Particulate Pollution in the San Joaquin Valley: Translating Science into Policy

Sources of Valley Organic Carbon

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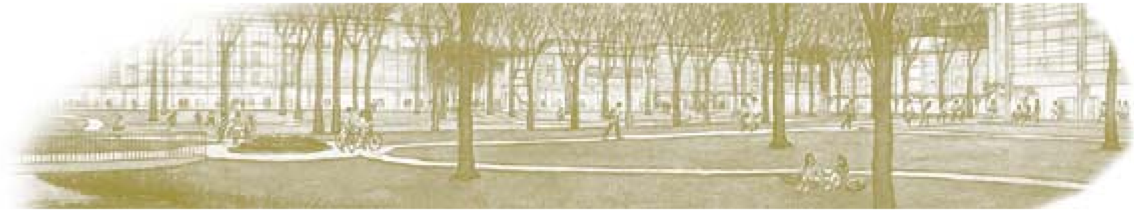


Expertise:

- Organic Aerosol Composition
- Organic Source Markers
- Characterization of Sources
- Ambient Organic PM Studies
    - Los Angeles
    - Pittsburgh
    - Baltimore
    - South Florida
- Source Apportionment

	Source Type	Organic Markers	
1	Cars	Yes	Rogge et al., 1993a
2	Diesel Trucks	Yes	Rogge et al., 1993a
3	Dual Fuel Power Cars	Yes	Rogge et al., 1996
4	Traffic Tunnel (Pittsburgh)	Yes	Bernardo, Rogge et al., 2005
5	Urban Road Dust Pasadena	No	Rogge et al., 1993b
6	Urban Road Dust Pittsburgh	No	Sevimoglu, Rogge, et al. 2005
7	Urban Road Dust San Joaquin Valley, CA	No	Rogge et al, 2010
8	Rural Road Dust San Joaquin Valley, CA	No	Rogge et al, 2010
9	Unpaved Road Dust San Joaquin Valley, CA	No	Rogge et al, 2010
10	Tire Wear Particles	Yes	Rogge et al., 1993c
11	Brake Lining Dust	No	Rogge et al., 1993c
12	Natural Gas Home Appliances	No	Rogge et al., 1993d
13	Industrial Oil Boilers	Yes	Rogge et al., 1997a
14	Coke-Oven	No	Bernardo, Rogge et al., 2005
15	Roofing Tar Pot	Yes	Rogge et al., 1997b

	Source Type	Organic Markers	
16	Restaurant Type Meat Cooking	Yes	Rogge et al., 1991
17	Residential Cooking for many Food Items	Yes & No	Rogge, 2000
18	Pine Logs burning in Fireplace	Yes	Rogge et al., 1998
19	Oak Logs burning in Fireplace	Yes	Rogge et al., 1998
20	Synthetic Logs burning in Fireplace	Yes	Rogge et al., 1998
21	Campfire burning of Pine Wood	Yes	Simoneit, Rogge et al., 2000
23	Thermal conversion of individual Biopolymers	Yes	Moncholi & Rogge, 2010
24	Leaf Surface Abrasions for Los Angeles Vegetation	Yes	Rogge et al., 1993e
25	Leaf Surface Abrasion for Pittsburgh Vegetation	Yes	Sevimoglu, Rogge, et al. 2005
26	Cigarette Smoke	Yes	Rogge et al., 1994
27	Fugitive Dust from Feedlots and Dairy Farms for San Joaquin Valley	Yes	Rogge et al., 2006
28	Fugitive Dust from Crop Fields for San Joaquin Valley	Yes	Rogge et al., 2007

Problem:

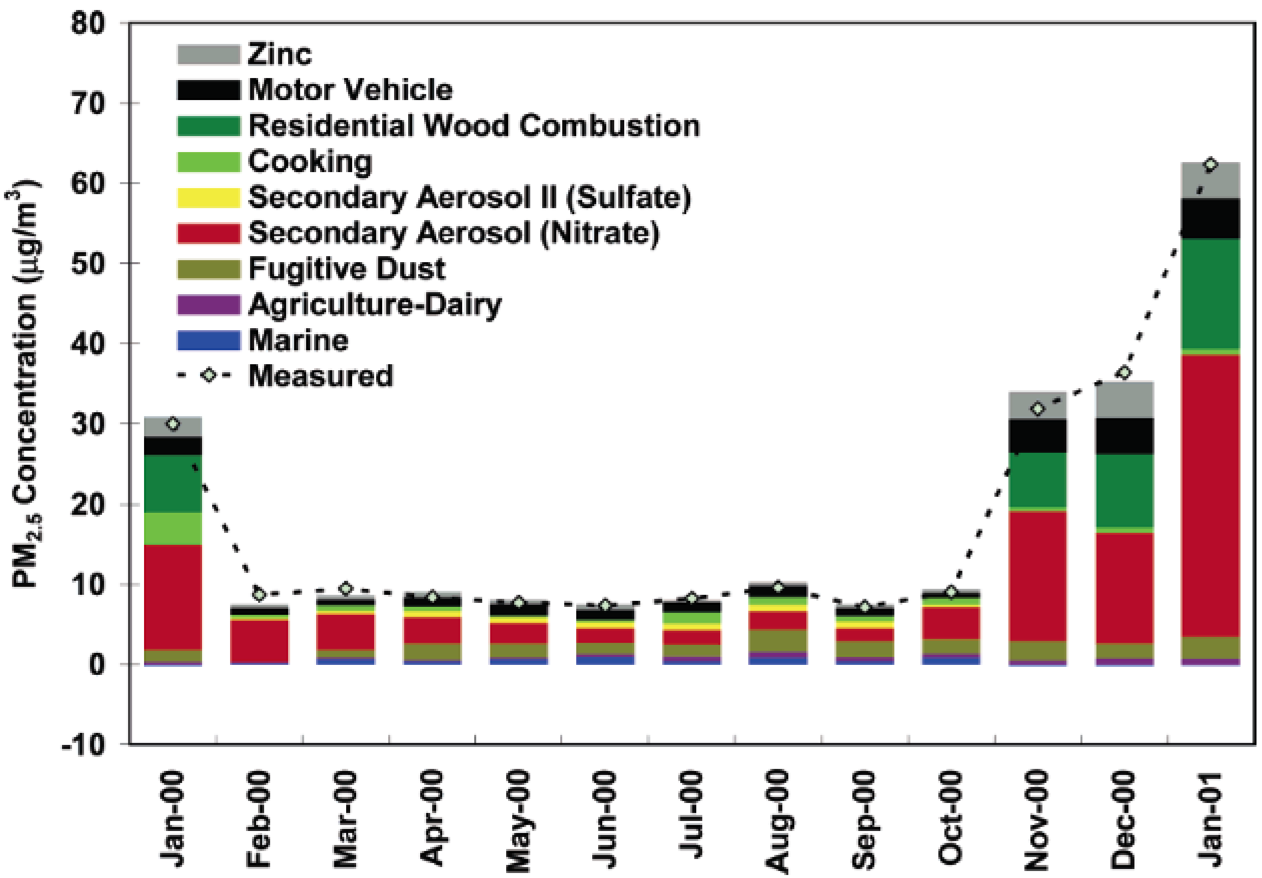
- San Joaquin Valley Air among highest PM levels in the Nation
- Organic Primary PM-Emissions may contribute to adverse health effects
- Atmospheric Chemistry is altering primary organic compounds and little is known about the potential for adverse health effects of aging organic aerosol
- Atmospheric Chemistry involving gaseous precursor organic compounds generates atmospheric PM2.5 (gas-to-particle conversion reactions)

Estimates for Selected Primary Sources of PM for the San Joaquin Valley in Tons/Day, 2008

Source Category	PM10	PM2.5
Stationary Fuel Combustion	7.1	6.8
Industrial Processes	17.8	10.4
Residential Fuel Combustion (Wood + Gas)	10.3	9.9
Cooking	3.6	2.1
Gasoline Powered Vehicles	3.5	2.2
Diesel Cars & Trucks	11.1	9.7
Off-Road & Farm Machinery	6.1	5.6
Subtotal Stationary & Residential & Mobile Sources	59.5	46.7
Agricultural Waste Burning	21.0	19.4
Paved Road Dust	43.9	6.6
Unpaved Road Dust	42.9	3.9
Construction & Demolition	10.8	1.1
Farming Operation	72.9	16.8
Windblown Dust	45.3	7.7
Subtotal Fugitive Dust Sources	236.8	55.5

Source: CARB

Monthly Contribution Estimates averaged over the 23 CRPAQS sites



California Regional PM10/PM2.5 Air Quality Study (CRPAQS)

Quantifying PM$_{2.5}$ Source Contributions for the San Joaquin Valley with Multivariate Receptor Models

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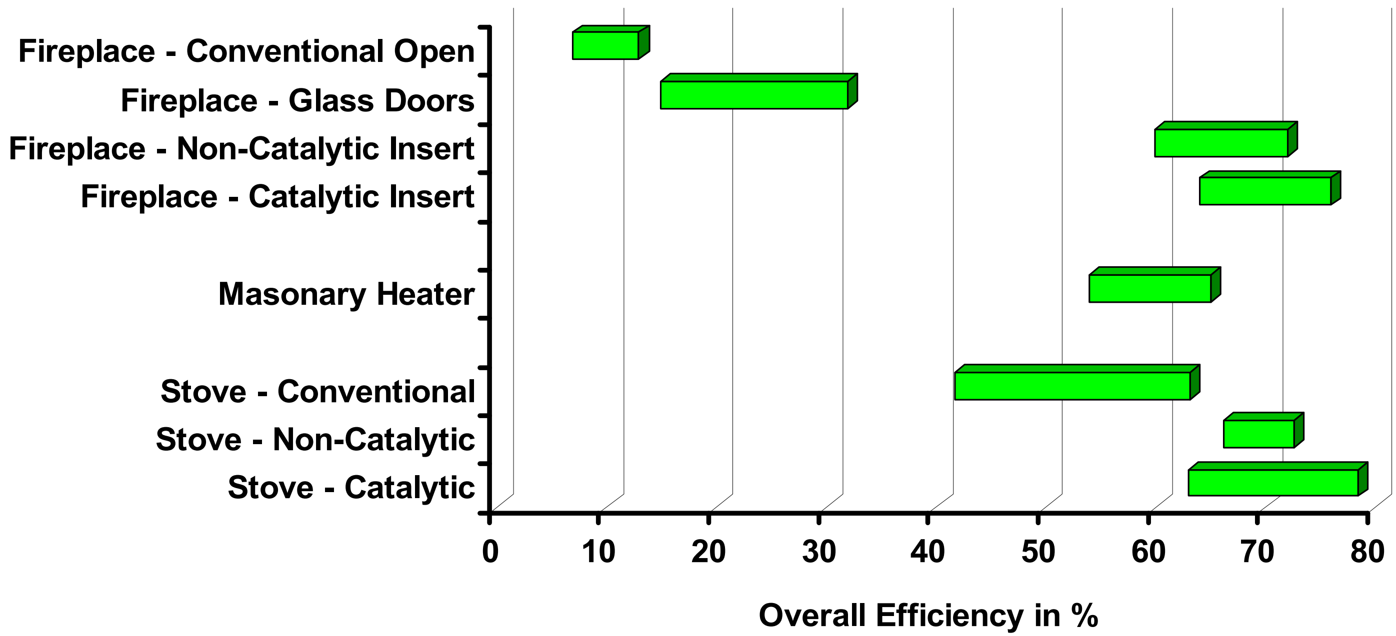
Environ. Sci. Technol. **2007**, *41*, 2818–2826

Organic Compounds associated with PM10 &PM2.5

Wood Burning and Agricultural Waste Burning (Biomass)

