Concentrations and Size Distributions of Particulate Matter Emissions from Catalyzed Trap-Equipped Heavy-duty Diesel Vehicles Operating on Ultra-low Sulfur EC-D Fuel

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Background

- Year-long industry-government collaborative program
  - Two rounds of vehicle tests to characterize exhaust emissions
  - Evaluation of ultra-low sulfur diesel formulations (ECD and ECD-1)
  - Several fuels and filters tested in Southern California fleets

- Results from the First Phase showed significant reductions in diesel PM, CO and HC emissions as compared to CARB diesel

- Second Phase tests were designed to:
  - Evaluate durability of the control devices
  - Conduct an extensive chemical characterization for a sub-set of vehicles

Test Program

- Six program vehicles selected for characterization
  - a school bus, two grocery trucks (tractor), and three transit buses.
- Vehicles tested with
  - original exhaust system
  - subsequently fitted with DPFs provided by Engelhard (DPX™) and Johnson-Matthey (CRT™).
- Test fuels used
  - market average CARB diesel
  - ECD, ECD-1, Fischer-Tropsch (F-T) diesel, and CNG

Test Matrix

Vehicle	Fuel	DPF Type
San Diego School Bus	CARB, ECD,	NONE
	ECD-1, FT	DPX
LA MTA	**ECD-1, CARB**	**NONE**
	ECD, ECD-1	**CRT**
	CNG (2 Vehicles: MY2000 and MY2001)	**NONE**
Ralphs Grocery	CARB, ECD-1	NONE
	ECD, ECD-1	CRT

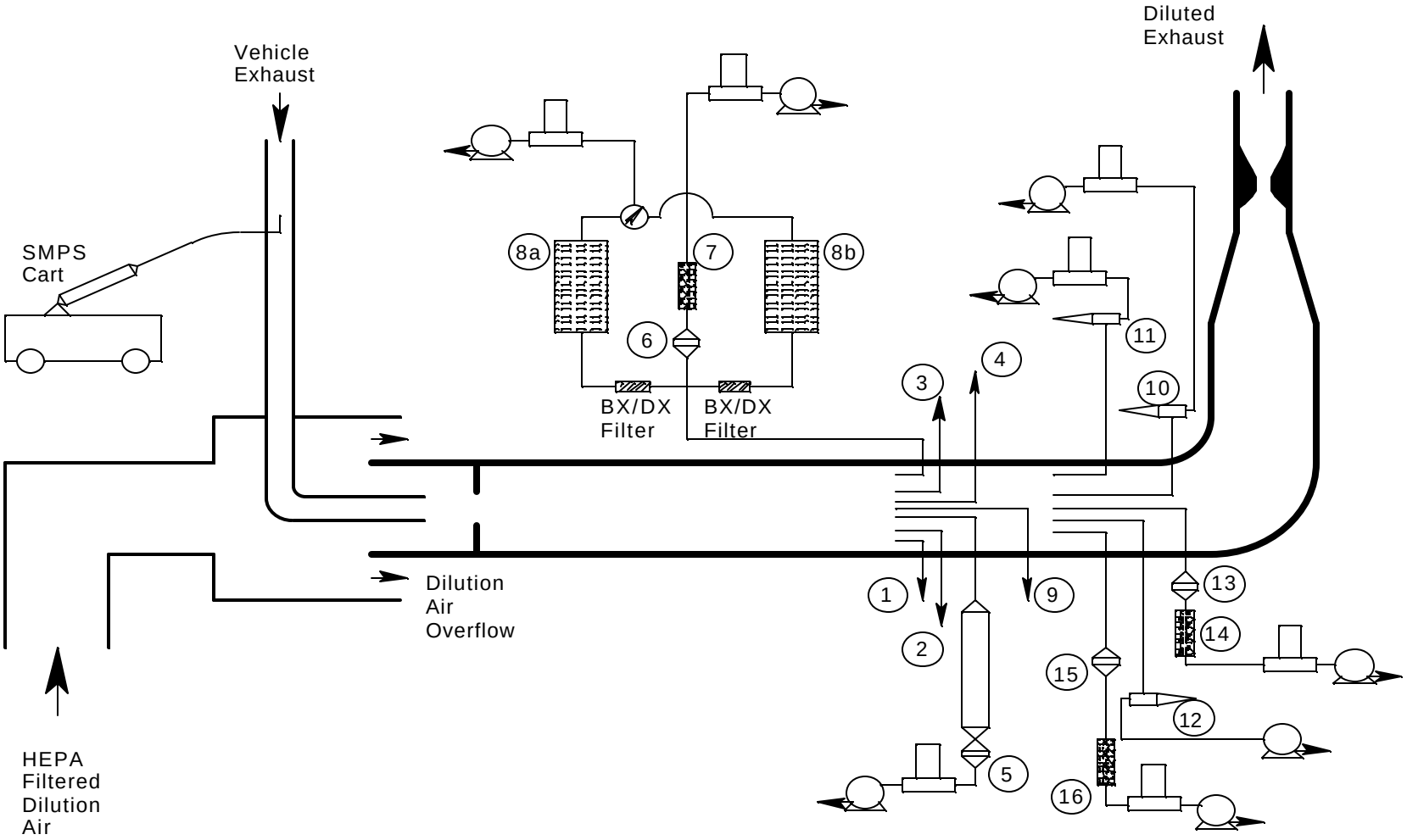
Fuel Analysis

Property	CARB	ECD	ECD-1
Cetane Number	54.1	64.7	51.3
Sulfur, ppm	121	7.4	13.1
SFC Aromatics			
Total, vol%	22.5	10.9	23.8
PNA, wt%	4.1	0.9	2.8

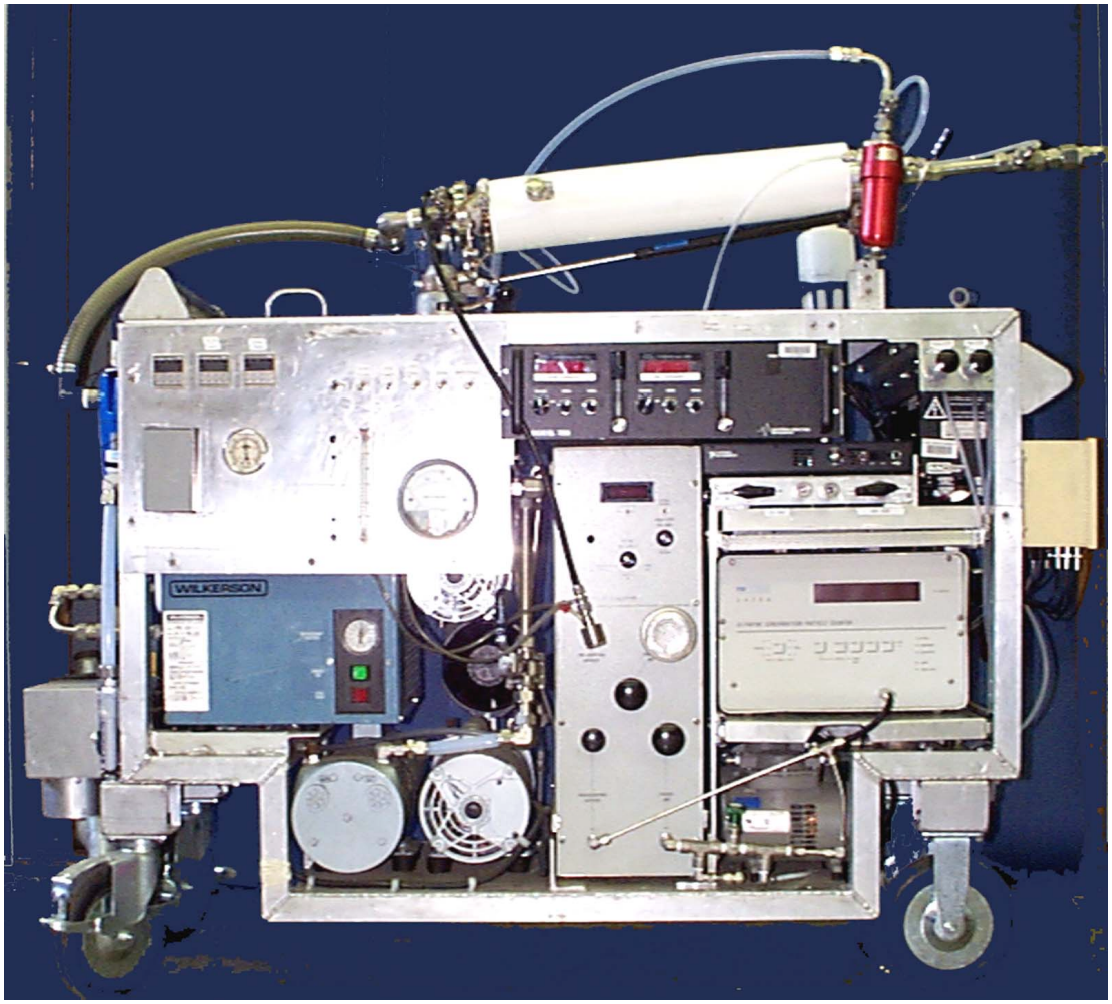
Chemical Characterization

- Particulate Matter
  - TPM, PM_{10}, $PM_{2.5}$
- Volatile Organic Compounds
  - Low molecular weight alkanes and olefins (C_2 – C_5)
  - Low molecular weight aromatics (BTEX)
- Elemental & Organic Carbon
- PAHs and n-PAHs
- Elemental Compounds
- Ionic Species
- Carbonyls
- Dioxins and Furans
- Bioassays

Sampling System



Particle Sizing Cart



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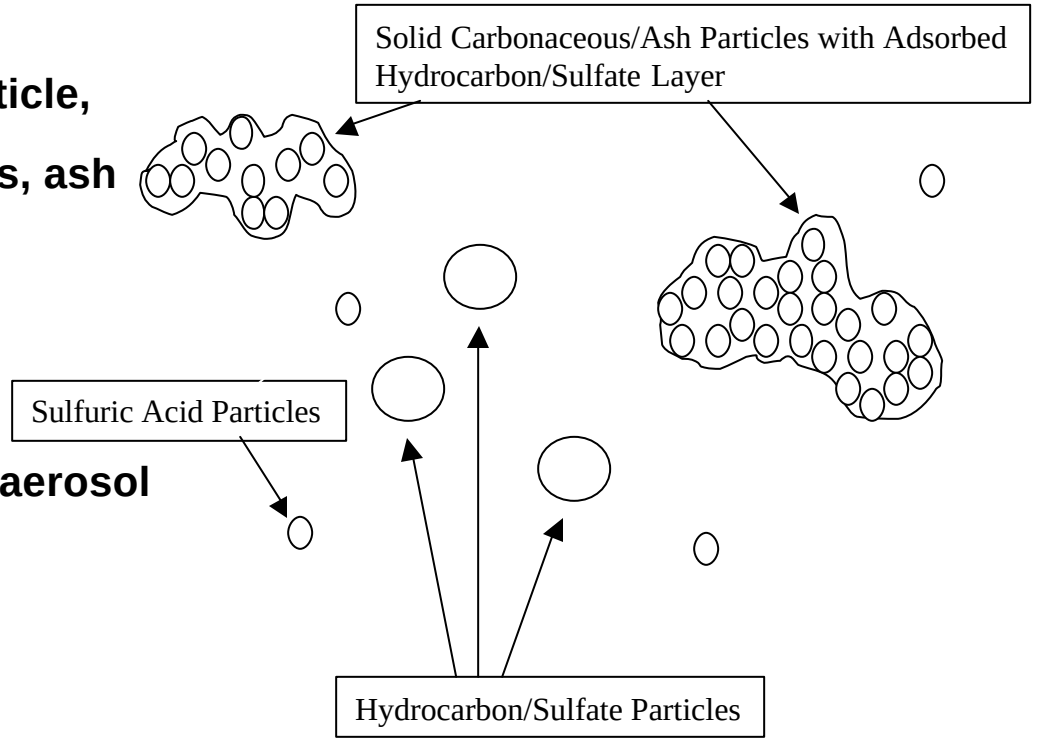
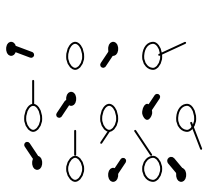
Typical Structure of Engine Exhaust Particles

- **Agglomerated solid carbonaceous particle, volatile organic, sulfur compounds, ash**
- **Most of sulfur in the fuel**
  - **– oxidized to SO_2, then**
  - **– oxidized to SO_3**
  - **– leads to sulfuric acid and sulfate aerosol**
- **Metal compounds in fuel and lube oil**
  - **– lead to inorganic ash**

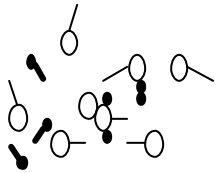


Nucleation Process

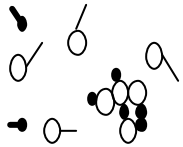
- **Homogeneous nucleation (Springer, 1978)**
  - **In the absence of condensation nuclei**
  - **Require large saturation ratio (S>1)**
- **Heterogeneous nucleation**
  - **Occurs on a foreign substance or surface, such as an ion or a solid particle**
- **Binary homogeneous nucleation**
  - **Two or more vapor species**



