ARB's Study of Emissions from "Late-model" Diesel and CNG Heavy-duty Transit Buses: *Toxic Compounds and PM Emissions*

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Briefing # 2 Content

RESULTS:

- Speciation of Gas-Phase Hydrocarbons
- Carbonyl Compounds
- Organic and Elemental Carbon and Elemental Composition of PM
- Phase distribution of PAH's
- Mutagenicity: Ames Bioassay Analysis
- *Emission Factors Summary Table*

Project Update

- *Majority of results already in …*

- Remaining PAH results expected early ‘02
- Remaining bioassay results expected early ’02
- ELPI results expected Dec ‘01

Test Fleet

	"CNG" "CNG re-test"	"Diesel (OEM)"	"CRT"
Model	2000 DDC Series 50G	1998 DDC Series 50	1998 DDC Series 50
Aftertreatment	None	OEM Catalyzed Muffler	CRT™
Fuel	CNG	ECD-1	ECD-1
Odometer	19,629	15,169	15,569
Weight	33,150 lbs	30,510	30,510

- Los Angeles County Metropolitan Transit Authority fleet
- 8.5 liter, 4-stroke, turbocharged, 4-cylinder, New Flyer Low 40 passenger transit buses

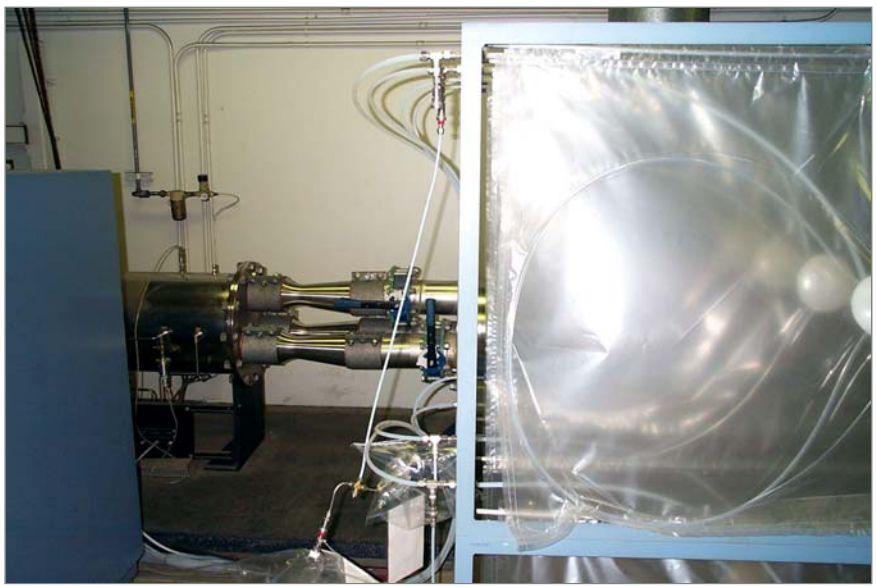
NOTE: CNG retest fuel sample below specification

Toxic Gas-Phase HC's - Sampling Methodology

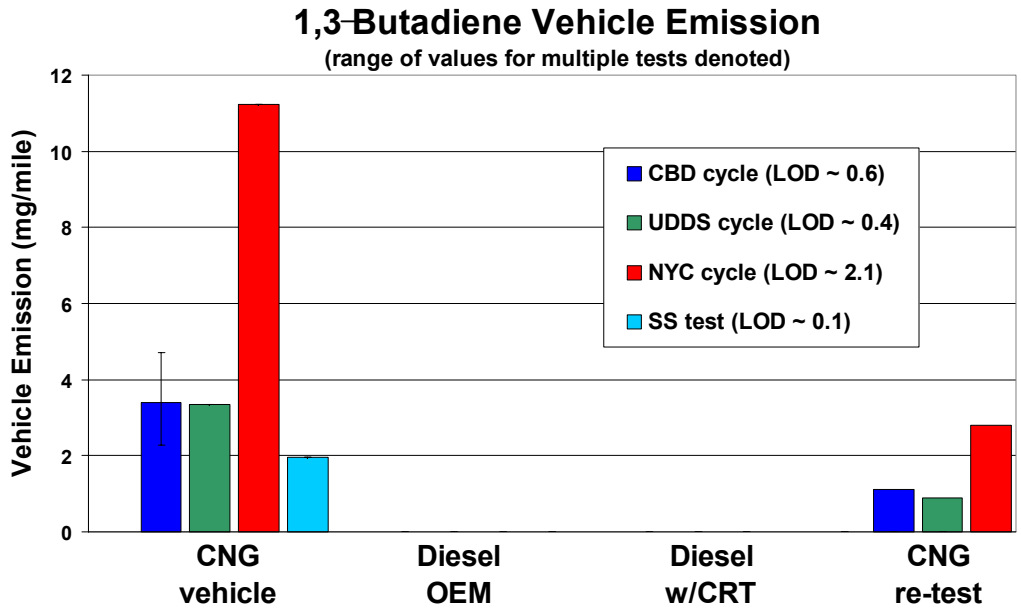
Target Analytes

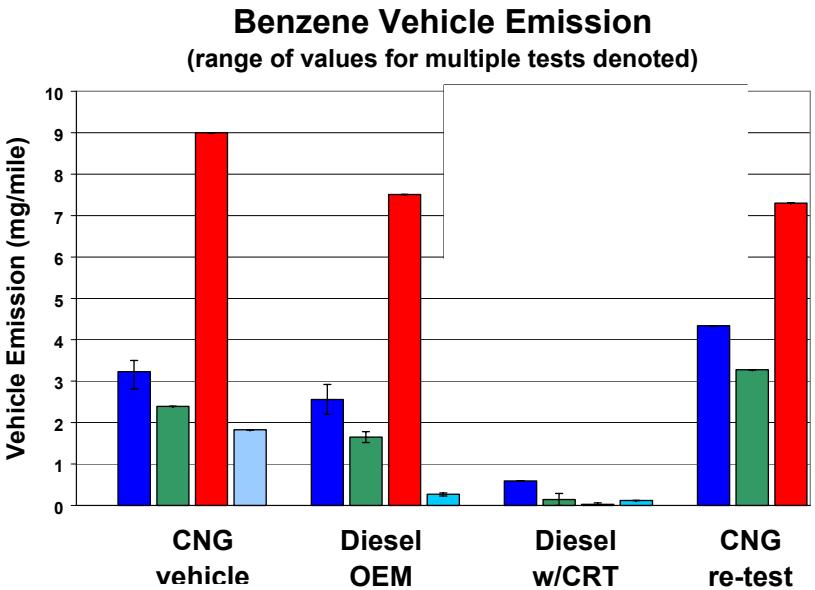
- 1,3-Butadiene
- Benzene
- Toluene
- Ethylbenzene
- m,p-xylene
- o-xylene
- Styrene

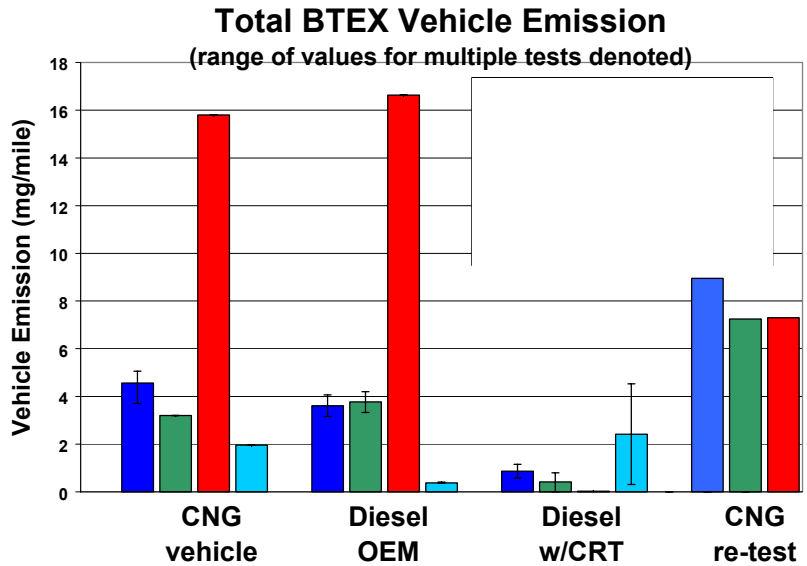
Tedlar Bag Collection



On-site GC-FID's


1,3-Butadiene Vehicle Emission
(range of values for multiple tests denoted)
Vehicle Emission (mg/mile)
0
2
4
6
8
10
12
CBD cycle (LOD ~ 0.6)
UDDS cycle (LOD ~ 0.4)
NYC cycle (LOD ~ 2.1)
SS test (LOD ~ 0.1)
CNG vehicle
Diesel OEM
Diesel w/CRT
CNG re-test


