Overview of Detailed Chemical Speciation and Particle Sizing for Diesel Exhaust, Both Real Time and Filter Based Measurements

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  - Cummins Engine Company, BP/ARCO, Lubrizol
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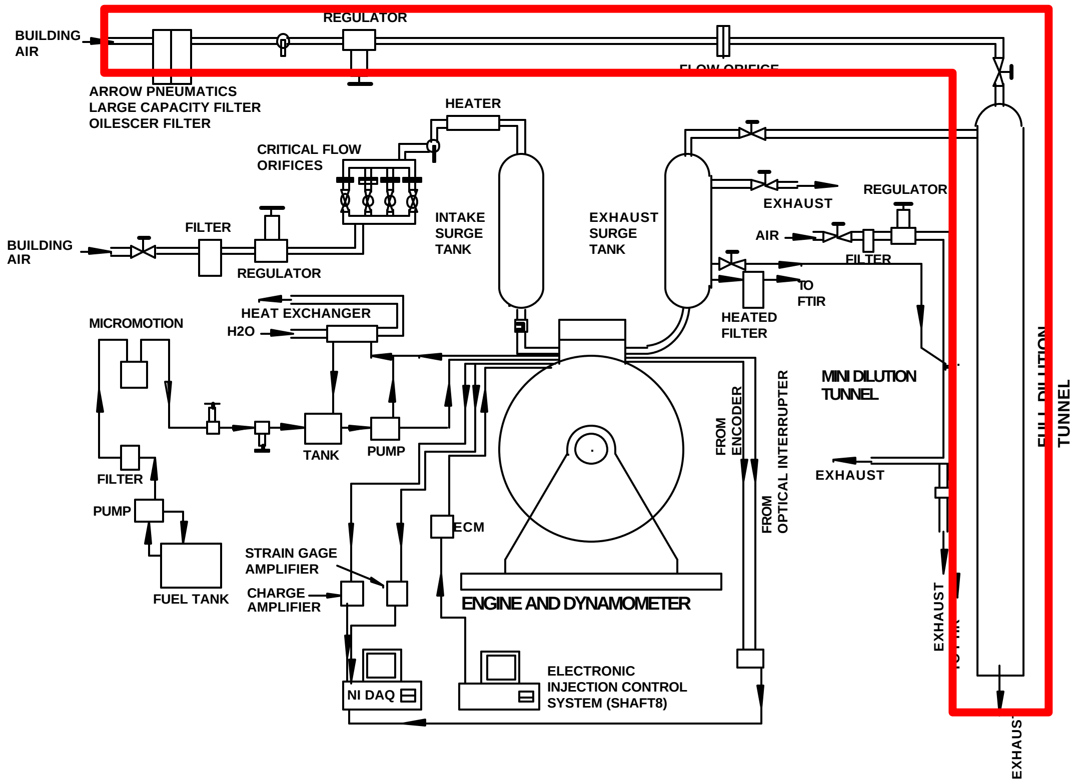
Objectives

- Develop methods that integrate advanced air pollution sampling and analysis techniques with state of the art engine research facilities
- Investigate the effects of changes in engine design and operating conditions, lubricants and fuels on physical and chemical properties of emissions
- Use these data on the detailed chemical composition of the engine emissions to enhance our understanding of subtle operational fundamentals of engine systems.
- Integrate this enhanced understanding into simulations through either correlations or fundamental relationships

Experimental Setup

Engine Bench Setup

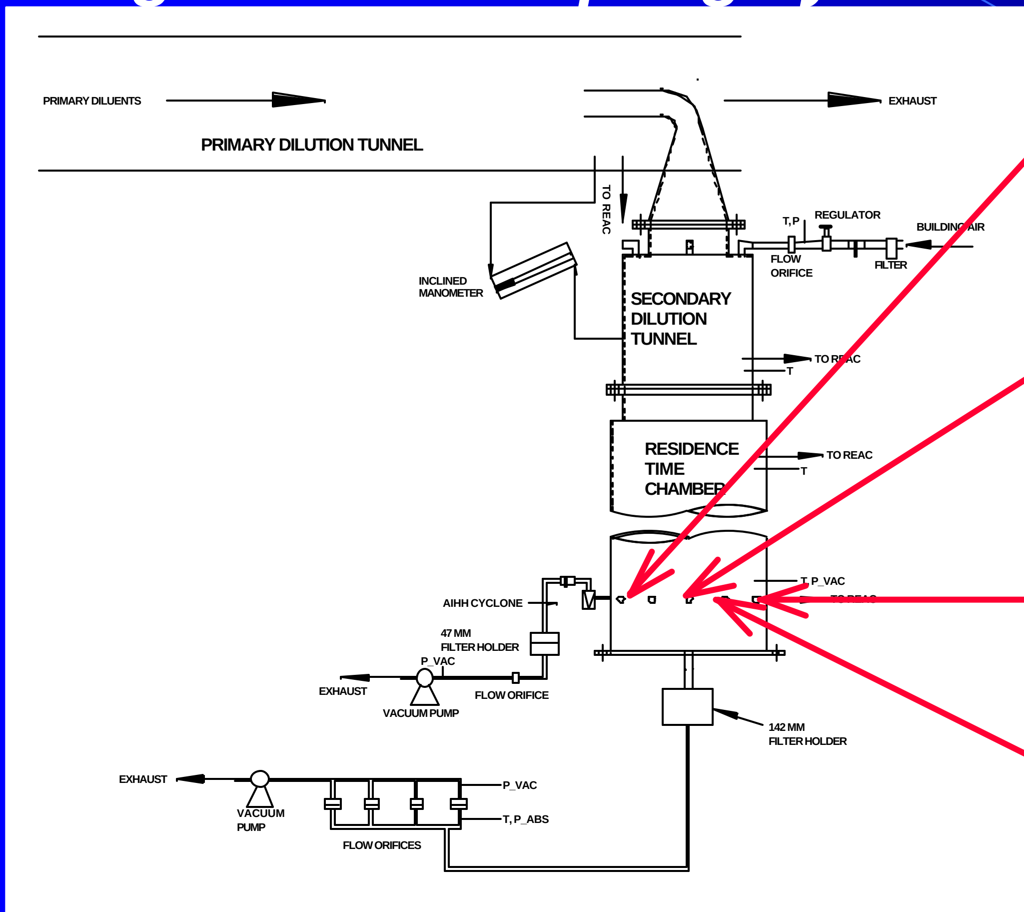


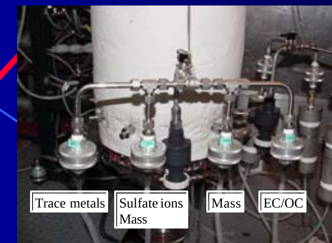
Engine Specs.

Engine Type	Cummins N14 Single Cylinder Diesel
Cycle	4-stroke
Combustion Chamber	Quiescent
Piston Chamber	Shallow Dish
Number of Intake Valves	2
Number of Exhaust Valves	2
Compression Ratio	13.1:1
Swirl Ratio	1.4
Displacement	2336 cc
Bore	139.7 mm
Stroke	152.4 mm
Combustion Chamber Diameter	97.8 mm
Connection Rod Length	304.8 mm
Piston Pin Offset	None
Injection System	Unit Injector, Direct Injection (DI)
Nozzle Dimension	$8 \times \Phi 0.2$ mm
Length/Diameter of holes (l/d)	4.1
Spray Angle	152°

Experimental Setup

Augmented sampling system





- Sulfate ions
- Trace metals
- EC/OC
- PM Con.

