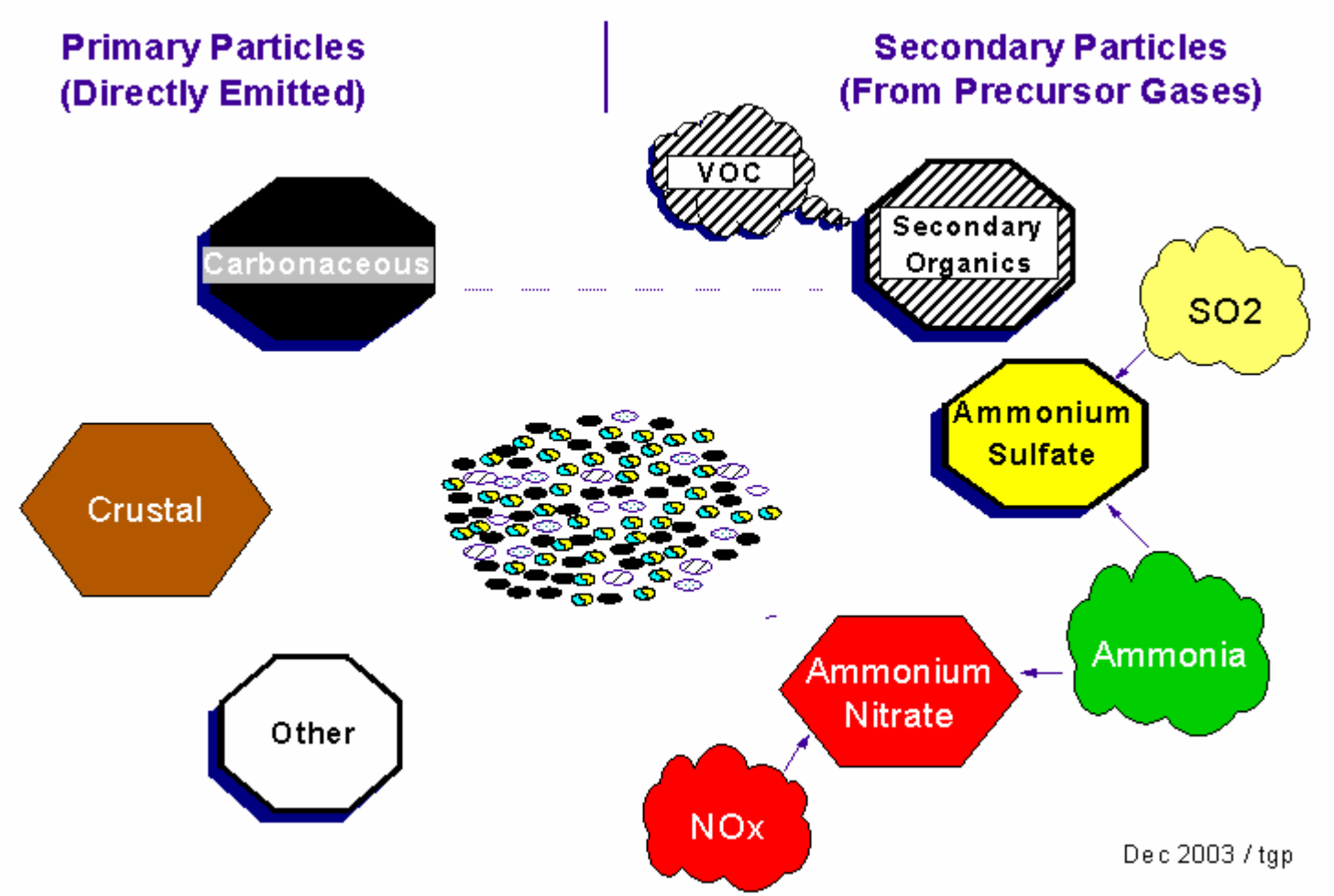
Preparation of Fine Particulate Emissions Inventories

Chapter 1 - $PM_{2.5}$ Overview

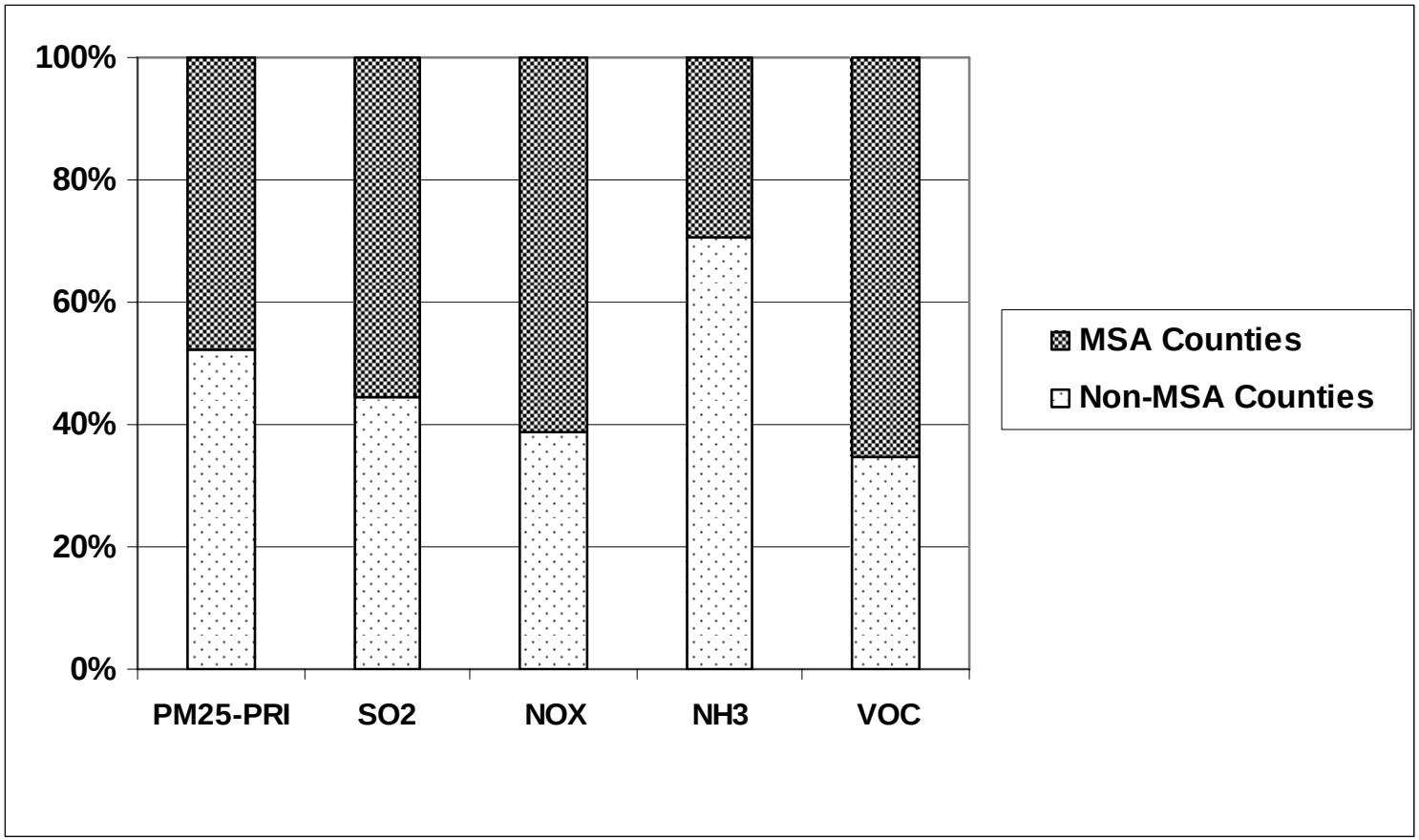
$PM_{2.5}$ In Ambient Air - A Complex Mixture



