Diesel- and Gasoline-Vehicle Chemical Emission Profiles for Use in the Apportionment of Atmospheric Carbonaceous Aerosol

Barbara Zielinska
Desert Research Institute
Reno, NV 89506

Contributors:

- DRI:
- Eric Fujita
- Terry Hayes
- John Sagebiel

- Others
- General Motors R&D Center (S.H.Cadle, P.Mulawa)
- Colorado School of Mines (M.S.Graboski,L.McCormick)
- Colorado State University (D. Lawson)

Objective:

- To develop distinct chemical emission profiles for various categories of motor vehicles (such as heavy- and light-duty diesel, light-duty gasoline, low and high particulate emitting, etc.) for use in the apportionment of atmospheric carbonaceous aerosol by Chemical Mass Balance (CMB).

FRACTIONAL ORGANIC AND ELEMENTAL CARBON ABUNDANCES IN DIESEL EMISSIONS

Location	Organic Carbon	Elemental Carbon	N[c]	Sources
Denver, CO[a]	19±8%	75±10%	15	NFRAQS, 1998
Denver, CO[a]	23±8%	74±21%	3	Watson et al., 1988
Los Angeles, CA[a]	36±3%	52±5%	2	Cooper et al., 1987
Los Angeles, CA[a]	33.6%	40.5%	2	Rogge et al., 1993
Bakersfield, CA[a]	49±13%	43±8%	3	Houck et al., 1989
Phoenix, AZ[b]	40±7%	22±8%	8	Chow et al., 1991
Phoenix, AZ[b]	64±11%	33±10%	7	Zielinska et al., 1997

NOTES:
(a) Modified Federal Test Procedures followed in dynamometer tests
(b) Roof monitoring at inspection station
(c) N = Number of samples

Studies:

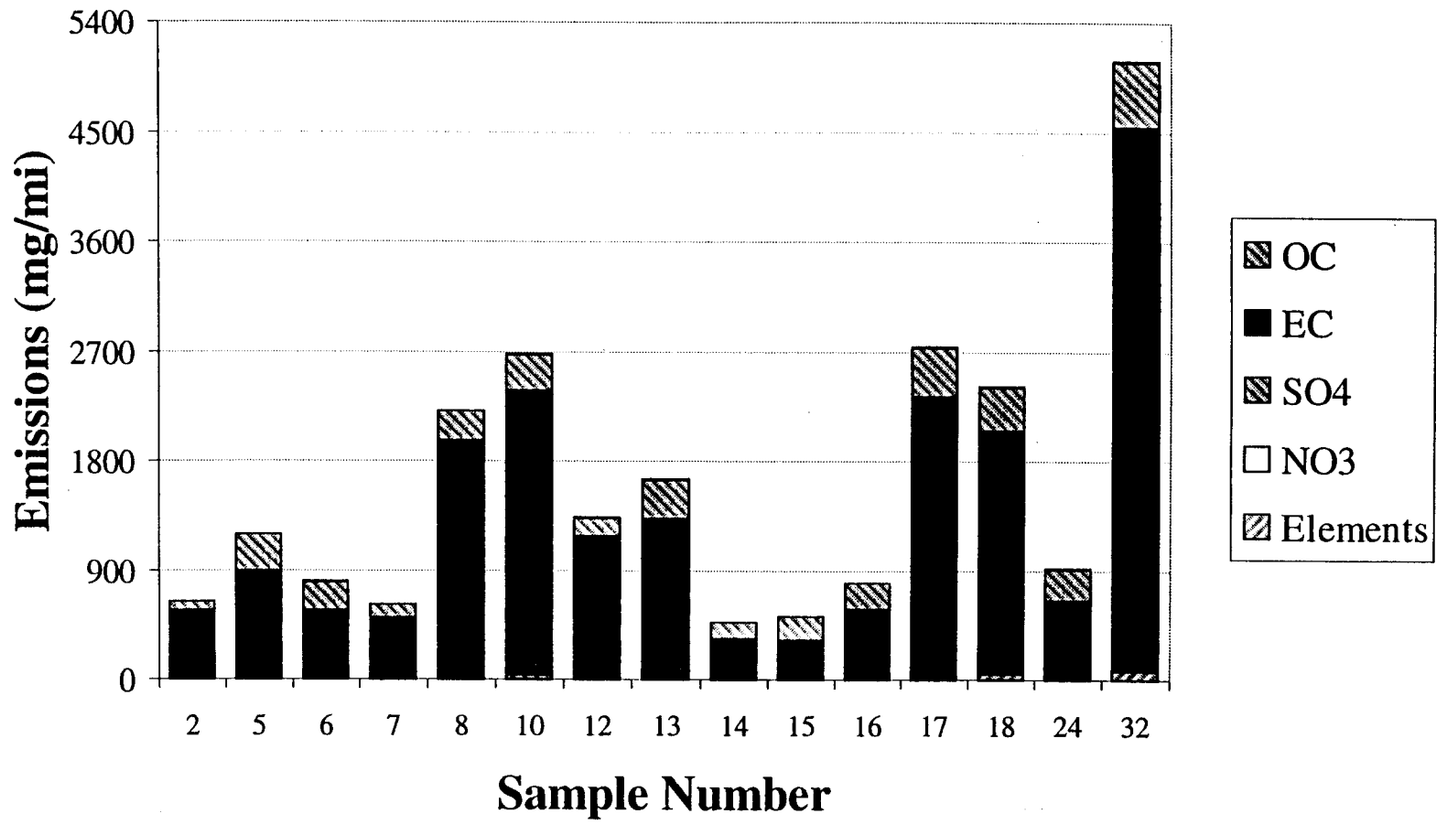
- Light-duty gasoline (LDG) and heavy-duty diesel (HDD) vehicle emissions sampling in I&M facilitiesin Phoenix, AZ (EPA Exploratory Grant, 1995)
- Dynamometer tests of in-service LDG vehicles in Nevada (part of Clark and Washoe Remote Sensing Study, 1994)
- Dynamometer tests of in-use HDD vehicles, by Colorado School of Mines (part of Northern Front Range Air Quality Study, Winter 1996-1997, http://charon.cira.colostate.edu/).

Heavy-Duty Diesel Test Summary (NFRAQS)[a]						
Sample ID	veh_use	GVWR	engine_mfg	odometer_mi[b]	opacity (%)[c]	cycle
HDD2	Food Delivery	33,000	International	142,242	27.6	WVT
HDD5	Lease	25,500	Navistar	122,406	16.3	CBD
HDD6	RTD Bus	38,000	DDC	85,200	10.7	CBD
HDD7	Replicate					HDTT
HDD8	Dump Truck	28,000	International	89,528	25	HDTT
HDD10	Lease	11,050	Isuzu	82,618	64.7	CBD
HDD12	School Bus	28,000	GMC	89,054	26.6	HDTT
HDD13	Replicate					CBD
HDD14	RTD Bus	38,000	DDC	85,200	5.8	HDTT
HDD15	Replicate					CBD
HDD16	Food Delivery	80,000	Cummins	47,797	46.8	CBD
HDD17	Dump Truck	80,000	Cummins	595,606	25.5	HDTT
HDD18	School Bus	30,000	Cummins	62,549	29.2	CBD
HDD24	Concrete Mixer	60,000	Cummins	96,262	6.9	WVT
HDD32	Garbage Hauler	50,000	Cummins	72,251	75.3	WVT

[a]Tests performed by Colorado School of Mines (CSM) Institute for Fuels and High Altitude Engine Research (CIFER), Graboski et al., 1997

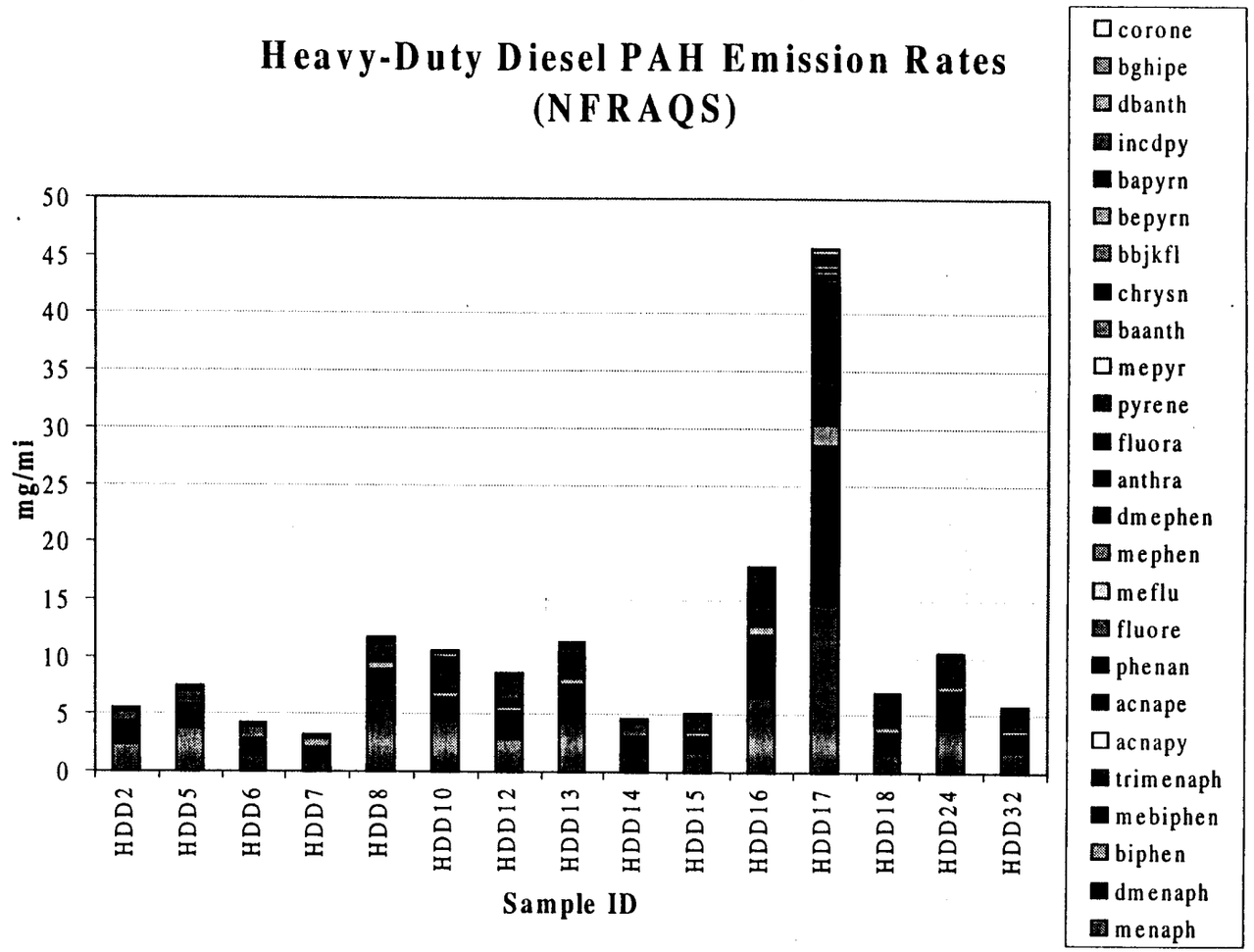
[b] Since rebuild [c] SAE J-1667 snap idle procedure

Heavy-Duty Diesel Emission Rates (NFRAQS)

