Application of Organic Molecular Markers for Ambient Apportionment of Fine Particulate Matter

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Bay Area Air Quality Management District
Community Air Risk Evaluation Task Force Meeting
San Francisco
February 23, 2006

Martis Fire on June 18 2001
near Reno, NV

View of Reno from DRI on clear day versus June 19, 2001


Martis Fire about 1 or 2 hours old


Martis Fire about 4-5 hours old

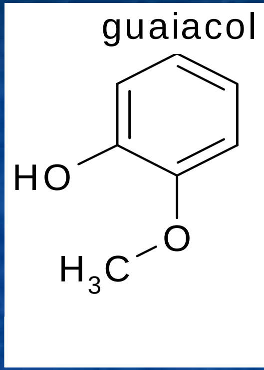
Residential Wood Combustion

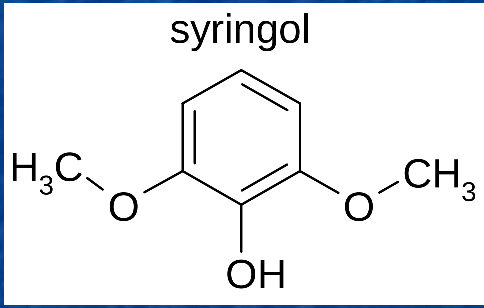
*McDonald et al., ES&T, **34**, 2080-2091, 2000*

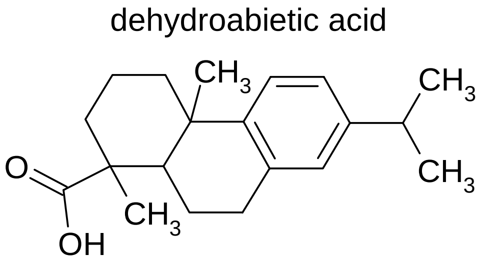
Rinehart et al., in preparation

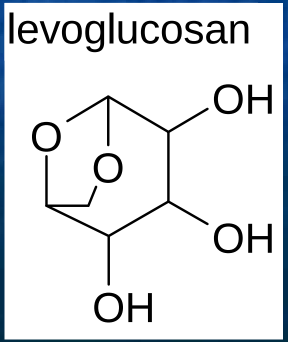
Organic Molecular Markers for Wood Combustion

- Lignin pyrolysis products
  - guaiacol (2-methoxyphenol), syringol (2,6-dimethoxyphenol) and derivatives
  - syringols/guaiacol ratios
    - ~ 0.01 for softwoods
    - ~ 1.0 for hardwoods
- Resin acids and oxidation products
  - Abietic acid, pimaric acid
  - Retene (1-methyl-7-isopropylphenanthrene)
  - 1,7-dimethylphenanthrene
- Cellulose pyrolysis product
  - Levoglucosan (1,6-anhydro-β-D-glucose)