Urban PM Sites

- Eastern U.S. data is very homogenous
- Comprised mostly of carbon
- Ammonium and sulfate components combined are comparable to carbon
- Crustal component is very small

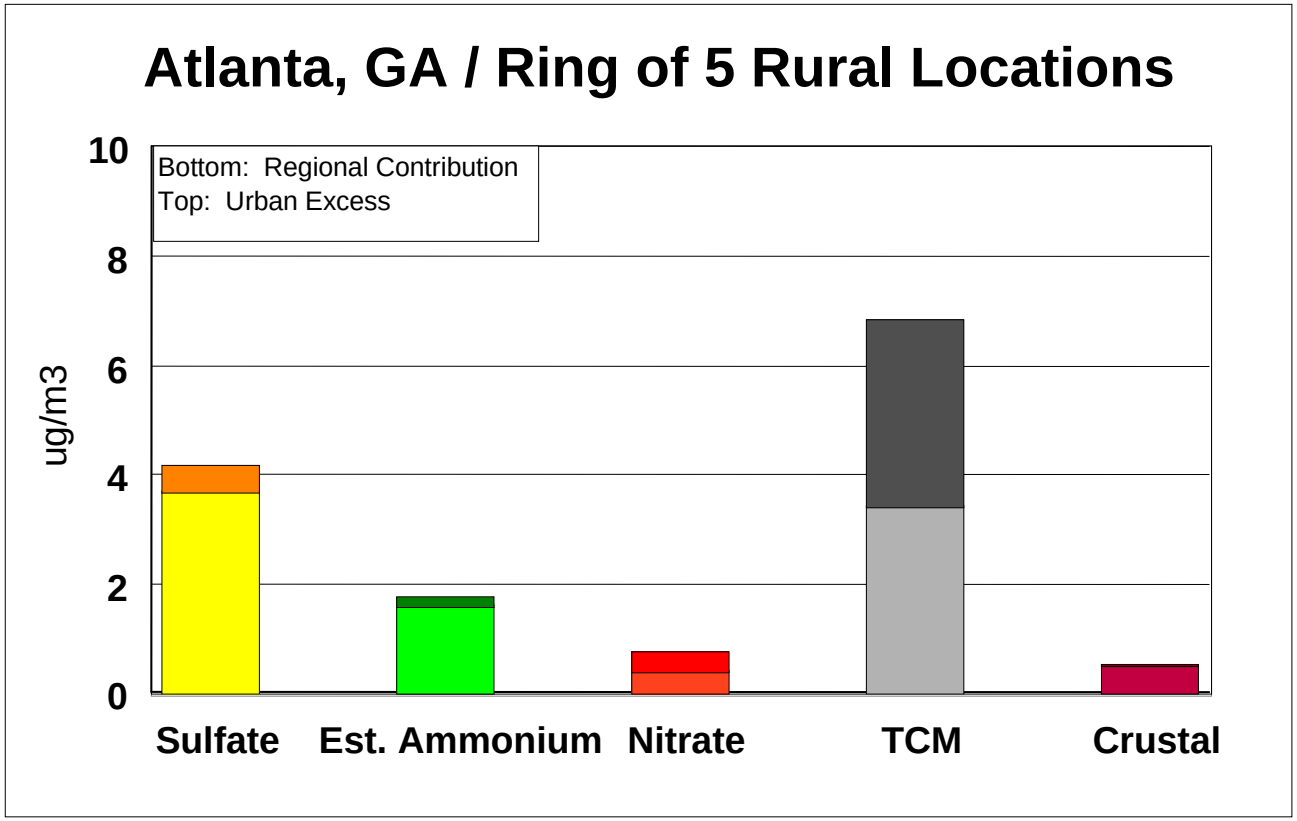
MSA to Non MSA Comparison of PM Emissions

