Issues associated with measuring nothing or almost nothing: Real-time Measurements of Metallic Ash Emissions from Engines

David Kittelson, Udayan Patwardhan, Darrick Zarling,
David Gladis, and Winthrop Watts,

Center for Diesel Research
Department of Mechanical Engineering
University of Minnesota

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Measuring nothing

- The EU has set a number based emission standards for light and heavy duty Diesel vehicles
  - The standards are based on “solid” particles larger than 23 nm
  - Light-duty, Euro 5b, September 2011
    - The standard is 6 x 10^{11} particles/km
    - The mass emission standard is 4.5 mg/km, but the number standard corresponds to about 0.15 to 0.7 mg/km, depending on DGN – a much tighter standard!
  - Heavy-duty, Euro VI, January 2013
    - The standards are 6 x 10^{11} and 8 x 10^{11} particles/kWh on the WHTC and the WHSC, respectively
    - The mass emission standard is 10 mg/kWh, but the number standard corresponds to about 0.2 to 0.9 mg/kWh, depending on DGN – again a much tighter standard!
- The US so far plans to limit measurements to mass
  - Current US heavy-duty standard is 13 mg/kWh
  - New US/CARB light-duty standards are 1.8 and 0.6 mg/km for 2017 and 2025 (maybe 2022), respectively. These correspond to roughly 8 and 3 mg/km
- It is very challenging to accurately measure filter mass at 13 mg/kWh. The new US/CARB standards represent an even greater challenge.
  - Stoichiometric burn SI engines have about 13% water – limiting lowest dilution factor
  - Light-duty cycle uses separate filters for 3 phases so a total mass of perhaps 30 μg is distributed on 3 filters each having 5+ μg artifact
  - We hope the CRC E99 project figures all of this out
- Unfortunately the US hates number measurements

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
- Method
- Initial engine results
- Calibration experiments
- New issues
- Conclusions

Acknowledgements

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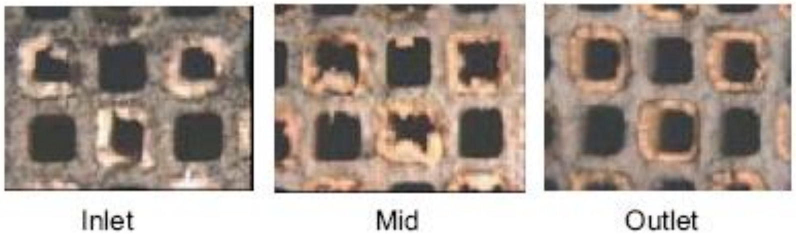
Background work

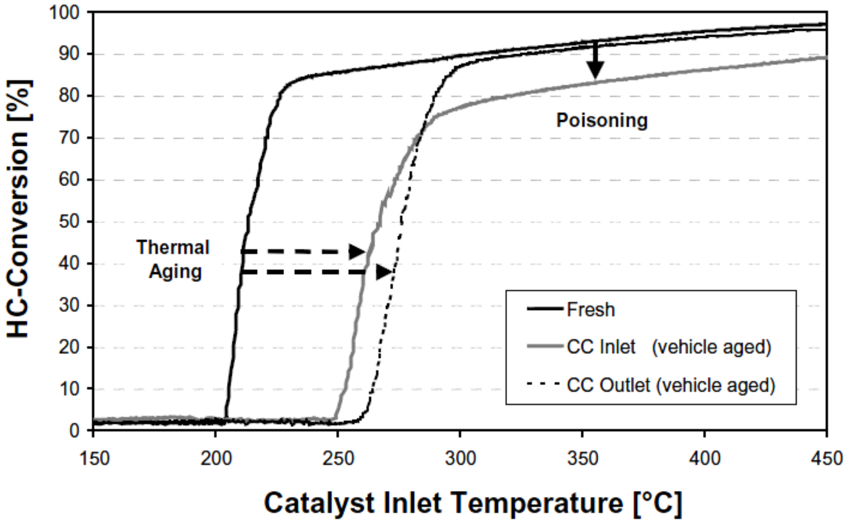
- Kim, J. (2005). High Temperature Oxidation Method for Real-Time Measurement of Metallic Ash in Diesel Exhaust, Plan B Paper in Partial Fulfillment of the Degree of Master of Science, University of Minnesota.
- Filice, M.,, W. F. Watts and D. B. Kittelson 2007. Near Real-Time Ash Measurement: A Preliminary 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

