Diesel and Gasoline Engine Emissions: Characterization of Atmosphere Composition and Health Responses to Inhaled Emissions

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"CONTEMPORARY" DIESEL EMISSIONS
(Now a "Baseline" for "Clean Diesel")

2000 Cummins 5.9L ISB 6 cyl. Turbo

D-2 Cert. Fuel (370 ppm S, 29% aromatics)

Shell Rotella-T® 15W-40 crankcase oil

Stock exhaust system with muffler

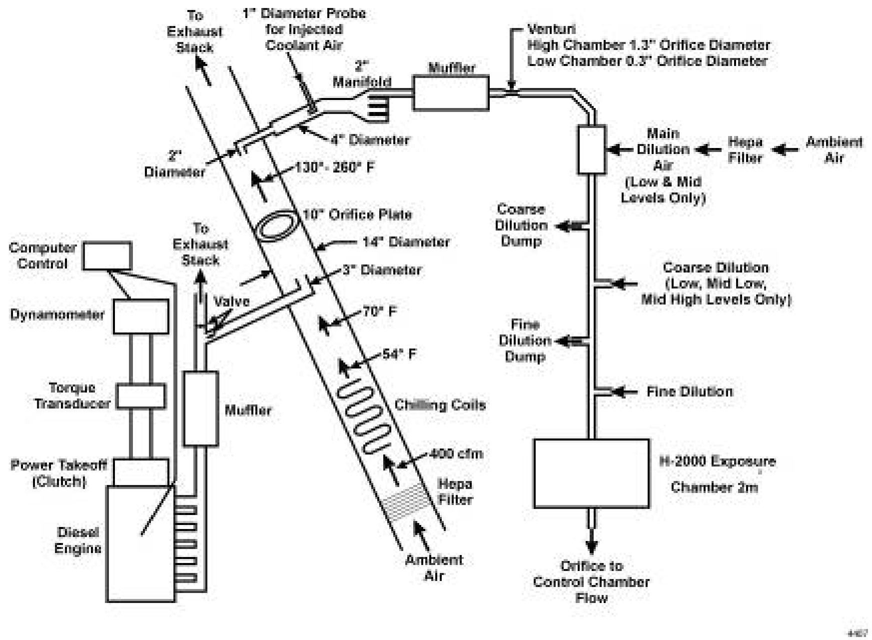
Repeated heavy-duty certification cycle

Cold start excluded

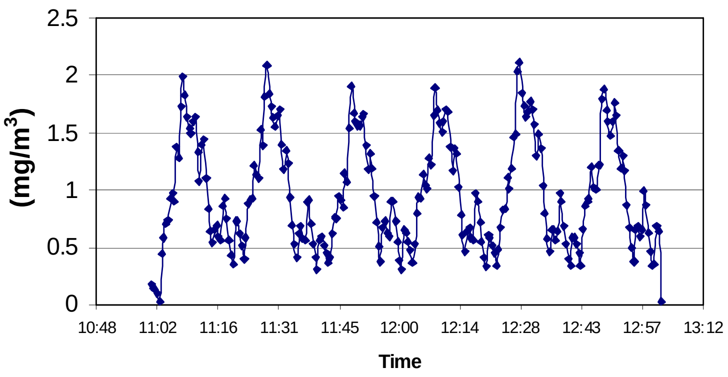
Emissions diluted with carbon- and HEPA-filtered air

Expose at 1000, 300, 100, 30, 0 µg PM/m^3
(dilutions ≈ 1:10 to 1:300)

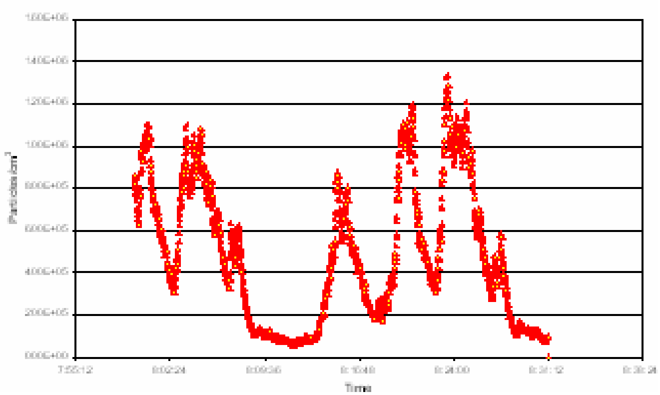
DIESEL EXPOSURE SYSTEM



PM Concentration in High Level Chamber During Multiple Cycles

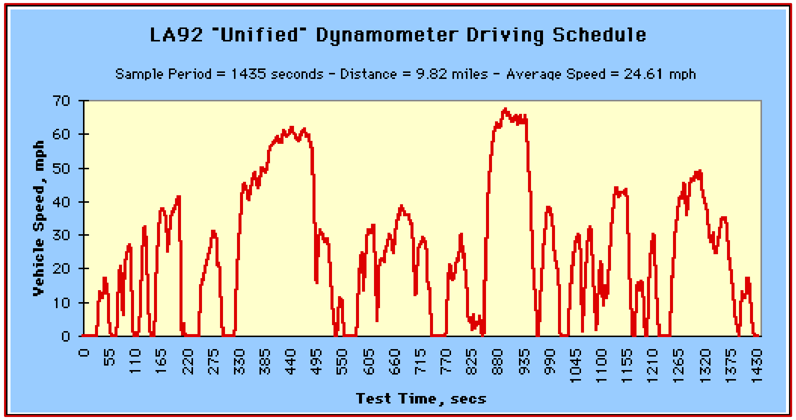


Number of 20 nm Particles/cc During One Cycle

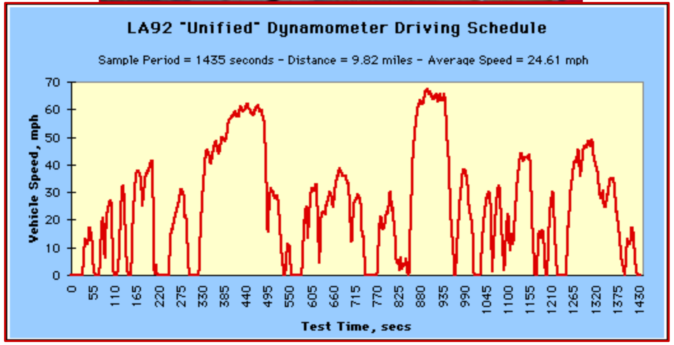


[McDonald et al., *Env. Sci. Technol*., 38: 2513, 2004]

Development of a Exposure Atmospheres: Gasoline Engine Emissions



GASOLINE EMISSION EXPOSURES



1996 4.3 L General Motors V-6 engines

- 3 in-use Chevrolet S-10 pickup trucks
- Mid-range mileage (40-70k miles)
- Normal emissions

(California) Unified Driving Cycle

- 3-phase cycle mapped from chassis dynamometer and modified for continuous use on engine stand
- Use 2 engines for 2 cold starts/day

Gasoline blended to 2002 U.S. national average regular unleaded

- No added oxygenates
- Reid vapor pressure =10.3 psia
- 275 ppm sulfur, 30% aromatics