(a) Binary Vapor



(b) Molecular Clusters

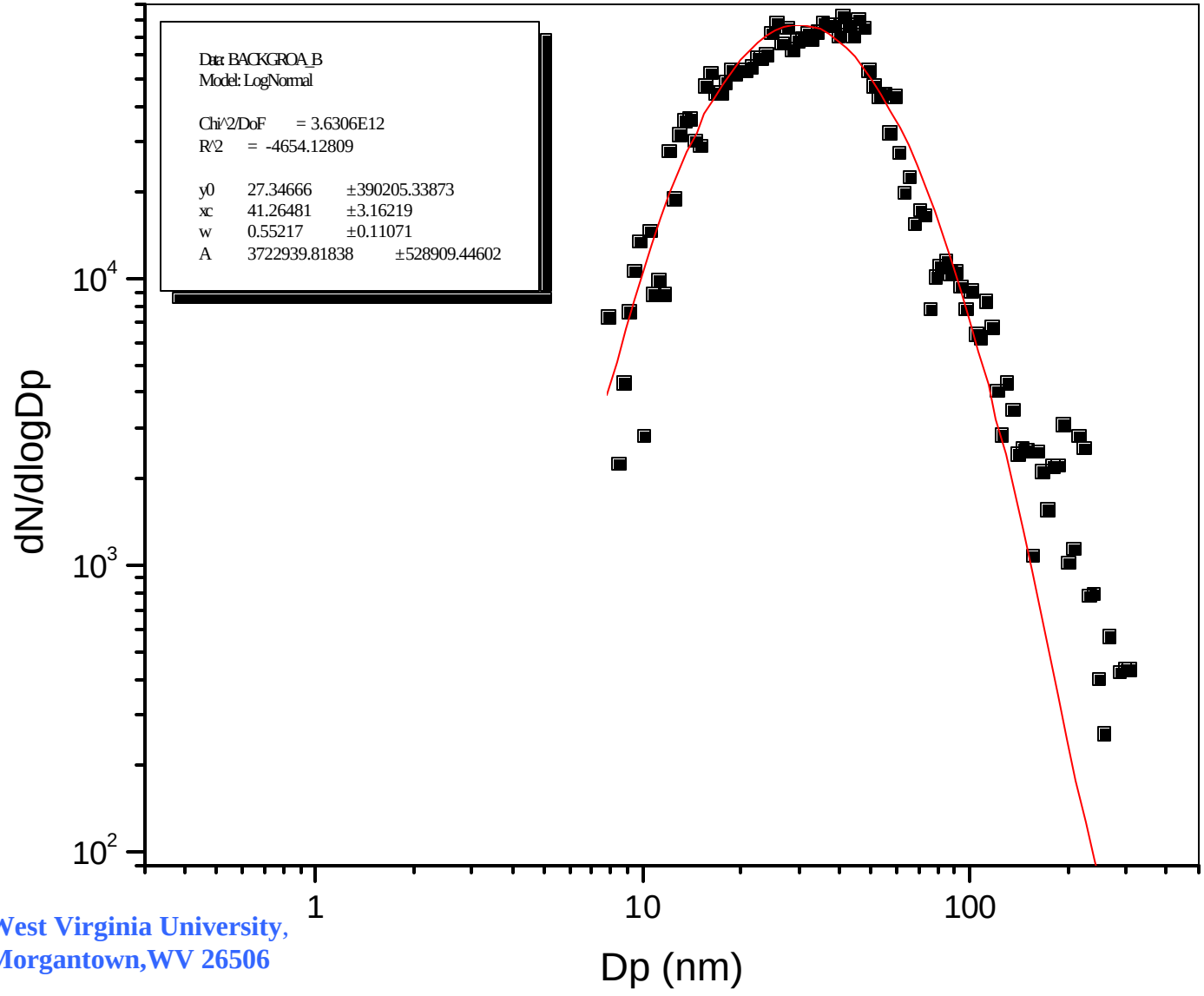


(c) Stable Nuclei

(d) Particle Growth

(Baumgard and Johnson, 1996)

TUNNEL BACKGROUND



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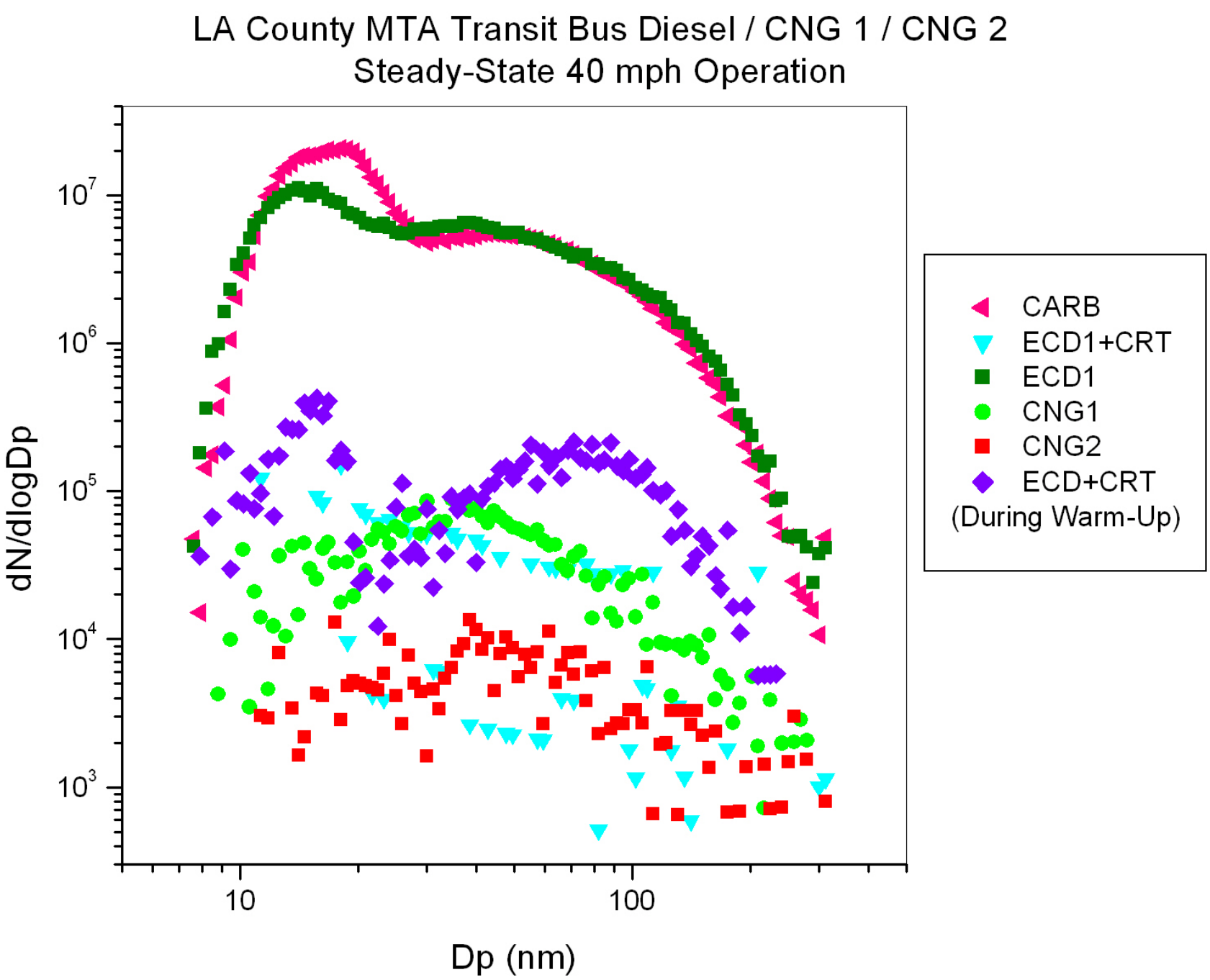
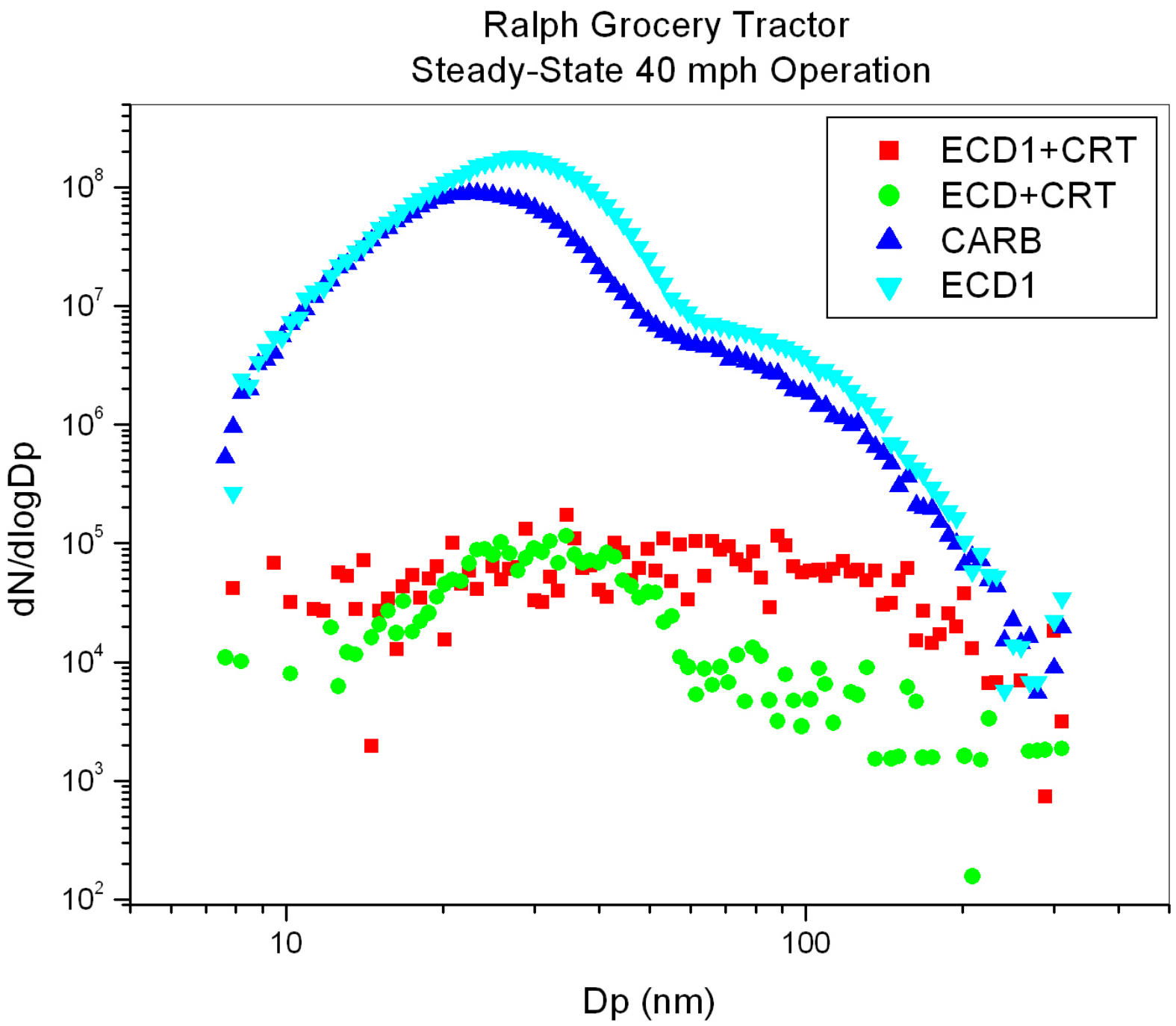
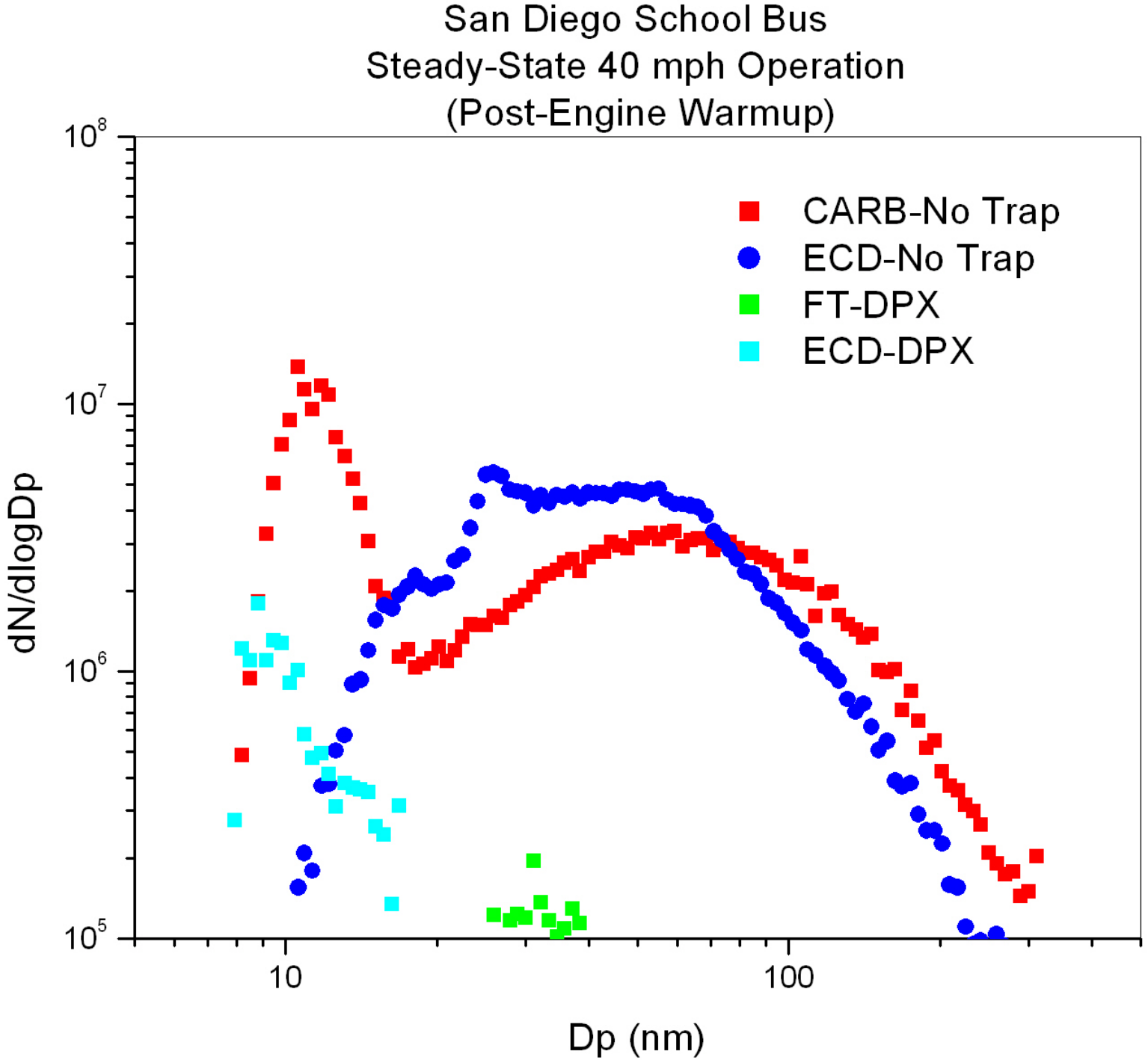
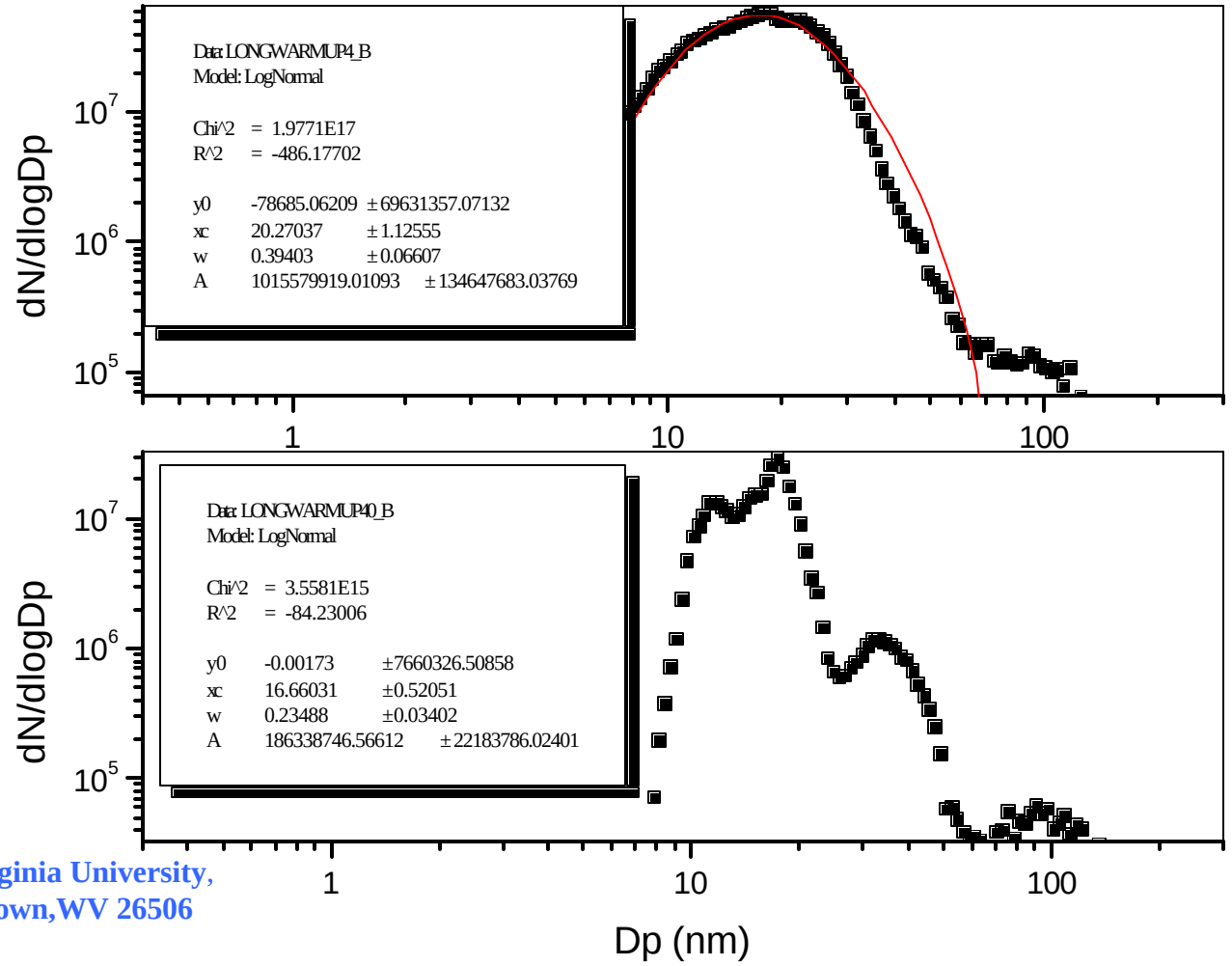