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

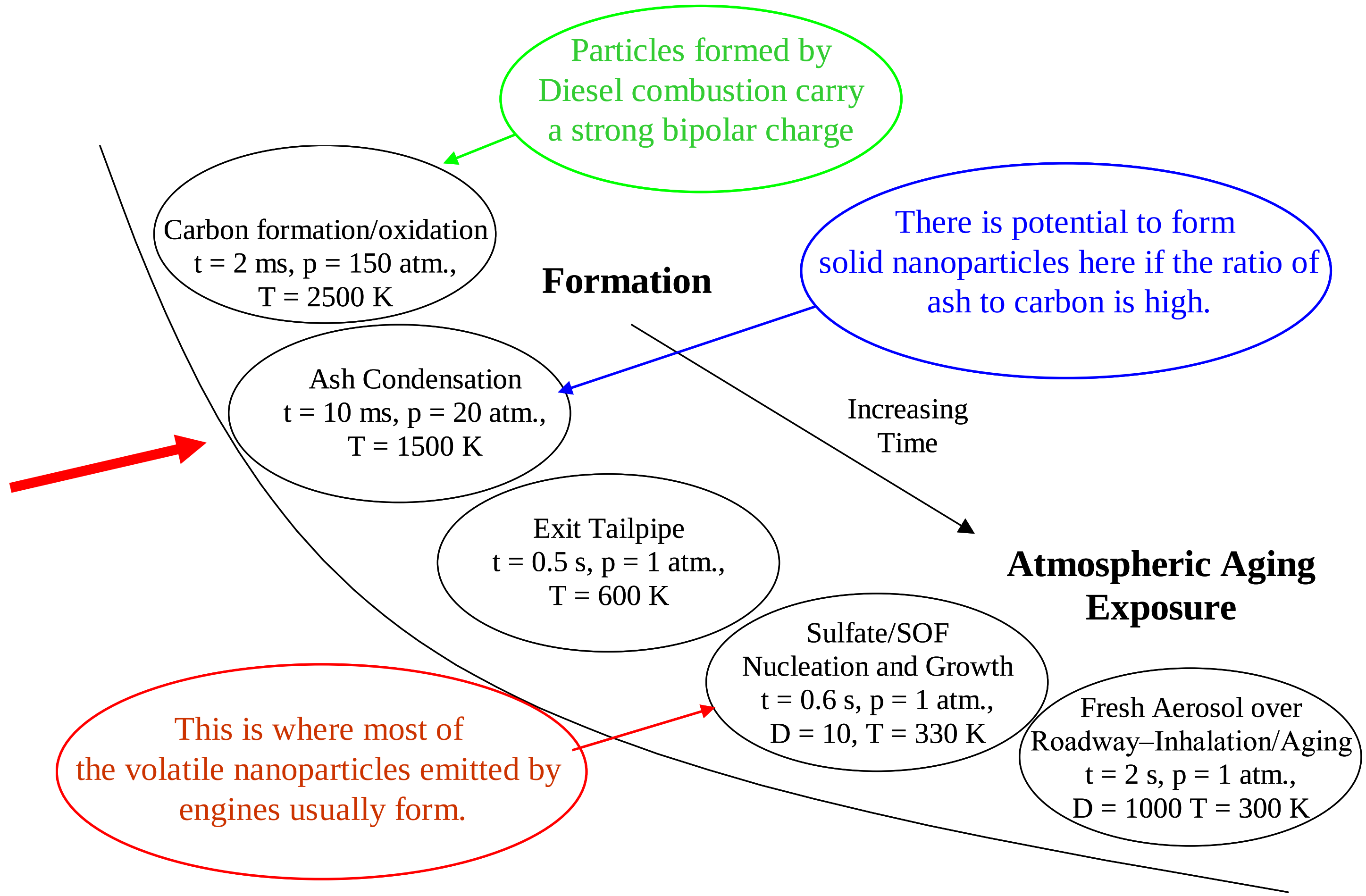


Ash distribution in exhaust filter channels (Heibel and Bhargava, 2007)