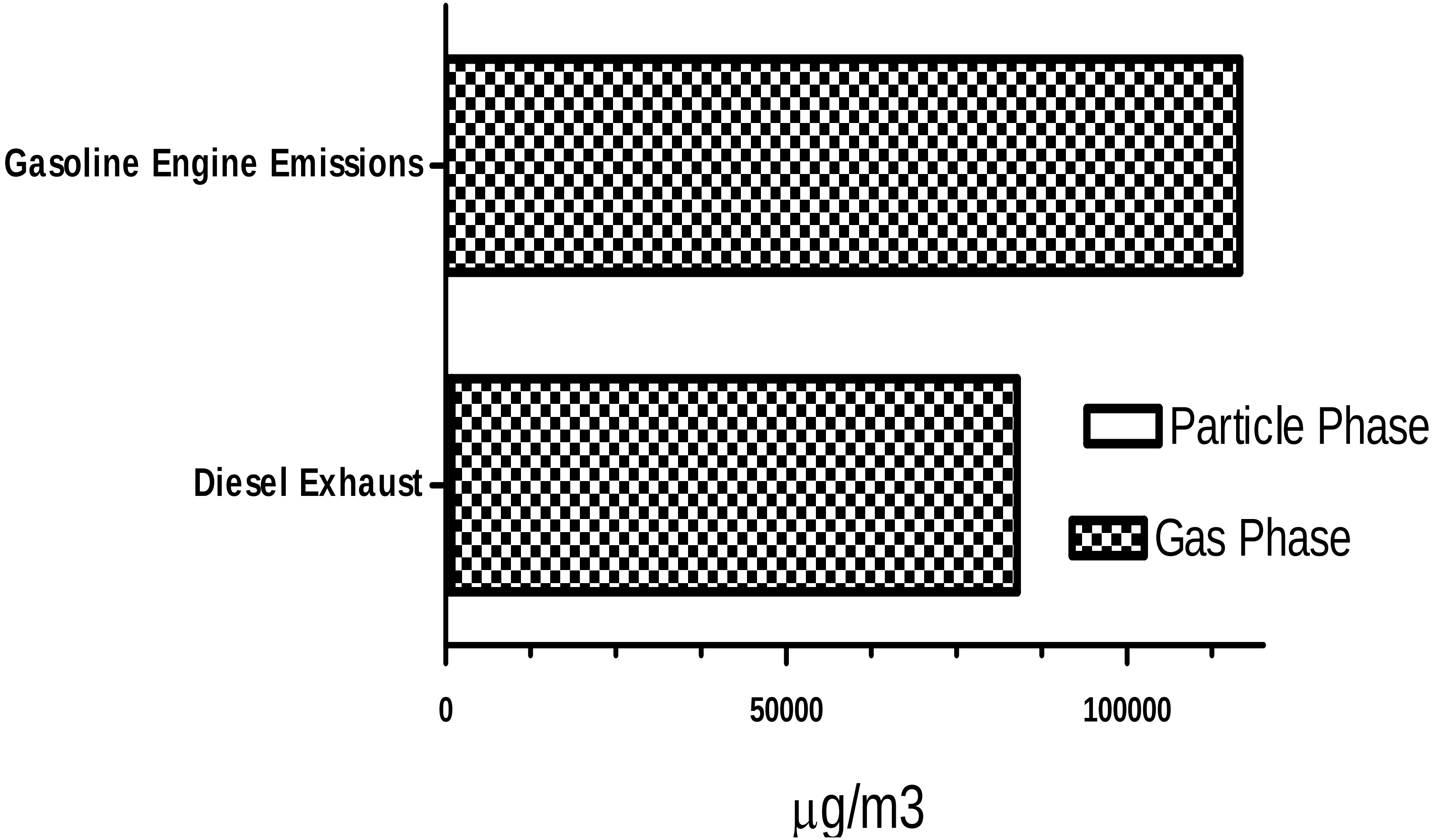
Pennzoil® multi-grade oil

AC Delco Duraguard® filters

Exposures at dilutions of ~12:1 (including filtered atmosphere at this dilution), 20:1, and 110:1

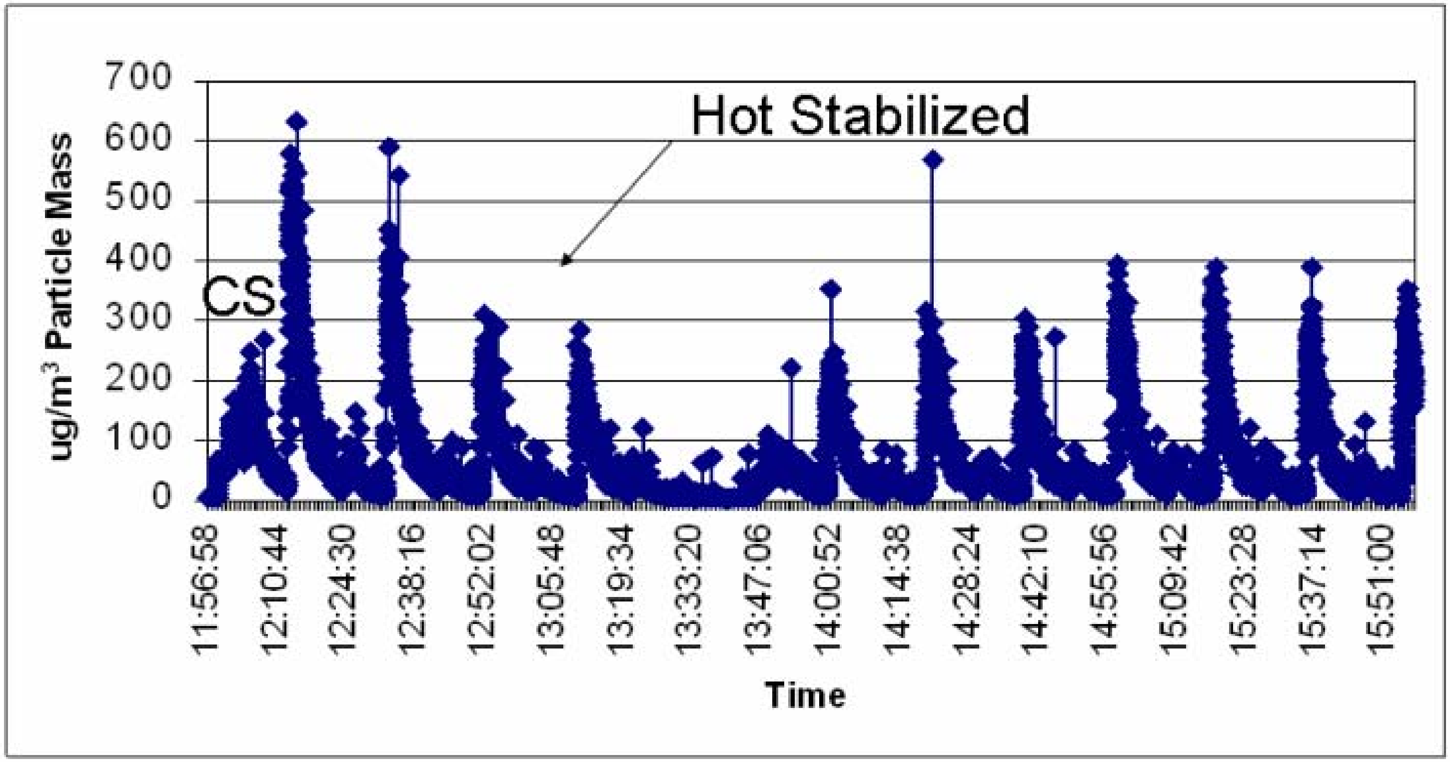
Exposure Atmospheres in Both Cases were Mostly Gases and Vapors