Benzene Vehicle Emission
(range of values for multiple tests denoted)
Vehicle Emission (mg/mile)
0
1
2
3
4
5
6
7
8
9
10
CNG vehicle
Diesel OEM
Diesel w/CRT
CNG re-test


Total BTEX Vehicle Emission
(range of values for multiple tests denoted)
Vehicle Emission (mg/mile)
0
2
4
6
8
10
12
14
16
18
CNG vehicle
Diesel OEM
Diesel w/CRT
CNG re-test

Carbonyl Compounds

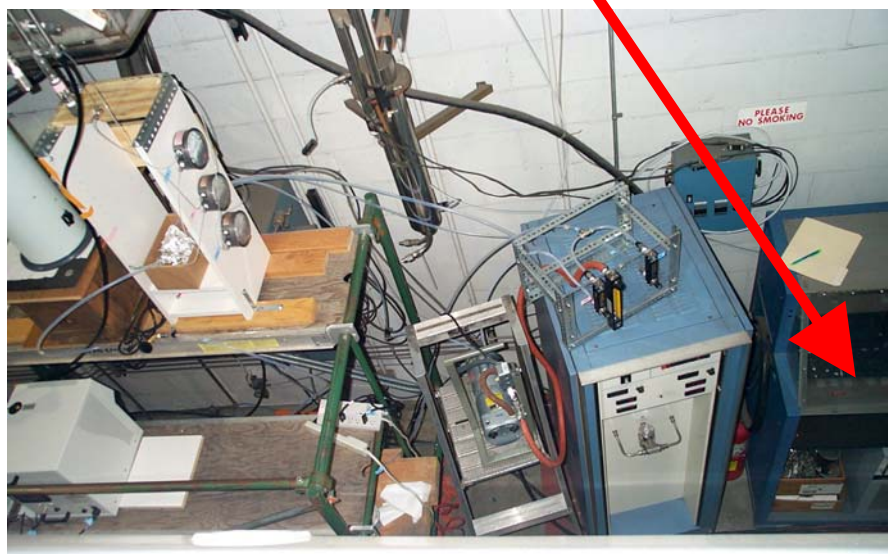
Sampling Methodology and Analysis

- Collection on DNPH cartridges
- High-precision Liquid Chromatography Analysis

Target Analytes

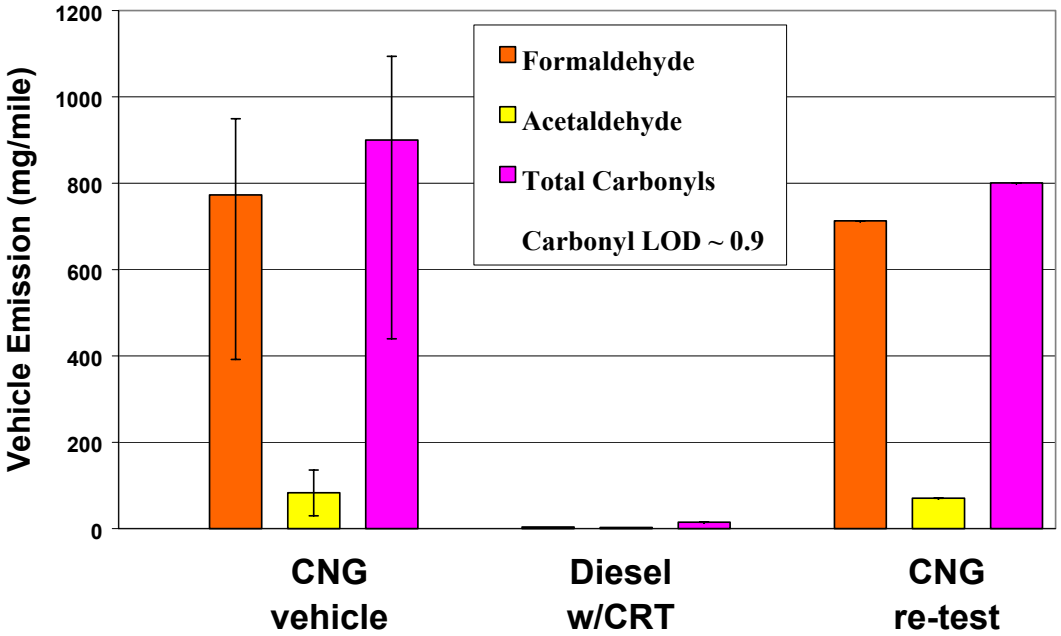
- Formaldehyde
- Acetone
- Propionaldehyde
- Methyl ethyl ketone
- Butyaldehyde
- Valeraldehyde
- Hexanal
- Acetaldehyde
- Acrolein
- Crotonaldehyde
- Methacrolein
- Benzaldehyde
- M-tolualdehyde

Aldehydes Bench



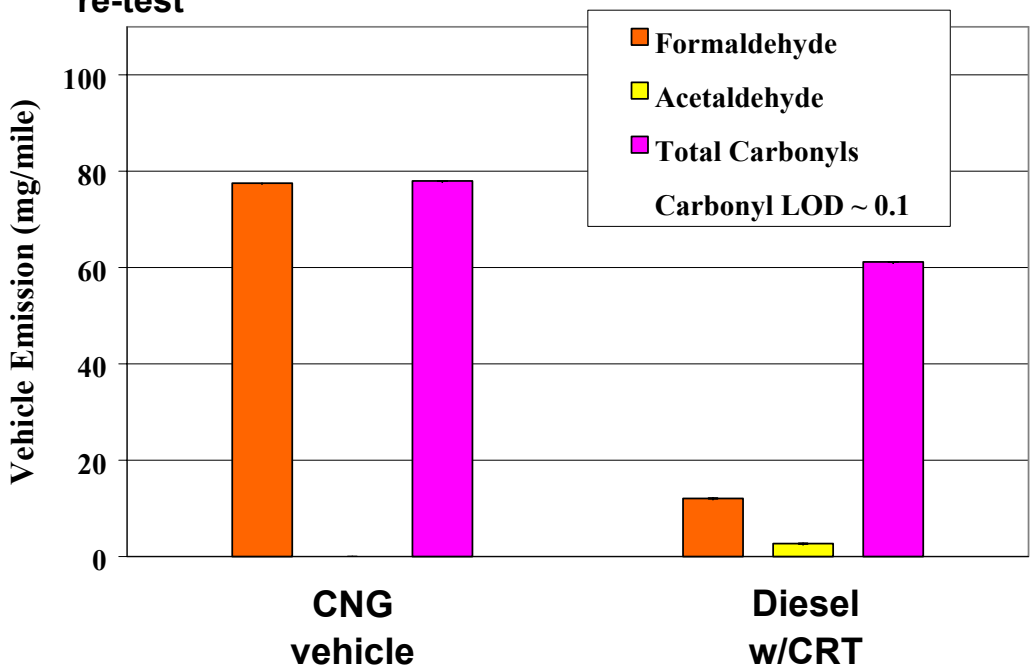
Carbonyl Emission for CBD Cycle

(range of values for multiple tests denoted)

