Estimating Contributions of Diesel Exhaust to Ambient PM

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Reno, Nevada

MATES III Technical Advisory Group Meeting

SCAQMD, Diamond Bar

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MATES II Approach

- Estimated ambient concentrations of diesel PM by applying a factor of 1.04 to the measured EC concentrations.
  - Factor assumes that diesel PM consists of 64% EC and 36 % OC.
  - Diesels account for 67 percent of the ambient fine particulate EC.
- Diesel PM accounted for 3.4 μg/m^3 of the eight-site annual average total $PM_{2.5}$ carbon of 9.8 μ g/m^3.
- Uncertainties
  - Factors are should be updated to current emissions.
  - The PM emission inventory does not reconcile with the ambient carbon measurements. Carbon too low relative to PM.
  - Secondary organic aerosols may be significant.
  - Source of two-third of the ambient $PM_{2.5}$ carbon was not identified in the MATE II report and no risk is attributed to this residual particulate carbon.

Overview

- On-road diesel and gasoline vehicle PM emissions trends.
- Variations in exhaust emission rates.
  - cold starts versus hot stabilized
  - engine load
  - smokers and other high-emitters
  - ambient temperature
- Chemical composition of motor vehicle fuels, lube oils, and exhaust.
  - organic and elemental carbon
  - PAH (gaseous, semi-volatile and particulate)
  - hopanes and steranes
  - elements
- Contributions of diesel and gasoline exhaust and other combustion sources to ambient PM
  - Chemical Mass Balance
  - Multiple Regression
- HEI Study: Assessing Exposure to Air Toxics in Microenvironments Dominated by Mobile Sources

On-Road Motor Vehicle PM Emissions Characterization Studies

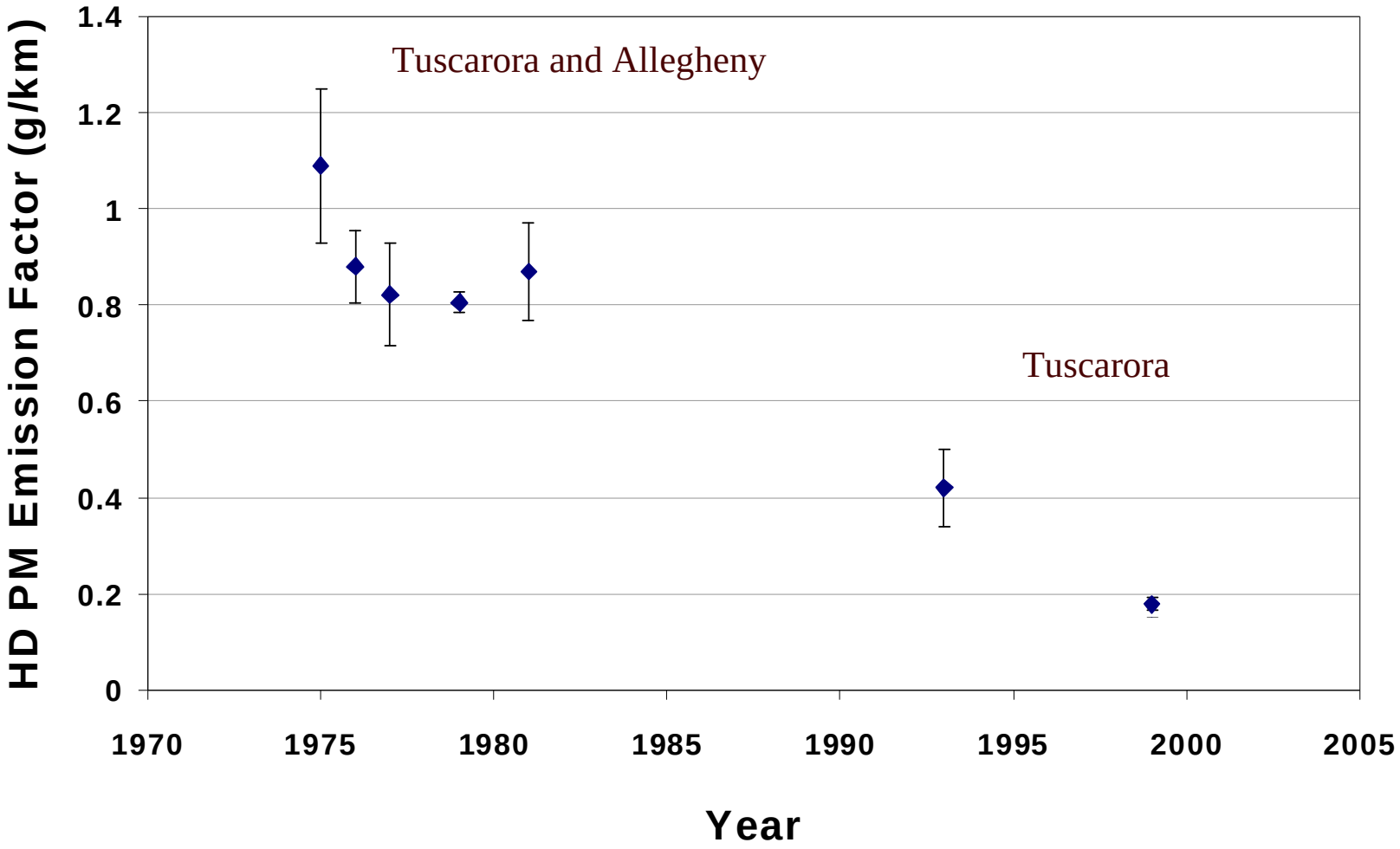
Completed Studies

- Northern Front Range Air Quality Study
- Comparative Toxicity Study (DOE OHVT-NREL)
- Characterization of PM Emissions from DoD Sources (DOD-SERDP)
- EC Diesel Fuel Emission Characterization Study (DOE OHVT-NREL)
- In-Use Light-Duty Gasoline Vehicle Particulate Matter Emissions on Three Driving Cycles (GM and CRC)

Current Studies

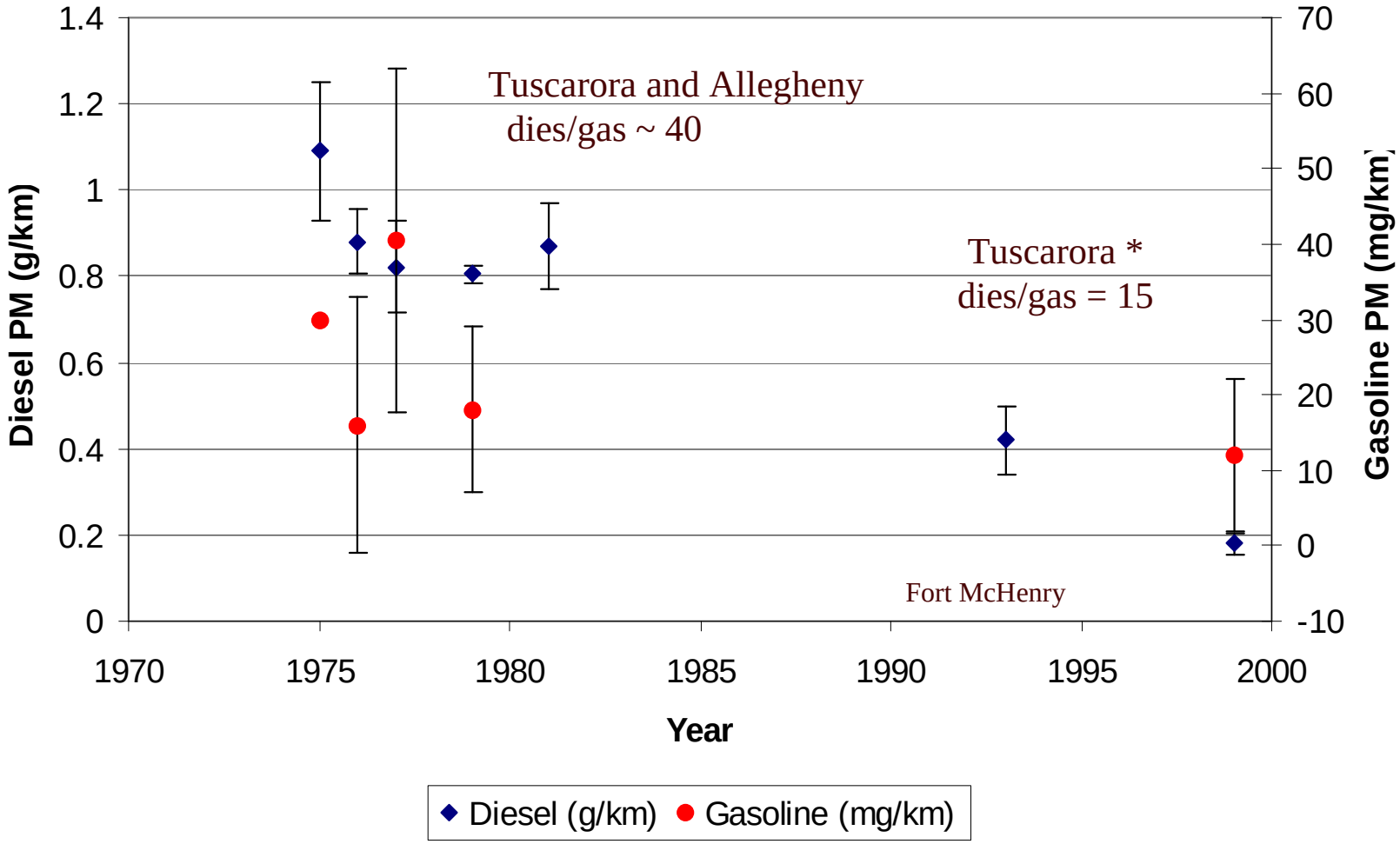
- Gas/Diesel Split (DOE OHVT-NREL)
- CRC E-55 - Heavy-Duty Vehicle Chassis Dynamometer Testing for Emission Inventory, Air Quality Modeling, Source Apportionment, and Air Toxic Inventory (DOE OHVT, CRC, EPA, others)

Trend in HDD PM_{10} Emission Rates
Roadway Tunnel Studies



Source: Gertler et al.