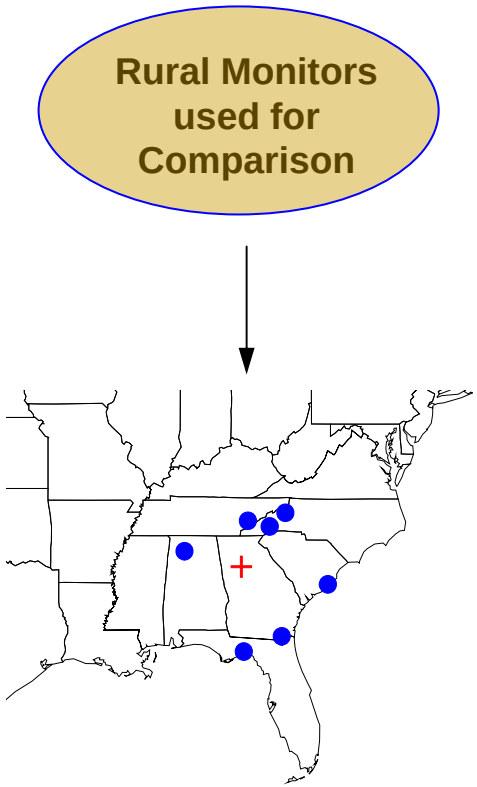


Comparison of Urban and Rural Data

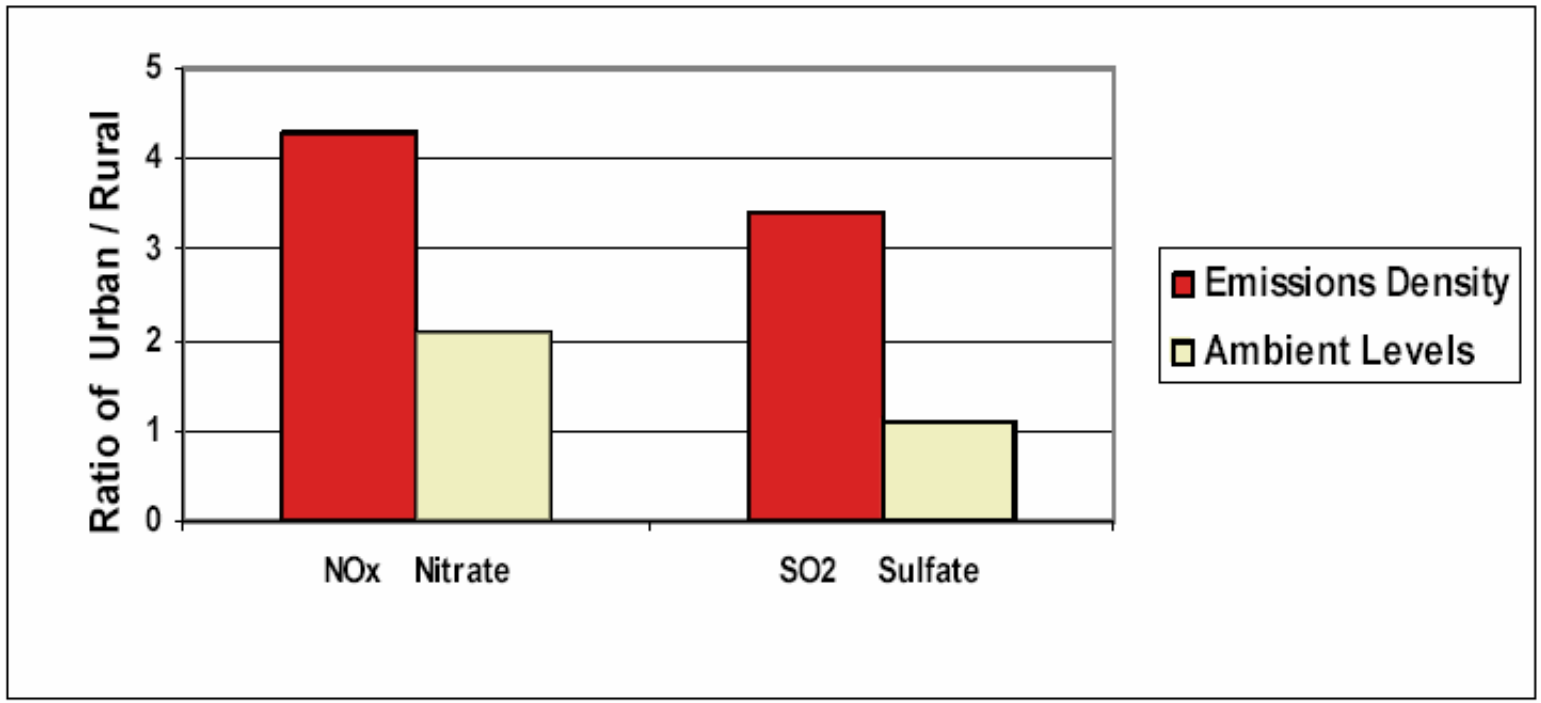
- More sulfate than carbon in non-urban sites
- Sulfate concentration slightly higher in urban areas
- Carbon concentrations substantially higher in urban areas
- Conclusions
  - Sulfate is a regional problem
  - Carbon has a regional component with urban excess
- Urban Excess definition

Example of "Urban Excess"



