Real-time Measurements of Metallic Ash Emissions from Engines

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Real time ash measurements
Outline

- **Introduction**
  - Why do we care about ash?
  - How do they form
    - Metals in lube oil – typically 0.5% metal, Ca, Zn, Mg,..
    - Wear metals
  - Structure and size
  - Oil consumption pathways
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- New issues
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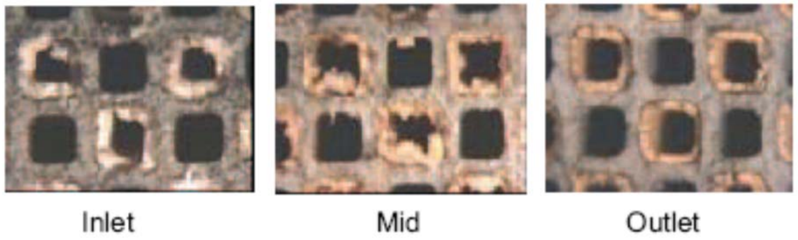
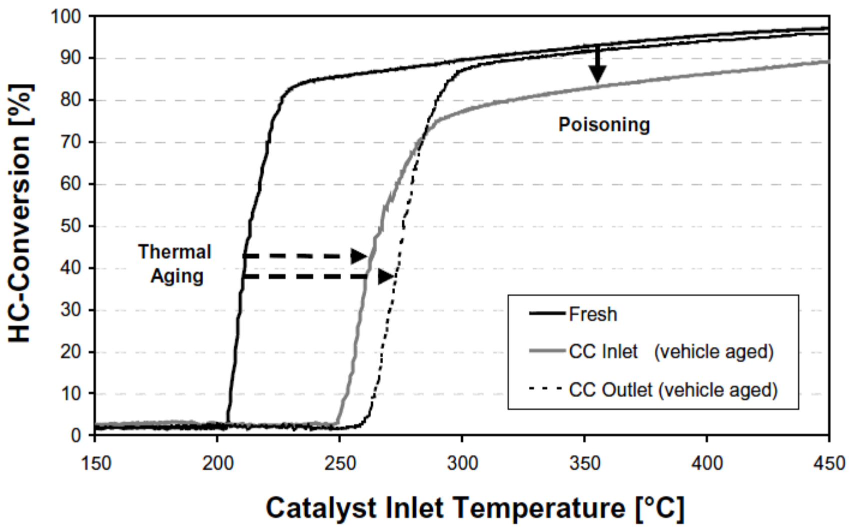
Importance of ash emissions

- Diesel engines - build-up and plugging of DPF
  - Increased pressure drop - eventually
  - Reduction of useful filter life, increased cleaning frequency
- Gasoline engines
  - Deposition in 3-way catalyst leads to poisoning
  - Same issues as diesel if GPF used
  - Solid nanoparticle emissions if GPF not used, especially with metallic additives
- Relationship to engine lube oil consumption mechanisms

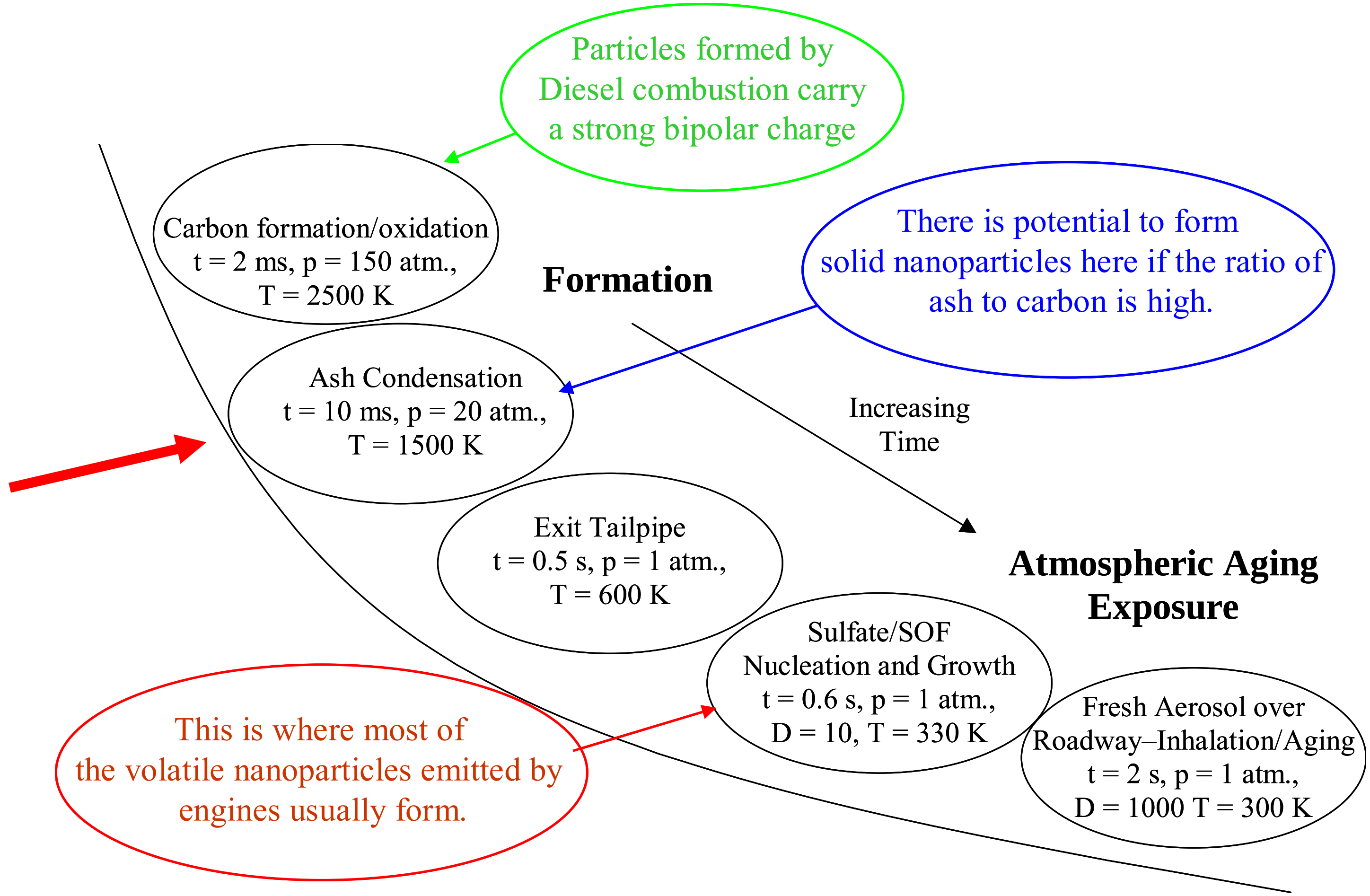


Ash distribution in exhaust filter channels (Heibel and Bhargava, 2007)



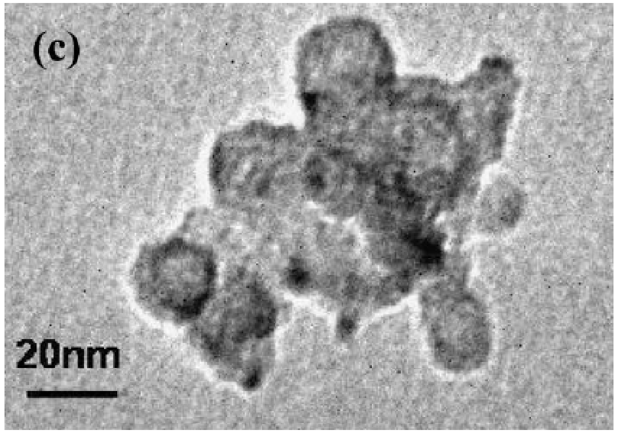
3-way catalyst poisoning by ash deposits (Franz, et al., 2005)

Particle formation history – 2 s in the life of an engine exhaust aerosol

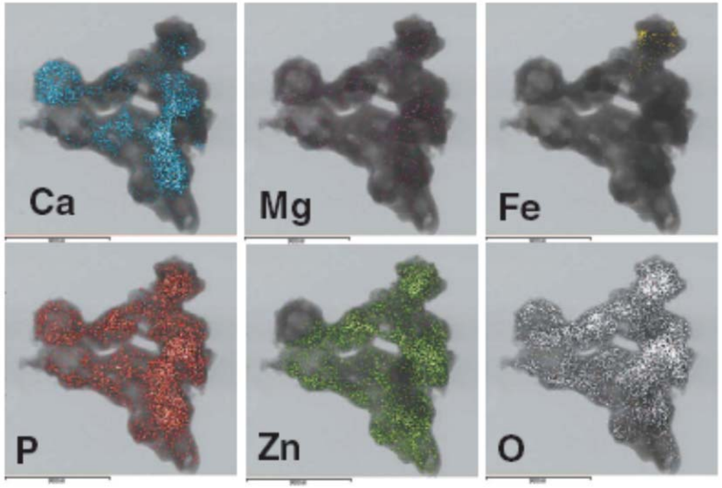


Kittelson, D. B., W. F. Watts, and J. P. Johnson 2006. “On-road and Laboratory Evaluation of Combustion Aerosols Part 1: Summary of Diesel Engine Results,” Journal of Aerosol Science 37, 913–930.

