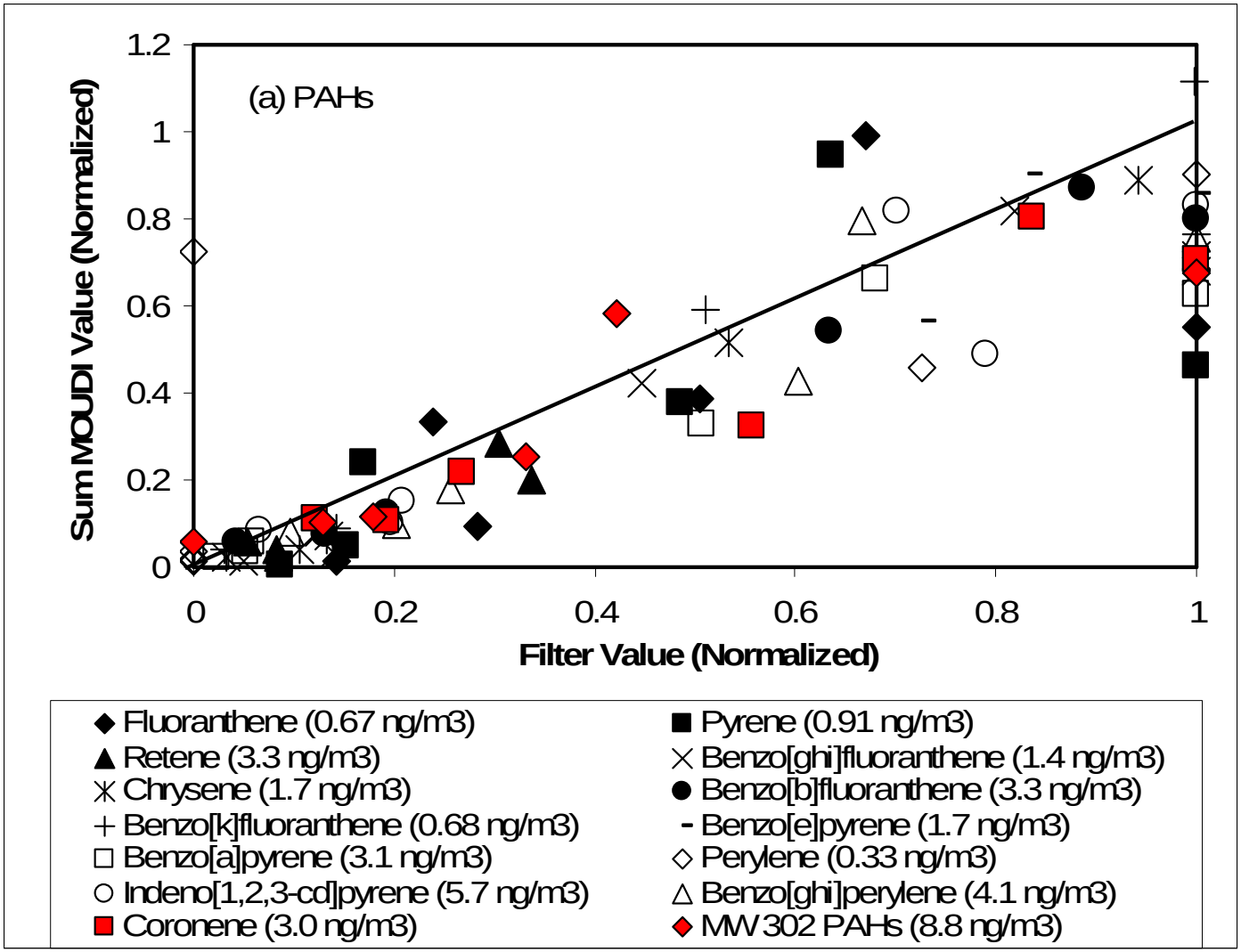
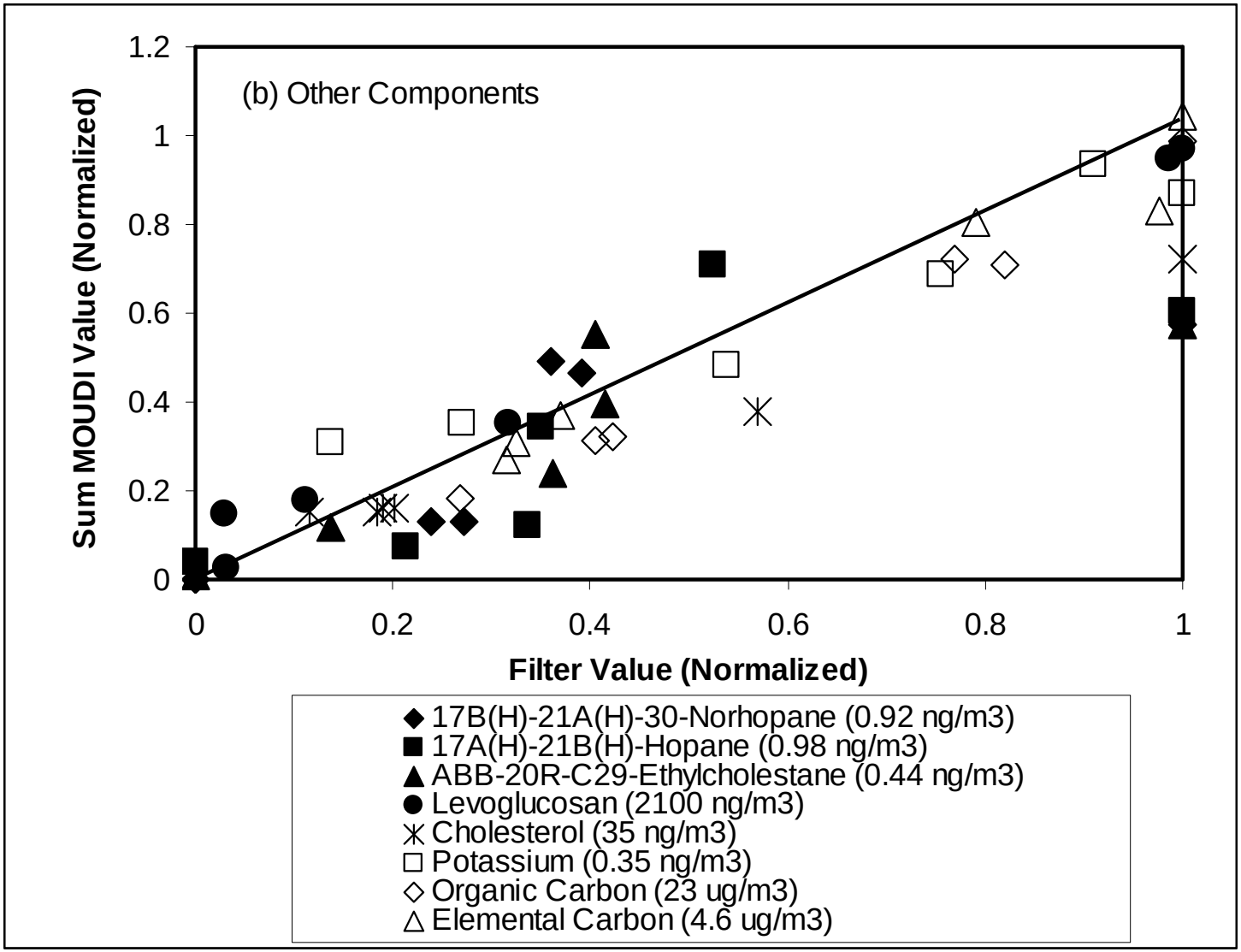
Co-Located Sample Agreement



Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, C.A. Jakober, P.M. Fine, M.D. Hays, J.J. Schauer, and M.P. Hannigan. Source Apportionment of Ultrafine Airborne Particulate Matter (PM0.1) During a Severe Winter Pollution Episode. Environmental Science and Technology, submitted for publication.