urban legends suggest otherwise



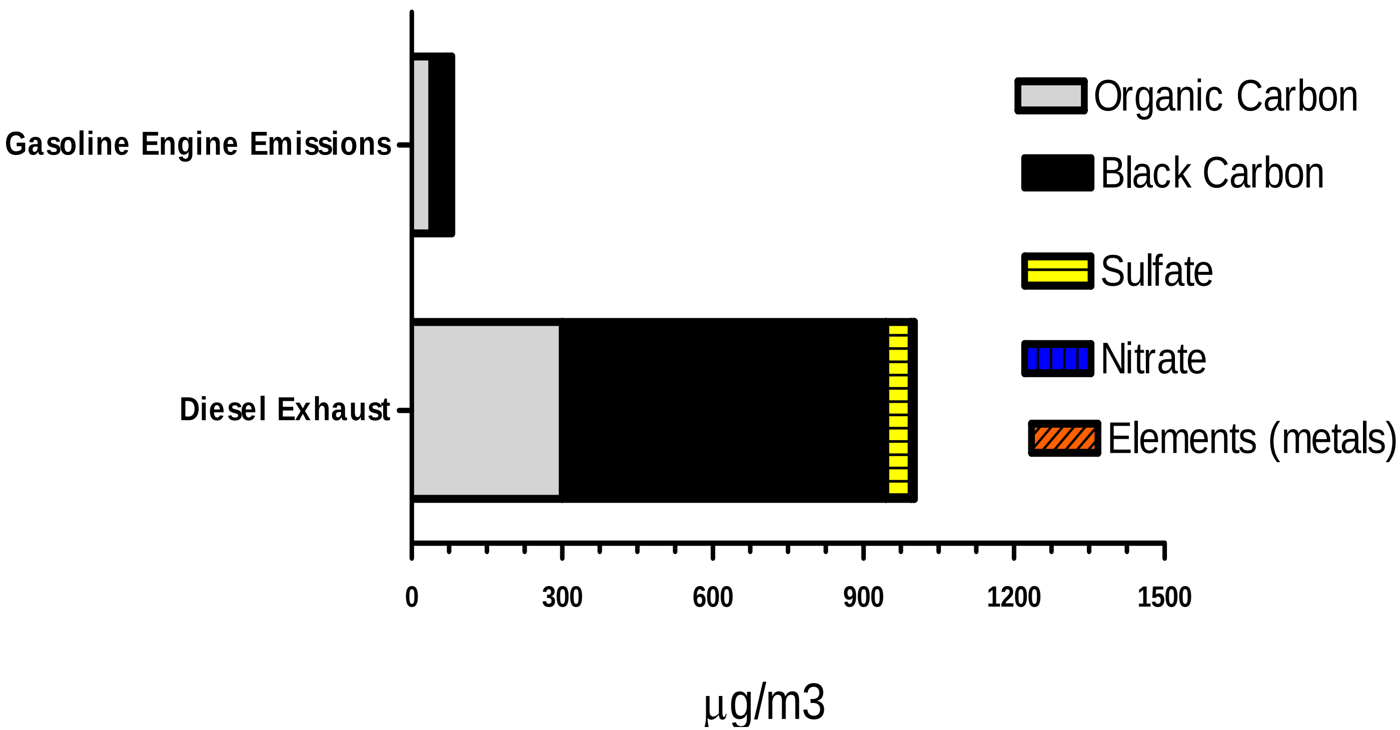
Yeah..Yeah.., but what did the particles look like?

Real-Time PM in High Level Gasoline Chamber



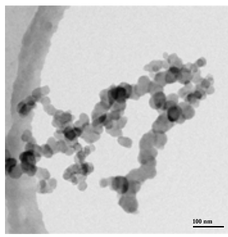
Note: Average PM emission rate (over 3 hours) = 5-10 mg/mile