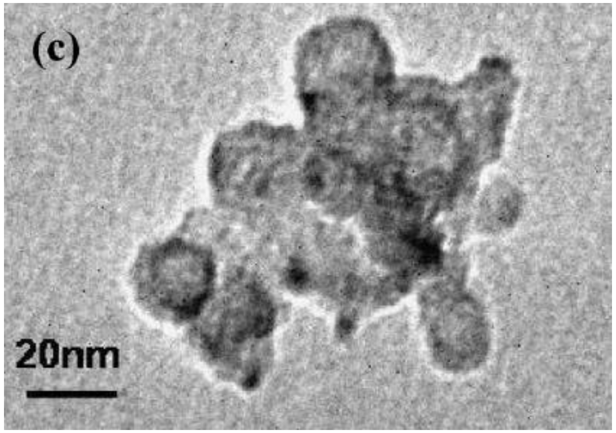
3-way catalyst poisoning by ash deposits (Franz, et al., 2005)

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

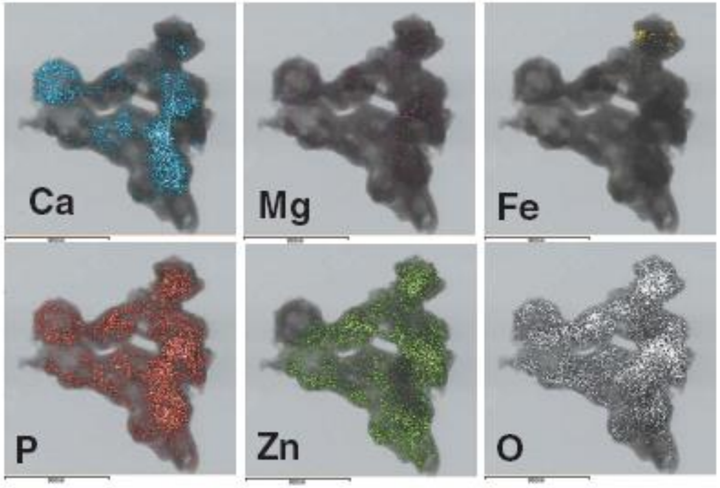


Kittelson, D. B., W. F. Watts, and J. P. Johnson 2006. "On-road and Laboratory Evaluation of Combustion Aerosols Part 1: Summary of Diesel Engine Results," Journal of Aerosol Science 37, 913–930.