Engine ash emissions

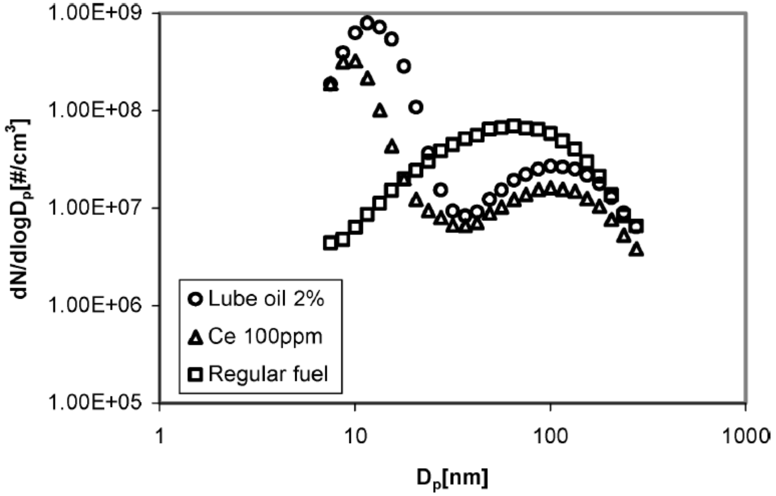


Jung, et al., 2005



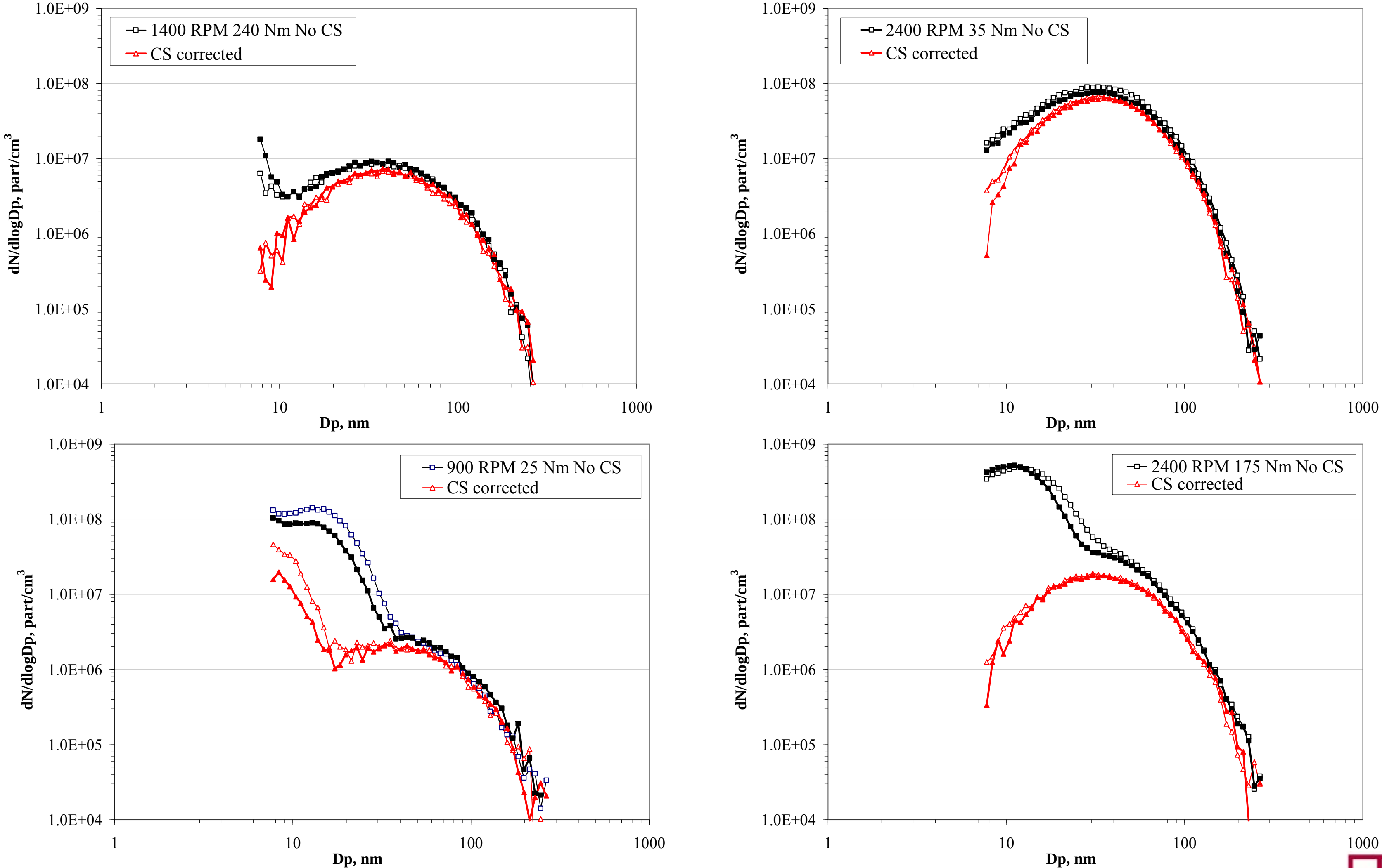
Sappok and Wong, 2007

- Non-combustible fraction of diesel aerosol
- Derived from metallic lube oil additives and engine wear metals
- Metallic particles tend to 'decorate' carbonaceous exhaust particles
- But form separate particles at sufficiently high metal to soot ratios



Jung and Kittelson, 2005

Catalytic stripper measurements - nuclei mode usually volatile but shows nonvolatile (ash) core at light load
4.5 liter Tier 4 offroad diesel engine



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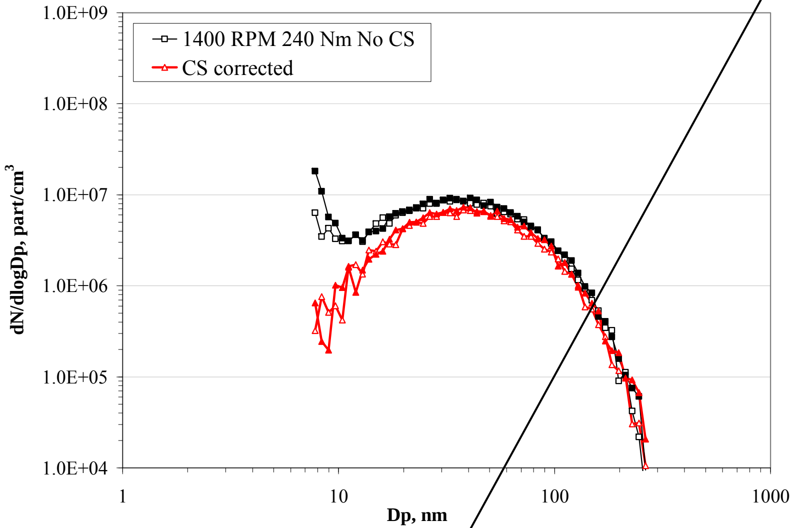
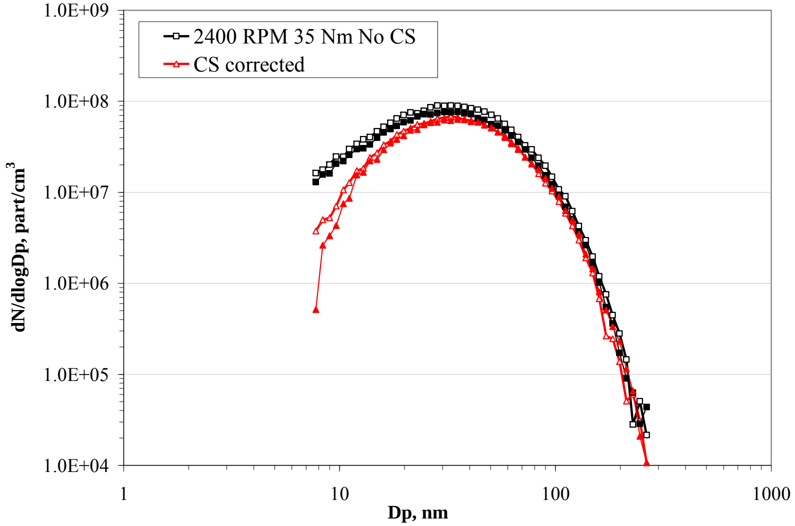
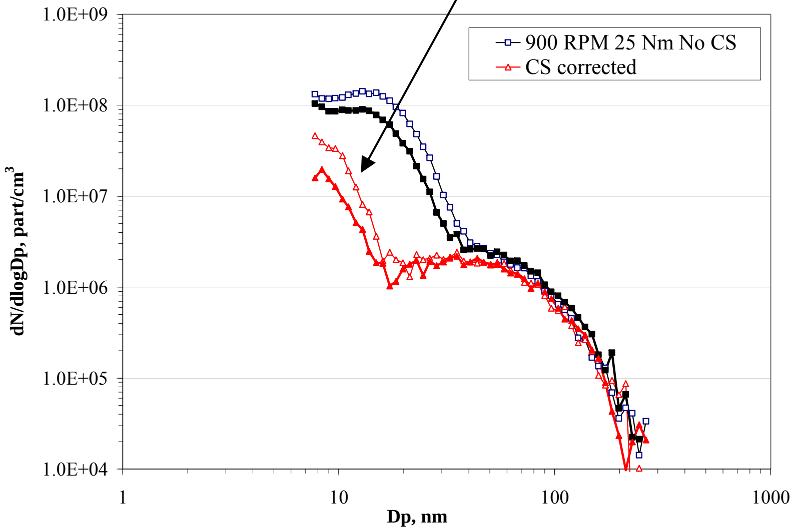
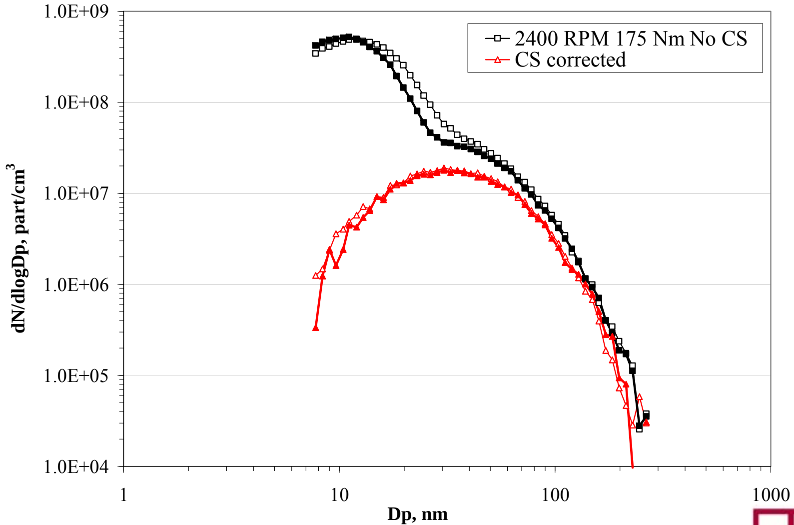
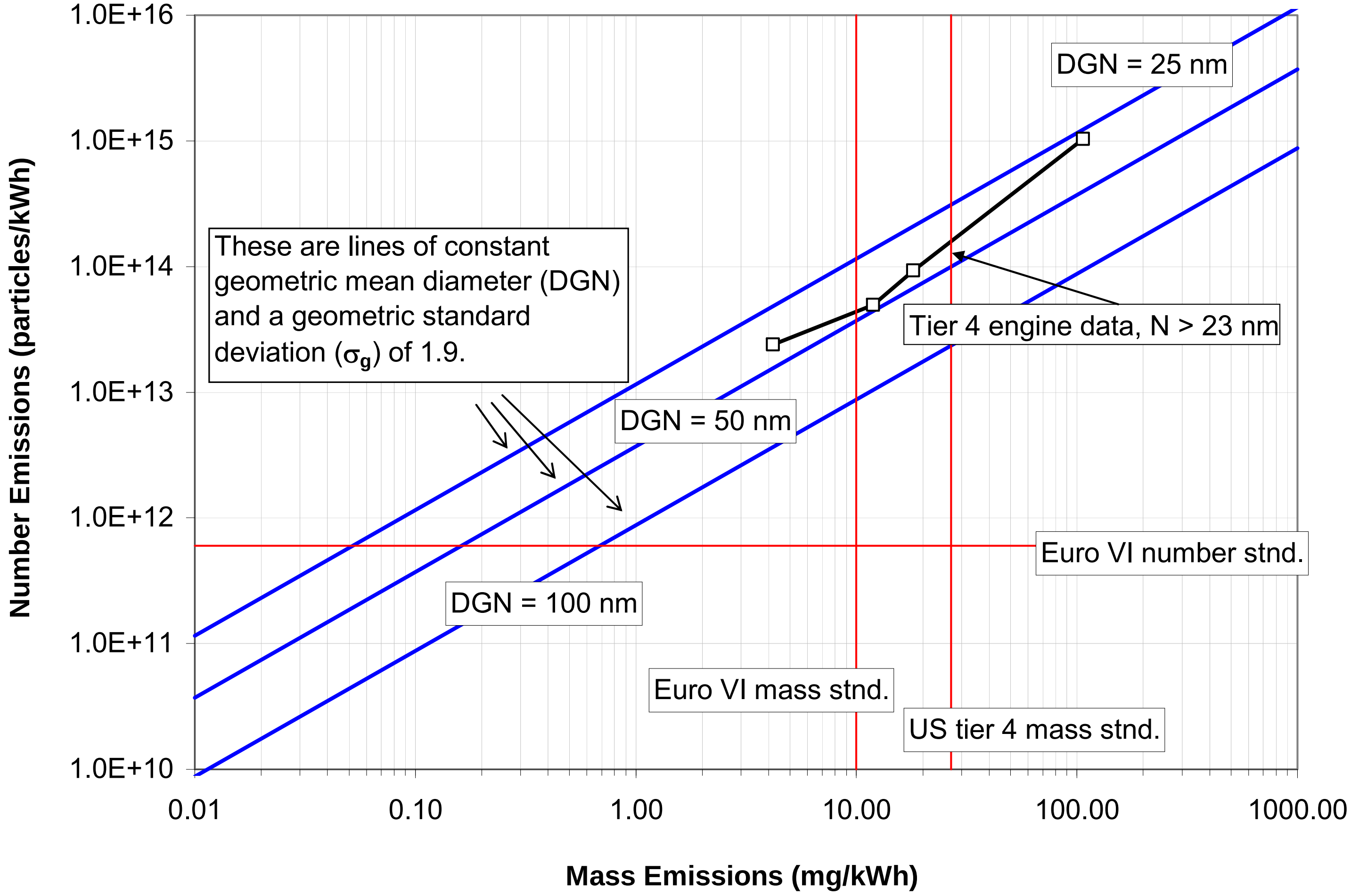