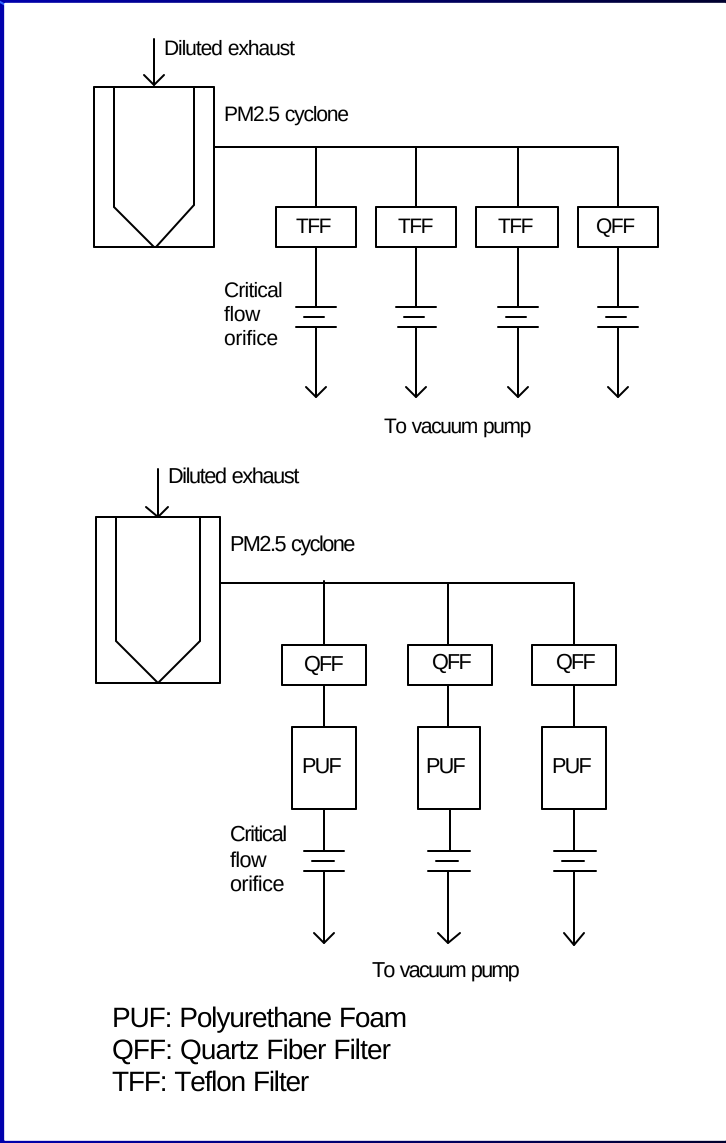
- Organics
- Semi-volatile organics

- Size dist.
  - number
  - mass
  - volume

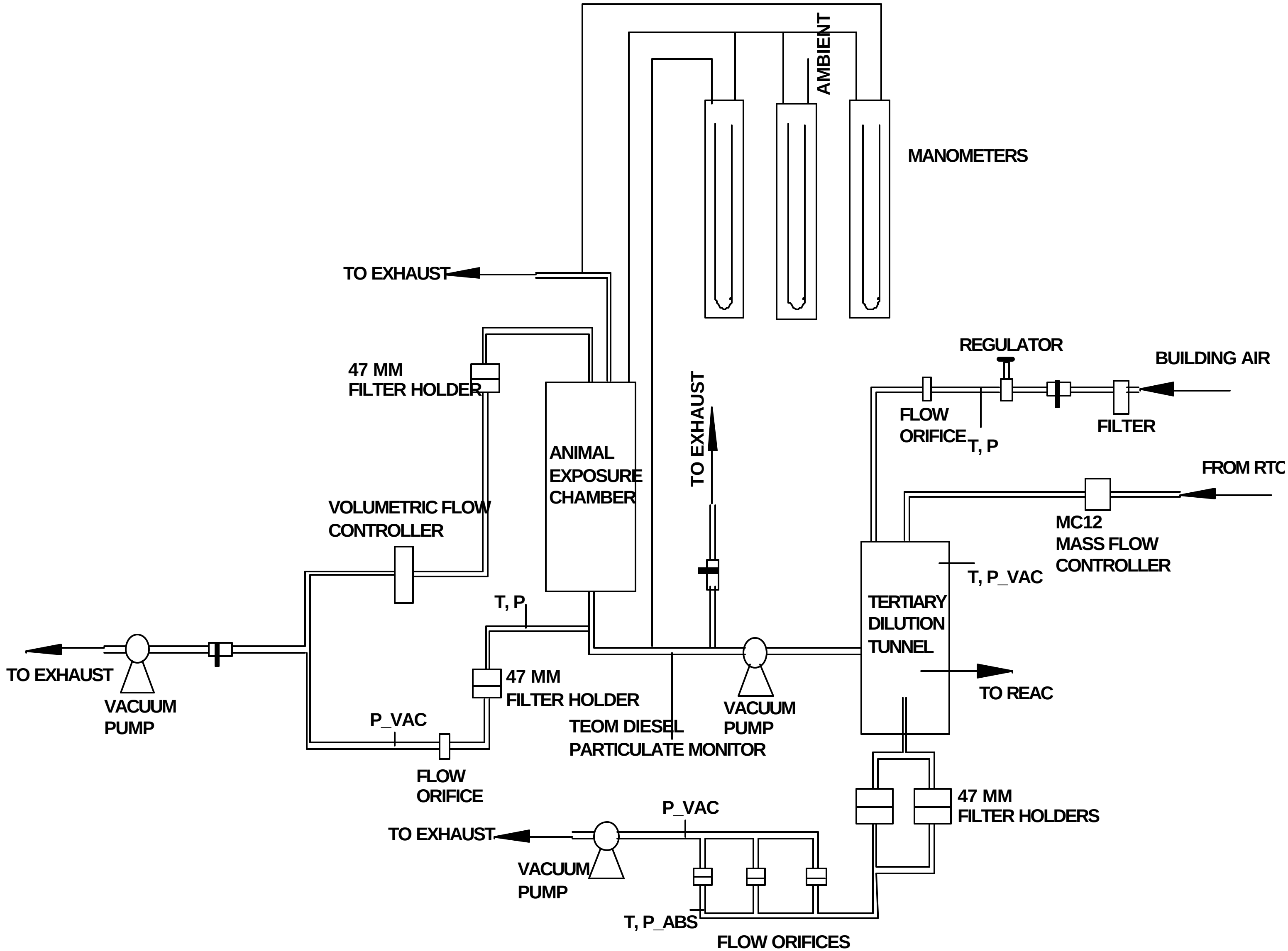
- Real-time PM
  - concentration
  - total mass
  - mass rate

Filter Sampling Systems

- PM2.5 Cyclone
- Teflon membrane filters
  - Gravimetric, sulfate ions, trace metals (ICPMS)
- Quartz fiber filter
  - EC/OC
- Quartz fiber filters
  - Particle phase organics
- Polyurethane filters (PUF)
  - Semi-volatile organic compounds



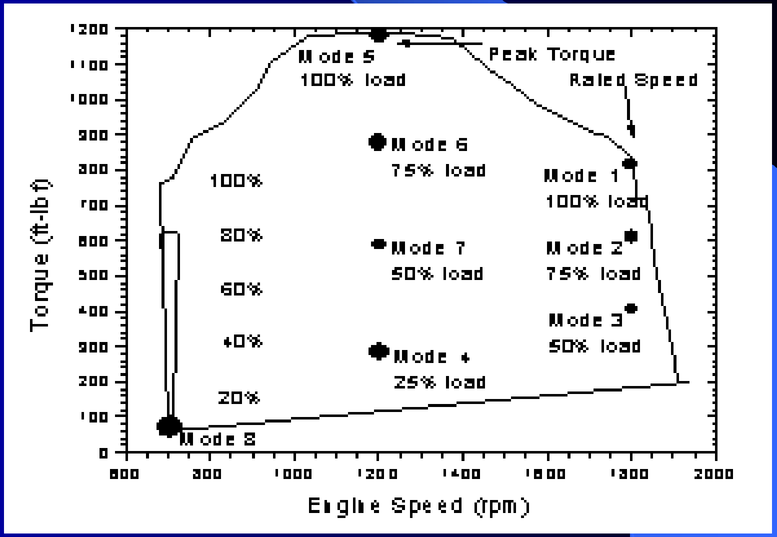
Animal Exposure Studies



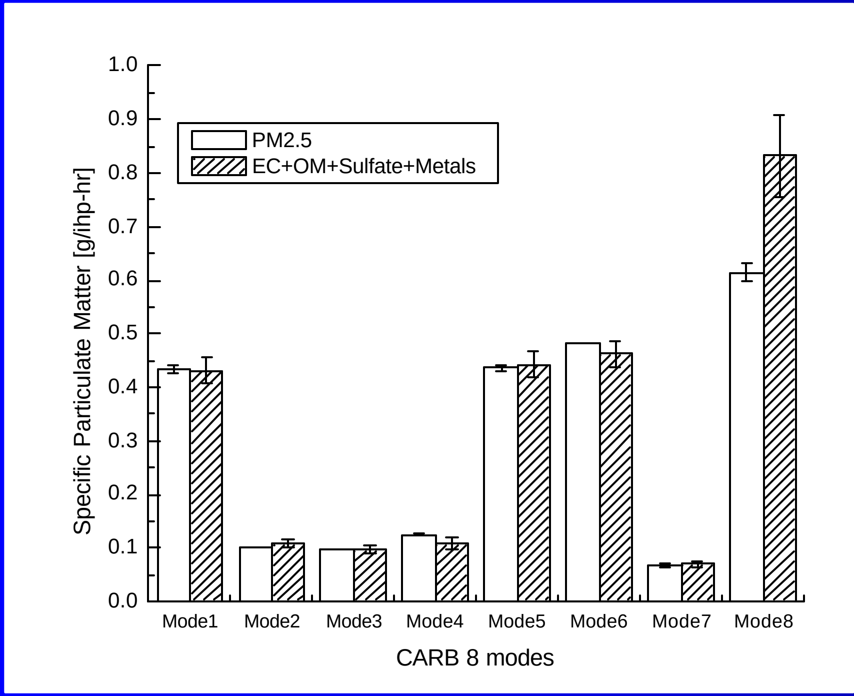
Fuels Tested and Operating Conditions

- Fuel 1 – Commercial Diesel Fuel
  - 352 ppm Sulfur
- Fuel 2 – EPA fuel 2006
  - 11 ppm Sulfur
- Fischer Tropsch fuel
  - Being tested now
- Primary testing was CARB 8 mode
  - A few additional operating conditions were examined