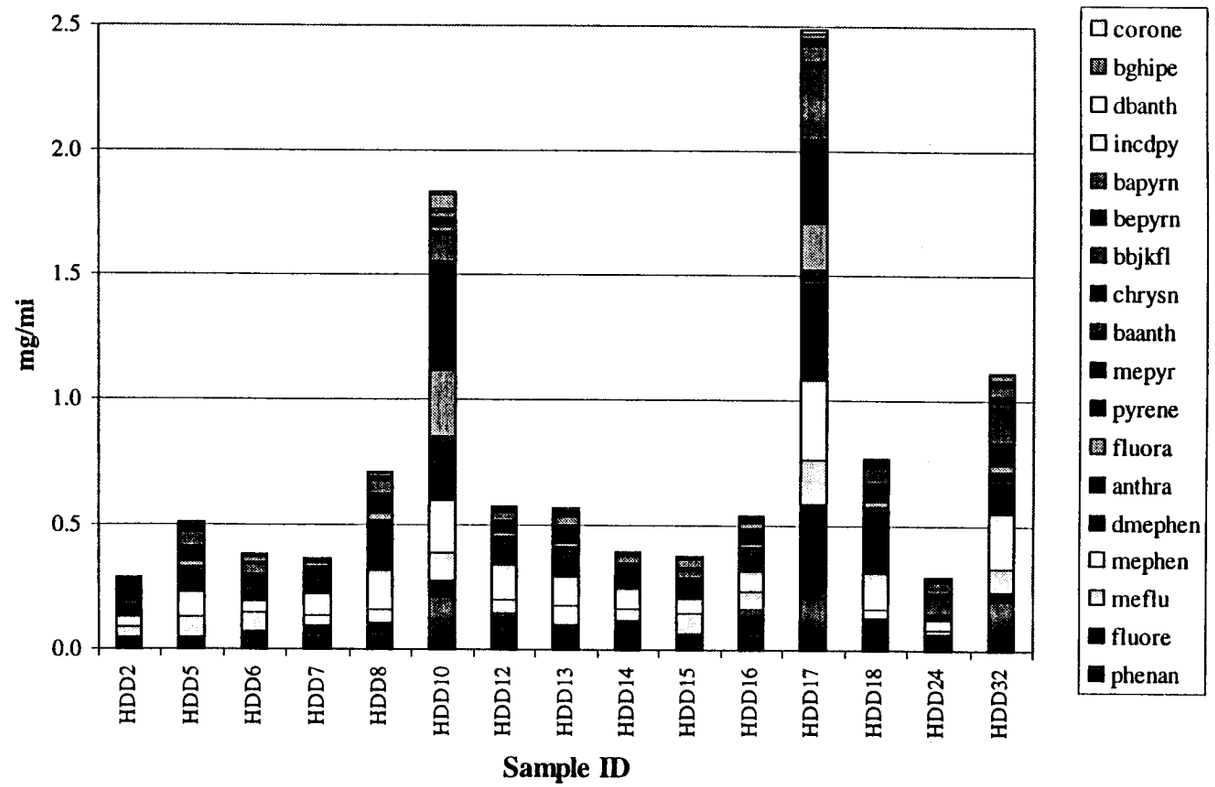


List of PAH (in order of elution)

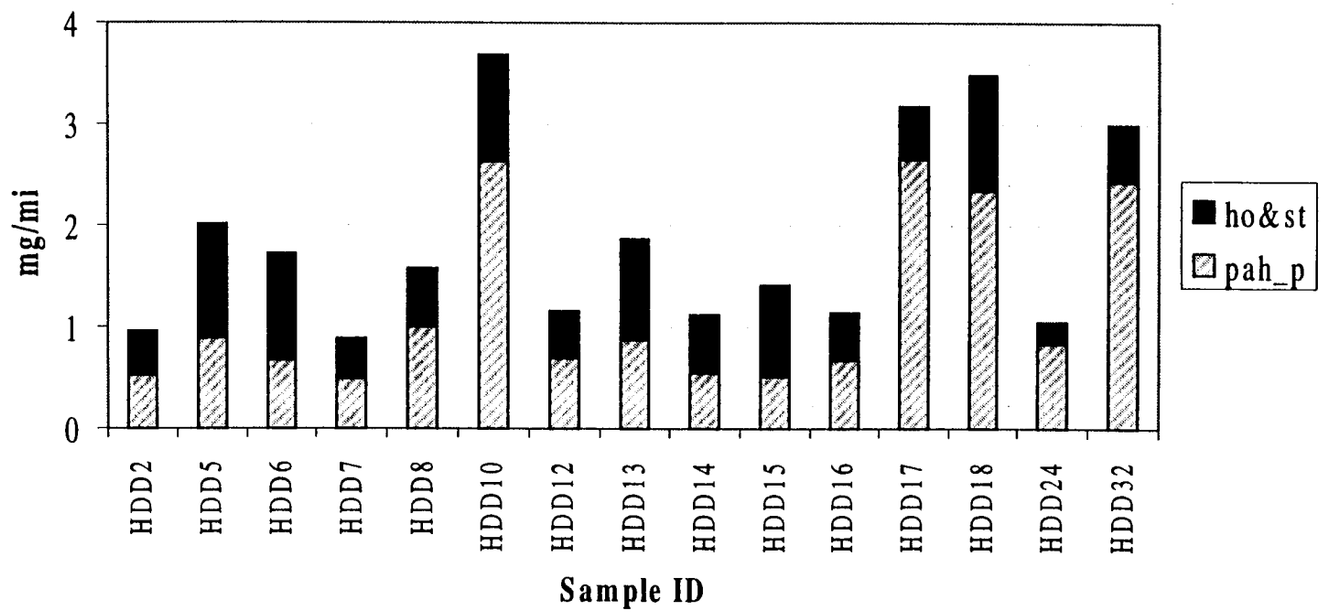
	Name		Name		Name
1	Naphthalene	24	Acenaphthylene	47	Pyrene
2	2-Menaphthalene	25	Acenaphthene	48	A-Methylpyrene
3	1-Menaphthalene	26	Phenanthrene	49	B-Methylpyrene
4	2,6+2,7-Dimenaphthalene	27	Fluorene	50	C-Methylpyrene
5	1,7+1,3+1,6-Dimenaphthalene	28	A-Methylfluorene	51	D-Methylpyrene
6	2,3+1,4+1,5-Dimenaphthalene	29	1-Methylfluorene	52	E-Methylpyrene
7	1,2-Dimenaphthalene	30	B-Methylfluorene	53	F-Methylpyrene
8	1,8-Dimenaphthalene	31	C-Methylfluorene	54	G-Methylpyrene
9	Biphenyl	32	A-Methylphenanthrene	55	Retene
10	2-Methylbiphenyl	33	2-Methylphenanthrene	56	Benzonaphthotiophene
11	3-Methylbiphenyl	34	B-Methylphenanthrene	57	Benz(a)anthracene
12	4-Methylbiphenyl	35	C-Methylphenanthrene	58	7-Methylbenz[a]anthracene
13	A-Trimethylnaphthalene	36	1-Methylphenanthrene	59	Chrysene
14	1-Ethyl-2-methylnaphthalene	37	3,6-Dimethylphenanthrene	60	Benzo(b+j+k)fluoranthene
15	B-Trimethylnaphthalene	38	A-Dimethylphenanthrene	61	Benzo(e)pyrene
16	C-Trimethylnaphthalene	39	B-Dimethylphenanthrene	62	Benzo(a)pyrene
17	2-Ethyl-1-methylnaphthalene	40	C-Dimethylphenanthrene	63	7-Methylbenzo[a]pyrene
18	D-Trimethylnaphthalene	41	1,7-Dimethylphenanthrene	64	Indeno[123-cd]Pyrene
19	E-Trimethylnaphthalene	42	D-Dimethylphenanthrene	65	Dibenz(ah+ac)anthracene
20	F-Trimethylnaphthalene	43	E-Dimethylphenanthrene	66	Benzo(b)chrysene
21	G-Trimethylnaphthalene	44	Anthracene	67	Benzo(ghi)Perylene
22	H-Trimethylnaphthalene	45	9-Methylanthracene	68	Coronene
23	1,2,8-Trimethylnaphthalene	46	Fluoranthene		


Heavy-Duty Diesel PAH Emission Rates
(NFRAQS)
mg/mi
0
5
10
15
20
25
30
35
40
45
50
HDD2
HDD5
HDD6
HDD7
HDD8
HDD10
HDD12
HDD13
HDD14
HDD15
HDD16
HDD17
HDD18
HDD24
HDD32
Sample ID
corone
bghipe
dbanth
incdpy
bapyrn
bepyrn
bbjkfl
chrysn
baanth
mepyr
pyrene
fluora
anthra
dmephen
mephen
meflu
fluore
phenan
acnape
acnapy
trimenaph
mebiphen
biphen
dmenaph
menaph

Heavy-Duty Diesel Particulate PAH Emission Rates (NFRAQS)



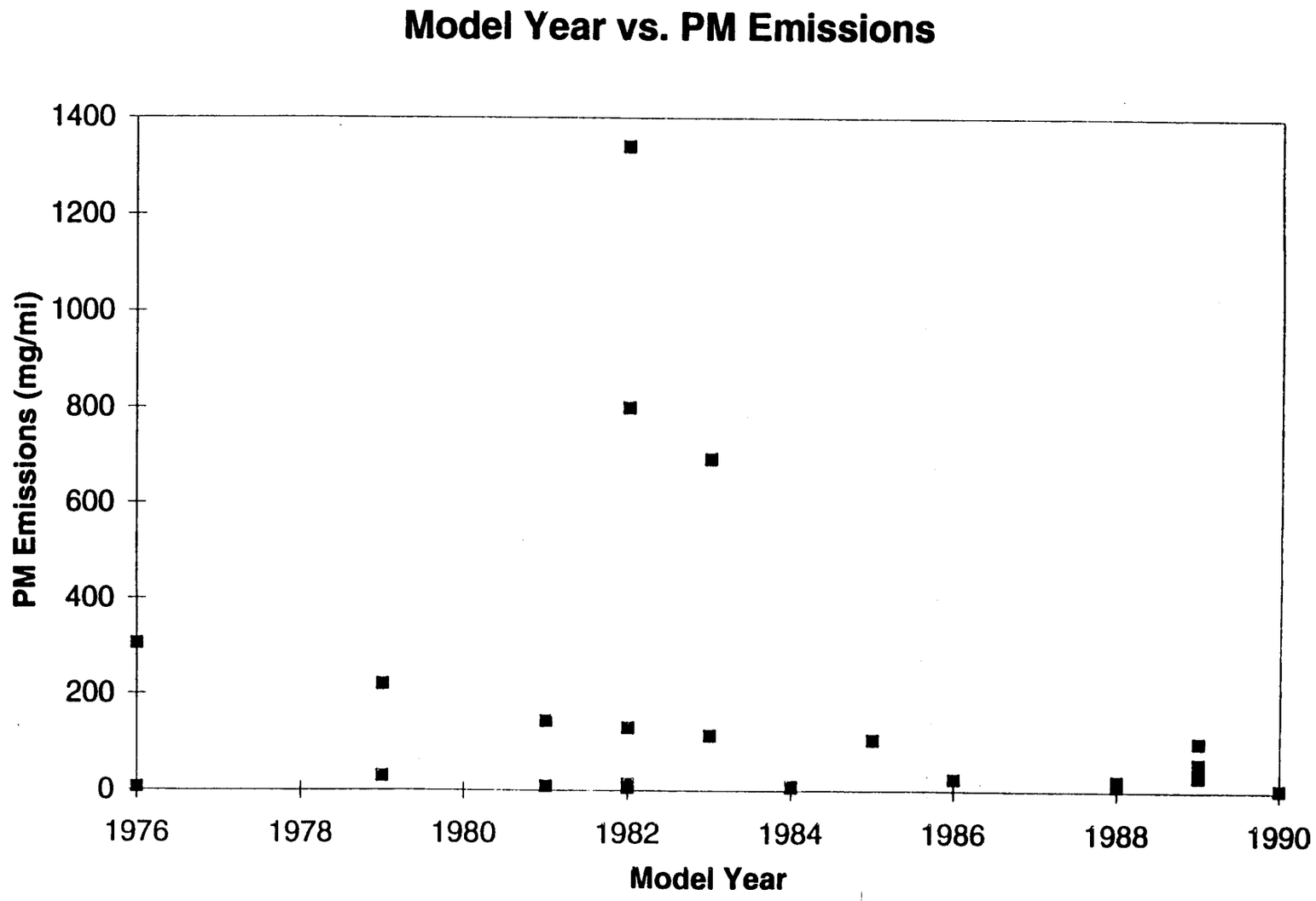
Heavy-Duty Diesel Particulate Organic Emission Rates (NFRAQS)