Co-Located Sample Agreement



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Source Apportionment Algorithm

1. Calculate biomass contributions to EC using levoglucosan as a tracer. Certainty = high.
2. Calculate motor oil contributions to EC using hopanes and steranes (expressed as equivalent concentration of 17α(H)-21β(H)-29-norhopane) as a tracer. Certainty = high.
3. Calculate gasoline-fuel contributions to EC using benzo[ghi]perylene and coronene (expressed as equivalent concentration of benzo[ghi]perylene) as a tracer. Certainty = high.
4. Calculate meat cooking contributions to EC using cholesterol as a tracer. Certainty = low.
5. Assign residual EC to diesel-fuel. Certainty = medium.
6. Calculate diesel-fuel contribution to OC using diesel-fuel EC as a tracer. Certainty = medium.
7. Calculate biomass contributions to OC using levoglucosan as a tracer. Certainty = high.
8. Calculate motor oil contributions to OC using hopanes and steranes (expressed as equivalent concentration of 17α(H)-21β(H)-29-norhopane) as a tracer. Certainty = high.
9. Calculate gasoline-fuel contributions to OC using benzo[ghi]perylene and coronene (expressed as equivalent concentration of benzo[ghi]perylene) as a tracer. Certainty = high.
10. Calculate meat cooking contributions to OC using cholesterol as a tracer. Certainty = low. Constrain meat cooking contributions to the amount of residual OC not already accounted for by other sources.

Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, C.A. Jakober, P.M. Fine, M.D. Hays, J.J. Schauer, and M.P. Hannigan. Source Apportionment of Ultrafine Airborne Particulate Matter (PM0.1) During a Severe Winter Pollution Episode. Environmental Science and Technology, submitted for publication.

Source Profiles (All Particle Sizes)

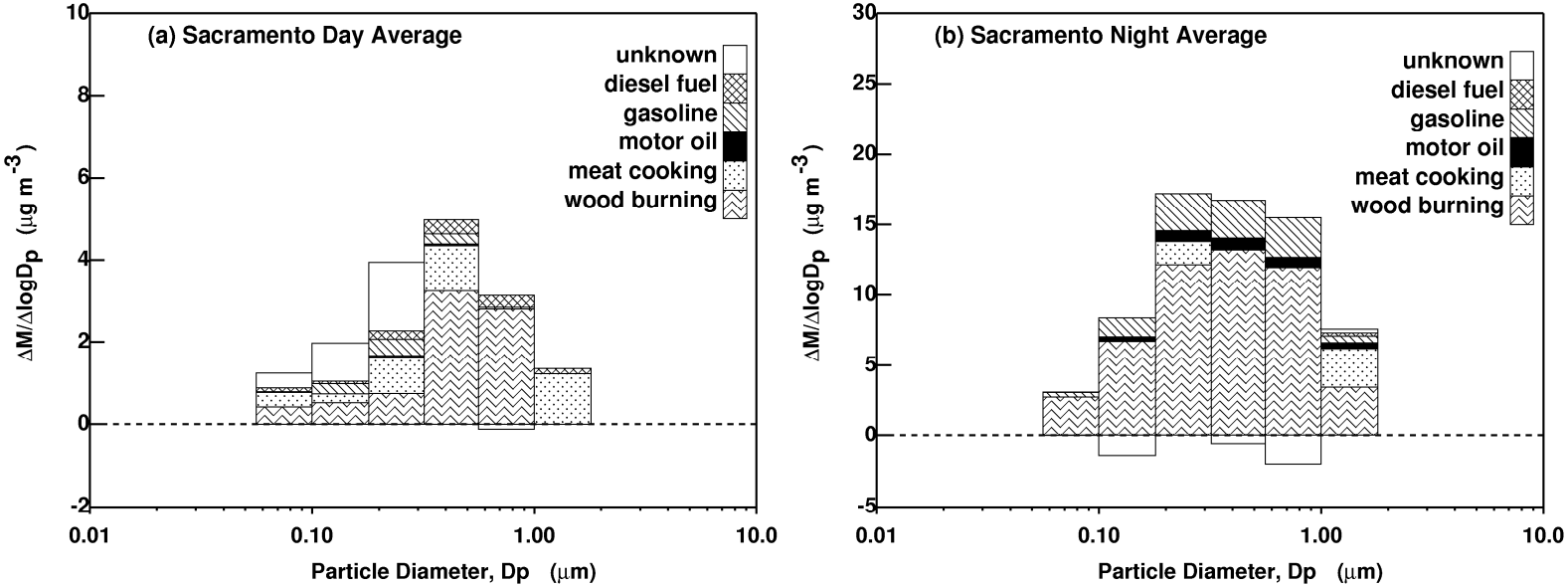
Source	Tracer	Tracer / OC	Tracer / EC
Diesel Fuel	EC[1]	2.56	1
Gasoline	Benzo[ghi]perylene[2,3]	0.0011	0.0006
Gasoline	Coronene[3]	0.0008	0.0004
Lubricating Oil	17α(H)-21β(H)-29-norhopane[#]	0.0006	0.0008
Lubricating Oil	17α(H)-21β(H)-hopane[3]	0.0006	0.0008
Lubricating Oil	αββ20R-C29-ethylcholestane[3]	0.0003	0.0004
Wood Burning	Levoglucosan	0.15	5.0
Meat Cooking	Cholesterol	0.0015	0.15

Notes:
1. Residual EC not explained by other sources was used as a tracer for diesel-fuel contributions to OC.
2. Gasoline engines were found to be the dominant source of benzo[ghi]perylene during source tests.
3. Coal combustion may also release these compounds but this source is not present in significant quantitites in California.