LA County MTA Transit Bus Diesel / CNG 1 / CNG 2
Steady-State 40 mph Operation
dN/dlogDp
10^7
10^6
10^5
10^4
10^3
10
100
Dp (nm)
CARB
ECD1+CRT
ECD1
CNG1
CNG2
ECD+CRT
(During Warm-Up)


Ralph Grocery Tractor
Steady-State 40 mph Operation
ECD1+CRT
ECD+CRT
CARB
ECD1
dN/dlogDp
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10
100
Dp (nm)


San Diego School Bus
Steady-State 40 mph Operation
(Post-Engine Warmup)
CARB-No Trap
ECD-No Trap
FT-DPX
ECD-DPX
dN/dlogDp
Dp (nm)
10
100
10^8
10^7
10^6
10^5

COLD START AT 40 MPH; DR=13:1
TRANSIT BUS
FUEL: ECD
EXHAUST AFTER-TREATMENT: JOHNSON-MATTHEY



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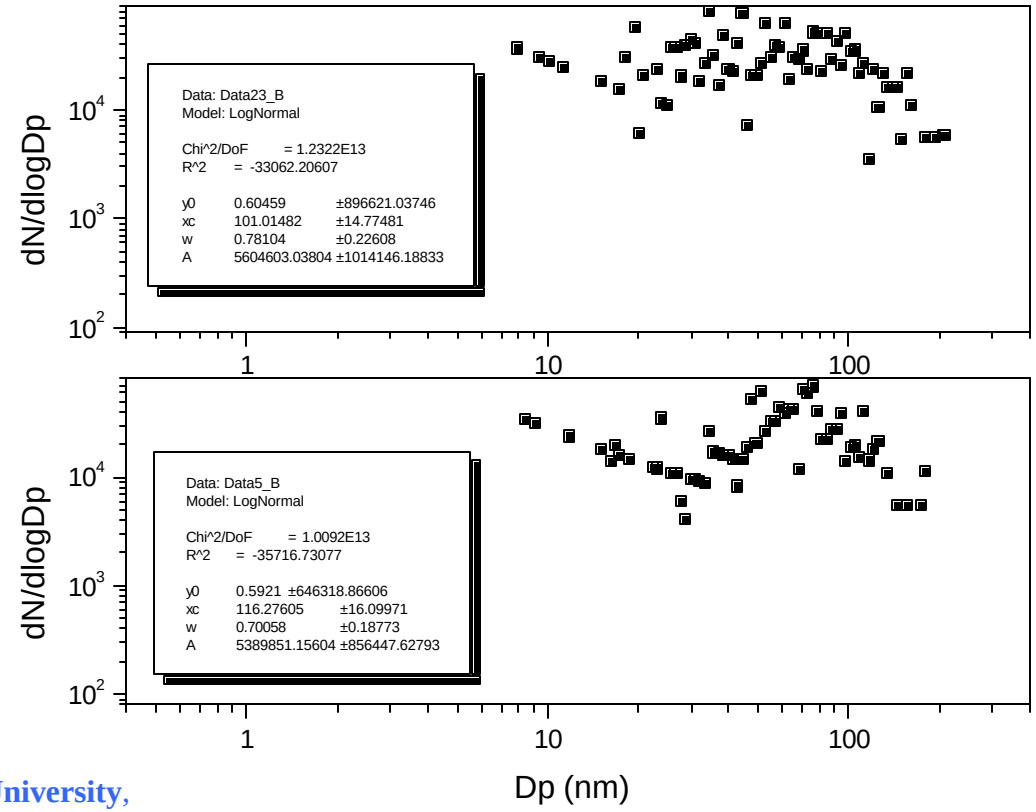
AFTER WARM-UP AT 20 MPH; DR=25:1
TRANSIT BUS
FUEL: ECD
EXHAUST AFTER-TREATMENT: JOHNSON-MATTHEY



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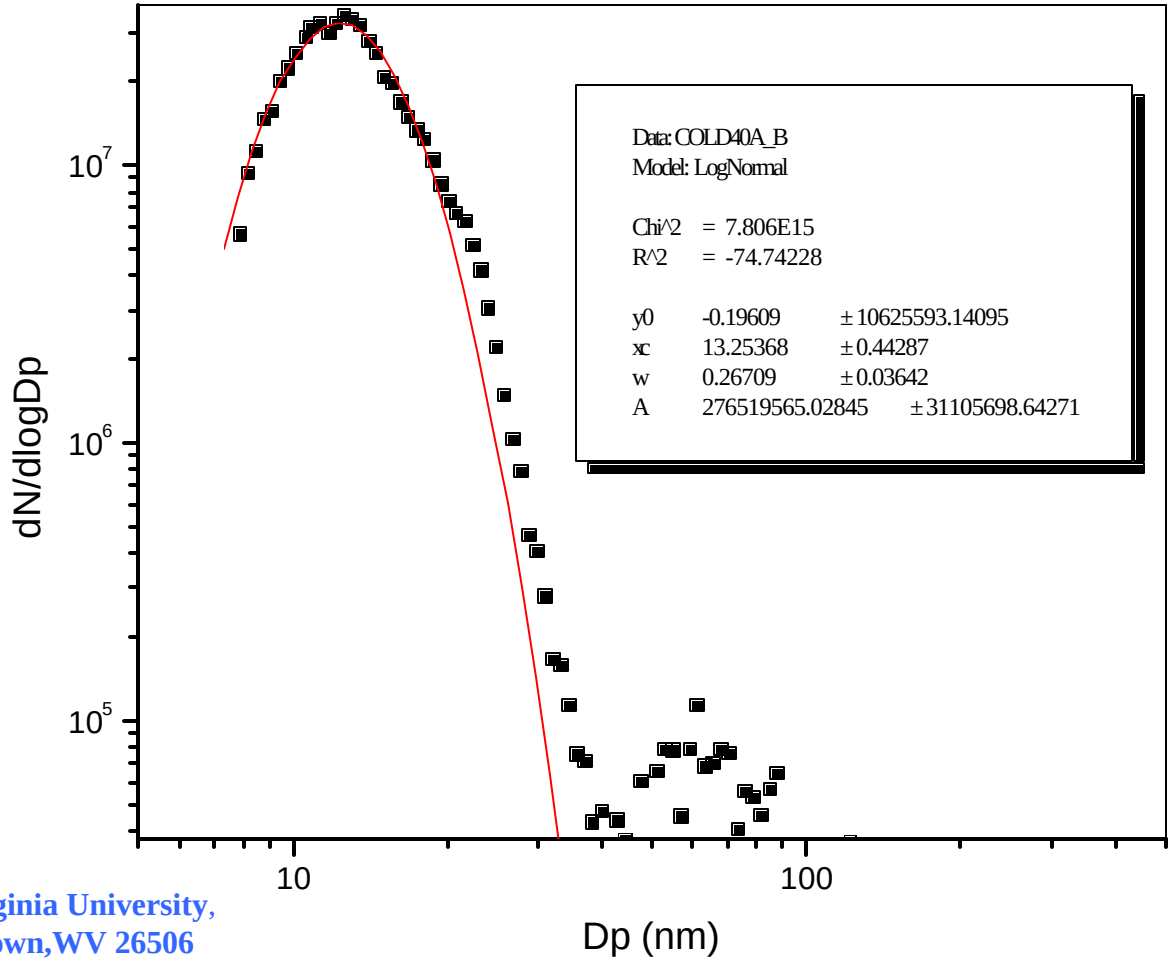
COLD START AT 40 MPH
TRANSIT BUS
FUEL: ECD 1
EXHAUST AFTER-TREATMENT: JOHNSON-MATTHEY