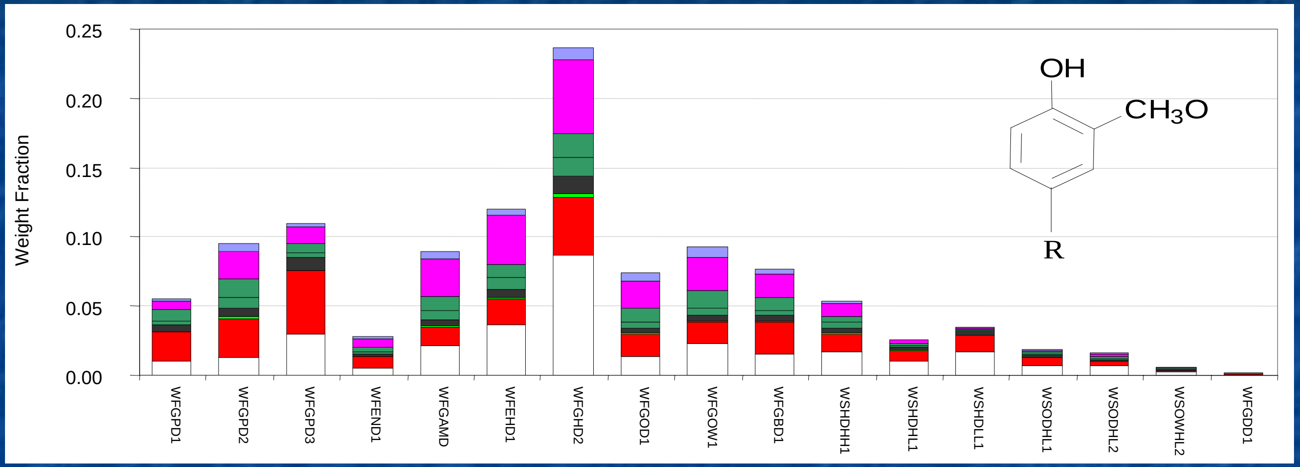




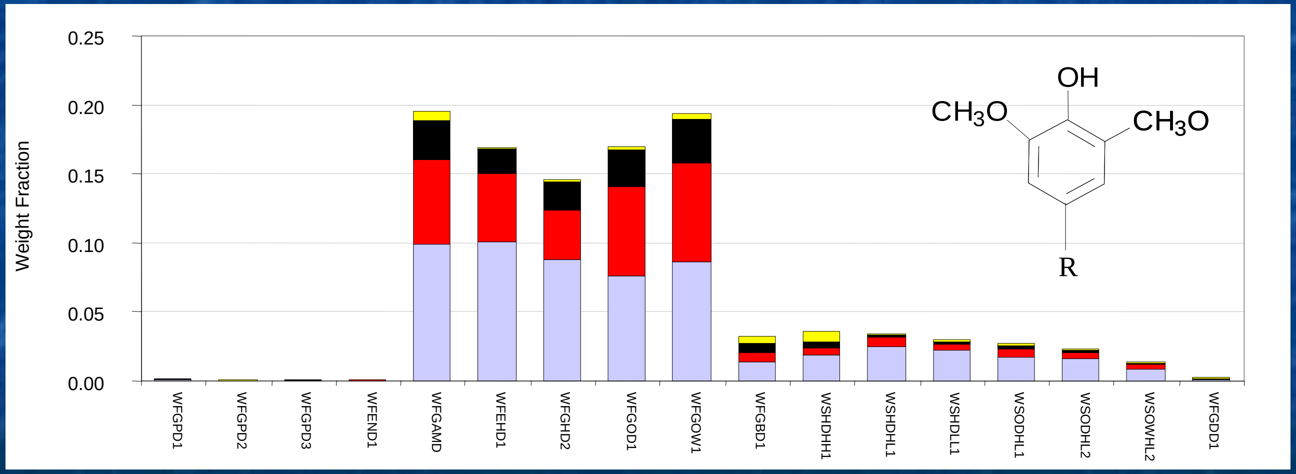


NFRAQS - Lignin Combustion Products

- Guaiacols

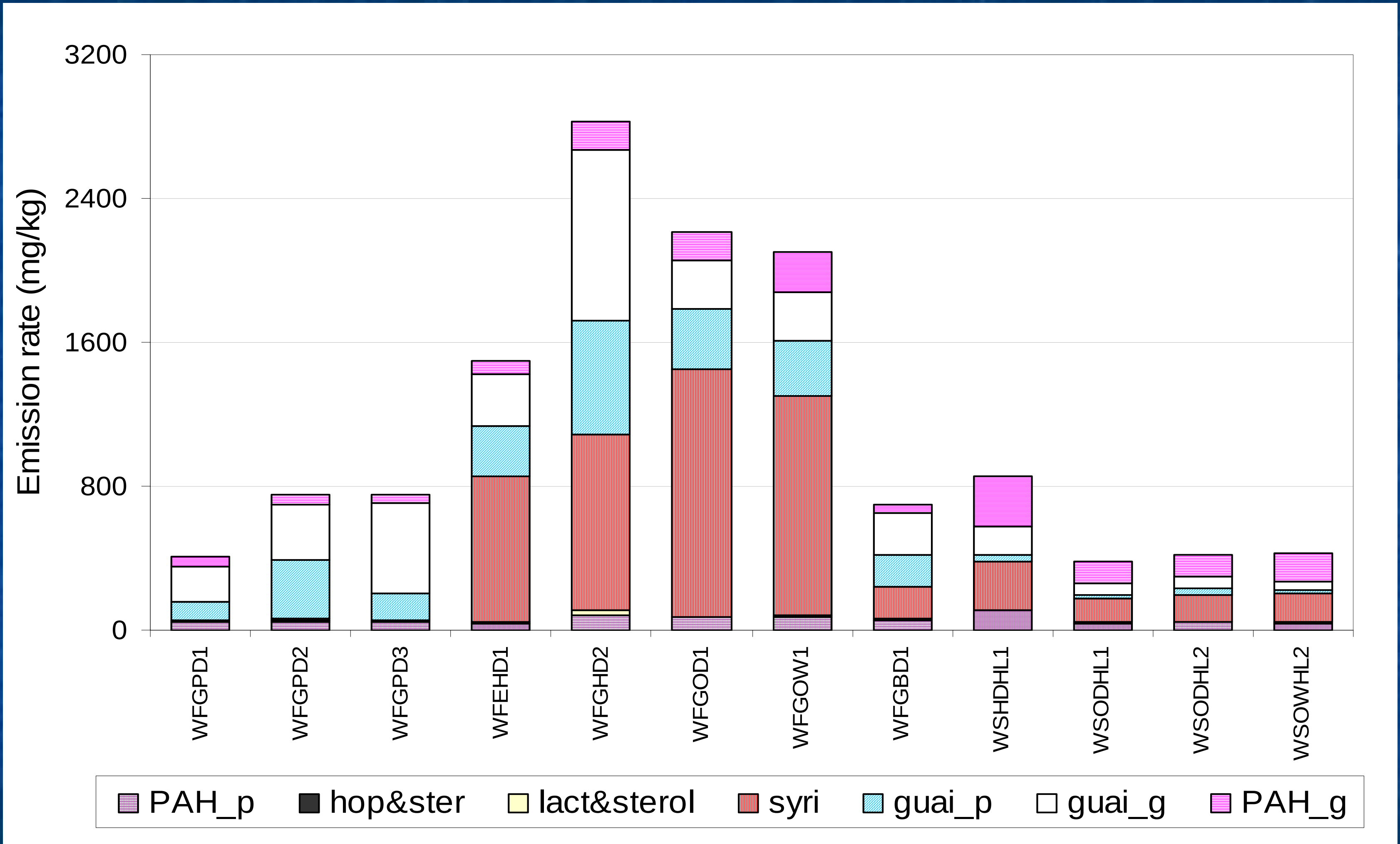


- Syringols



Fireplace Softwood	Fireplace Hardwood	Woodstove Hardwood

NFRAQS - Other Organic Compounds in Woodsmoke

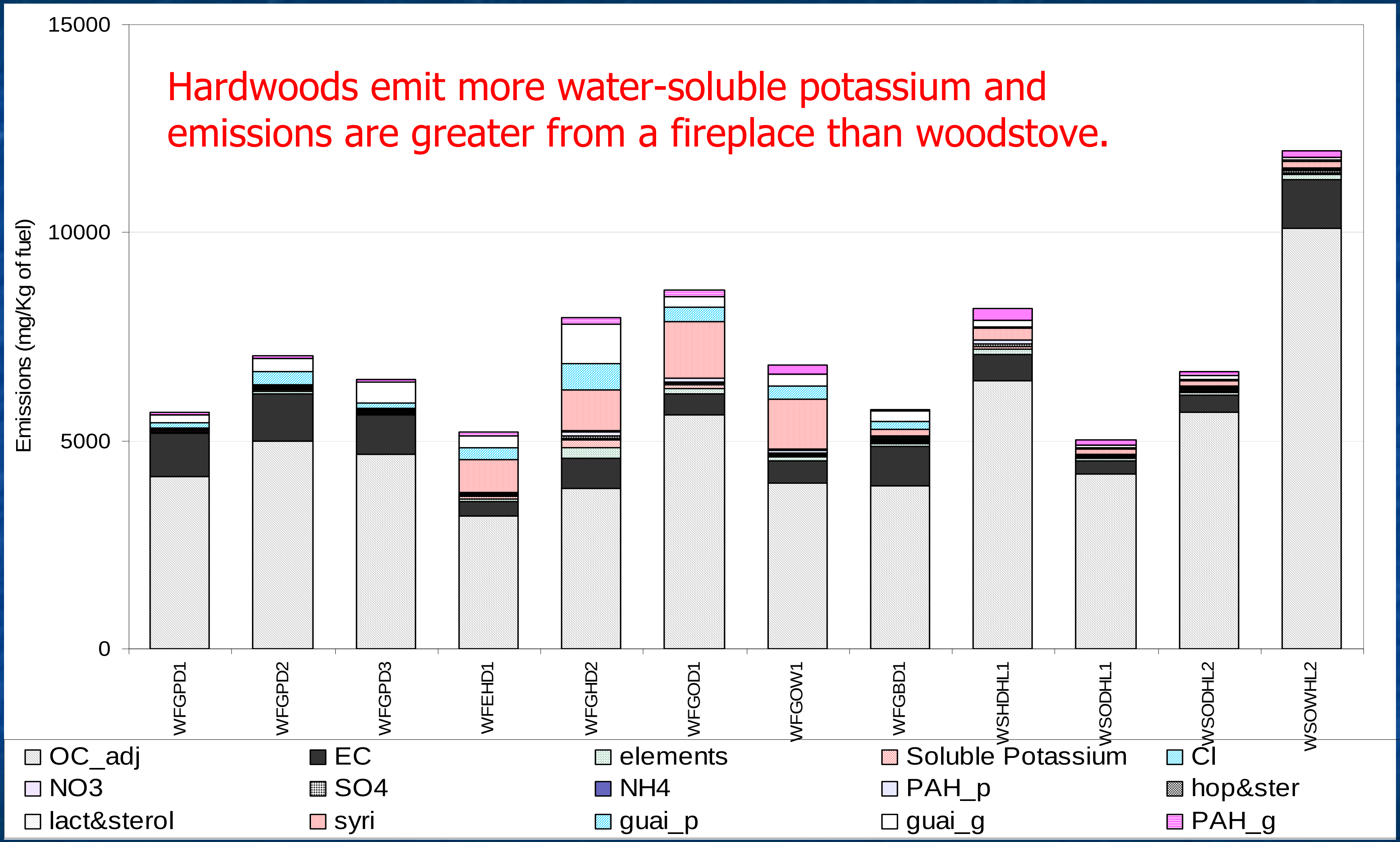


Fireplace Softwood

Fireplace Hardwood

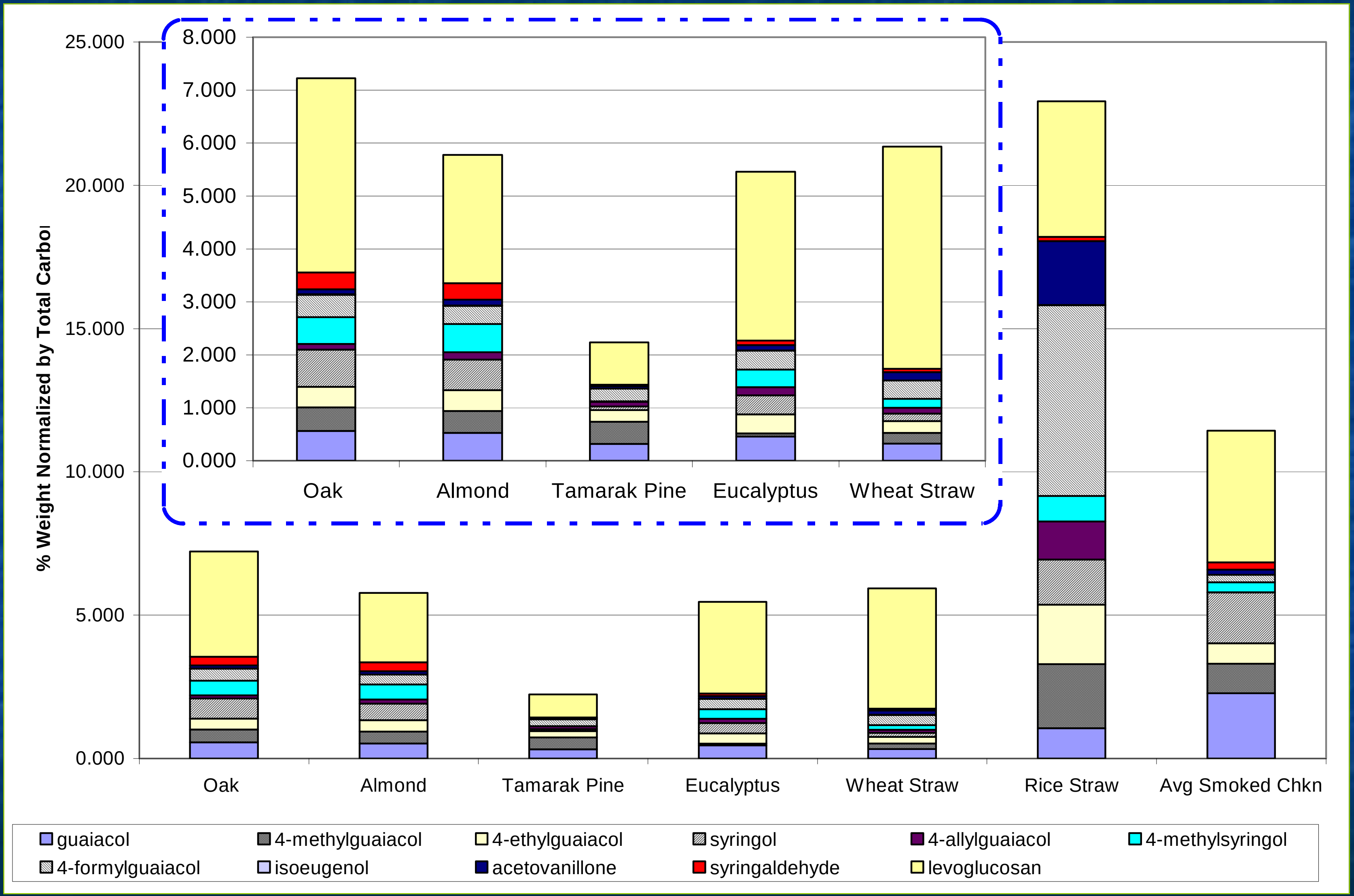
Woodstove Hardwood

NFRAQS - Chemical Composition of Wood Smoke



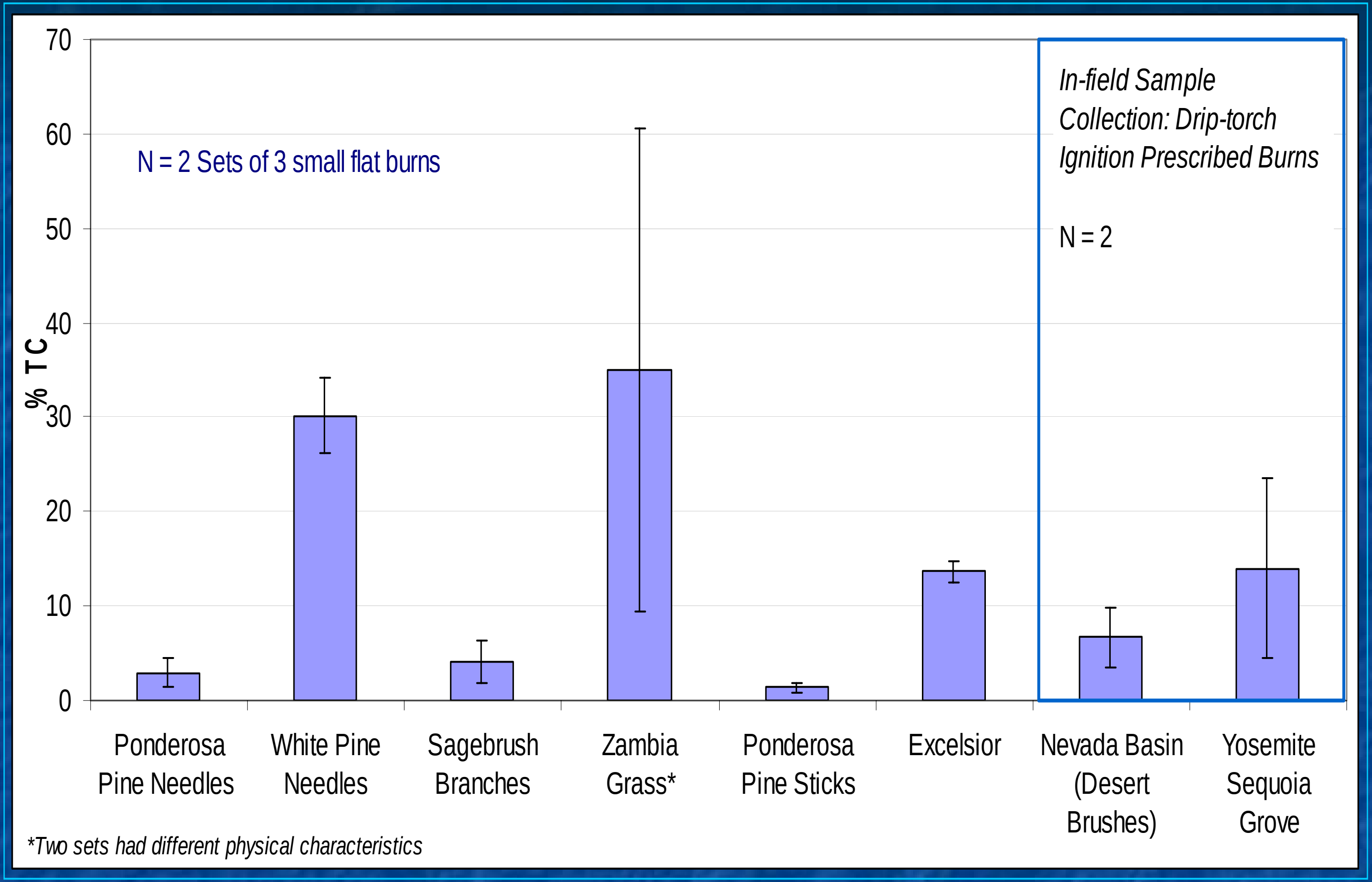
Fireplace Softwood | Fireplace Hardwood | Woodstove Hardwood

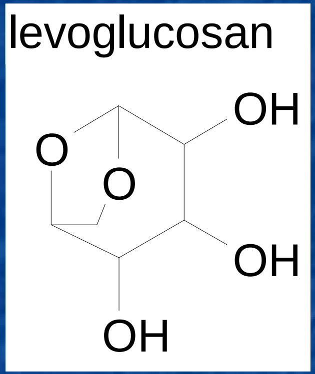
Abundance of Levoglucosan & Selected Methoxy Phenols in Residential Woods & Agricultural Straws



Source: L.R. Rinehart Ph.D. Dissertation 2005.

Levoglucosan in Wildland Fuels and Prescribed Burns



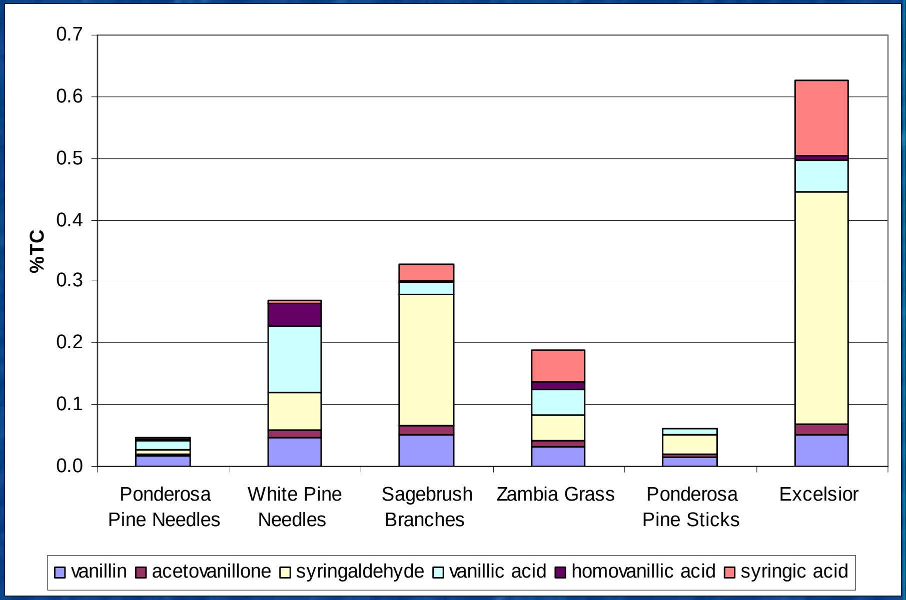


- The abundance of levoglucosan varies for the different plant types, however it is a large portion of the total carbon, measured by IMPROVE-TOR analysis.
- Levoglucosan is found in higher abundance in pine needles & grasses than woods.

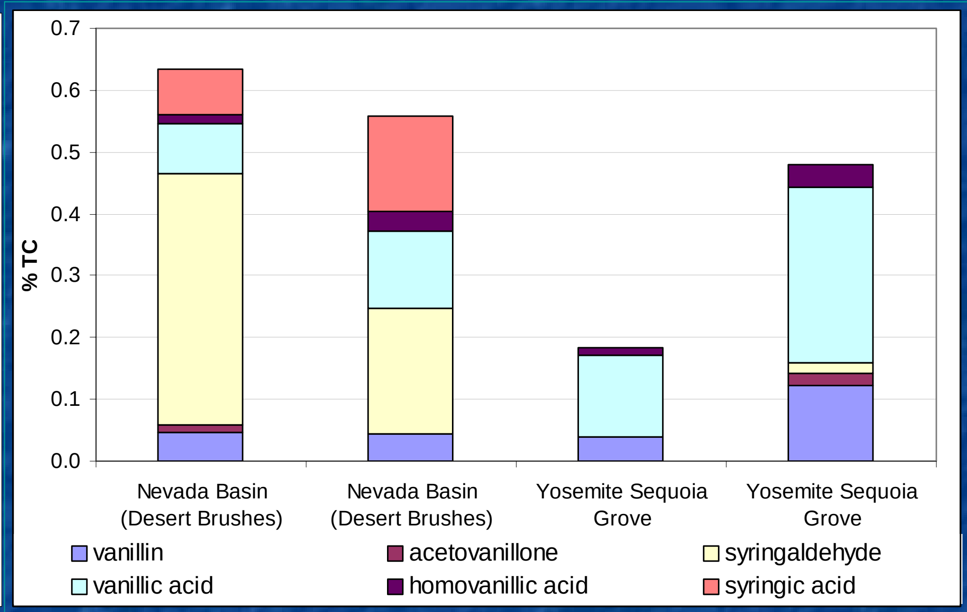
Source: L.R. Rinehart Ph.D. Dissertation 2005.

Lignin Combustion Products - Methoxy Phenols & Acids in Wildland Fuels & Prescribed Burns

Laboratory Experiments



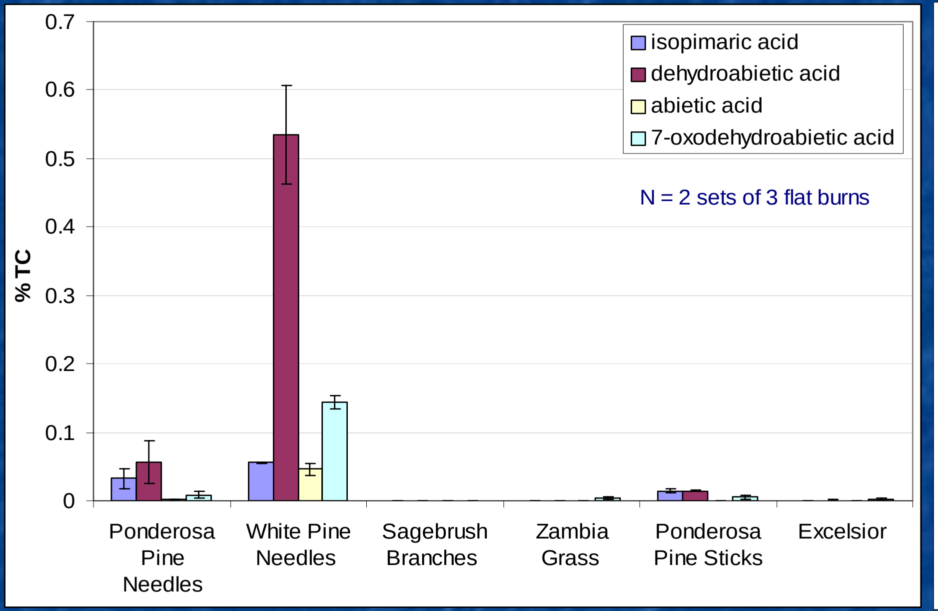
Prescribed Burns



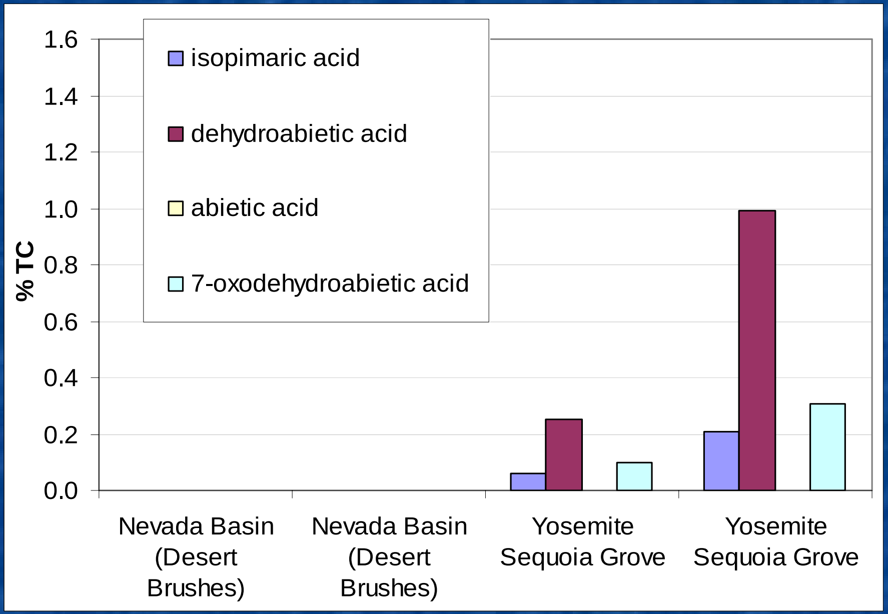
Source: L.R. Rinehart Ph.D. Dissertation 2005.