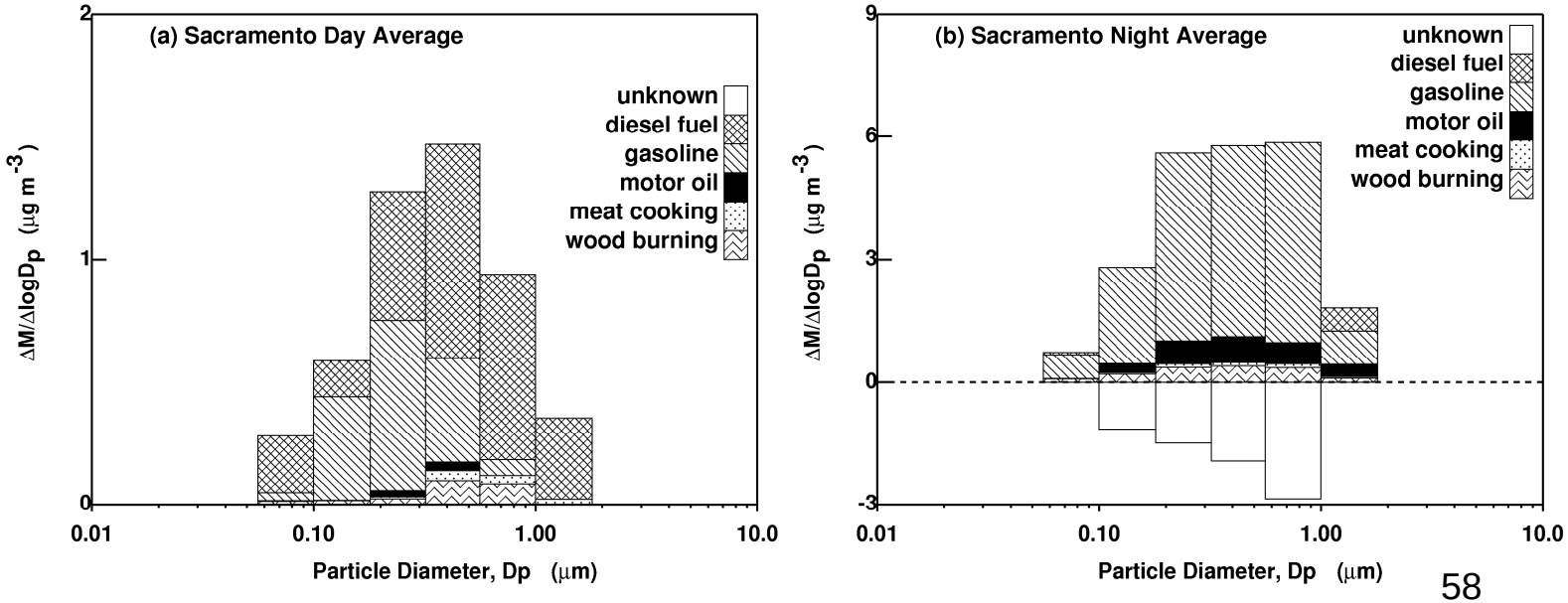
Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, C.A. Jakober, P.M. Fine, M.D. Hays, J.J. Schauer, and M.P. Hannigan. Source Apportionment of Ultrafine Airborne Particulate Matter (PM0.1) During a Severe Winter Pollution Episode. Environmental Science and Technology, submitted for publication.