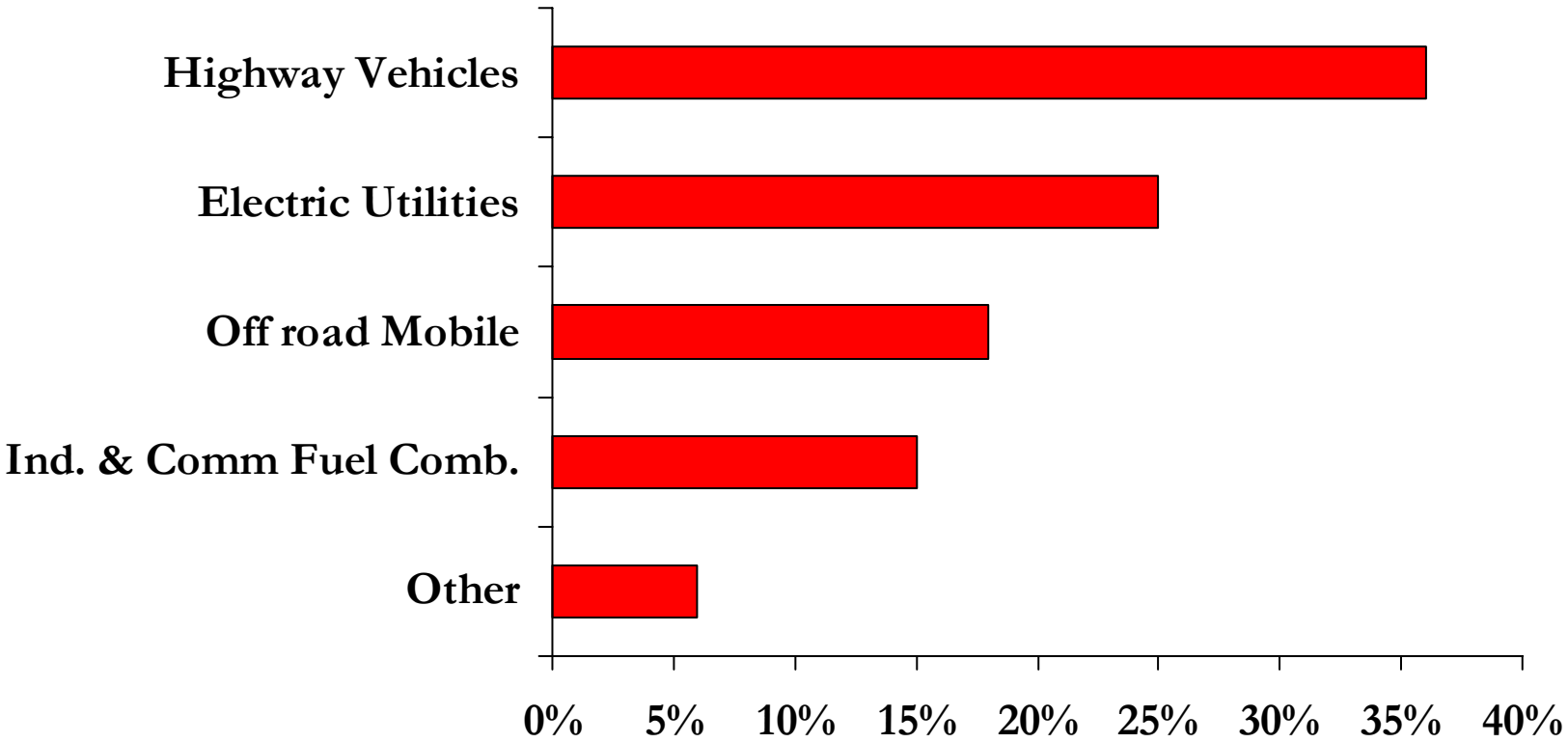


Comparison of Urban~Rural Ratios

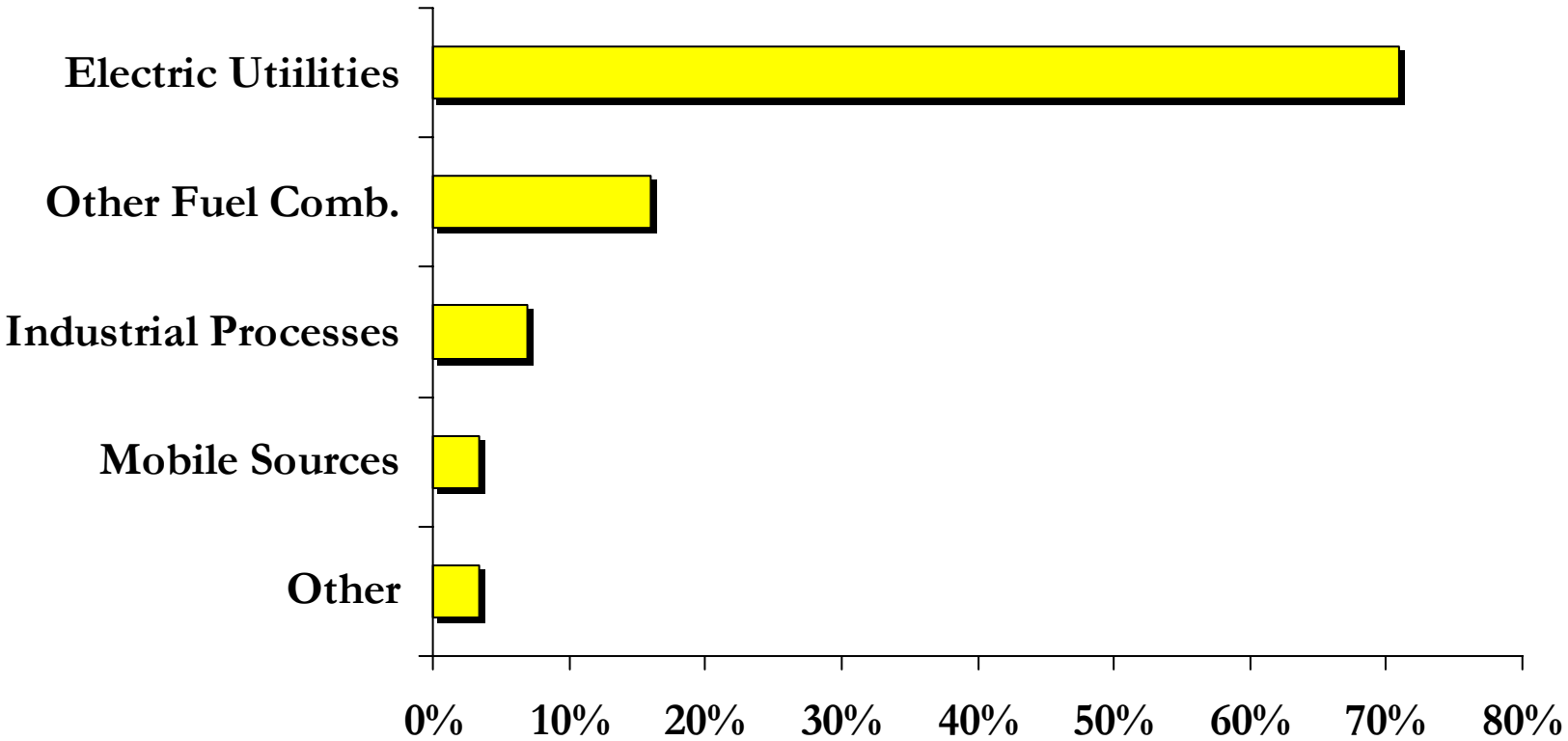


Note: Sulfate particles are more stable and thus have longer lifetime in the atmosphere than Nitrate. Sulfate is therefore more subject to transport

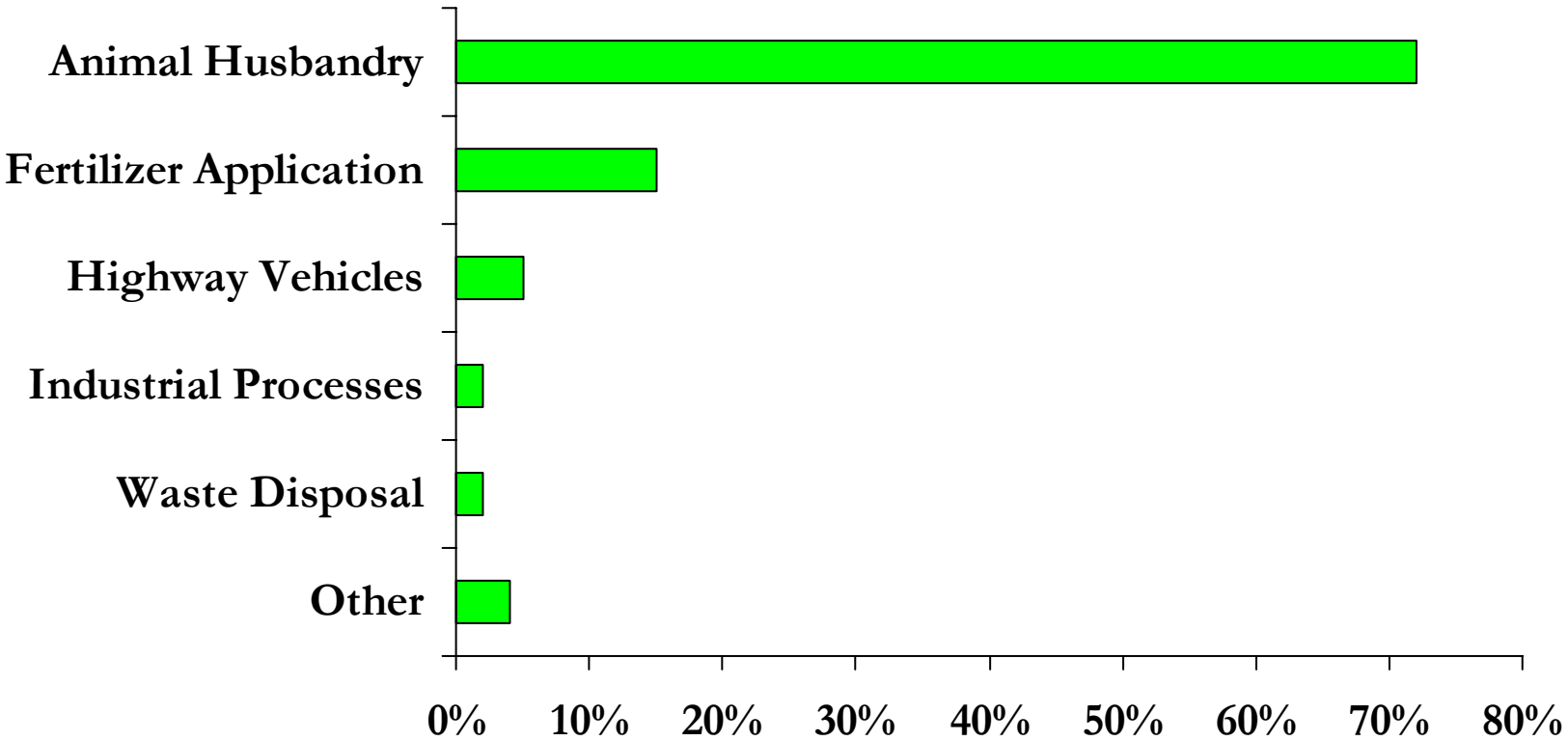
National NOx Emissions



SO2 National Emissions



NH3 National Emissions



Crustal Material

- Main Sources:
  - Unpaved roads
  - Agricultural tilling
  - Construction
  - Wind-blown dust
  - Fly ash (less significant)