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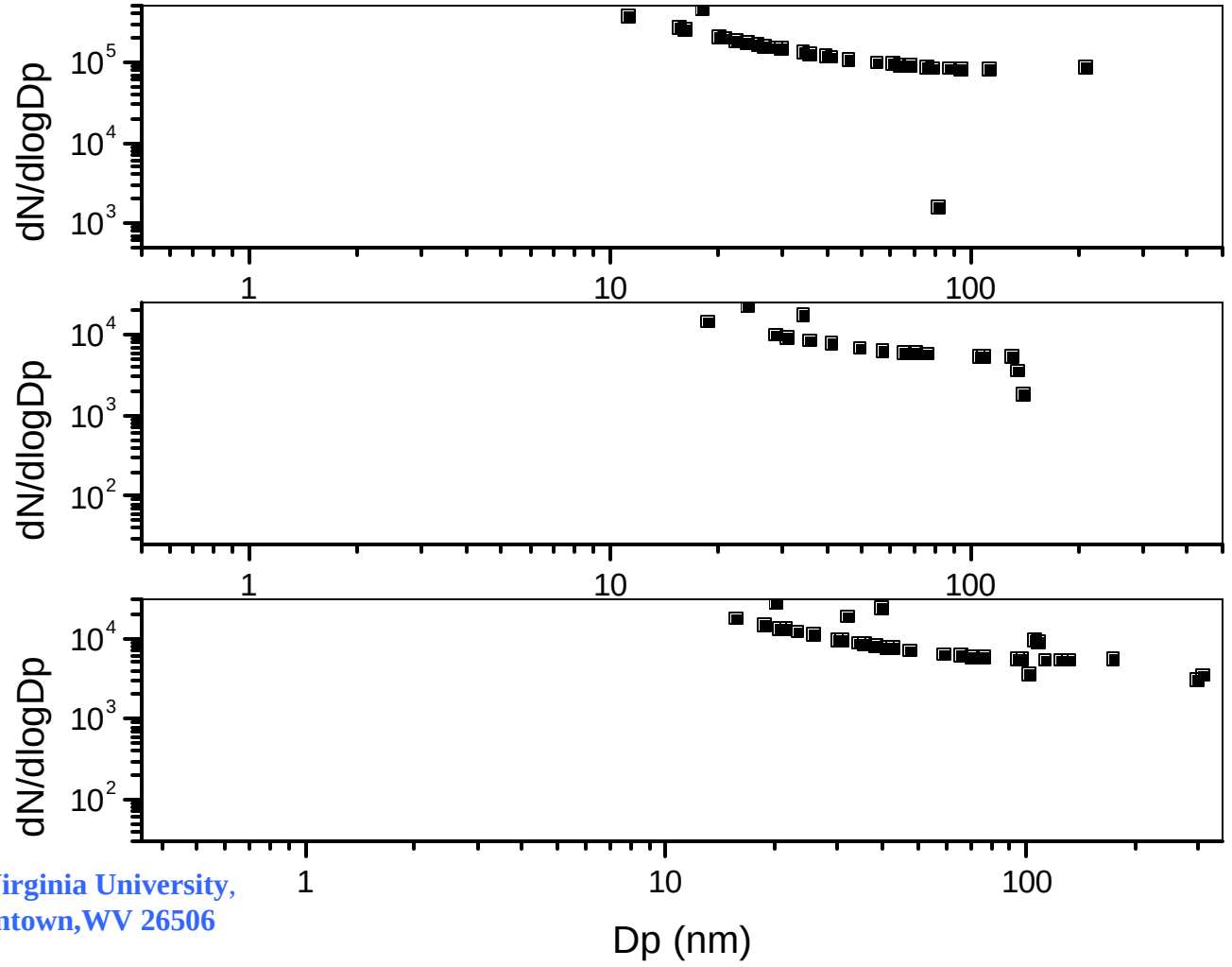
AFTERWARM-UP AT 40 MPH
TRANSIT BUS
FUEL: ECD1
EXHAUST AFTER-TREATMENT: JOHNSON-MATTHEY



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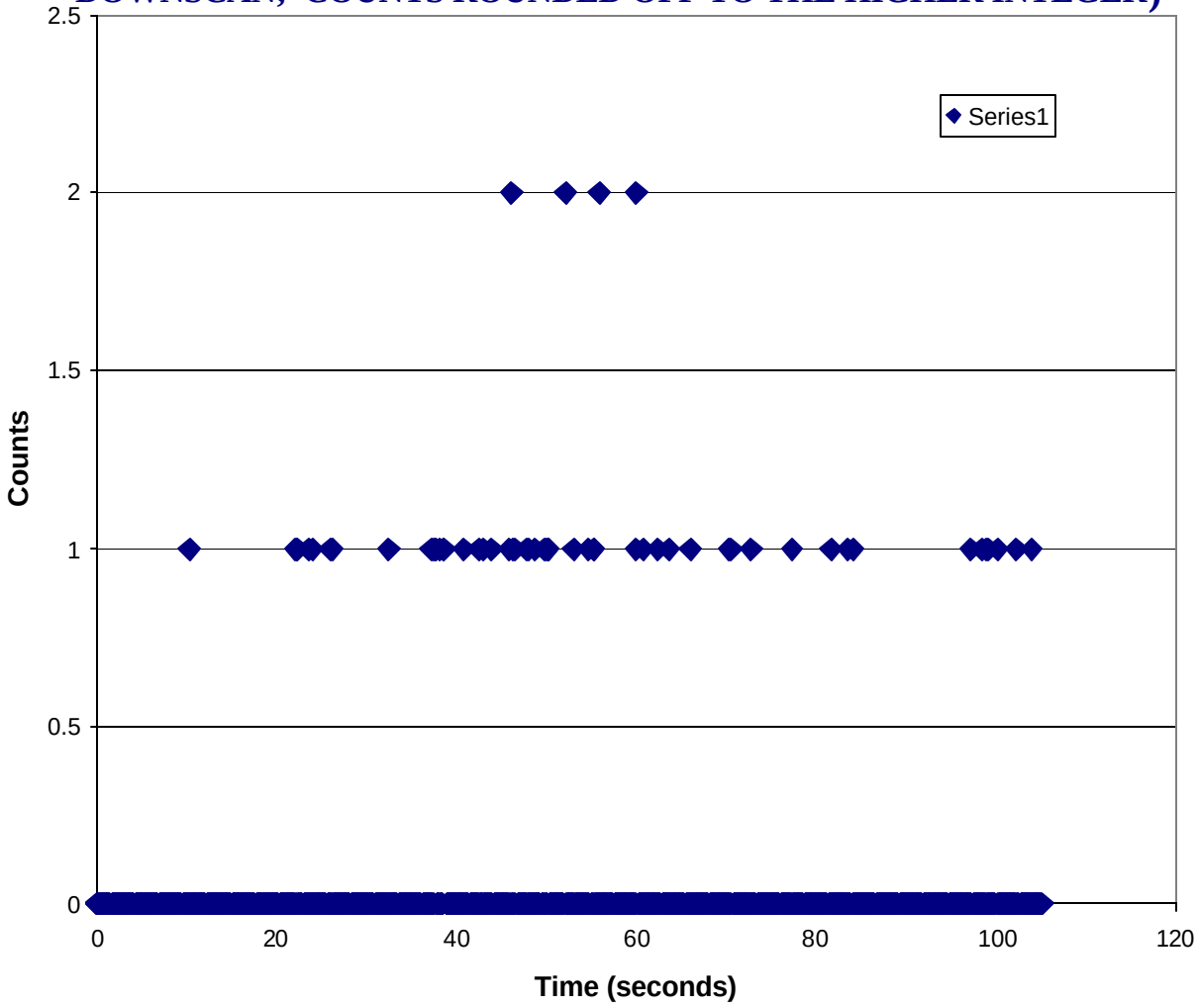
IDLE: RAW PM COUNT DATA FROM CPC

(INCLUDES 90 SECONDS OF UPSCAN AND 15 SECONDS OF DOWNSCAN; COUNTS ROUNDED OFF TO THE HIGHER INTEGER)



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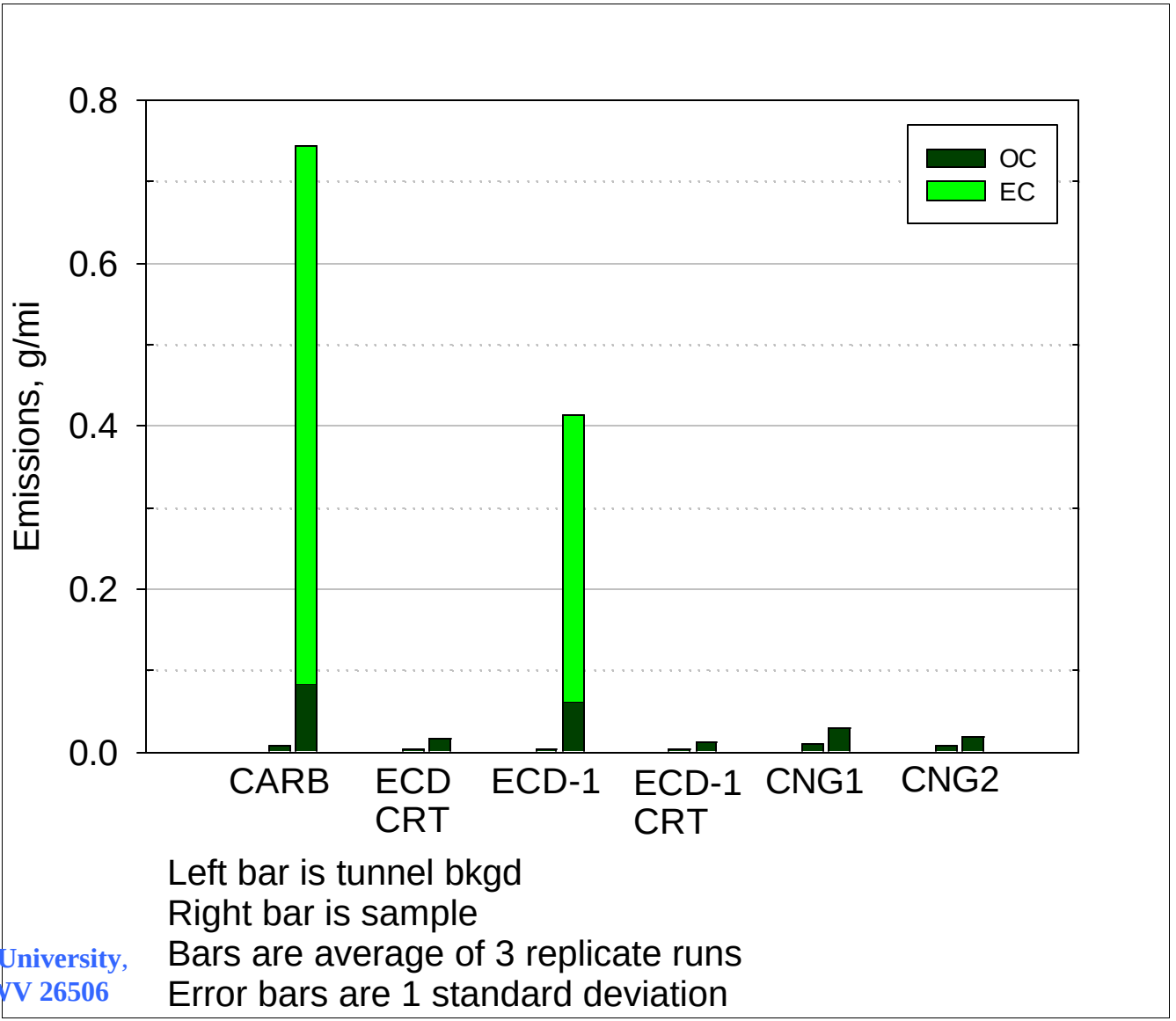
EC/OC



Left bar is tunnel bkgd
Right bar is sample
Bars are average of 3 replicate runs
Error bars are 1 standard deviation

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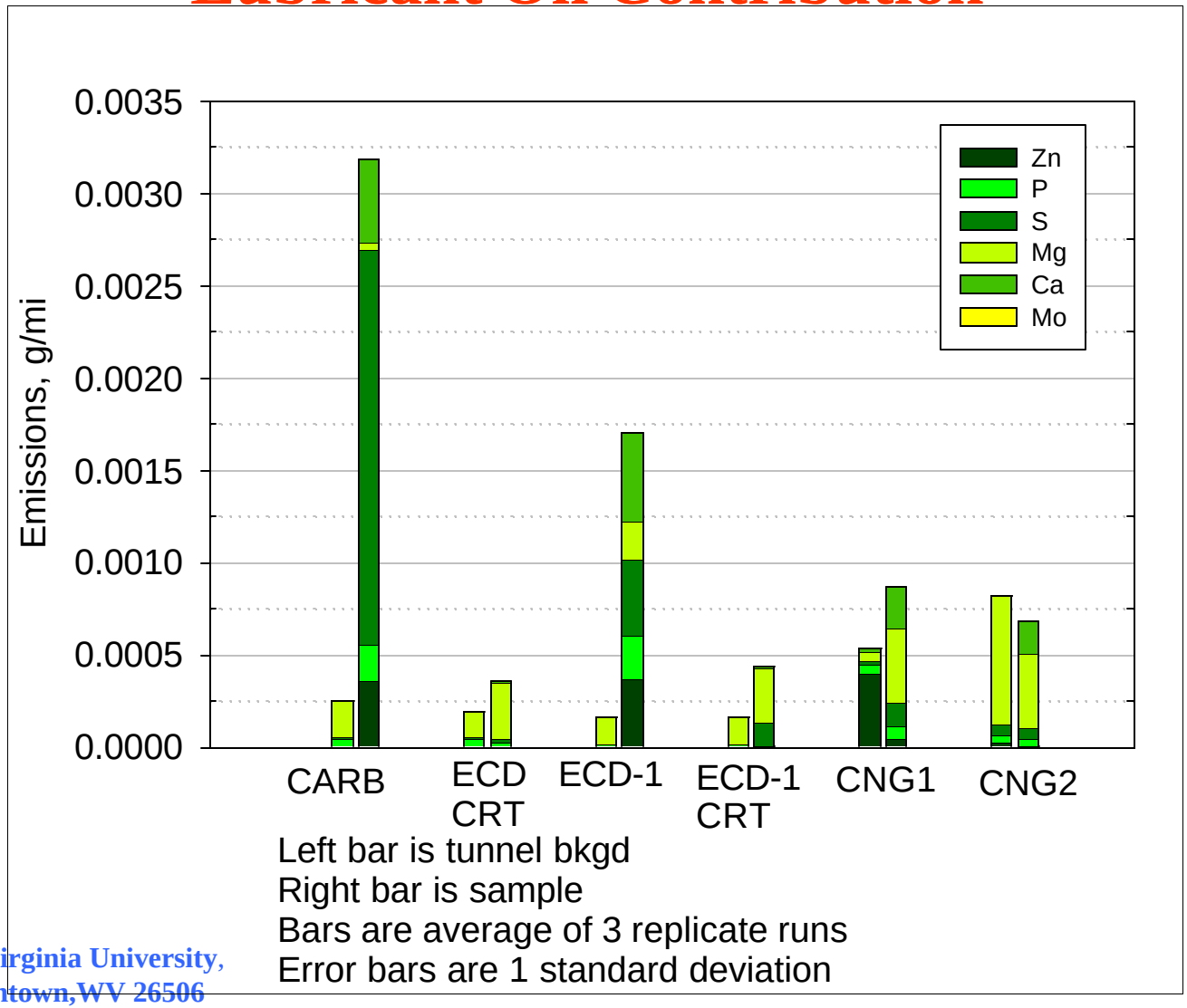
Elemental Analysis:
Lubricant Oil Contribution