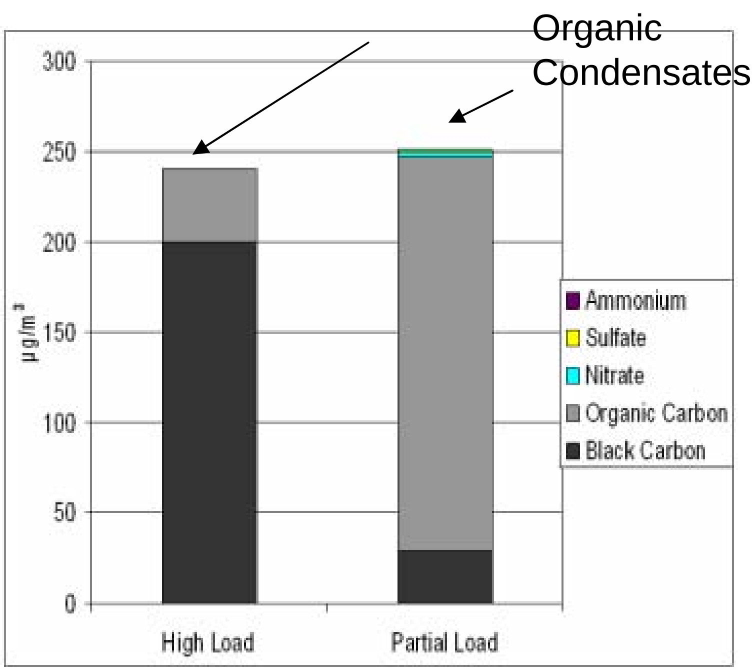
PM similar in Composition, but depends…

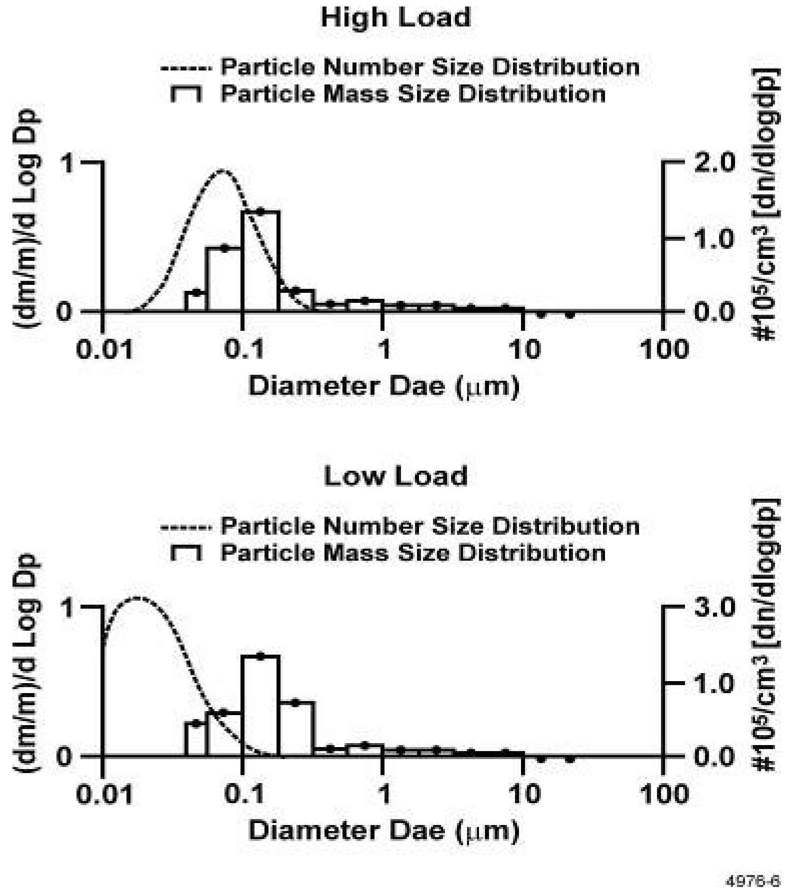


Comparative composition of <u>particulate fraction</u>

Diesel Exhaust:Particle Composition and Size with Engine Load

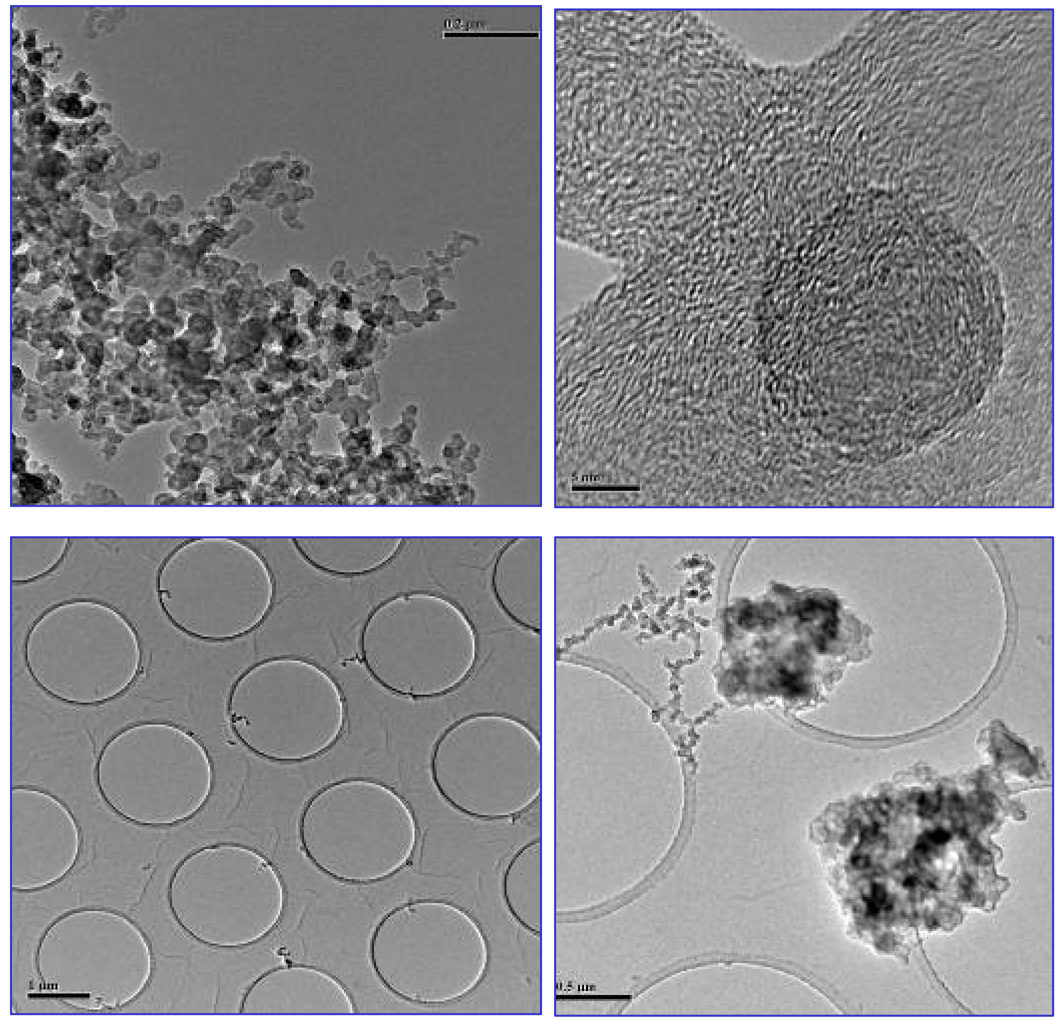




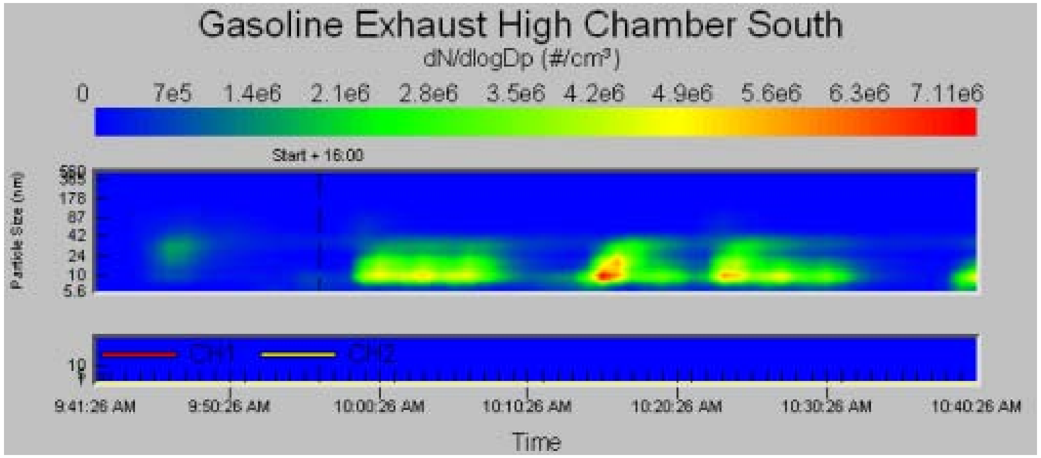


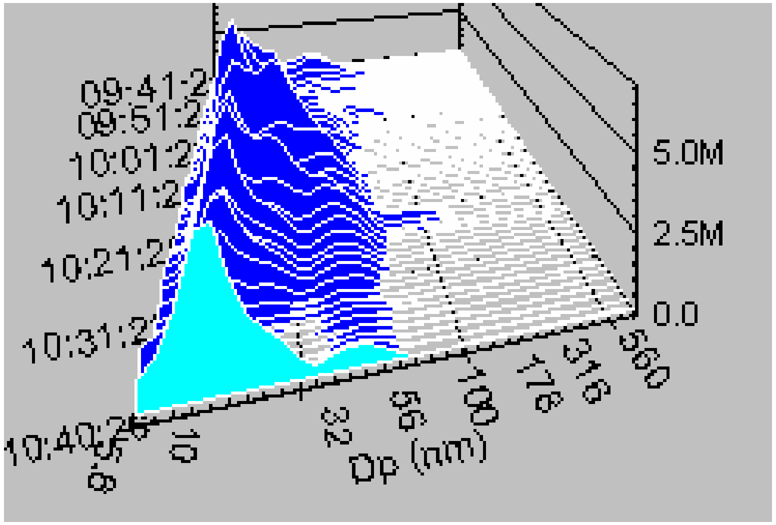
Particle Morphology

- Particle Morphology by EM only characterizes solid non-volatile PM.
- Non-volatile gasoline PM is nearly identical to diesel PM.
- Most particles (by number) can not be defined because they are semi-volatile amorphous liquids.