Engine ash emissions

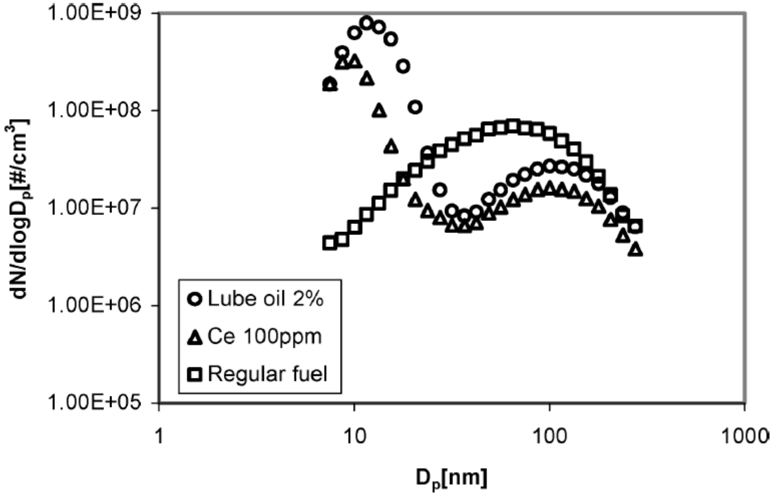


Jung, et al., 2005



Sappok and Wong, 2007

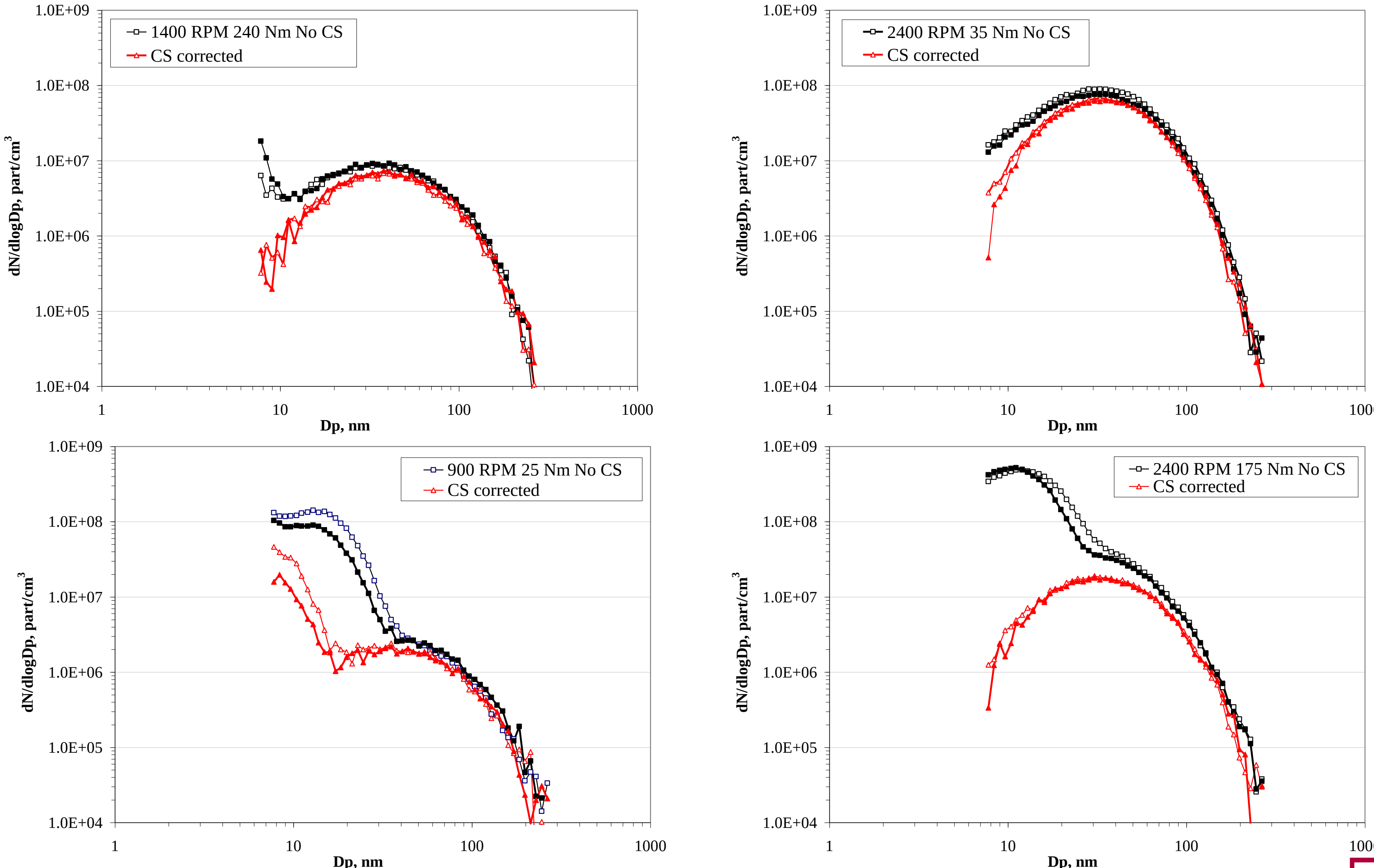
- Non-combustible fraction of diesel aerosol
- Derived from metallic lube oil additives and engine wear metals
- Metallic particles tend to ‘decorate’ carbonaceous exhaust particles
- But form separate particles at sufficiently high metal to soot ratios