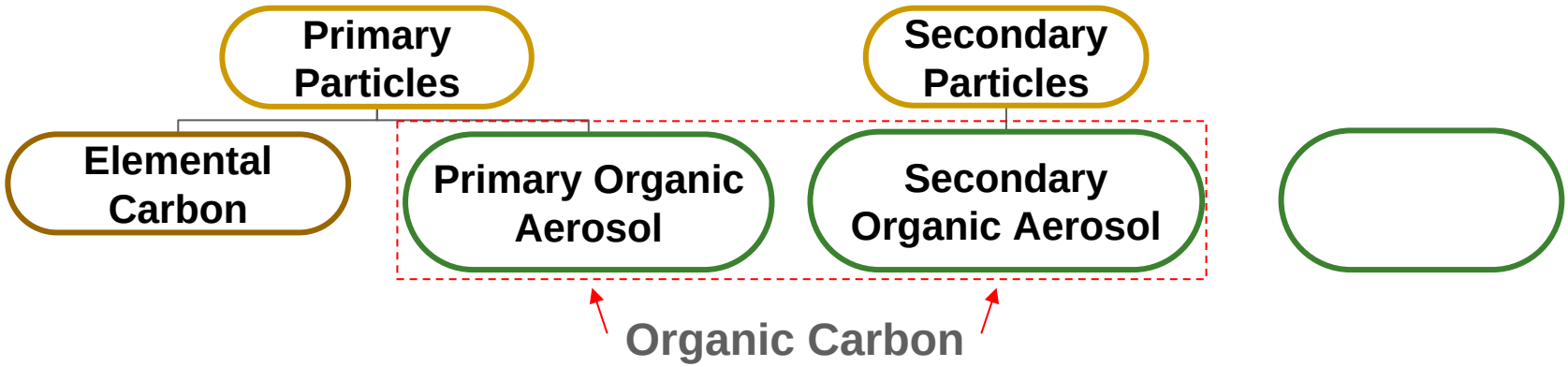
Crustal Material (cont.)

- Huge Disparity Between EI & Ambient Data
  - Ambient Data
    - < 1 ug/m3 in most of US
    - Exception: > 1 ug/m3 in much of Southwest
    - Emissions: 2.5M TPY (comparable to Carbon Emissions)

Crustal Material (cont.)

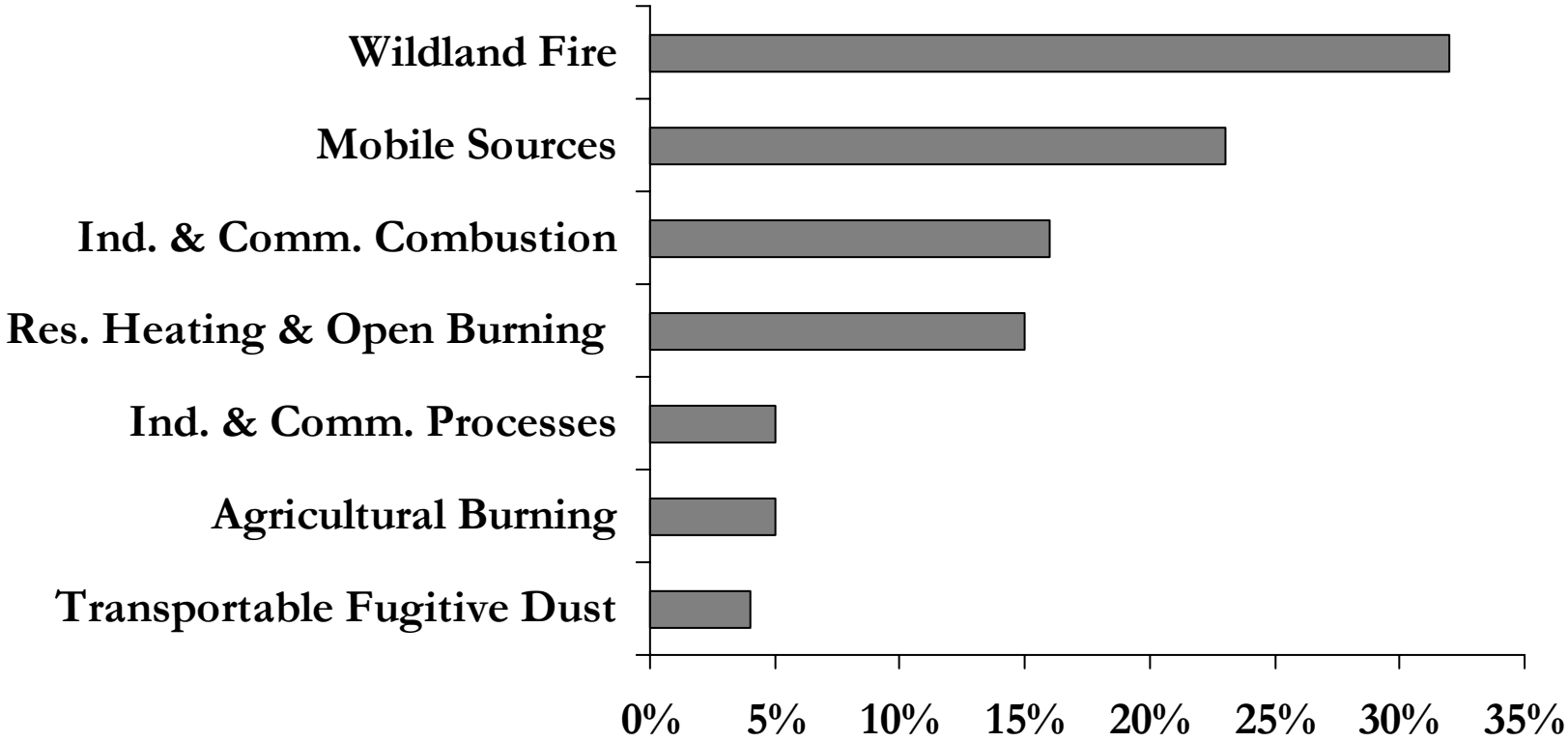
- Fugitive Dust has low “Transportable Fraction
- Crustal materials are a relatively small part of PM2.5 in the ambient air
- Fugitive dust is released near the ground and surface features often capture the dust near its source
- As much as 50-90% may be captured locally