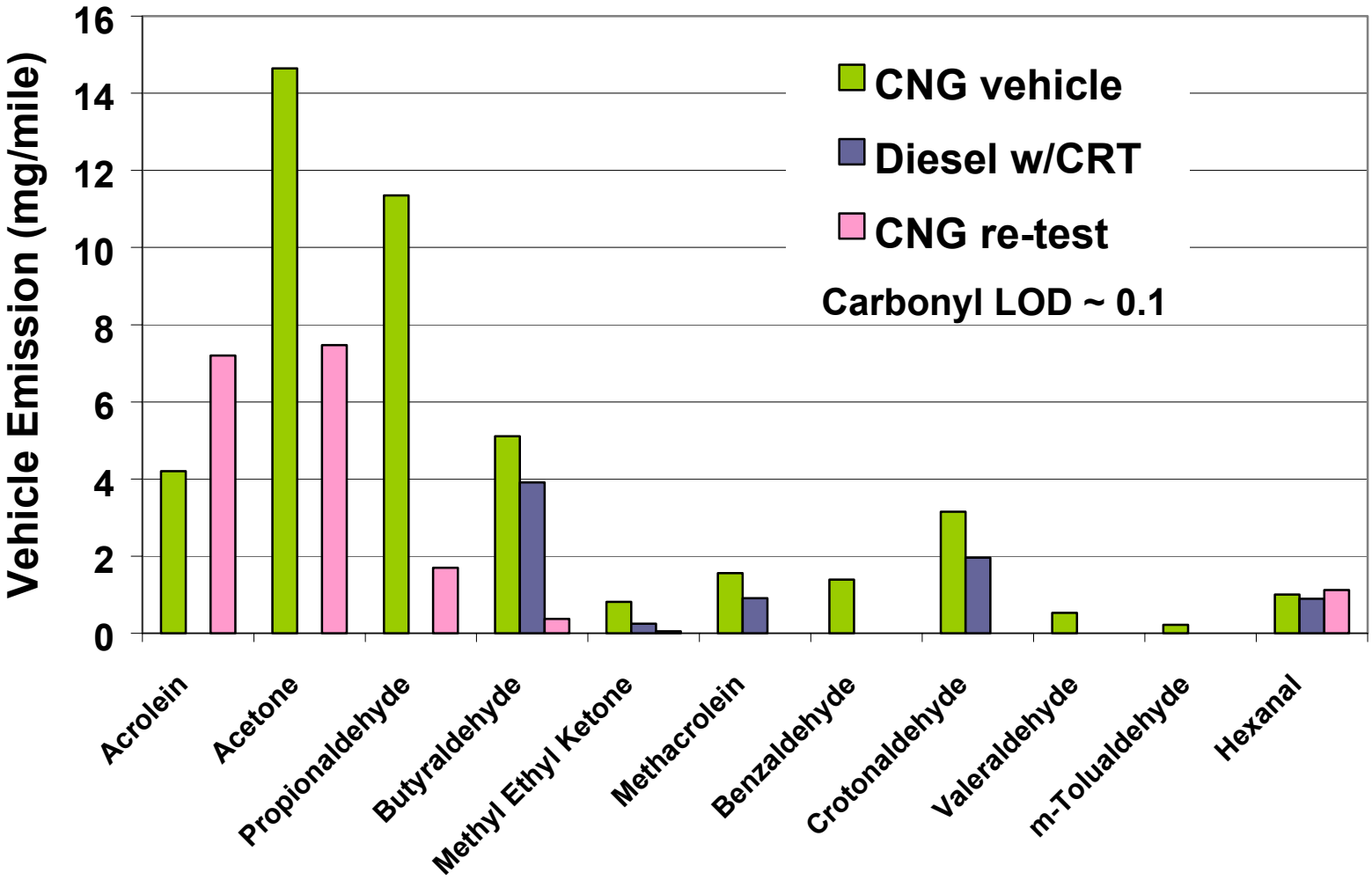


Carbonyl Emission for SS tests

(range of values for multiple tests denoted)



Additional Carbonyls for CBD Cycle



EC/OC and Elemental Analysis

EC/OC Procedure

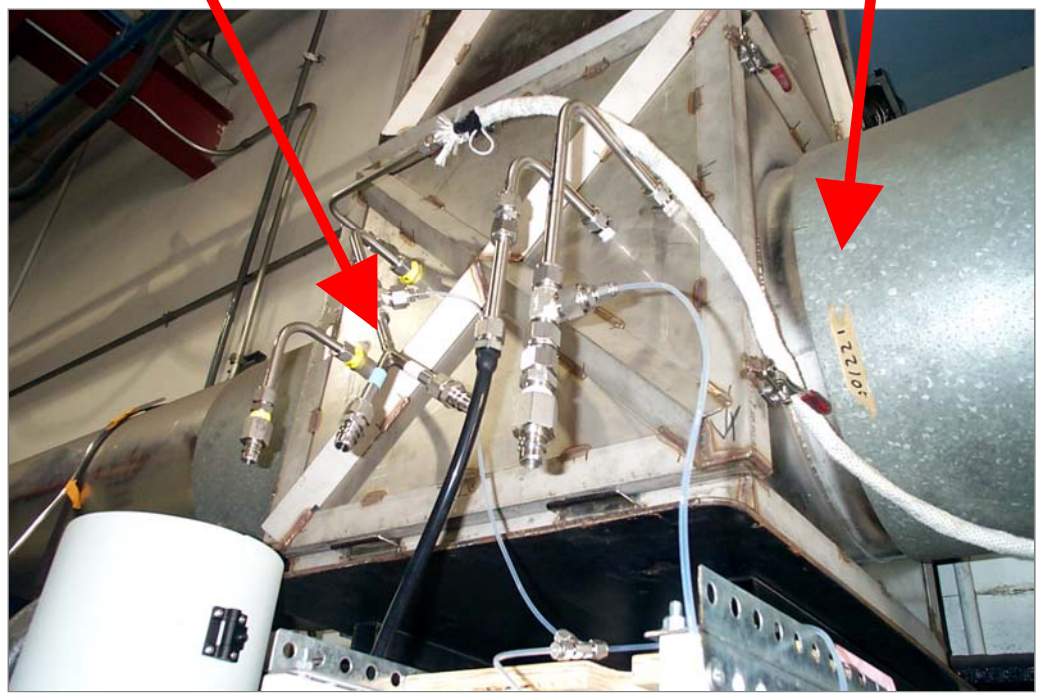
- Quartz-Filter Collection of PM
- DRI/IMPROVE Optical/Thermal Analysis

Elemental Analysis

- Teflon-Filter Collection of PM
- X-ray Fluorescence

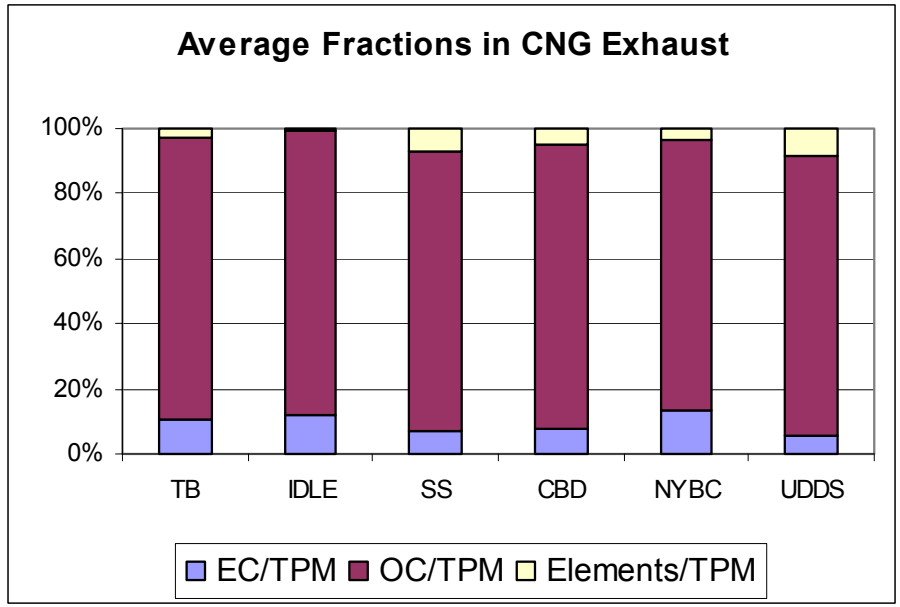
Primary Dilution Tunnel

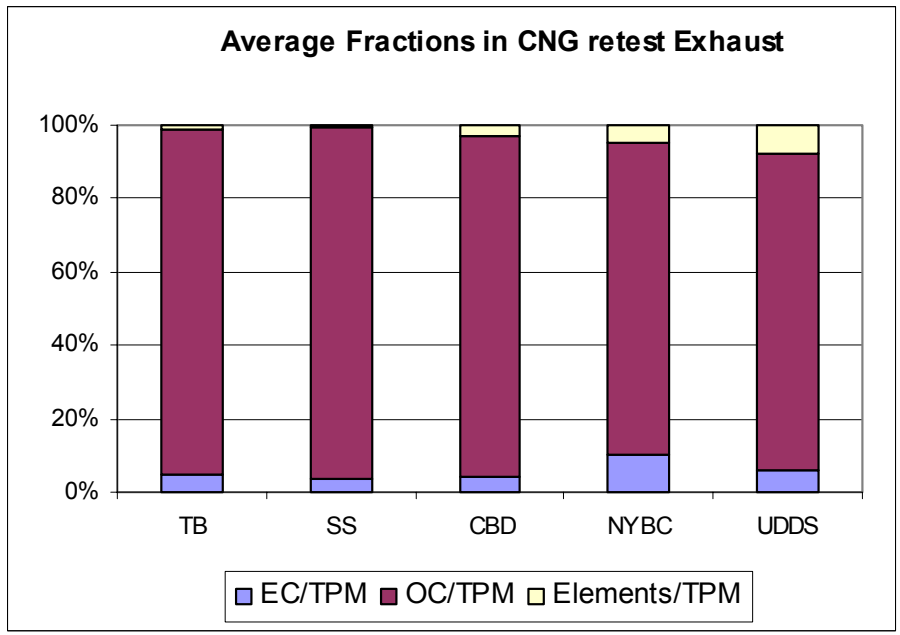
Sampling Probes



Average Composition of PM

- OC dominates CNG PM composition across all cycles
- Similar tunnel blank composition