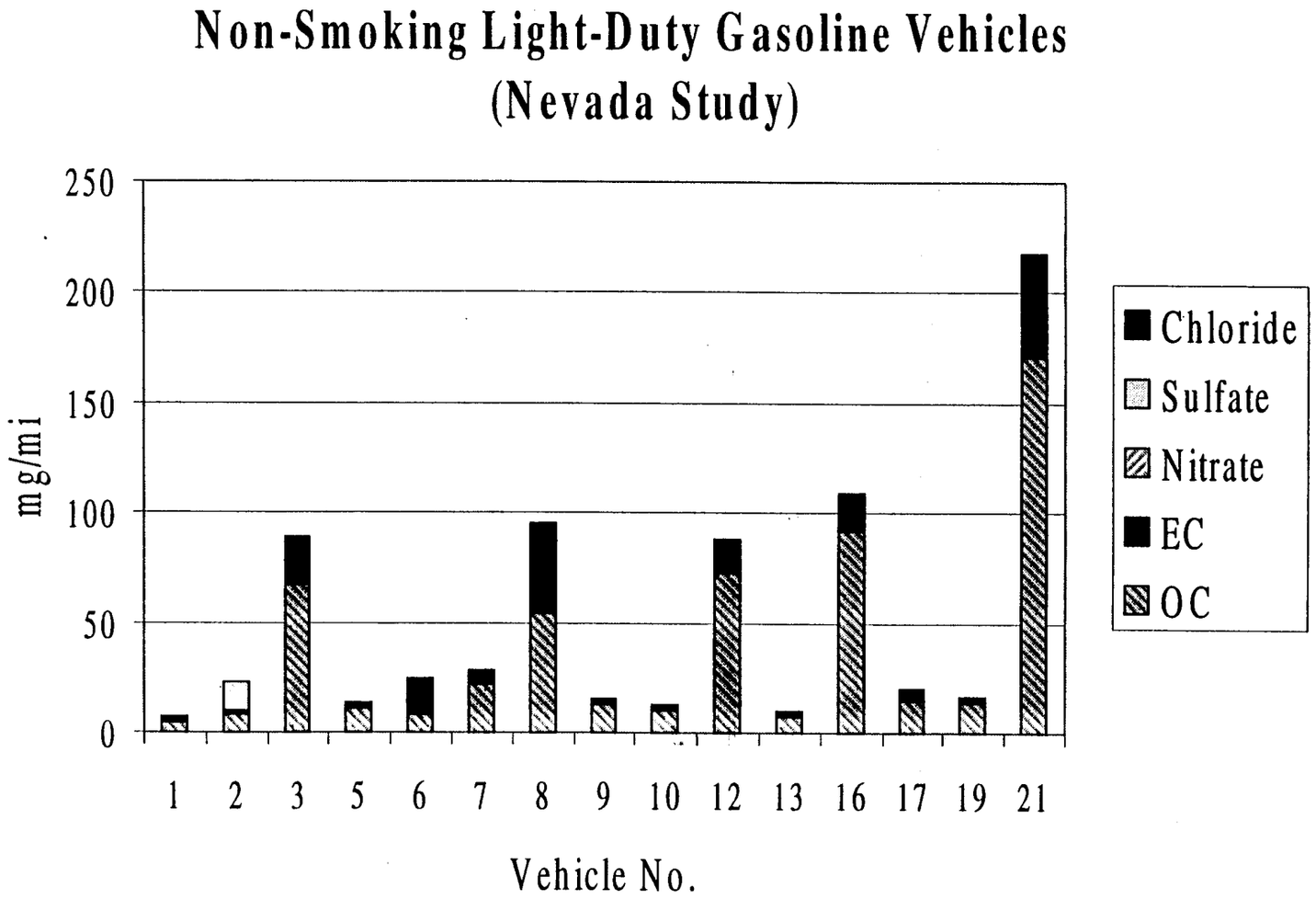


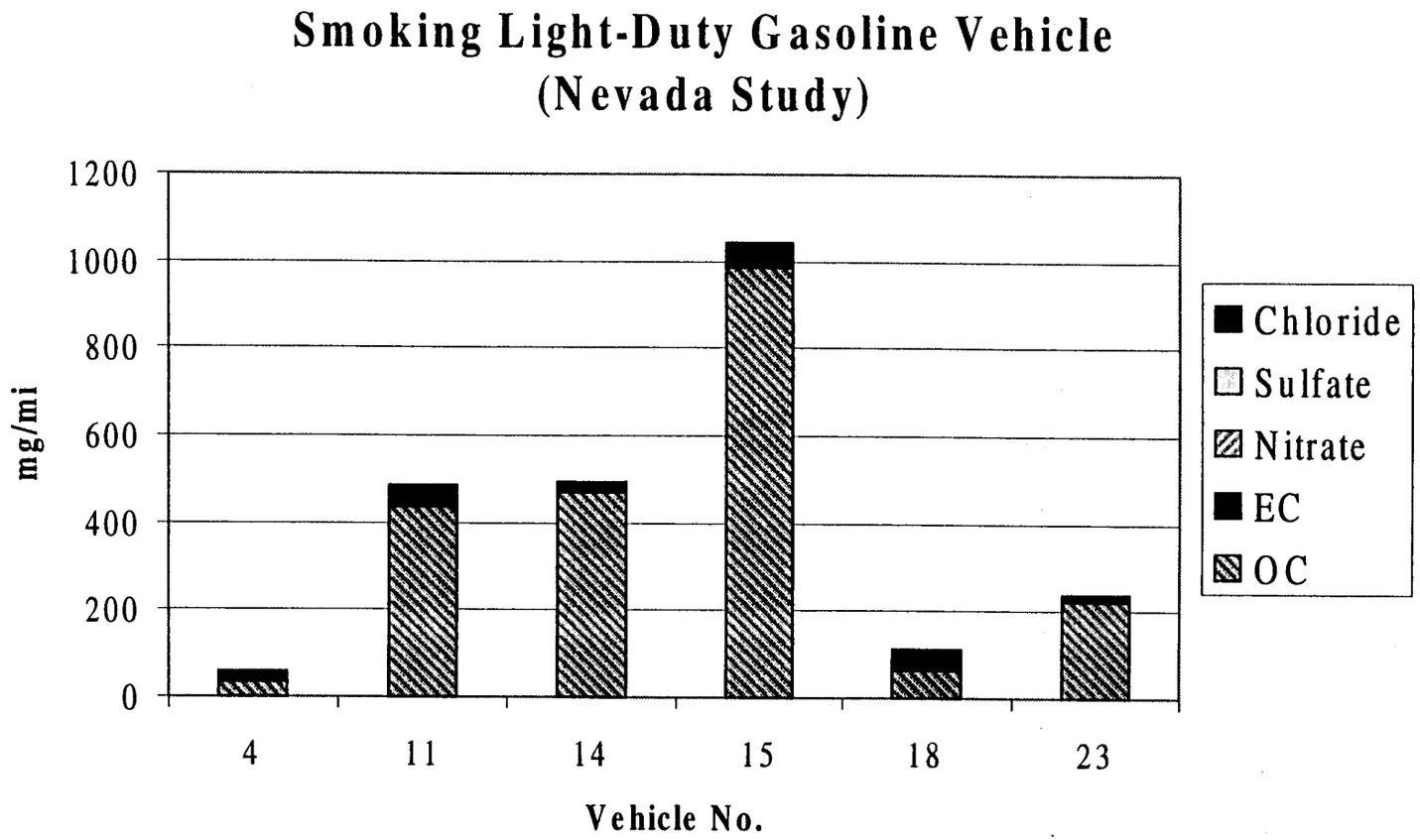
Summary of vehicles tested and emissions. Vehicles are ordered by model year.
Averages are presented for all vehicles and for those that emitted visible smoke and those that did not.