Carbon Particles: Composition & Terminology



- Primary Particles
  - Elemental (Black) Carbon
  - Primary Organic Aerosol (POA)
  - Primary Carbon = EC (BC) + Primary Organic Aerosol (POA)

Primary Carbon in PM2.5



% of PM2.5 Primary Carbon Emissions
(National Emissions ~ 2M TPY)

POA & EC Characteristics of Primary Carbon Emissions

Category	Ratio of organic carbon mass* to elemental carbon mass (average)	Potential range of ratios
Forest Fires	9.9	6 – 28
Managed Burning	12	6 – 28
Agricultural Burning	12	2.5 – 12
Open Burning - Debris	9.9	
Non-road Diesel Engines & Vehicles	**0.4**	**0.4 – 3**
On-road Diesel Vehicles	**0.4**	**0.4 – 3**
Trains, Ships, Planes	**0.4**	**0.4 – 25**
Non-road Gas Engines & Vehicles	14	0.25– 14
On-road Gas Vehicles	4.2	0.25 – 14
Fugitive Dust - Roads	22	3 – 65
Woodstoves	7.4	3 – 50
Fireplaces	7.4	3 – 50
Residential Heating - Other	26	
Commercial Cooking	111	13 – 111

Primary Organic Aerosols (POA)

- Certain organic carbon excluded
- Organic carbon matter = primary organic aerosol (POA).
- The OC to POA multiplier for “fresh” POA in the emissions is usually estimated
- Particles “age” through oxidation.
- A different “multiplier” is applied to the POA by the chemical transport models to account for the “aging”

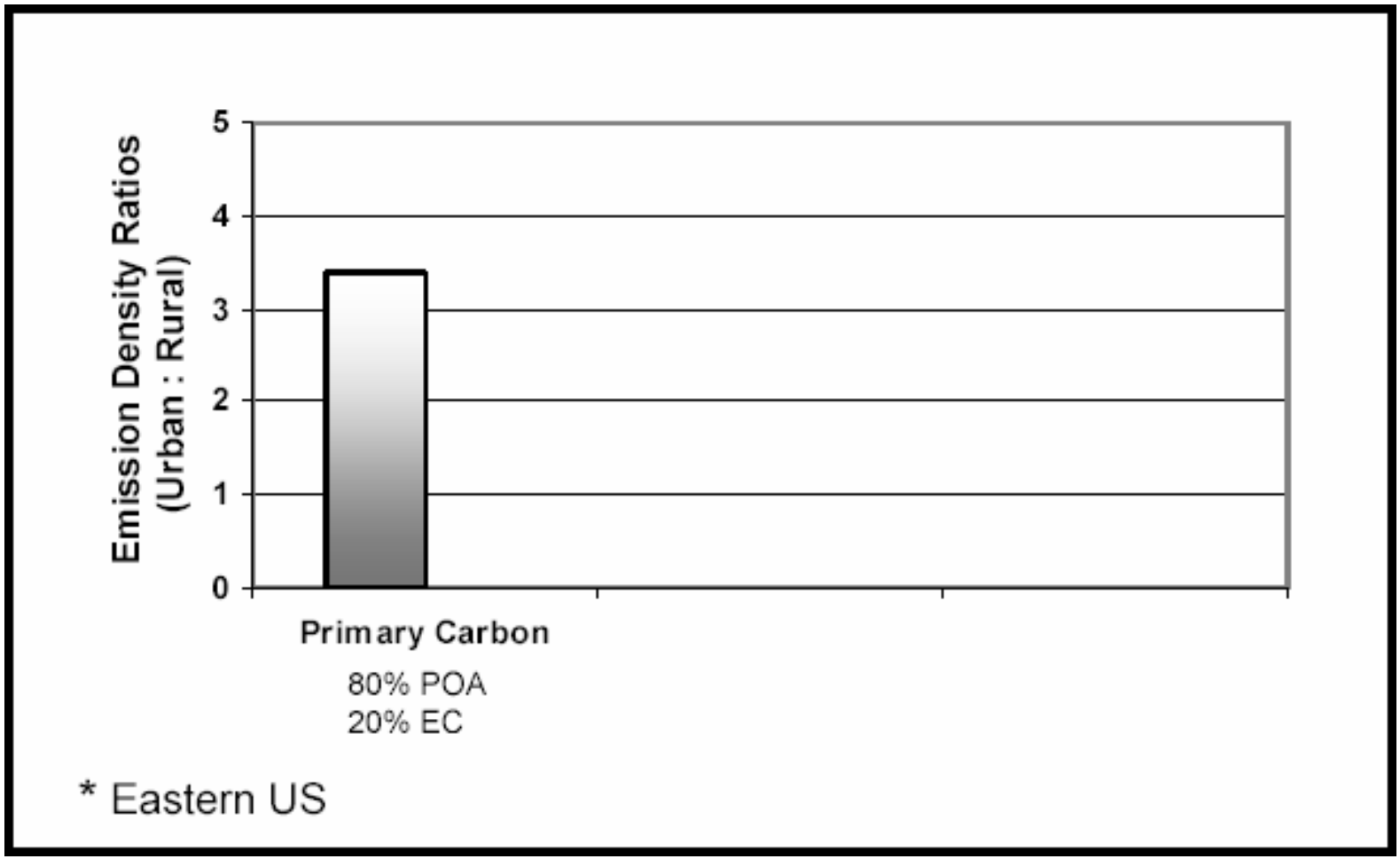
Primary Organic Aerosols (cont.)

- Models only apply the additional multiplier to the POA, not the EC or SOA
- Multiplier is not related to the model's estimate of secondary organic aerosol formed in the atmosphere from precursor gases
- Only accounts for further oxidation of primary particle emissions as the aerosol "ages"
- Transport models contain a separate module to simulate the amount of secondary organic carbon formed in the atmosphere from precursor