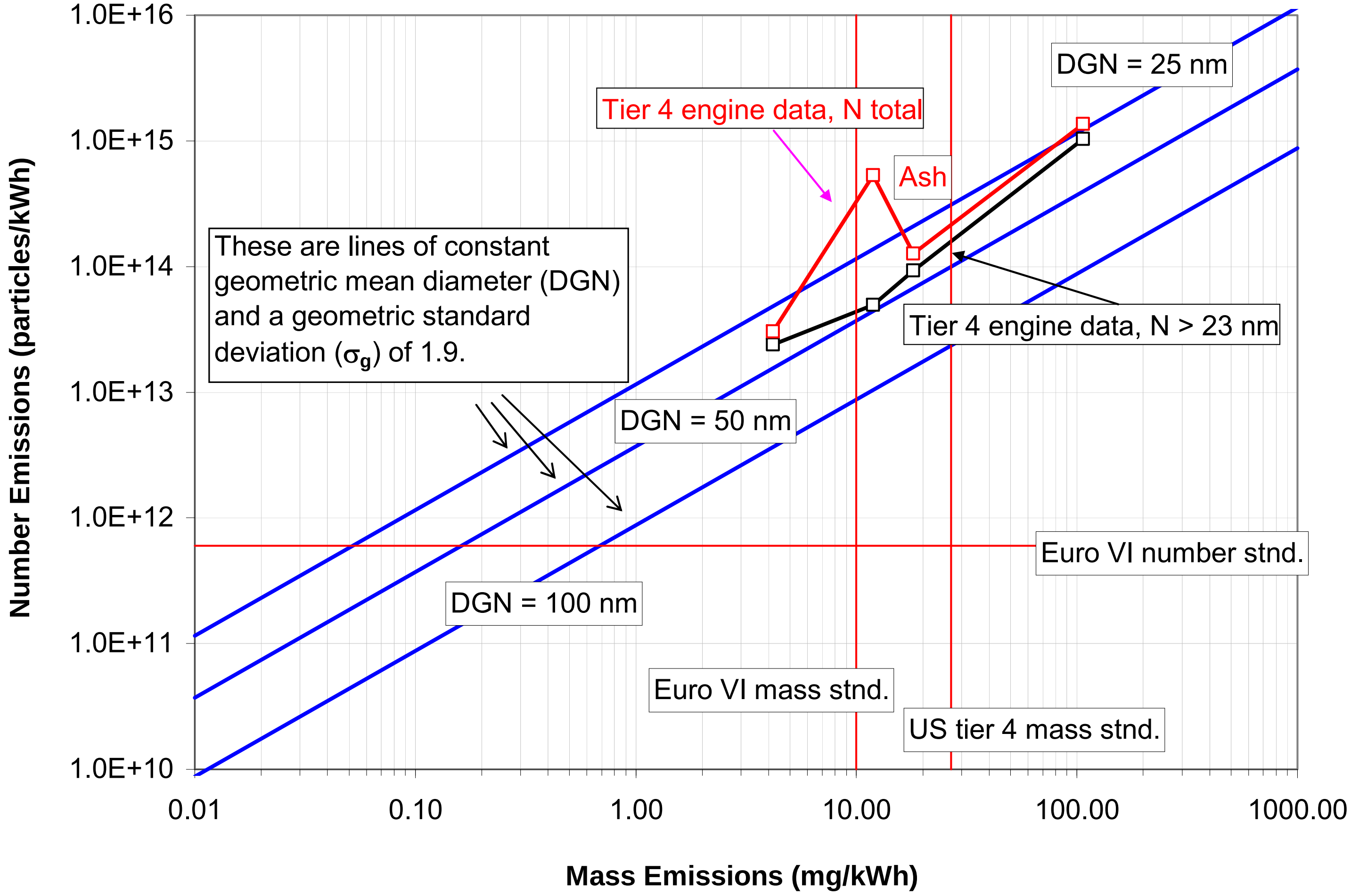




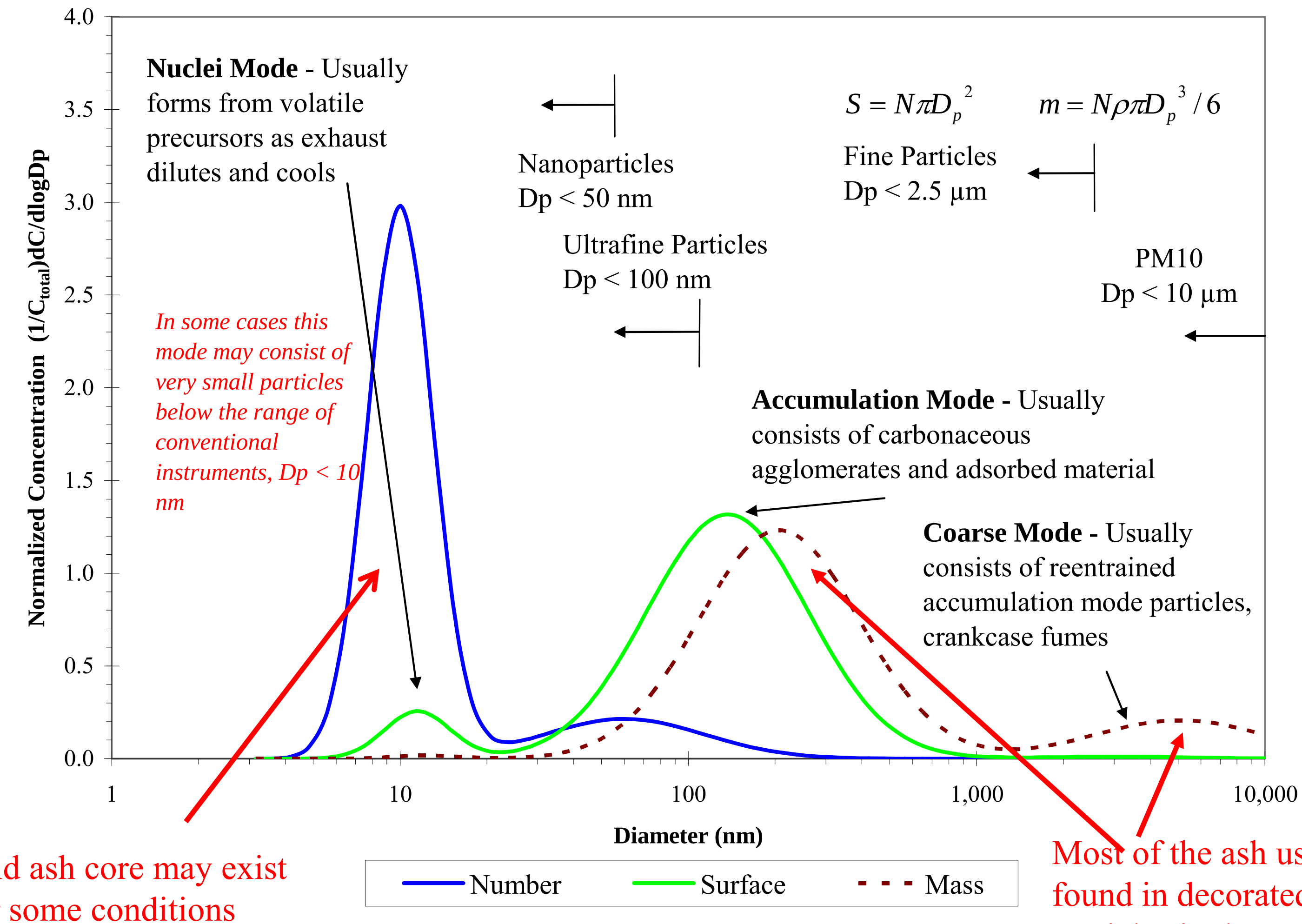
Mass and number emissions and standards



Mass and number emissions and standards – note the impact of counting all the ash



Typical engine exhaust particle size distribution by mass, number and surface area



A solid ash core may exist under some conditions

Most of the ash usually found in decorated particles in these 2 modes

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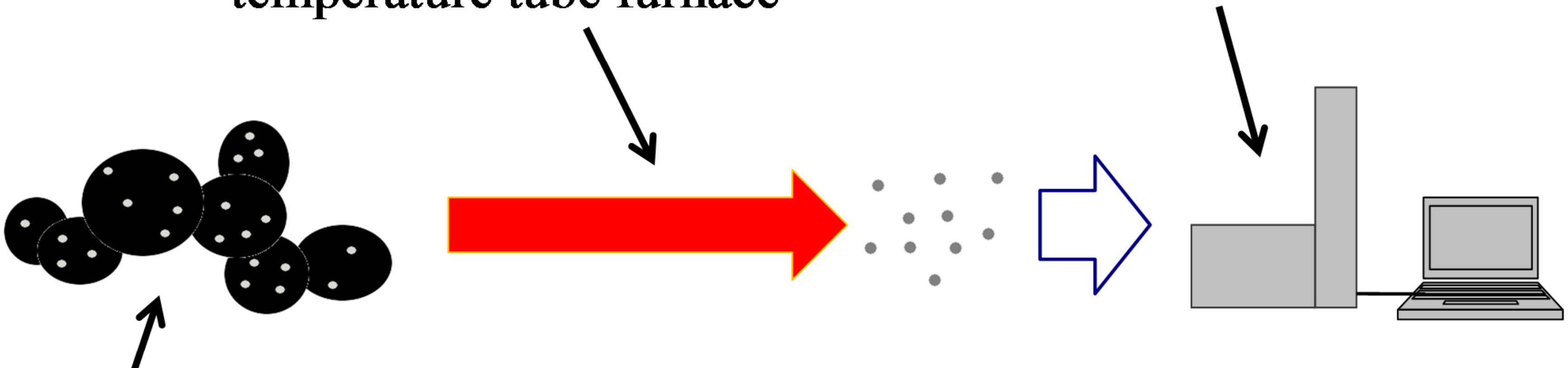