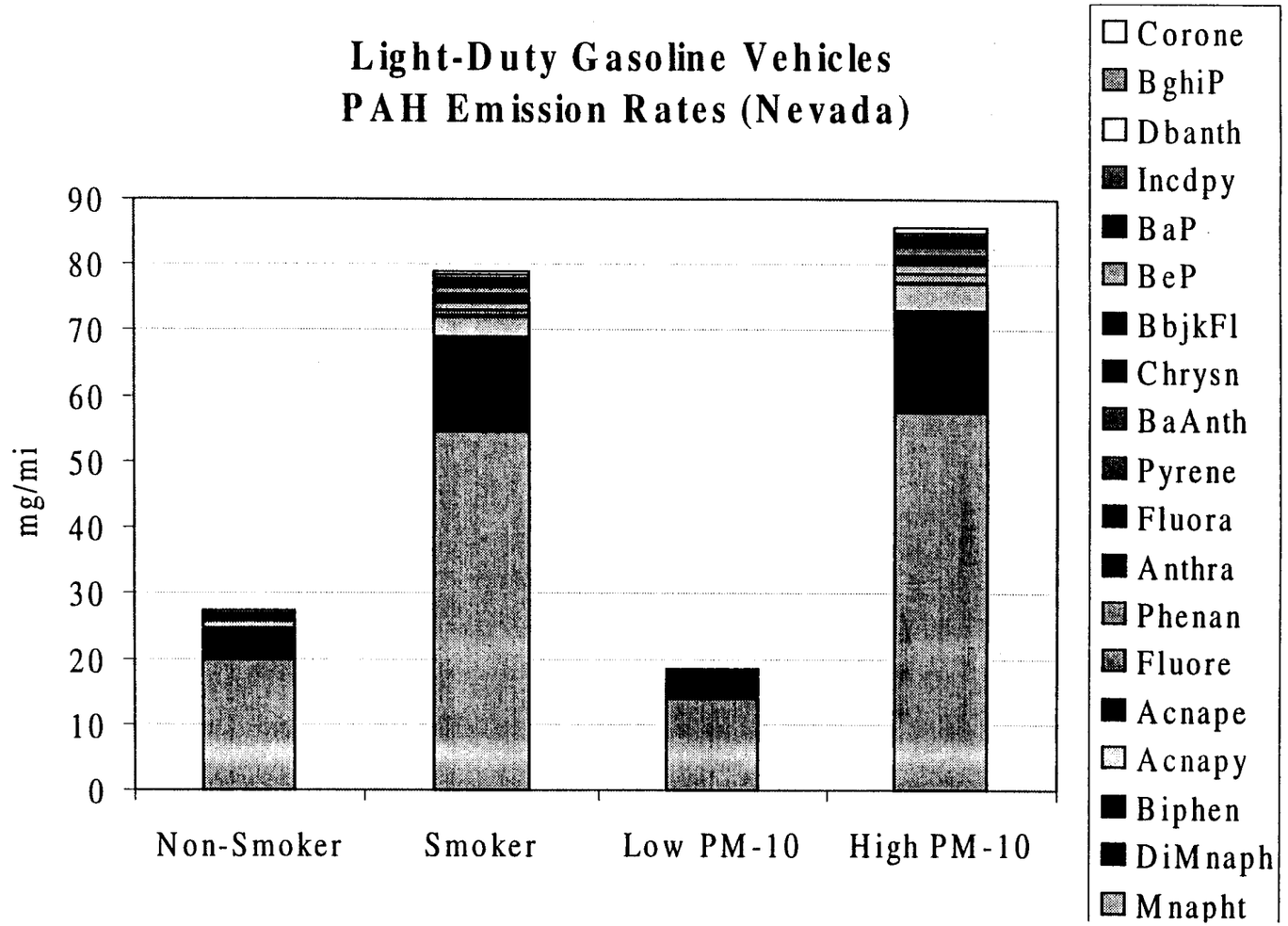
				IM240 Emission Rate				
				(mg/mile)		(g/mile)		
Vehicle #	Model Year	Make	Model	Mass	HC	CO	NOx	Field Notes
1	1990	Mercury	Sable Wagon	5.6	0.05	1.76	0.44	possible cold start
2	1989	Ford	Pony	32.4	0.14	8.46	0.18	
3	1989	Yugo	2-door	103.0	2.63	40.08	0.24	
4	1989	Isuzu	Pickup	59.0	4.42	78.90	0.66	visible black smoke
5	1988	Honda	CRX Si	13.4	2.17	13.79	1.33	
6	1988	Nissan	Sentra	22.0	1.42	36.84	1.25	
7	1986	VW	Cabriolet	25.6	1.31	57.34	1.74	
8	1985	Chevrolet	S-10 Blazer	106.4	2.63	58.80	1.22	
9	1984	Toyota	Pickup	10.1	2.12	26.23	6.11	
10	1984	Chevrolet	Celebrity	7.8	0.60	27.52	0.14	
11	1983	Ford	Ranger Pickup	693.4	7.87	46.01	1.44	visible smoke
12	1983	Ford	Ranger Pickup	115.9	4.57	69.44	1.09	
13	1982	Ford	Station Wagon	6.8	3.12	22.17	2.12	
14	1982	Ford	Escort	801.0	3.69	34.92	2.19	visible smoke
15	1982	Ford	Mustang	1341.8	6.41	62.80	1.31	visible smoke
16	1982	Toyota	Pickup	131.8	4.47	78.96	1.41	
17	1982	Mazda	626	14.3	2.12	30.11	1.96	
18	1981	Ford	F150 Pickup	145.8	11.04	117.45	0.26	visible smoke
19	1981	Olds	Toronado	10.0	2.29	35.11	3.01	
20	1979	Buick	Regal	30.1	1.84	38.05	0.07	overheated
21	1979	Ford	Mustang	221.4	10.10	92.02	2.00	
22	1976	Olds	Cutlass	7.2	2.37	18.24	5.87	
23	1976	Mercury	2dr Sedan	306.1	3.65	40.73	3.53	visible smoke
		Average of all vehicles		183.08	3.52	45.03	1.72	
		Average of smokers (n=6)		557.85	6.18	63.47	1.57	
		Average of non-smokers (n=17)		50.81	2.59	38.52	1.78	

From Sagebiel et al., 1997

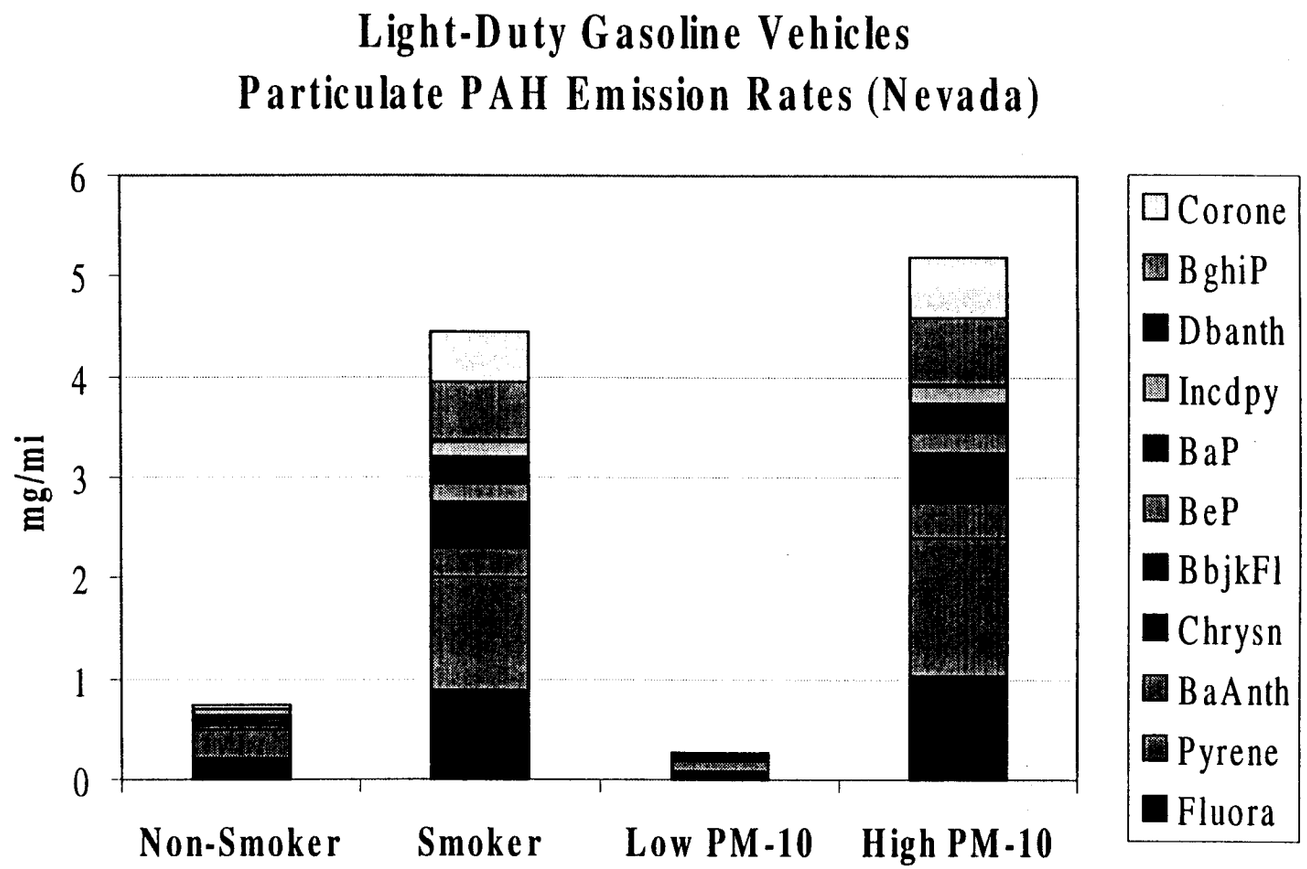

Model Year vs. PM Emissions
PM Emissions (mg/mi)
1400
1200
1000
800
600
400
200
0
1976
1978
1980
1982
1984
1986
1988
1990
Model Year


Non-Smoking Light-Duty Gasoline Vehicles
(Nevada Study)
250
200
150
100
50
0
mg/mi
1
2
3
5
6
7
8
9
10
12
13
16
17
19
21
Vehicle No.
Chloride
Sulfate
Nitrate
EC
OC

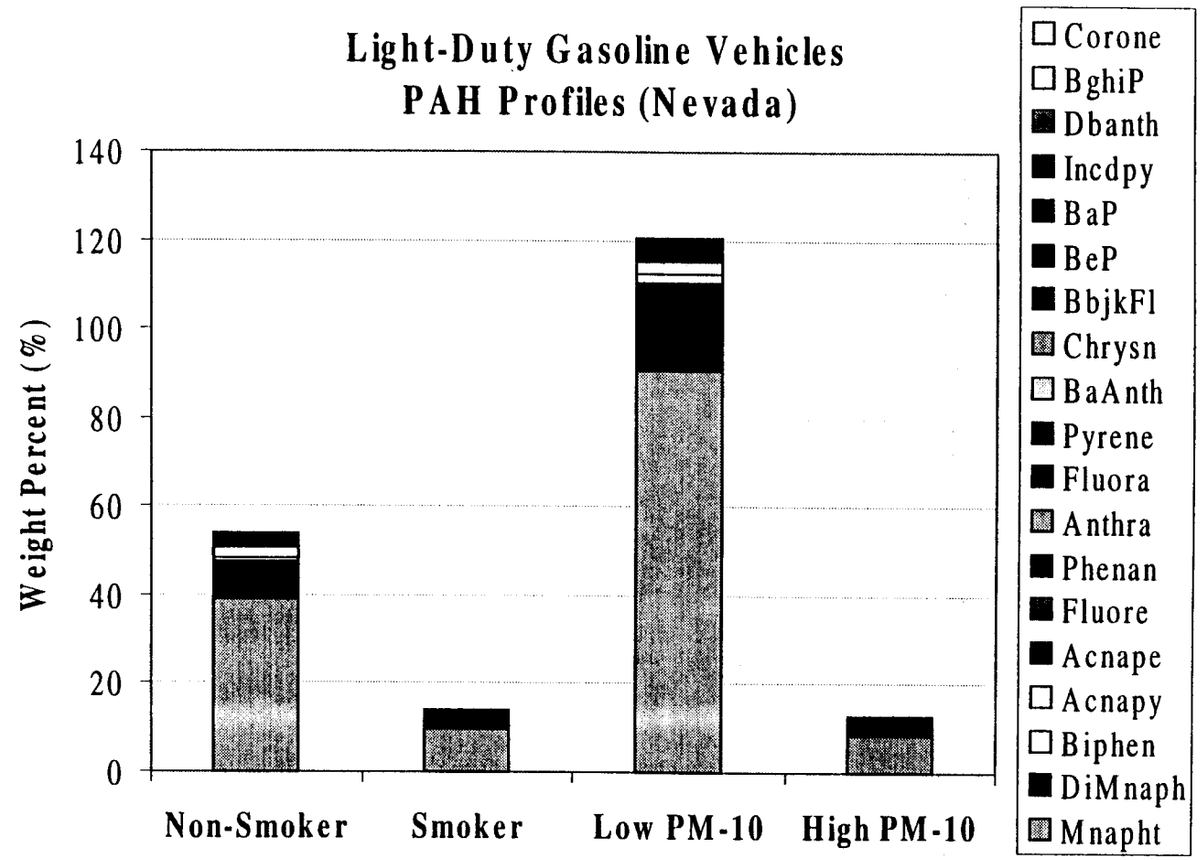

Smoking Light-Duty Gasoline Vehicle
(Nevada Study)
1200
1000
800
600
400
200
0
mg/mi
4
11
14
15
18
23
Vehicle No.
Chloride
Sulfate
Nitrate
EC
OC