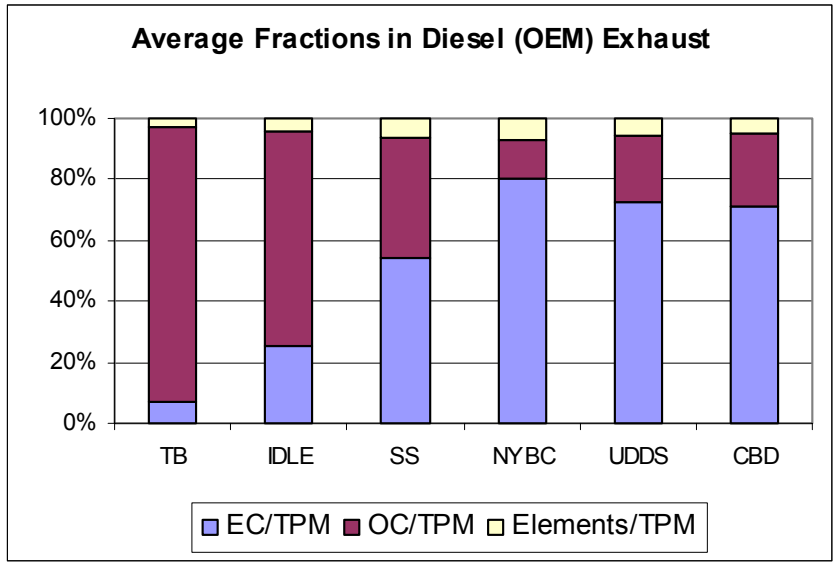


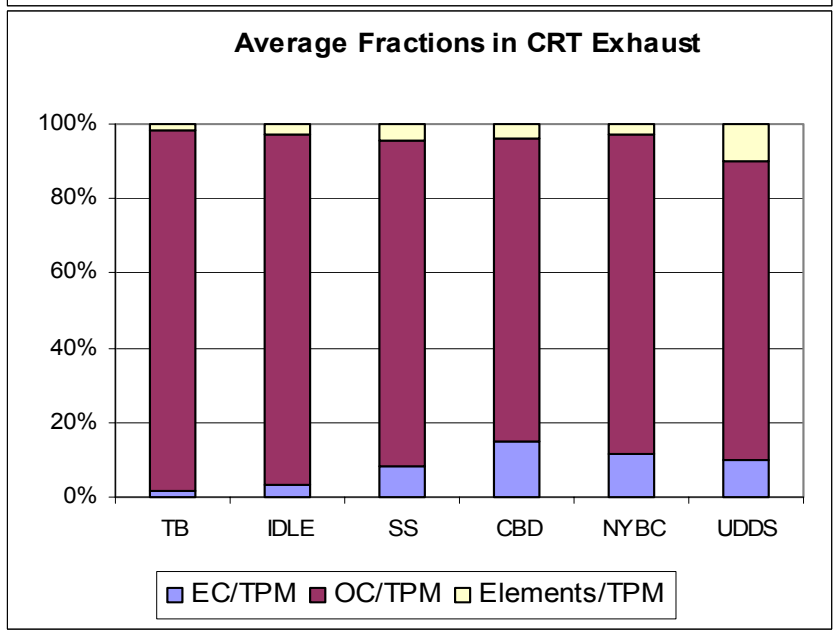
NOTE: TPM=Total PM= EC+OC+Elements

Average Composition of PM (cont'd)

- EC/OC fraction in Diesel (OEM) PM shows strong cycle dependence
- OC dominates CRT PM composition across all cycles

NOTE: TPM=Total PM= EC+OC+Elements



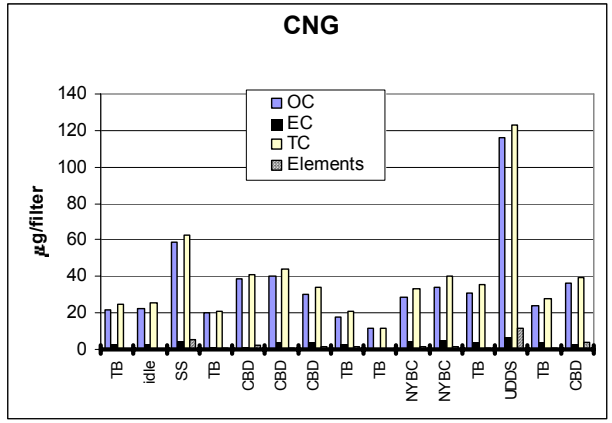


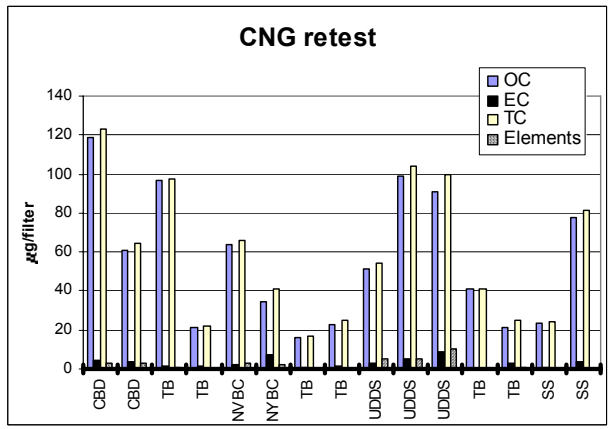
EC/OC/Elements-Total Emissions

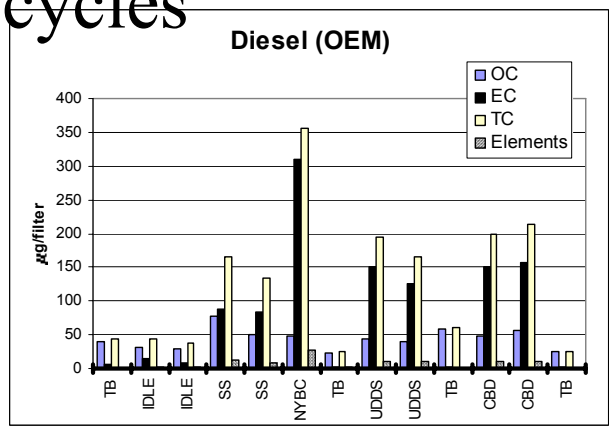
- EC/OC/Elements fractions show cycle dependence and variability
- In general, emissions:

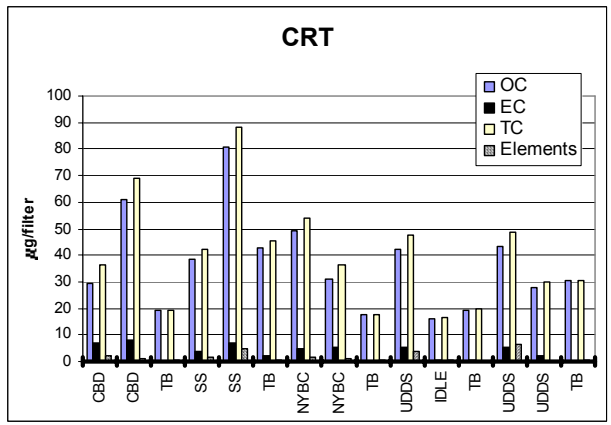
Diesel (OEM) > CNG > CRT

TB ~ Idle < other cycles







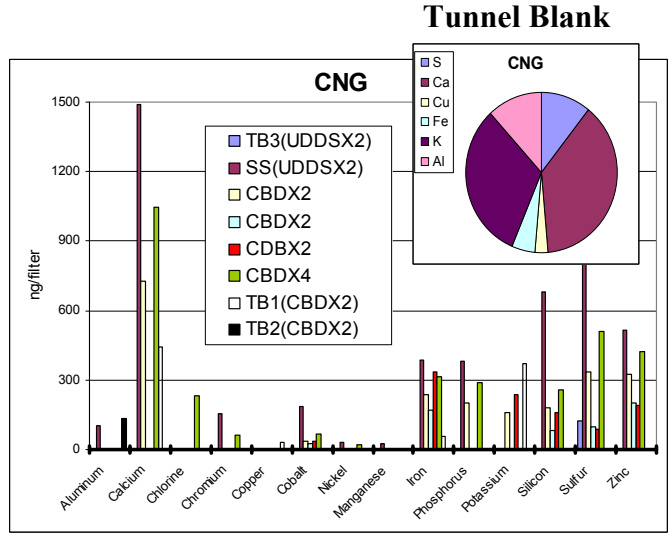


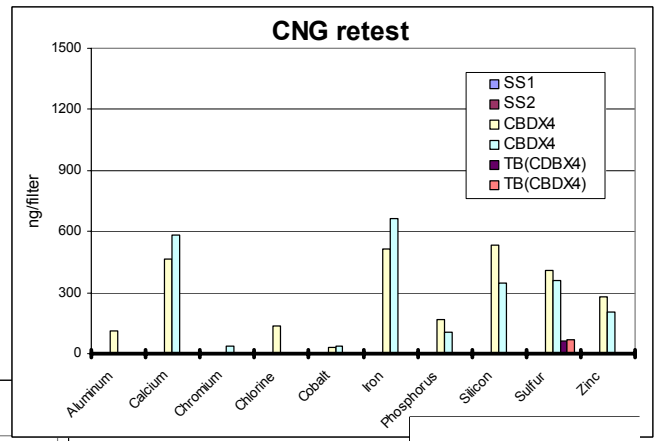
NOTE: Cumulative results per test sequence, not per cycle

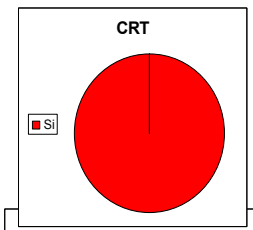
Elemental Analysis Results

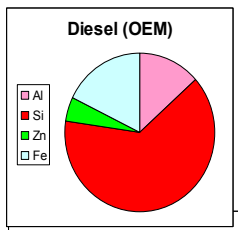
- Ca, Cl, P, Zn, S are oil components
- Fe from engine wear
- Si source unknown
- Si emissions: Diesel (OEM) >> CNG ~ CRT
- In general, TB << SS and CBD

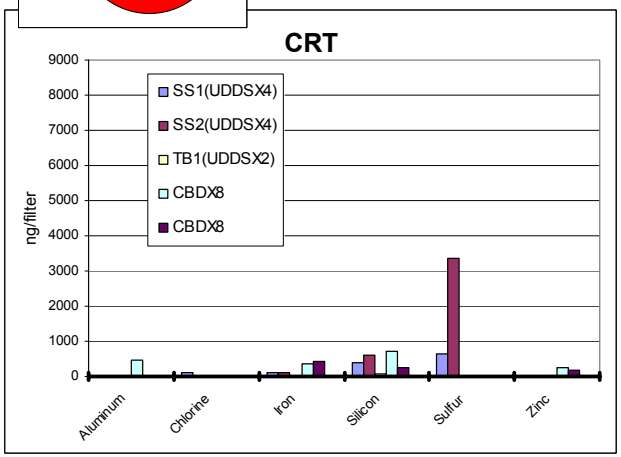
NOTE: Cumulative results per test sequence, not per cycle