Sacramento Size-Resolved Source Apportionment

Total Organic Compounds

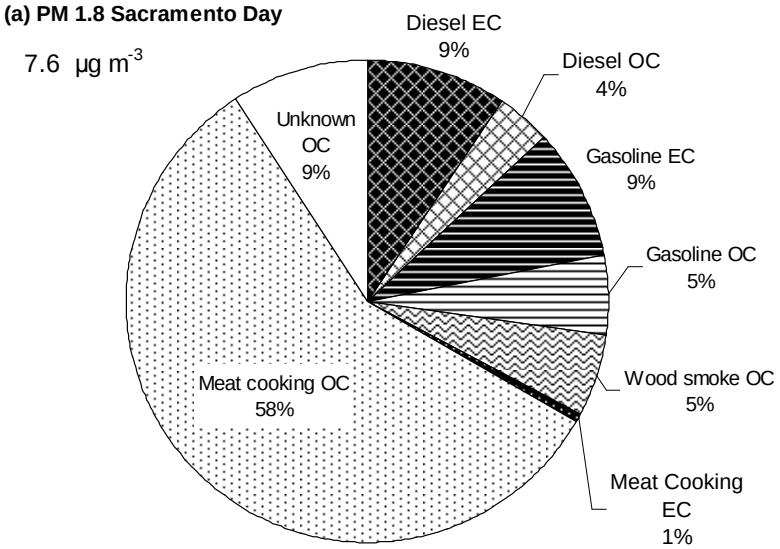


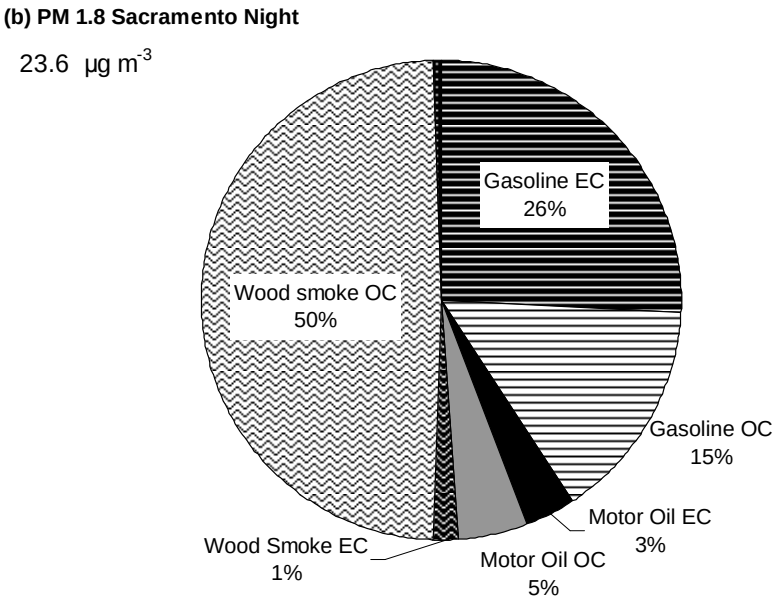
Elemental Carbon

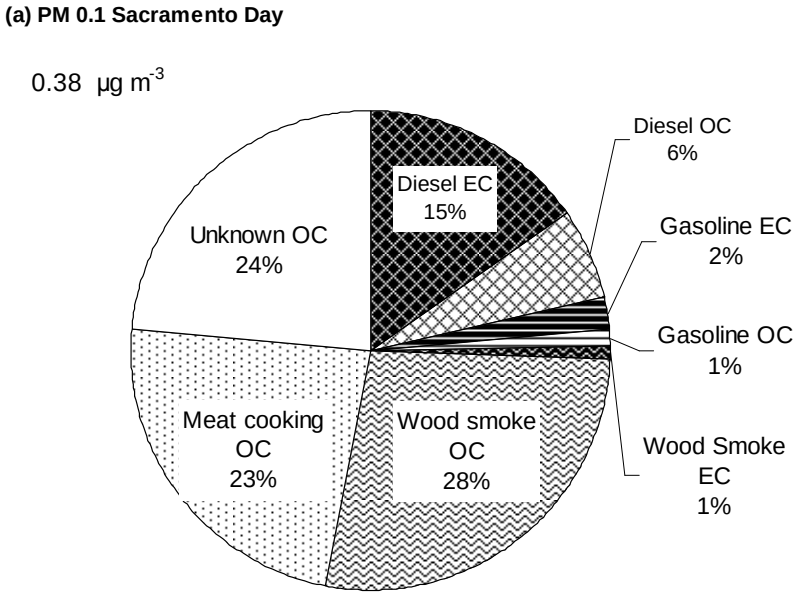


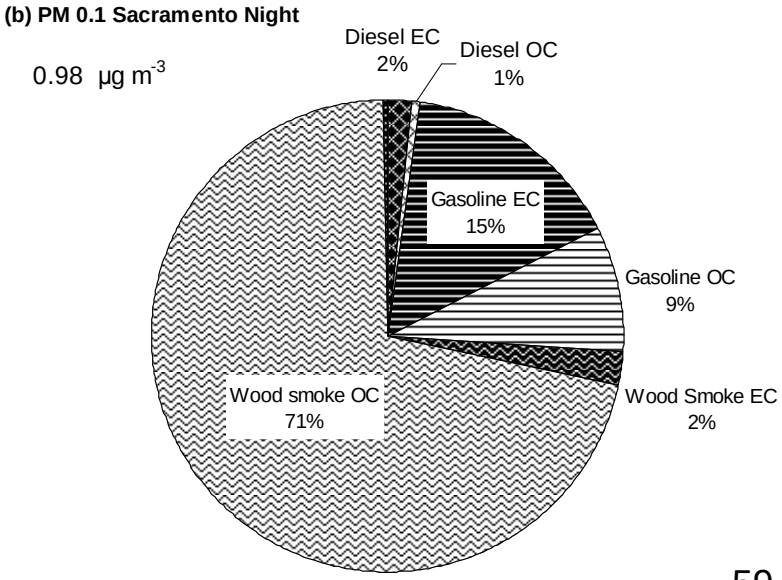
Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, C.A. Jakober, P.M. Fine, M.D. Hays, J.J. Schauer, and M.P. Hannigan. Source Apportionment of Ultrafine Airborne Particulate Matter (PM0.1) During a Severe Winter Pollution Episode. Environmental Science and Technology, submitted for publication.

Sacramento PM1.8 and PM0.1





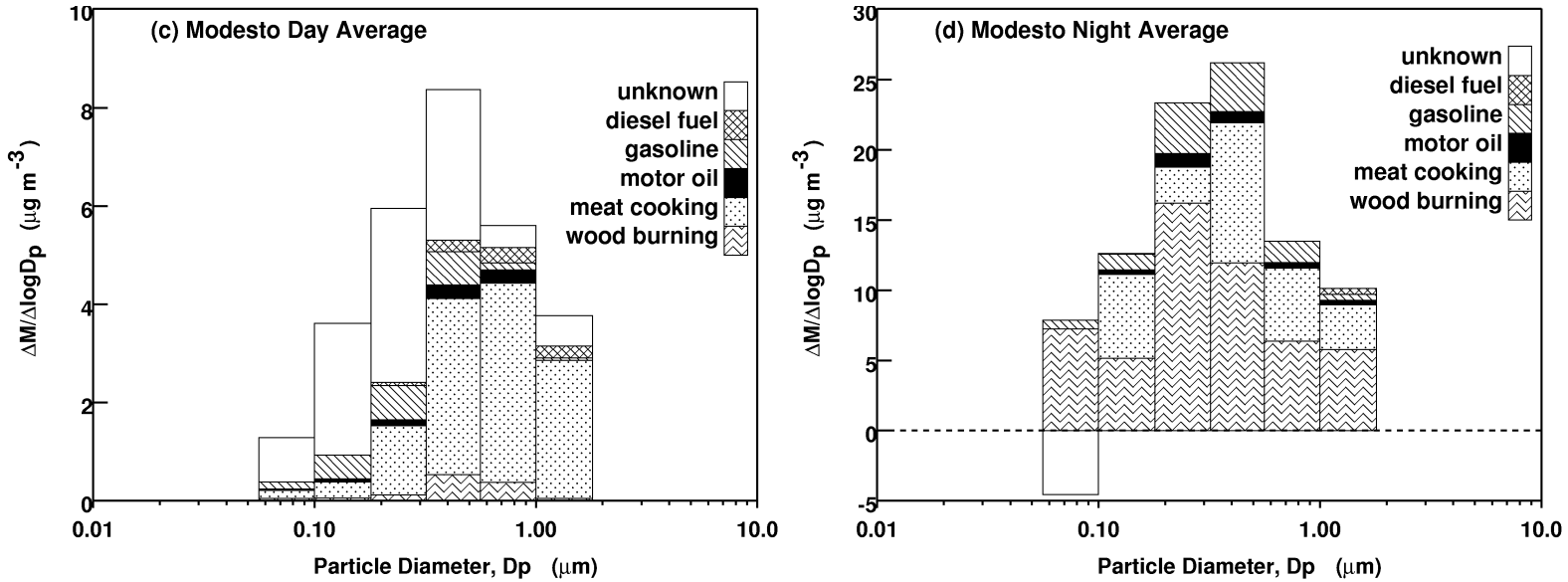




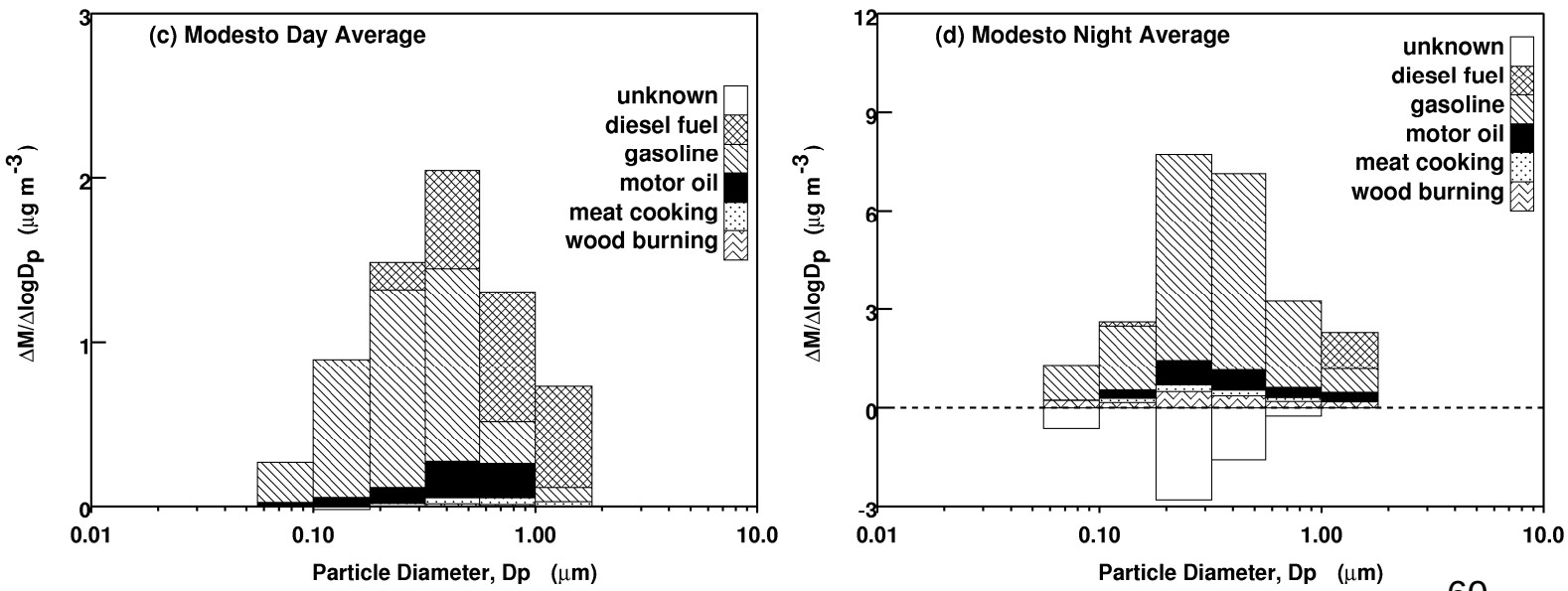
Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, C.A. Jakober, P.M. Fine, M.D. Hays, J.J. Schauer, and M.P. Hannigan. Source Apportionment of Ultrafine Airborne Particulate Matter (PM0.1) During a Severe Winter Pollution Episode. Environmental Science and Technology, submitted for publication.