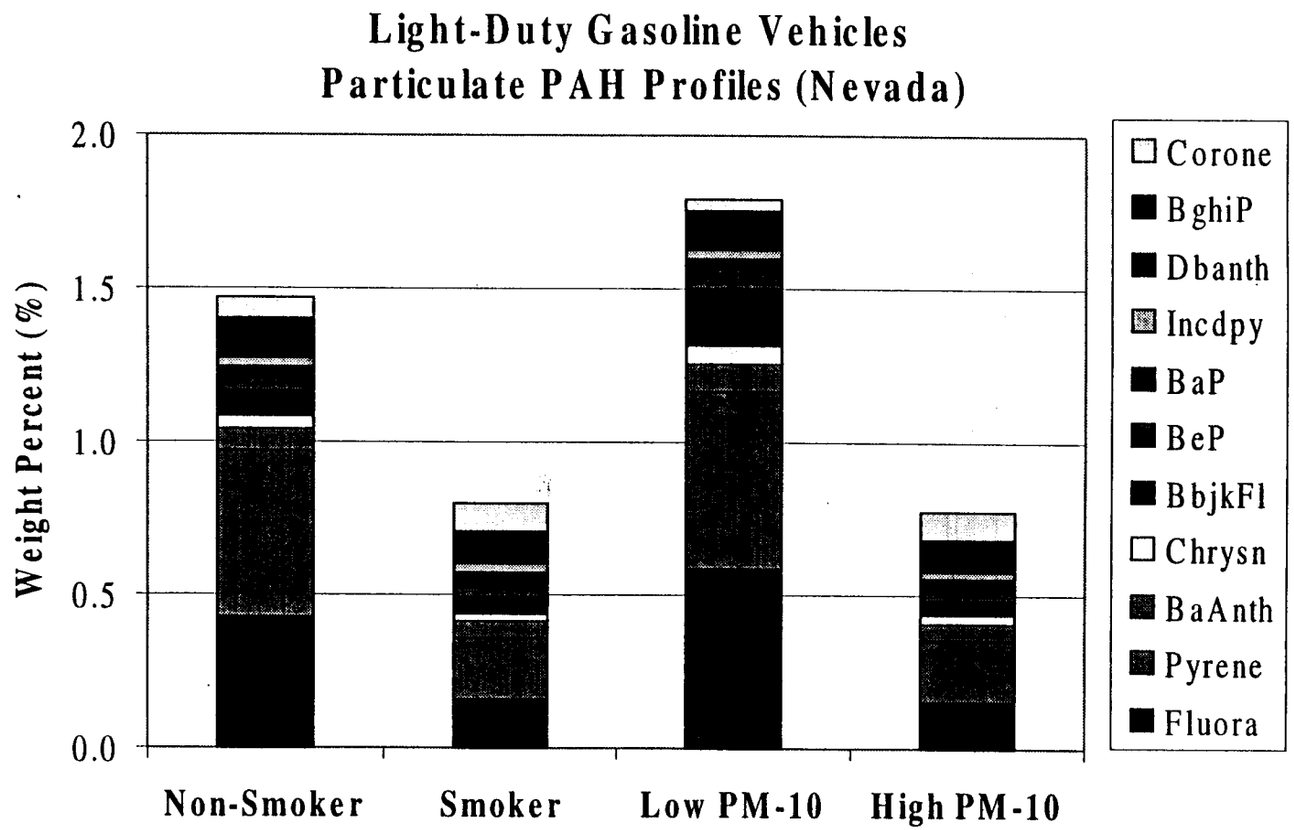


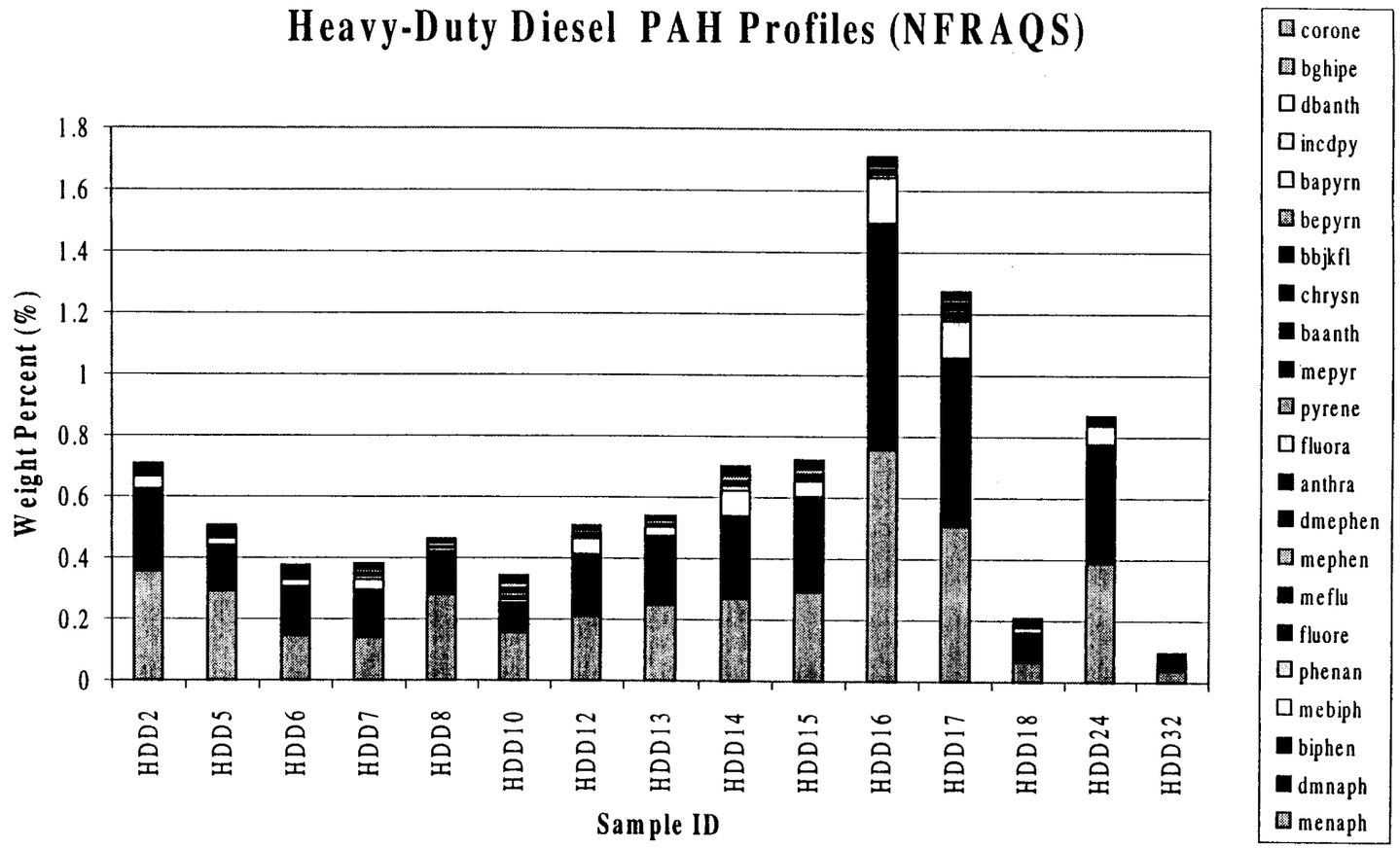
Low PM-10 is the average for vehicles emitting < 50 mg/mi and high PM-10 is for vehicles over 150 mg/mi.
PAH listed in the order of elution from GC column (from methylnaphthalenes to coronene)



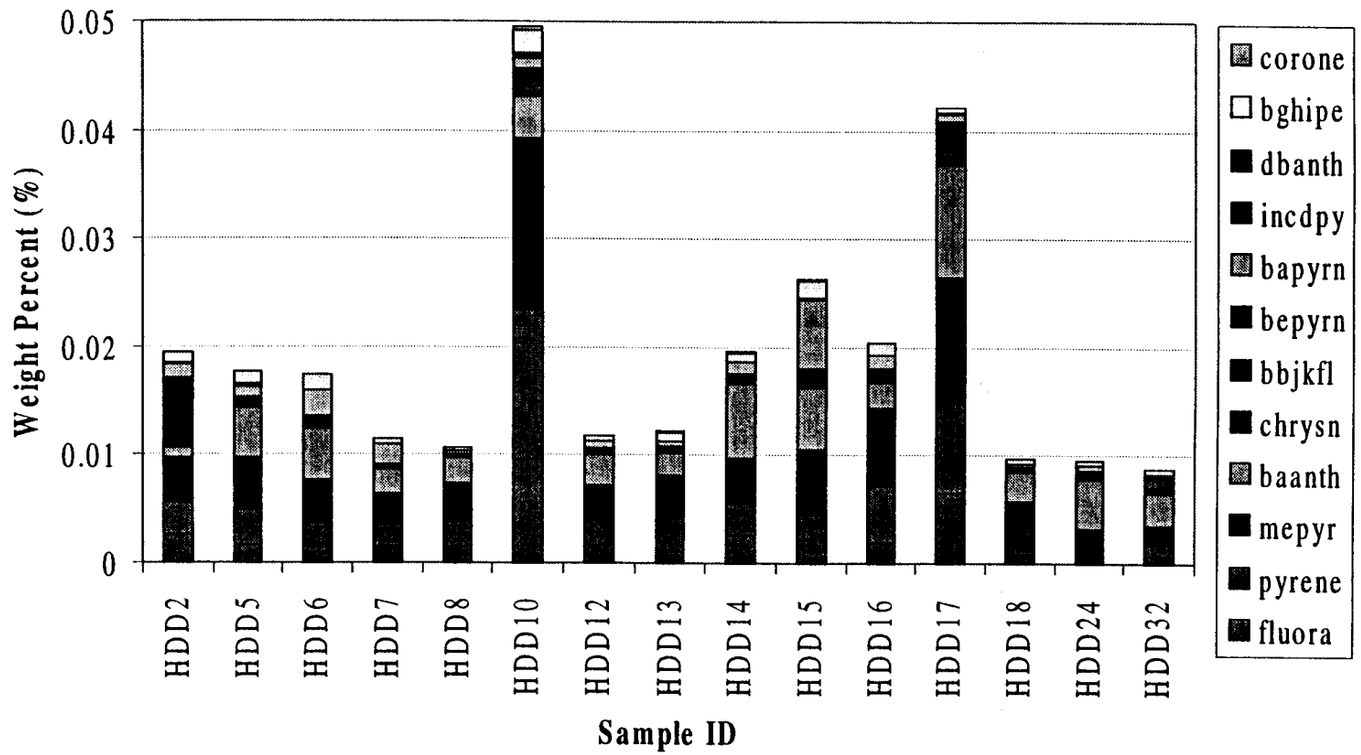
Low PM-10 is the average for vehicles emitting < 50 mg/mi and high PM-10 is for vehicles over 150 mg/mi.
PAH listed in the elution order from GC column (from fluoranthene to coronene)


Light-Duty Gasoline Vehicles
PAH Profiles (Nevada)
Weight Percent (%)
140
120
100
80
60
40
20
0
Non-Smoker
Smoker
Low PM-10
High PM-10
Corone
BghiP
Dbanth
Incdpy
BaP
BeP
BbjkFl
Chrysn
BaAnth
Pyrene
Fluora
Anthra
Phenan
Fluore
Acnape
Acnapy
Biphen
DiMnaph
Mnapht


Light-Duty Gasoline Vehicles
Particulate PAH Profiles (Nevada)
Weight Percent (%)
2.0
1.5
1.0
0.5
0.0
Non-Smoker
Smoker
Low PM-10
High PM-10
Corone
BghiP
Dbanth
Incdpy
BaP
BeP
BbjkFl
Chrysn
BaAnth
Pyrene
Fluora