CARB 8 Modes



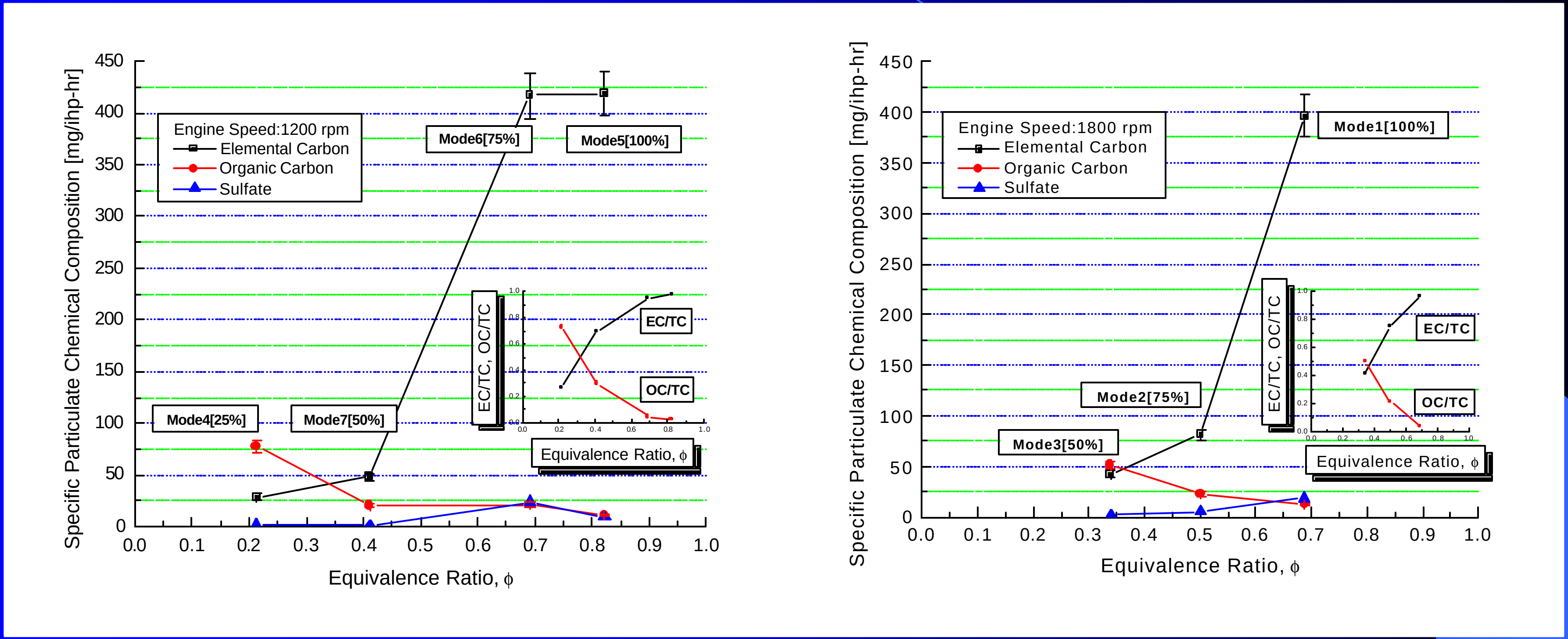
Comparison of Filter Mass Measurements and the Analytical EC/OC, Metals Measurements



Comparison of PM concentration and sum of EC, OC, sulfates, and metals of interest for CARB 8 modes.

- There is good agreement between the sum of EC-OC and the filter mass measurement.
- Mode 8 shows poor agreement – probably because the light load is subject to large uncertainty when emissions are reported as gm/hp-hr

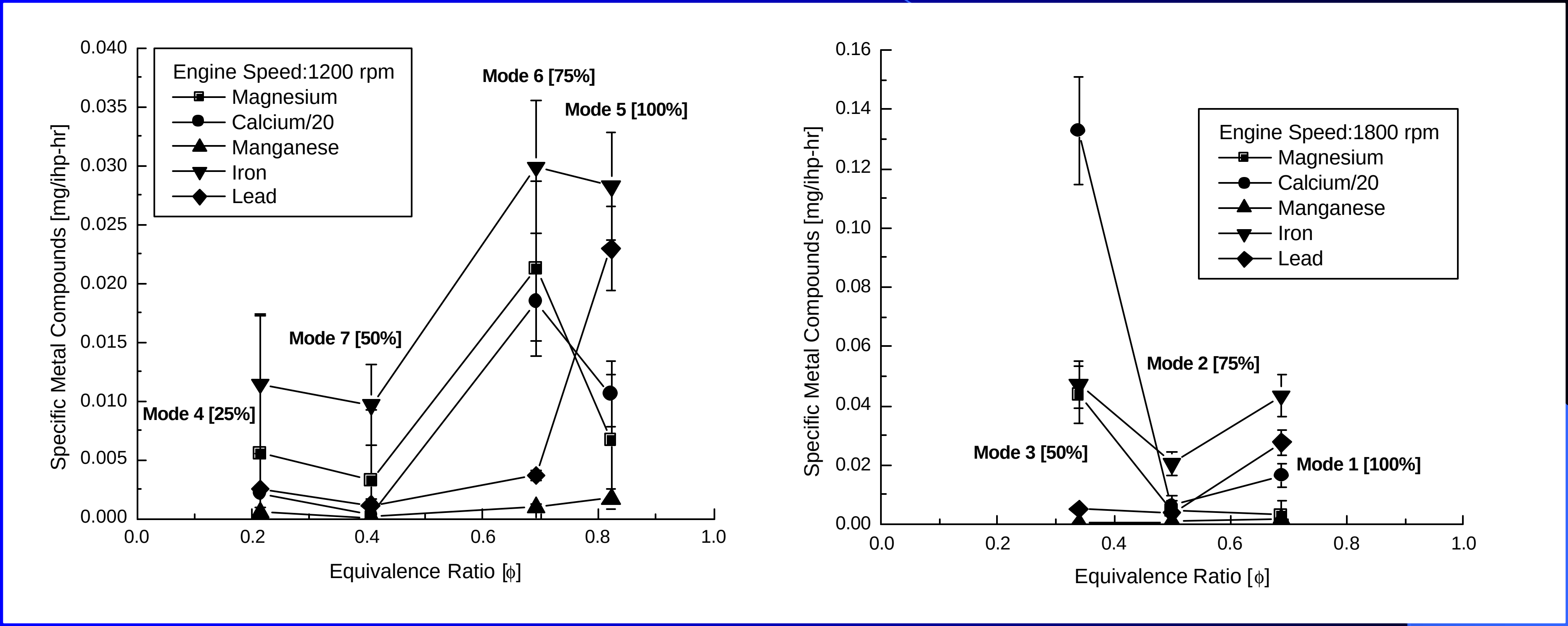
EC, OC and Sulfates vs Load Fuel 1



•Specific elemental carbon, organic carbon, and sulfates versus equivalence ratio at the engine speeds of 1200 rpm(left) and 1800 rpm (right).

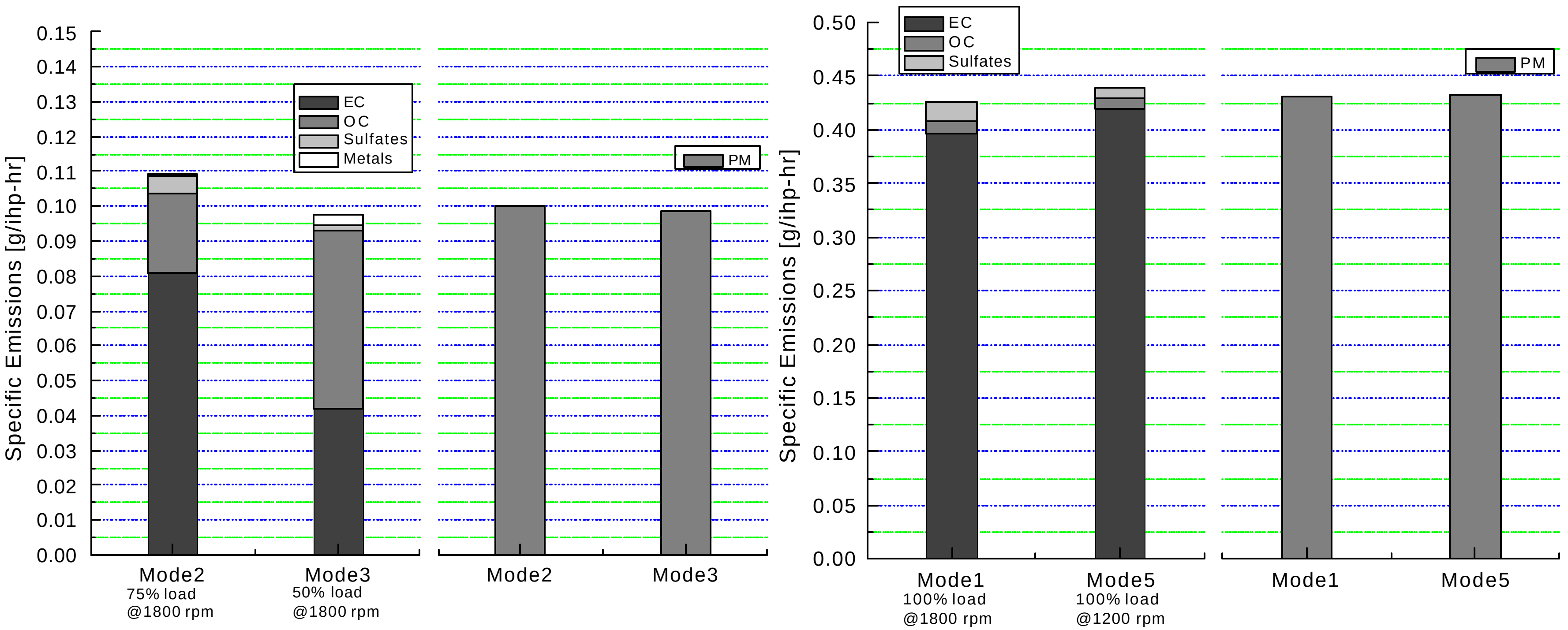
•Observe the shift is EC, OC and Sulfates with engine load