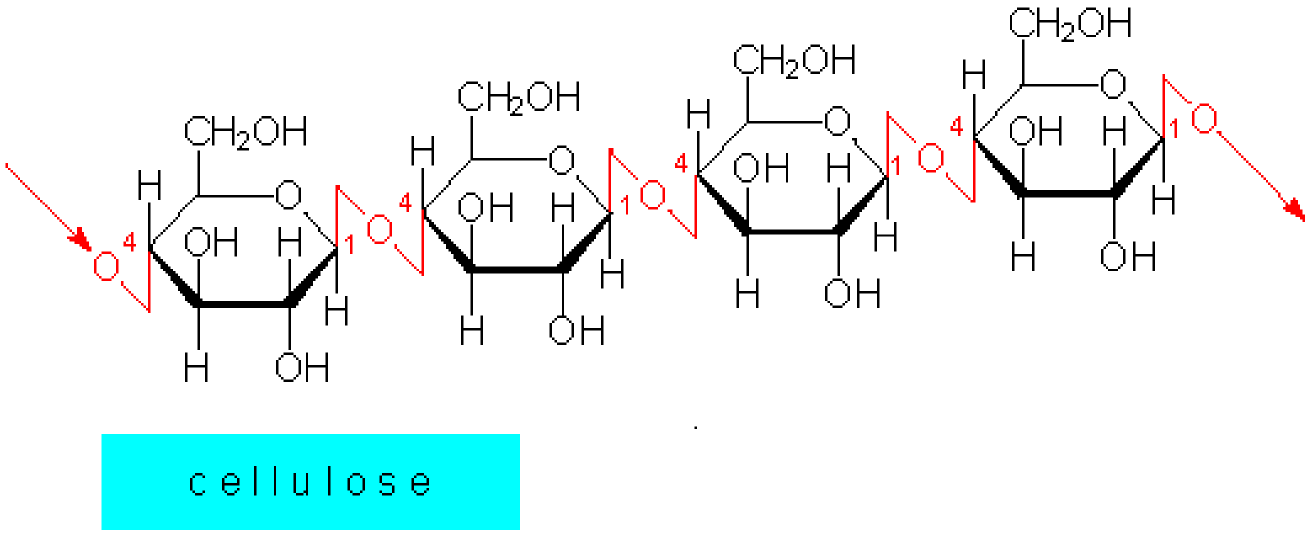
Overall Thermal Efficiencies for Residential Wood Combustors

US-EPA, AP-42



<table>
<tr><th colspan="2">Wood Constituents</th><th>Conifers (gymnosperms) “Softwood”</th><th>Deciduous Trees (angiosperms) “Hard Wood”</th></tr>
<tr><td rowspan="3">Polymers
Major</td><td>Cellulose</td><td colspan="2">40 – 50%</td></tr>
<tr><td>Hemicelluloses</td><td colspan="2">25 – 35%</td></tr>
<tr><td>Lignins</td><td>30 – 40%</td><td>20 – 30%</td></tr>
<tr><td rowspan="4">Minor</td><td rowspan="3">Extraneous Substances</td><td colspan="2">4 – 10%</td></tr>
<tr><td>Resins</td><td>Gums</td></tr>
<tr><td colspan="2">Fats, waxes, starches, terpenes, tannins, phenolics, pectins, sugars, sapins, mucilages, glycosides, essential oils, sterols, others</td></tr>
<tr><td>Inorganics (Ash)</td><td colspan="2">< 1%</td></tr>
</table>

Cellulose

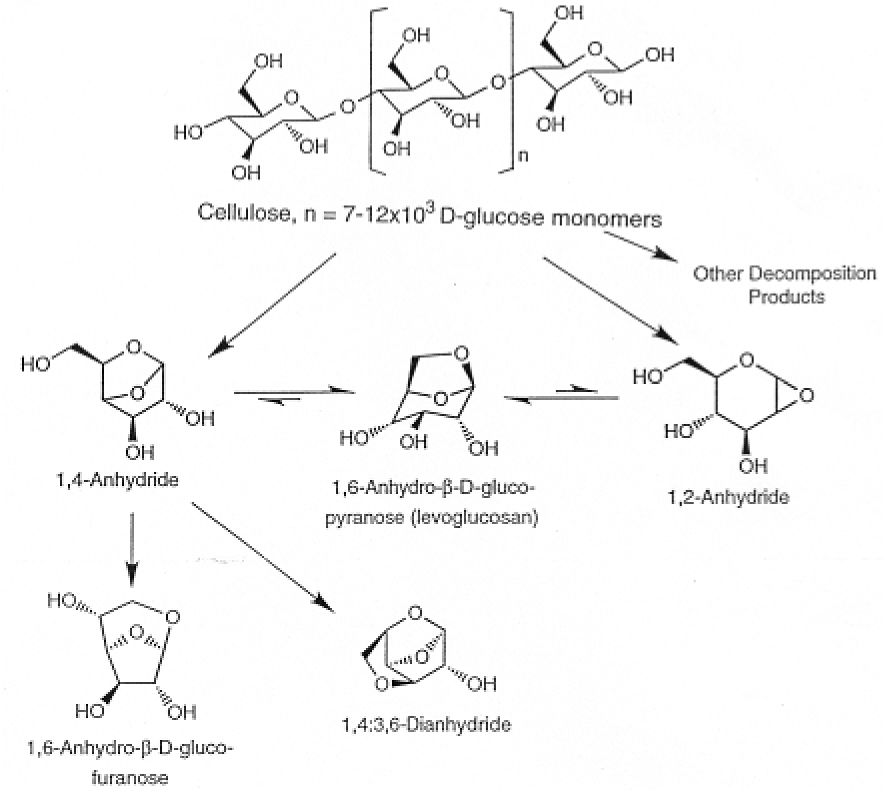


- **Most abundant organic polymer on earth**
- **Long straight chain of glucose monomers (degree of polymerization ~ 5,000 – 10,000)**

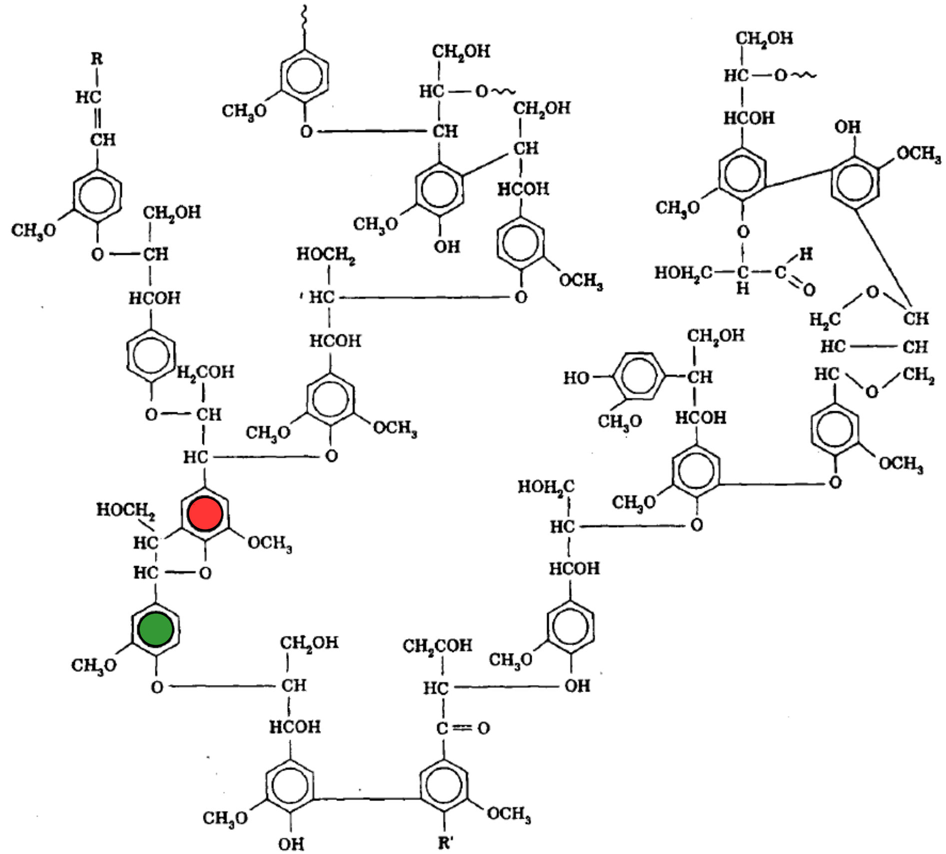
Markers for Wood- and Cellulose-Burning

Any Wood, Biomass, Paper, Wood Products, Cellulose containing Products:

Levoglucosan



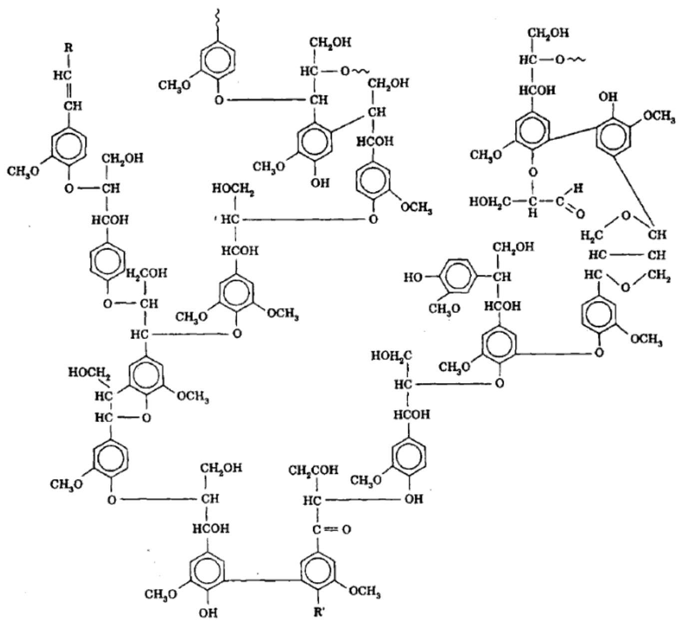
Lignins

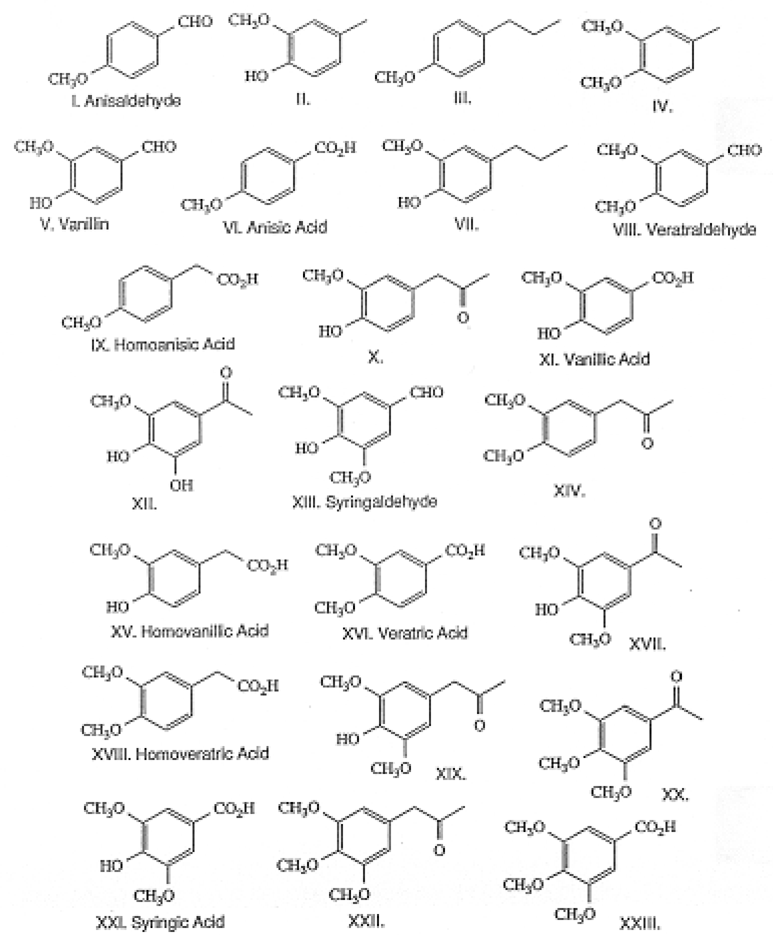


- Second most abundant organic polymer on earth
- Complex 3 dimensional polymer of phenylpropane units (degree of polymerization ~ 70 - 150)
- Hardwoods have about 50% guaiacyl and 50% syringyl units
- Softwoods have 90% - 100% guaiacyl units