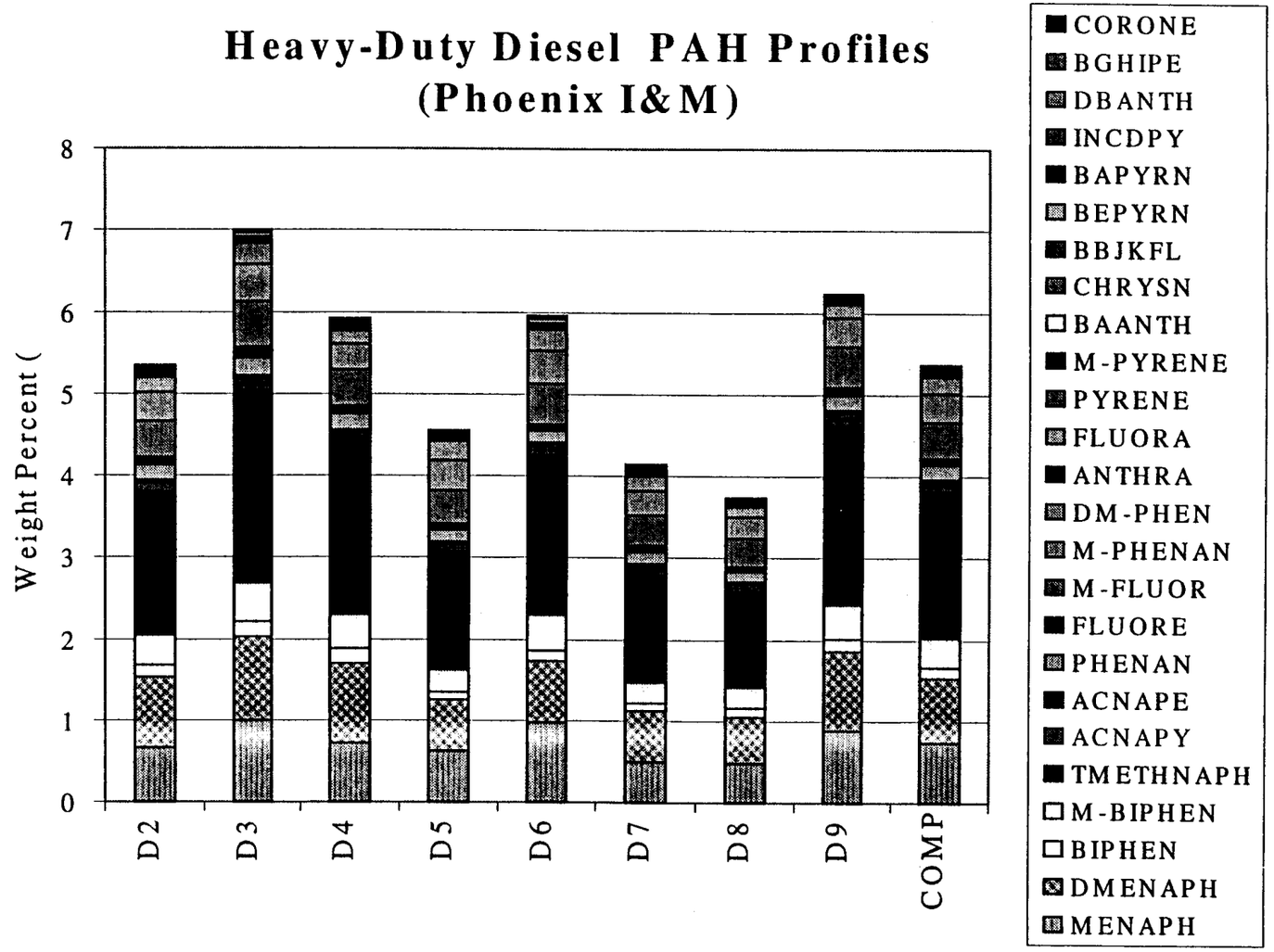

Heavy-Duty Diesel PAH Profiles (NFRAQS)
Weight Percent (%)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
HDD2
HDD5
HDD6
HDD7
HDD8
HDD10
HDD12
HDD13
HDD14
HDD15
HDD16
HDD17
HDD18
HDD24
HDD32
Sample ID
corone
bghipe
dbanth
incdpy
bapyrn
bepyrn
bbjkfl
chrysn
baanth
mepyr
pyrene
fluora
anthra
dmephen
mephen
meflu
fluore
phenan
mebiph
biphen
dmnaph
menaph

Heavy-Duty Diesel Particulate PAH Profiles (NFRAQS)

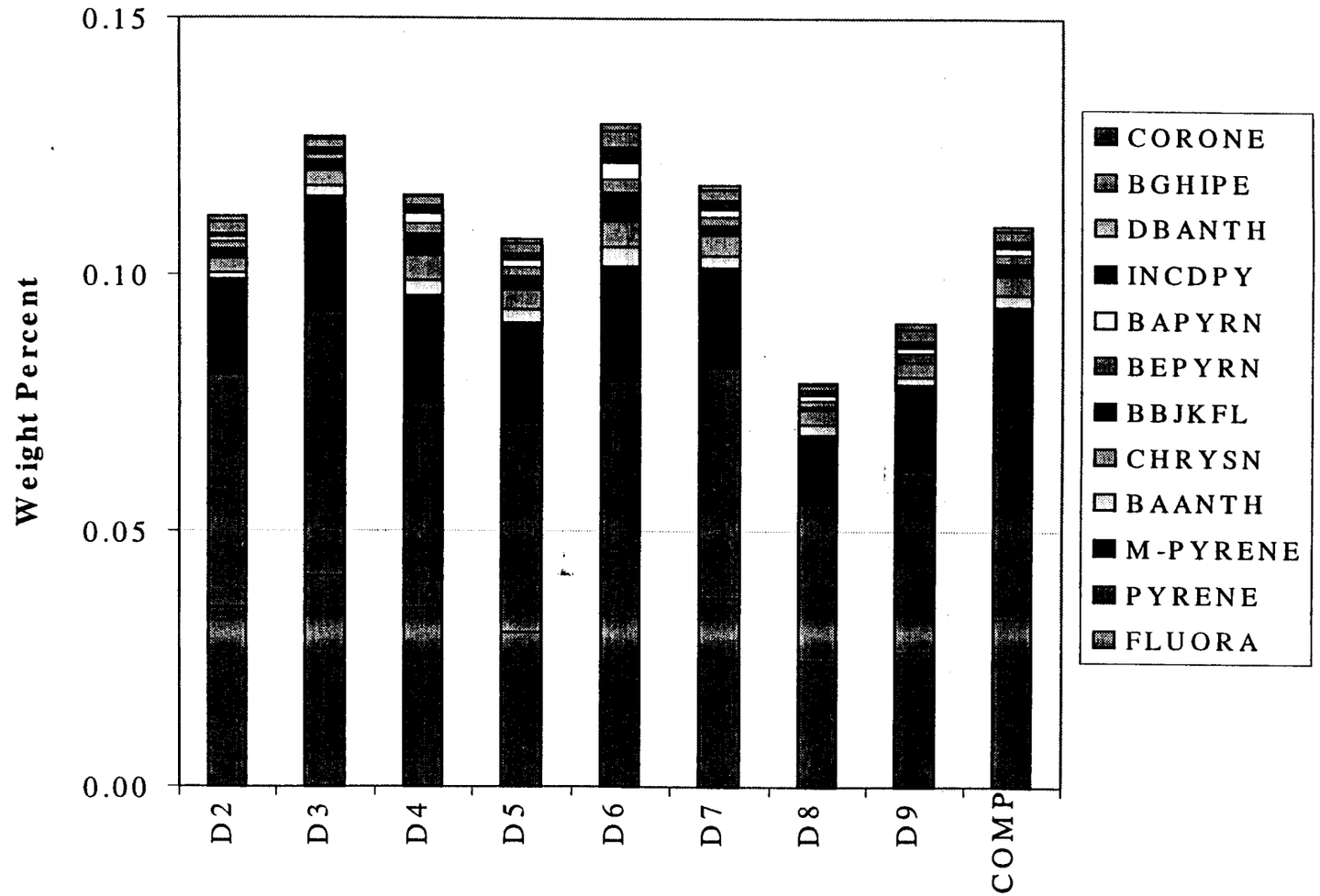


Heavy-Duty Diesel Vehicles (Phoenix, I&M)

Run No.	No. of HDD Trucks	Notes
2	15	All pass; two (1978 and 1983) 6% opacity
3	12	All pass; one (1989) 4.3% opacity
4	13	All pass; one (1984) 7.2%, one (1986) 6.5% opacity
5	15	All pass; one (1989) 8.2%, heavy white smoke; one (1977) 8.1% and one (1994) 15% opacity
6	17	One fails (1978) 29% opacity; one (1990) 7.8% opacity
7	12	All pass; two (1982 & 1986) 11%; one (1993) 10% opacity
9	15	All pass; one (1989) 13.4% opacity
Total	**99**	

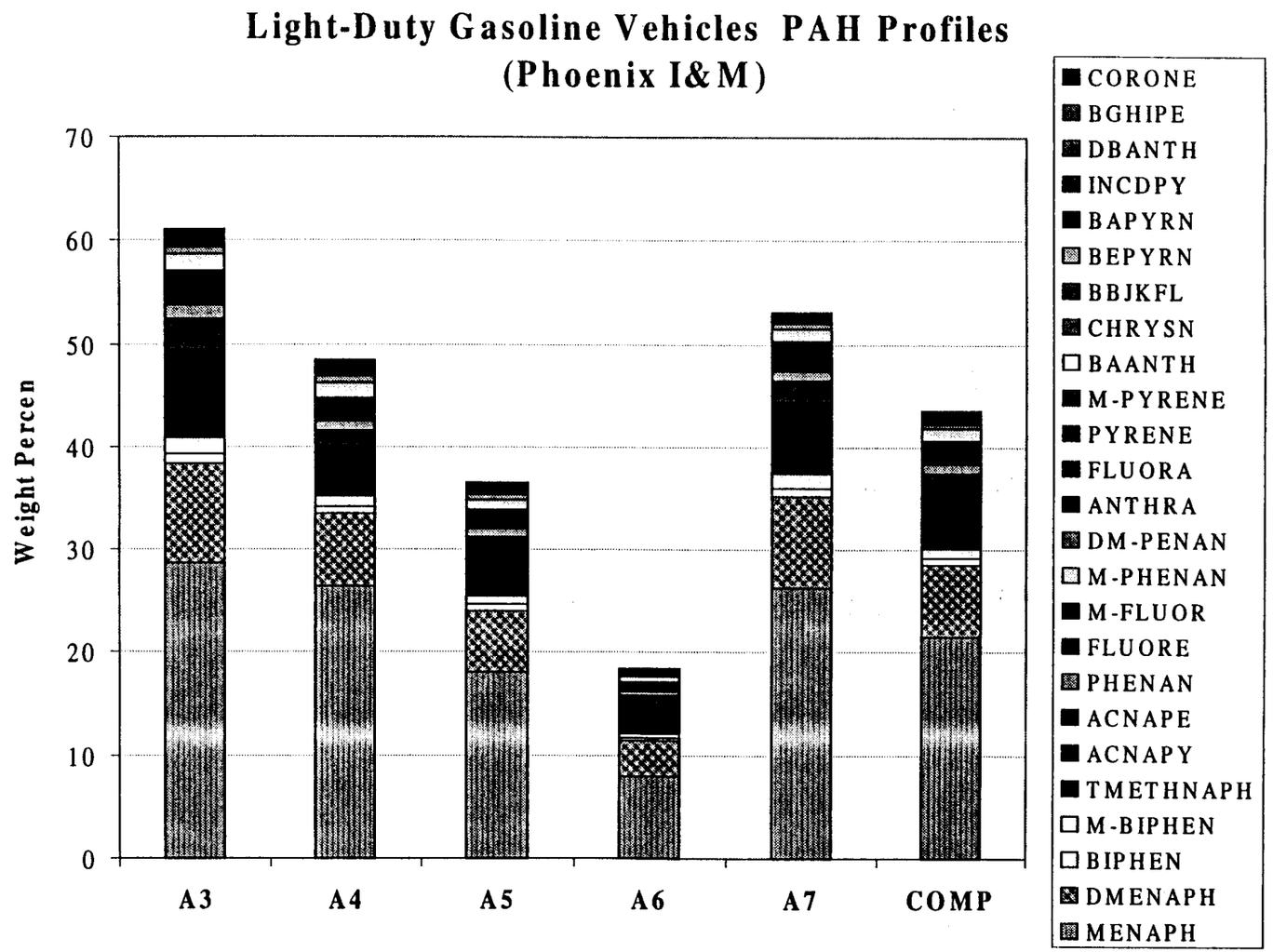

Heavy-Duty Diesel PAH Profiles
(Phoenix I&M)
Weight Percent (
0
1
2
3
4
5
6
7
8
D2
D3
D4
D5
D6
D7
D8
D9
COMP
CORONE
BGHIPE
DBANTH
INCDPY
BAPYRN
BEPYRN
BBJKFL
CHRYSN
BAANTH
M-PYRENE
PYRENE
FLUORA
ANTHRA
DM-PHEN
M-PHENAN
M-FLUOR
FLUORE
PHENAN
ACNAPE
ACNAPY
TMETHNAPH
M-BIPHEN
BIPHEN
DMENAPH
MENAPH