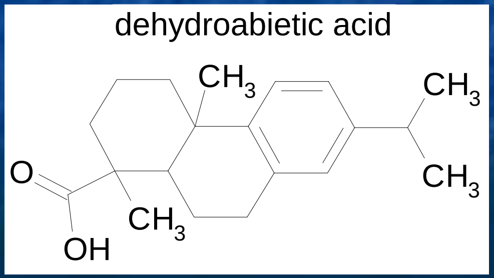
Variability of Resin Acids for Wildland Fuels

Laboratory Experiments



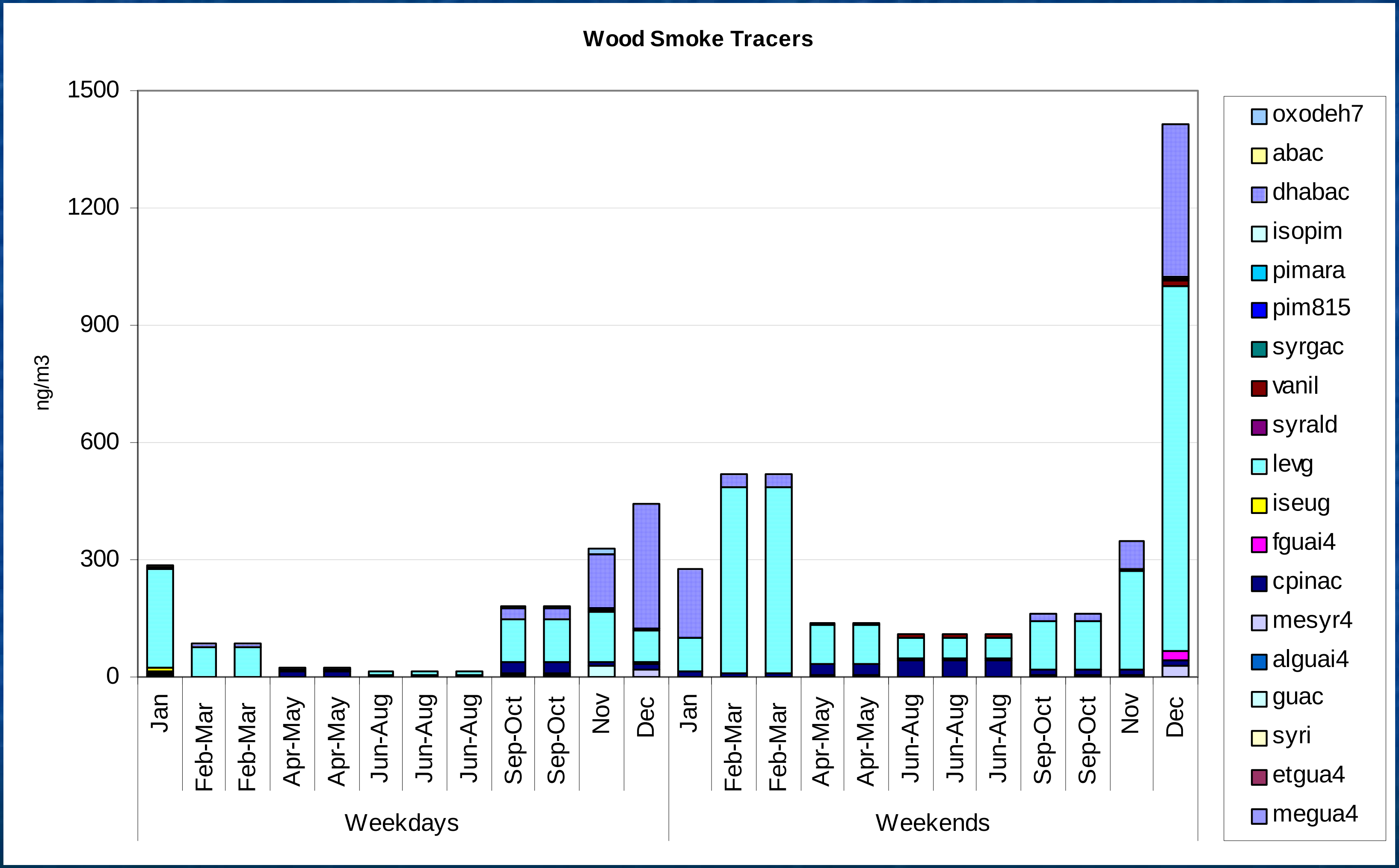
Prescribed Burns





Source: L.R. Rinehart Ph.D. Dissertation 2005.

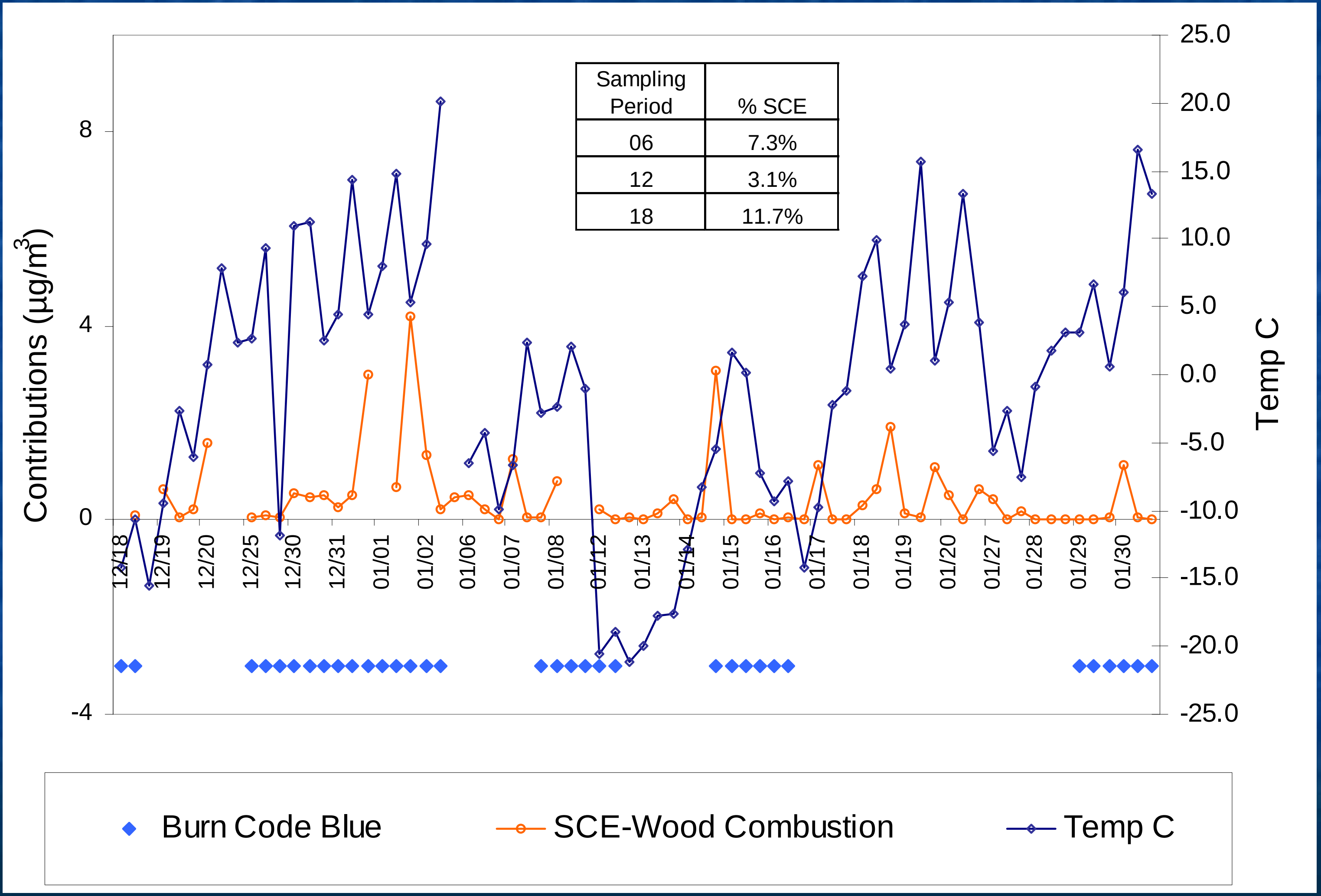
Monthly Average Ambient Concentrations of Organic Markers for Wood Combustion at San Jose, CA in 2004



NFRAQS

Northern Front Range Air Quality Study

$PM_{2.5}$ Carbon from Wood Burning Versus Temperature at Welby

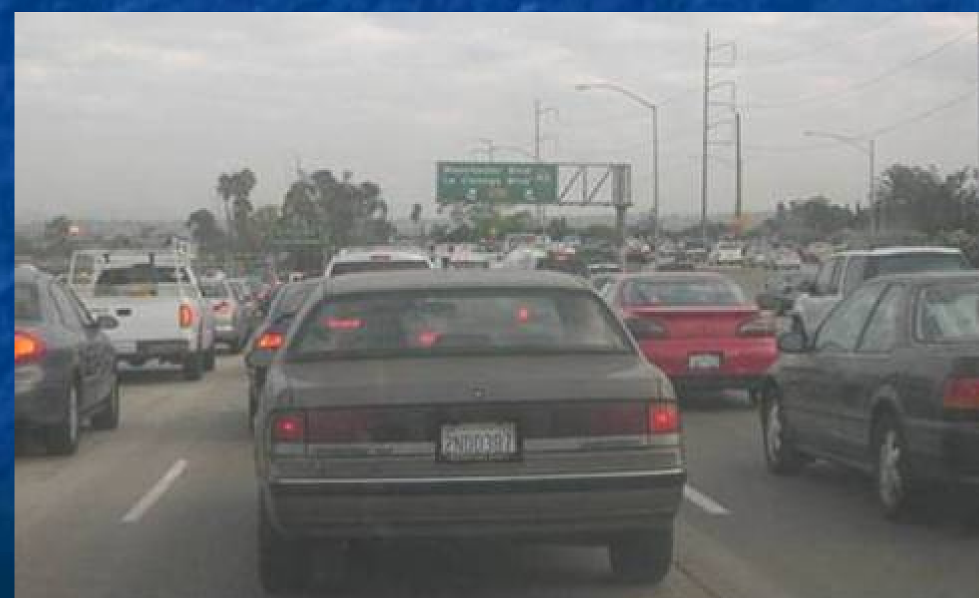


Sampling Period	% SCE
06	7.3%
12	3.1%
18	11.7%

Finding of the NFRAQS Regarding Woodburning

- Source Contributions of Residental wood combustion.
  - Moderate contributor, on average, constituting 8.0 ± 1.6% at Welby and 3.8 ± 0.8% of total carbon at Brighton.
  - CMB apportionments of motor vehicle exhaust (80% of TC) are consistent with fractions of fossil carbon by 14C analysis (77%).
  - Larger woodburning contributions at nighttime and morning near Christmas and New Year's holidays and on 12/19 and 1/14, 1/17, and 1/29 30. These periods coincided with some of the coldest temperatures and were blue code (burning allowed) except 1/17. The contributions of woodburning to total carbon on these days were 25 to 50%.
- Effect of Woodburning Restrictions.
  - Woodburning contributions during Winter 97 were substantially lower than during the winter of 1987/88, when woodburning contributions at Welby were comparable to those from motor vehicle exhaust. The 1987/88 woodburning contributions were estimated prior to woodburning controls in the Denver area.

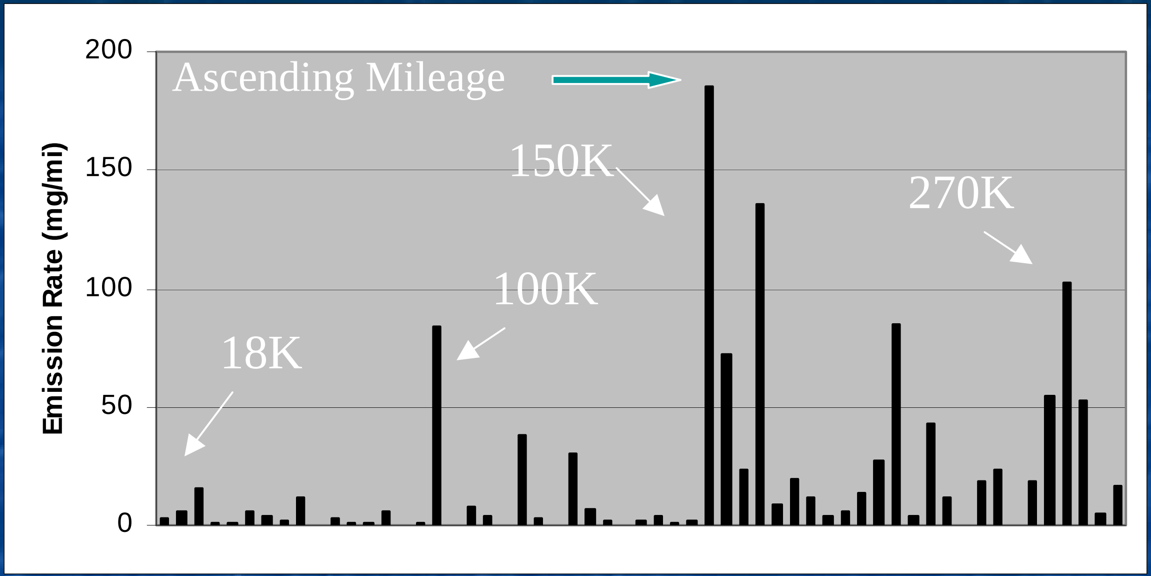

costco
AIR-RIDE EQUIPPED



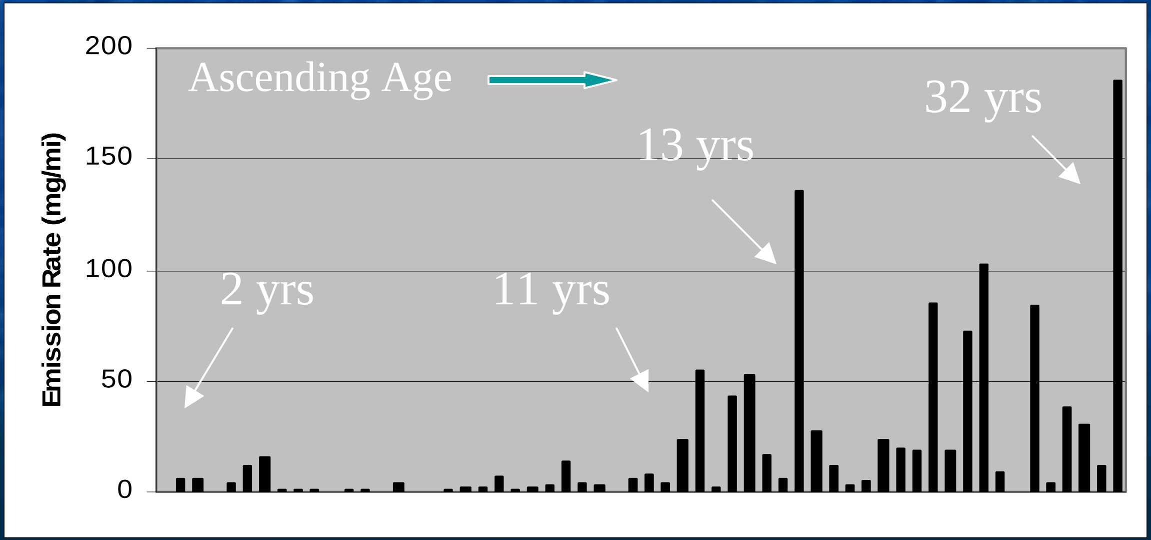
Dynamometer Tests of PM Emissions in Vehicle Exhaust
Gasoline / Diesel PM Split Study

$PM_{2.5}$ emissions versus mileage and age show that most vehicles less that 11 years and 150 K miles are clean.