Thermal Breakdown Products of Lignins:

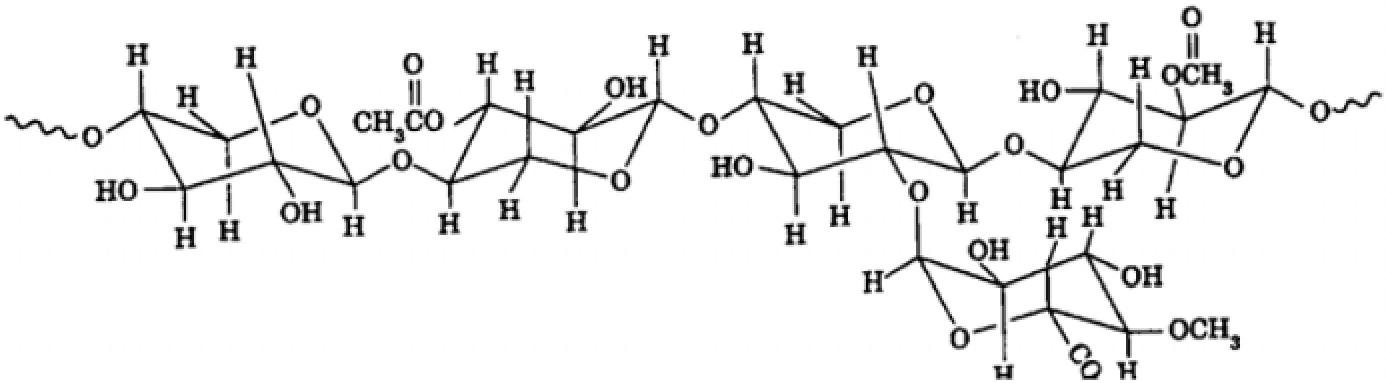
- Combustible Gases
- Hydroxy-/Methoxy-Phenols





Naeher et al., Inhalation Toxicology, 67-106, 2007: Methoxy-Phenols are irritant, carcinogenic, teratogenic.

Hemicelluloses



- Branched polymers (random, 3-dimensional amorphous structures) containing:

  Pentoses:

  - Xylose
  - Arabinose
  - Mannose

  Hexoses:

  - Galactose
  - Glucose

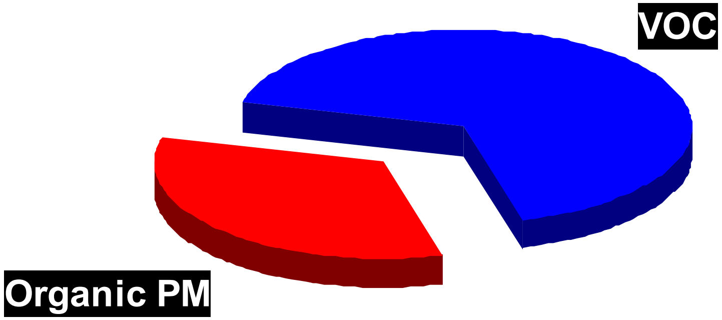
Xylans: predominate in hardwoods

Galactoglucomannans: predominate in softwoods

- (degree of polymerization ~ 70 – 150)

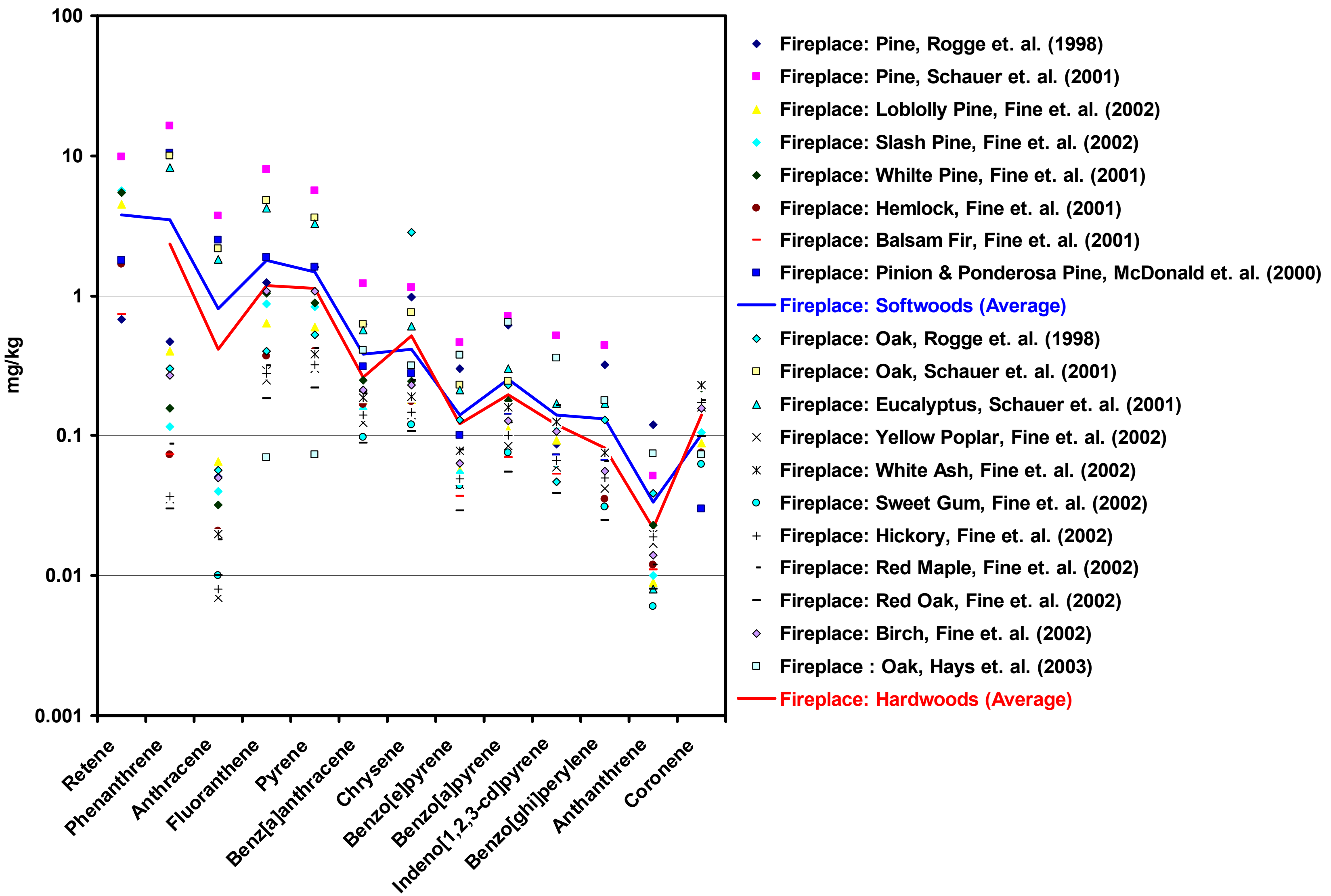
Non-Methane Organic Wood Smoke Emissions

Total Emissions: 10 to 100 g/kg of wood burned

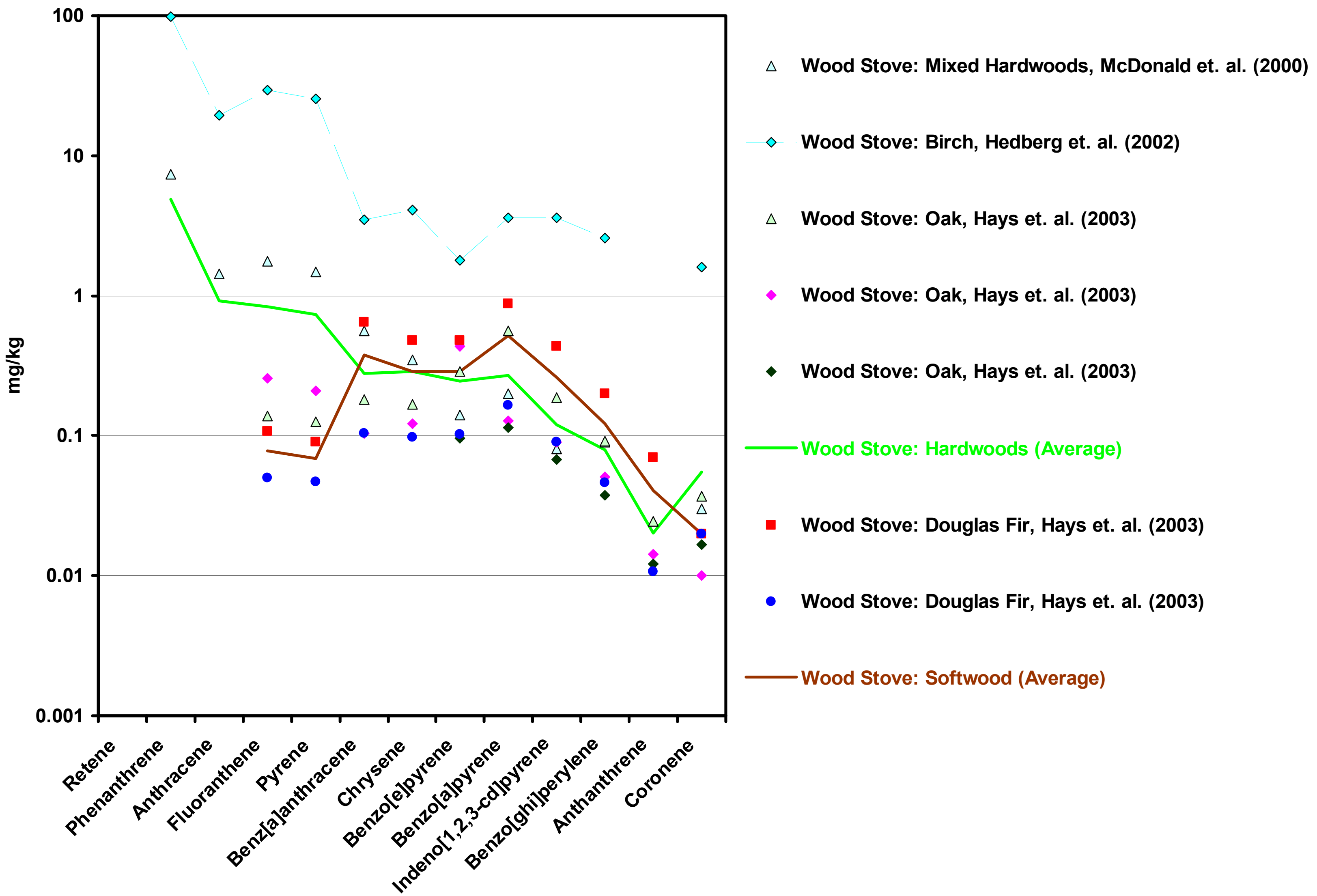


- Aliphatic & Olefinic Aldehydes
- Ketones
- Carbonyls
- Alkanes & Alkenes
- Alkanoic Acids & Alkenoic Acids
- Alkynes
- Diolefins
- Cycloalkanes & Cycloalkens
- Aromatic Hydrocarbons
- Polyaromatic Hydrocarbons (PAHs)
- Phenols & substituted Phenols
- Resin Acids
- Anhydrosugars
- Others