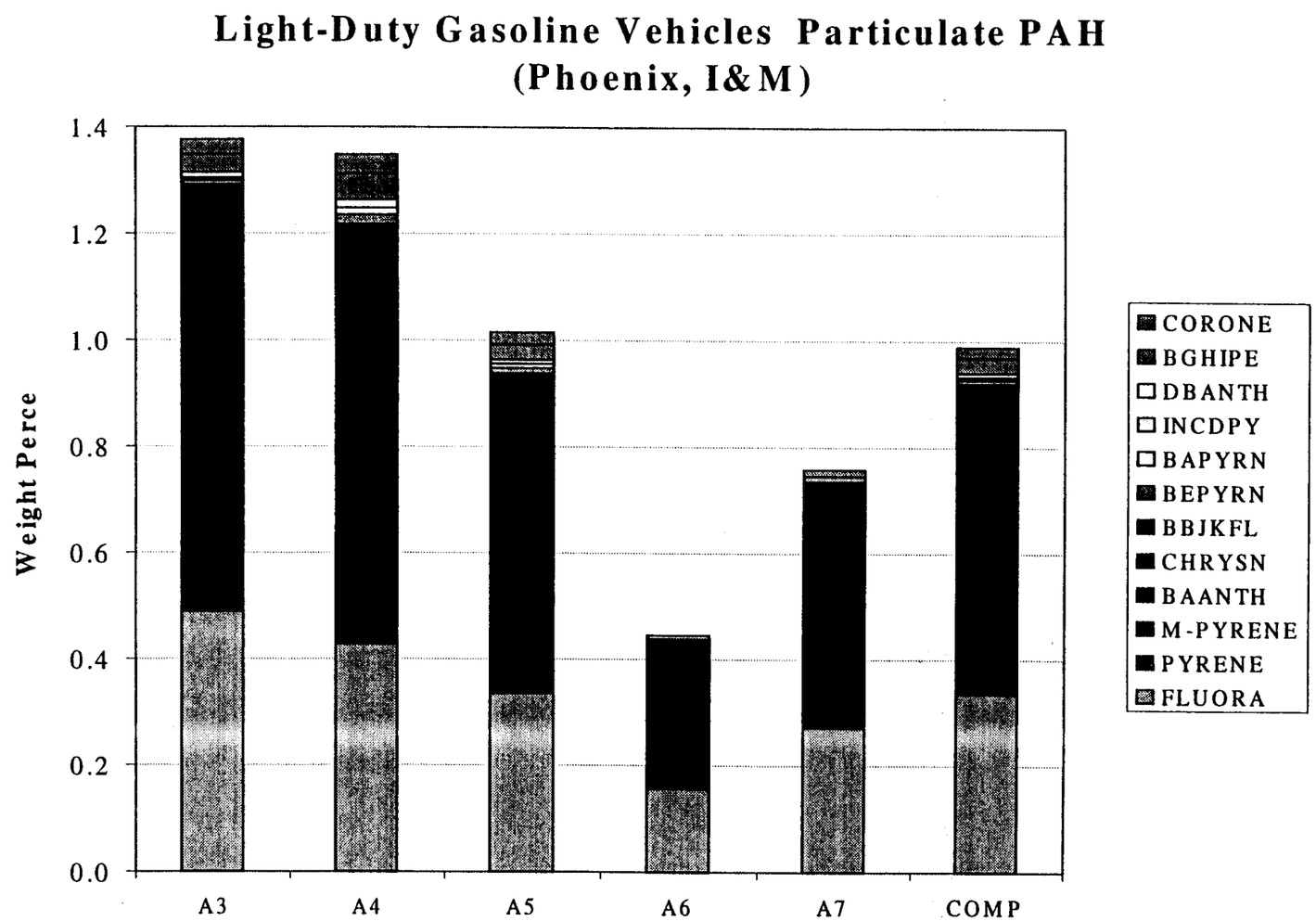
Heavy-Duty Diesel Particulate PAH (I&M)



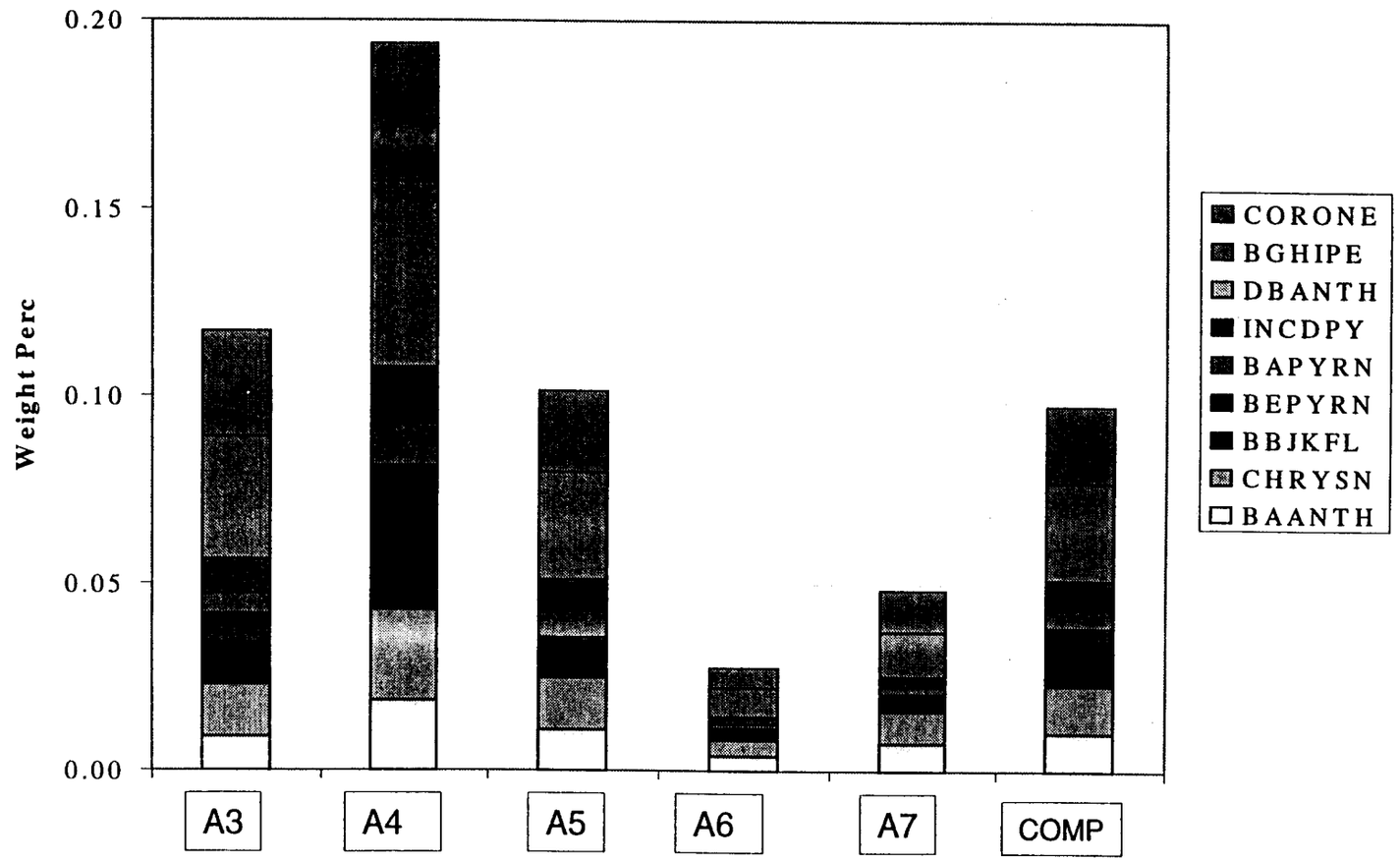
Light-Duty Gasoline Vehicles (Phoenix, I&M)

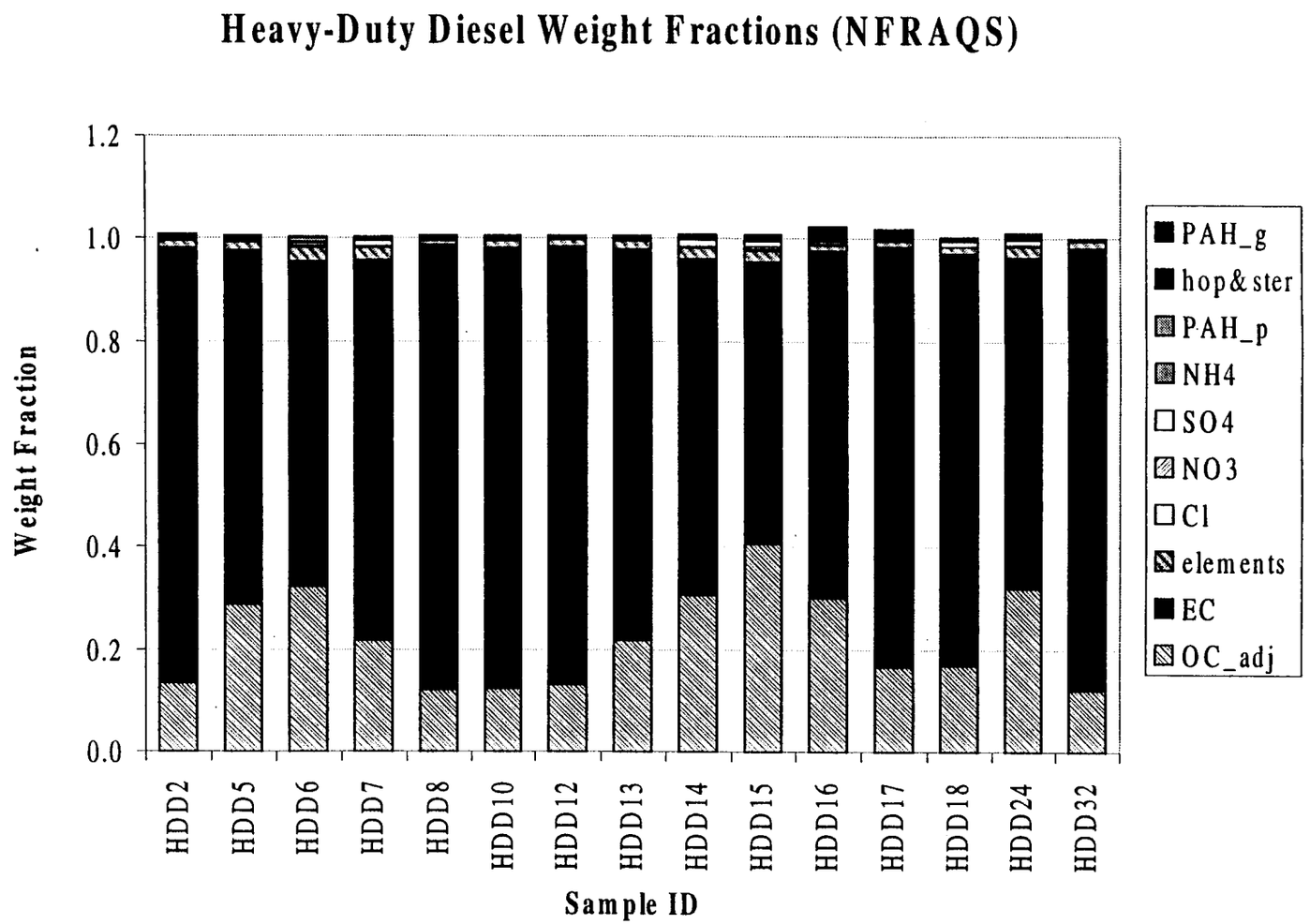
Run No.	No. of Vehicles	Notes
2	18	Model year 1973 to 1995; 3 high HC emitters (>100 ppm); one fail
3	19	Model year 1972 to 1995; 2 high HC emitters; all pass
4	26	Model year 1967 to 1995; no high HC (>100 ppm) emitters, 2 cars ~ 50 ppm HC; all pass
5	17	Model year 1976 to 1995; 1 high HC (>100 ppm) emitter, 3 cars >50 ppm; 1 fail
6	15	Model year 1968 to 1993; 2 high HC (>100 ppm) emitters, 2 cars>50 ppm; 2 fail
7	26	Model year 1969 to 1995; 2 high HC (>100 ppm) emitters, 3 cars>50 ppm; all pass
Total	**121**	