Mileage Effect
Note: The 16 vehicles
< 98K mi had emission
rates <20 mg/mi.
(weighted emission rates)



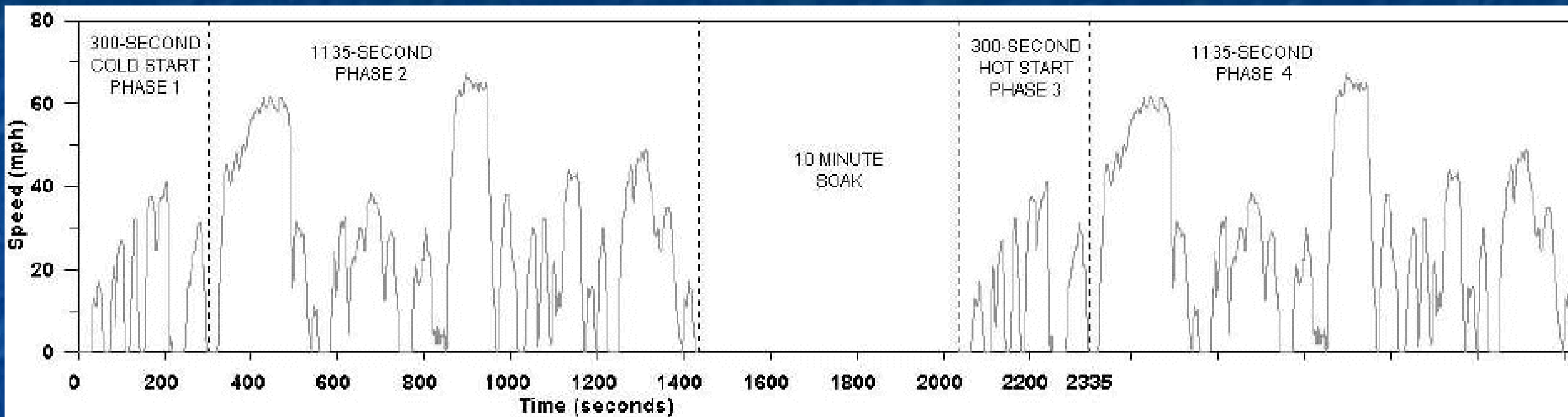
Age Effect
Note: The 31vehicles
<11 yr. had emission
rates <20 mg/mi.



Source: P. Gabele (2003)
NREL Gas/Diesel Split Study

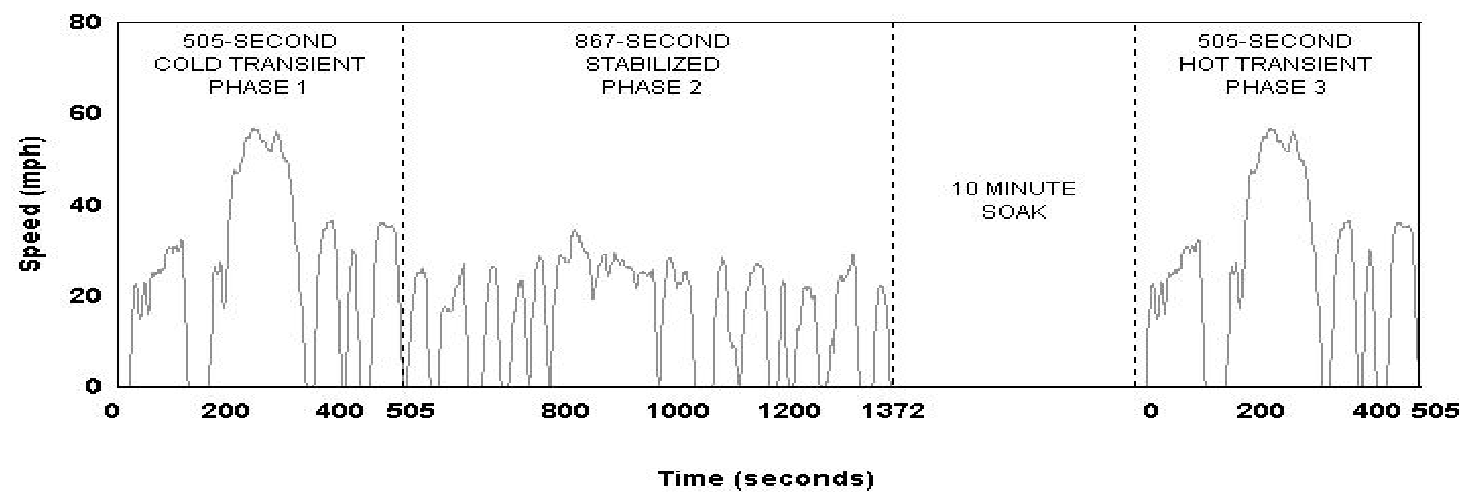
Test cycles may affect vehicle emission rate and composition.

Modified Unified Driving Cycle (LA92)

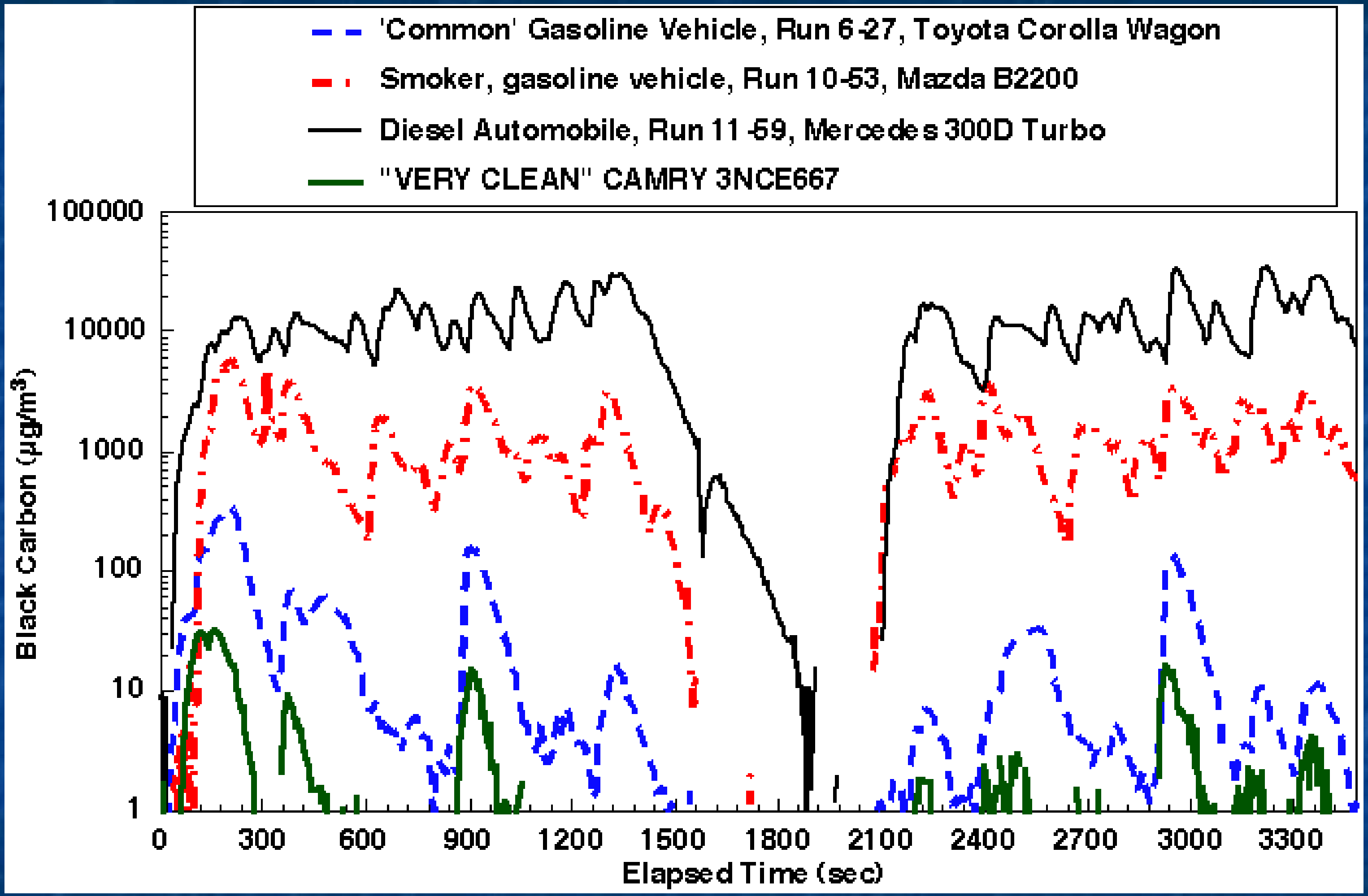


Cold UDC **Warm UDC**

Federal Test Procedure



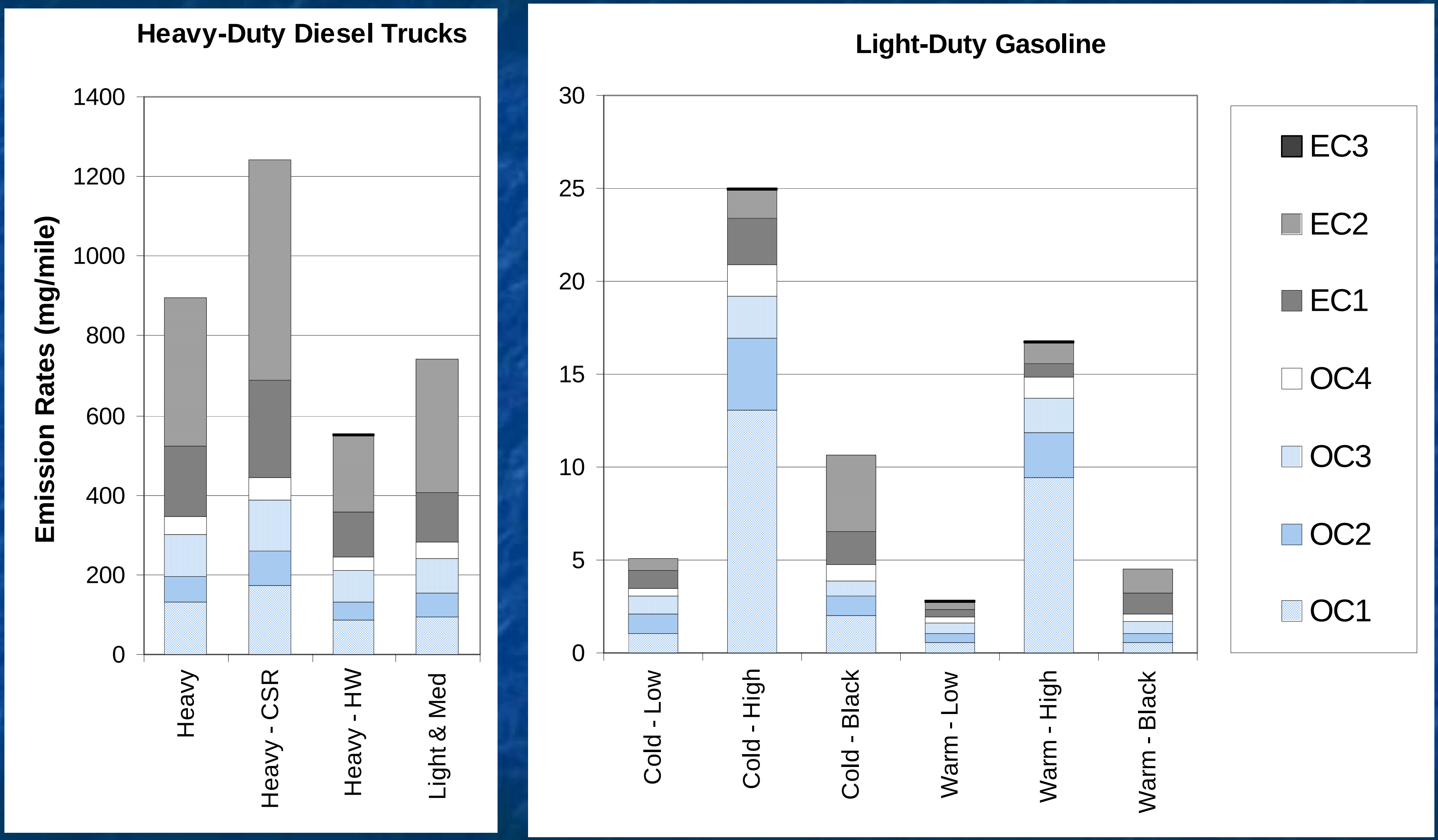
Black Carbon Emissions Rates During UDC



Source: Pat Arnott (2003)
NREL Gas/Diesel Split Study

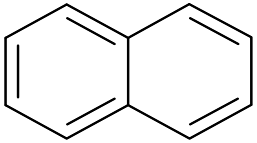
Most PM emissions during UDC from cold start and hard accels with higher fraction of black carbon.