High temperature oxidation method (HTOM) overview

Oxidize soot and hydrocarbons within high temperature tube furnace

Cooled particles measured using real/near-real time particle instruments



Diesel exhaust or other metallic ash containing aerosol

Stable metal oxides and other refractory metal compounds are formed or survive high temperature tube furnace

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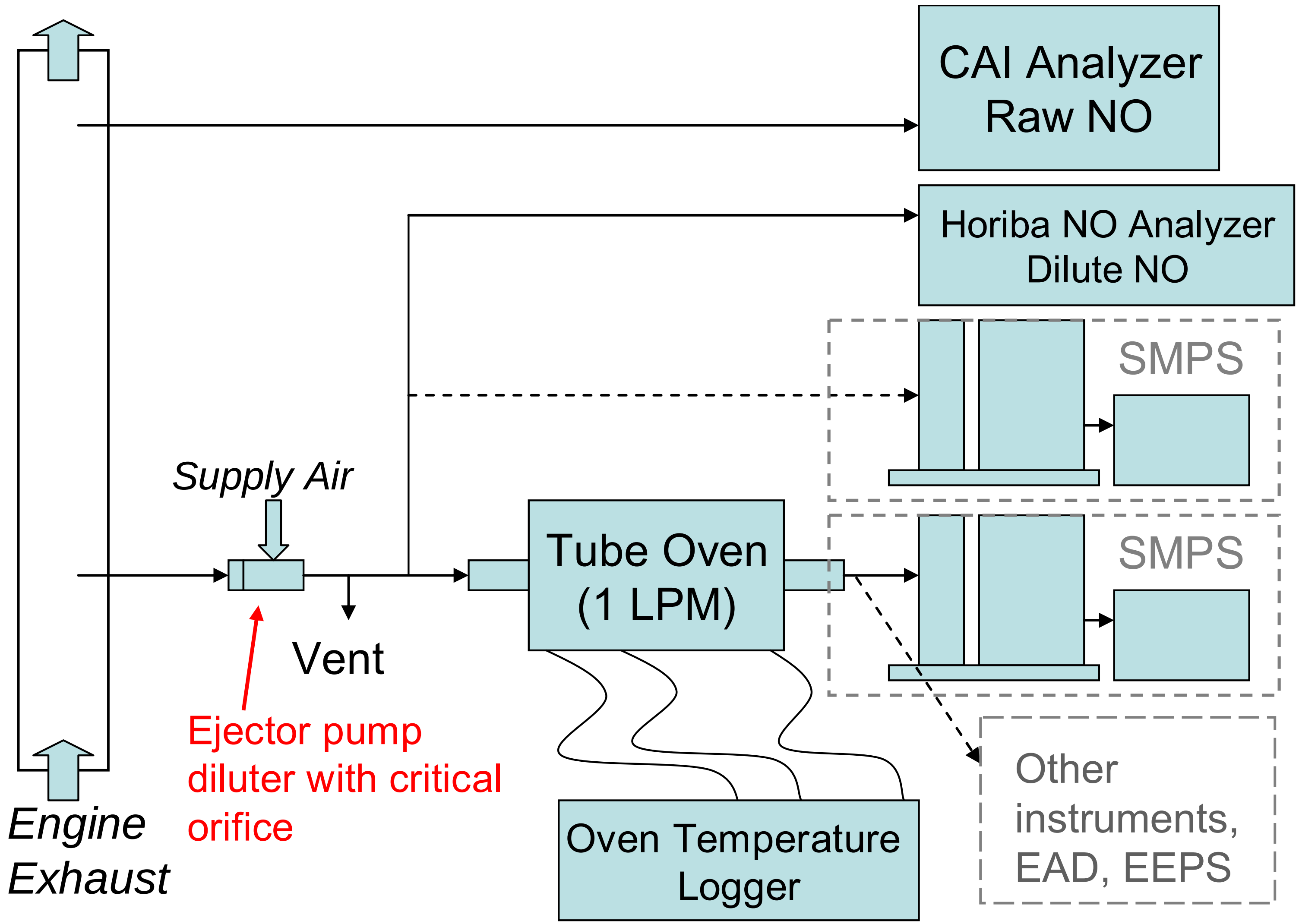
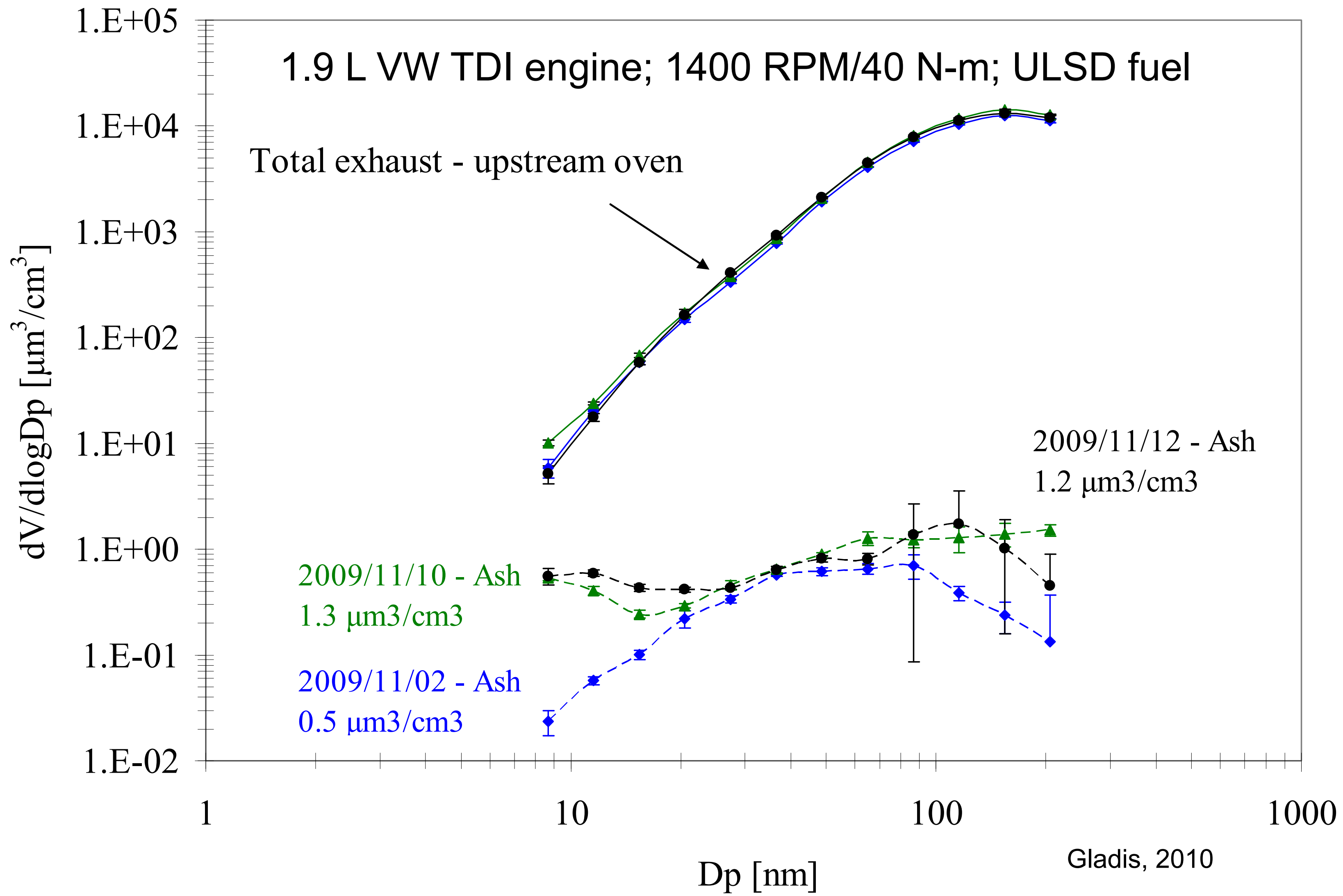
Engine exhaust apparatus