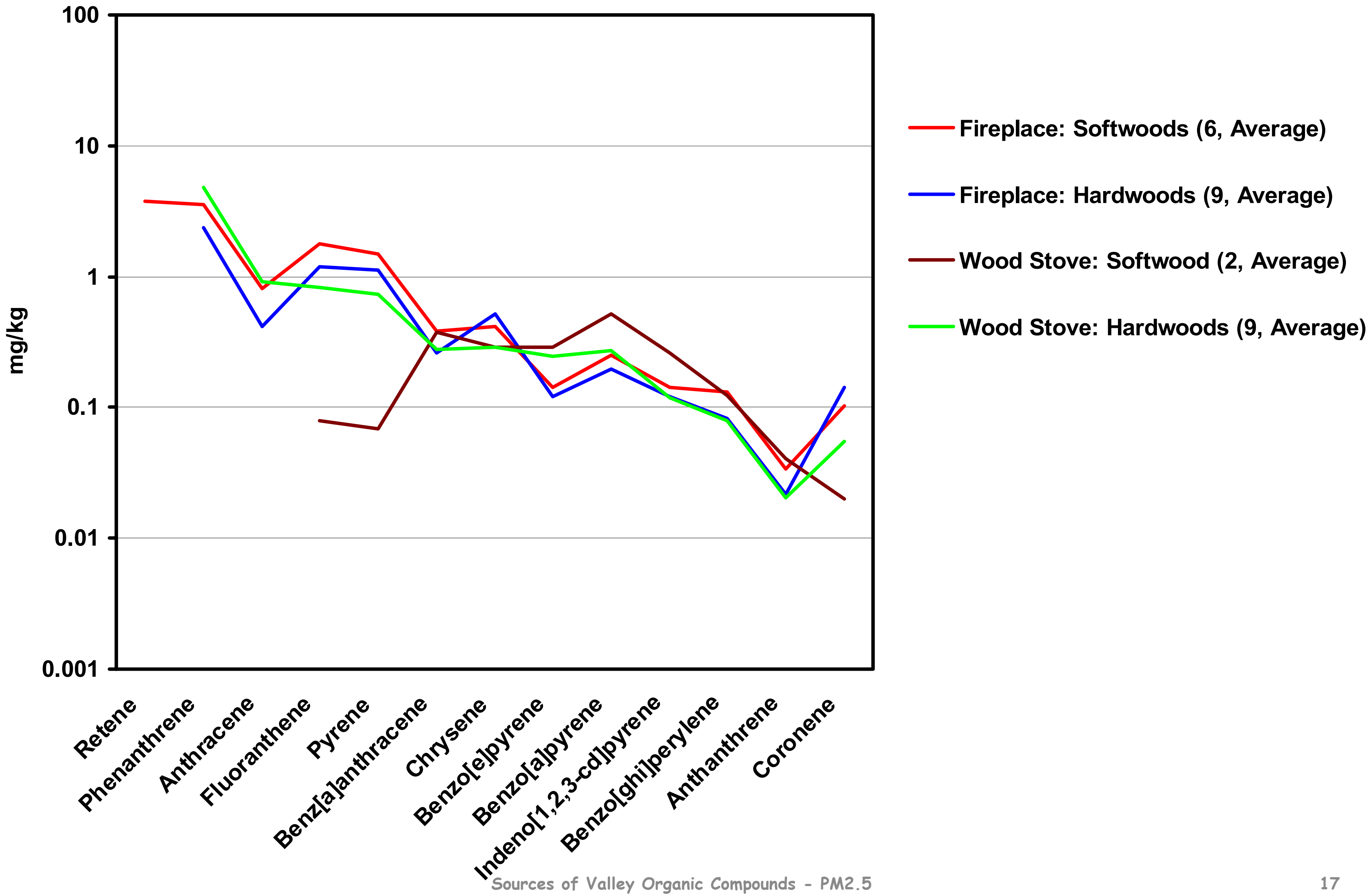
PAHs Emission Factors: Fireplaces



PAHs Emission Factors: Wood Stoves



PAHs Emission Factors (Average): Fireplaces vs. Wood Stoves



Organic Compounds associated with PM2.5

Residential Cooking

Study was supported by the Center for Indoor Air Research and American Lung Association

Emissions from Cooking:

1. Indoor:

•After cigarette smoking, residential cooking is the next major indoor source

•Often, no exhaust system available or if usually not very efficient

•Cook is typically close to cooking range

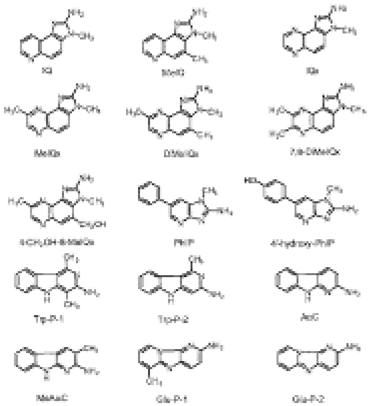
•Cooking and indoor activities are side by side

•Central AC: Dispersion of pollutants throughout entire house

2. Outdoor:

•In urbanized areas, emissions from food cooking are comparable to that of major source categories, e.g., gasoline powered vehicles

Organic Speciation:



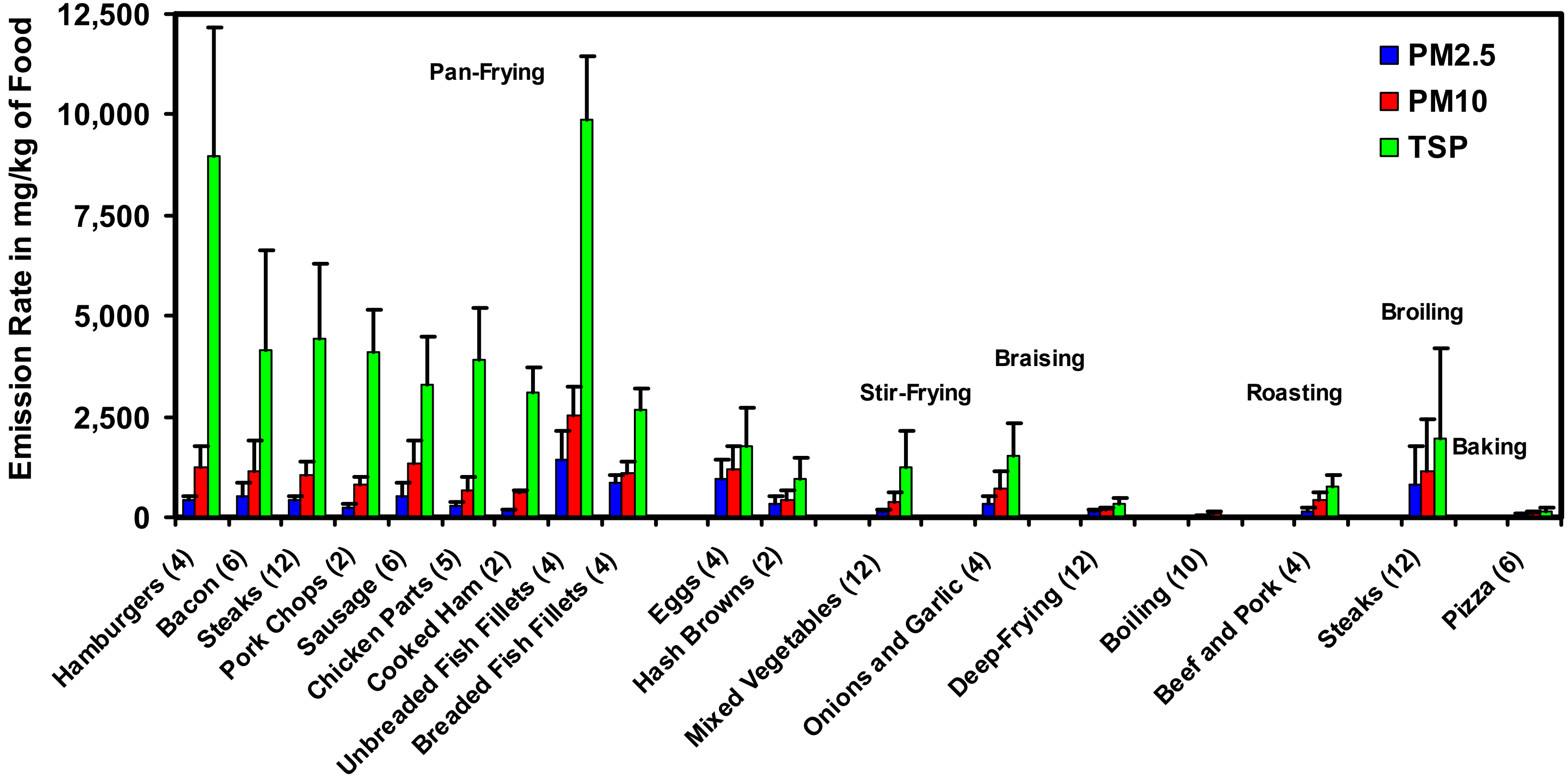
- **GC/MS:**
  - n-Alkanes (C14-C31)
  - n-Alkanoic Acids (C6-C28)
  - n-Alkenoic Acids (Palmitoleic-, Oleic, & Linoleic Acid)
  - n-Alkanols (C7-C18)
  - n-Alkan-2-ones (C7-C19)
  - Aliphatic Dicarboxylic Acids (C3-C9)
  - Furans
  - Furanones
  - Amides (Palmit-, Olea-, Stearamide)
  - PAH (Naphthalene,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

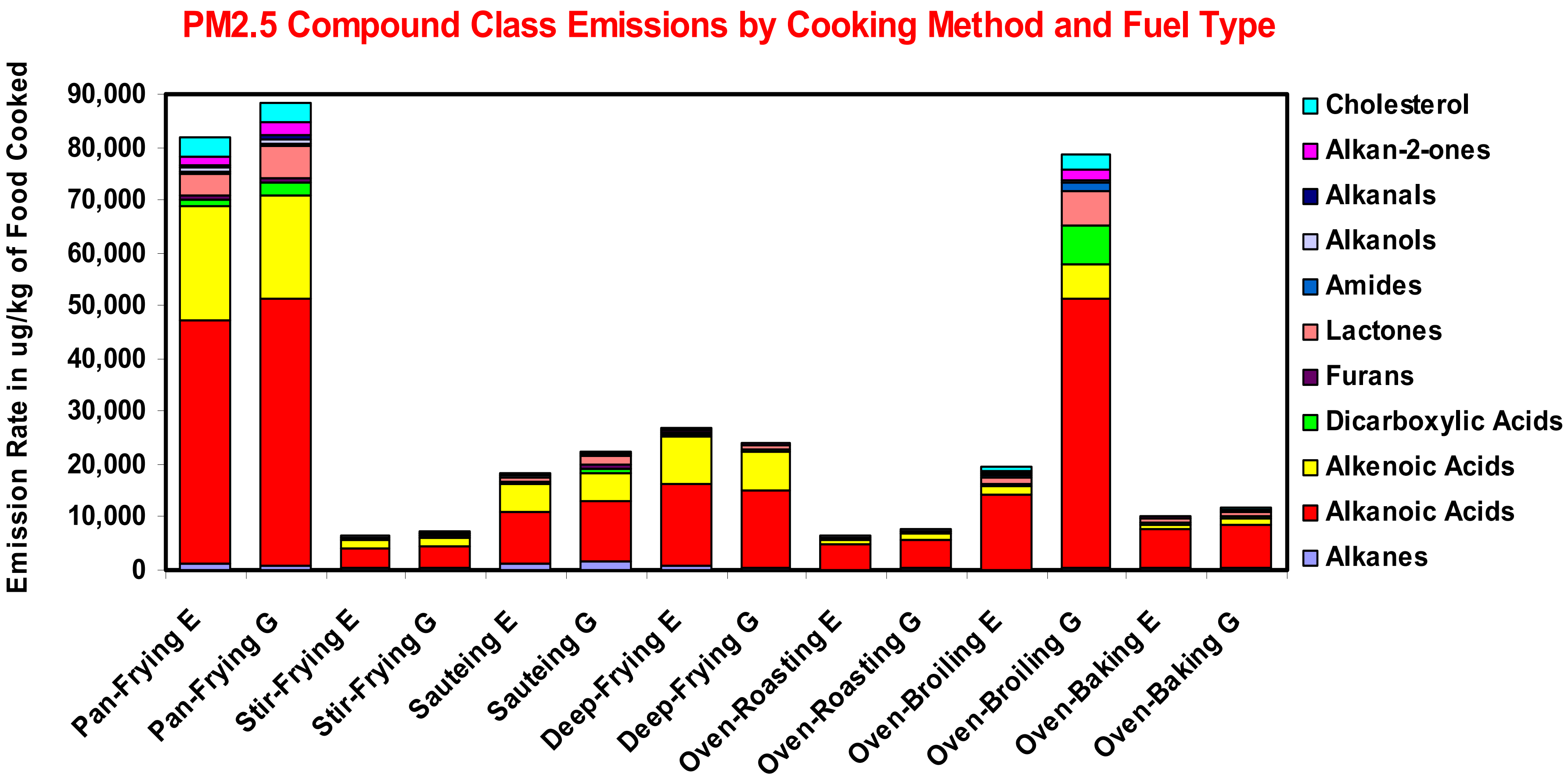
T. Sugimura et al., *Cancer Science*, 95, 290-299, 2004. HAAs are potent carcinogens