Vehicle Profiles – Carbon Fractions by IMPROVE-TOR

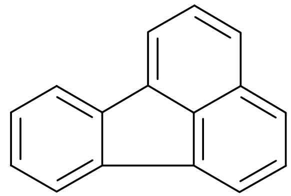


Gasoline/Diesel PM Split Study, Fujita et al., 2005

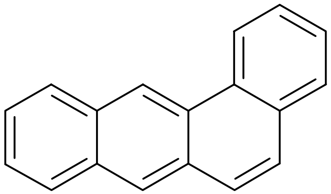
naphthalene



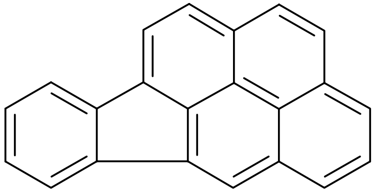
fluoranthene



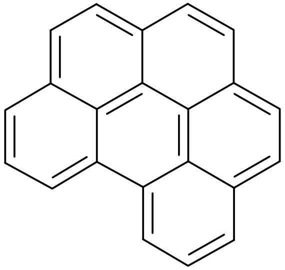
benz(a)anthracene



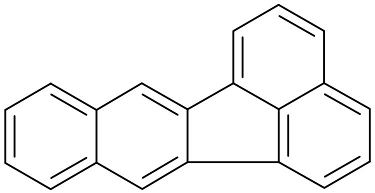
indeno(1,2,3-cd)pyrene



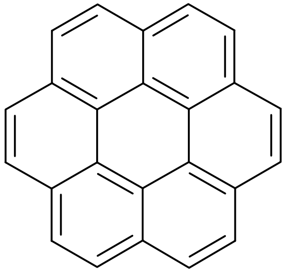
benzo(ghi)perylene



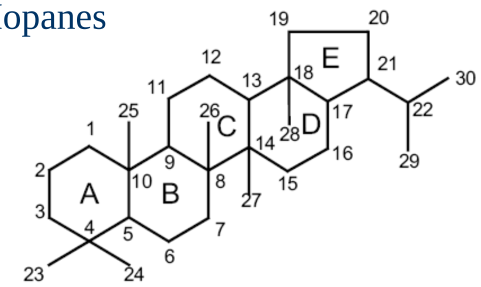
benzo(k)fluoranthene



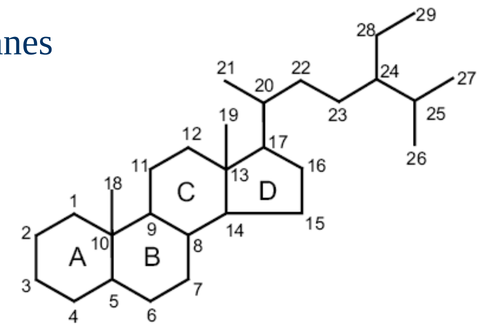
coronene



Hopanes

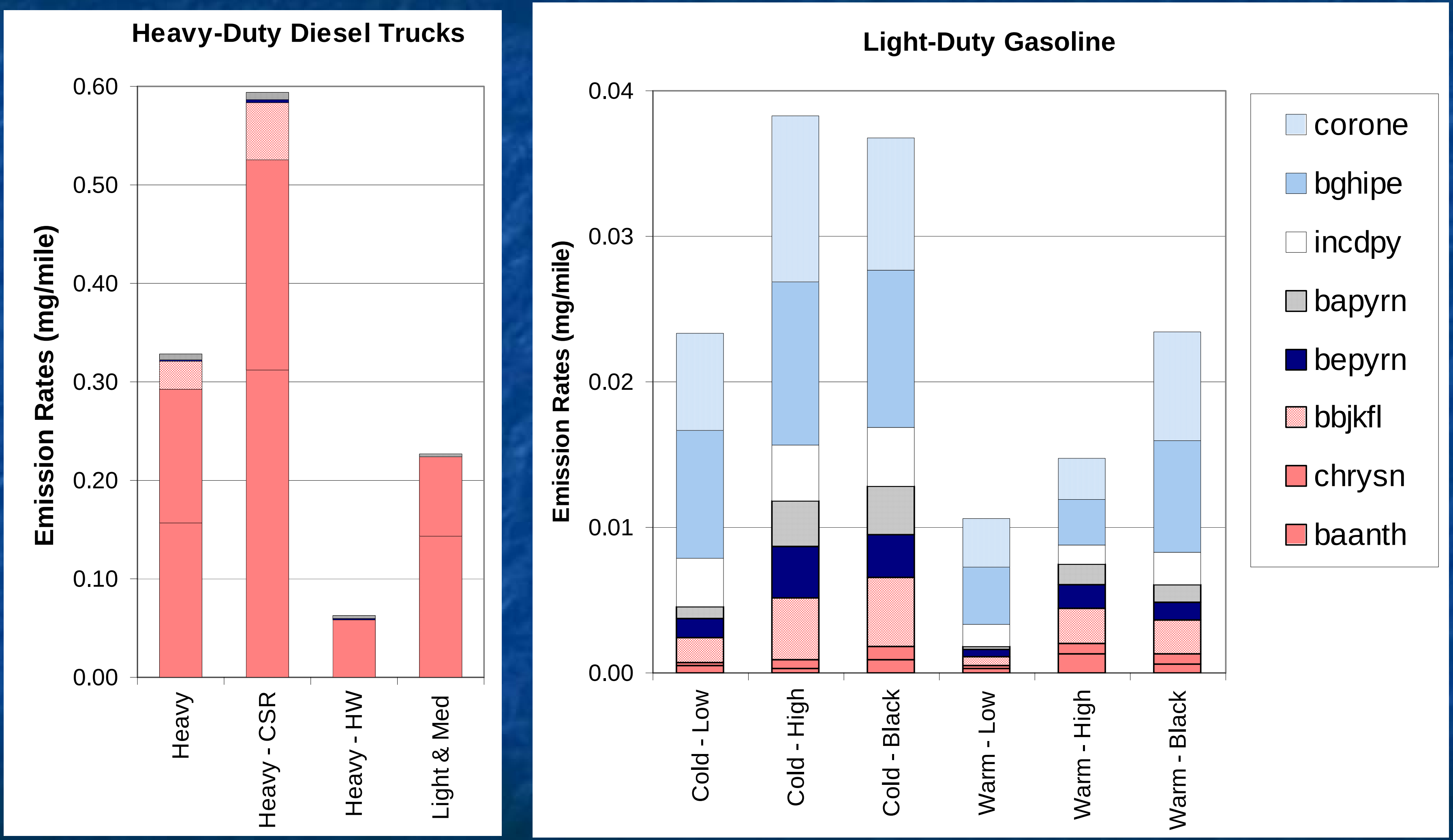


Steranes



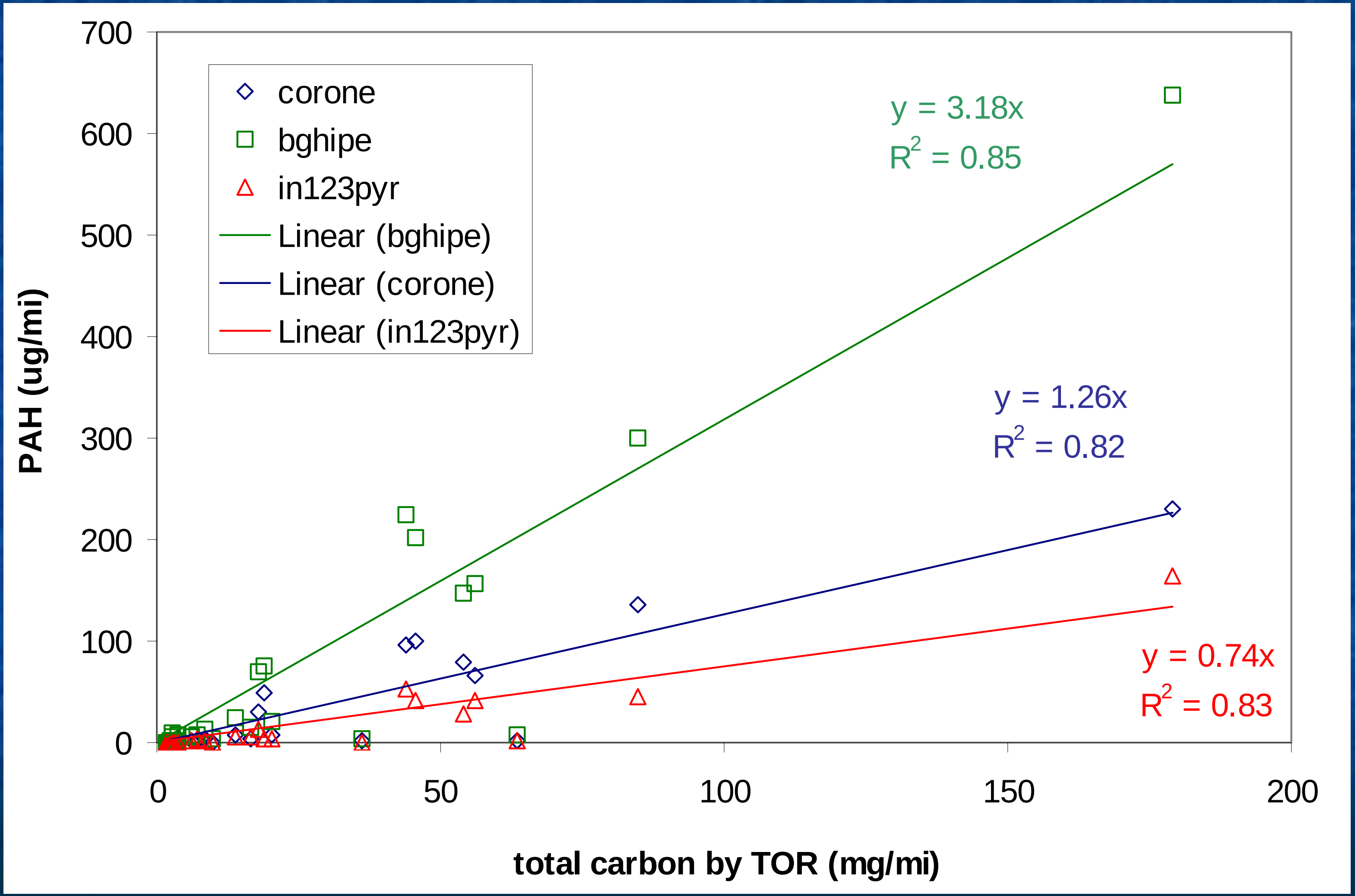
Emission Rates of Particulate PAH

Potential molecular markers exist for vehicle exhaust

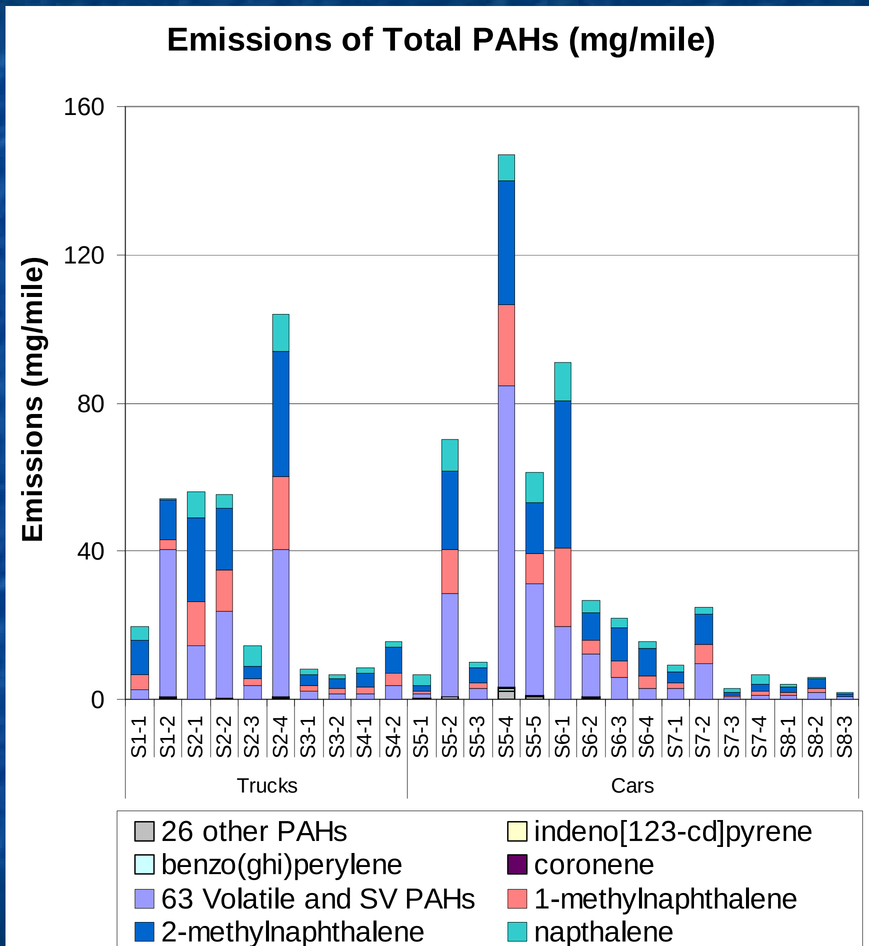


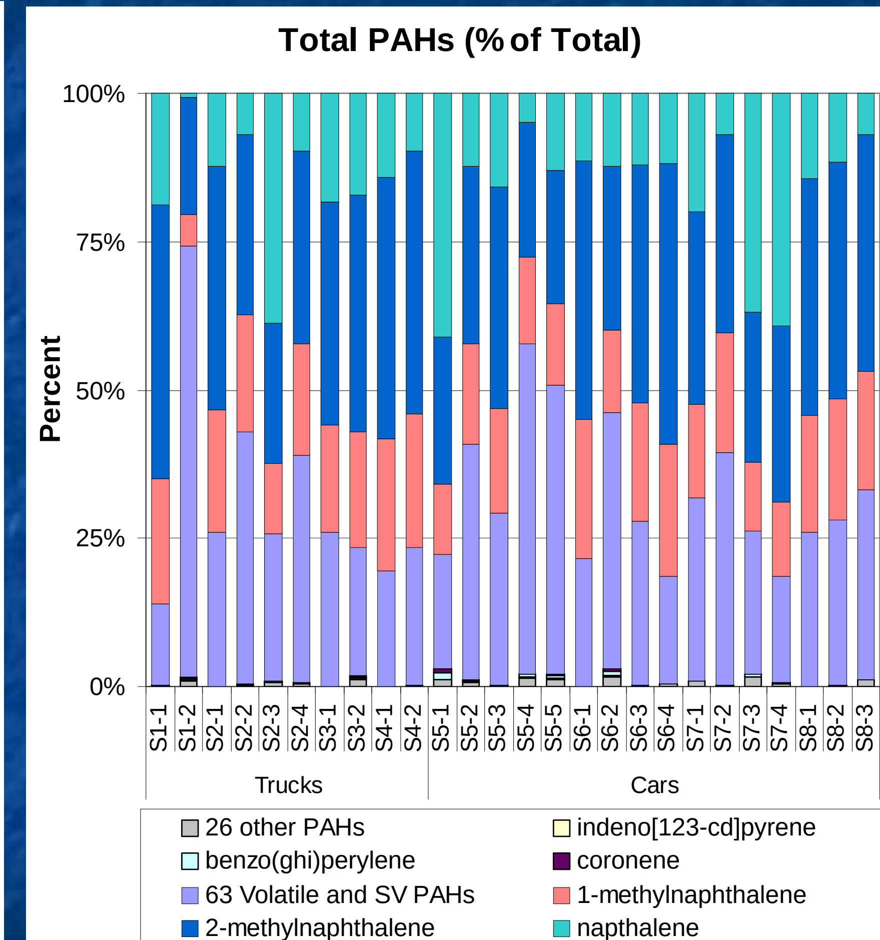
Gasoline/Diesel PM Split Study, Fujita et al., 2005

Kansas City Vehicle Characterization Study
Correlation of Potential Marker PAHs with TC



Kansas City Vehicle Characterization Study Volatile, Semi-Volatile and Particulate PAHs