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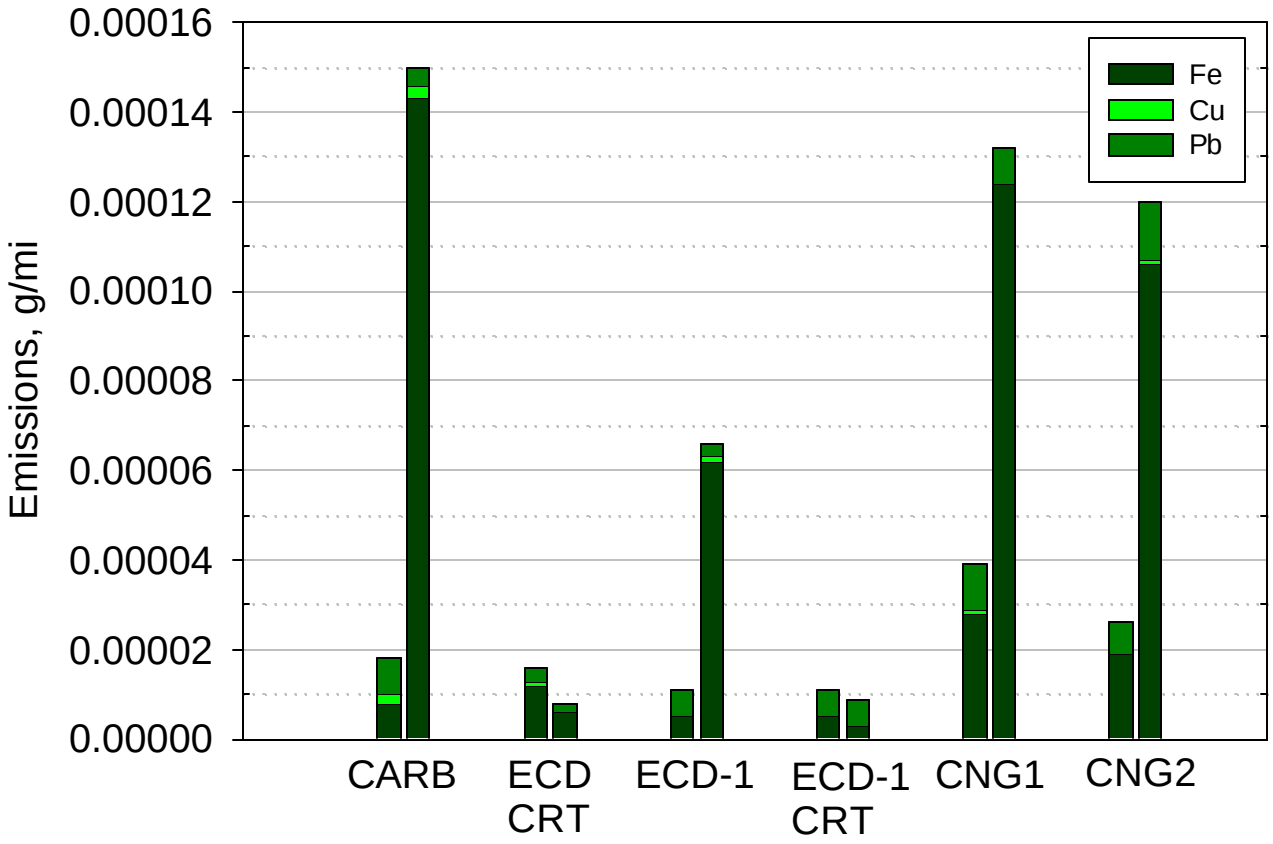
Engine Wear Contribution



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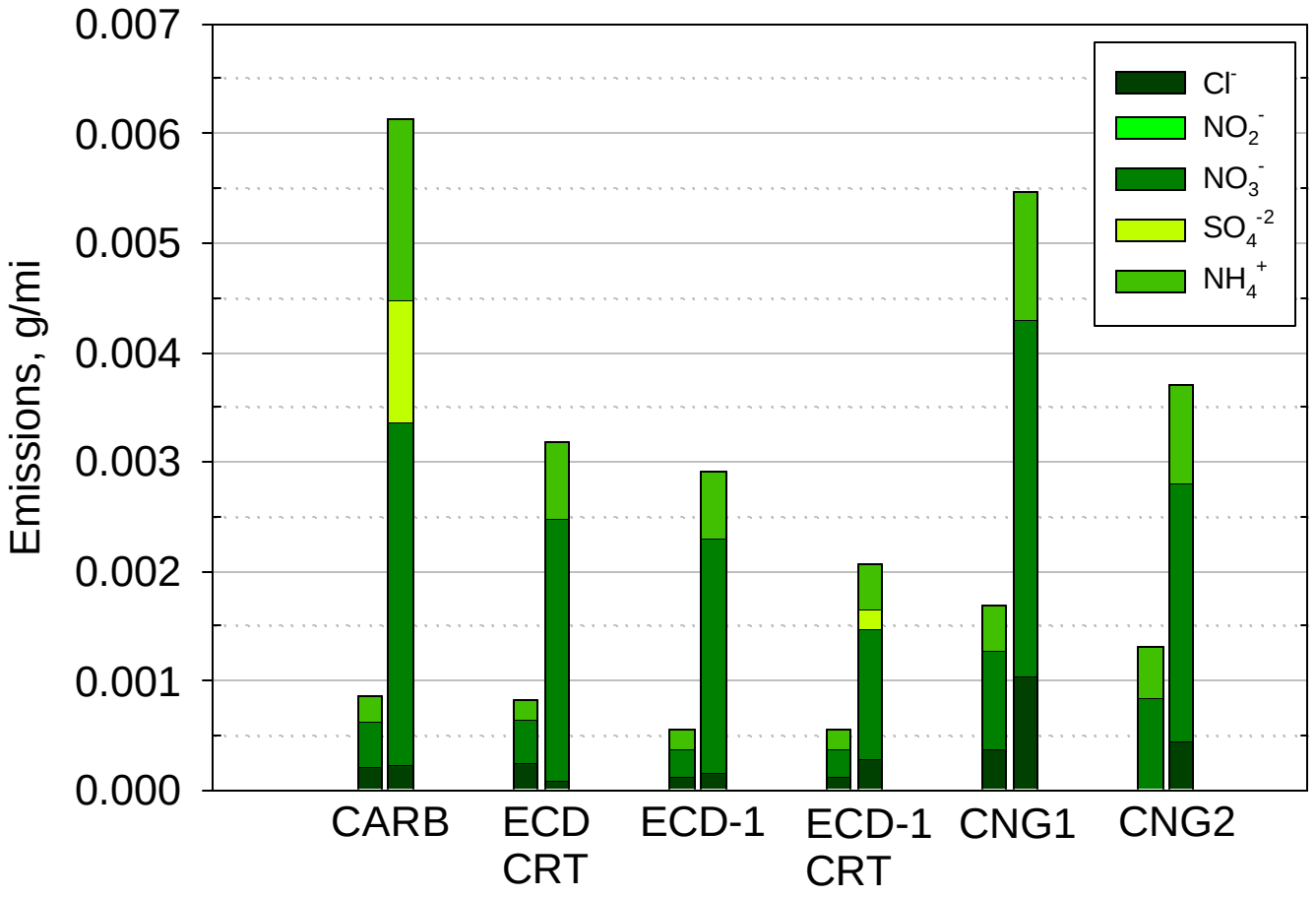
Inorganic Ionic Species



Left bar is tunnel bkgd
Right bar is sample
Bars are average of 3 replicate runs
Error bars are 1 standard deviation

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Carbonyl Compounds
(Air Toxics)

Formaldehyde

Acetone

Propionaldehyde

Methyl ethyl Ketone (MEK)

Butanal

Glyoxal

Tolual

Acetaldehyde

Acrolein

Croton

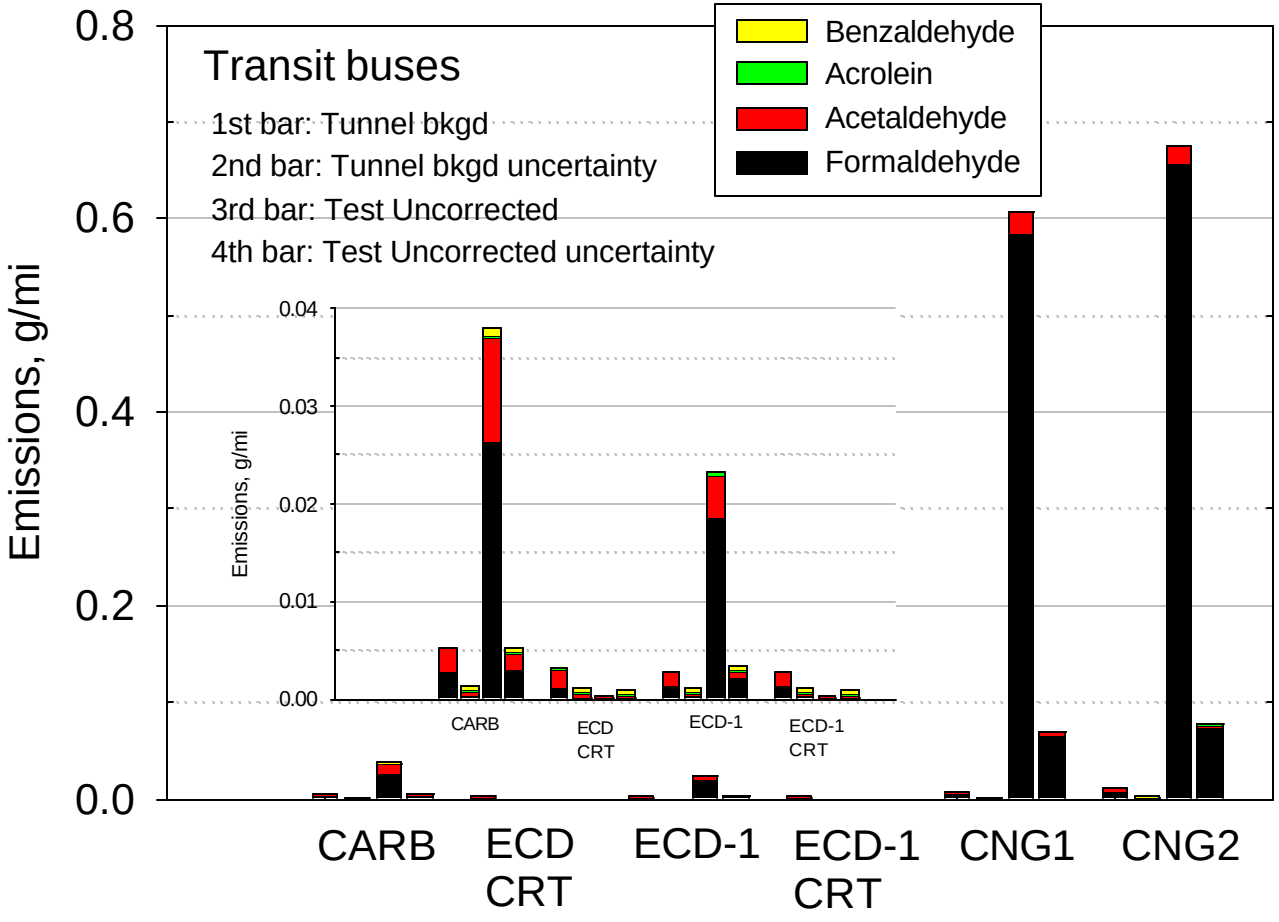
Methylacrolein

Benzaldehyde

Valal

Hexanal

Carbonyls



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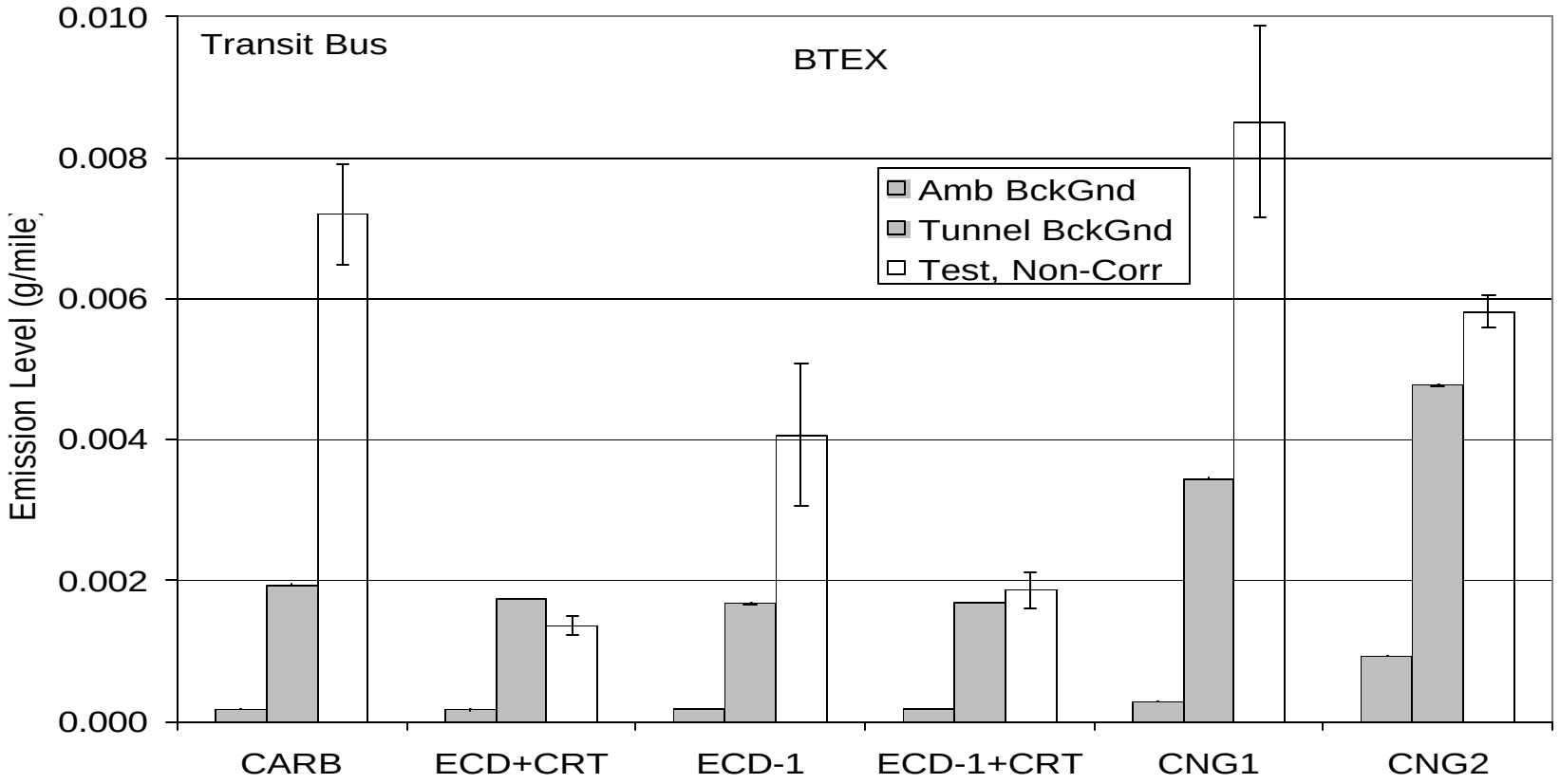
BTEX