- **HPLC:**
  - Heterocyclic Aromatic Amines (HAAs)

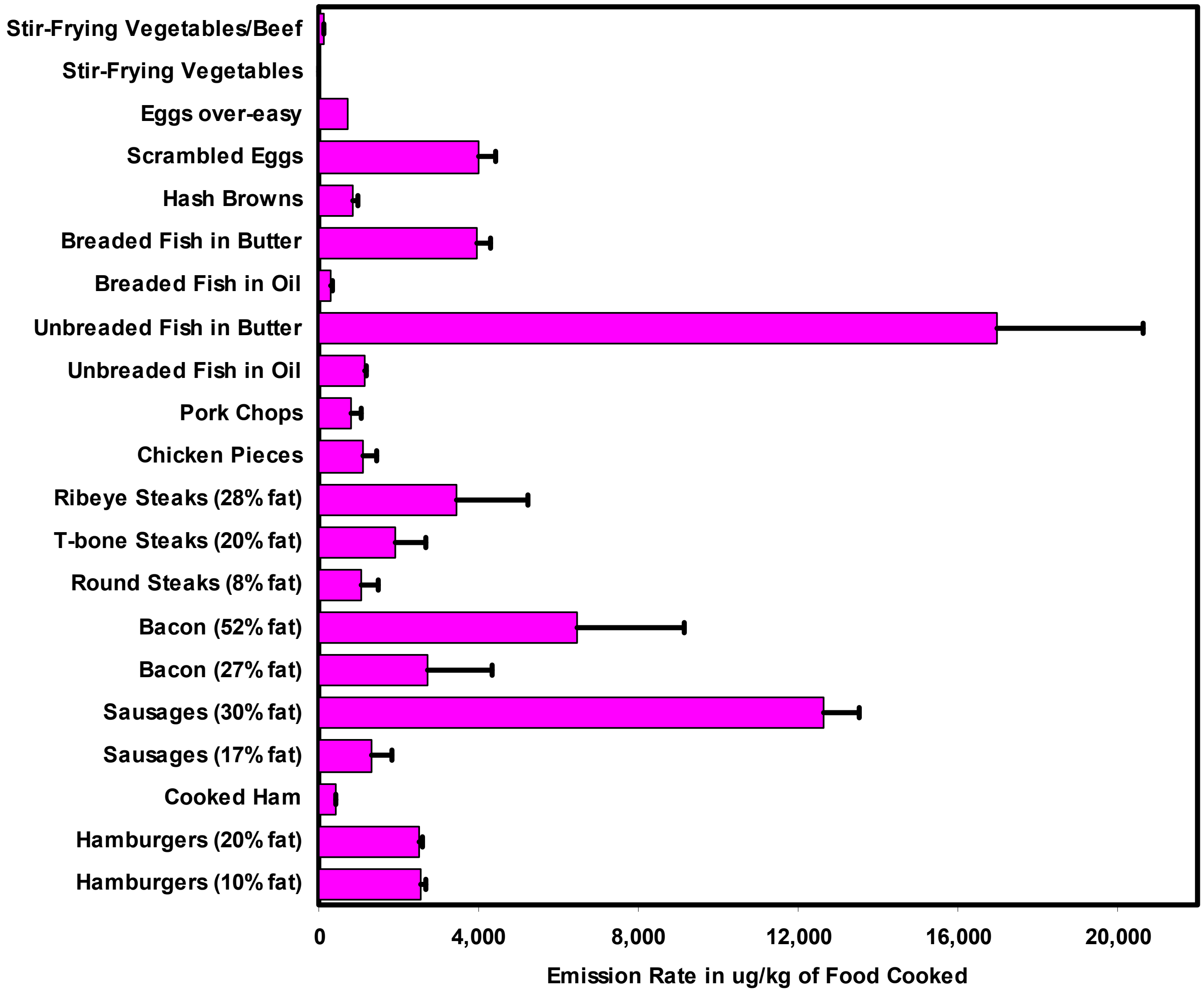
Abbreviation	Name
IQ	2-amino-3-methylimidazo(4,5-f)quinoline
MeIQ	2-amino-3,4-dimethylimidazo(4,5-f)quinoline
IQx	2-amino-3-methylimidazo(4,5-f)quinoxaline
MeIQx	2-amino-3,8-dimethylimidazo(4,5-f)quinoxaline
4,8-DiMeIQx	2-amino-3,4,8-trimethyl-3H-imidazo(4,5-f)quinoxaline
7,8-DiMeIQx	2-amino-3,7,8-trimethyl-3H-imidazo(4,5-f)quinoxaline
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

Emissions of Particulate Matter from Residential Cooking

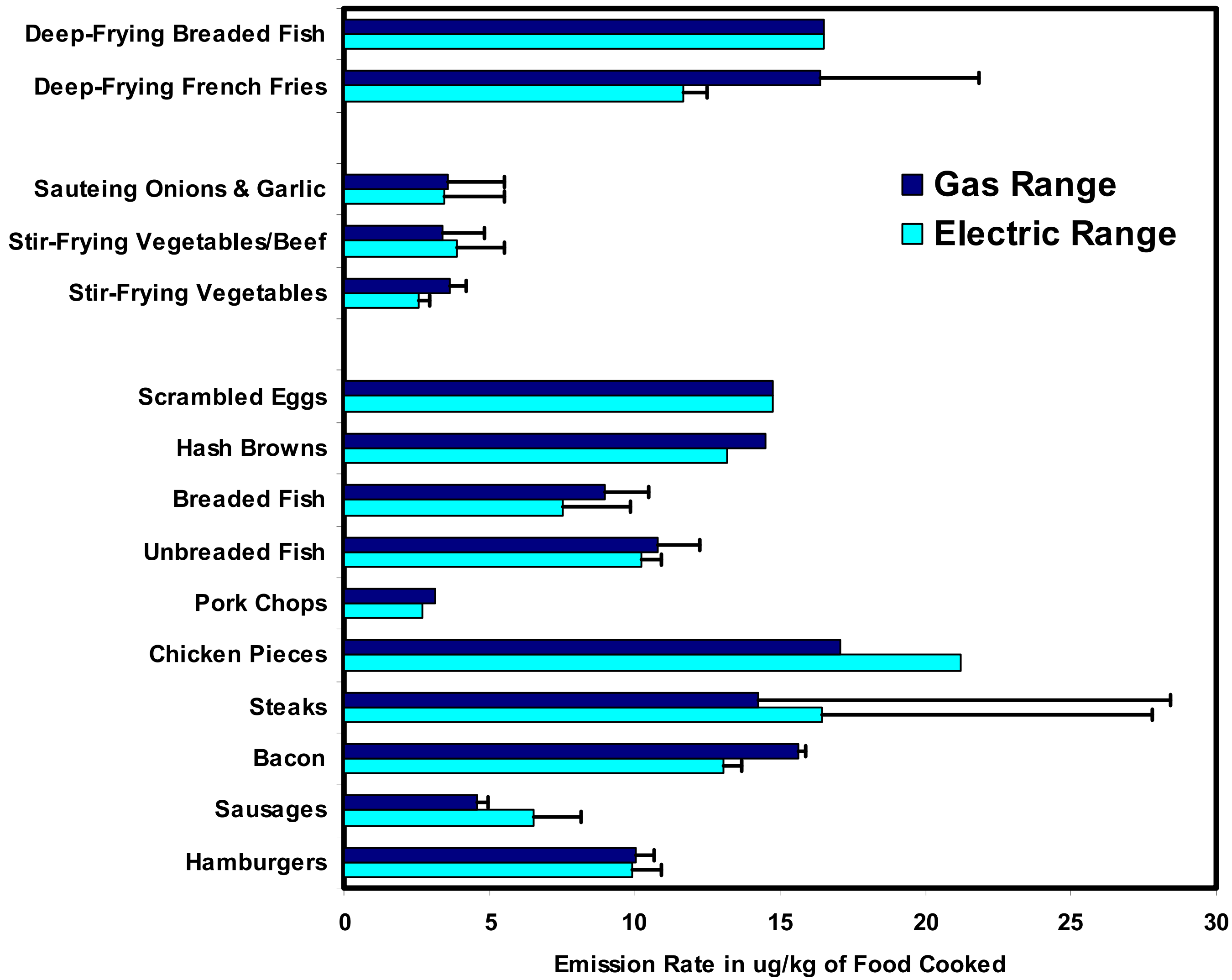



PM2.5 Compound Class Emissions by Cooking Method and Fuel Type
Emission Rate in ug/kg of Food Cooked
90,000
80,000
70,000
60,000
50,000
40,000
30,000
20,000
10,000
0
Pan-Frying E
Pan-Frying G
Stir-Frying E
Stir-Frying G
Sauteing E
Sauteing G
Deep-Frying E
Deep-Frying G
Oven-Roasting E
Oven-Roasting G
Oven-Broiling E
Oven-Broiling G
Oven-Baking E
Oven-Baking G
Cholesterol
Alkan-2-ones
Alkanals
Alkanols
Amides
Lactones
Furans
Dicarboxylic Acids
Alkenoic Acids
Alkanoic Acids
Alkanes