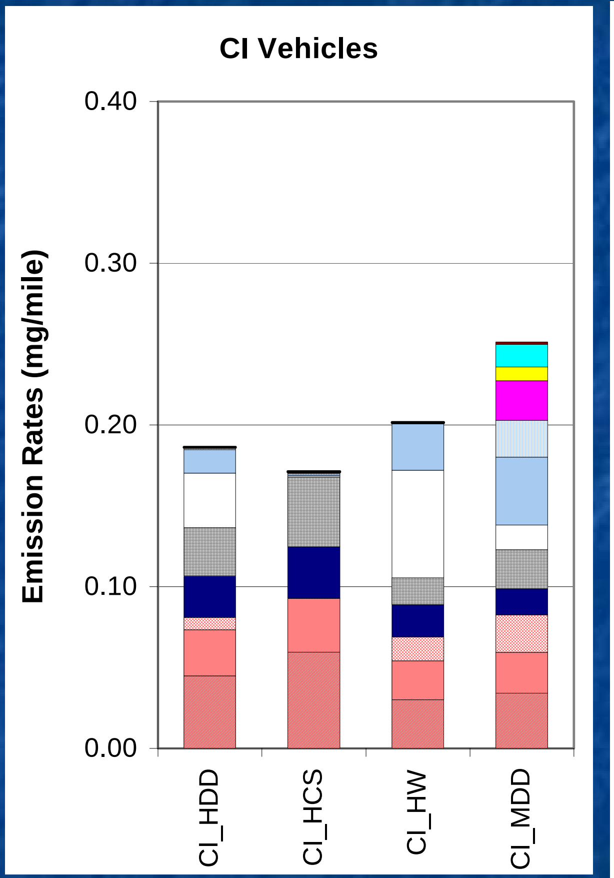


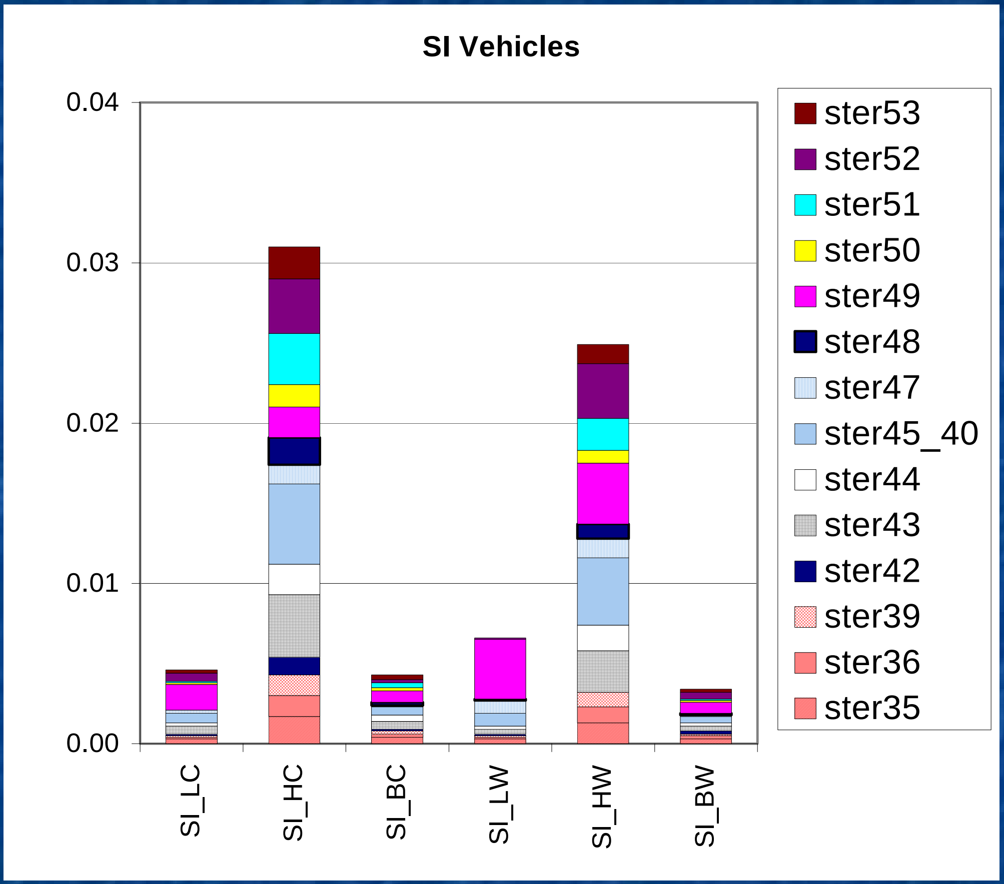


63 volatile and semi-volatile PAHs = sum of biphenyl to 1-methylpyrene.

DRI - Presented at the 15th CRC On-Road Vehicle Emissions Workshop, 2005

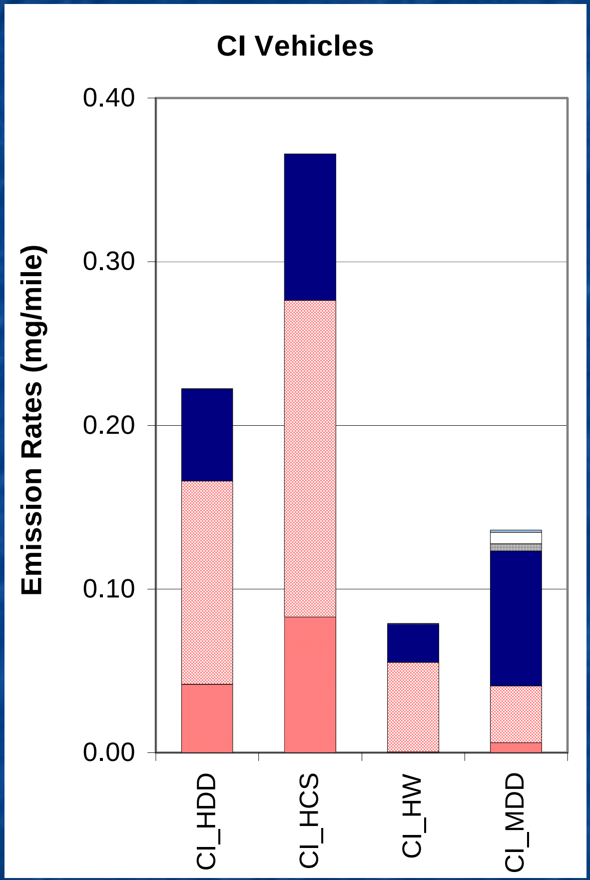
Steranes in Vehicle Exhaust Profiles

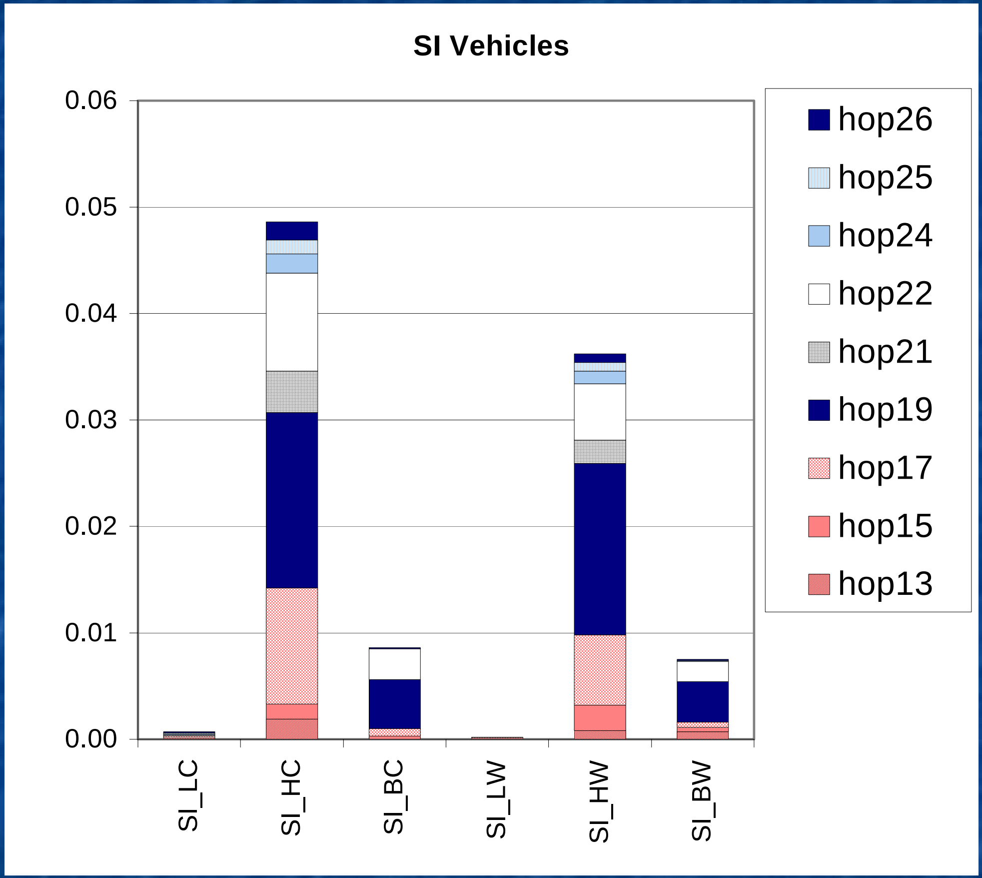




Gasoline/Diesel PM Split Study, Fujita et al., 2005

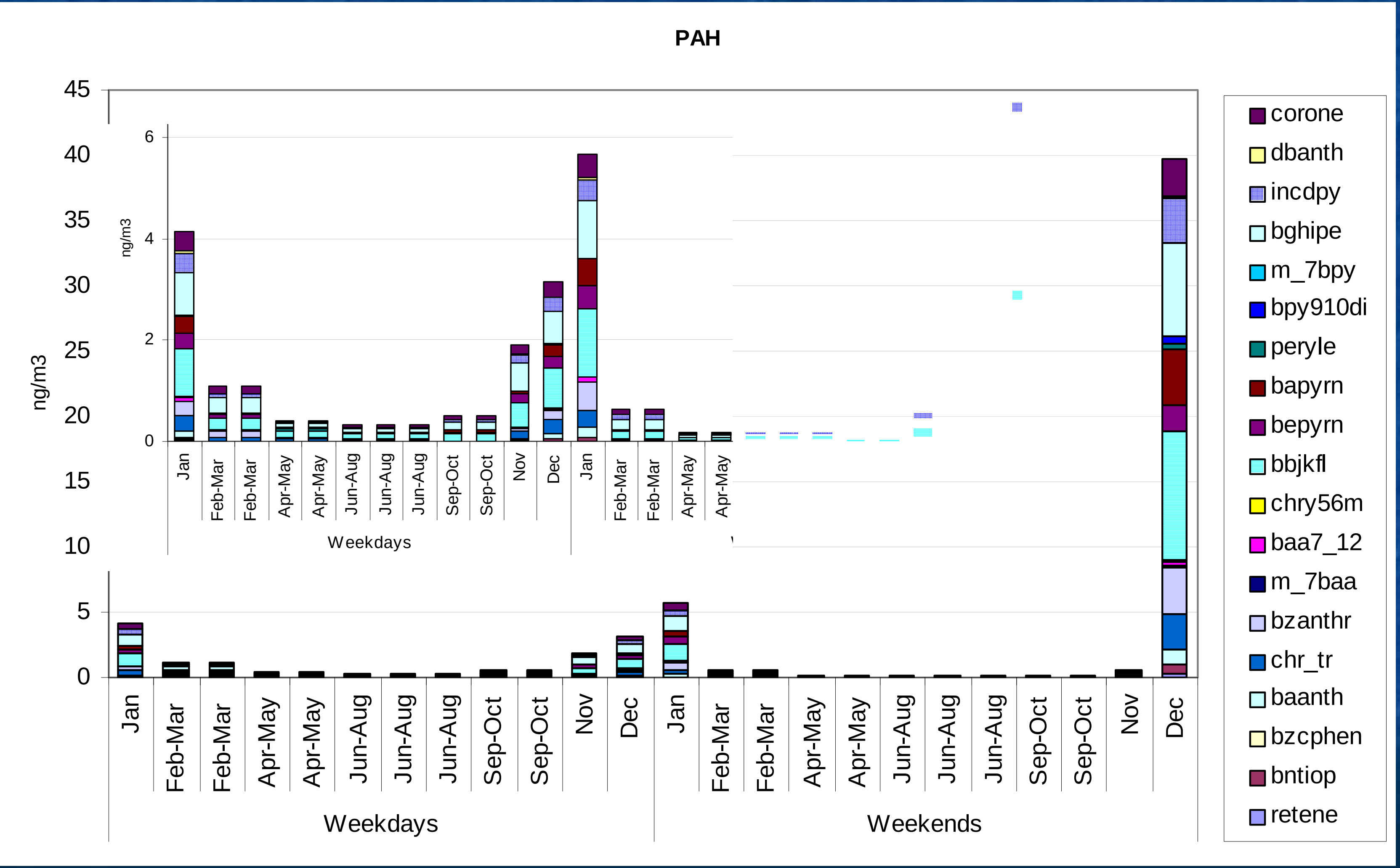
Hopanes in Vehicle Exhaust Profiles





Gasoline/Diesel PM Split Study, Fujita et al., 2005

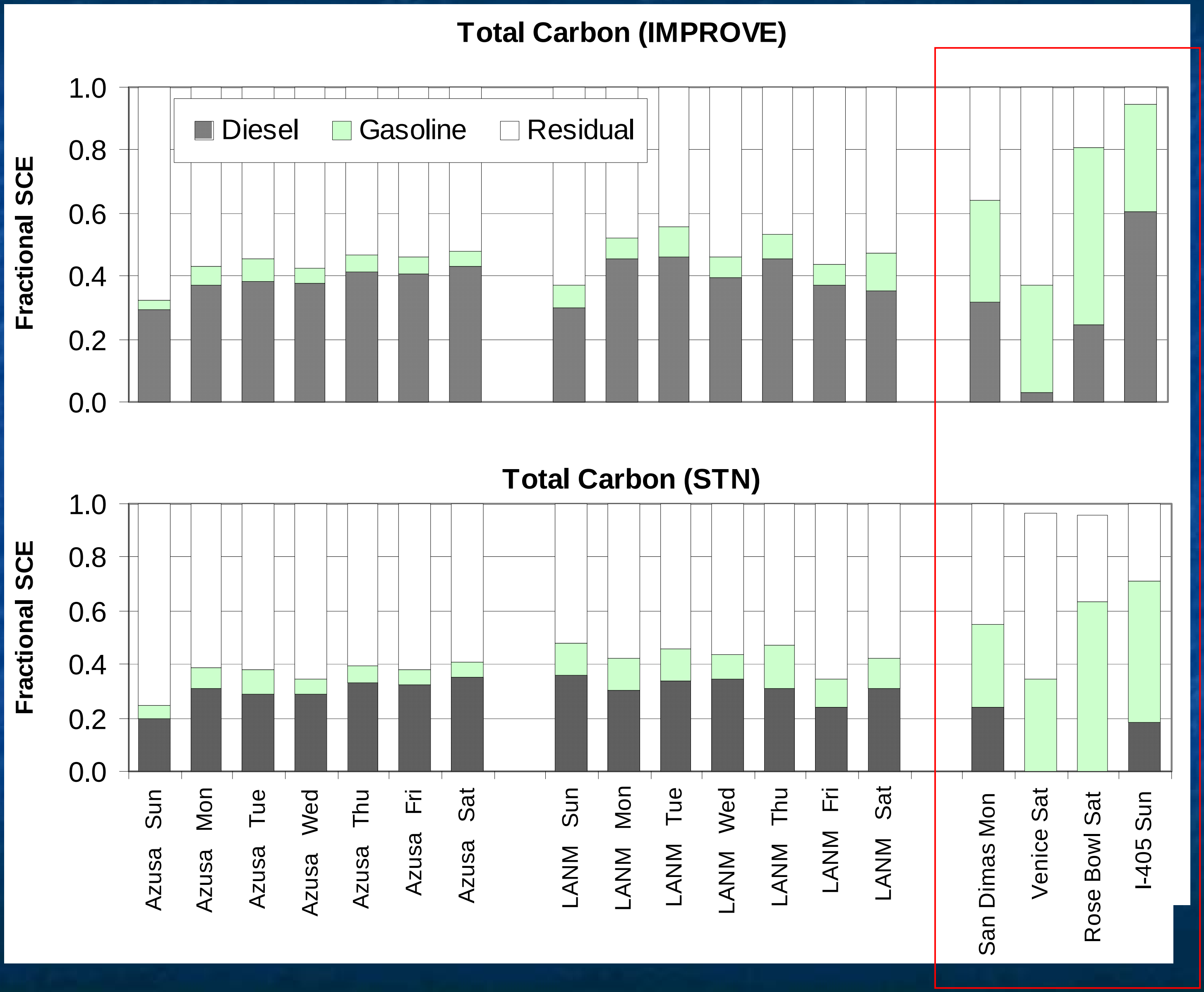
Monthly Average Ambient Concentrations of Particle-Phase PAHs at San Jose, CA in 2004