Metals Loading vs Load Fuel 1



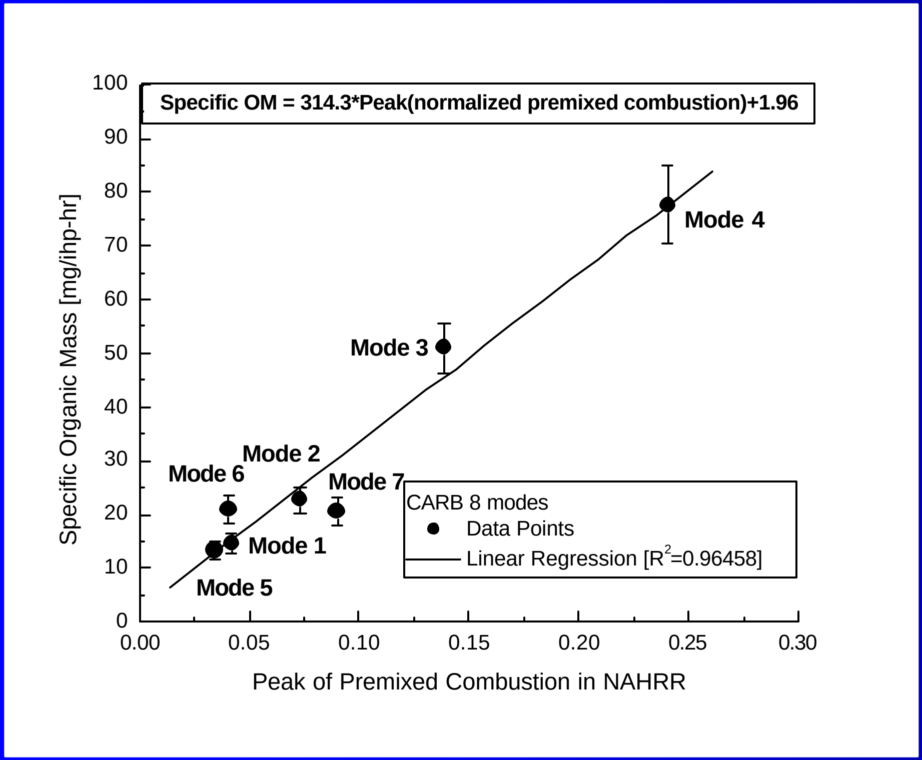
- Specific metal compounds versus equivalence ratio at the engine speeds of 1200 rpm (left) and 1800 rpm (right)
- Significant variation in metals loading with changes in load
- Trace metals, ex. Ca, can be correlated with oil consumption
- Iron is probably from engine wear

Particulate Composition Different Operating Conditions with Similar Particulate Loading



- Comparison of the PM and the sum of EC, OC, sulfates, and metals when two different operating conditions exhibit almost the same PM concentrations
- Similar particulate loads may have very different chemical composition

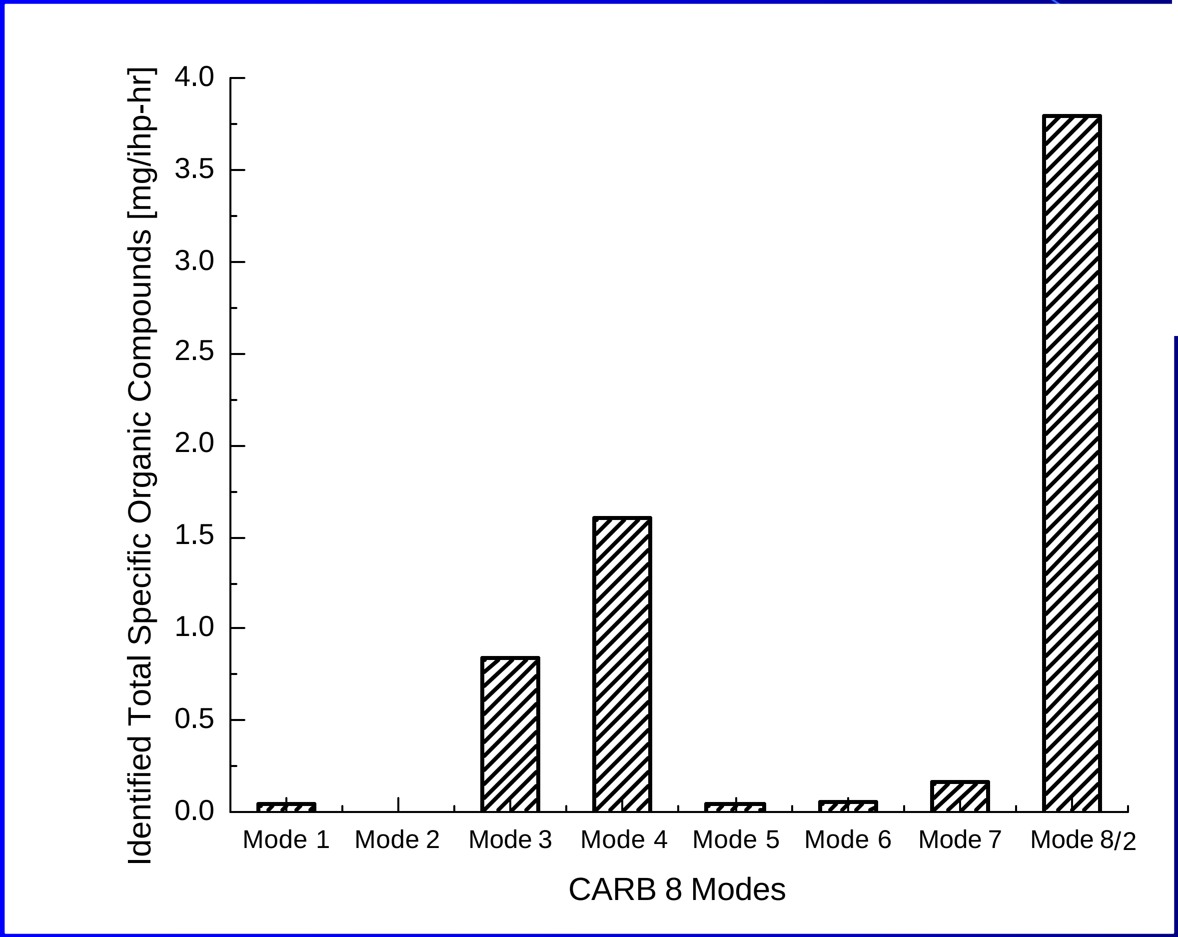
Organic Carbon for Different Operating Conditions

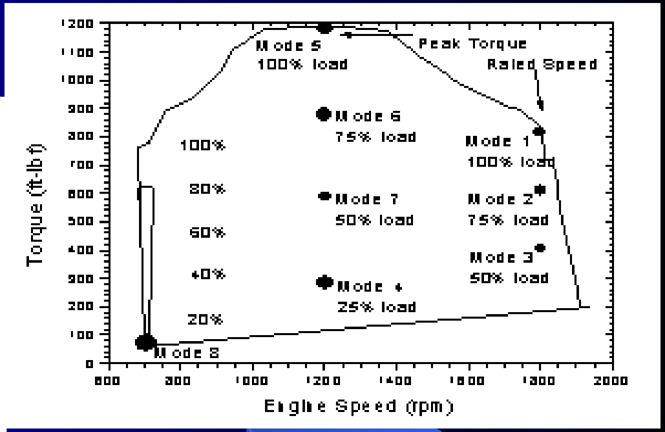


Specific organic carbon as a function of the peak value of the premixed combustion of the normalized apparent heat release rate (NAHRR).

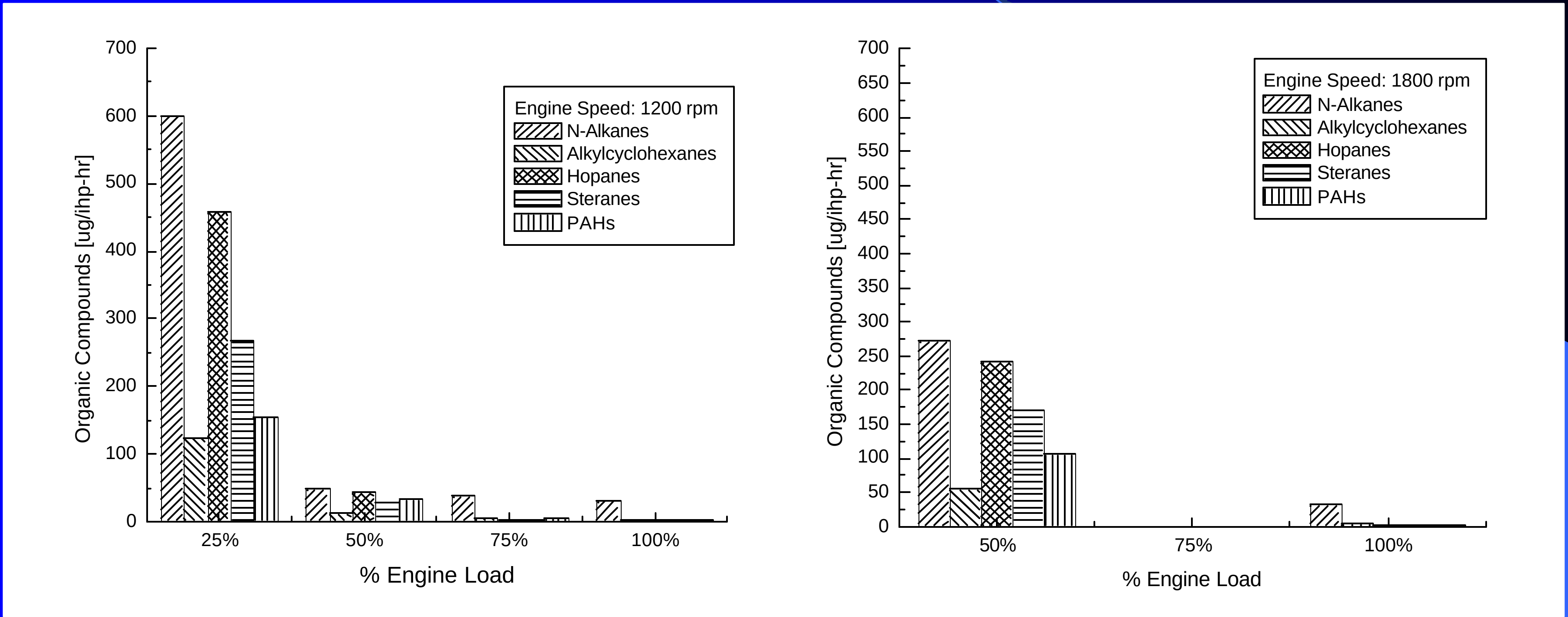
- The appears to be a correlation between the premixed burn fraction and the organic carbon content
- This correlation appears to hold over all ranges of speeds and loads tested