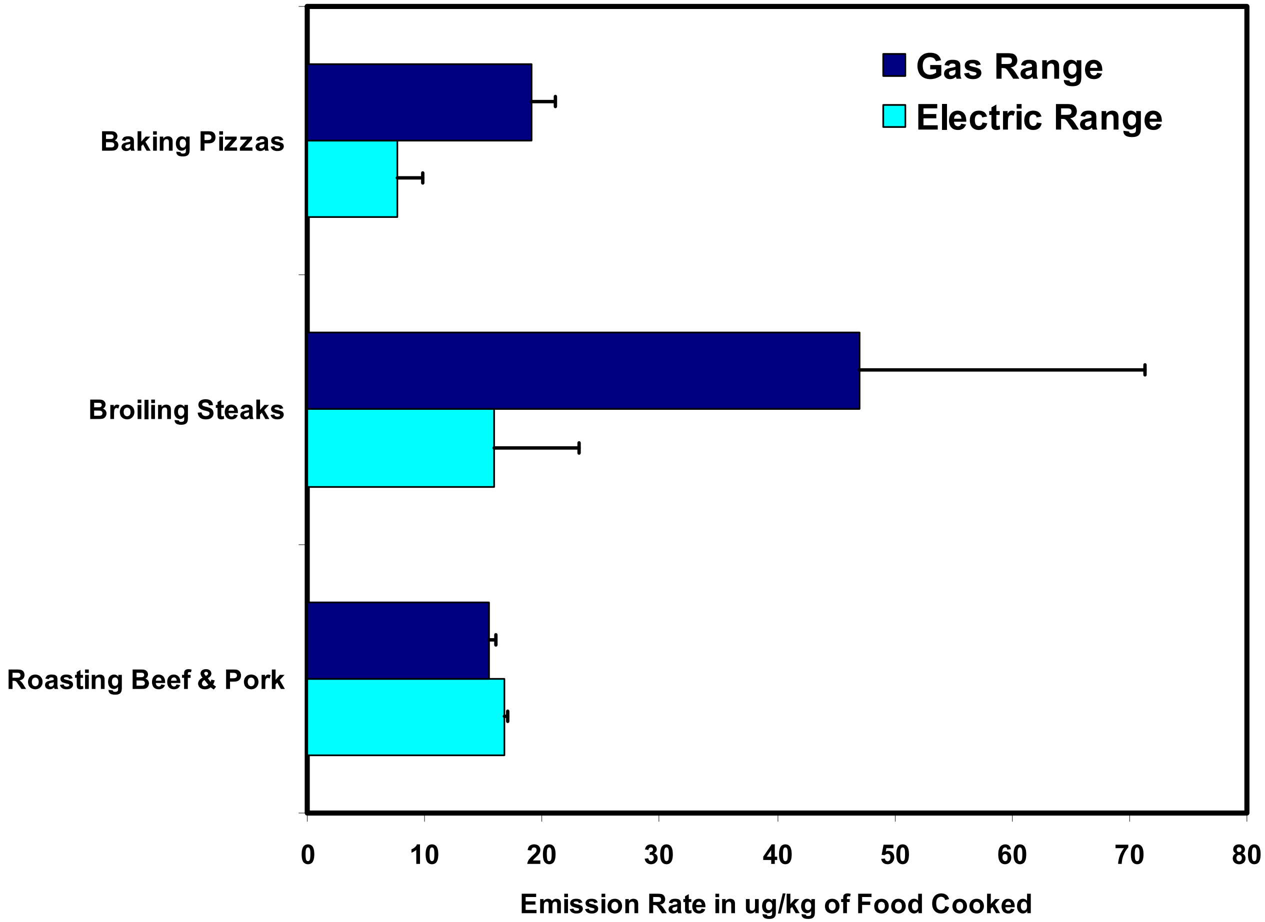
Cholesterol Emissions from Pan-Frying and Stir-Frying