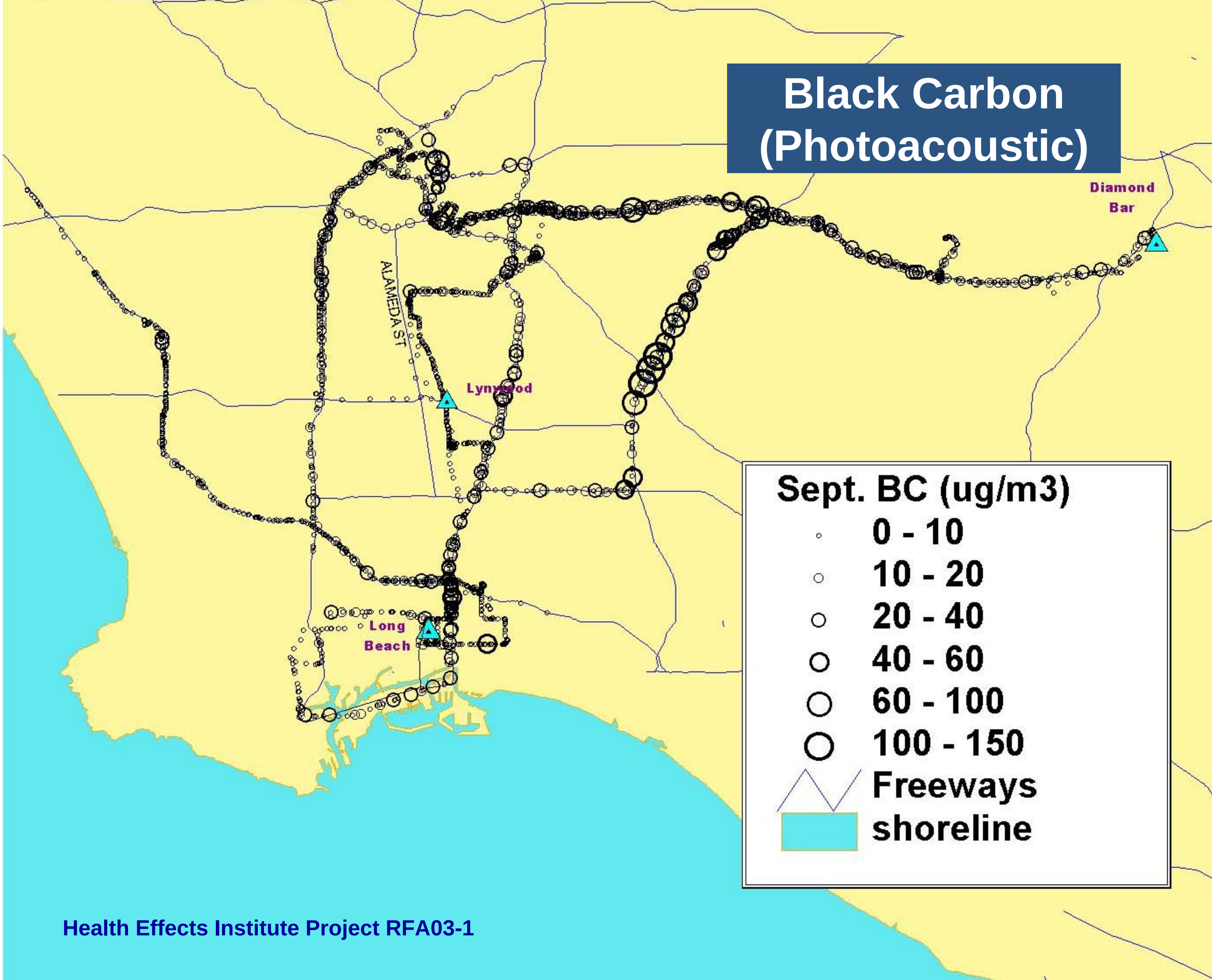
Variations in Source Contribution Estimates (Percent of Total) Azusa and Los Angles Weekday Ambient Samples

	Compression-Ignition			**Spark-Ignition**		
	IMPROVE	STN	STN no PAH	IMPROVE	STN	STN no PAH
TC						
Mean	**40.9**	**30.8**	**31.3**	**6.6**	**9.4**	**11.4**
Std Dev	3.7	3.0	2.7	1.3	3.3	3.5
Std Err	1.2	1.0	0.9	0.4	1.0	1.1
OC						
Mean	**22.1**	**15.8**	**16.1**	**7.4**	**10.4**	**12.2**
Std Dev	2.6	2.0	1.9	1.7	3.6	3.7
Std Err	0.8	0.6	0.6	0.5	1.1	1.2
EC						
Mean	**90.3**	**93.3**	**65.9**	**4.5**	**5.2**	**7.2**
Std Dev	3.3	3.4	5.9	1.0	2.1	2.0
Std Err	1.0	1.1	1.9	0.3	0.7	0.6

Total Carbon Source Contributions

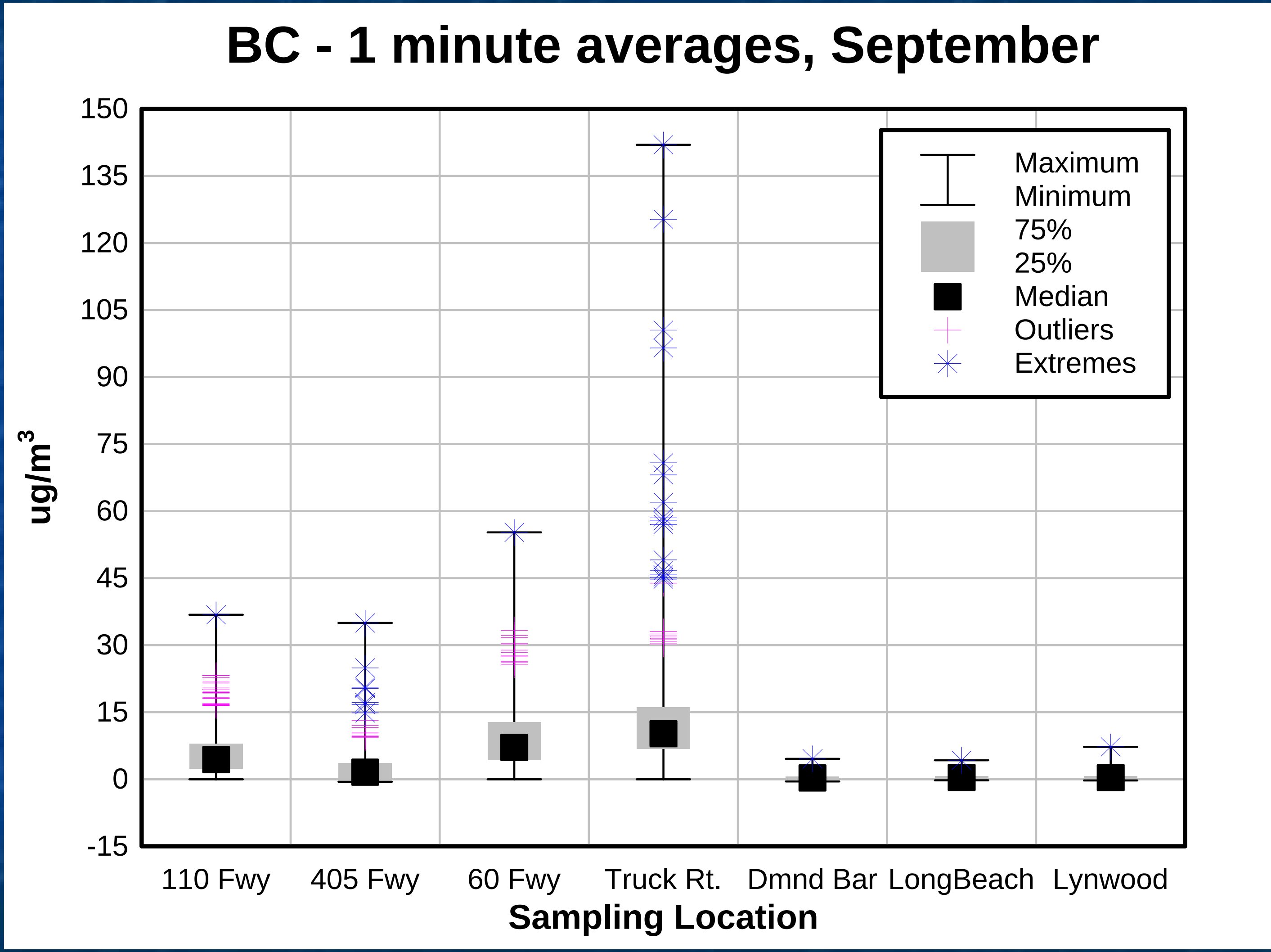


Black Carbon (Photoacoustic)



Health Effects Institute Project RFA03-1

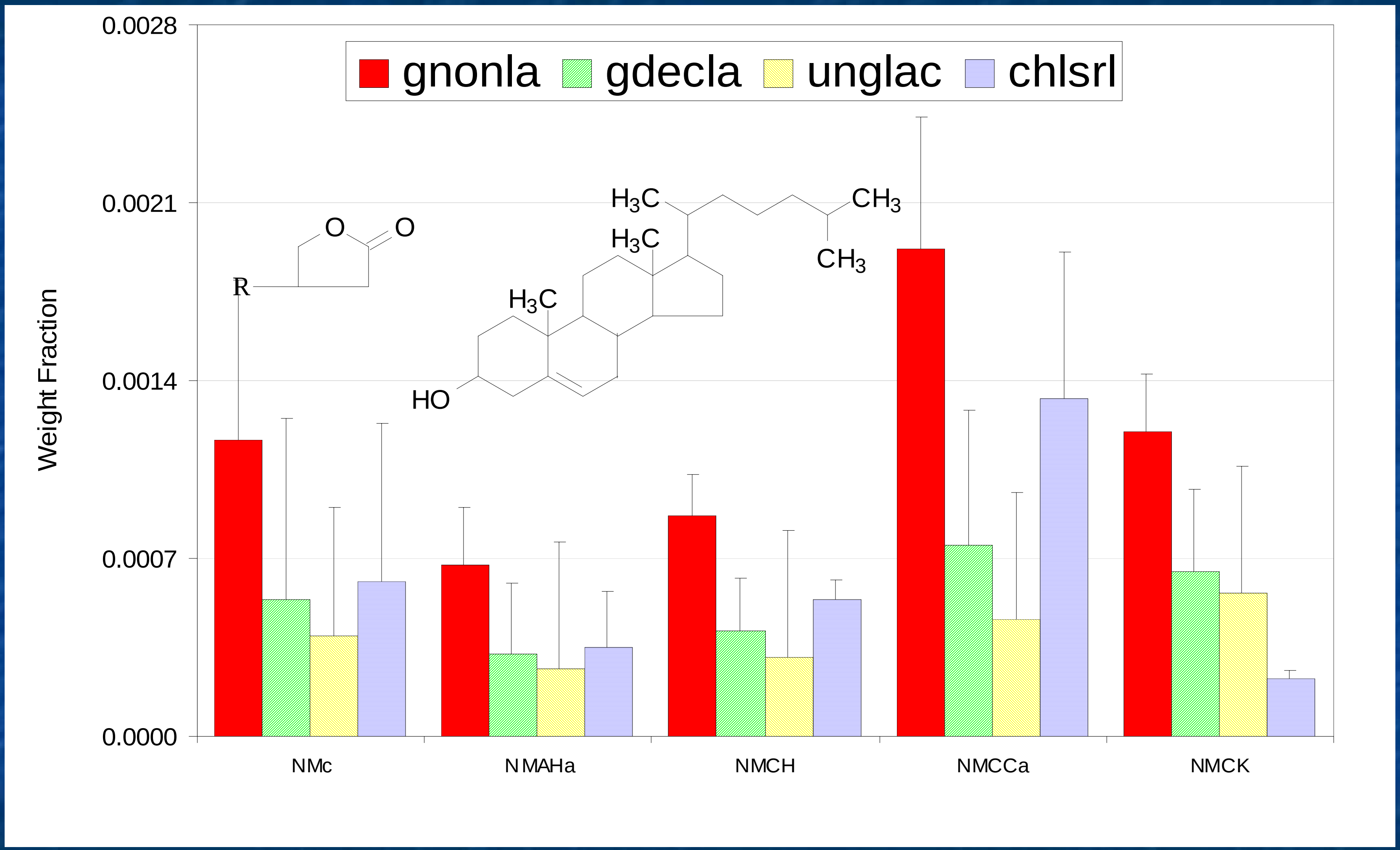
On-Road and Near-Road Exposures to Black Carbon



Organic Molecular Markers for Meat Cooking

- Fatty Acids
  - palmitic acid
  - stearic acid
  - oleic acid
- Sterols
  - cholesterol
- Lactones
  - lactonization of β-hydroxy fatty acids
  - oxidation of alkenals and oleic acid