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Conclusions

- **Changes from CARB to ECD and ECD-1 without a DPF had minimal impact on particle size distributions and concentrations.**
- **DPF's provided dramatic reductions in particle concentrations across the nanoparticle size range, and in unregulated emissions.**
- **Further investigations of cold-start nanoparticle emissions with the use of a DPF is recommended**
  - **Number count and chemical analyses**
  - **Particle concentrations same order as background**
  - **Bioassays on size-selective PM emissions**

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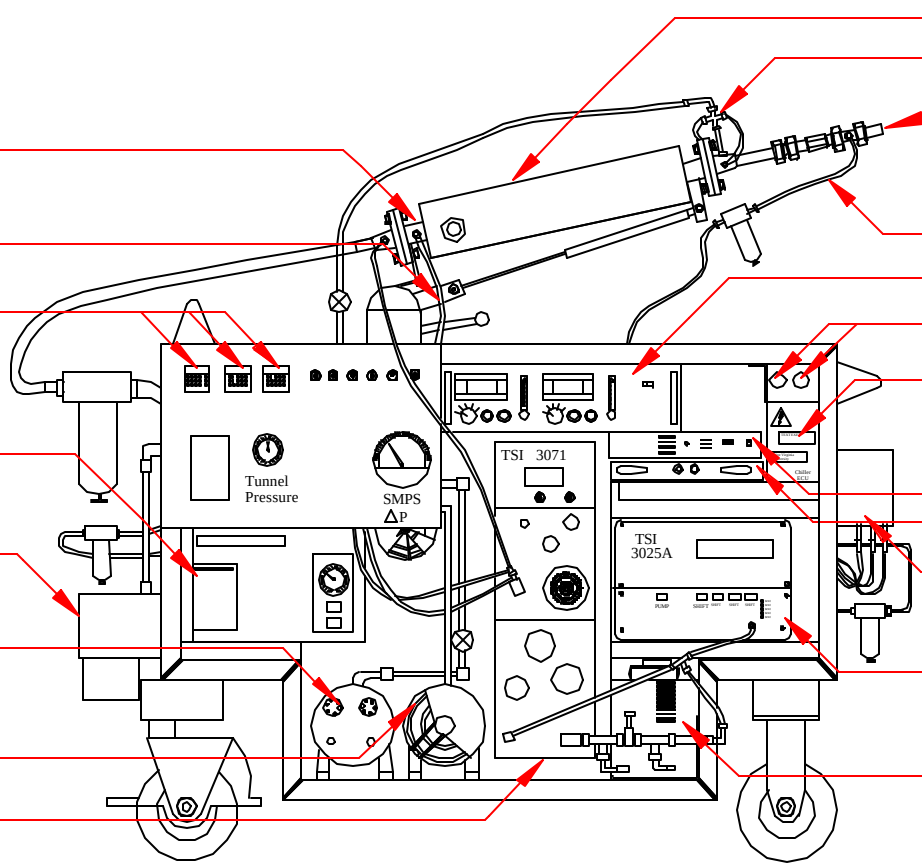
Approach

- **INSULATED RAW EXHAUST TRANSFER TUBE (FROM EXHAUST STACK TO THE DILUTION TUNNEL)**
- **SINGLE STAGE DILUTION OF RAW EXHAUST WITH A MASS FLOW CONTROLLER-BASED DILUTION SYSTEM**
- **MEASURE CONCENTRATIONS AND PARTICLE SIZE DISTRIBUTIONS ON STEADY-STATE OPERATION**
- **COLLECT DATA DURING WARM-UP TO OBSERVE THE EFFECT OF CATALYST LIGHT-OFF ON PARTICLE SIZE DISTRIBUTIONS**
- **BASED UPON THE STEADY-STATE PARTICLE SIZE DISTRIBUTIONS, SELECT A FEW KEY PARTICLE SIZES FOR TRACKED DURING THE TRANSIENT OPERATION**

Particle Sizing Cart



Heater Insulation
Dilution Air Manifold
Raw Exhaust
Mini Dilution Tunnel
Raw Exhaust Co_2 Sample
Diluted Exhaust Co_2 Sample
Dual Co_2 Analyzers (Raw & Dilute)
Temperature Controllers
Co_2 Sample Bypass Valves
Thermo-Electric Chiller (Co_2 Sample Conditioning)
Refrigerated Dryer (Dilution Air)
Data Acquisition System
Co_2 Analyzer Calibration Ports
Heat Exchanger (Dilution Air)
Mass Flow Controller Power Supply
Mini Tunnel Vacuum Pump (Dilution Air)
Condensation Nuclei Counter
Dilution Air Pump
Co_2 Bypass Pumps
Electrostatic Classifier

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Nucleation Process (Cont'd)

- **Certain number of H_2O and H_2SO_4 molecules collide**

  For critical cluster- sufficient energy to be stable

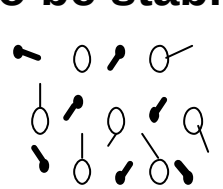
  - Greater than critical size, grow (less, shrink)

  - Rate of nucleation (H_2SO_4 hydrate (embryo) formation predicted by Reiss, 1950):

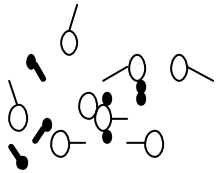
$$J = C\exp(-\Delta G^* / kT)$$

  (Grow past critical size)

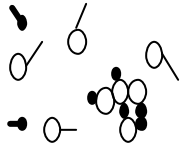
- **Higher nucleation rate occurs at higher relative humidity, and lower temperature**



(a) Binary Vapor



(b) Molecular Clusters



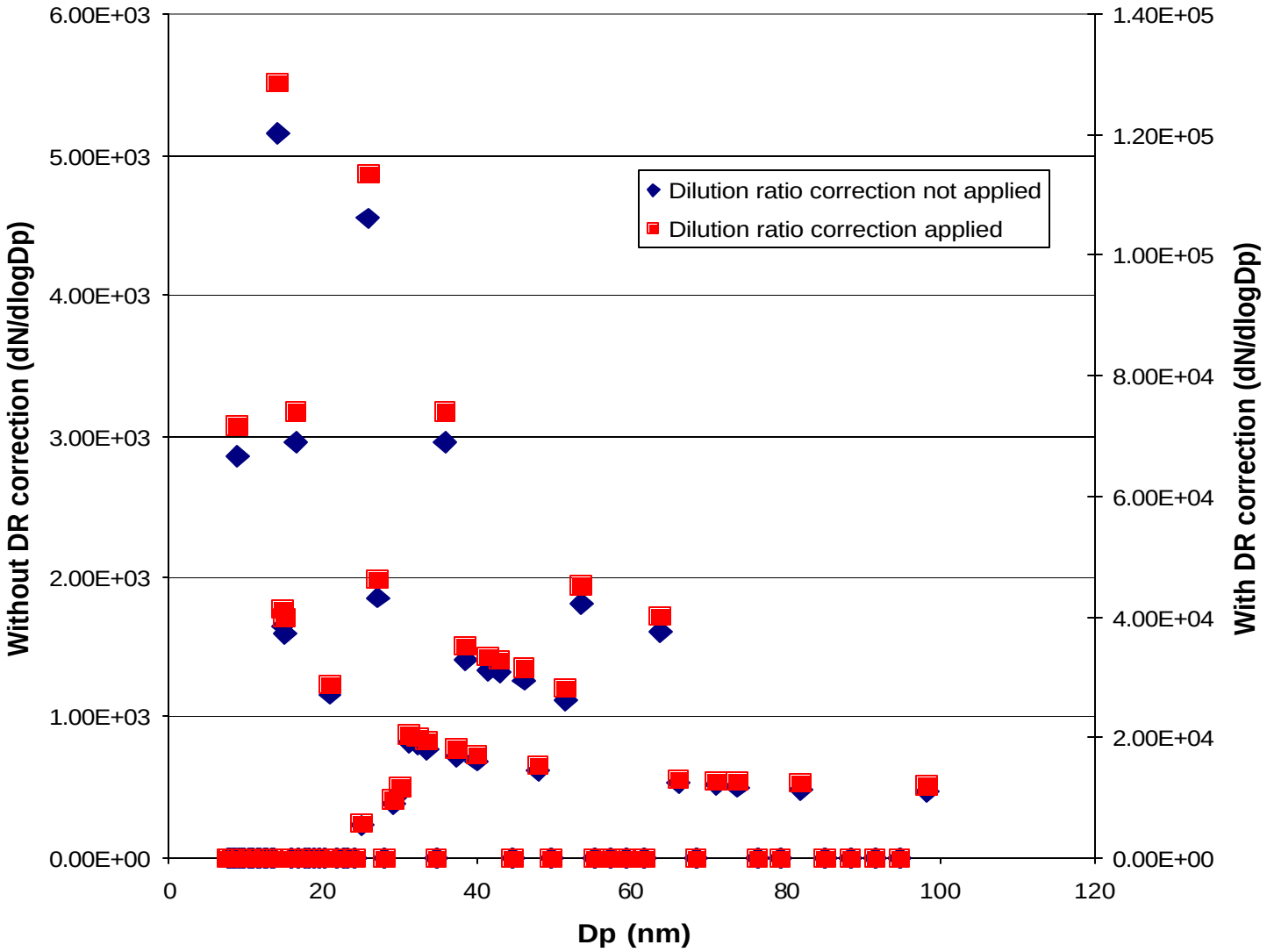
(c) Stable Nuclei

(d) Particle Growth

(Baumgard and Johnson, 1996)

C is the frequency factor, k is the Boltzmann's constant, T is the temperature and ΔG is the free energy required to form an embryo

IDLE : PM CONCENTRATION AND SIZE DISTRIBUTION



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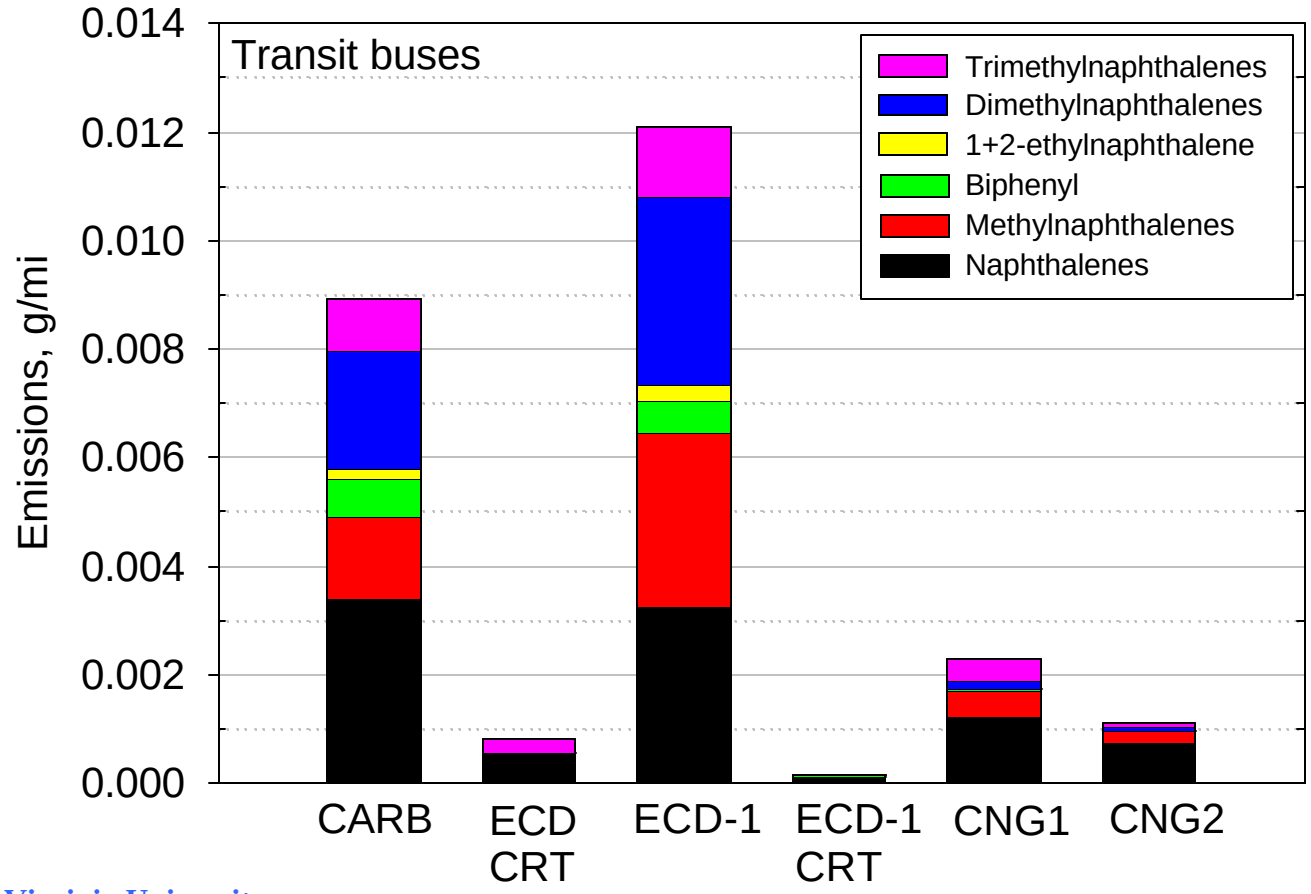
2-Ring PAH