Trends in Particulate Emission Rates Measured in Highway Tunnels



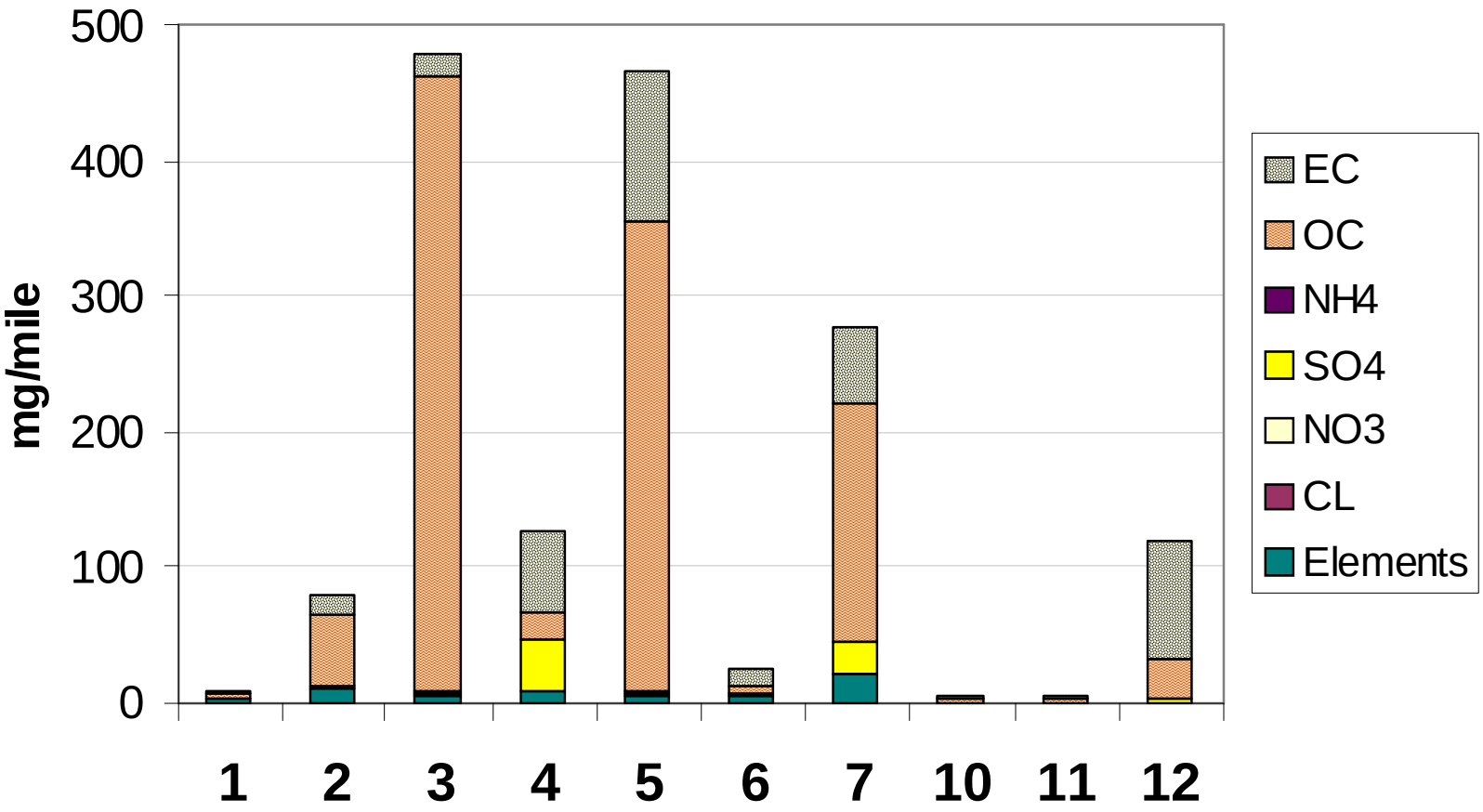
* Source: Preliminary results from HEI Project 98-3 courtesy of Gertler et al. Desert Research Institute.

Average PM Emission Rates (mg/mi)

		FTP						
Emission Class	Fuel	Phase 1	Phase 2	Phase 3	Composite		Hot UC	REP05
Tier 0 (1990-95)	Nonoxy	42.8	1.6	2.3	10.3		4.0	14.7
	Oxy	24.7	2.1	2.9	7.0		5.2	15.3
Tier 1 (1994-97)	Nonoxy	18.2	0.6	1.3	4.4		1.7	7.5
	Oxy	12.8	0.6	1.3	3.3		1.2	6.2
High Emitter	Nonoxy	95.9	5.0	17.9	27.4		31.0	56.9
	Oxy	63.5	3.7	44.1	27.2		27.2	49.6
Source: Cadle et al. (1998). CRC Project E-24-1								

	FTP	Hot UC	REP05
Ave speed, mph	19.6	24.6	51.5
Max speed, mph	56.7	67.2	80.3
Max accel&decel, mph/s	3.3	6.9	8.5

DOE Comparative Toxicity Study

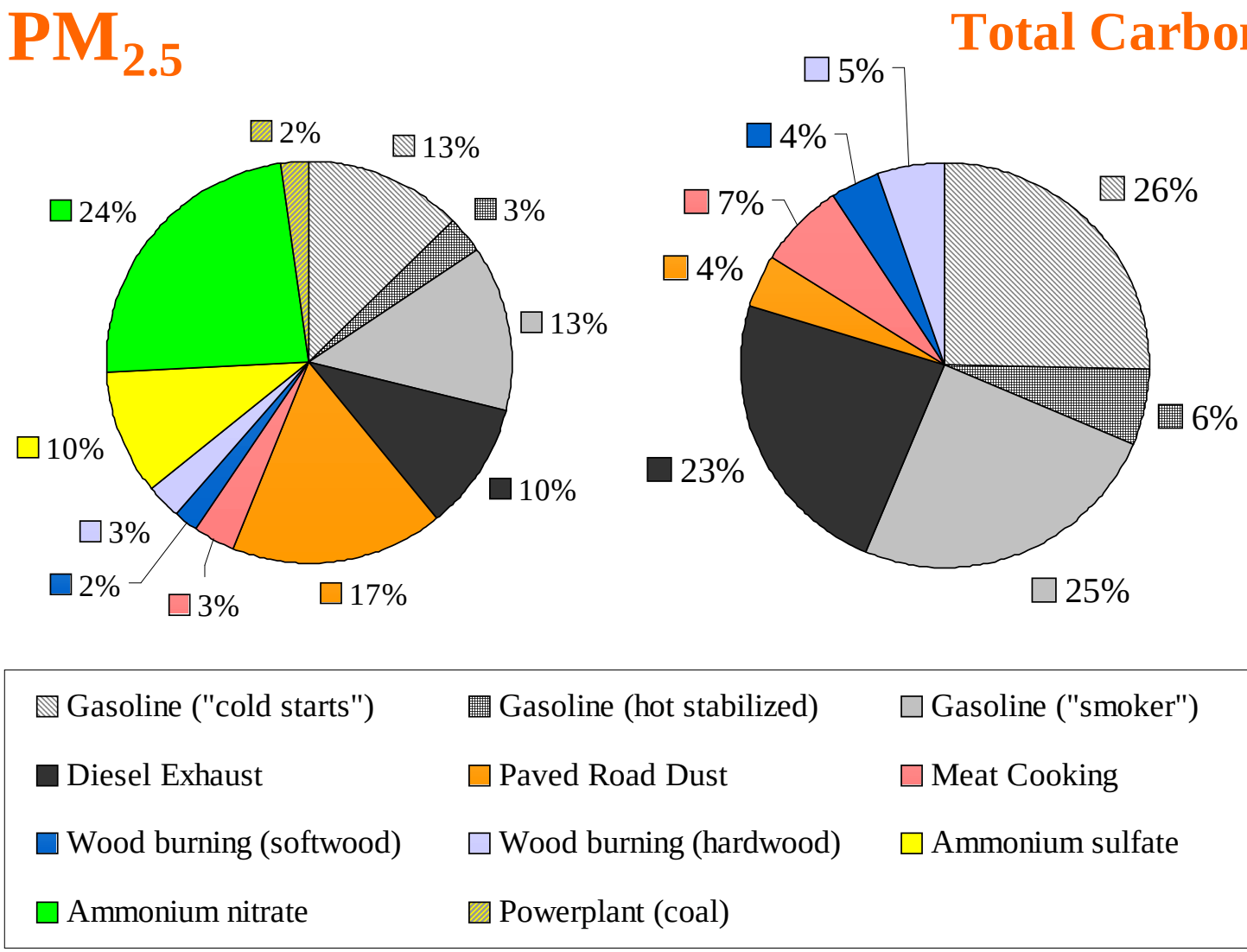


1. Gasoline Average
2. Gasoline Black Smoker
3. Gasoline White Smoker
4. Diesel Current
5. Diesel High Emitter

6. Set No. 1 at 30 °F
7. Set No. 4 at 30 °F

10. New Technology, Gasoline A
11. New Technology, Gasoline B
12. New Technology, Diesel

$PM_{2.5}$ and Total Carbon Source Contribution Estimates



Source: Northern Front Range Air Quality Study

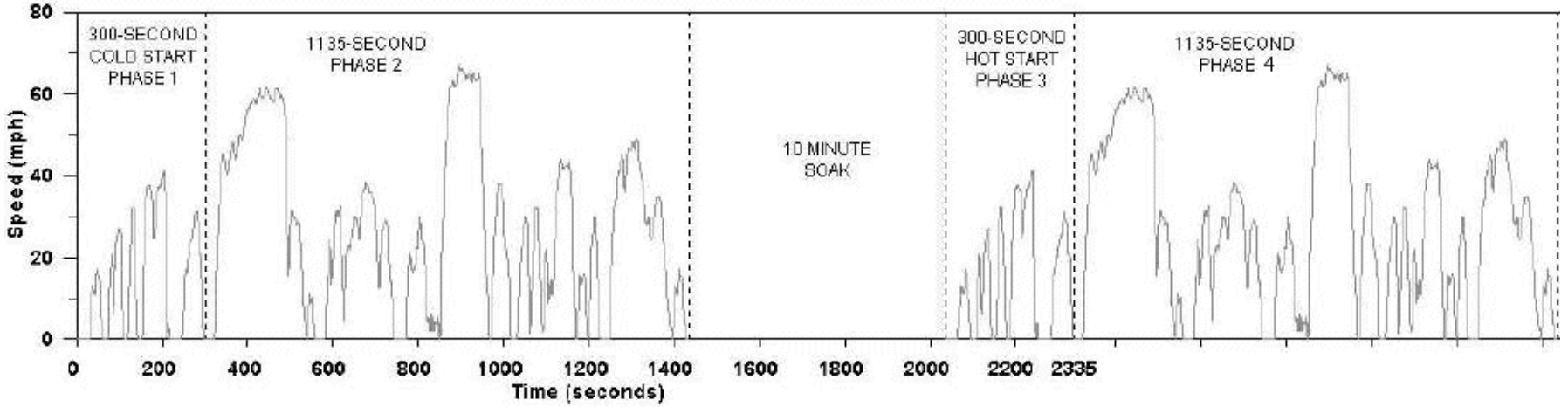
Gasoline/Diesel PM Split Study Participants