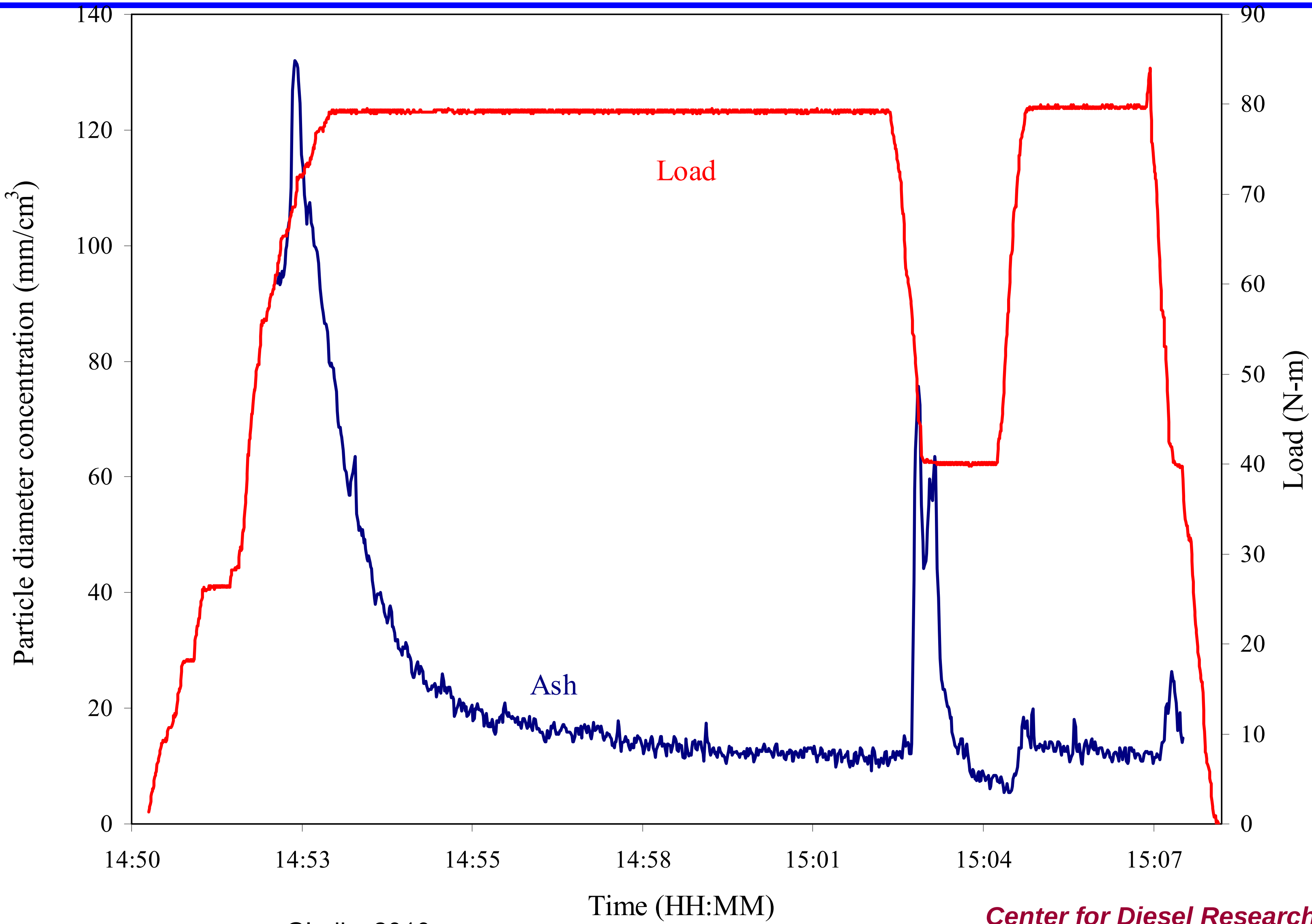


Engine exhaust measurements: volume weighted size distributions



Gladis, 2010

Transient ash emissions



Gladis, 2010

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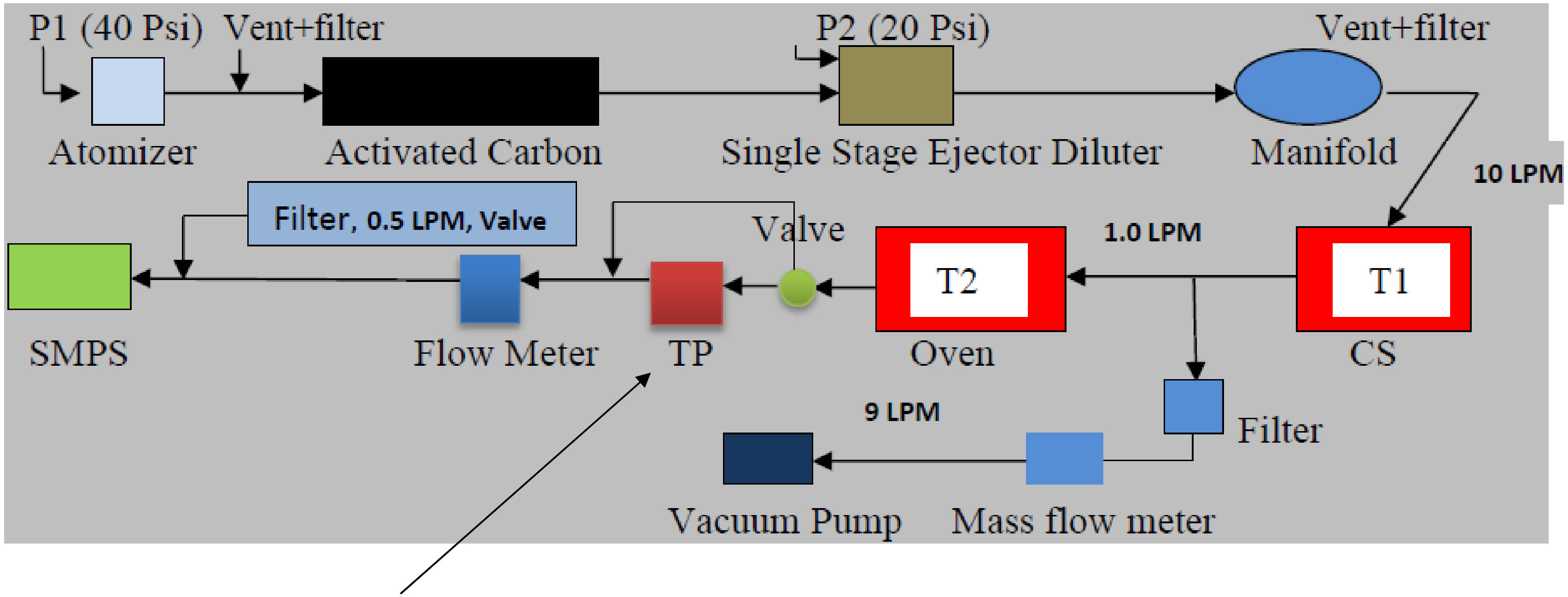
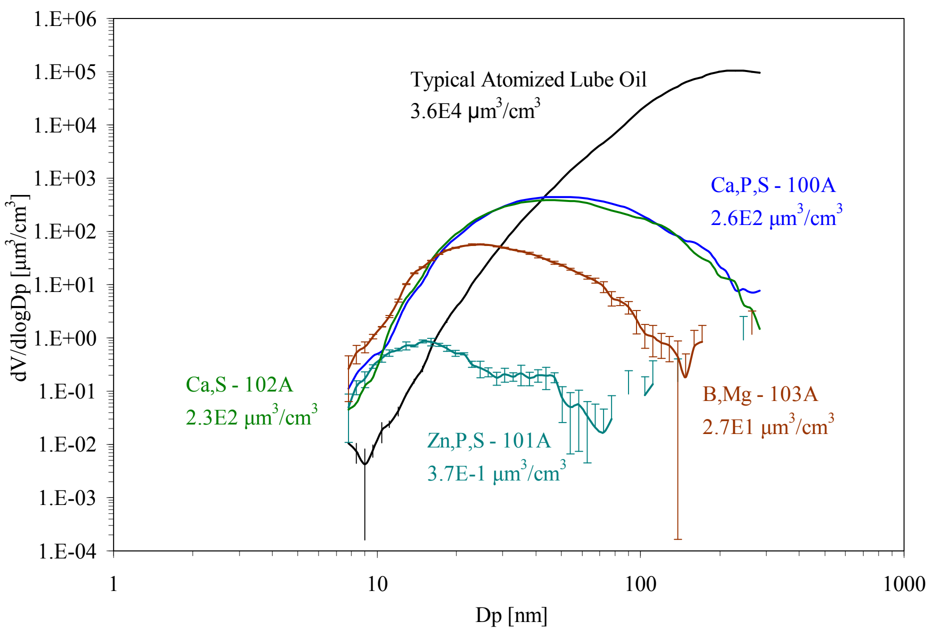
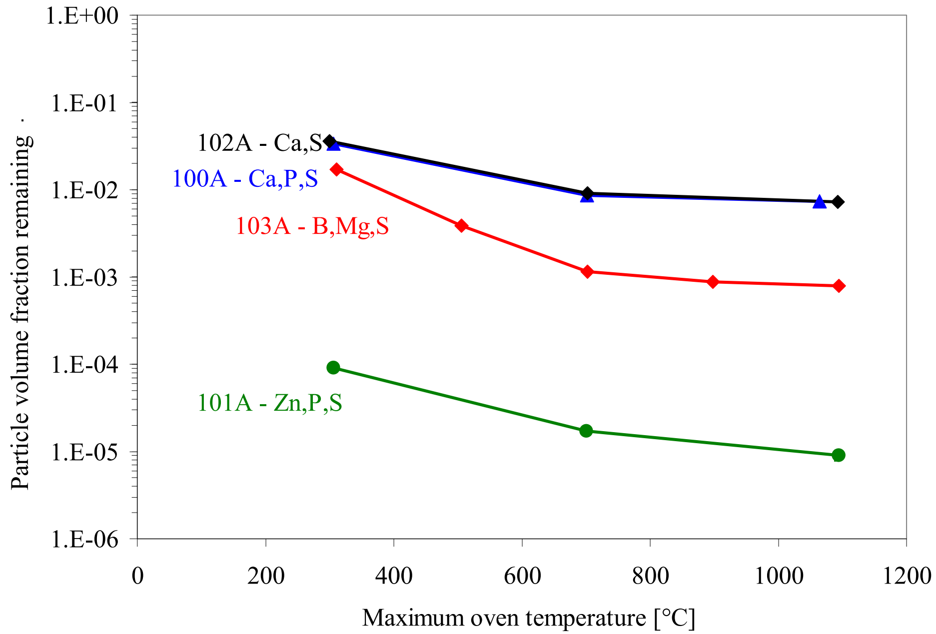
Spray calibration system with thermal precipitator for collection of TEM samples



Thermal Precipitator

Lube oil spray results: evaporation and oxidation of specially blended lube oils





Gladis, 2010 ***Center for Diesel Research***

Lube oil spray results: composition of specially blended lube oils and ash survival fraction

Oil composition, ppm, mass