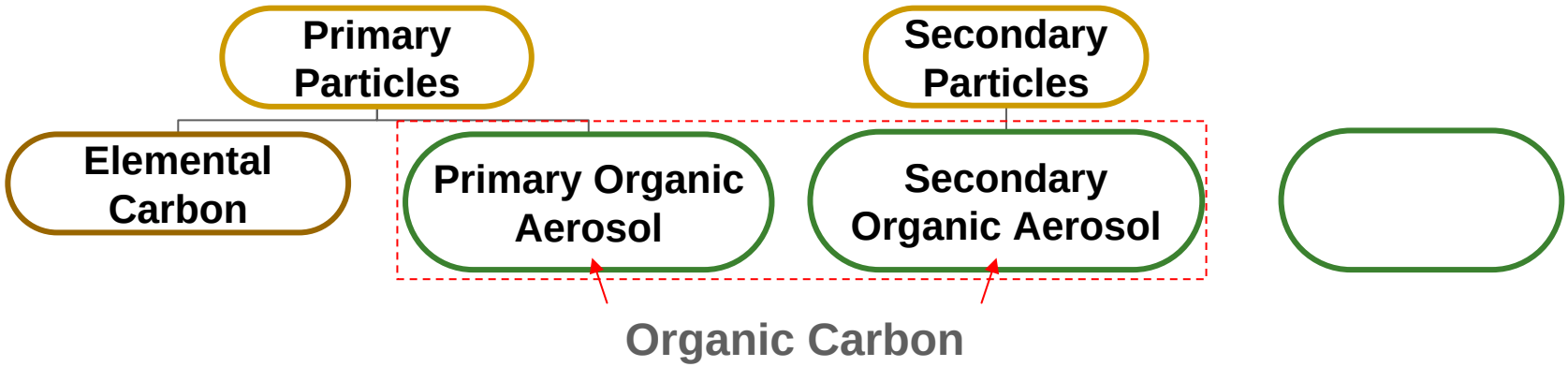
Primary Organic Aerosols (cont.)

- The derivation of a multiplier for ambient OC is much more complicated
- Use of a single multiplier introduces error
- A multiplier of 1.4 to 2.4 is often used for ambient data
- No agreed upon standard adjustment

Primary Carbon Emissions Emission Density Ratios



Carbon Particles: Composition & Terminology



- Primary Particles
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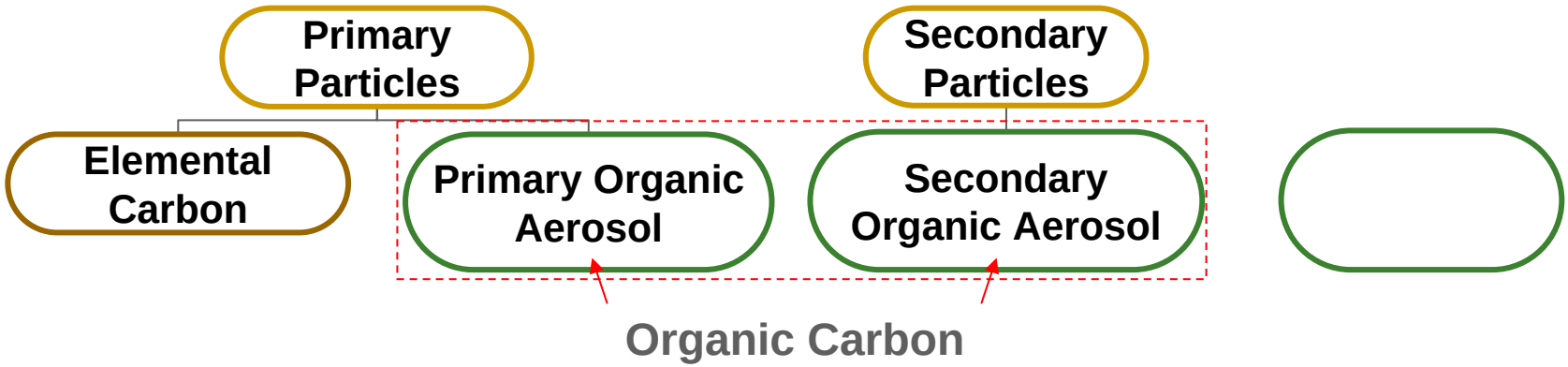
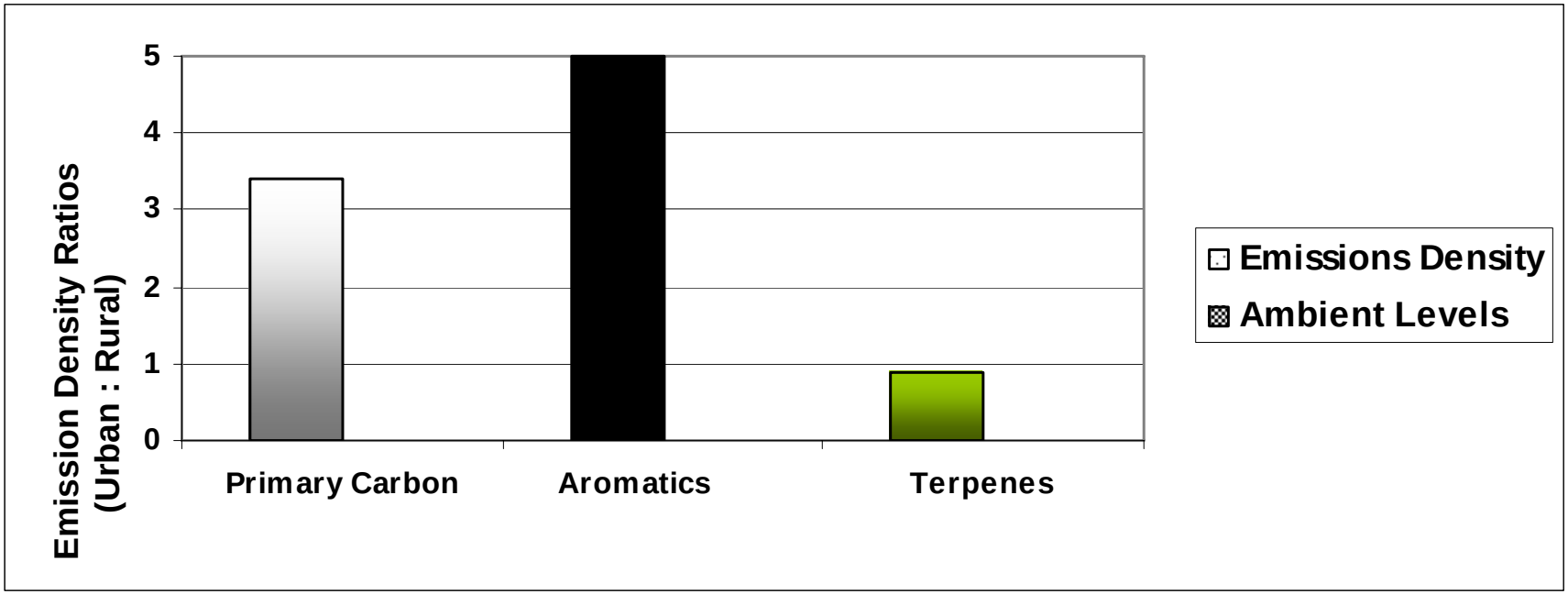
Carbon Particles: Composition & Terminology (cont.)