Light-Duty Gasoline Vehicles PAH Profiles
(Phoenix I&M)
Weight Percen
70
60
50
40
30
20
10
0
A3
A4
A5
A6
A7
COMP
CORONE
BGHIPE
DBANTH
INCDPY
BAPYRN
BEPYRN
BBJKFL
CHRYSN
BAANTH
M-PYRENE
PYRENE
FLUORA
ANTHRA
DM-PENAN
M-PHENAN
M-FLUOR
FLUORE
PHENAN
ACNAPE
ACNAPY
TMETHNAPH
M-BIPHEN
BIPHEN
DMENAPH
MENAPH

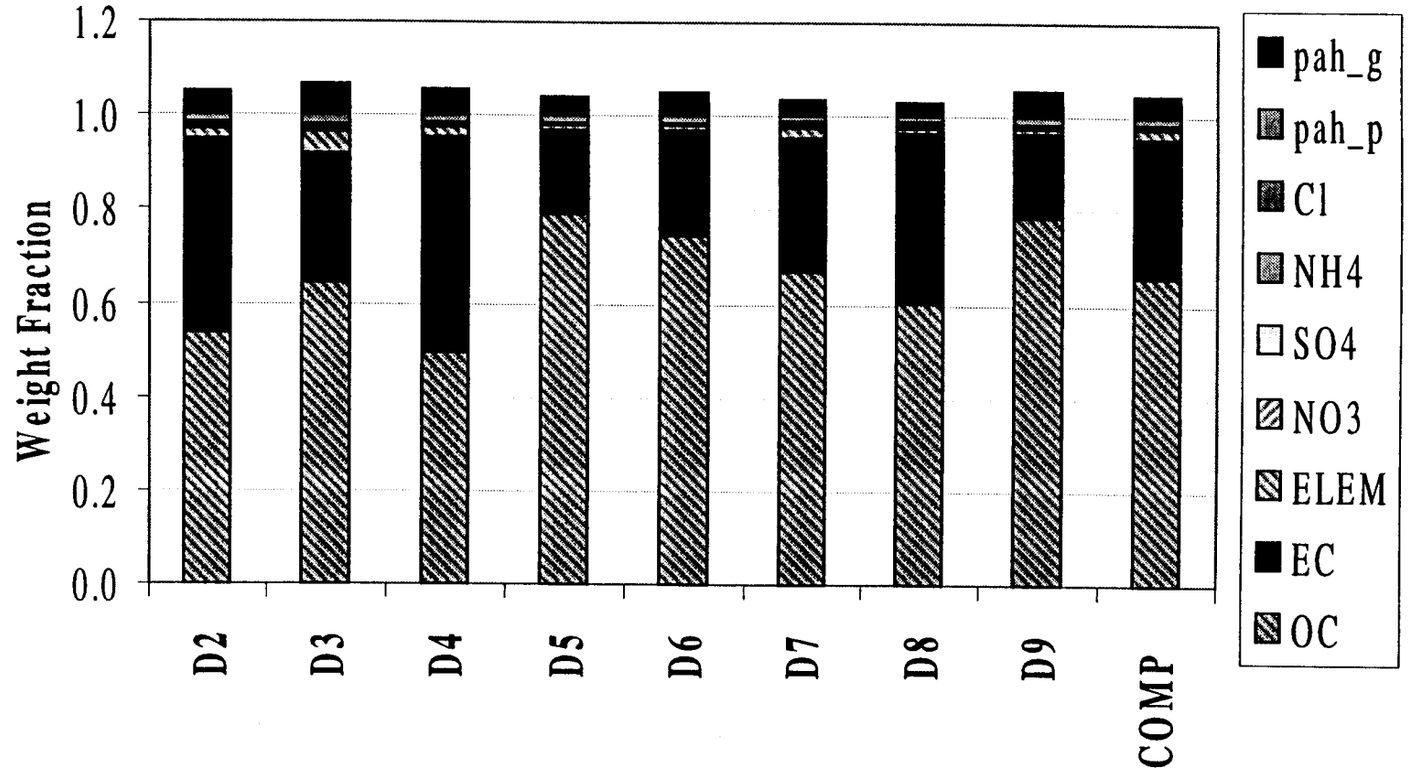

Light-Duty Gasoline Vehicles Particulate PAH
(Phoenix, I&M)
Weight Perce
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
A3
A4
A5
A6
A7
COMP
CORONE
BGHIPE
DBANTH
INCDPY
BAPYRN
BEPYRN
BBJKFL
CHRYSN
BAANTH
M-PYRENE
PYRENE
FLUORA

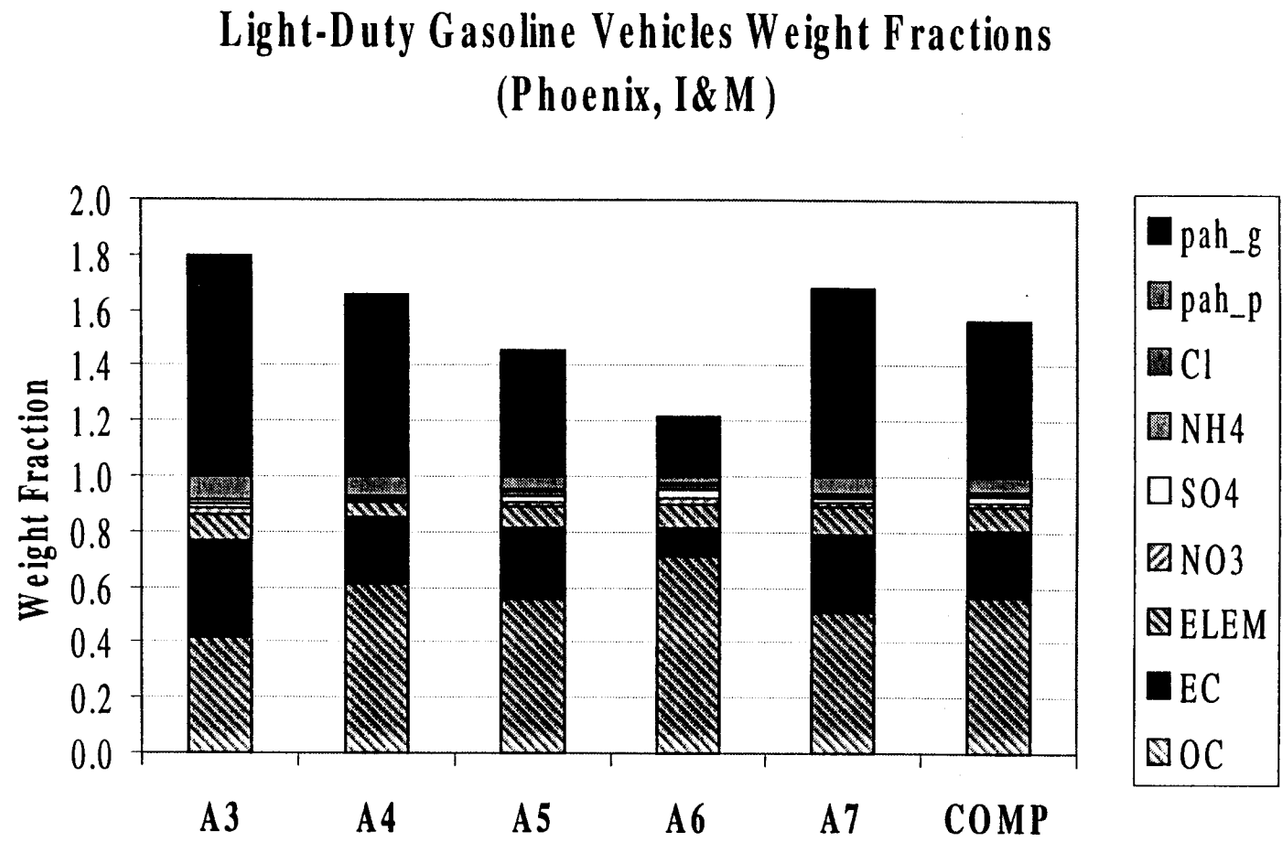
Light-Duty Gasoline Vehicle Heavy PAH Profile (Phoenix, I&M)




Heavy-Duty Diesel Weight Fractions (NFRAQS)
Weight Fraction
1.2
1.0
0.8
0.6
0.4
0.2
0.0
HDD2
HDD5
HDD6
HDD7
HDD8
HDD10
HDD12
HDD13
HDD14
HDD15
HDD16
HDD17
HDD18
HDD24
HDD32
Sample ID
PAH_g
hop&ster
PAH_p
NH4
SO4
NO3
Cl
elements
EC
OC_adj

Heavy-Duty Diesel Weight Fractions (Phoenix, I&M)




Light-Duty Gasoline Vehicles Weight Fractions
(Phoenix, I&M)
Weight Fraction
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
A3
A4
A5
A6
A7
COMP
pah_g
pah_p
Cl
NH4
SO4
NO3
ELEM
EC
OC

Conclusions:

- Most of the particulate matter emissions from light-duty gasoline vehicles come from older, poorly maintained vehicles
- Mixed-phase profiles (gas- and particle-phase species) can be utilized to apportion fine particulate matter emitted from gasoline- and diesel-powered vehicles
- Extended profiles (inorganic and organic species) are useful in CMB apportionment of fine particulate matter emitted from different vehicle categories
- Most of the discriminatory power of the mixed-phase extended profiles resides in the polycyclic aromatic hydrocarbons (PAH)

ACKNOWLEDGMENTS

Financial support for this work was provided by the Northern Front Range Air Quality Study through Colorado State University and by the U.S. Environmental Protection Agency and General Motors Research and Development Center.