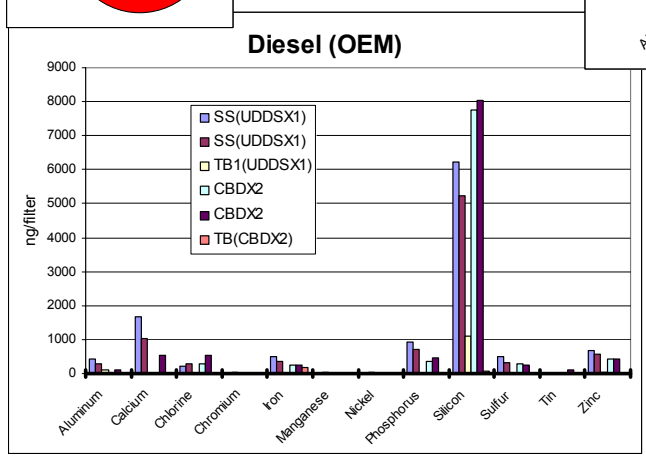






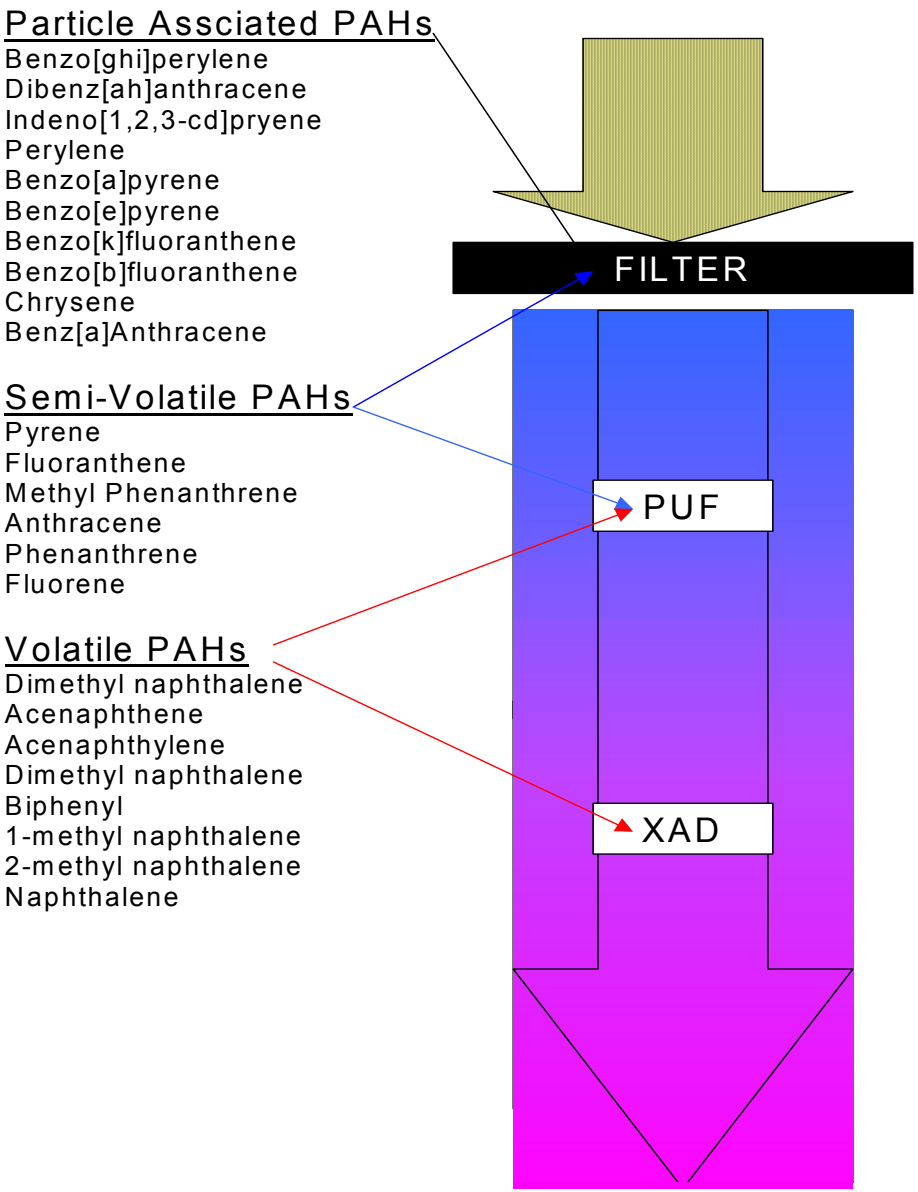






Polycyclic Aromatic Hydrocarbons

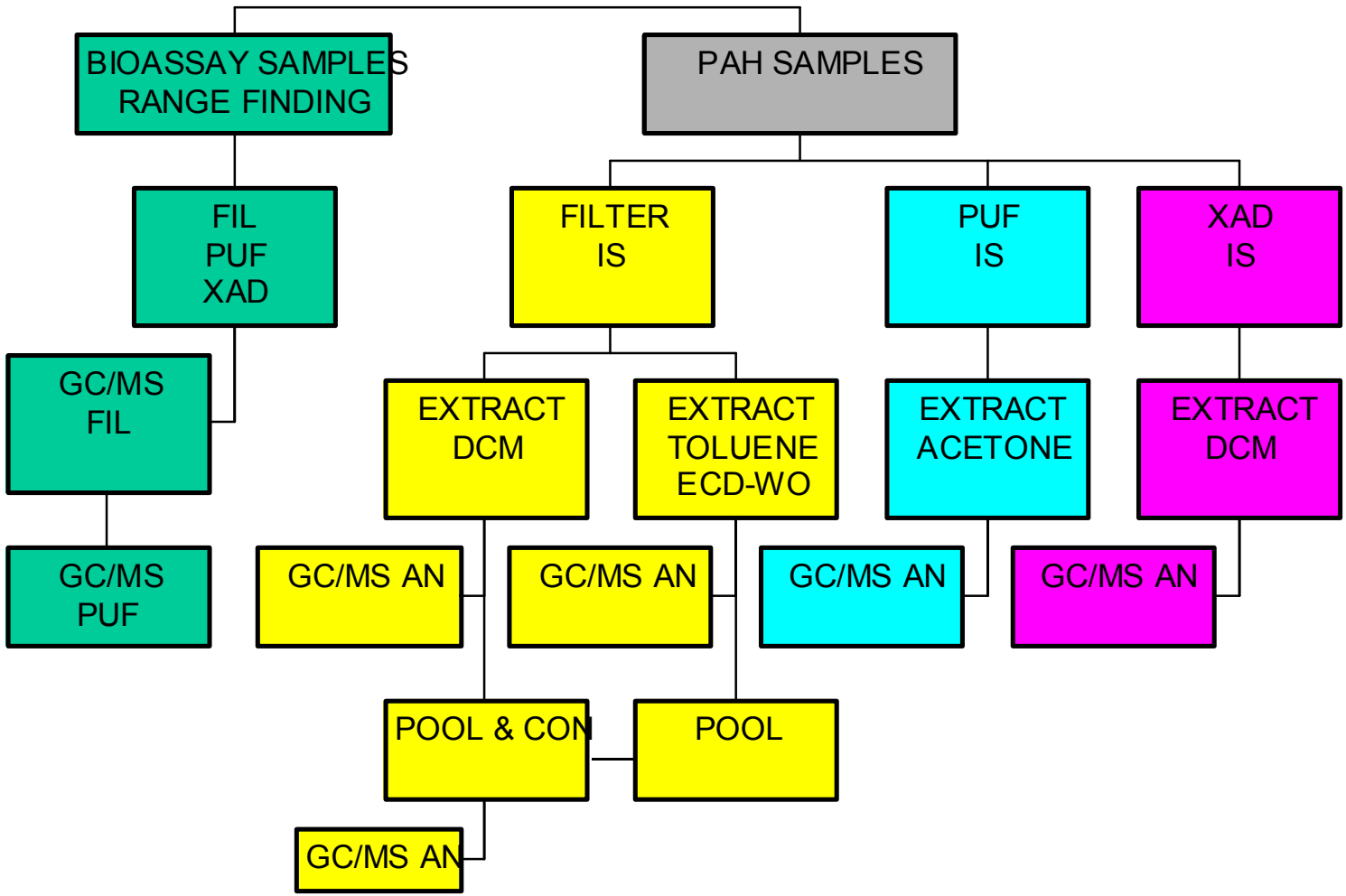
TARGET PAHS



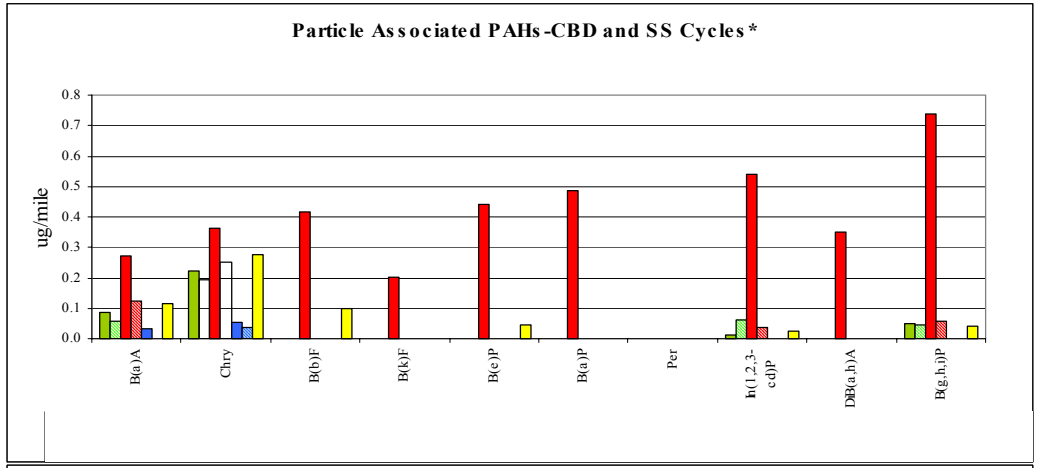
Particle Associated PAH's	OEHHA Unit risk for cancer by inhalation per million (ug/m3)E-1
Benz[a]anthracene	
Chrysene	**11**
Benzo[b]fluoranthene	**110**
Benzo[k]fluoranthene	**110**
Benzo[a]pyrene	**1100**
Dibenz[ah]anthracene	**1200**

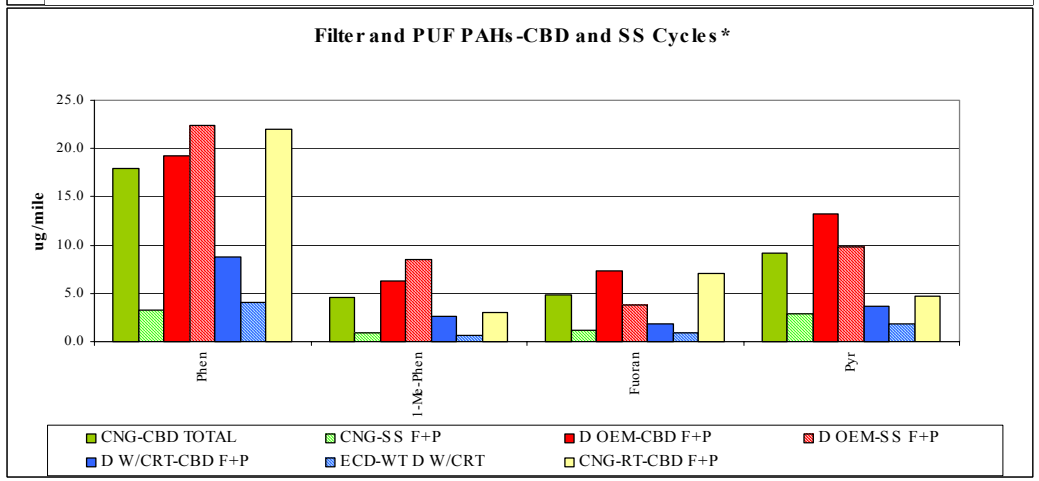
Expected PAH phase distribution in ambient and CARB diesel exhaust samples