Modesto Size-Resolved Source Apportionment

Total Organic Compounds



Elemental Carbon



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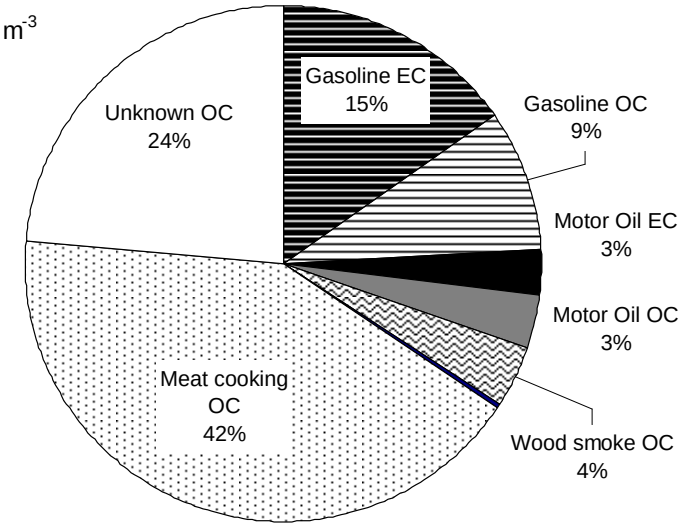
Modesto PM1.8 and PM0.1