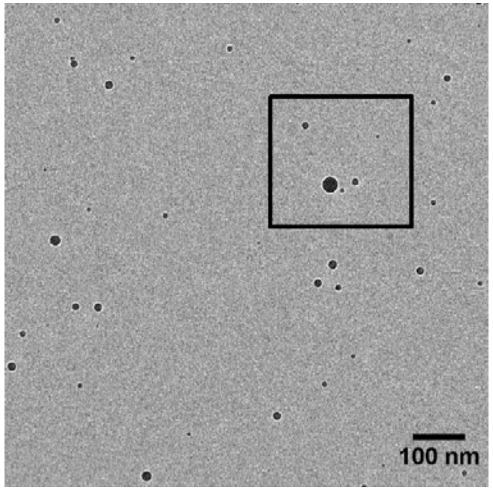
	Base stock 104A	101A	100A	103A	102A
B	<5	<5	<5	285	<5
Ca	<2	<2	3946	<2	3724
Mg	<2	<2	8	~500	<2
P	2	976	1052	<10	13
S	55	1998	802	57	8804
Zn	<5	1008	<5	<5	<5

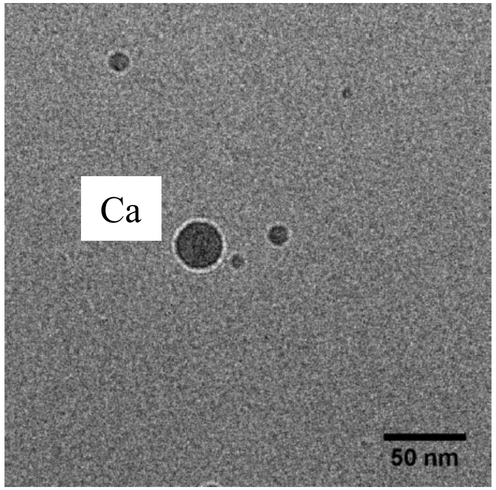
Ash compound survival fraction

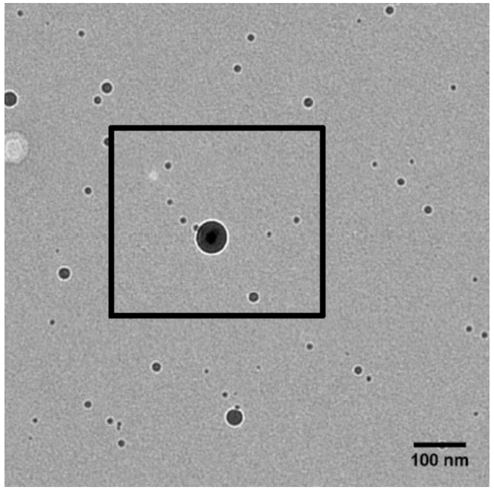
				Metallic Volume Fraction		
Blend #	Element	Compound	Concentration [ppm]	Expected	Measured	Measured/Expected
100A	Ca	CaCO3	3946	2.9E-03	7.3E-03	2.51
101A	Zn	ZnSO4	1008	5.9E-04	9.6E-06	0.02
102A	Ca	CaSO4	3724	3.4E-03	7.2E-03	2.10
103A	Mg	MgCO3	500	5.3E-04	7.8E-04	1.48

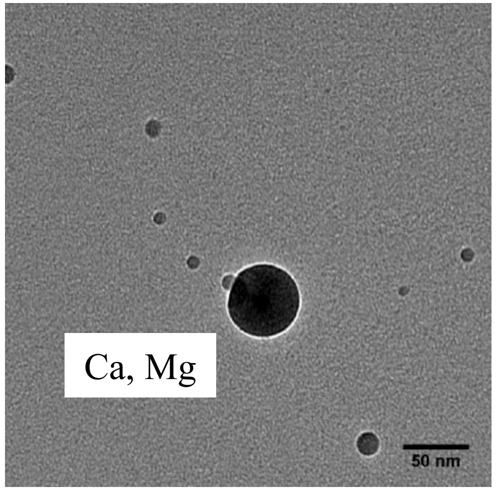
What happened to the zinc compounds?
Why is survival fraction so high for Ca and Mg?