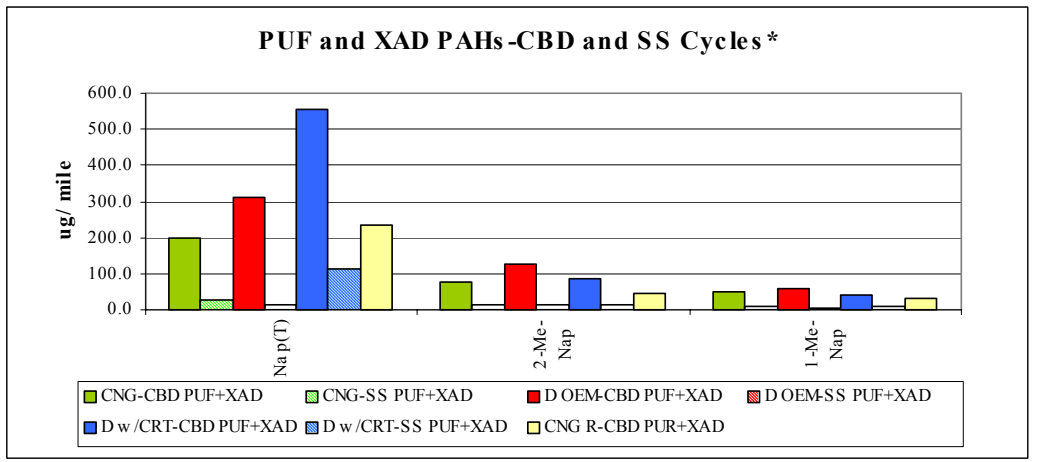
PAH ANALYSIS



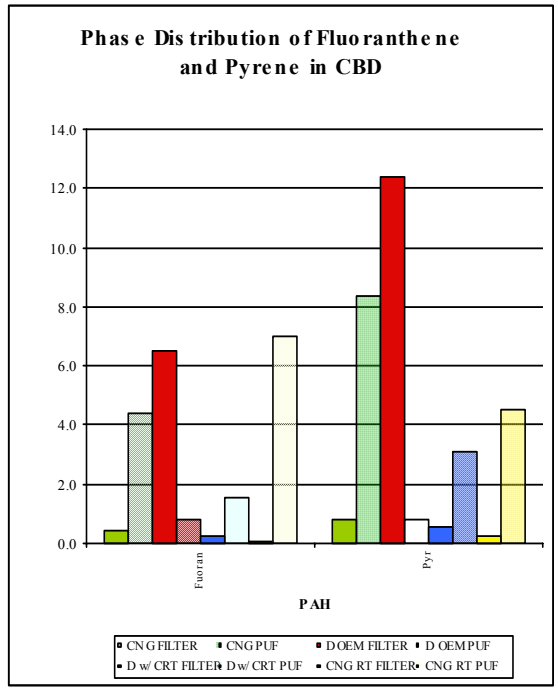
*All results not corrected for tunnel blanks and XAD values corrected for background contamination

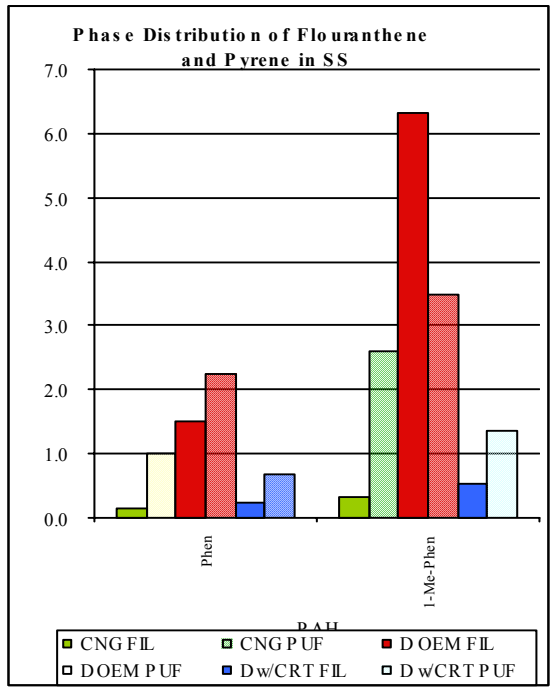






- **CBD and SS Results PAHs in PM**
  - –Diesel (OEM)-Most PAHs Detected
  - –CNG CBD - Most PAHs m.w. 252 Not Detected except for BaP
  - –CNG SS- All PAHs m.w. 252 Not Detected
  - –CRT- CBD and SS Only Benz[a]anthrancene and Chrysene Detected
- **CBD and SS Semi-volatile PAHs**
  - –Diesel (OEM) Generally the Highest Levels
  - –CNG Similar Levels to Diesel OEM
  - –CRT Lowest Levels
- **CBD and SS Volatile PAHs**
  - –At Similar Levels
- **Fluoranthene and Pyrene Phase Distribution**
  - –CBD Diesel(OEM)-Primarily in Filter
  - –SS Distributed more evenly between the Filter and PUF
  - –CRT and CNG-Primarily in PUF

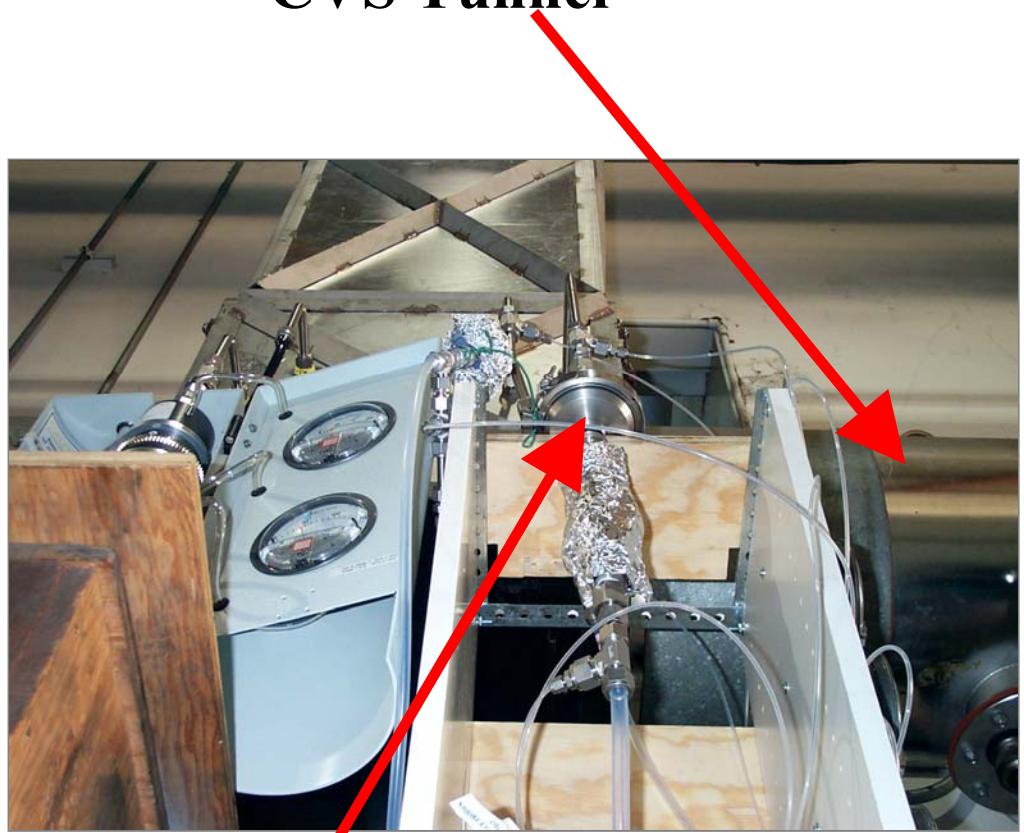




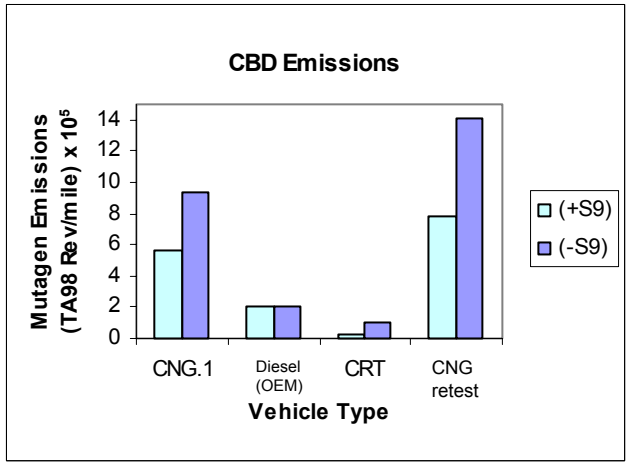
Bioassay Analysis

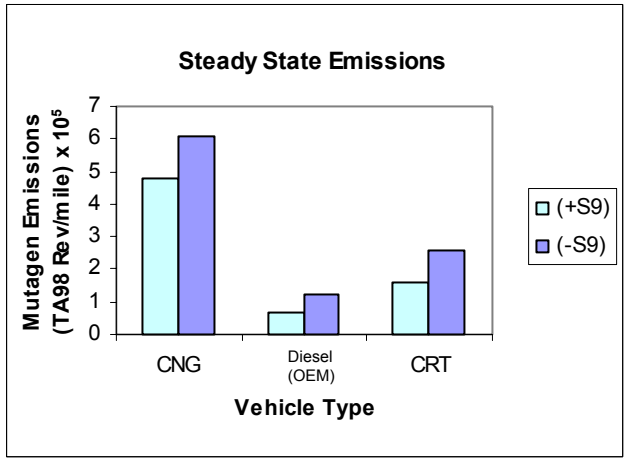
Procedure

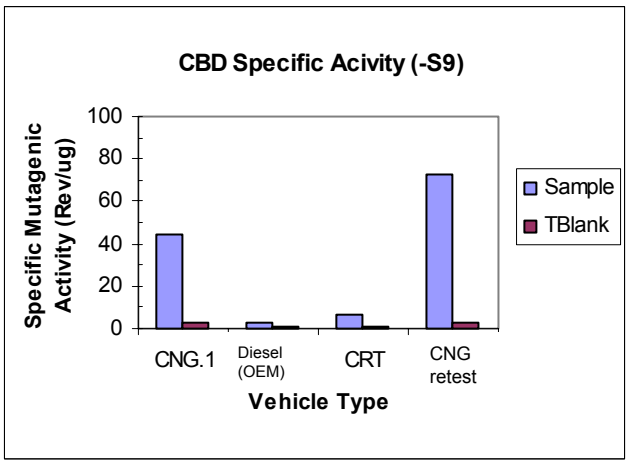
- Collection of PM on Filter
- Collection of vapor-phase on PUF
- Solvent Extraction
- Salmonella/Microsuspension procedure
- TA98 and TA 100 Tester Strains with and w/o +S9 Metabolic Enzymes