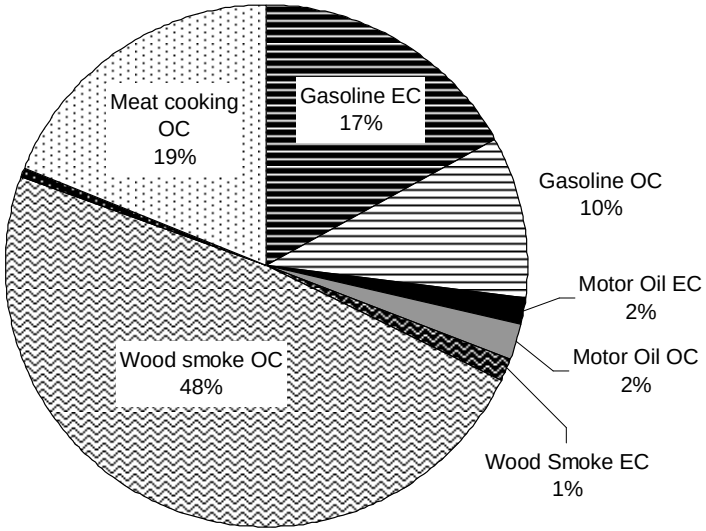
(c) PM 1.8 Modesto Day

11.0 μg m^{-3}



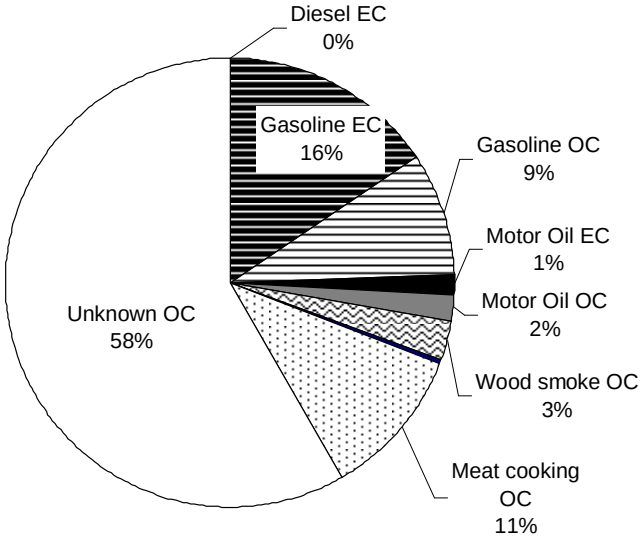
(d) PM 1.8 Modesto Night

27.9 μg m^{-3}



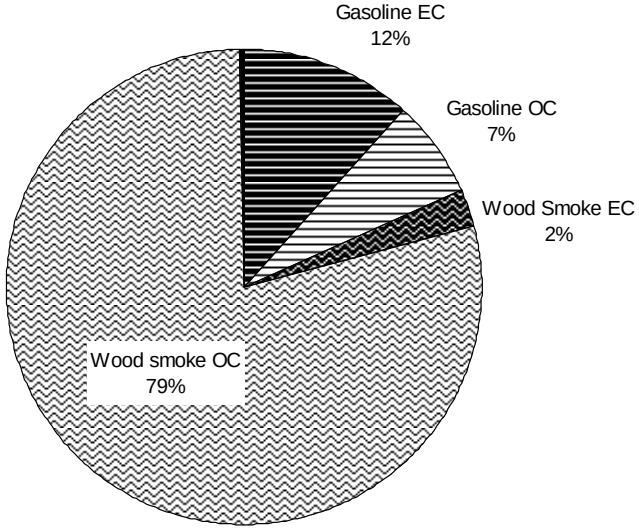
(c) PM 0.1 Modesto Day

0.39 μg m^{-3}



(d) PM 0.1 Modesto Night

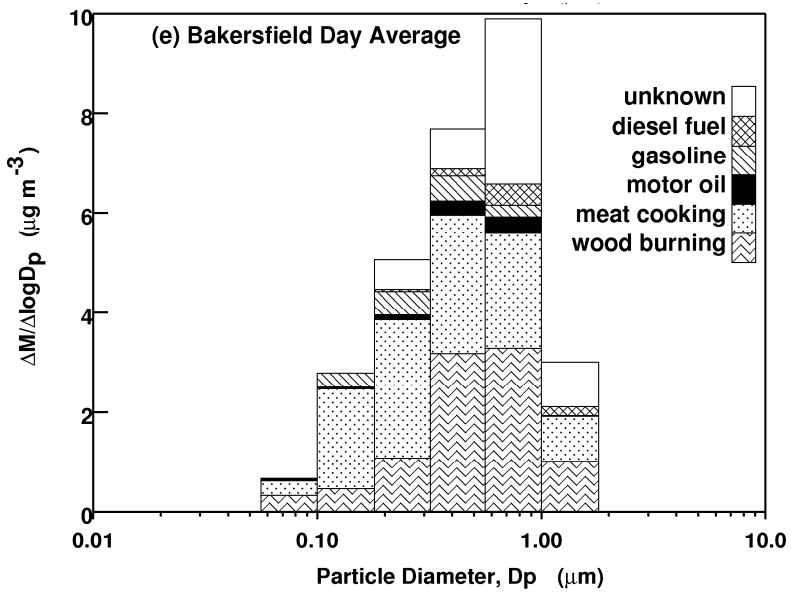
1.1 μg m^{-3}

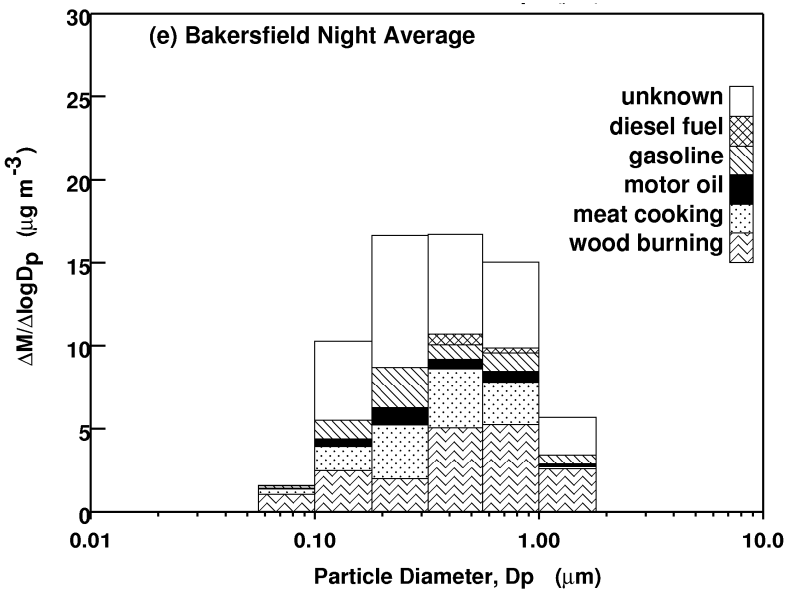


Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, C.A. Jakober, P.M. Fine, M.D. Hays, J.J. Schauer, and M.P. Hannigan. Source Apportionment of Ultrafine Airborne Particulate Matter (PM0.1) During a Severe Winter Pollution Episode. Environmental Science and Technology, submitted for publication.

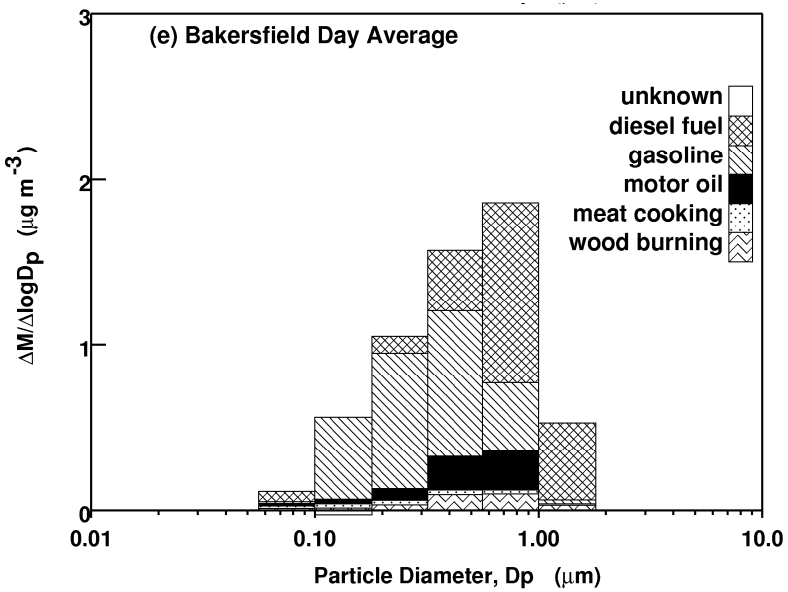
Bakersfield Size-Resolved Source Apportionment