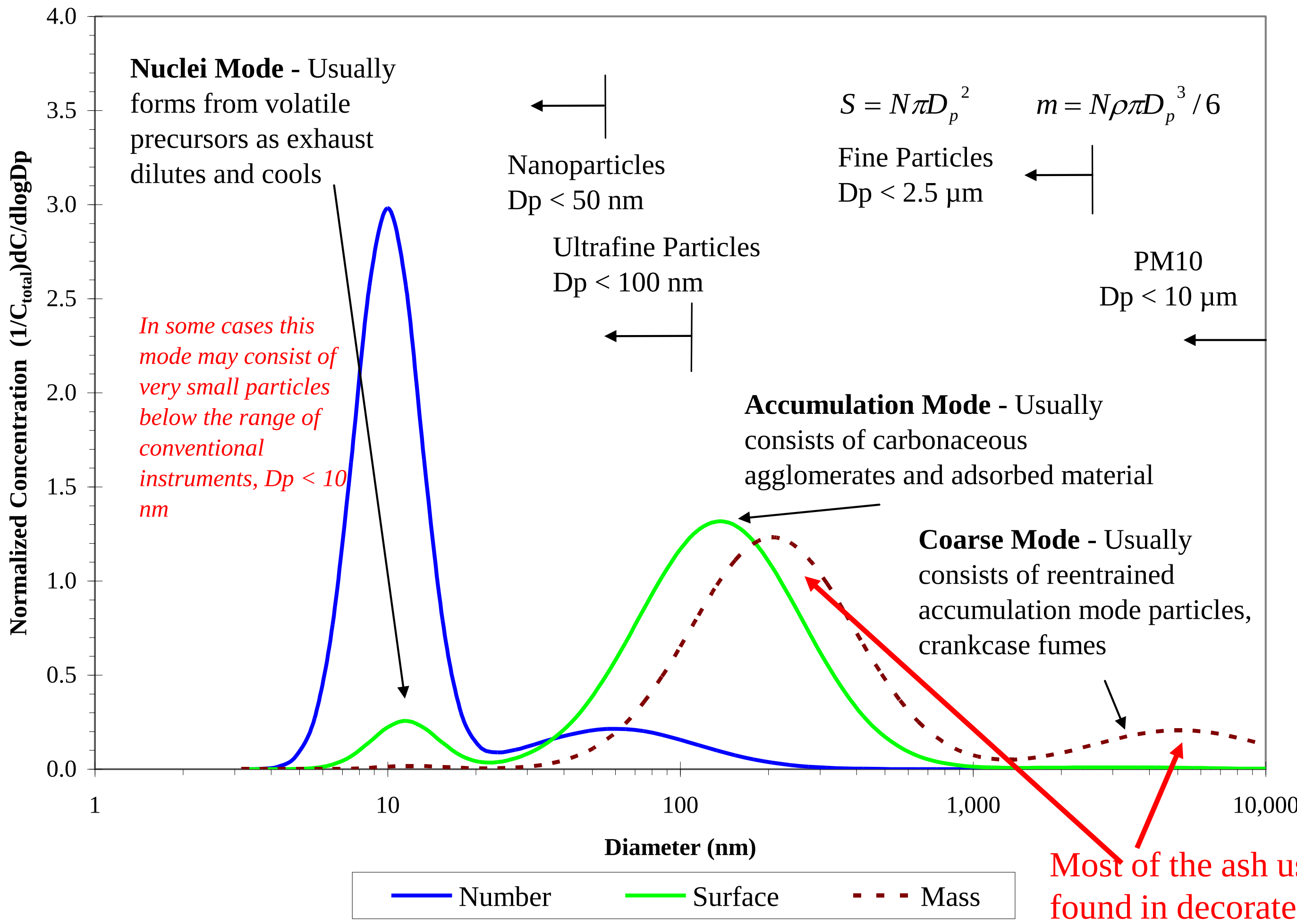
Jung and Kittelson, 2005

Catalytic stripper measurements - nuclei mode usually volatile but shows nonvolatile (ash) core at light load

4.5 LTier 4/Interim IIIB offroad diesel engine



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



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

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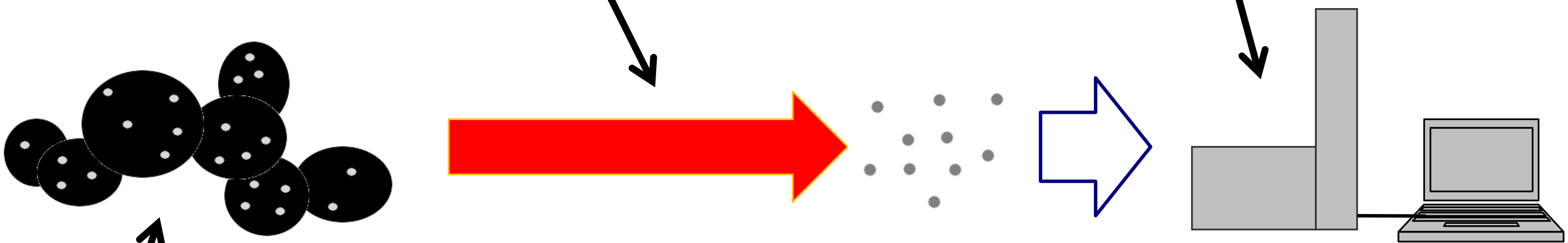
High temperature oxidation method (HTOM) overview