Particle Size and Number Analysis - Gasoline





Role of Volatile Particle Contribution to PM

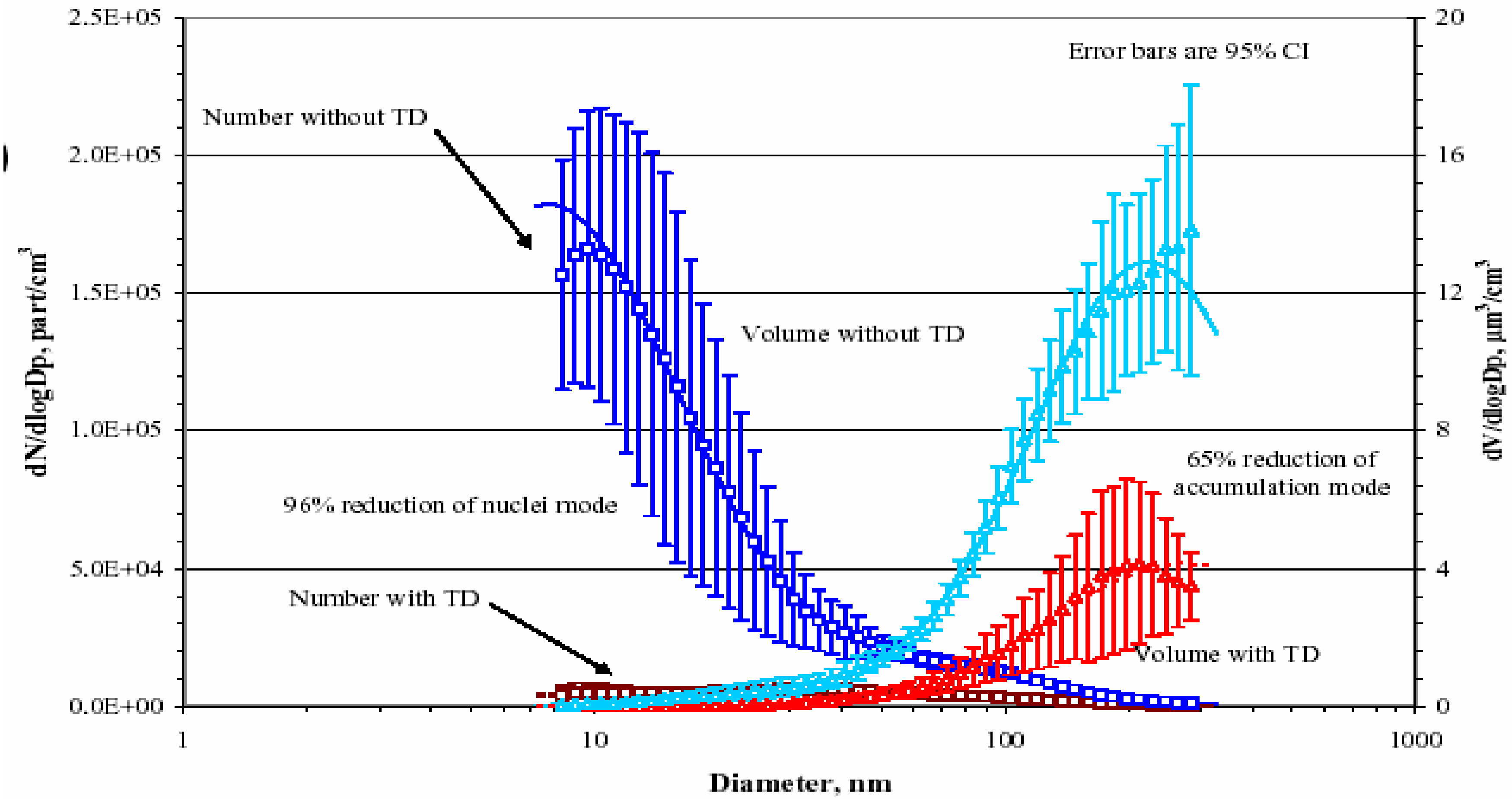
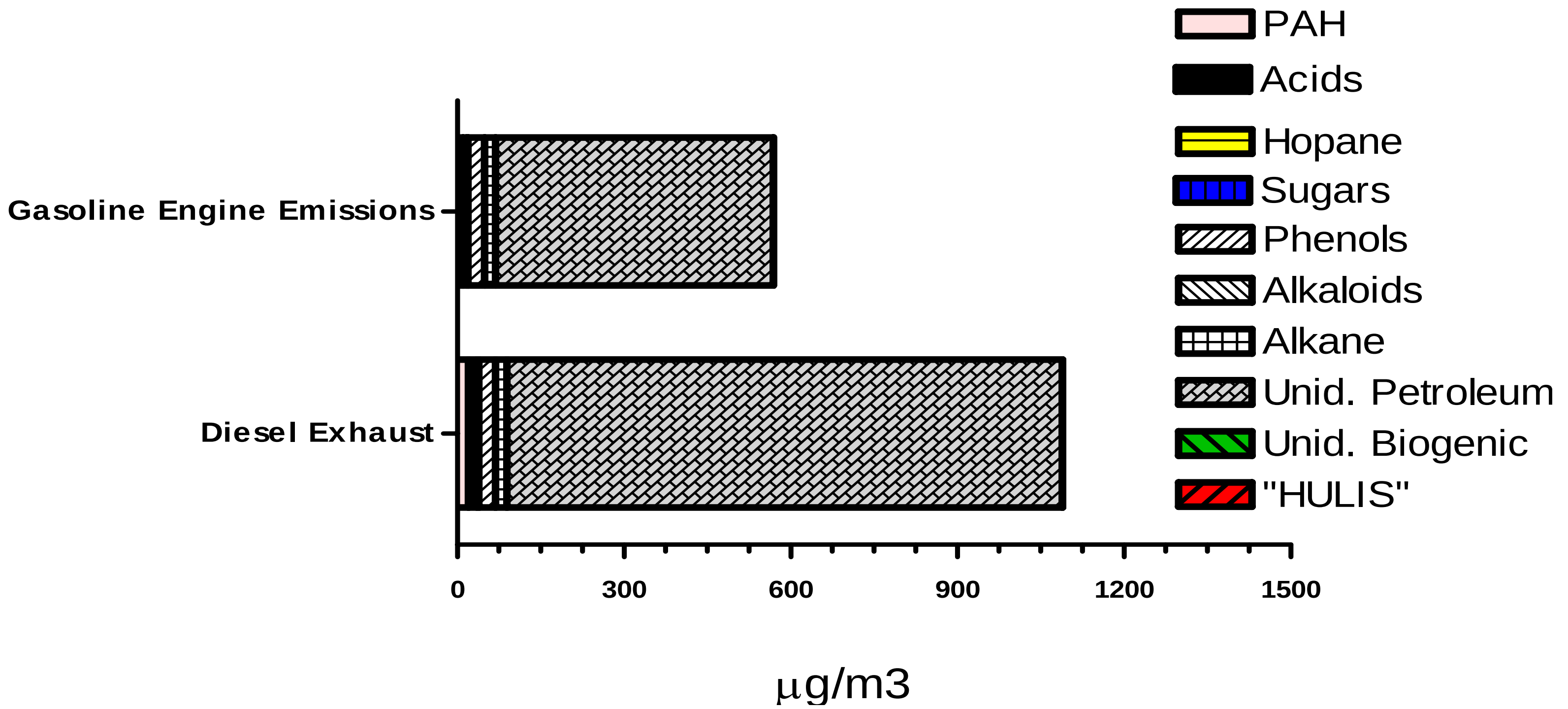


Figure obtained from D. Kittelson, U of Minn.

What the Heck is that Stuff?