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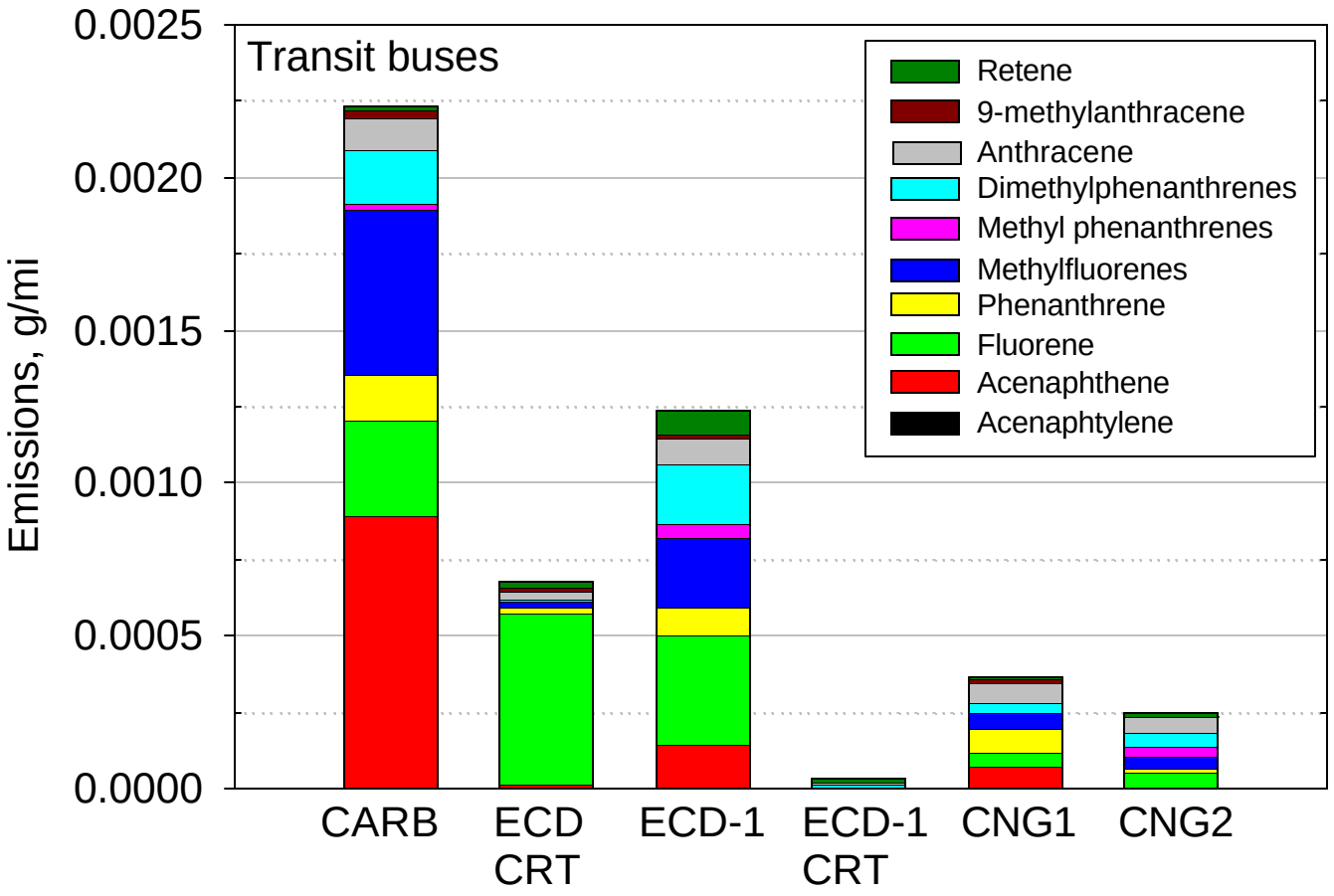
3-Ring PAH



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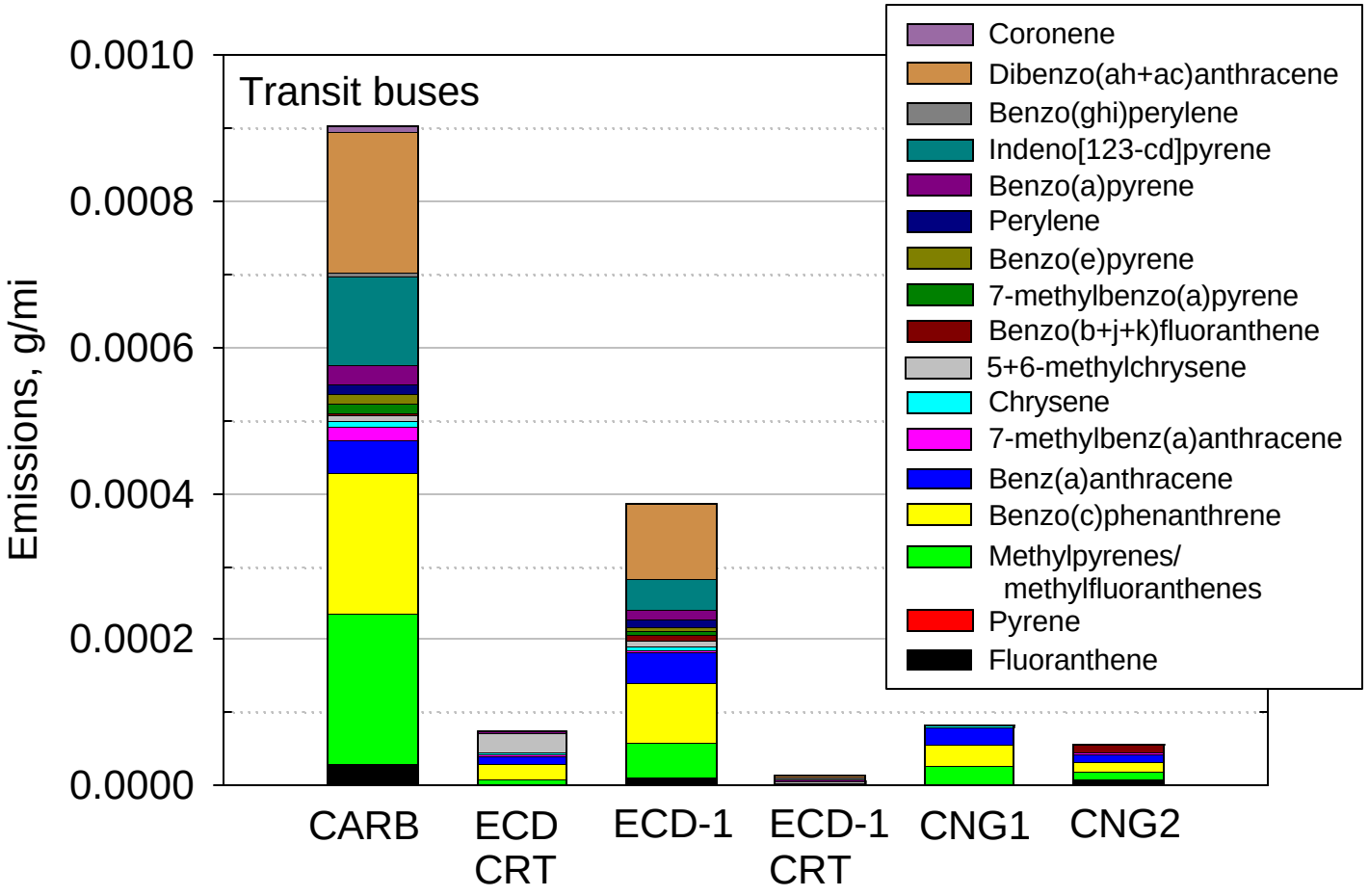
4-Ring PAH



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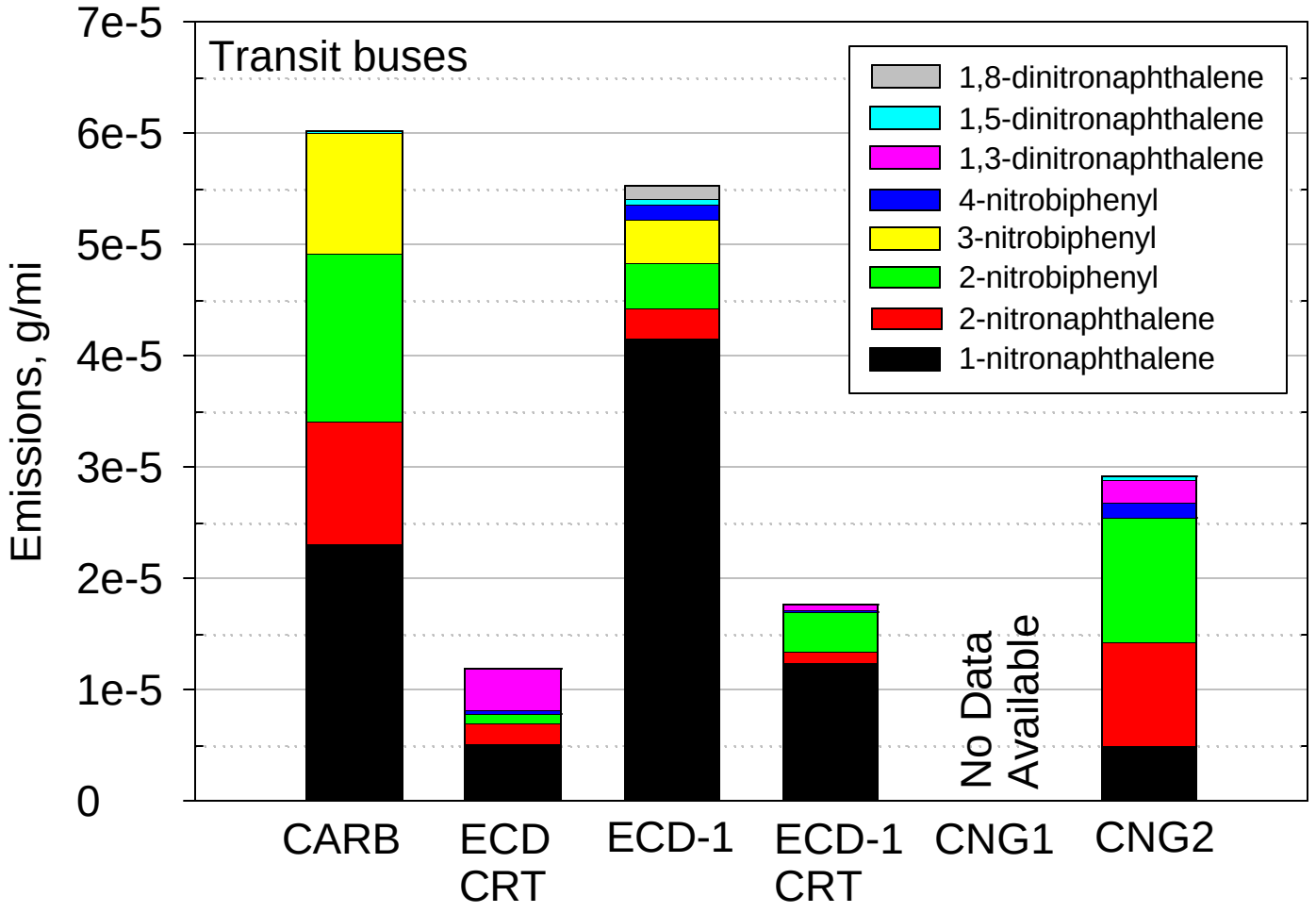
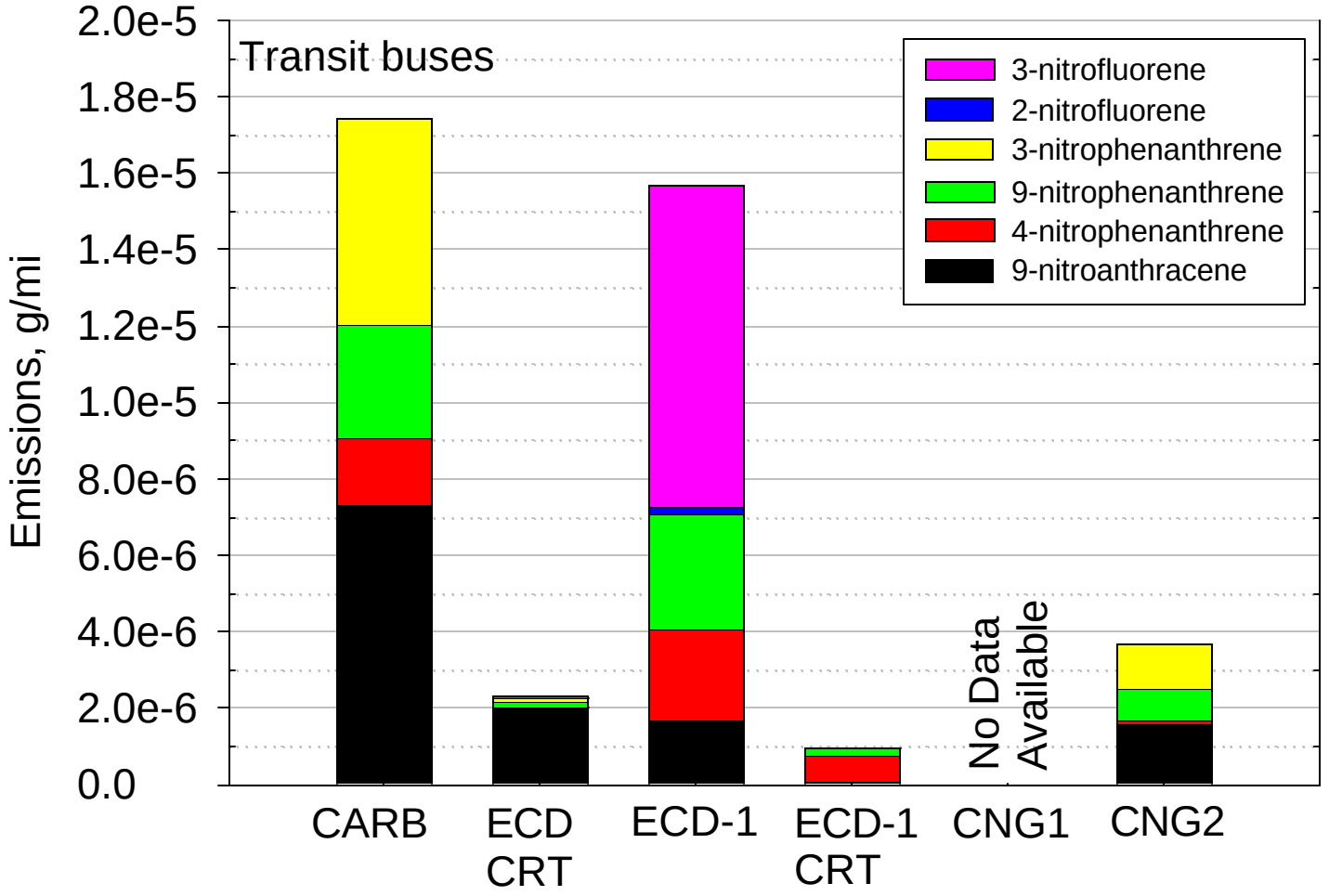
2-Ring n-PAH