- Bureau of Automotive Repair and SCAQMD
  - Light-duty vehicle recruitment
  - Smog check
- California Trucking Associations
  - Heavy-duty vehicle recruitment
- Ralphs Grocery Distribution Center
  - Test site and logistics
- U.S. Environmental Protection Agency and Clean Air Vehicle Technology Center
  - LD vehicle dynamometer measurements
- West Virginia University
  - MDD and HDD Truck dynamometer measurements
- Desert Research Institute and University of Wisconsin Madison
  - Source and ambient measurements and source apportionment

Gasoline/Diesel PM Split Study
LD Vehicle Recruitment Sample

Category	Model Year	Odometer (miles)	Number of Vehicles	Number of Composites
1	1996 and newer	low mileage (< 50,000)	4	1
2	1993-95	low mileage (< 75,000)	4	1
3	1996 and newer	high mileage (> 100,000)	4	1
4	1990-92	lower mileage (< 100,000)	4	1
5	1993-95	higher mileage (> 125,000)	8	2
6	1990-92	> 125,000	9	3
7	1986-89	> 125,000	6	3
8	1981-85	> 125,000	6	3
9	1980 and earlier	> 125,000	6	3
10	Smoker	no model year or odometer criteria	6	6
11	LD Diesel	no model year or odometer criteria	2	2
		Total	59	26

Gasoline/Diesel PM Split Study –
Light-Duty Vehicle Driving Cycle:
Modified Unified Driving Cycle (LA92)



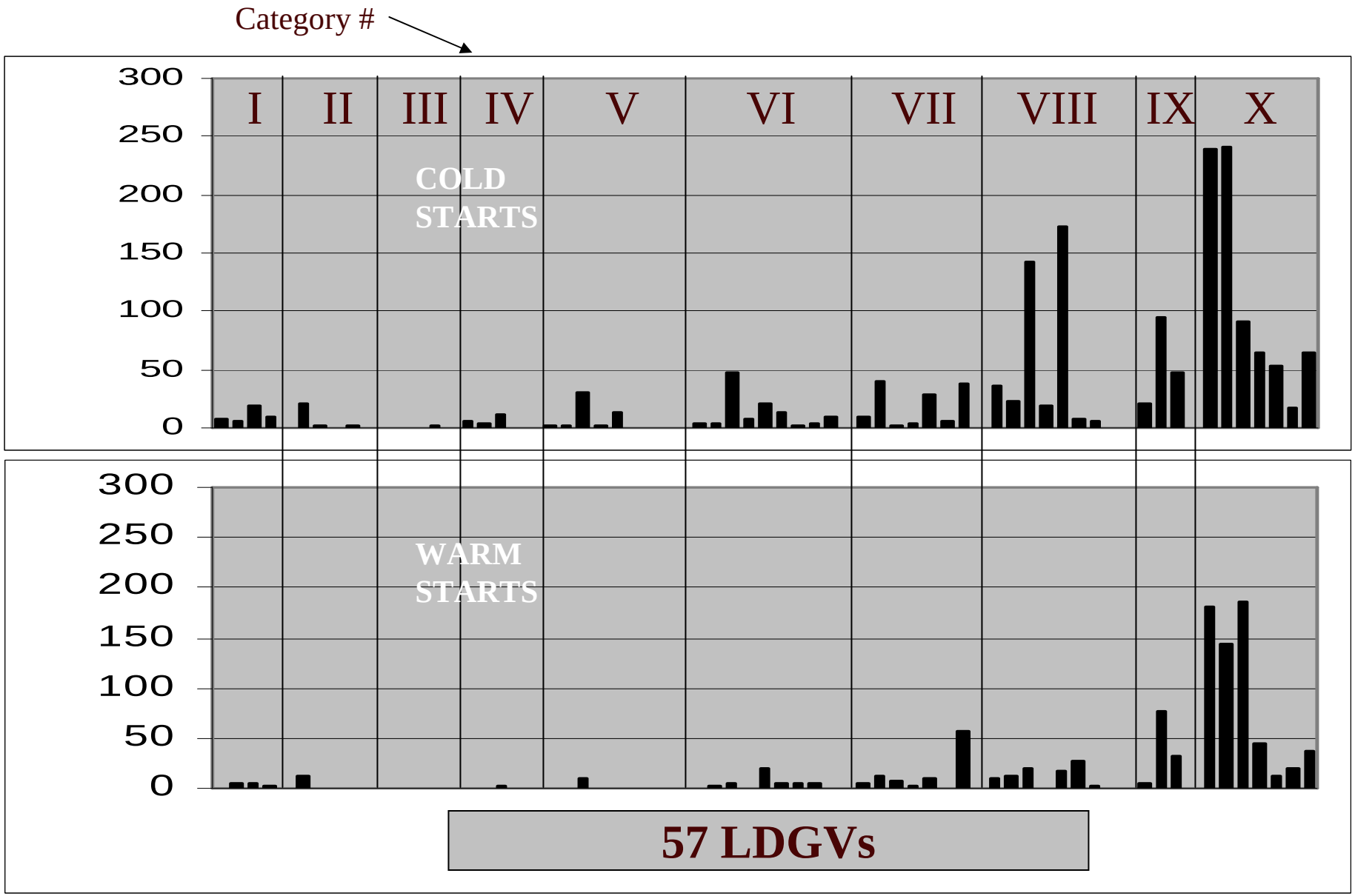
- Modified Unified Cycle – Phases 3 and 4 are a warm repeat of phases 1 and 2
- 2 sampling phases: “Cold” phase and “Hot” phase, each lasting 1435 seconds; 24.6 mph ave. speed