Comparative composition of <u>organics in PM and vapor-phase SVOCs</u>



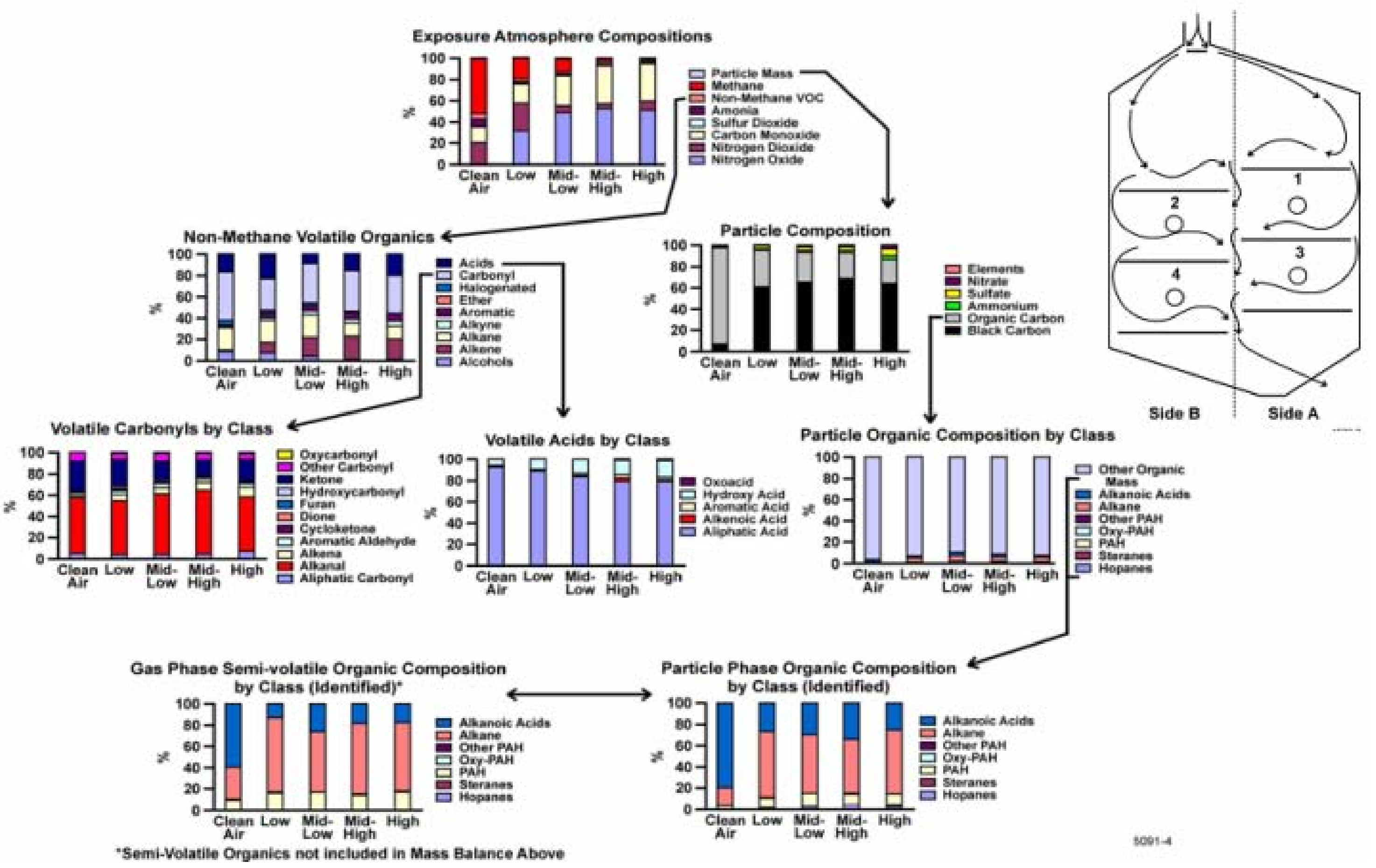
- **Unidentified organic mass predominates petroleum fuel emissions**

  Also large portion of biomass emissions
  Need to include this mass as a "class" in multivariate analyses

- **PAHs are very small portions of exposure mass**

  Effects would have to be strong to appear without adding atmospheres having larger mass portions – or many more atmospheres

Diesel Exhaust Atmosphere Composition

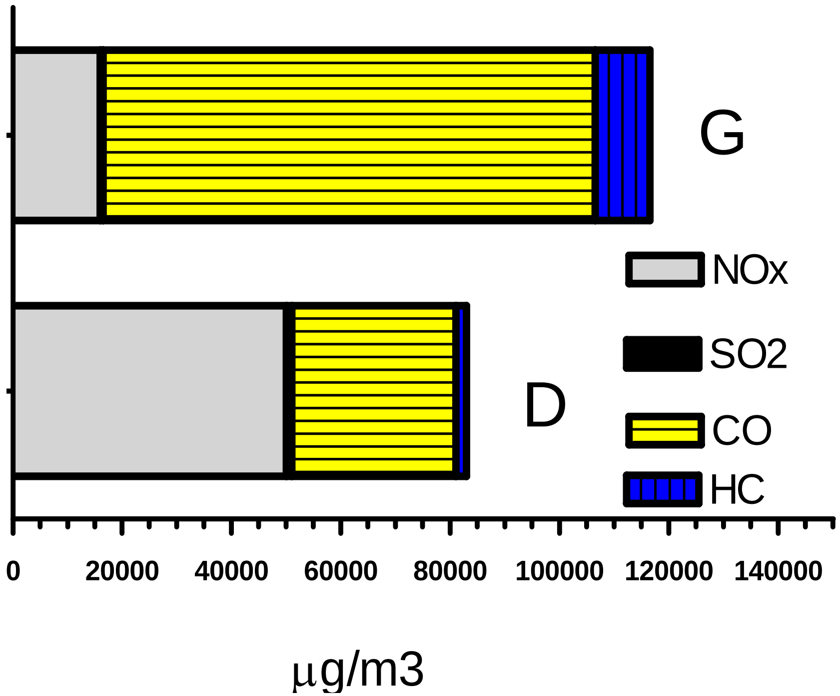


[McDonald et al., *Env. Sci. Technol*. 38: 2513, 2004]

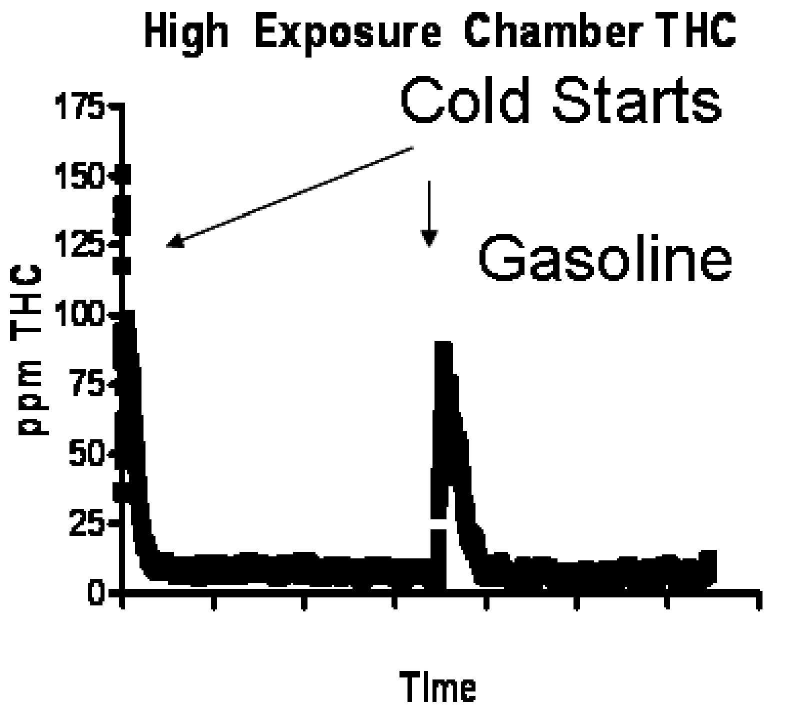
Conclusions Regarding Particles

- Diesel and gasoline exhaust atmospheres similar in phase (solid versus “liquid”), morphology, and total particle number (despite significant differences in mass).
- Another similarity is that we know little about the precise composition of the particle/semi-volatile phases (contrasts gas/vapor phase)
- The atmospheres in both cases vary greatly during the engine cycle, with significant proportions of particles in the nano-range that mimic other characterization data (on-road and laboratory).