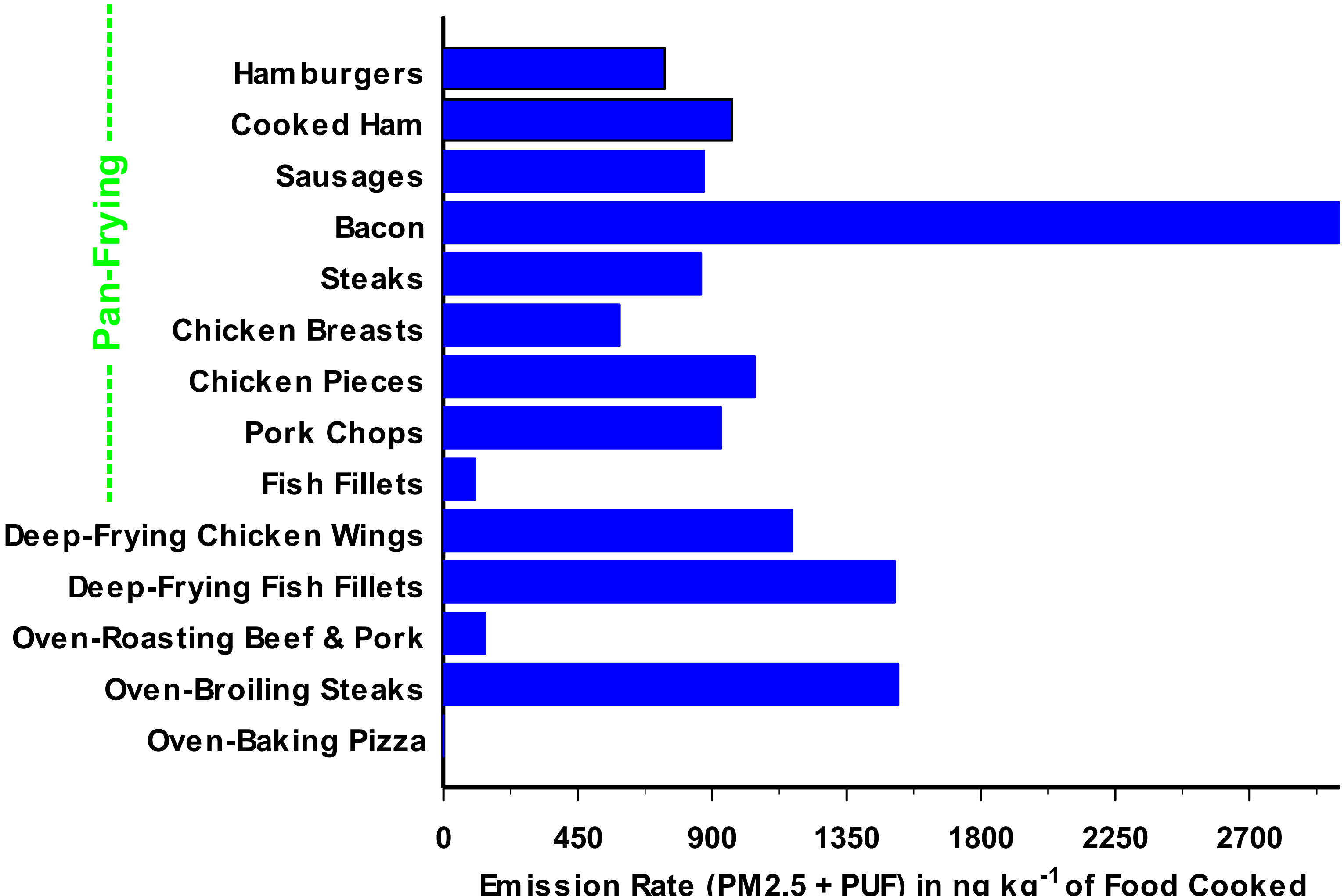
PAH Emissions from Stove-Top Cooking



PAH Emissions from Oven Cooking

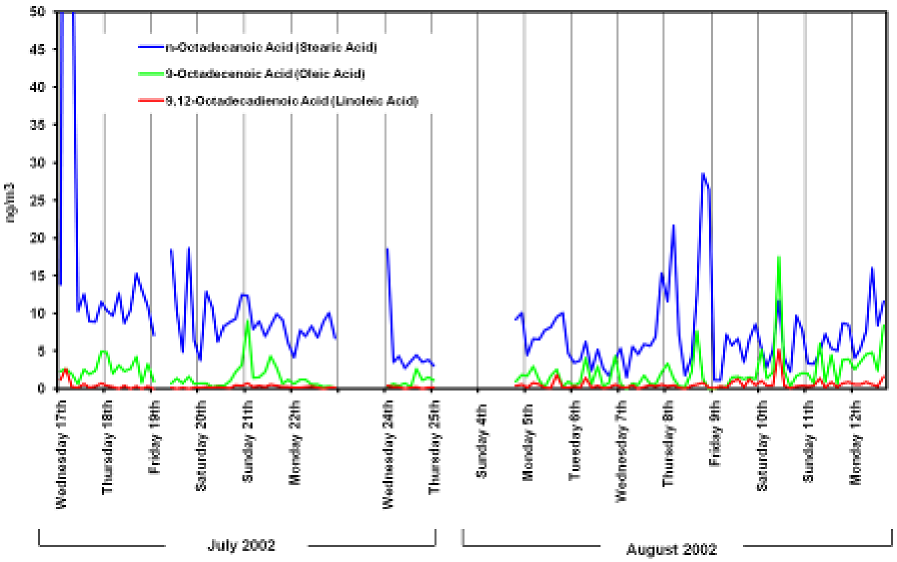


Heterocyclic Amines (HAAs) in Cooking Fumes from Residential Cooking

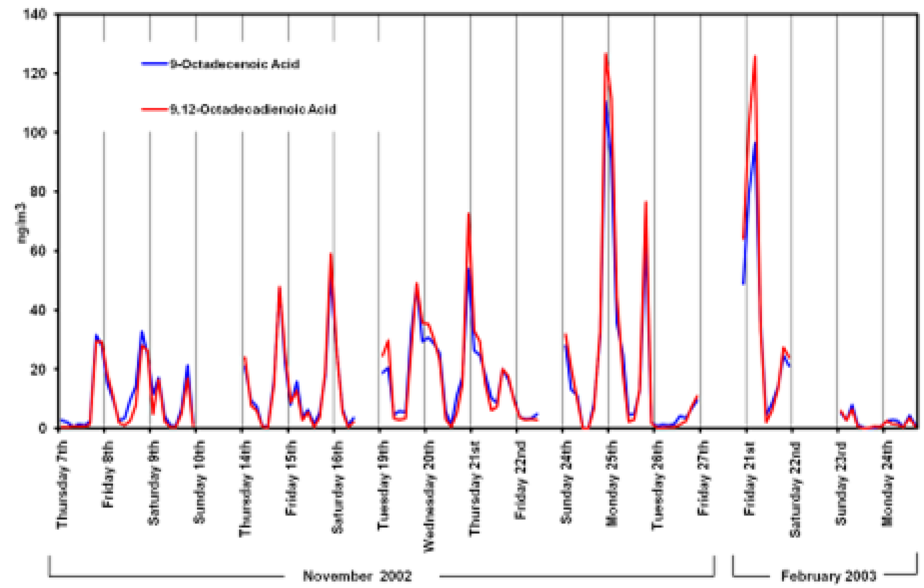


Baltimore Supersite: 3-Hourly PM2.5 Sampling Campaigns: 2002-2003

Summer 2002: Ambient Concentrations of F18 Saturated and Unsaturated Fatty Acids



Winter 2002/03: Ambient Concentrations of F18 Unsaturated Fatty Acids



Study was supported by US-EPA

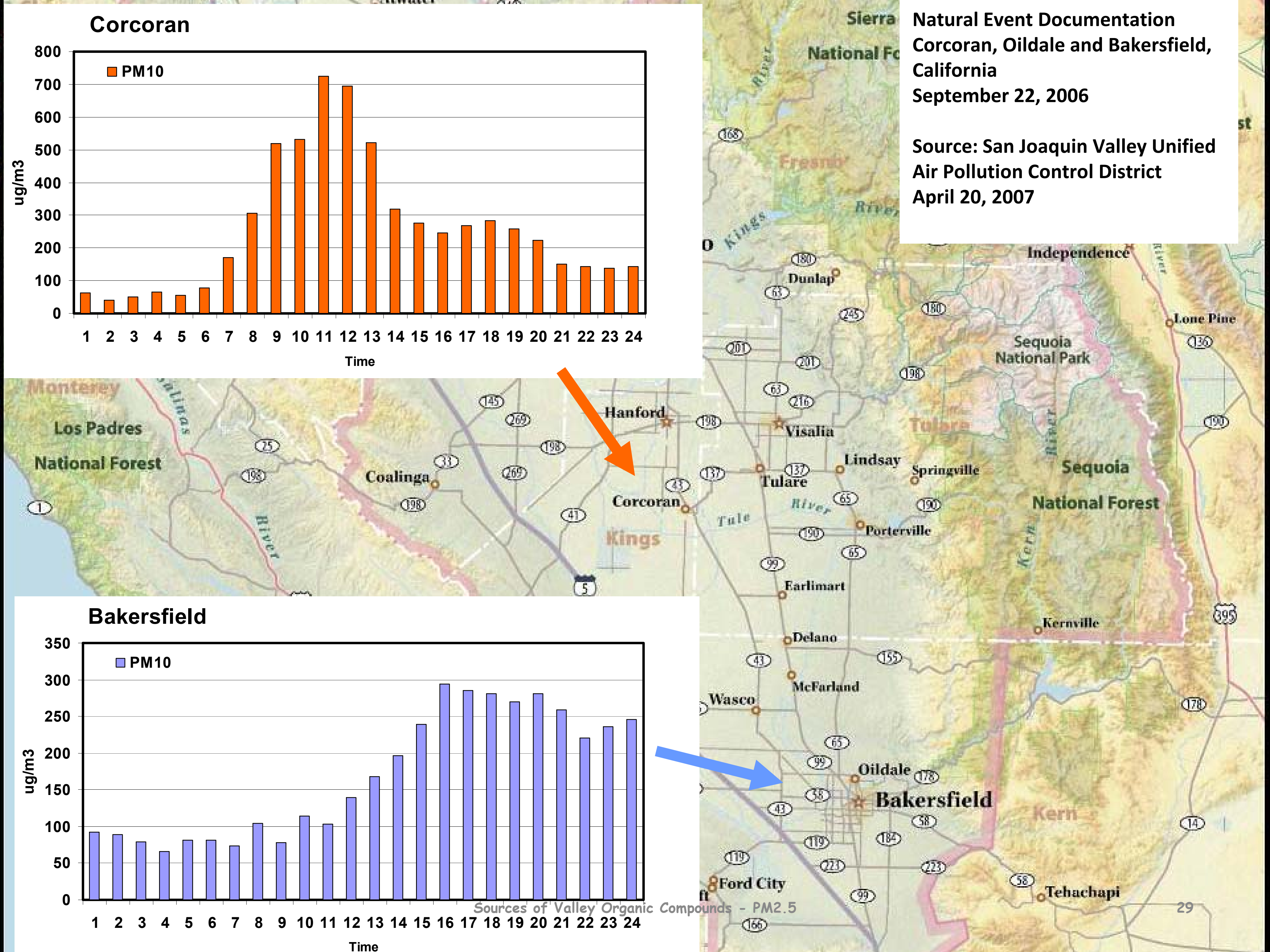
Organic Compounds associated with PM10 &PM2.5

Fugitive Dust from Fields
and
Windblown Dust

Study was supported by the California Air Resources Board

Natural Event Documentation
Corcoran, Oildale and Bakersfield, California
September 22, 2006

Source: San Joaquin Valley Unified Air Pollution Control District
April 20, 2007

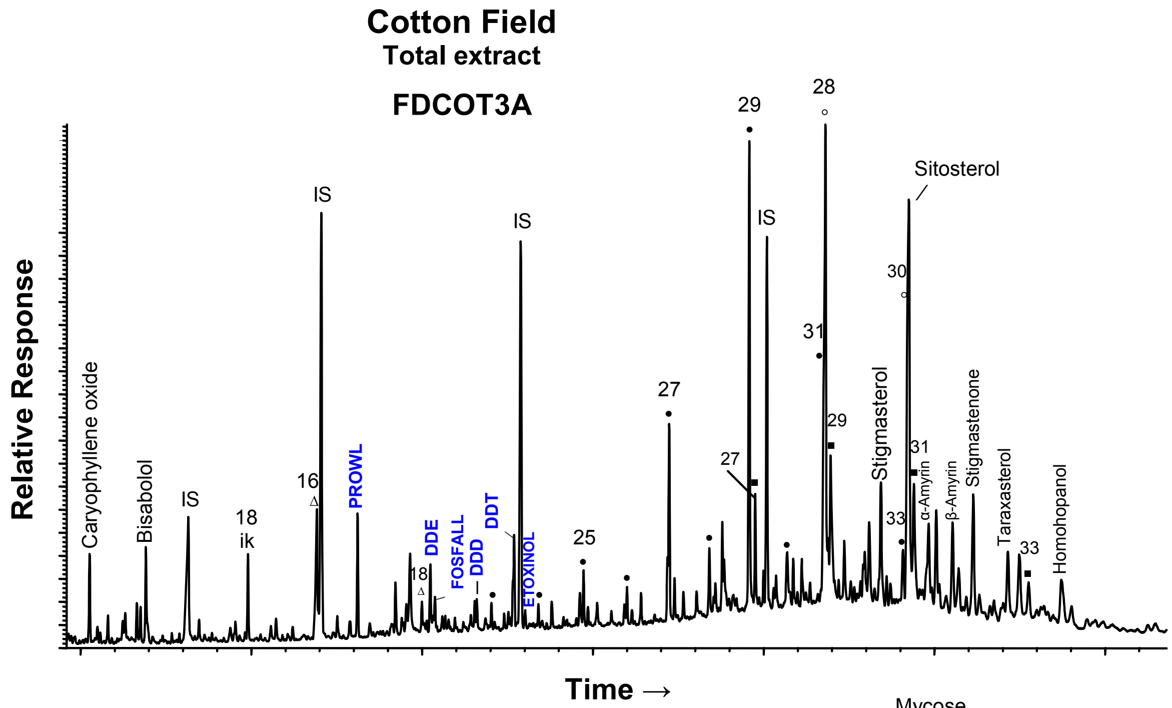


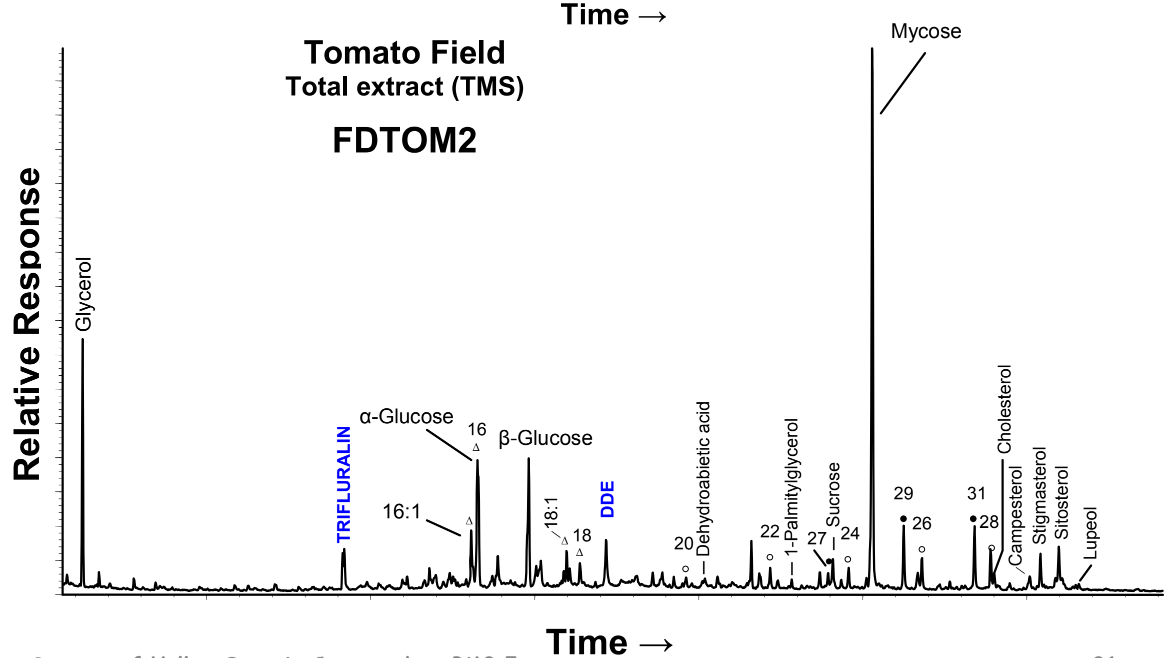
Major Crops in the San Joaquin Valley

Type	Acreage	SJV Rank in US	US Rank in World
Cotton	800,000 - 900,000	2	2
Safflower	100,000 - 150,000	2	1
Tomato	300,000 - 350,000		
Almonds	500,000 - 600,000	1	1
Grapes & Resins	800,000 - 900,000		

Fugitive dust exposes humans to:

- "Natural dust"
- Pesticides
- Pharmaceuticals
- Microorganisms
  - San Joaquin Valley fever (Coccidioidomycosis)





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Organic marker compounds in surface soils of crop fields from the San Joaquin Valley fugitive dust characterization study

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Received 12 January 2007; received in revised form 22 May 2007; accepted 23 June 2007

- **Fugitive dust exposes humans to:**
  - *Agricultural Waste Burning Products*
    - *e.g., Polycyclic Aromatic Hydrocarbons (PAHs)*

Average concentration of organic compounds in surface soils of crop fields (reported as $ng\,g^{-1}$)[a]

Compounds	Cotton fields (12)	Safflower fields (3)	Tomato fields (5)	Almond orchards (6)	Vineyards (3)	Compd ID[b]
PAHs						
Phenanthrene		3.2±3.4	0.6±0.1	3.4±1.7	12.3±19.6	a
Anthracene		0.7±0.7		4.4±2.2	1.9±2.8	a
4H-Cyclopentaphenanthrene					1.2±2.1	a
Fluoranthene		2.1±1.2	0.5±0.2	5.8±4.1	38.6±63.9	a
Pyrene		1.7±0.7	0.4±0.2	5.3±3.8	35.6±58.6	a
Benz[a]anthracene			0.2±0.2		13.8±22.6	a
Chrysene/triphenylene			0.3±0.3		26.2±42.7	a
Benzo[b]fluoranthene			0.5±0.2	4.2±3.0	35.5±58.6	a
Benzo[k]fluoranthene					12.7±21.0	a
Benzo[j]fluoranthene					2.1±3.3	a
Benzo[e]pyrene			0.3±0.2		21.5±34.9	a
Benzo[a]pyrene					21.0±34.6	a
Perylene					4.1±6.6	a
Indeno[123-cd]pyrene					29.4±48.8	a
Benzo[ghi]perylene					22.3±36.5	a
Dibenz[ah]anthracene					20.2±33.5	a
Coronene					6.4±10.0	a

Organic Compounds associated with PM10 &PM2.5

Fugitive Dust from Feedlots and Dairy Farms

Study was supported by the California Air Resources Board

Organic Marker Compounds for Fugitive Dust from Feedlots and Dairy Farms

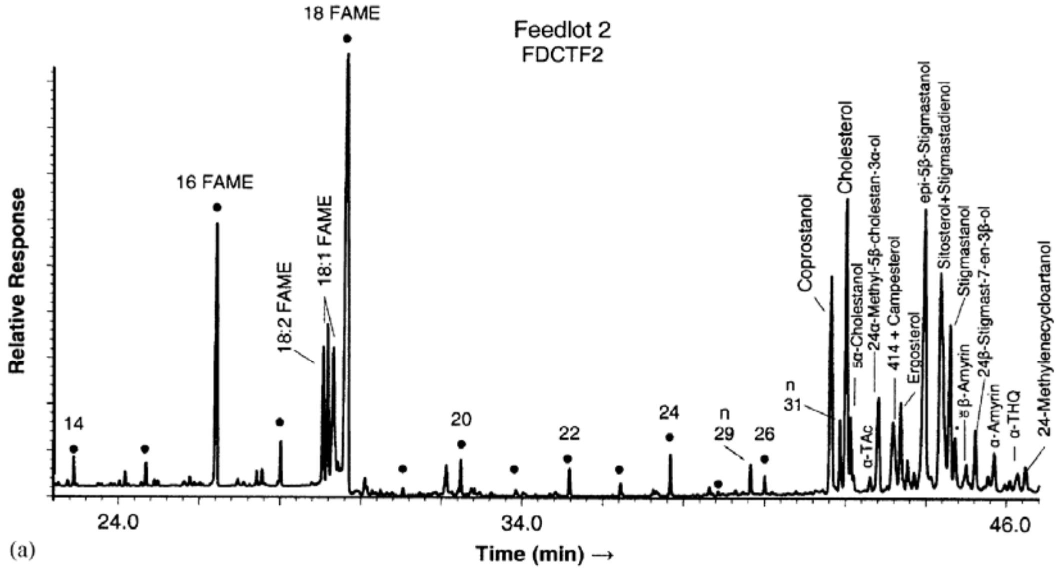
Cattle Population in the San Joaquin Valley