MX-6
mazda
3SJB343

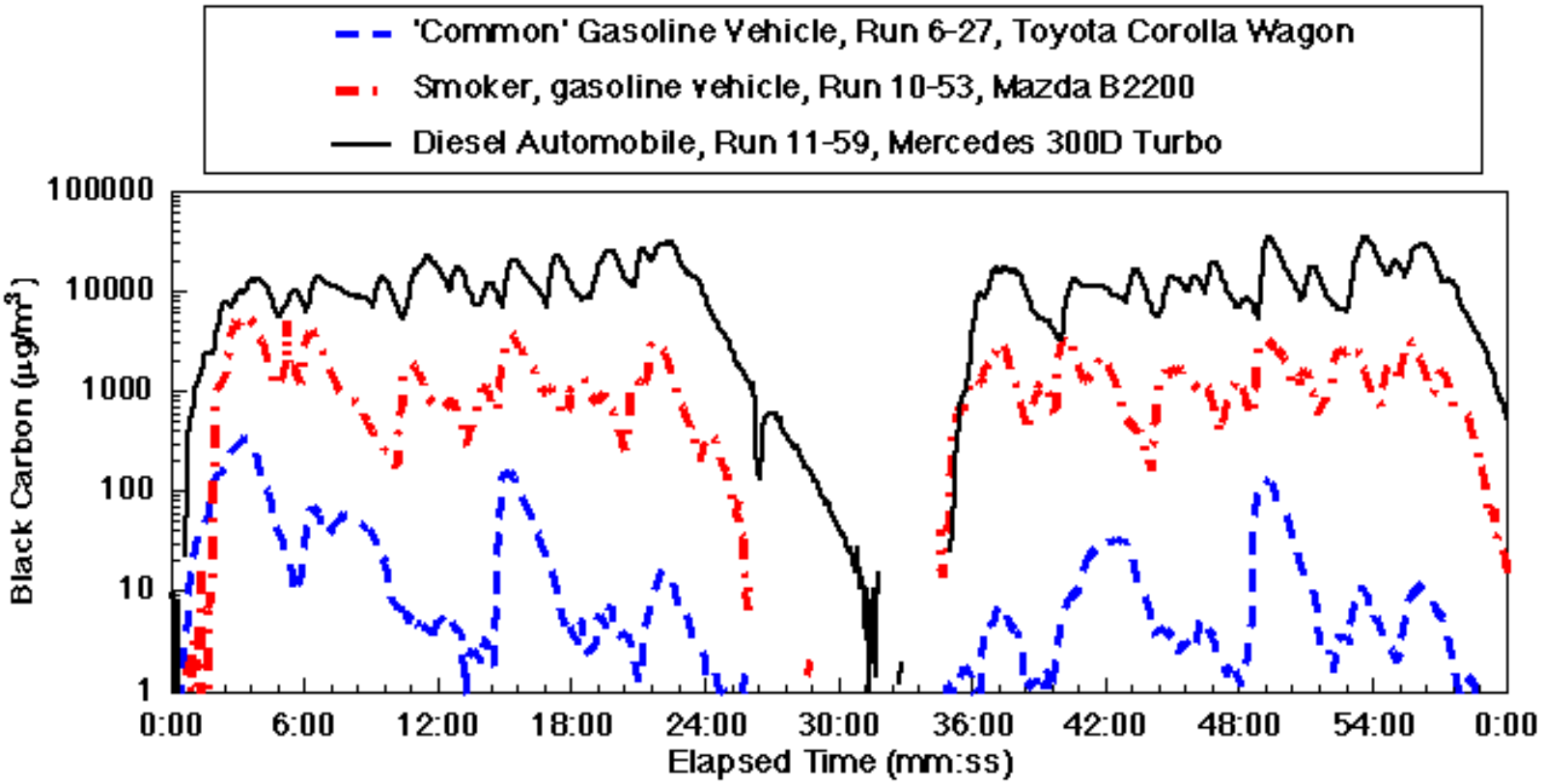

UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY

LDV and HDV Exhaust Sampling Systems

PM2.5 Emission Rates (mg/mi) for LDGVs

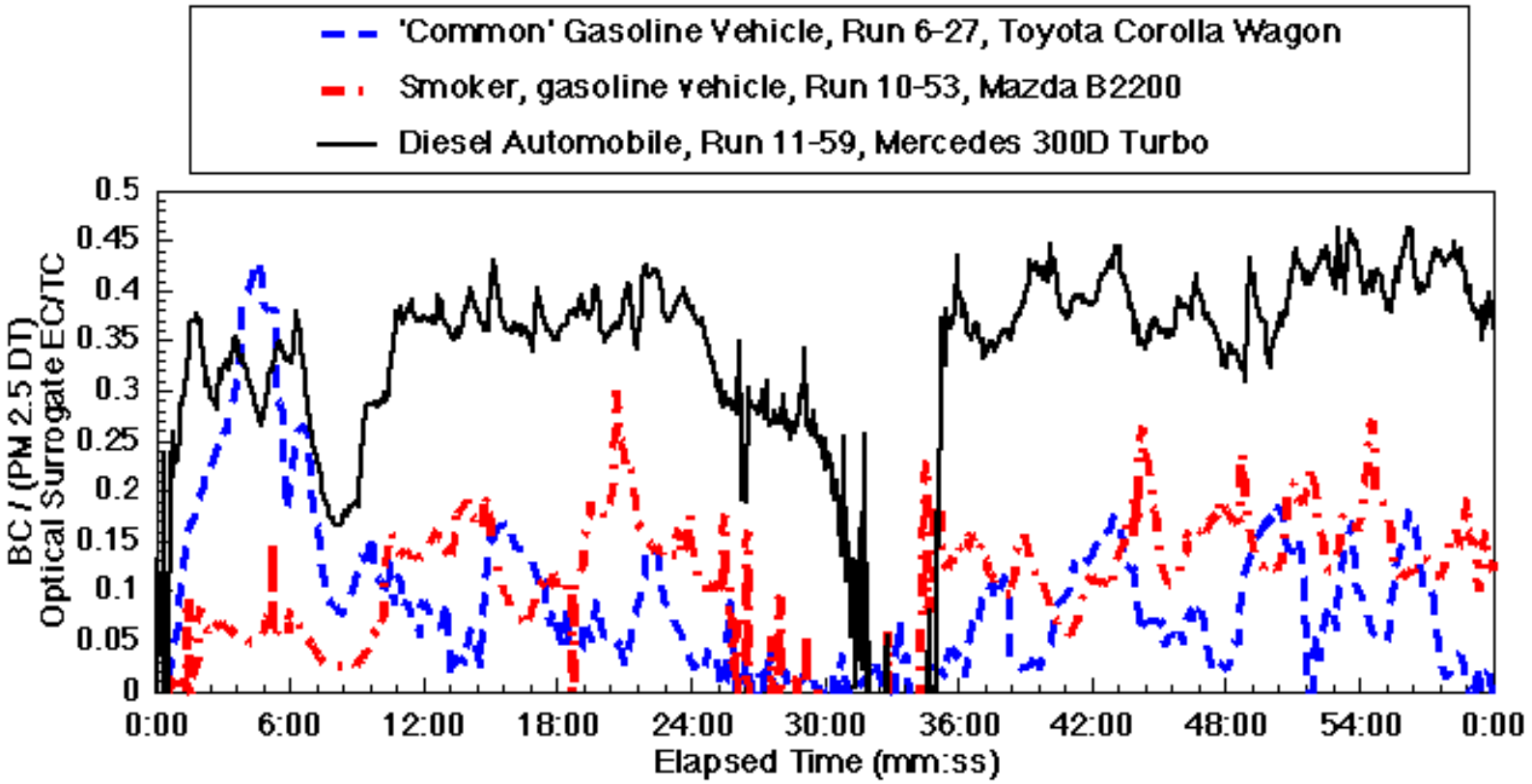


PRELIMINARY



Source: Pat Arnott (2001), NREL Gas/Diesel Split Study

PRELIMINARY



Source: Pat Arnott (2001), NREL Gas/Diesel Split Study

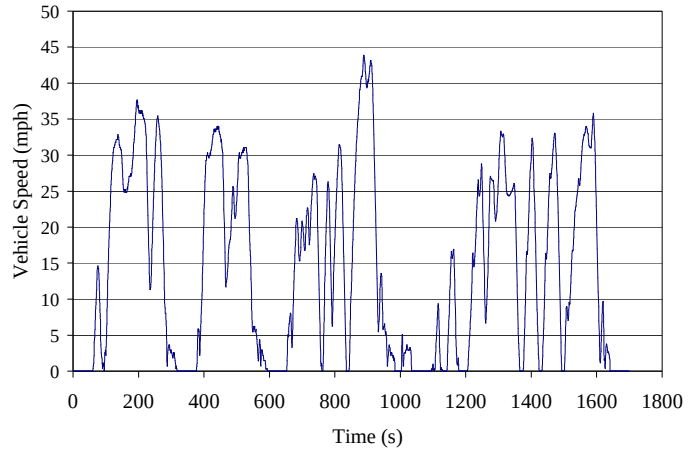
Soot is produced by spark-ignition vehicles…
(from the tailpipe of relatively new Toyota Prius at NREL)

Gasoline/Diesel PM Split Study
Heavy-Duty Vehicle Sampling

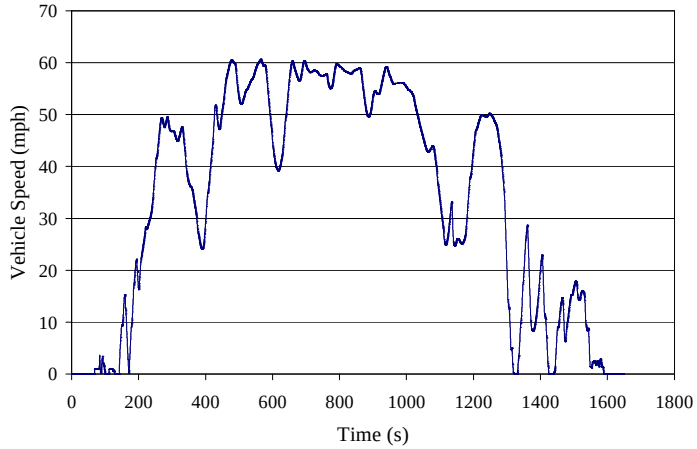
- 34 HD vehicles grouped by model year; tested over a variety of cycles, including cold starts and idle
  - 2 transit buses
  - 16 >33,000 lbs. GVW
  - 8 14,000-33,000 lbs. GVW
  - 8 <14,000 lbs. GVW
- All vehicles tested with CA diesel fuel; 5 tested with federal diesel fuel

Gasoline/Diesel PM Split Study
Heavy-Duty Vehicles Tested Over Several Driving Cycles

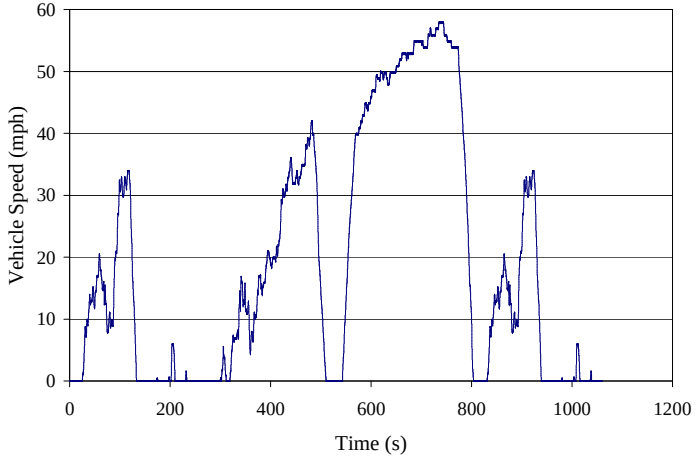
Gasoline/Diesel PM Split Study –
Heavy-Duty Vehicle Test Cycles



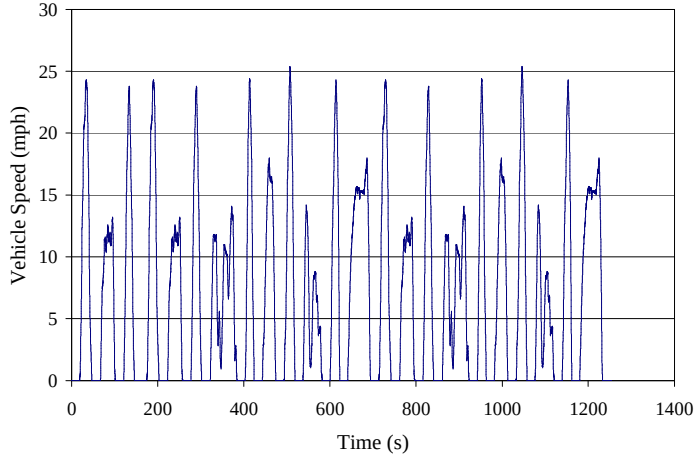
City/Suburban Heavy Vehicle Route (CSHVR)