Engine lube oil spray TEMs

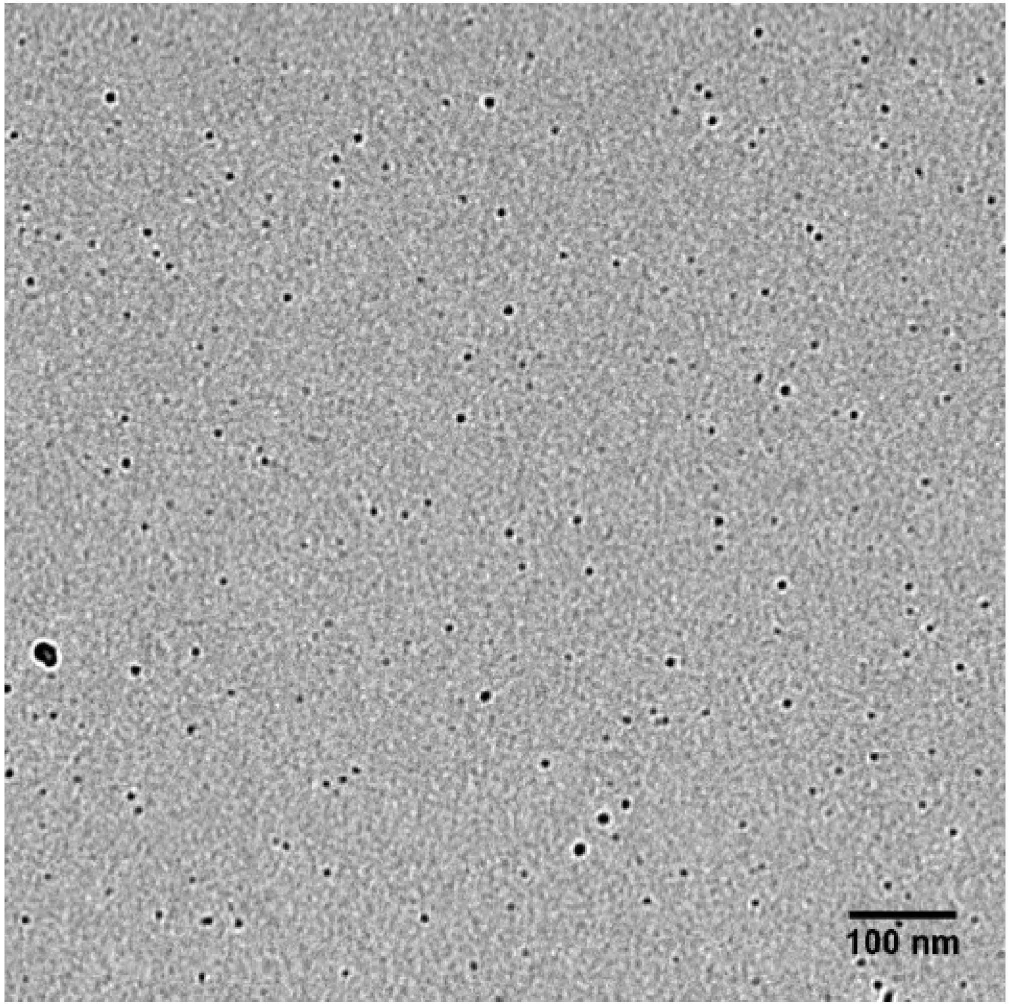








TEMs from engine oil ash, very small particles, leftover from decorated soot



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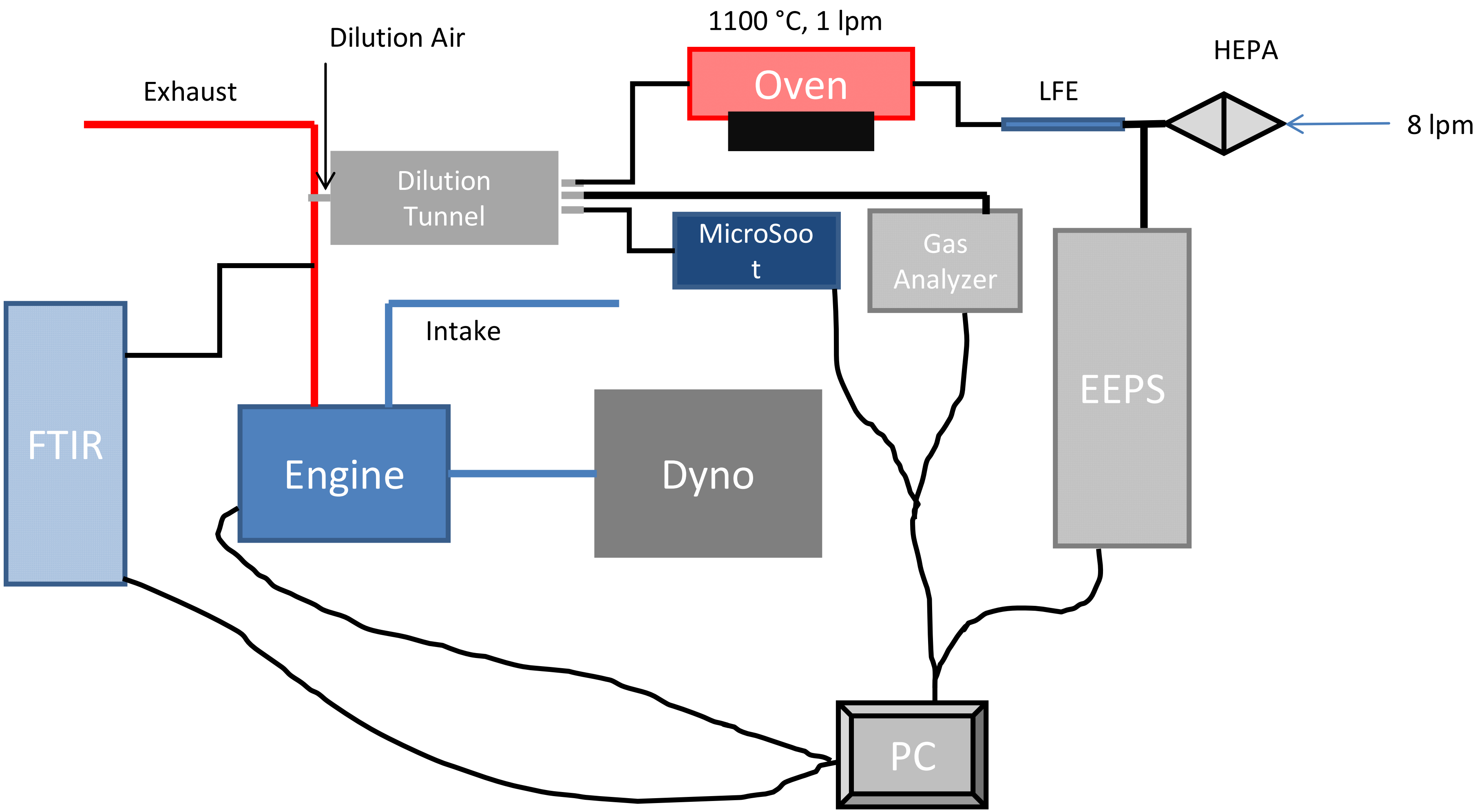
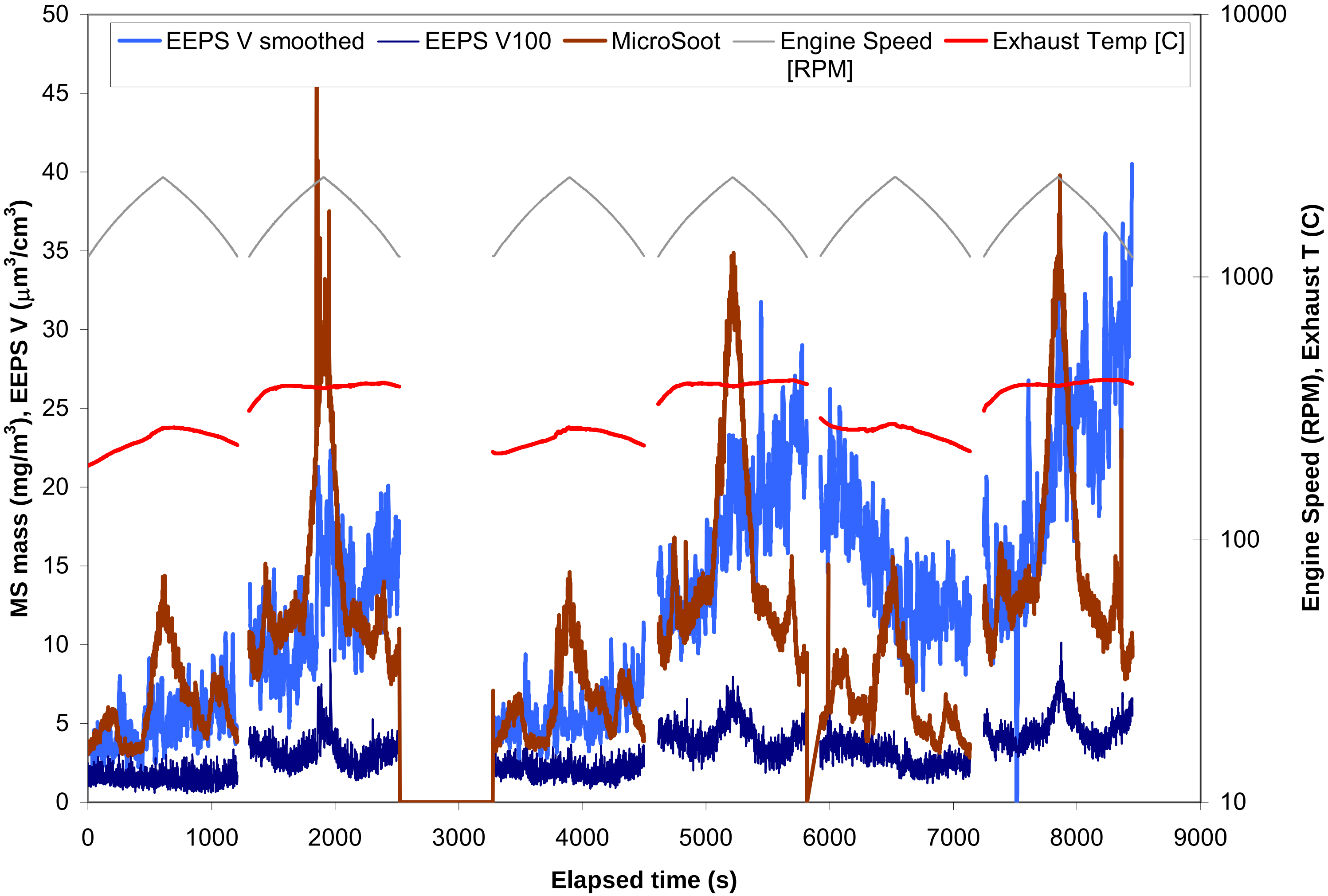
New setup for transient ash measurements