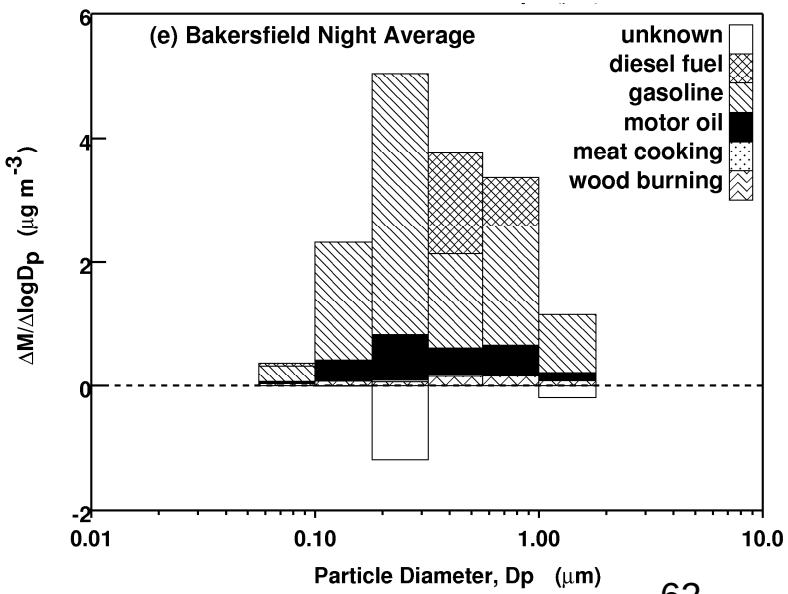
Total Organic Compounds





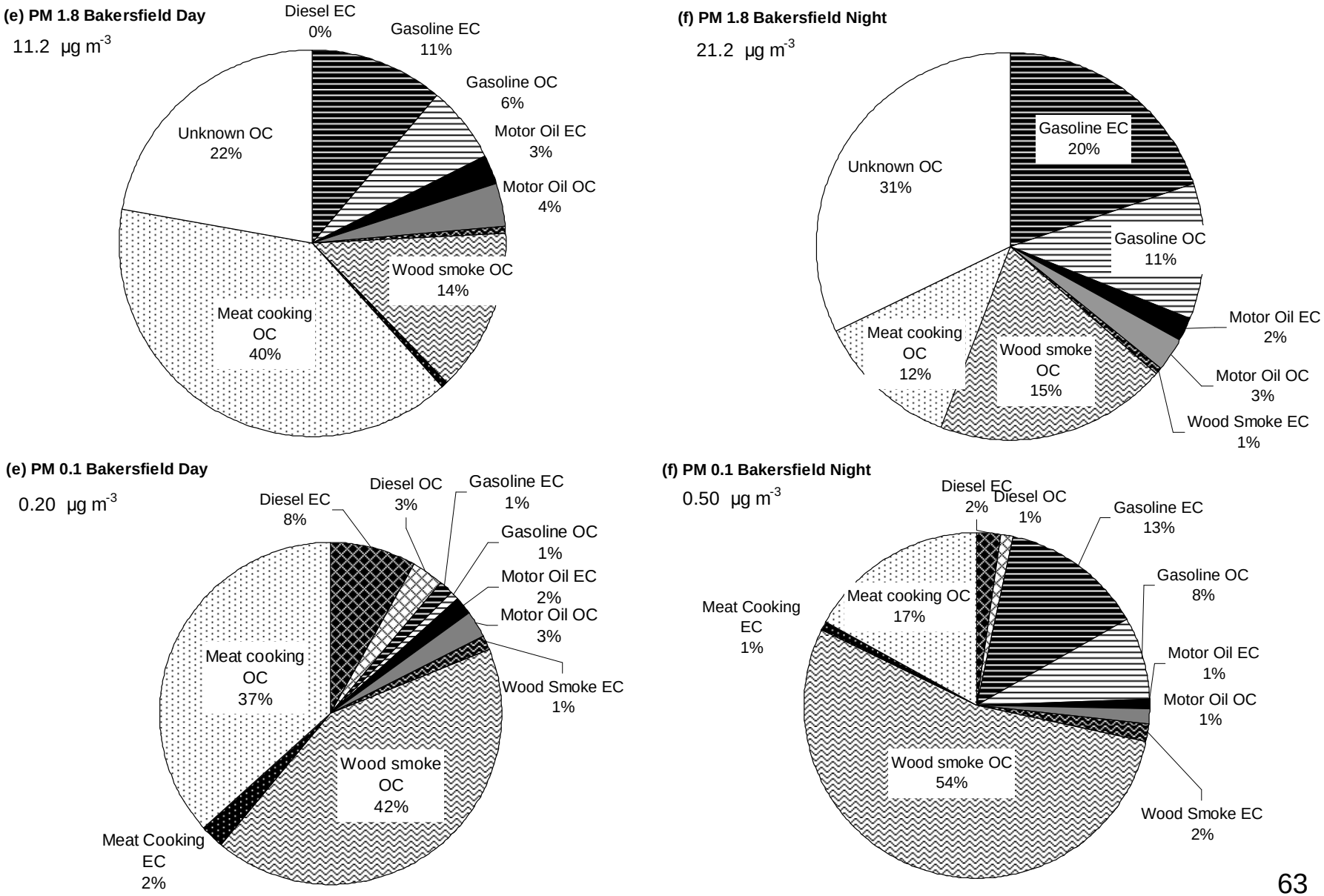
Elemental Carbon





Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, C.A. Jakober, P.M. Fine, M.D. Hays, J.J. Schauer, and M.P. Hannigan. Source Apportionment of Ultrafine Airborne Particulate Matter (PM0.1) During a Severe Winter Pollution Episode. Environmental Science and Technology, submitted for publication.

Bakersfield PM1.8 and PM0.1



Source: 2008 Kleeman, M.J., S.G. Riddle, M.A. Robert, C.A. Jakober, P.M. Fine, M.D. Hays, J.J. Schauer, and M.P. Hannigan. Source Apportionment of Ultrafine Airborne Particulate Matter (PM0.1) During a Severe Winter Pollution Episode. Environmental Science and Technology, submitted for publication.

Conclusions

- Size-resolved emissions of hopanes, steranes, and PAHs have been measured from light duty gasoline and heavy duty diesel vehicles under realistic driving cycles.
- The elemental carbon and organic carbon emissions from LDGVs and HDDVs are not perfectly correlated with hopanes and steranes.
- It is likely that lubricating oil and fuel make separate contributions to PM emissions from these sources.
- These measurements provide the basis for ultrafine source apportionment of LDGV and HDD exhaust particles in the atmosphere

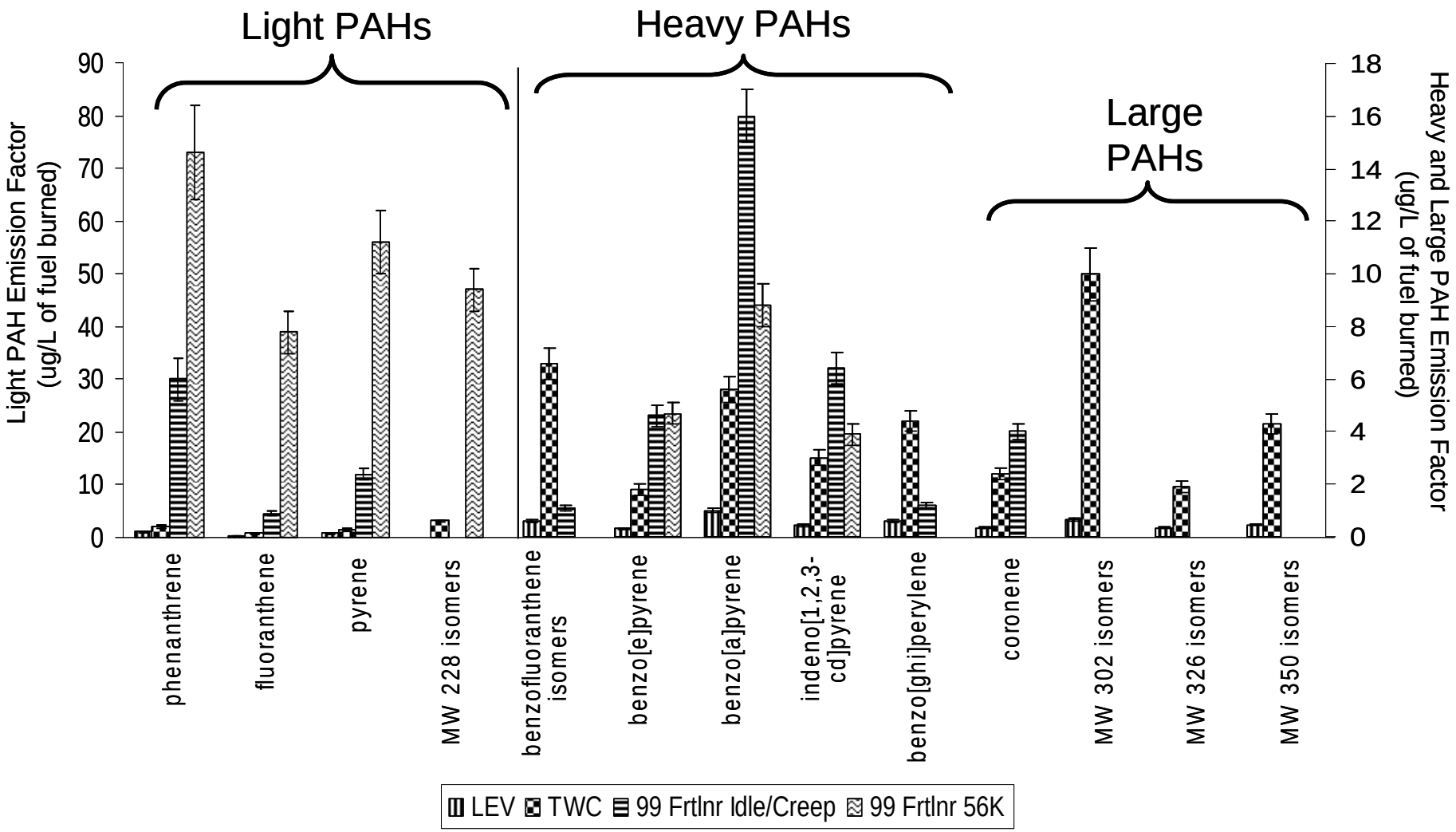
Conclusions

- Biomass combustion and food cooking had relatively uniform composition as a function of particle size
- PM0.1 in a roadside environment is dominated by diesel and gasoline engines
- PM0.1 in urban California cities is dominated by biomass combustion and food cooking during winter stagnation events