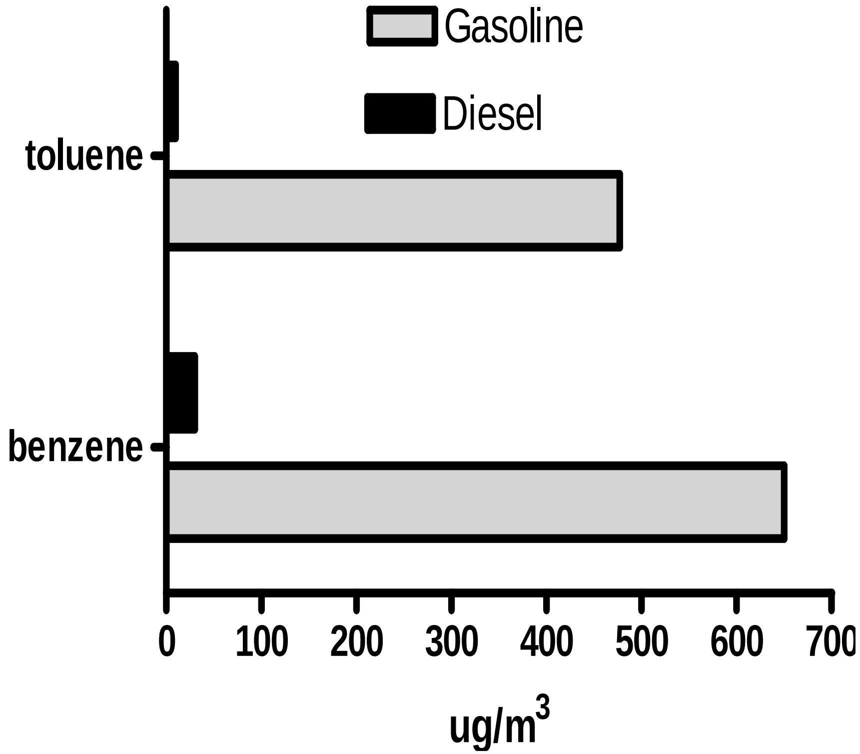
Back to the Majority of the Story



At similar dilutions, Gasoline had more “stuff” than Diesel

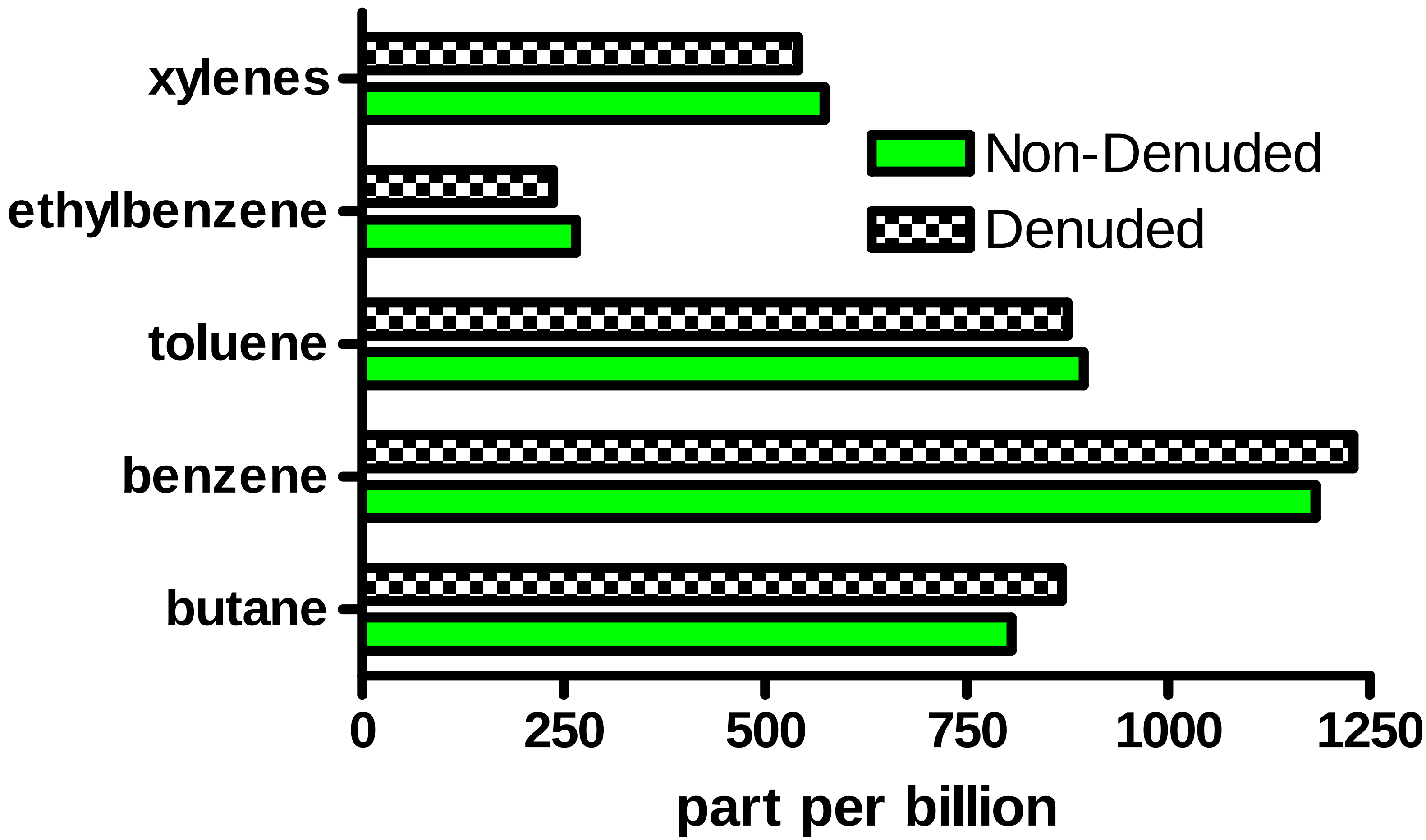


Comparison of Selected Aromatic VOCs (High Exposure Level)