Mass of Organic Compounds Measured at Each Operating Mode



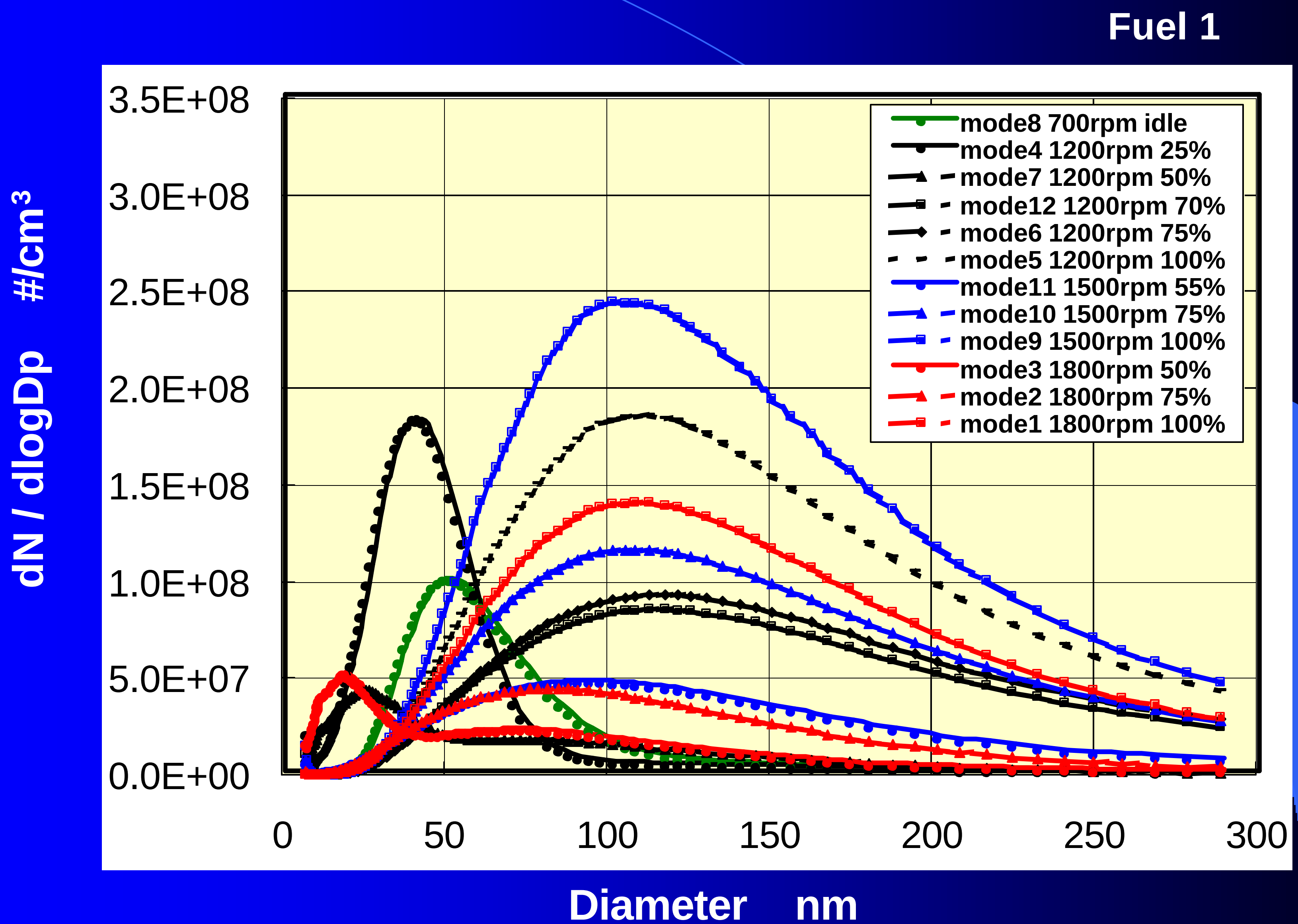


Distribution of Chemical Compounds in Organic Component



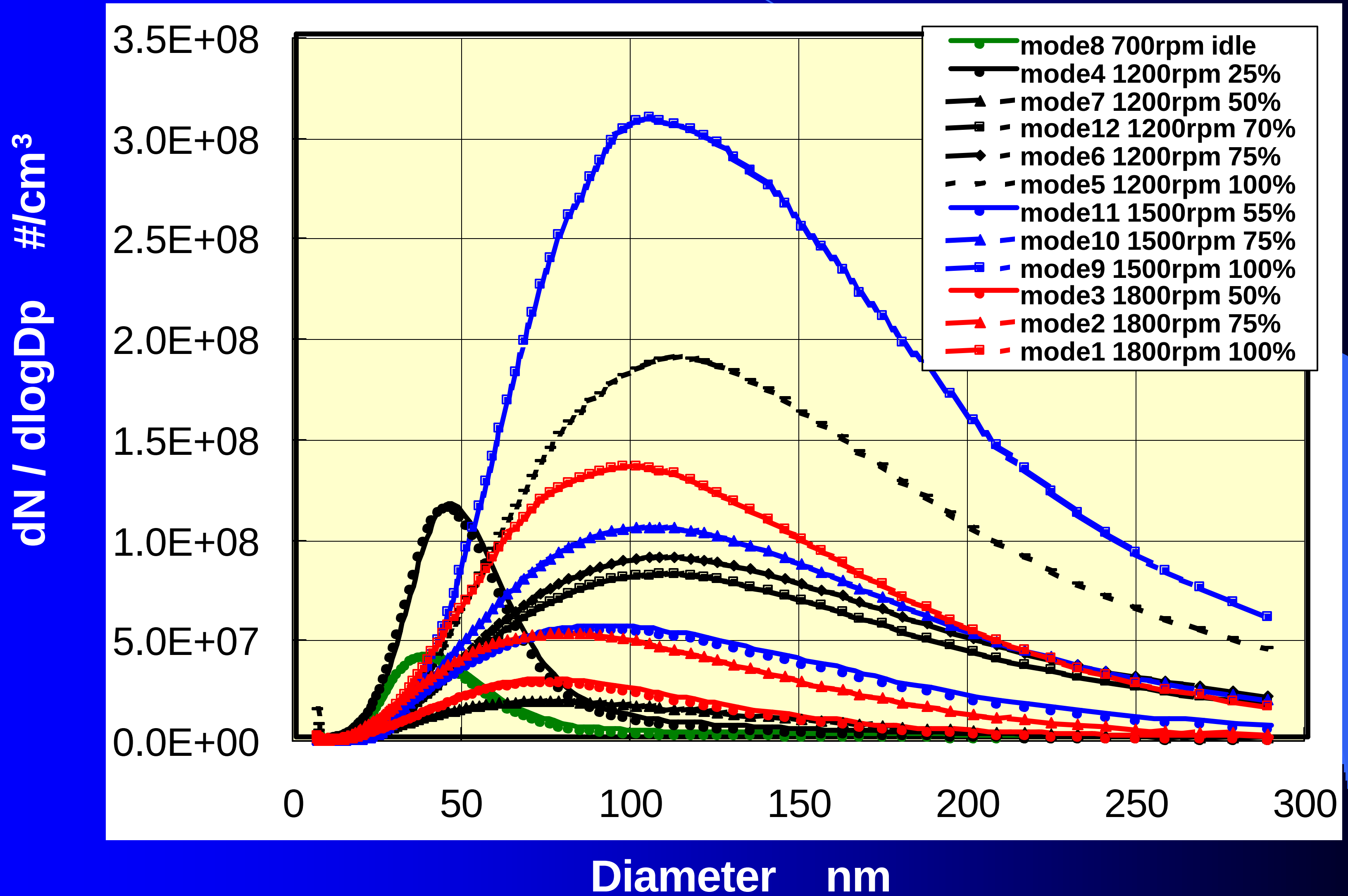
•Specific species identification within each class of compounds are also available

12 modes


Fuel 1
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
0
50
100
150
200
250
300
dN / dlogDp #/cm3
Diameter nm
mode8 700rpm idle
mode4 1200rpm 25%
mode7 1200rpm 50%
mode12 1200rpm 70%
mode6 1200rpm 75%
mode5 1200rpm 100%
mode11 1500rpm 55%
mode10 1500rpm 75%
mode9 1500rpm 100%
mode3 1800rpm 50%
mode2 1800rpm 75%
mode1 1800rpm 100%