- Secondary Particles
  - Secondary Organic Aerosol (SOA)
- Organic Carbon = POA & Secondary Organic Aerosols

Comparison of Emission Density Ratios



	Primary Carbon	Aromatics	Terpenes
	80% POA 20% EC	70% Mobile	Biogenic
Emissions:	**2.2M tpy (Ann)**	**3.7 M tpy (Ann)**	**.35 M tpy (July)**

***** Eastern US

Summary of Important PM2.5 Source Categories

DIRECT EMISSIONS

Combustion [a, b]

- **Open Burning (all types)**
- **Non-Road & On-Road Mobile**
- **Residential Wood Burning**
- **Wildfires**
- Power Gen
- Boilers (Oil, Gas, Coal)
- Boilers (Wood)

Crustal / Metals [b]

- **Fugitive Dust**
- Mineral Prod Ind
- Ferrous Metals

PRECURSOR EMISSIONS

SO2 [c]

- **Power Gen (Coal)**
- **Boilers (Coal)**
- Power Gen (Oil)
- Boilers (Oil)
- Industrial Processes

NOx

- **On-Road Mobile (Gas, Diesel)**
- **Power Gen (Coal)**
- **Non-Road Mobile (Diesel)**
- **Boilers (Gas, Coal)**
- Residential (Gas, Oil)
- Industrial Processes

NH3

- **On-Road Mobile**
- **Animal Husbandry**
- **Fertilizer Application**
- Wastewater Treatment
- Boilers

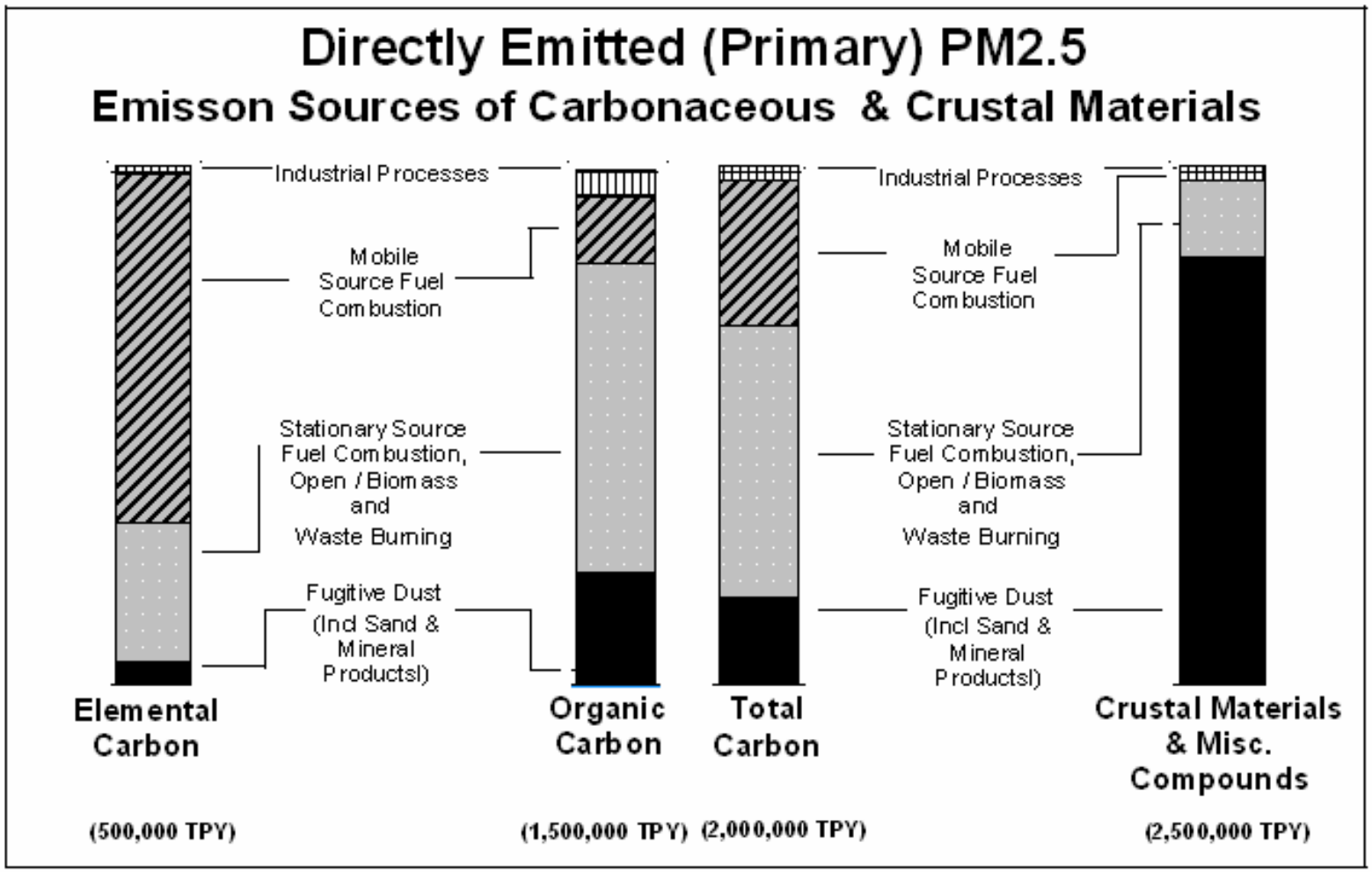
VOC [d]

- **Biogenics**
- **Solvent use**
- **On-Road (Gas)**
- Storage and Transport
- Residential Wood
- Petrochemical Industry
- Waste Disposal

a Includes primary organic particles, elemental carbon and condensible organic particles; also some flyash
b Impact of carbonaceous emissions on ambient PM 5 to 10 times more than crustal emissions impact
c Includes SO_2, and SO_3 and H_2SO_4 condensible inorganics
d Contributes to formation of secondary organic aerosols

NOTE: Categories in **BOLD** are most important nationally. Their relative importance varies among and between urban and rural areas.

PM2.5 Primary Emissions Sources - Summary



$PM_{2.5}$ In Ambient Air - A Complex Mixture

A Review of Precursor Interrelationships

Secondary Organics

- VOC from Vegetation (Terpenes)
  - Relatively fast reaction
- VOC from Mobile Sources (Aromatics)
  - Slower than Terpenes
- Reducing Aromatics >> lower SOA

Ammonium Sulfate

- SO2 from Sulfur in Fuels
- Compared to Ozone:
  - Sulfate forms & deposits more slowly
- If insufficient Ammonia ~
  - Ammonium bisulfate or
  - Sulfuric acid
- Reducing SO2 >> lower Ammonium Sulfate

Ammonium Nitrate

- NOx from fuel combustion
  - Relatively fast reaction
- If insufficient Ammonia ~
  - Sulfate formed before nitrate
- Higher temperatures, lower rH >> Equilibrium shift
  - Less nitrate - more nitric acid
  - Sampling losses
- Reducing NOx may reduce Nitrates, Sulfates & SOA but outcomes very complicated, cannot be generalized

Ozone

- Generally, less Ozone >> less SOA, Sulfate & Nitrate