Highway

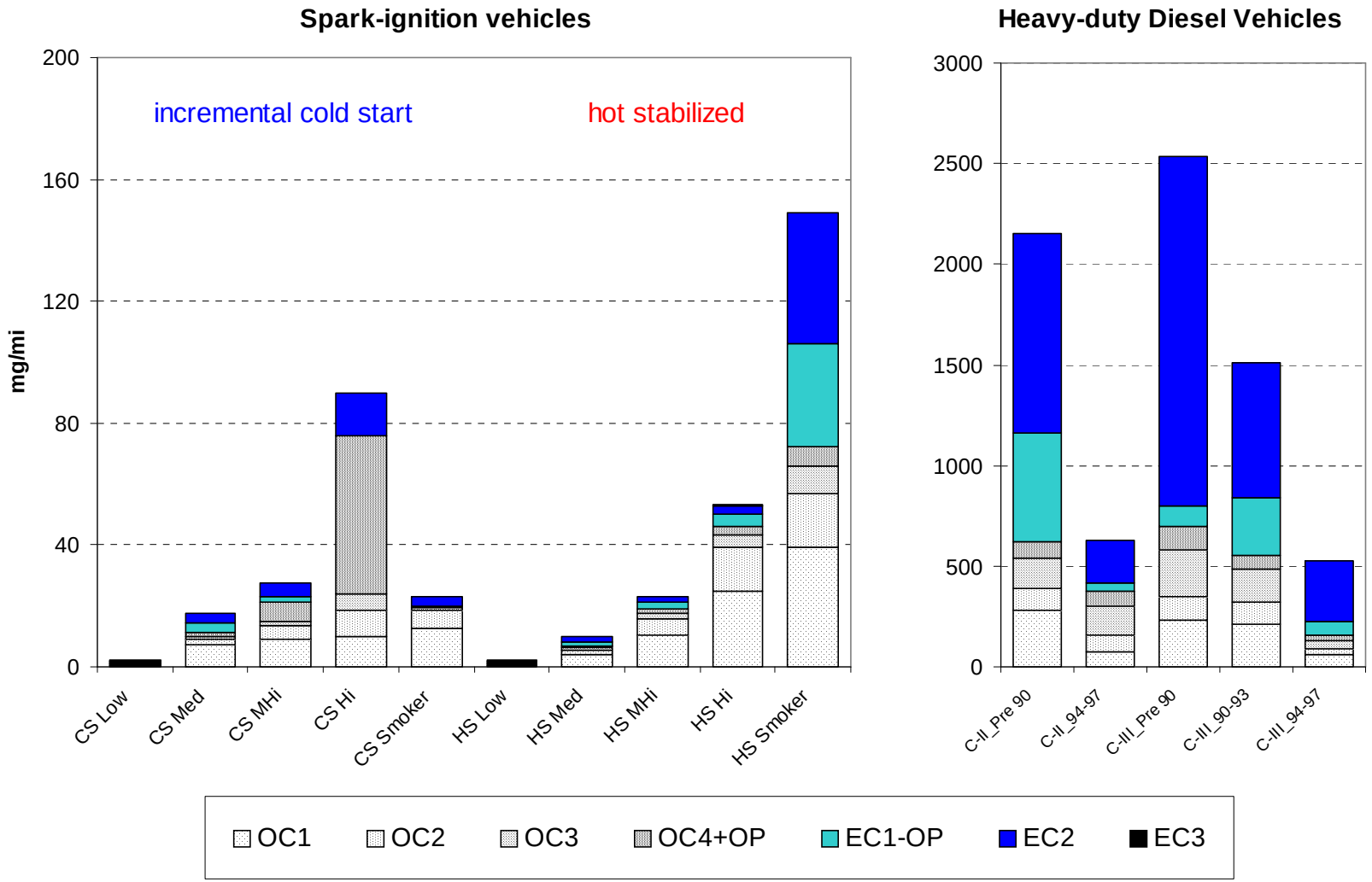


HD Urban Dynamometer Driving Schedule (UDDS)

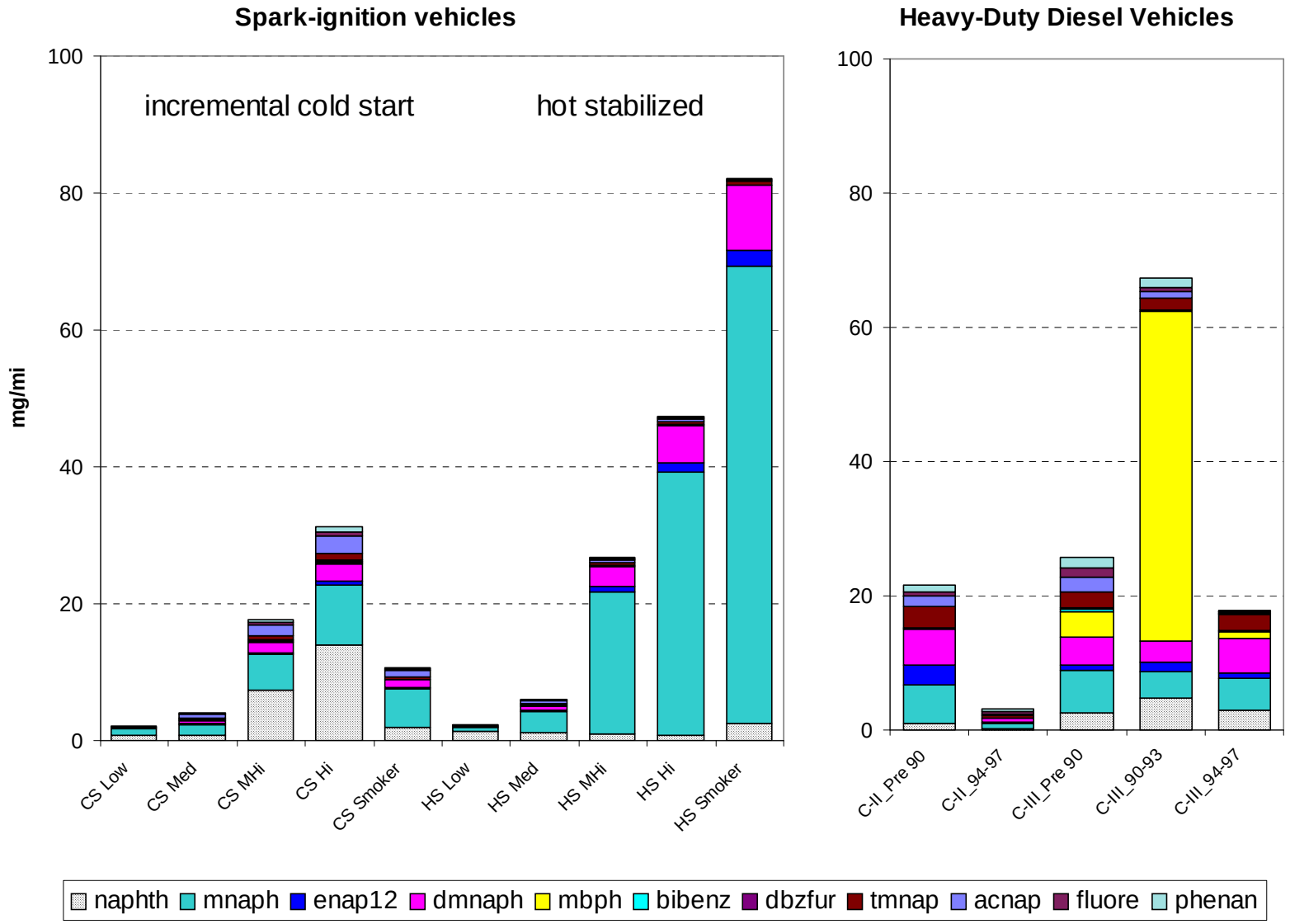


Manhattan

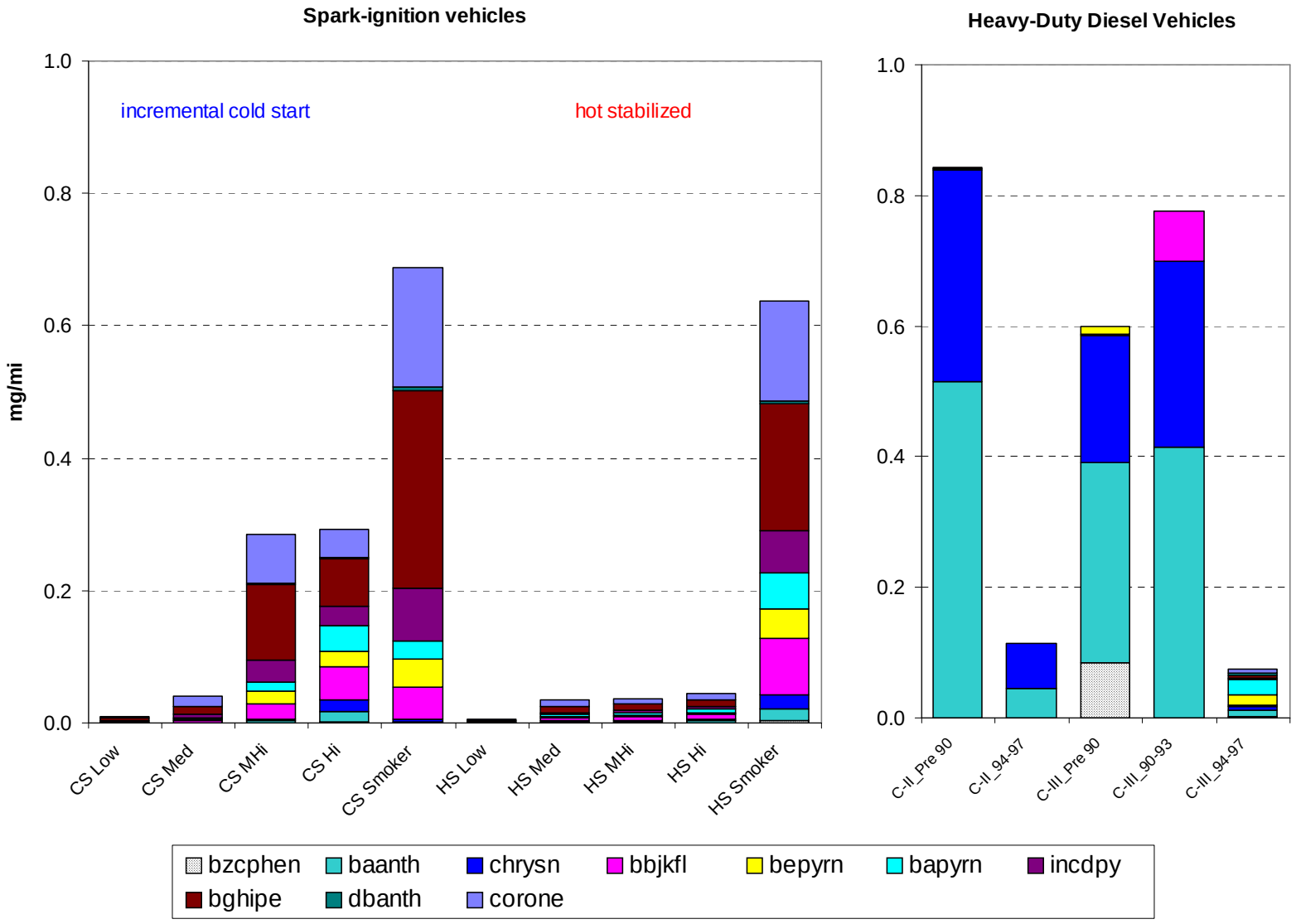
Gas Diesel PM Split Study
IMPROVE TOR OC and EC Emission Rates