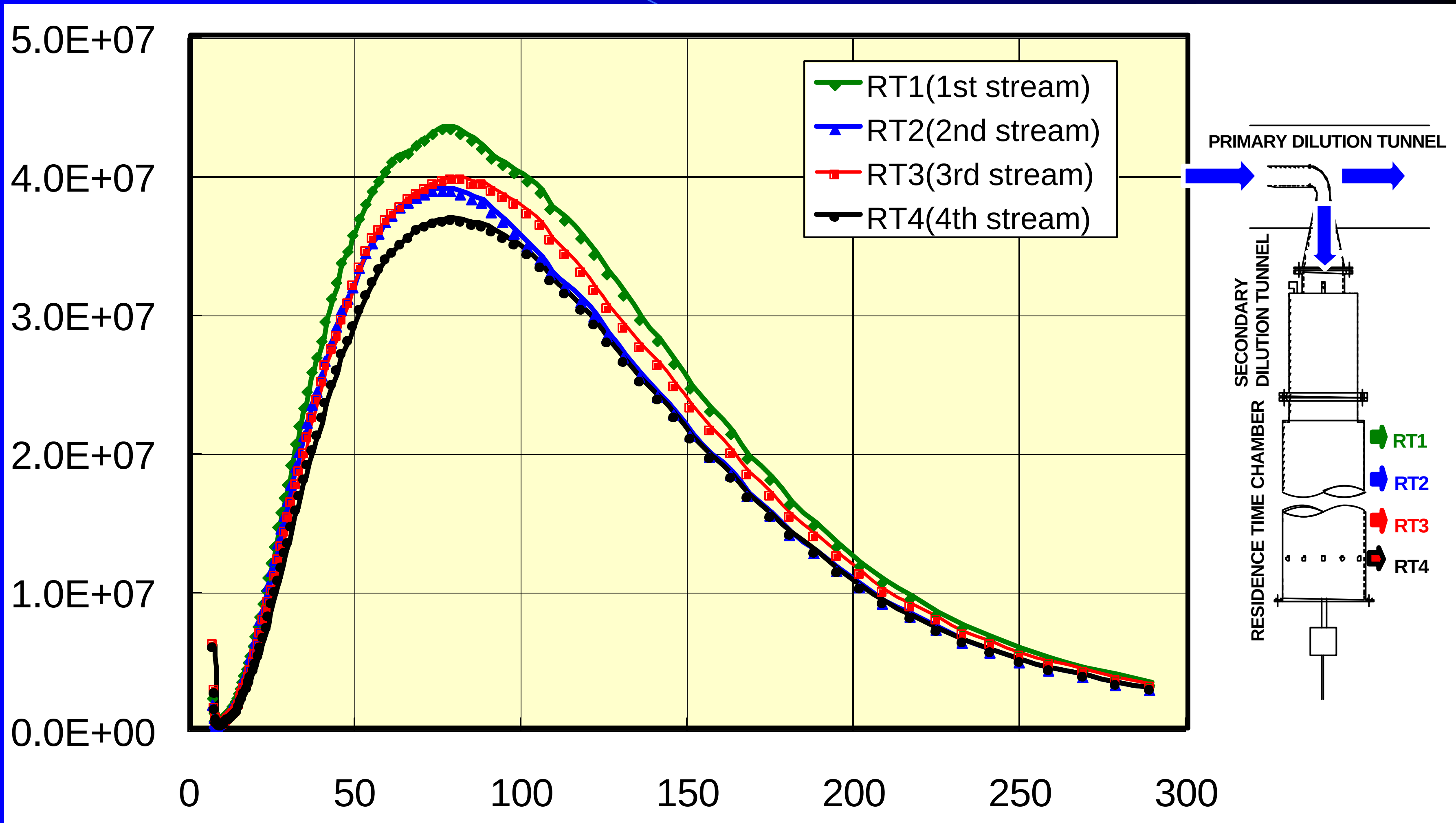
12 modes

Fuel 2



Residence Time Change

Dilution Ratio 18.1
Mode 2
Fuel 1

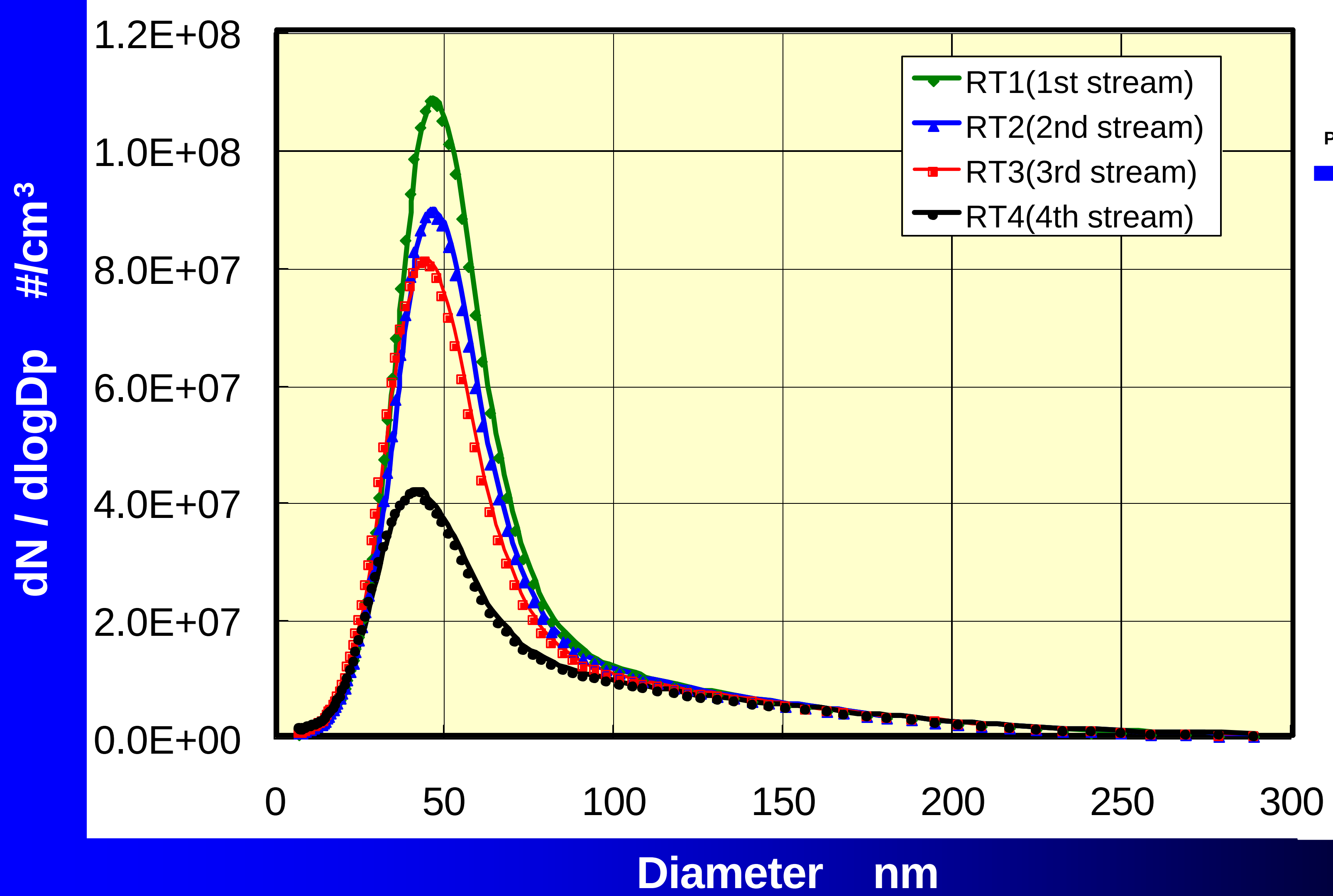


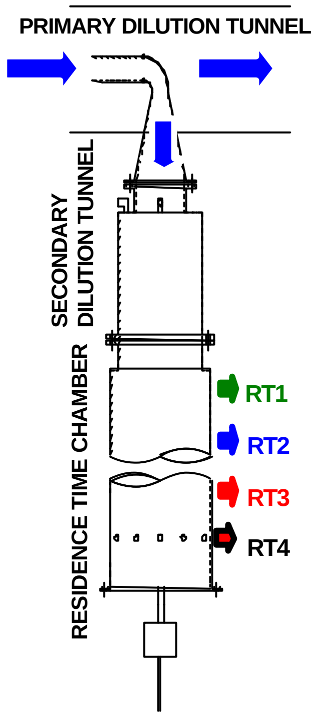
dN / dlogDp #/cm^3

Diameter nm

Residence Time Change

Dilution Ratio 20.0
Mode 4
Fuel 2

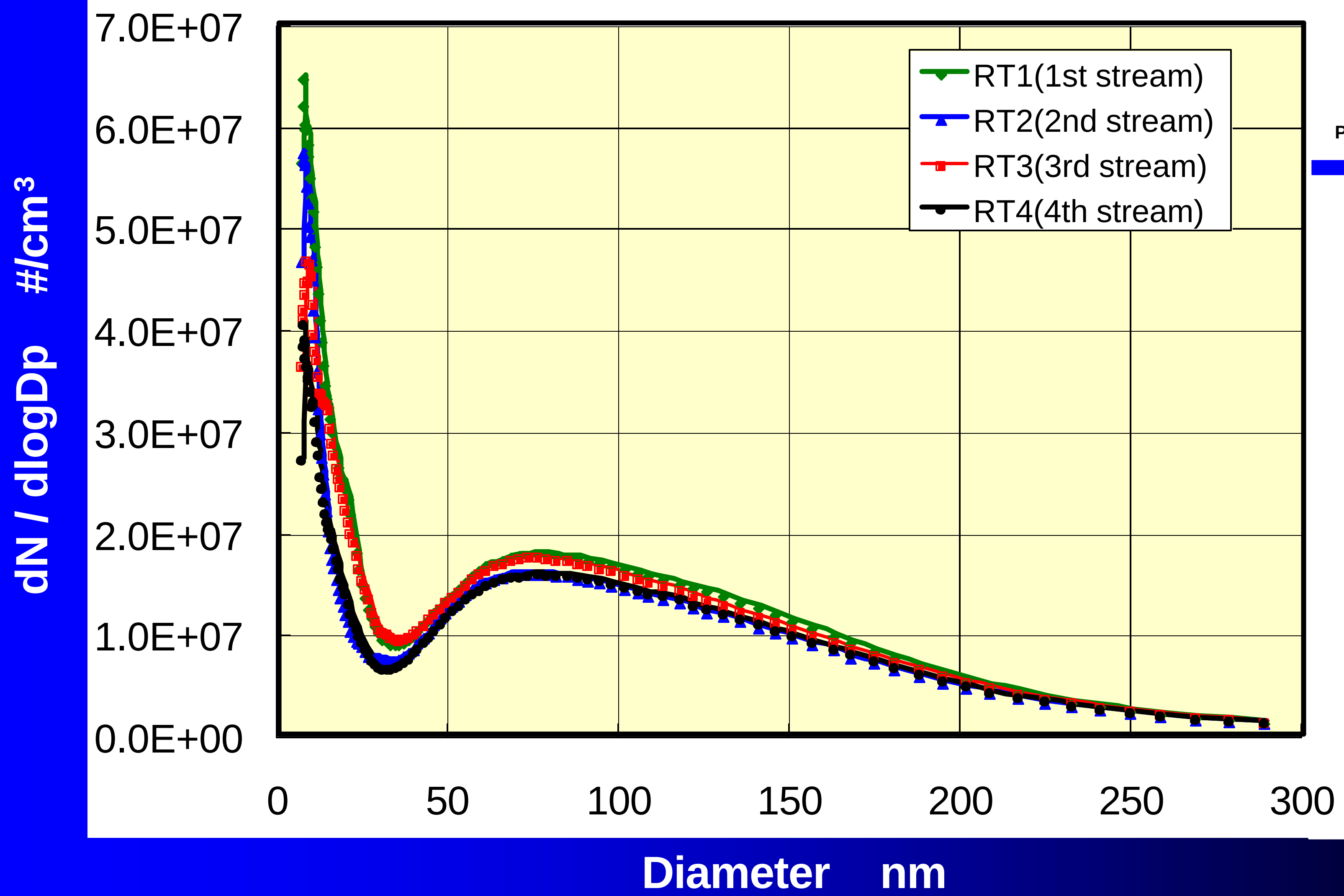


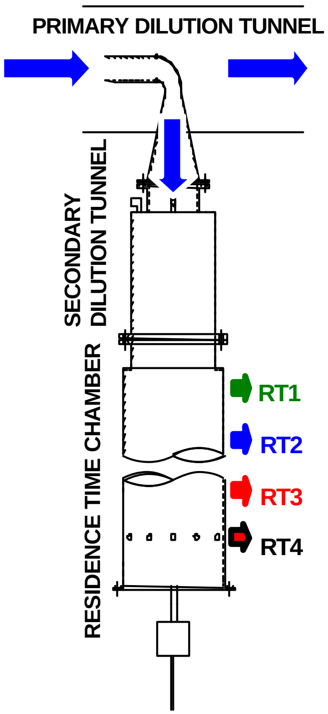


31.0sec
37.3sec
43.5sec
51.6sec

Residence Time Change

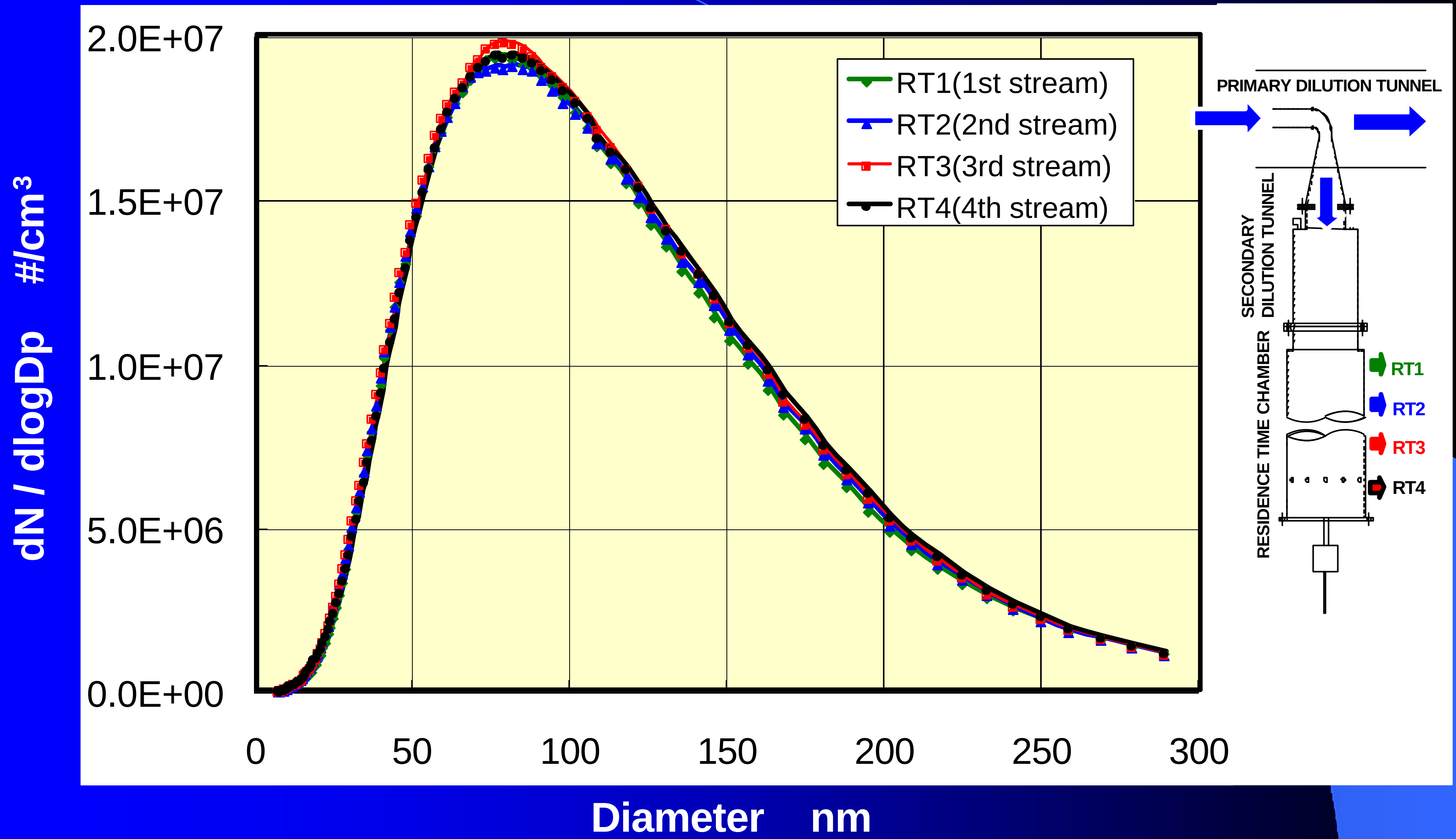
Dilution Ratio 25.1
Mode 7
Fuel 1





Residence Time Change

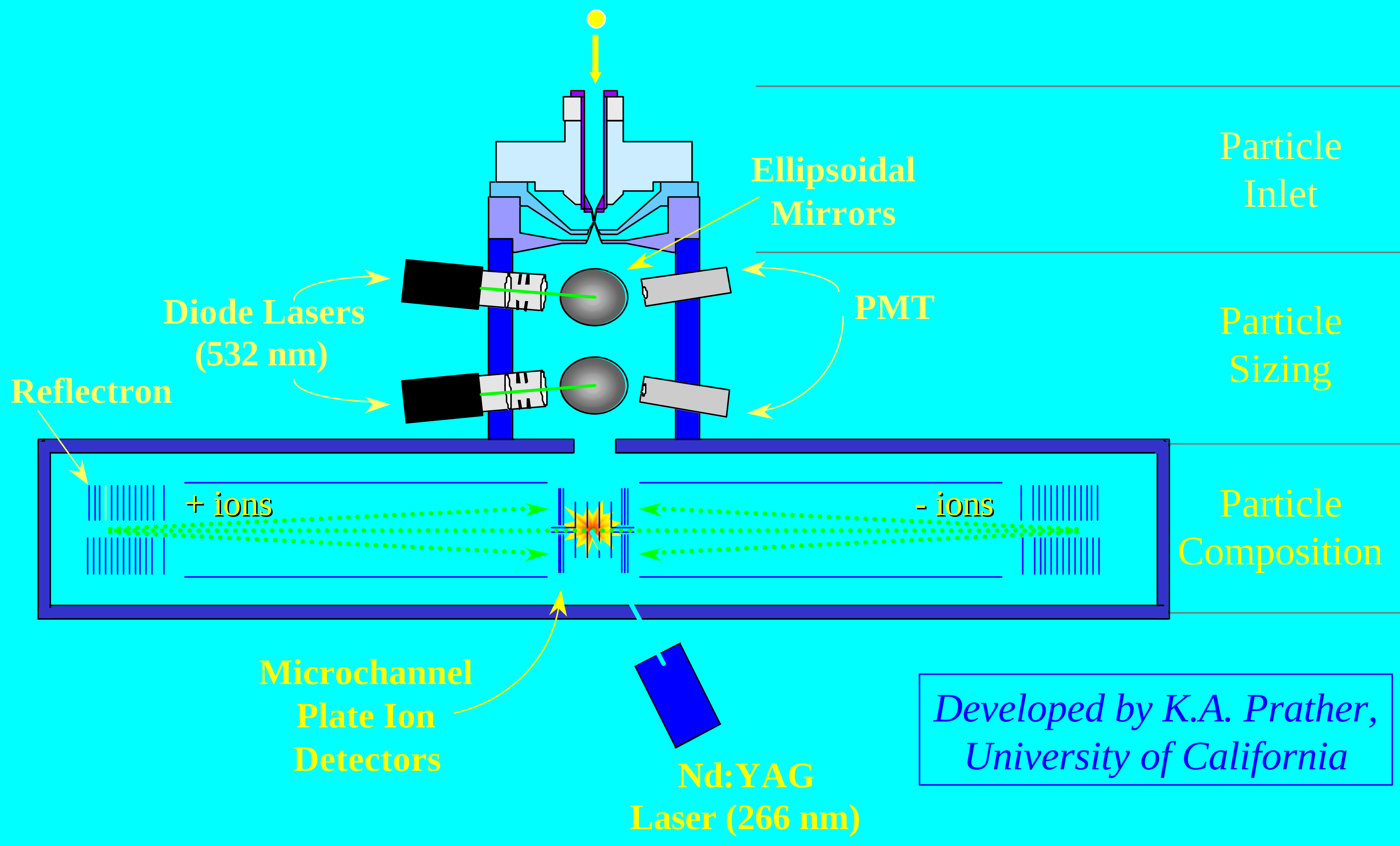
Dilution Ratio 19.5
Mode 7
Fuel 2



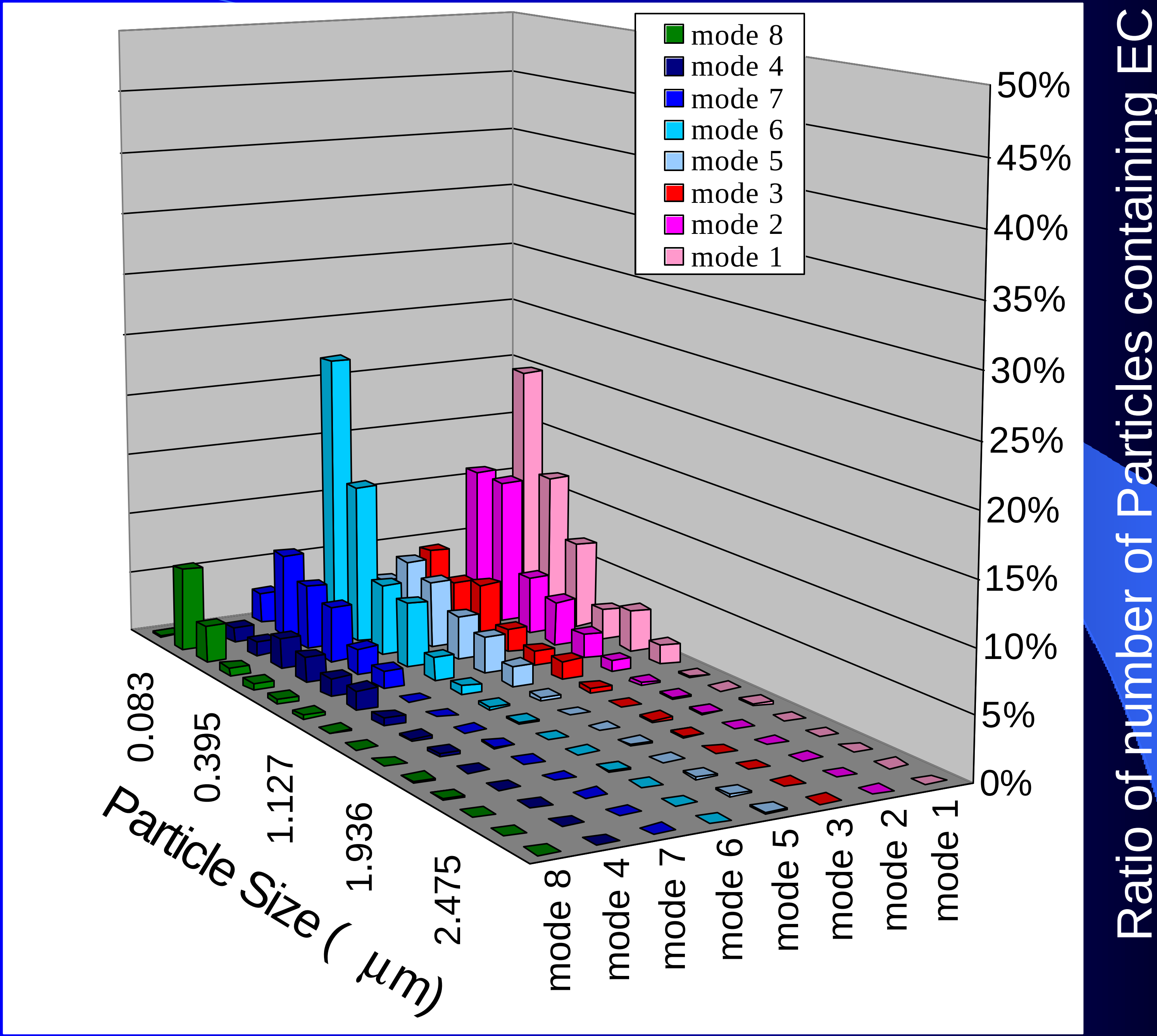
ATOFMS Background

- Aerosol Time-of-Flight Mass Spectrometry (ATOFMS)
- Single Particle Mass Spec Instruments have been developed over the past decade