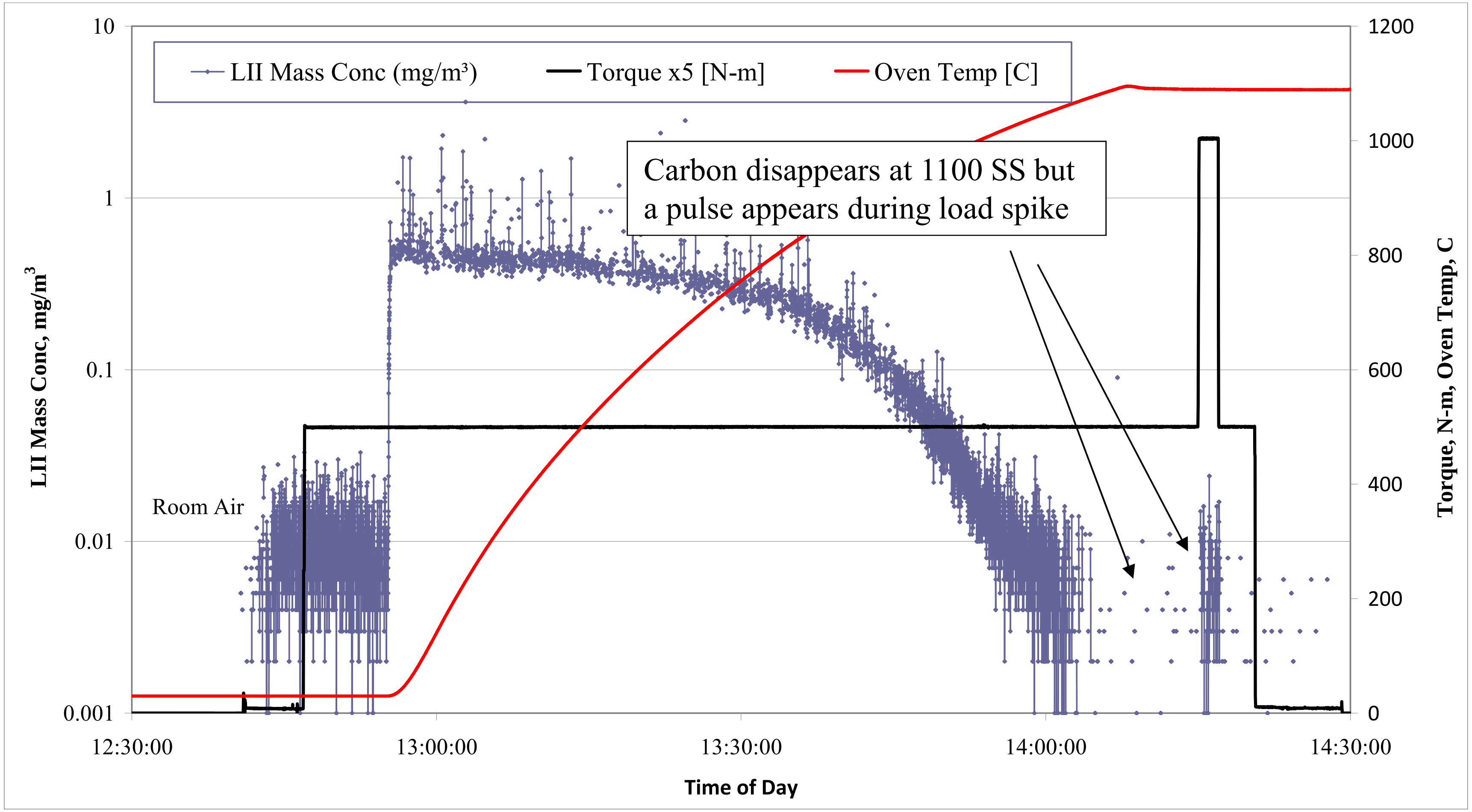
Transient ash measurements during speed ramps at heavy and light loads



Real time black carbon and real time ash show similar time response

- This is reasonable as we expect much of the ash to be decorating soot particles (black carbon)
- But it could also mean that there is carbon breakthrough, incomplete oxidation of particles
- Concentrations of ash downstream of oven are very low so downstream ash measurements are challenging
- Measured carbon breakthrough with LII instrument

Black carbon measured downstream of oven using Artium LII300 during temperature ramp



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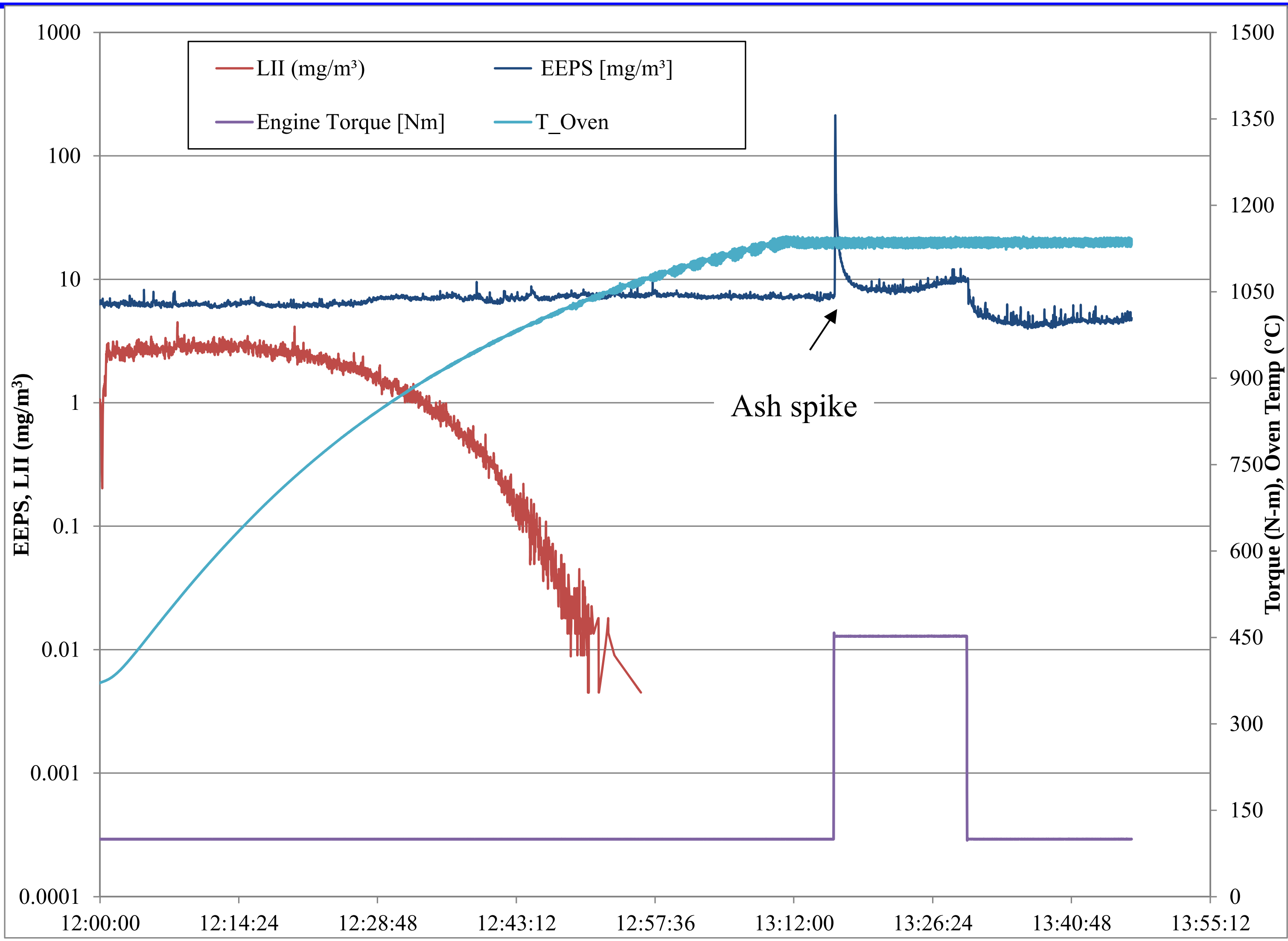
Further tests show no carbon breakthrough on load transient



Moving forward

- Carbon breakthrough, interference - solved using 1150 C
- New spray calibration experiments with pure salts
  - $CaSO_4$, $MgSO_4$, $ZnSO_4$, $Zn_3(PO_4)_3$
  - Zinc compounds show higher losses than Ca, Mg?
- Tests with new oils
- Steady state and transient ash emissions

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Conclusions

- We have developed a method that allows us to measure exhaust ash emissions from engines in near real time.
- Results suggest significant ash emission during engine transients, both up and down in load and speed

Acknowledgements

- We would like to thank BP and Corning for their support of this work.
- The work was also partially supported by internal funding from the U of M

Questions

Background work

- Kim, J. (2005). High Temperature Oxidation Method for Real-Time Measurement of Metallic Ash in Diesel Exhaust, Plan B Paper in Partial Fulfillment of the Degree of Master of Science, University of Minnesota.
- Filice, M.,, W. F. Watts and D. B. Kittelson 2007. Near Real-Time Ash Measurement: A Preliminary Study. Extended Abstract, Poster prepared for Seminar on Industrial Emissions and Immissions: New Problems Caused By Ultrafine Particulate. 11th International Trade Fair of Material & Energy Recovery and Sustainable Development, November 7-10, 2007, Rimini, Italy.
- Apple, James, David Gladis, Winthrop Watts, and David Kittelson, 2009. "Measuring Diesel Ash Emissions and Estimating Lube Oil Consumption Using a High Temperature Oxidation Method," *SAE Int. J. Fuels Lubr.* 2(1): 850-859, 2009, also SAE paper number 2009-01-1843.
- Gladis, David Daniel, A Real-time Method for Making Engine Exhaust Ash Measurements, University of Minnesota, M.S. Thesis, September 2010

New results, upstream and downstream number concentration, downstream size distribution