NFRAQS Meat Emissions - Tracer Compounds



Composite

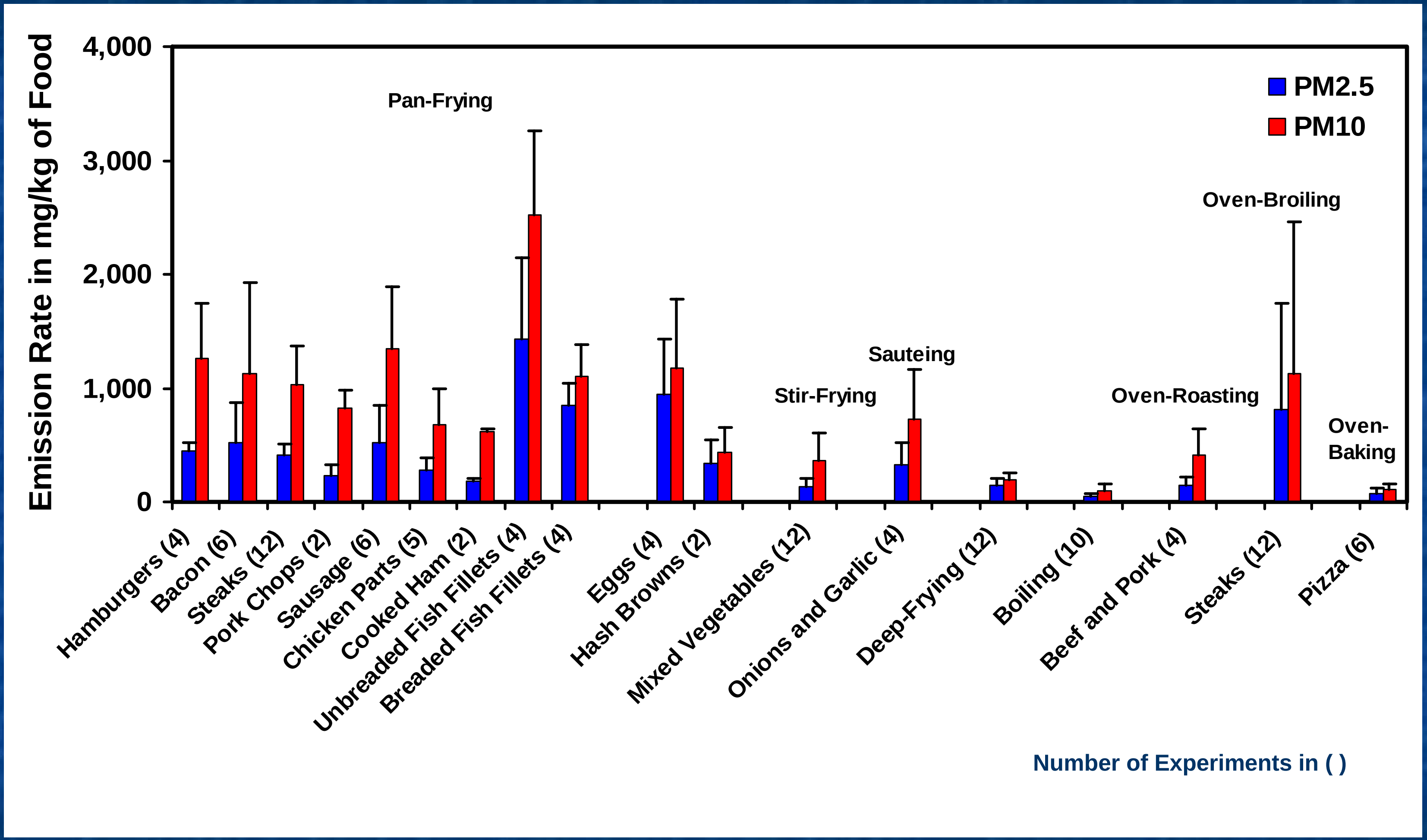
Automated Charbroiled Hamburger

Charbroiled Hamburger

Charbroiled Chicken With Skin

Charbroiled Steak

Emissions of Particulate Matter from Residential Cooking



Source: Wolfgang Rogge et al., Organic PM2.5 emissions from residential cooking. Presented at the International State of Science Workshop on Organic Speciation in Atmospheric Aerosol Research, Las Vegas, NV April 5-7, 2004.

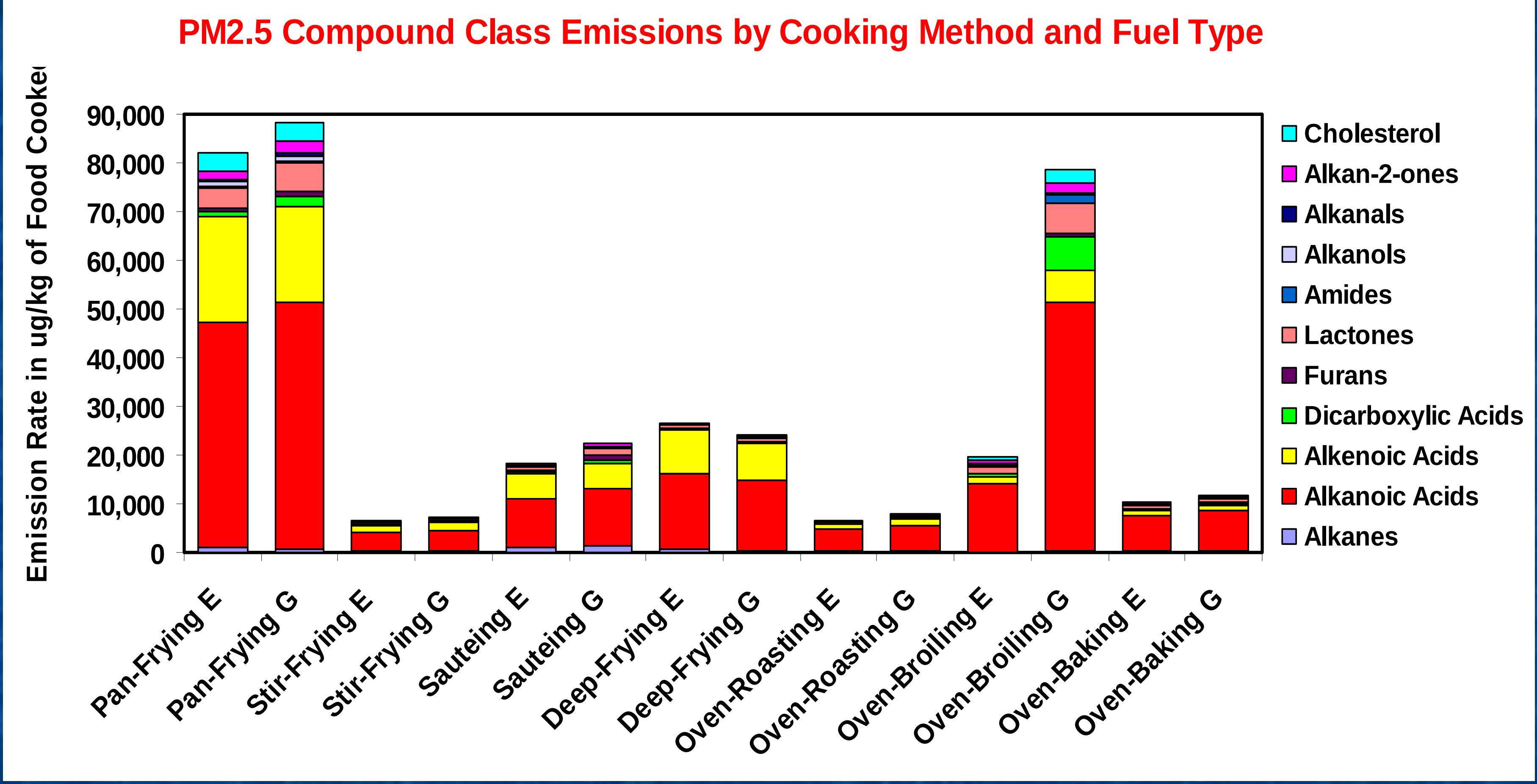
Organic Speciation:

- **GC/MS:**
  - n-Alkanes (C14-C31)
  - n-Alkanoic Acids (C6-C28)
  - n-Alkenoic Acids (Palmitoleic-, Oleic, & Linoleic Acid)
  - n-Alkanols (C7-C18)
  - n-Alkan-2-ones (C7-C19)
  - Aliphatic Dicarboxylic Acids (C3-C9)
  - Furans
  - Furanones
  - Amides (Palmit-, Olea-, Stearamide)
  - PAH (Naphthalene, Fluorene, Phenanthrene, Methyl(Phenanthrenes/Anthracenes), Dimethyl(Phenanthrenes/Anthracenes), Fluoranthane, Pyrene, Benzo[b]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Perylene)
  - Steroids (Cholesterol, Campesterol)
  - Others

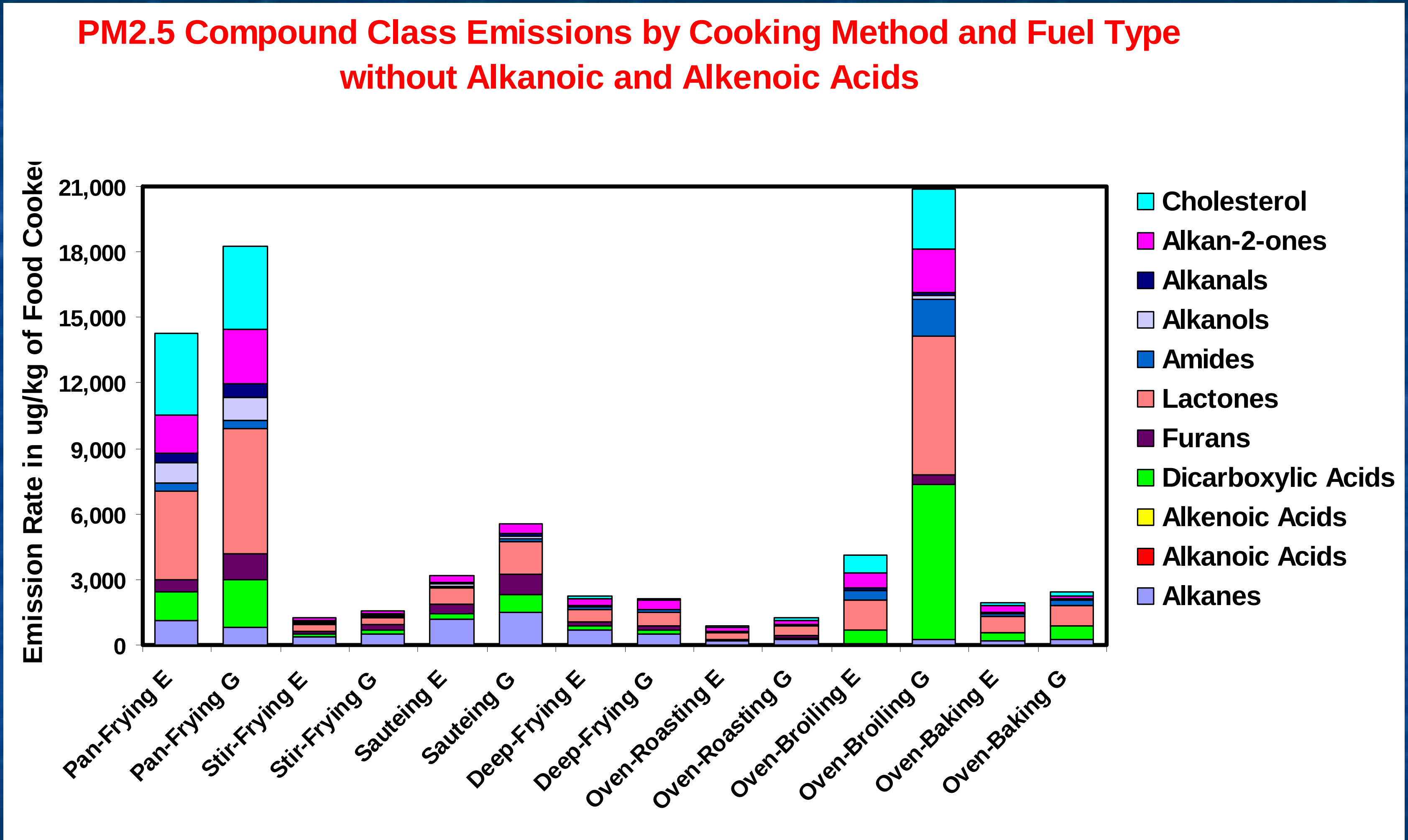
- **HPLC:**
  - Heterocyclic Amines

Abbreviation	Name
IQ	2-amino-3-methylimidazo(4,5-f)quinoline
MeIQ	2-amino-3,4-dimethylimidazo(4,5-f)quinoline
IQx	2-amino-3-methylimidazo(4,5-f)quinoxaline
MeIQx	2-amino-3,8-dimethylimidazo(4,5-f)quinoxaline
4,8-DiMeIQx	2-amino-3,4,8-trimethyl-3H-imidazo(4,5-f)quinoxaline
7,8-DiMeIQx	2-amino-3,7,8-trimethyl-3H-imidazo(4,5-f)quinoxaline
4,7,8-TriMeIQx	2-amino-3,4,7,8-tetramethyl-3H-imidazo(4,5-f) quinoxaline
PhIP	2-amino-1-methyl-6-phenylimidazo(4,5-b)pyridine
GLU-P-1	2-amino-6-methyldipyrido(1,2-a:3',2'-d)imidazole
GLU-P-2	2-aminodipyrido(1,2-a:3',2'-d)imidazole
AαC	2-amino-9H-pyrido(2,3-b)indole
MeAαC	2-amino-3-methyl-9H-pyrido(2,3-b)indole
Trp-P-1	3-amino-1,4-dimethyl-5H-pyrido(4,3-b)indole
Trp-P-2	3-amino-1-methyl-5H-pyrido(4,3-b)indole
Harman	1-methyl-9H-pyrido(3,4-b)indole
Norharman	9H-pyrido(3,4-b)indole

Source: Wolfgang Rogge et al., Organic PM2.5 emissions from residential cooking. Presented at the International State of Science Workshop on Organic Speciation in Atmospheric Aerosol Research, Las Vegas, NV April 5-7, 2004.



Source: Wolfgang Rogge et al., Organic PM2.5 emissions from residential cooking. Presented at the International State of Science Workshop on Organic Speciation in Atmospheric Aerosol Research, Las Vegas, NV April 5-7, 2004.



Source: Wolfgang Rogge et al., Organic PM2.5 emissions from residential cooking. Presented at the International State of Science Workshop on Organic Speciation in Atmospheric Aerosol Research, Las Vegas, NV April 5-7, 2004.

Summary

- Organic markers exists for most combustion sources.
  - Abundances of organic markers are variable and profiles must be specific to the region.
  - Analytical method for OC/EC must be specified.
- Source Contributions.
  - Mobile sources are the major source of carbonaceous aerosols in urban areas.
  - Relative contributions of PM emissions from diesel and gasoline vehicles depend greatly upon mix of local traffic.
  - Residential wood combustion and wildfires can be significant sources of PM during the winter and summer respectively. Restrictions on residential wood combustions have been effective.
  - PM emissions from meat cooking can be significant indoor source of PM but is a minor contributor to ambient PM except near sources (e.g. charbroiling restaurants).