Some Final Thoughts

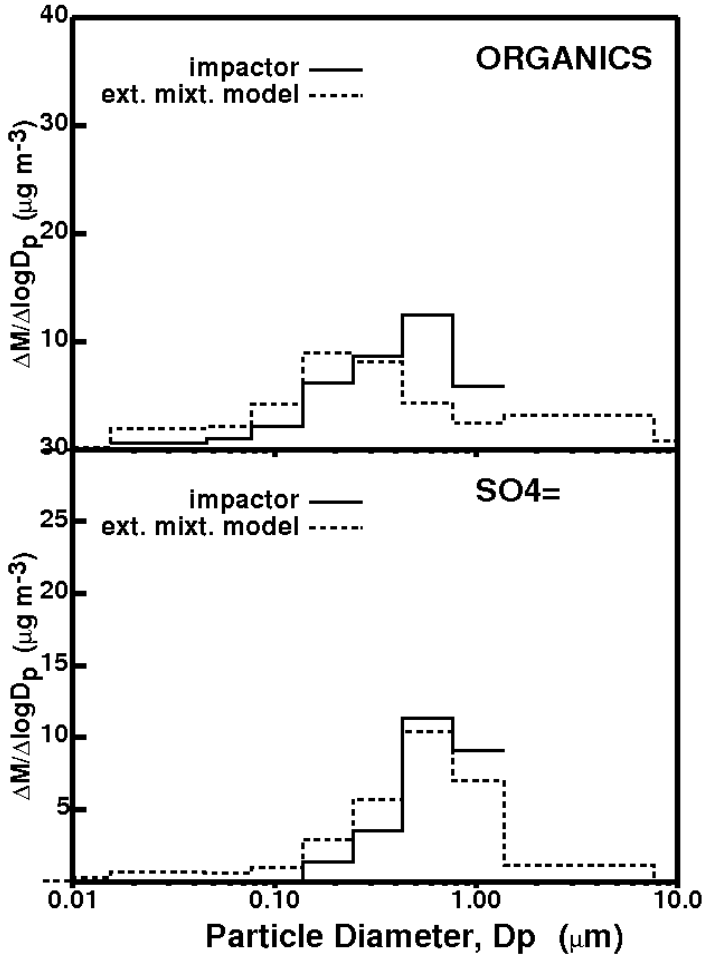
- What other interesting things did we find?

PAHs Heavier Than Coronene Exist in Gasoline Exhaust



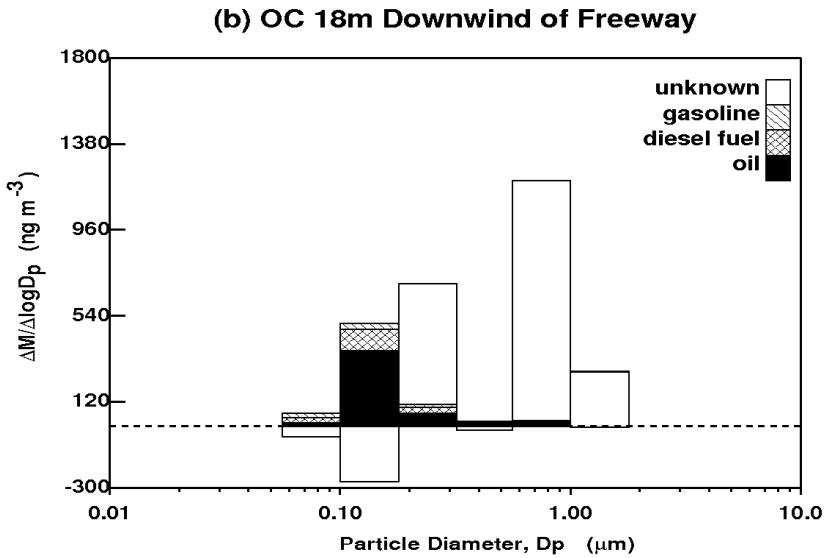
Source: 2007 Riddle, S.G., C.A. Jakober, M.A. Robert, T.M. Cahill, M.J. Charles and M.J. Kleeman. Large PAHs detected in fine particulate matter emitted from light-duty gasoline vehicles. Atmospheric Environment, 41, pp8658-8668.

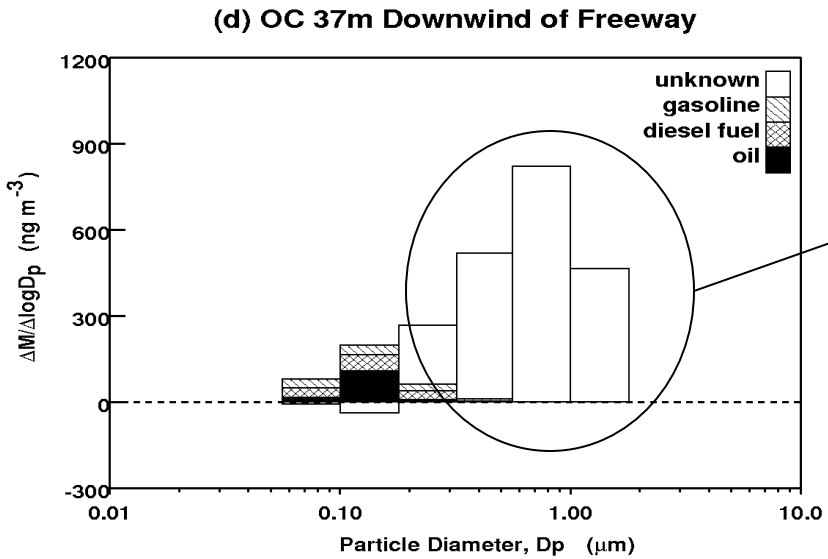
Predicted vs. Observed PM Concentrations at Riverside on 9/25/1996



Source: 2001 Kleeman M.J., G.R. Cass. A 3D Eulerian source-oriented model for an externally mixed aerosol. Environmental Science and Technology, 35: 4834-4848.

Size Distribution of Unexplained Particle Organic Carbon In Roadside Environment





Unexplained OC has the same size distribution as background sulfate (not shown)

Source: 2008 Riddle, S., M.A. Robert, C.A. Jakober, M.P. Hannigan, and M.J. Kleeman. Size-resolved Source Apportionment of Airborne Particulate Matter in a Roadside Environment. Environmental Science and Technology, 42, pp6580-6586.