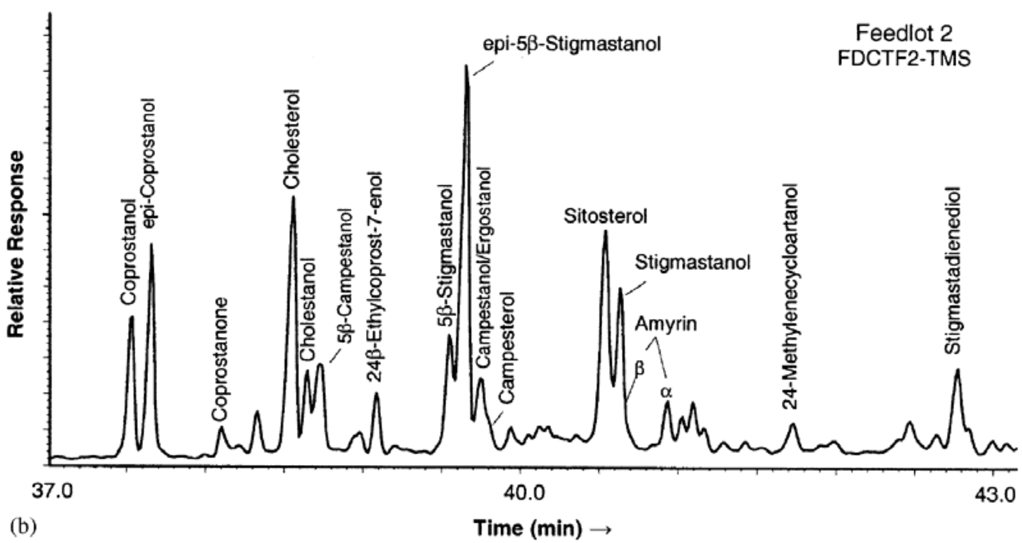
- Dairy Cattle ~ 2,000,000
- Range Cattle ~ 400,000
- Feedlot Cattle ~ 300,000

Dust Emissions depend on:

- Size of herd
- Type – dairy farms vs. feedlot
- Daily temp. & rainfall
- Lot design, manure management
- Activity pattern of cattle

Organic Marker Compounds for Fugitive Dust from Feedlots and Dairy Farms





Searching for unique markers, investigated:

- Food
- Food additives
- Metabolic conversion products of food chemicals

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Organic marker compounds for surface soil and fugitive dust from open lot dairies and cattle feedlots

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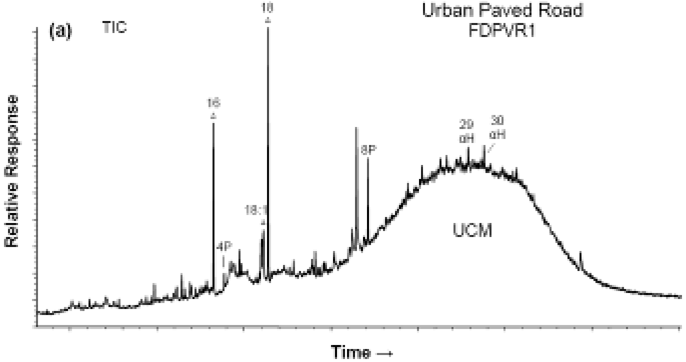
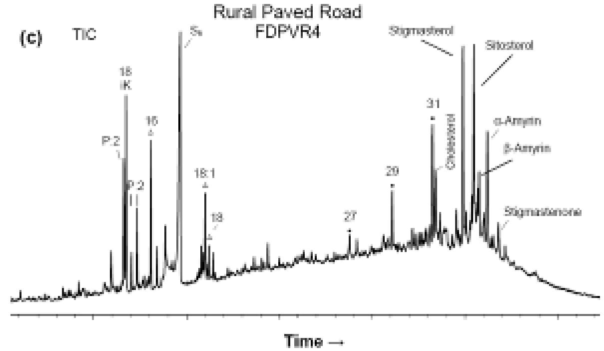
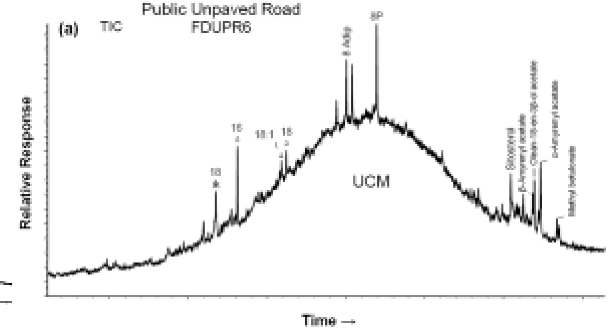
Organic Compounds associated with PM10 &PM2.5

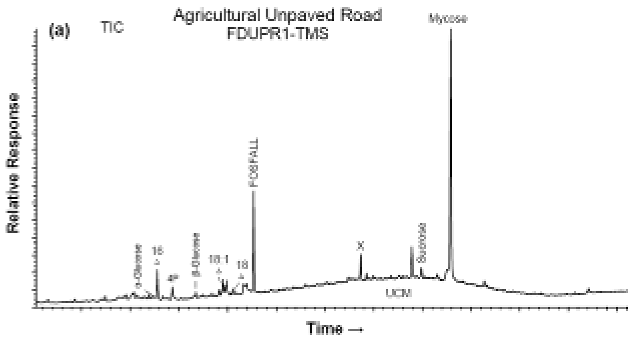
Fugitive Dust from Paved and Unpaved Roads

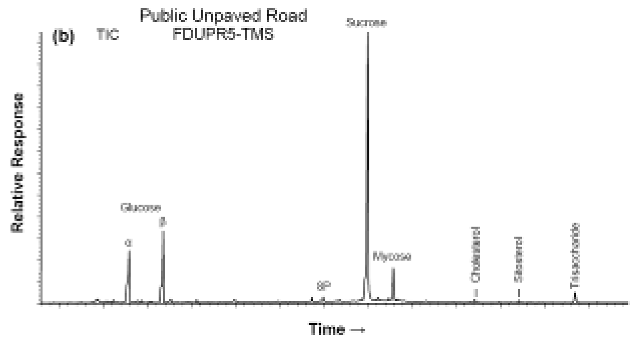
Study was supported by the California Air Resources Board

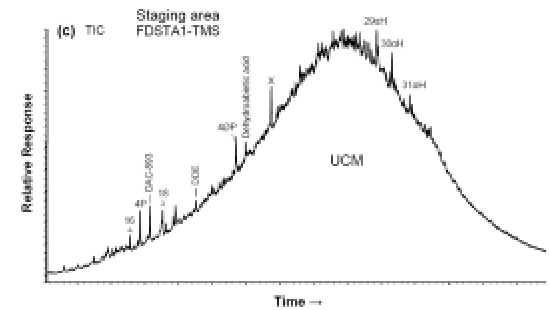


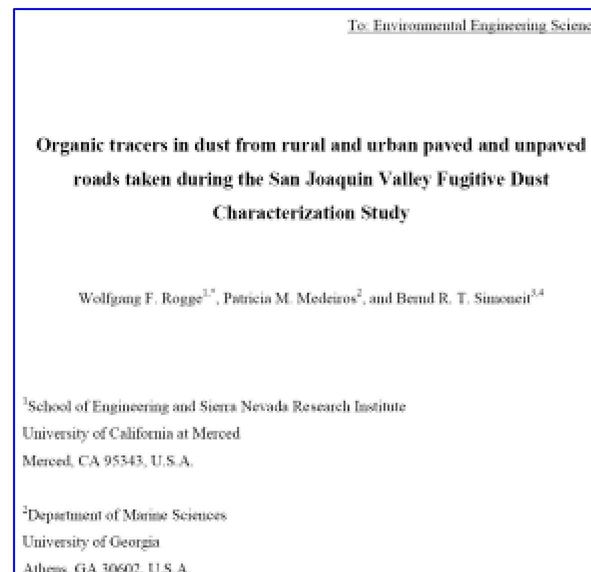












To: Environmental Engineering Science

Organic tracers in dust from rural and urban paved and unpaved roads taken during the San Joaquin Valley Fugitive Dust Characterization Study

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Table 2 - Concentrations of organic compounds in dust samples from paved and unpaved roads (reported as ng g^{-1}).

Compounds	Paved road: Urban	Paved road: Rural[a]	Unpaved road: Agricultural[b]	Unpaved road: Public[c]	Unpaved road: Staging area
Benzothiazoles					
Benzothiazole	928.0	706.1	6.5	17.6	nd
2-Hydroxybenzothiazole	1314.0	79.5	nd	nd	nd
TOTAL	**2242.0**	**785.6**	**6.5**	**17.6**	**-**
Pesticides/Plasticizers					
Dacthal (DAC-893, DCPA)	nd	nd	nd	nd	237.8
Fosfall	nd	nd	152.9	nd	nd
DDE	nd	nd	13.4	nd	78.5
Benzyl butyl phthalate	nd	nd	nd	nd	378.7
Dibutyl phthalate	3.5	nd	nd	nd	198.2
Diethylhexyl phthalate	14.1	nd	nd	49.5	nd
Diethylhexyl adipate	nd	nd	nd	10.9	nd
TOTAL	**17.6**	**-**	**166.2**	**60.4**	**893.2**

	Road Urban Paved	Road Rural Paved		Road Agriculture Unpaved			Road Public Unpaved		
Sample Name:	**FDPVR1**	**FDPVR3**	**FDPVR4**	**FDUPR1**	**FDUPR2**	**FDUPR3**	**FDUPR4**	**FDUPR5**	**FDUPR6**
PAHs									
Naphthalene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Acenaphthylene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Acenaphene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fluorene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Phenanthrene	28.5	54.1	0.0	0.7	3.6	0.9	1.1	2.8	8.9
Anthracene	7.8	7.1	0.0	0.2	4.9	0.1	0.1	0.1	3.1
4H-Cyclopentaphenanthrene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.7
Fluoranthene	28.1	41.5	3.5	0.4	0.9	0.3	1.1	2.1	36.9
Pyrene	36.3	97.3	3.6	0.6	1.2	0.5	0.9	1.7	42.4
Benzo[a]anthracene	42.5	43.1	1.5	0.0	0.0	0.0	0.0	0.2	22.1
Chrysene/Triphenylene	107.6	658.8	6.9	0.0	0.0	0.0	0.0	2.2	28.9
Benzo[b]fluoranthene	110.2	139.2	3.5	0.0	0.0	0.0	0.0	0.9	20.3
Benzo[k]fluoranthene	25.7	10.9	0.4	0.0	0.0	0.0	0.0	0.2	8.5
Benzo[j]fluoranthene	3.9	2.1	0.5	0.0	0.0	0.0	0.0	0.2	2.6
Benzo[e]pyrene	113.4	239.9	5.7	0.0	0.0	0.0	0.0	1.2	11.7
Benzo[a]pyrene	48.5	29.4	1.3	0.0	0.0	0.0	0.0	0.2	14.8
Perylene	12.4	14.3	1.8	0.0	0.0	0.0	0.0	0.2	2.7
Indeno{1,2,3-cd]pyrene	87.2	25.8	1.0	0.0	0.0	0.0	0.0	0.0	10.2
Benzo[g,h,i]perylene	135.3	48.3	3.2	0.0	0.0	0.0	0.0	0.9	8.3
Dibenzo[a,h]anthracene	60.7	23.0	0.5	0.0	0.0	0.0	0.0	0.0	5.8
Coronene	76.4	8.5	1.7	0.0	0.0	0.0	0.0	1.0	2.8

Thank you

Questions?