Transit buses
Emissions, g/mi
7e-5
6e-5
5e-5
4e-5
3e-5
2e-5
1e-5
0
1,8-dinitronaphthalene
1,5-dinitronaphthalene
1,3-dinitronaphthalene
4-nitrobiphenyl
3-nitrobiphenyl
2-nitrobiphenyl
2-nitronaphthalene
1-nitronaphthalene
No Data Available
CARB
ECD CRT
ECD-1
ECD-1 CRT
CNG1
CNG2

3-Ring n-PAH



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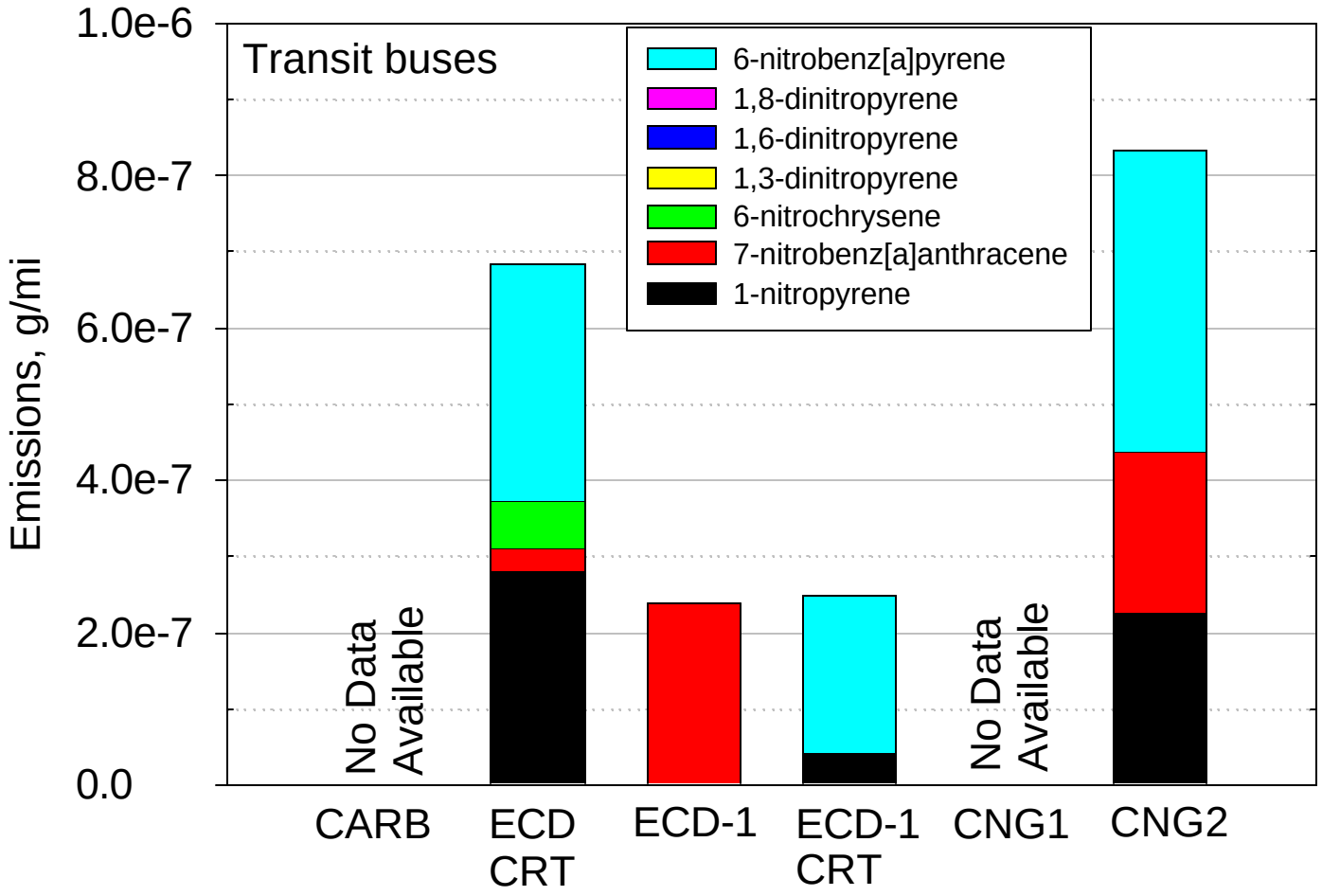
4-Ring n-PAH



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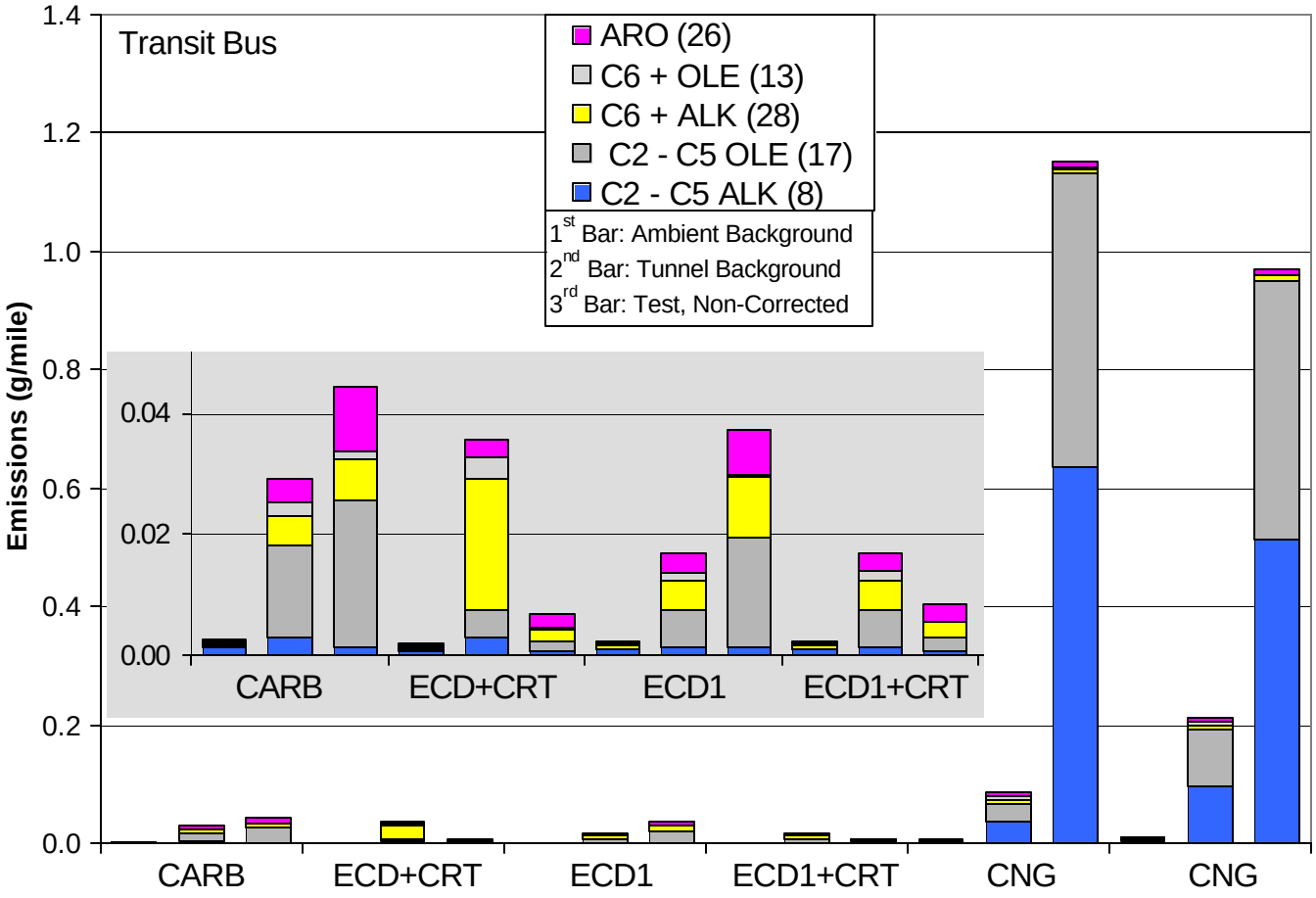
VOC's
(Grouped by Compound Classes)



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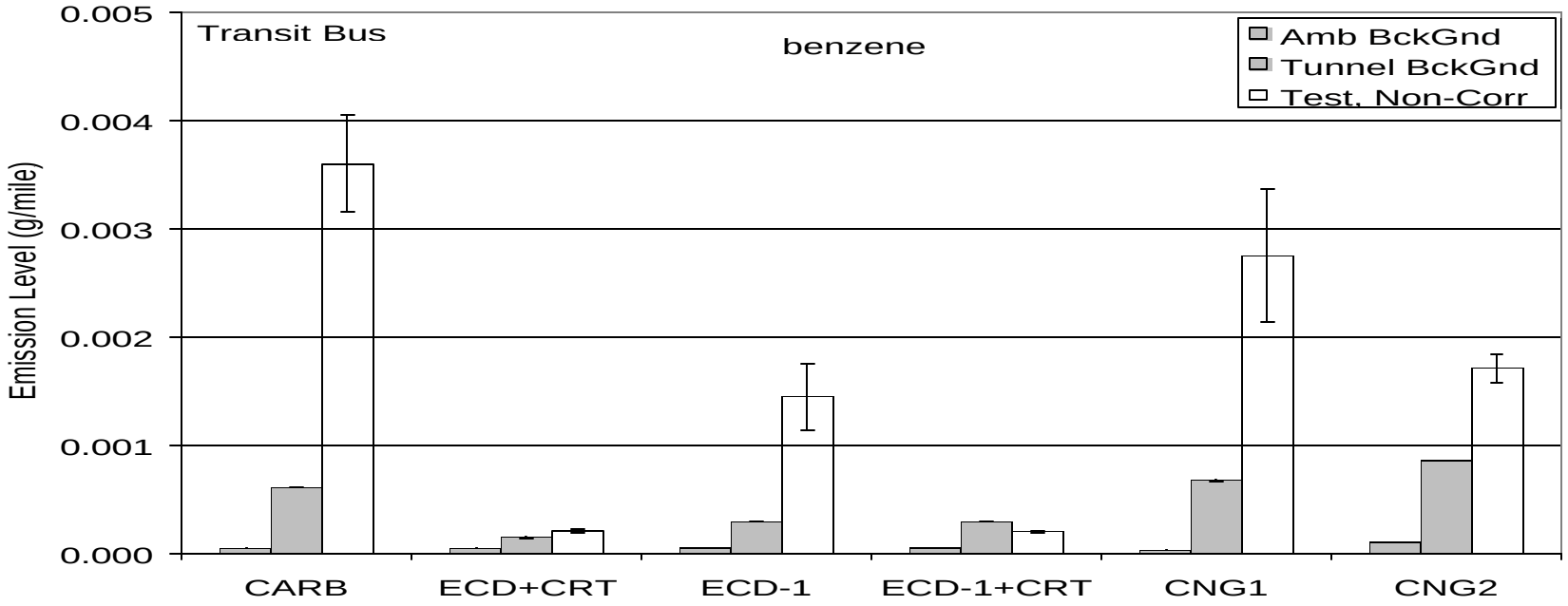
Benzene



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