  - Real time instruments : 100 – 150 particles per minute
  - Size individual particles: 0.15 to 5.0 μm
  - Semi-quantitative measure of individual particle chemical composition
  - Portable
- ATOFMS was developed at UC-Riverside under the direction of Prof. Kim Prather
- ATOFMS was commercialized by TSI in 1999

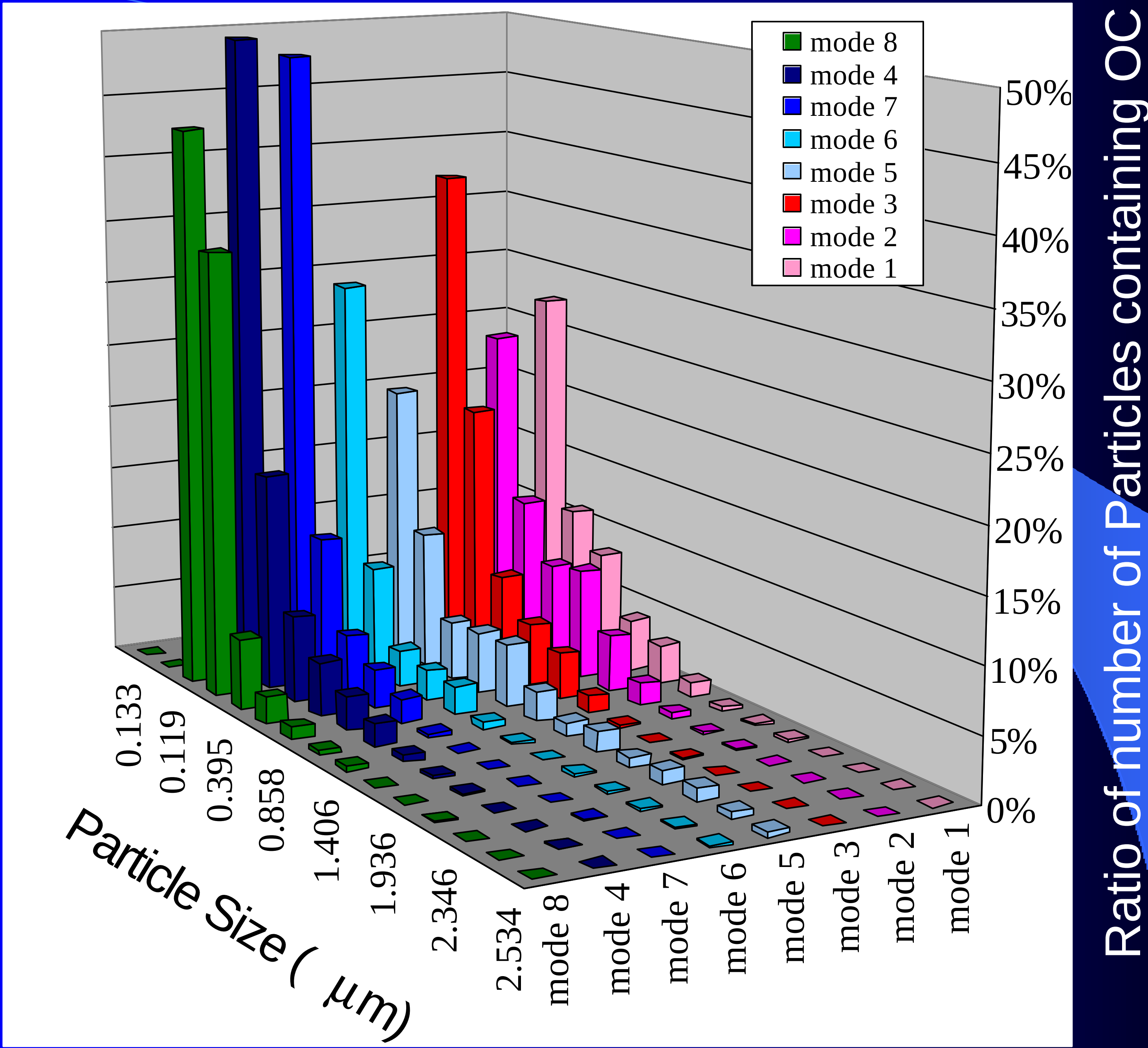
Aerosol Time-of-Flight Mass Spectrometry



Developed by K.A. Prather, University of California



mode 8
mode 4
mode 7
mode 6
mode 5
mode 3
mode 2
mode 1
50%
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%
0.083
0.395
1.127
1.936
2.475
Particle Size (μm)
mode 8
mode 4
mode 7
mode 6
mode 5
mode 3
mode 2
mode 1
Ratio of number of Particles containing EC


mode 8
mode 4
mode 7
mode 6
mode 5
mode 3
mode 2
mode 1
50%
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%
0.133
0.119
0.395
0.858
1.406
1.936
2.346
2.534
Particle Size (µm)
mode 8
mode 4
mode 7
mode 6
mode 5
mode 3
mode 2
mode 1
Ratio of number of Particles containing OC

Summary of Data for the Single Cylinder Research Engine

- Data is still being analyzed
- There are large differences in the chemical composition of the particulates as the engine operating conditions are changed
- Operating conditions with similar particulate loading can have very different chemical compositions
- Small nano-particle formation is strongly dependent on time history of exhaust gas system before sampling
- There may be correlations between particle size and chemical composition