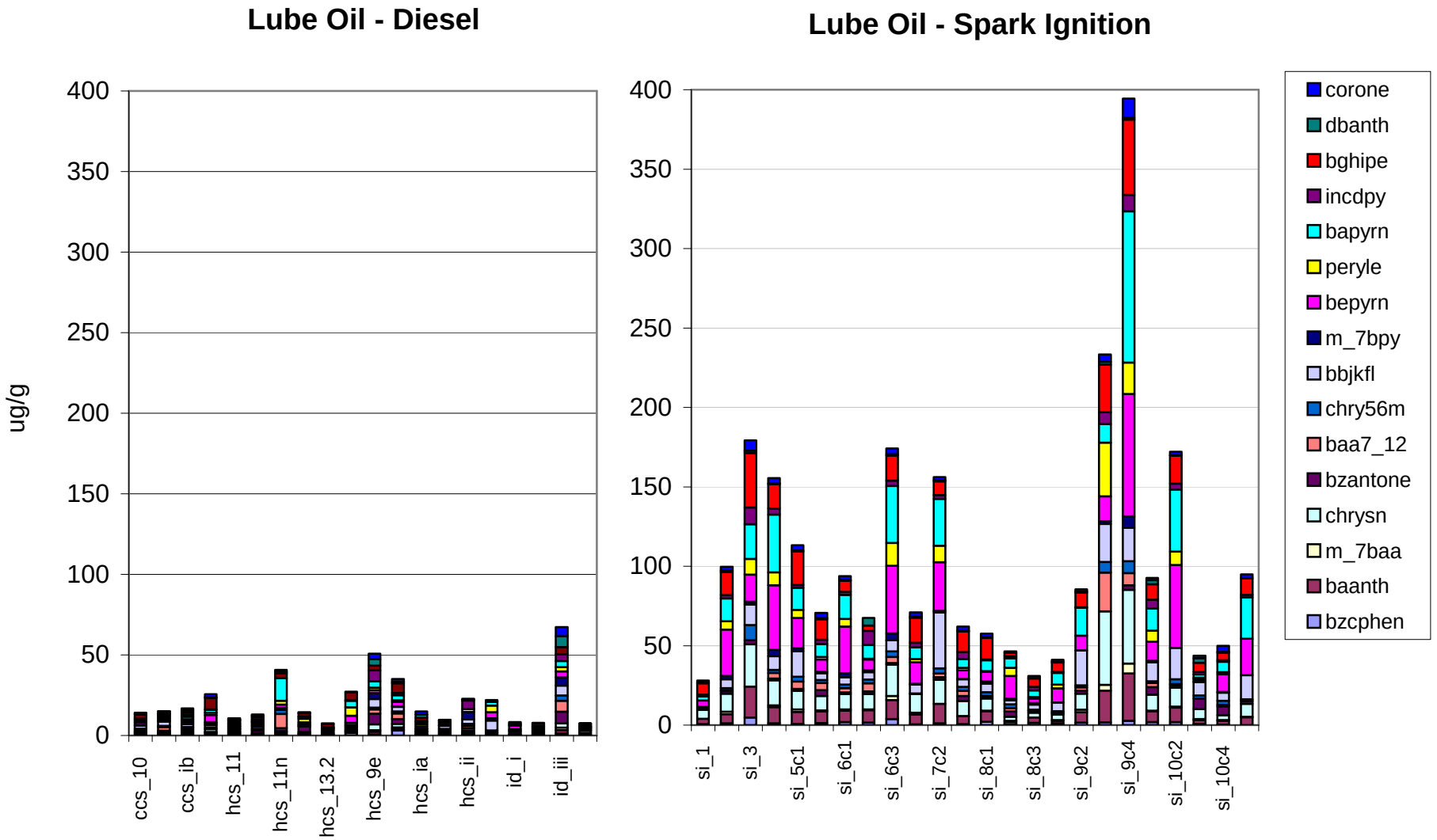
Gas Diesel PM Split Study – Volatile PAH



Gas Diesel PM Split Study – Particle PAH



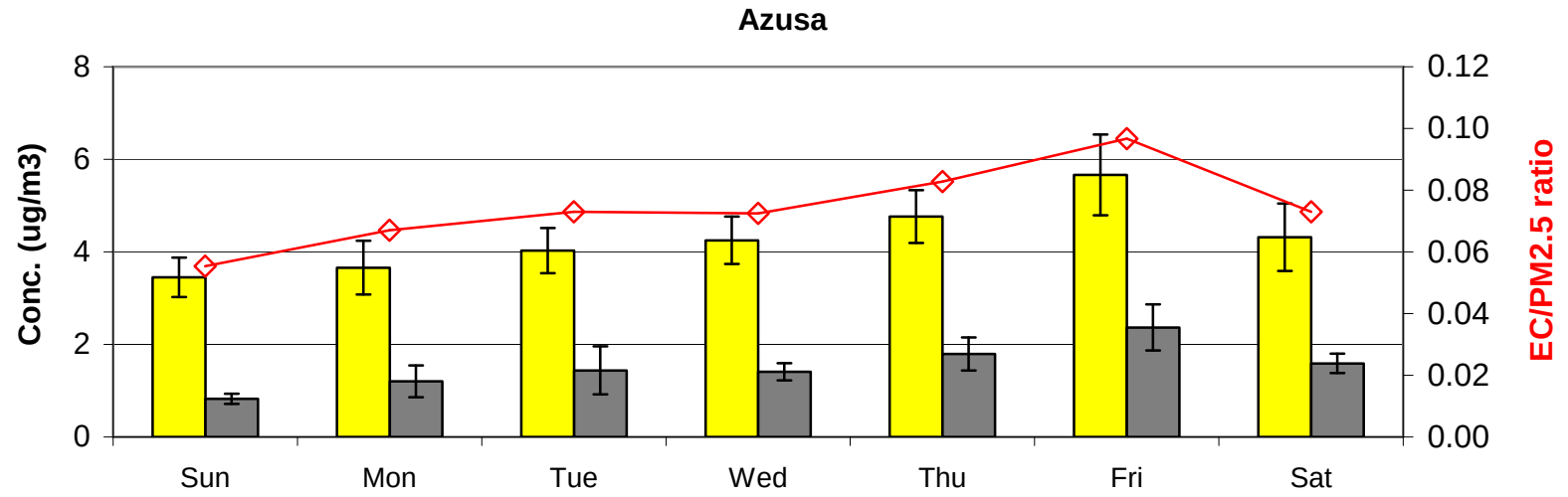
DOE Gasoline/Diesel PM Split Study
Particle-Phase PAH in Lubrication Oil

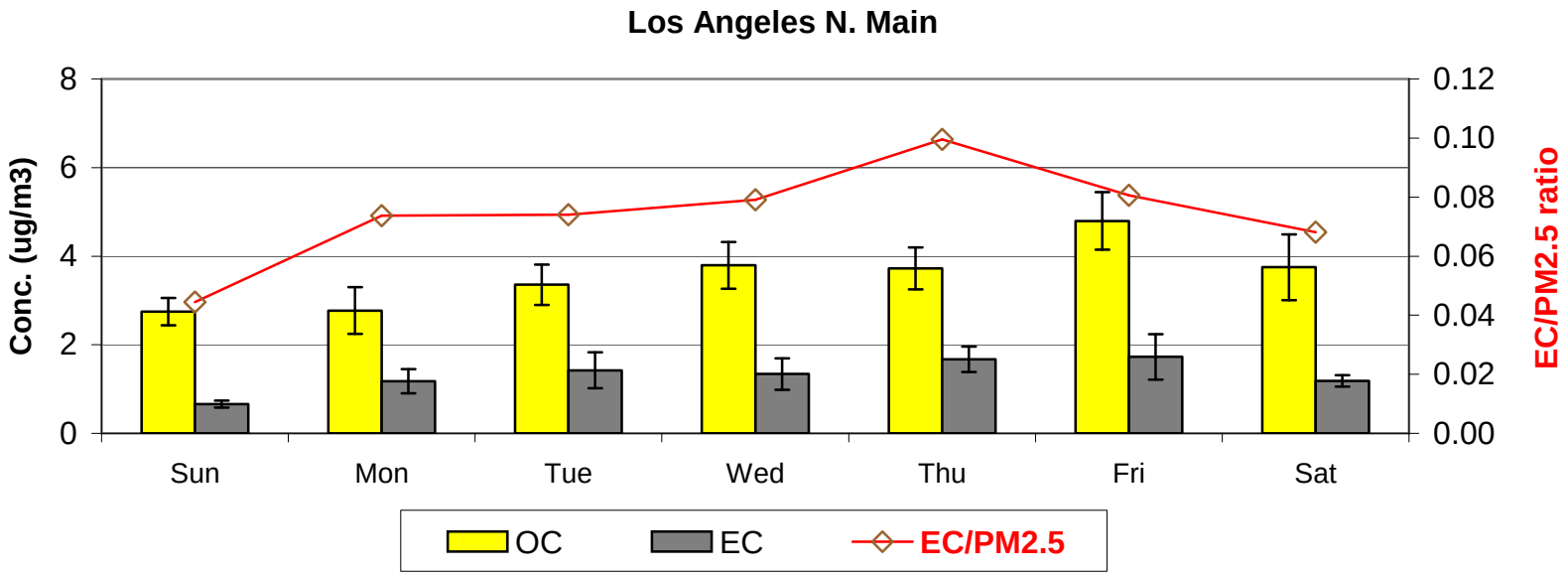


DOE's Gasoline/Diesel PM Split Study – Ambient Samples

- $PM_{2.5}$ Measurements
  - Gravimetric mass
  - Ions by IC, Colorimetry, AA
  - Elements by XRF
  - PM organic speciation by TIGF/PUF/XAD and GC/MS (PAH, hopanes, steranes, alkanes, polars)
  - Continuous black carbon by photoacoustic spectrometer
  - Continuous $PM_{2.5}$ by DustTrak
- Fixed Site Monitoring
  - Los Angeles-N. Main and Azusa
  - Daily 24 hr, from midnight PST; July 7-27, 2000
  - Composite by day of week
- Mobile Sampling
  - Regional background
  - Spark-ignition vehicle dominated
  - Compression-ignition vehicle dominated
  - SI and CI mix
  - Specific mixed samples

DOE's Gasoline/Diesel PM Split Study
Ambient Samples – IMPROVE TOR OC, EC and EC/$PM_{2.5}$ Ratios





Chemical composition of fuels, lubrication oils, and engine exhaust

- Diesel exhaust is the dominant source of elemental carbon. However, fractions of EC in gasoline exhaust increase during cold starts and hard accels.
- Hopanes and steranes are present in lubrication oil with similar composition for both gasoline and diesel vehicles. Much higher for high emitters.
- Gasoline exhaust contains higher proportions of high molecular weight PAH (e.g., indeno(cd)pyrene, benzo(ghi)perylene, and coronene) and volatile PAHs
- Combustion produced particle-phase PAHs tend to build up in lubricating oil of gasoline vehicles. This is not the case for diesel vehicles.
- Diesel emissions are enriched in methylated PAHs contained in diesel fuel.