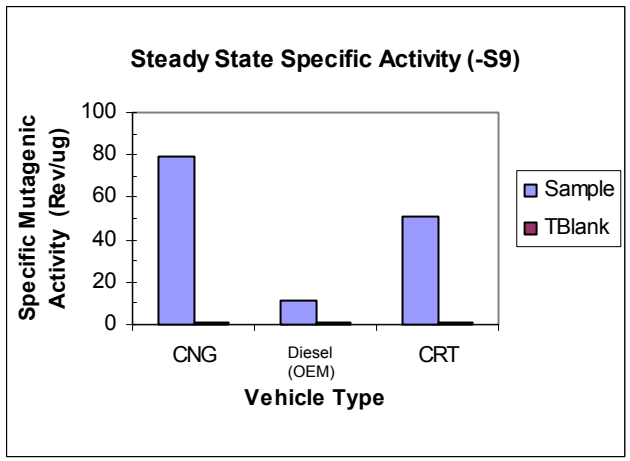


Mutagenicity Results









Emission Factor Summary

CBD				
	CNG emission rate mg/mi	**CRT** emission rate mg/mi	**Diesel(OEM)** emission rate mg/mi	OEHHA Unit risk for cancer by inhalation per million (ug/m3)E-1
Total PM	40.0	14.0	119.0	**300***
Butadiene	3.5	0.0	0.0	**170**
Benzene	3.2	0.6	1.6	**29**
Formaldehyde	780.0	0.0	**	**6**
Acetaldehyde	90.0	0.0	**	**2.7**
Total PAH's	0.58	0.78	0.80	
heavy	0.0004	0.0001	0.0038	
semi-vol	0.04	0.02	0.05	
volatile	0.54	0.77	0.75	
B[a]a	9.0E-05	4.0E-05	2.7E-04	**110**
Chr	2.3E-04	5.0E-05	3.7E-04	**11**
B[b]f	0	0	4.1E-04	**110**
B[k]f	0	0	2.0E-04	**110**
B[a]p	***	***	4.5E-04	**1100**
Dib[ah]a	0	0	3.5E-04	**1200**
Spec.Mut. Activity** ((TA98 Rev/mi)X10E5)	**9.6/6**	**1/2.5**	**2/1.2**	

* For diesel total PM only from ARB TAC document

** Data not available

*** Emission factor under development

****CBD/Steady State

Challenges

- **Test Low-emission Technologies: CNG and CRT**
  - Current methodologies needed improvement or required modification
- **Emissions Testing**
  - Large Test Matrix
  - Extremely low levels of PM requiring large number of samples to be collected
  - Interferences from the Tunnel Background
- **Analytical**
  - Low levels of PM and gaseous emissions require lower detection limits
- **Logistics**
  - Short Turn-Around Time
  - Limited Resources

Meeting the Challenge

- **Developed ARB in-house Expertise**
- **Modified existing sample collection and analysis methods:**
  - For PAH's, 1) concentrated samples, 2) required different solvent to extract samples, and 3) developed a faster method to extract XAD
- **Required Pooling of Samples to Obtain sufficient Sample for analysis**

What Was Learned From This Study?

- **Not Routine…Research Effort**
- **Tunnel Background Interferences**
  - To evaluate accurately low-emission technologies will require new sampling methodologies including different types of dilution tunnels to address tunnel background interferences
- **Changes to Sampling Methodology**
  - Need samplers that can collect greater PM mass
  - Apply what was learned from this study to improve on future studies
- **Analytical Techniques**
  - Methodology for particle number/size characterization is needed
  - For PAH's, may need to develop additional clean-up procedures to eliminate interferences
  - For PAH's, automate sample preparation
  - Develop techniques that lower the Method Detection Limit

Final Remarks

Toxic Hydrocarbons and Carbonyl Compounds

- Butadiene was only detected in CNG vehicle exhaust (with 1 exception: Diesel without trap idle test).
- Generally, BTEX concentrations in CVS exhaust samples were close to ambient levels
- Generally, BTEX emission follows the order: CNG > Diesel (OEM) > CRT
- Carbonyl emissions from CNG vehicle were much higher than from CRT-equipped vehicle
- Total carbonyl emissions (by mass) from CNG vehicles are two orders of magnitude higher than BTEX and 1,3 Butadiene emissions
- CNG vehicle carbonyl emissions are dominated (>80%) by formaldehyde

Final Remarks (cont'd)

Composition of PM

- OC dominates CNG PM composition across all cycles
- Similar tunnel blank composition
- EC/OC fraction in Diesel (EOM) PM shows strong cycle dependence
- OC dominates CRT PM composition across all cycles
- EC/OC/Elements fractions show cycle dependence and variability
- Emission of EC/OC/Elements: Diesel (OEM) > CNG > CRT
- Ca, Cl, P, Zn, S are oil components
- Fe from engine wear
- Si source unknown
- Si emissions: Diesel (OEM) >> CNG ~ CRT

Final Remarks (cont'd)

PAH's and Bioassay

- Emission rates (ug/mi) for most PAH's were higher in the CBD than SS
- Emission rates for CNG retest were generally higher than CNG
- Differences were observed in the properties of PM from CNG, Diesel (OEM), and CRT
- New substrate is needed to replace XAD because of backgrounds of some PAH's approach the low PAH levels in tunnel blank and samples
- CRT PAH levels are similar levels to TB's
- Generally, CNG and Diesel (OEM) are higher than TB's
- Emissions of mutagenic compounds showed cycle dependence
- For CBD, bioassay follows: CNG > Diesel (OEM) > CRT
- For SS, bioassay follows: CNG > CRT > Diesel (OEM)

"Bottom Line" and Next Step

- *Thus far, the cumulative results in this study suggest that the "adverse" impact from emissions follows:*

  Total PM Mass: Diesel(OEM)>CNG>CRT

  Secondary PM: CRT>Diesel (OEM)> CNG

  Particle Size/Counts: CNG>Diesel(OEM)>CRT

  Toxicity/Mutagenicity: CNG>CRT$\overset{?}{\sim}$Diesel(OEM)

- *Results show cycle dependence*
- *PM is not PM and is not PM !*

What is next?

- SCAQMD Briefing
- Finish data analysis and subject it to peer review
- Report back once publications accepted

IDEAS FOR FOLLOW-UP STUDY:
Investigation of Toxics from Interim and "2007" Heavy-Duty Emission Controls

Scope Cuts Across Applications:

- Baseline
- CRT and SCRT on bus or truck (*in-house*)
- DPX and DPX/EGR on bus or truck (*in-house*)
- SCR/DPF engine tests (*piggy back on current work: DOE or EPA)*
- NO_x Adsorber/DPF engine tests (*piggy back on current work: DOE or EPA*)
- CNG/Catalyst, "Advanced" CNG, CNG/H_2, or CNG/Trap?? bus (*in-house*)
- Other? (*i.e.*, fuel-borne cat, active PM trap)

Approach:

- Duplicate samples, one fuel, one oil, one or two duty cycles

FOLLOW-UP STUDY (*cont'd)*

Emissions of Concern:

- DPF Ash
- Regulated Emissions
- Elements
- Toxic VOC's and Carbonyls
- PAH's and Nitro-PAH's
- Bioassay Analysis
- Characterization of Particle Number and Size
- Dioxins
- Other? (HONO, N_2O, etc.)

Participants:

- Lead Team: RD, SSD, MSCD
- In-house Testing: RD, MSCD
- Analysis: UCD, MLD, NREL, EPA, Private Lab
- Data Reduction: RD, SSD, MSCD