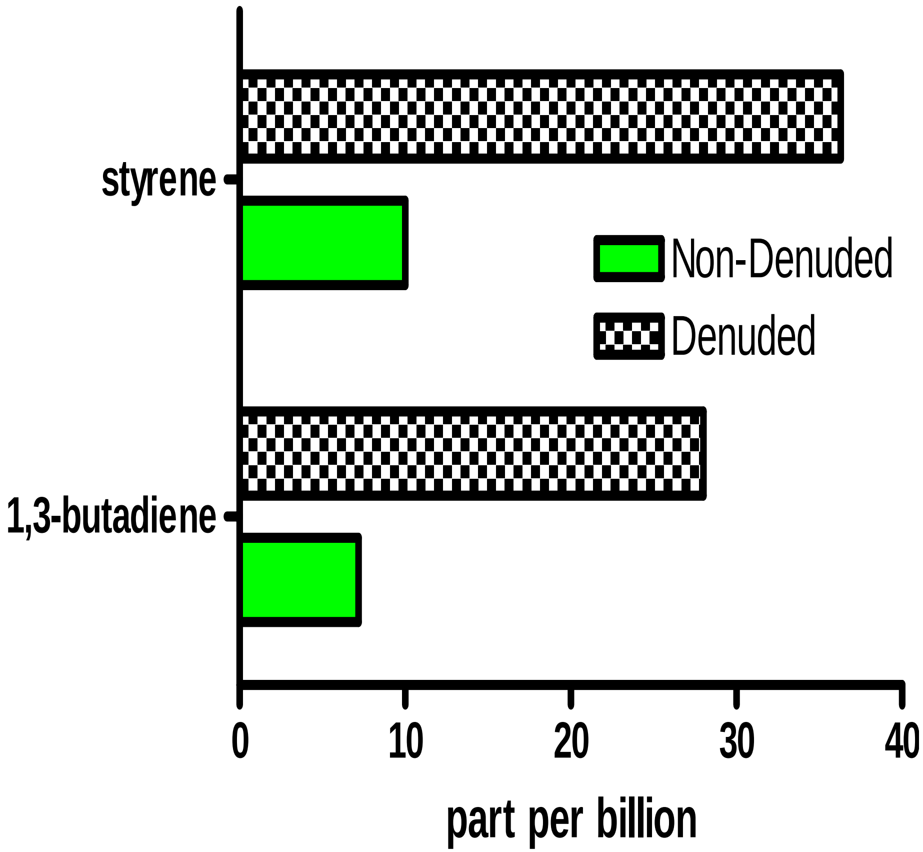


With the exception of select classes of organics, the gasoline atmosphere has much higher volatile organics, including “air toxics”

Newly-Developed DRI NOx Denuder-Canister Sampler Was Used to Test NOx-VOC Stability



Data on Reactive Compounds Measured in Exhaust Are Currently Underestimated



- New sampling technology has exposed an engine emissions sampling artifact

- Diesel 1,3-butadiene concentrations were likely underestimated due to NOx reactivity

Summary

- **Compared with Diesel, Gasoline had:**
  - **Higher “mass” exposures (if gas and particle phase are summed)**
  - **Lower particle mass exposures**
  - **Similar particle number and size**
- **Advances in measurement techniques enabled:**
  - **Measurement of reactive VOC with minimized artifact**

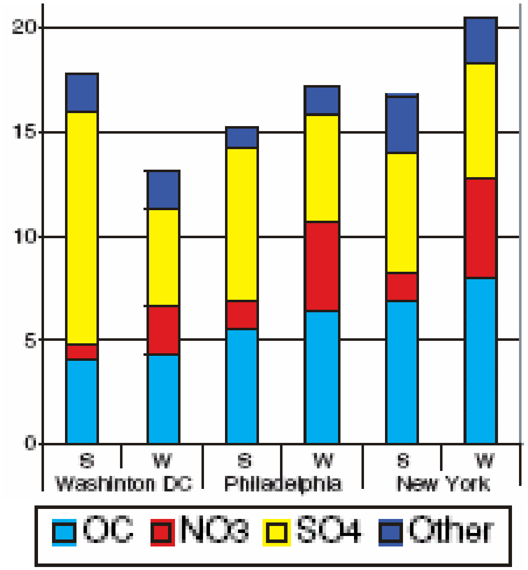
That Was Easy: Now How do We Extend These Comparisons to Health Data?

- Comparing health responses and defining risk gets a little more tricky….
- One goal may be comparative health response by head-to head exposures…jury still out.
- A “higher” goal is to define characteristics that do cause health effects
  - so we may potentially eliminate these through engineering

Often The "Higher Goals" Are Toughest To Achieve

Example: Contribution of sulfate to health effects of fine PM

- **Sulfate constitutes a substantial portion of fine PM mass in the eastern U.S.**
- **Mass-based standards presume that sulfate contributes a proportional share of health impact**
- **Because most sulfate is formed from SO_2, this health burden is charged to SO_2 sources, the largest of which is coal combustion**



However:

Information to date indicates that most sulfate has very low toxicity
(e.g., Grahame & Schlesinger, *Inhal. Toxicol.* 17:15, 2004)

Much less attention has been given to the organic fraction

HOW CAN WE IDENTFY CAUSAL POLLUTANTS ?

1. **Study every pollutant individually**

2. **Predict effects using structure-function models**

   We don't have structure-response or exposure-response data for many classes, and almost none for combinations

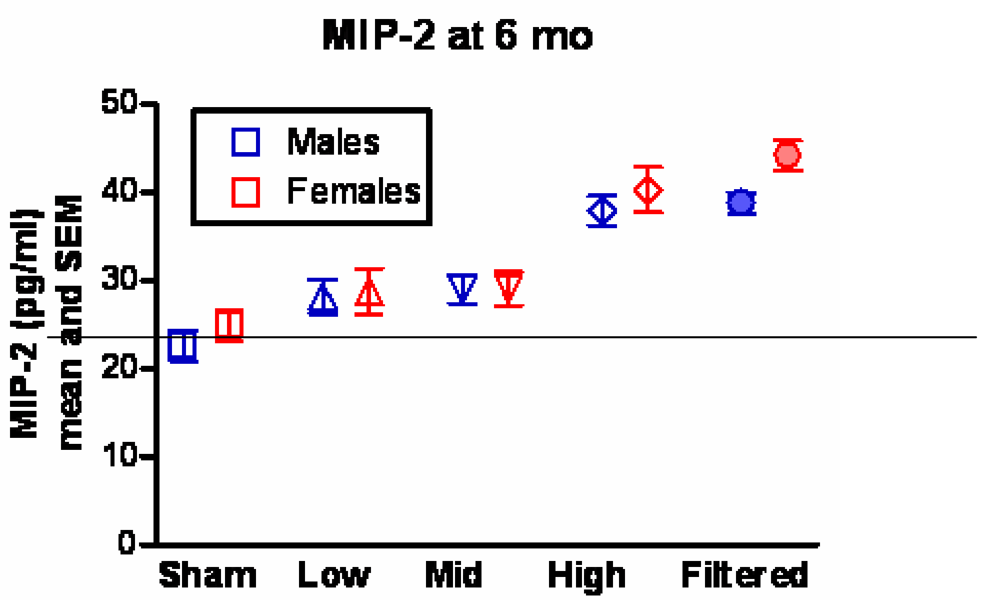
3. **Study combinations of selected species to test for interactions**

   More than 3 become intractable (A, B, C, A+B, A+C, B+C, control)

4. **Apply multivariate analysis to a database produced by identical studies of mixtures that vary in <u>composition</u> and <u>toxicity</u>**

   A plausible approach - <u>if</u> you have such a database

One Approach that Adds “Texture” to Those Types Of Data is to “Fractionate” Atmospheres



- **MIP-2 increase indicator of inflammation**
- **Filtered high dose ≈ high dose**

There was no change in MIP-2 for equal exposure time to Diesel Exhaust

Danger in Current Methods of Comparison

- Certainly PM does not look to be important for this response
- However, without that information we might be tempted to compare based on PM mass
  - Gasoline PM would be much more “toxic” per unit.
  - Particle number/morphology would not be important
  - We would all be mis-led……..

Acknowledgments

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NERC

NIEHS

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- Organic Analytical Lab-VOC
- Environmental Analysis Facility-Carbon/Ions

BP: Global Fuels Technology Group

- Donation of BP-15 fuel