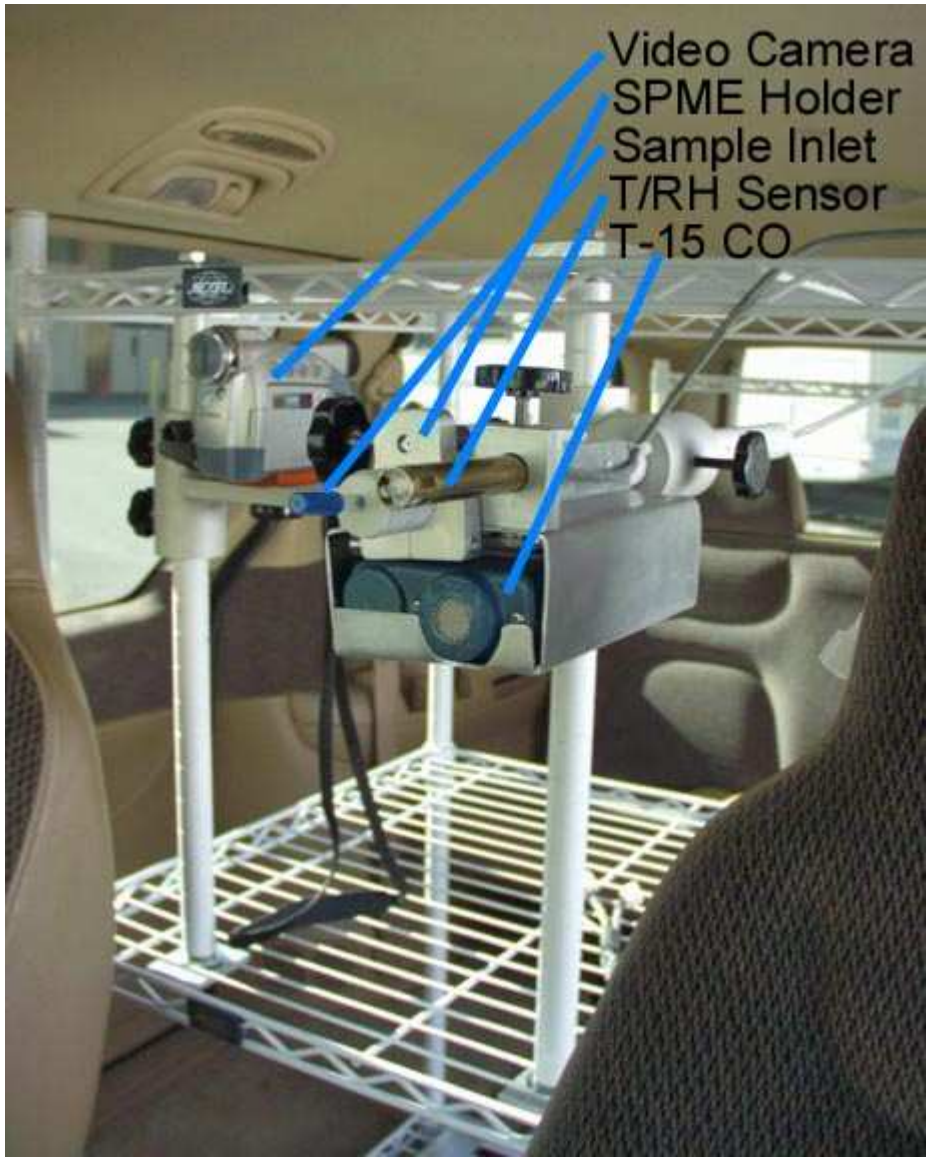
Contributions of Diesel and Gasoline Vehicles to Ambient concentrations of fine PM and SVOC

- PM emissions from heavy-duty diesel trucks have decline over past 30 years.
- Most gasoline vehicles have low PM emissions in hot-stabilized mode. These emissions rates have changed little over time.
- Directly-emitted particles (exhaust and road dust) from mobile sources plus nitrate from mobile NOx can account for about 80% of the ambient $PM_{2.5}$ (NFRAQS).
- Tunnel measurements and PART 5 emission rates do not reflect higher emissions due to:
  - Cold Starts
  - Colder temperature
  - Hard accelerations (non-FTP)
  - High emitters (not necessarily visible smokers)
- Current inventories do not include emissions of semi-volatile organics, which may be important precursors to secondary organic aerosols.

Recent Studies Involving Mobile Sampling

- Weekend Ozone Study (Department of Energy)
  - CO, NOx, black carbon and speciated hydrocarbons
- Gasoline/Diesel Split Study (Department of Energy)
  - PM mass, black carbon, PAH and other organics
- Weekend Nitrate Study (Department of Energy)
  - ozone, CO, NOx, NO_2, PAN, nitrate, ammonia,
- Section 211(B) Tier 2 High End Exposure Screening Study of Baseline and Oxygenated Gasoline (American Petroleum Institute)
  - BTEX, MTBE, 1,3-butadiene, formaldehyde, acetaldehyde
- Assessing Exposure to Air Toxics in Microenvironments Dominated by Mobile Sources (Health Effects Institute)
  - BTEX, MTBE, 1,3-butadiene, formaldehyde, acetaldehyde, PM (diesel PM?)

Measuring In-Cabin Exposures



Integrated and Semi-Continuous Methods

Method	Integrated			Semi-Cont.
	Canister	DNPH	Adsorbent	SPME
Applicable Environments	all	all	all	all
Time Resolution	60 min	60 min	60 min	10 min
Detection Limits	0.05 ppbC	0.1 ppbv	0.2 ppbv	0.2 ppbv
Data Application	Reference (R)	Reference (R)	Reference (R)	Confirmatory (C)
CO	R			
PID				
BTEX	R			C
1,3- Butadiene	R			
MTBE	R			
Formaldehyde		R		
Acetaldehye		R		
Ethanol			R	
NMHC	R			

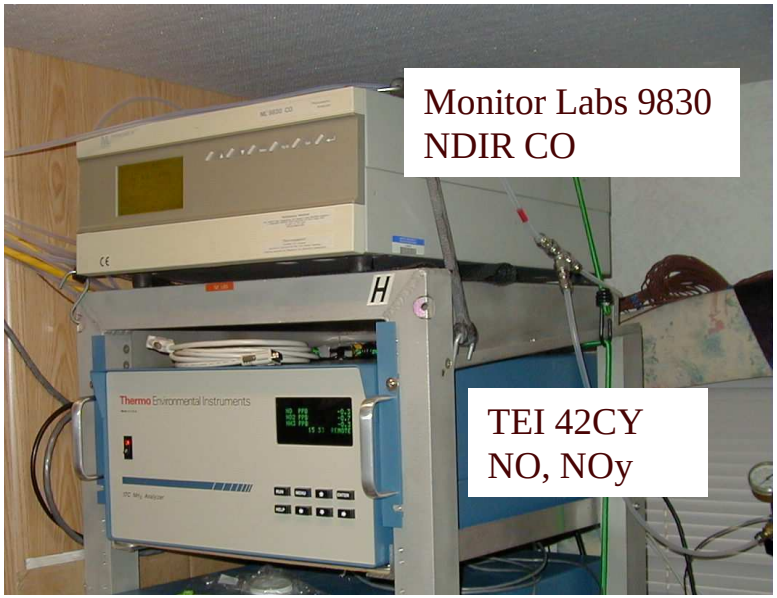
Continuous Methods

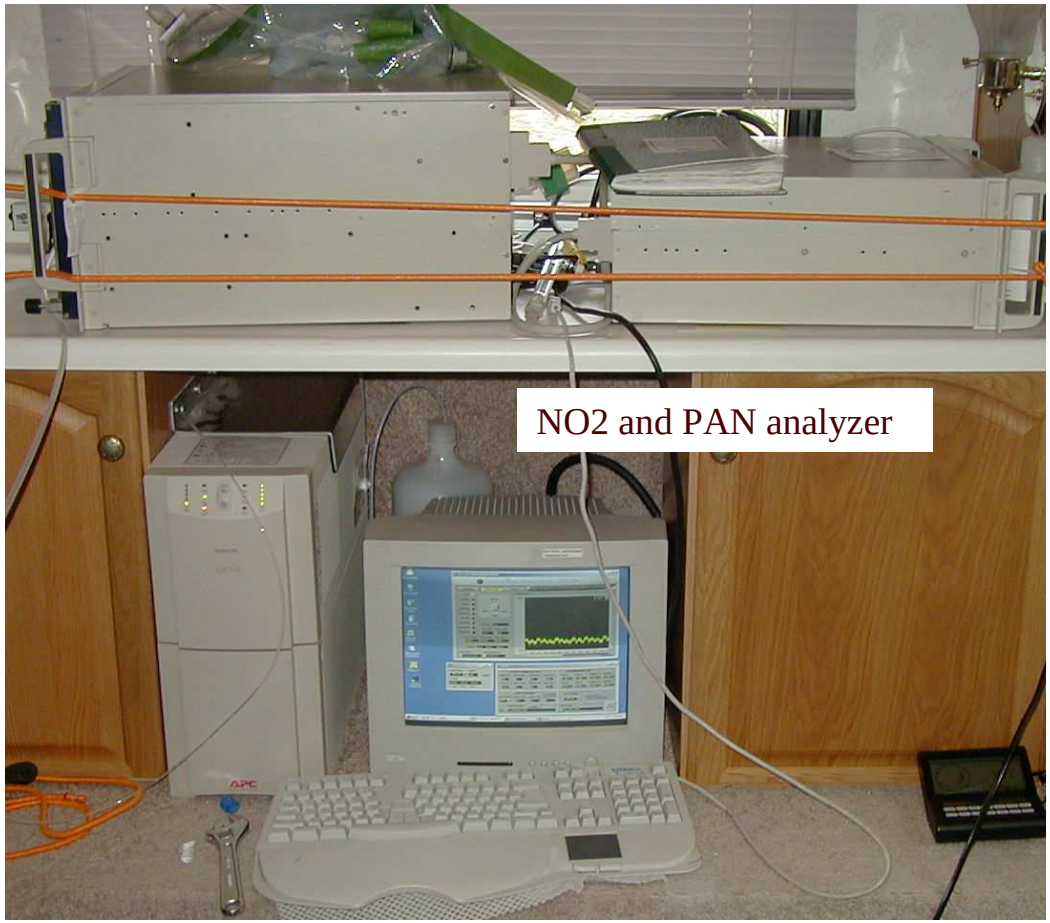
Method	Continuous				
	T15 CO	NDIR CO	ppbRAE	MS200	HCHO
Applicable Environments	outdoor and in-cabin w/high vent.	all	outdoor	higher end	all
Time Resolution	seconds	seconds	seconds	1 min	1 min
Detection Limits	0.1 ppm	0.04 ppm	1 ppb	1-3 ppbv	1 ppbv
Data Application	Surrogate (S)	Surrogate (S)	Surrogate (S)	Confirmatory (C)	Confirmatory (C)
CO	Surrogate	Surrogate			
PID			Surrogate		
BTEX	S (a)	S (a)	S (c)	C	
1,3-Butadiene	S (a)	S (a)	S (c)		
MTBE	S (a)	S (a)	S (c)		
Formaldehyde	S (b)	S (b)	S (d)		C
Acetaldehye	S (b)	S (b)	S (d)		S (g)
Ethanol	S (e)	S (e)	S (f)		
NMHC	S (a)	S (a)	S (c)		

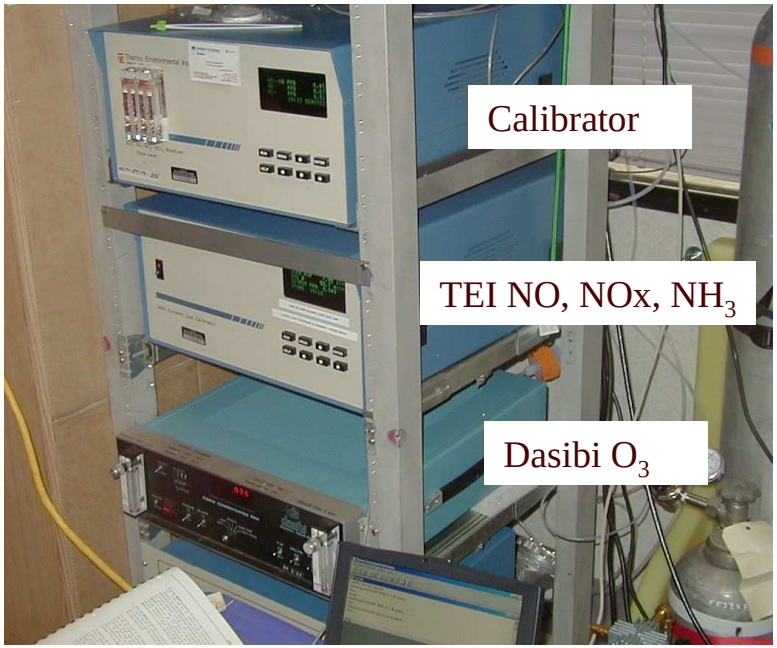
S (a). Time series reconstructed from canister/CO ratio for exhaust-dominated samples.
S (b). Time series reconstructed from DNPH/CO ratio for exhaust-dominated samples except outdoor daytime samples.
S (c). Time series reconstructed from canister/PID ratio for exhaust- or evap-dominated samples in outdoor MEs.
S (d). Time series reconstructed from DNPH/PID ratio for exhaust-dominated samples except outdoor daytime samples.
S (e). Time series reconstructed from solid adsorbent/CO ratio for exhaust-dominated samples.
S (f). Time series reconstructed from solid adsorbent/PID ratio for exhaust and evap-dominated samples.
S (g). Time series reconstructed from $CH3CHO_{DNPH}/HCHO_{Cont}$ ratio for exhaust dominated samples.


DRI Mobile
Sampling Station

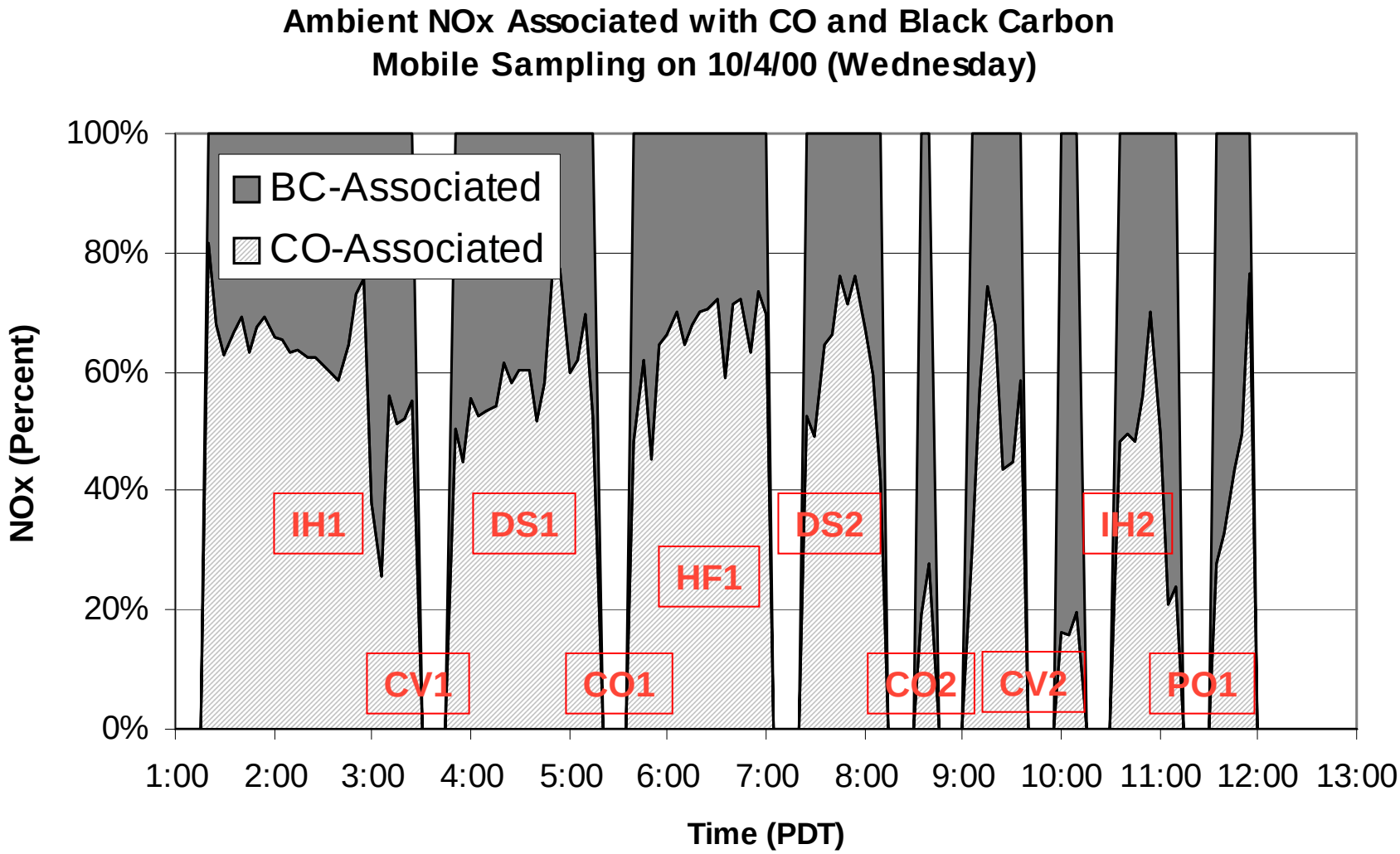
Instruments in the DRI Mobile Sampling Station







R&P Nitrate Analyzer


Ambient NOx Associated with CO and Black Carbon
Mobile Sampling on 10/4/00 (Wednesday)
BC-Associated
CO-Associated
NOx (Percent)
100%
80%
60%
40%
20%
0%
IH1
DS1
HF1
DS2
IH2
CV1
CO1
CO2
CV2
PO1
1:00
2:00
3:00
4:00
5:00
6:00
7:00
8:00
9:00
10:00
11:00
12:00
13:00
Time (PDT)

Assessing Exposure to Air Toxics in Microenvironments Dominated by Mobile Sources Sponsored by the Health Effects Institute

- Objectives
  - Quantify exposure to air toxics for two highly exposed populations
    - In-cabin exposure during commute
    - Residential area adjacent to freeways (Boyle Heights?)
- Approach
  - Mobile sampling using DRI's sampling van and mobile sampling station
  - Diesel Apportionment
    - Chemical Mass Balance
    - Regression
    - Multivariate Analysis (PMF, Unmix?)
- Potential complement to MATES III
  - Diesel apportionment
  - Characterization of gradient between source and receptor areas.
- Schedule: Field campaigns in summer 04 and winter 04/05.