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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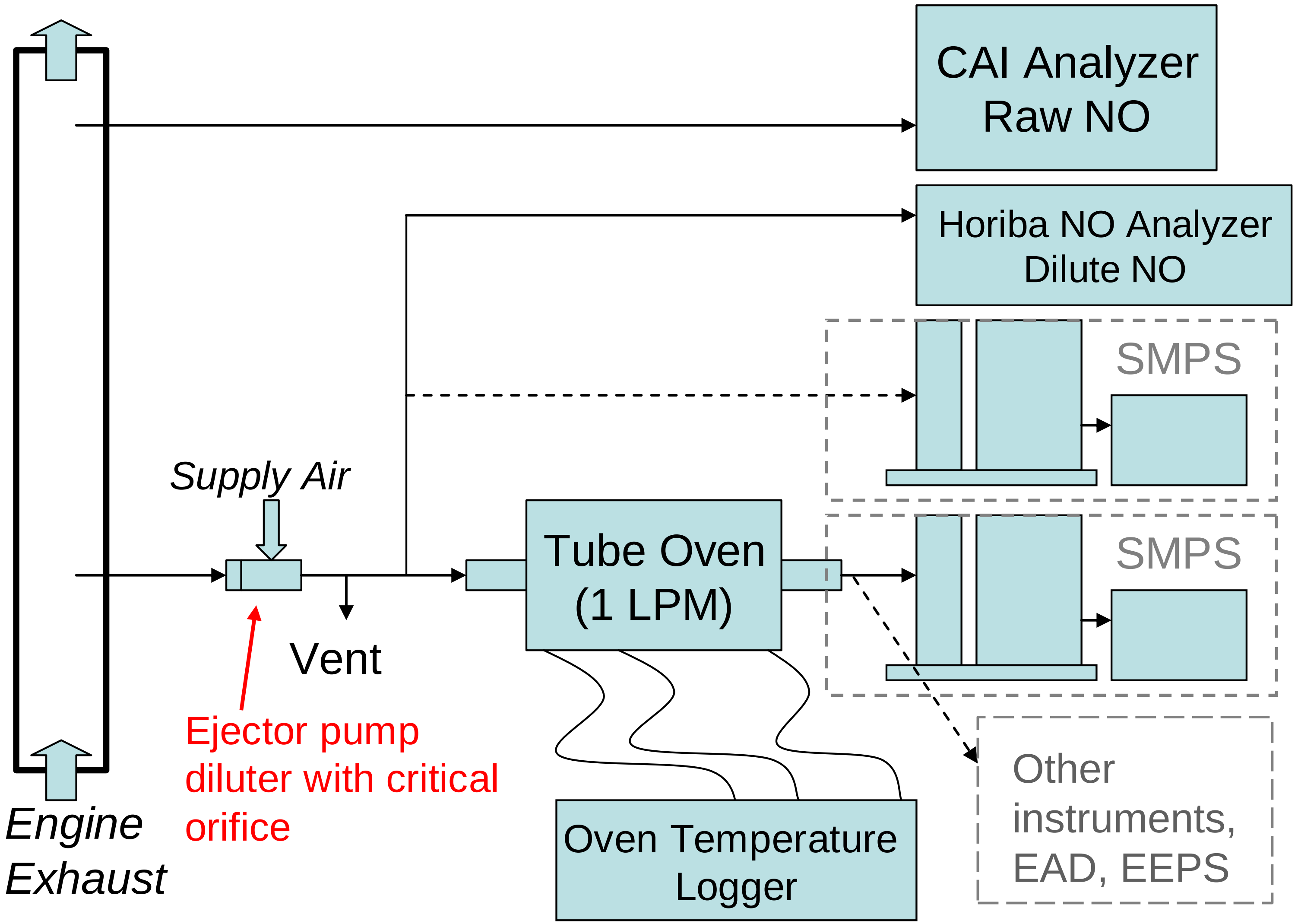
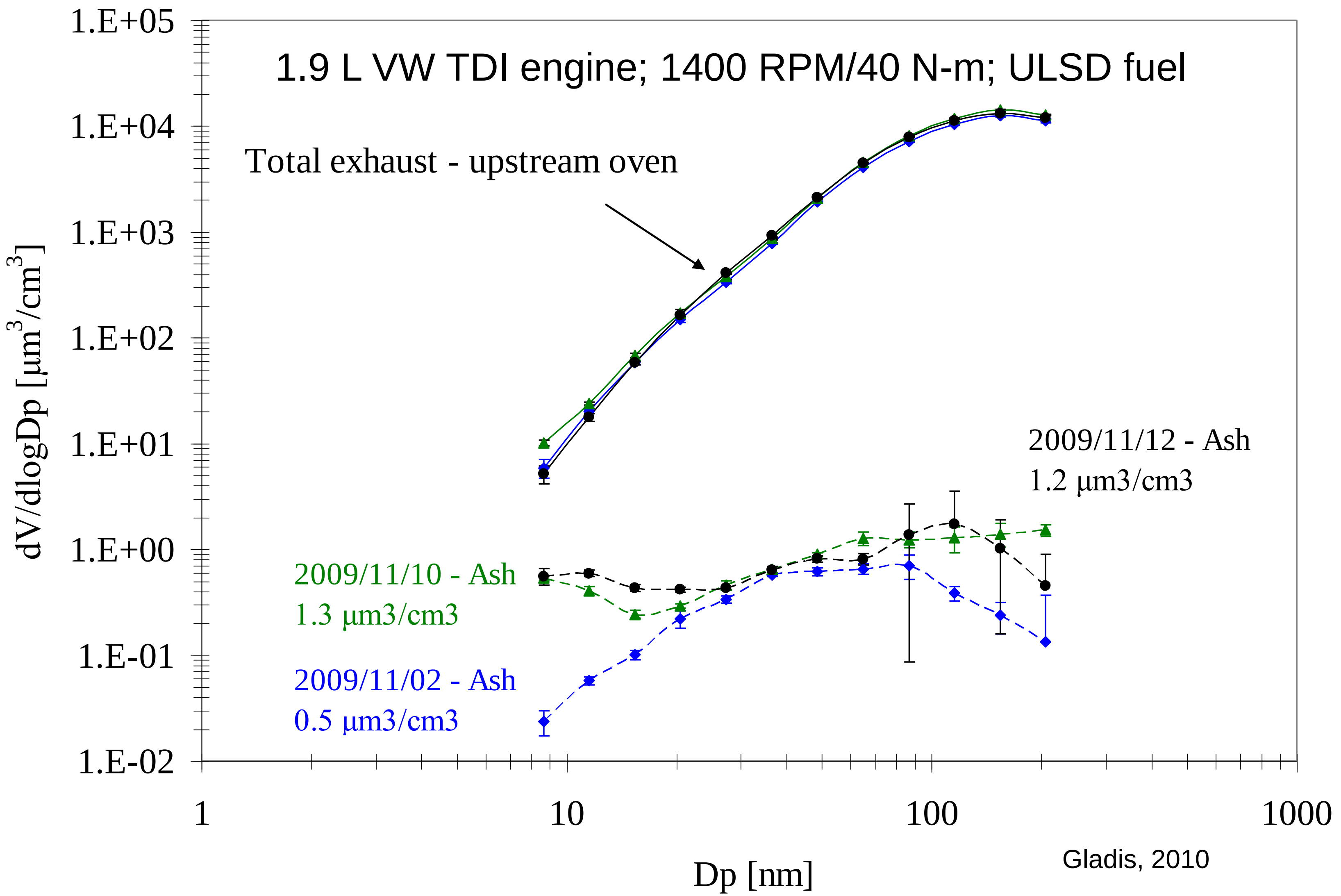
Engine exhaust apparatus

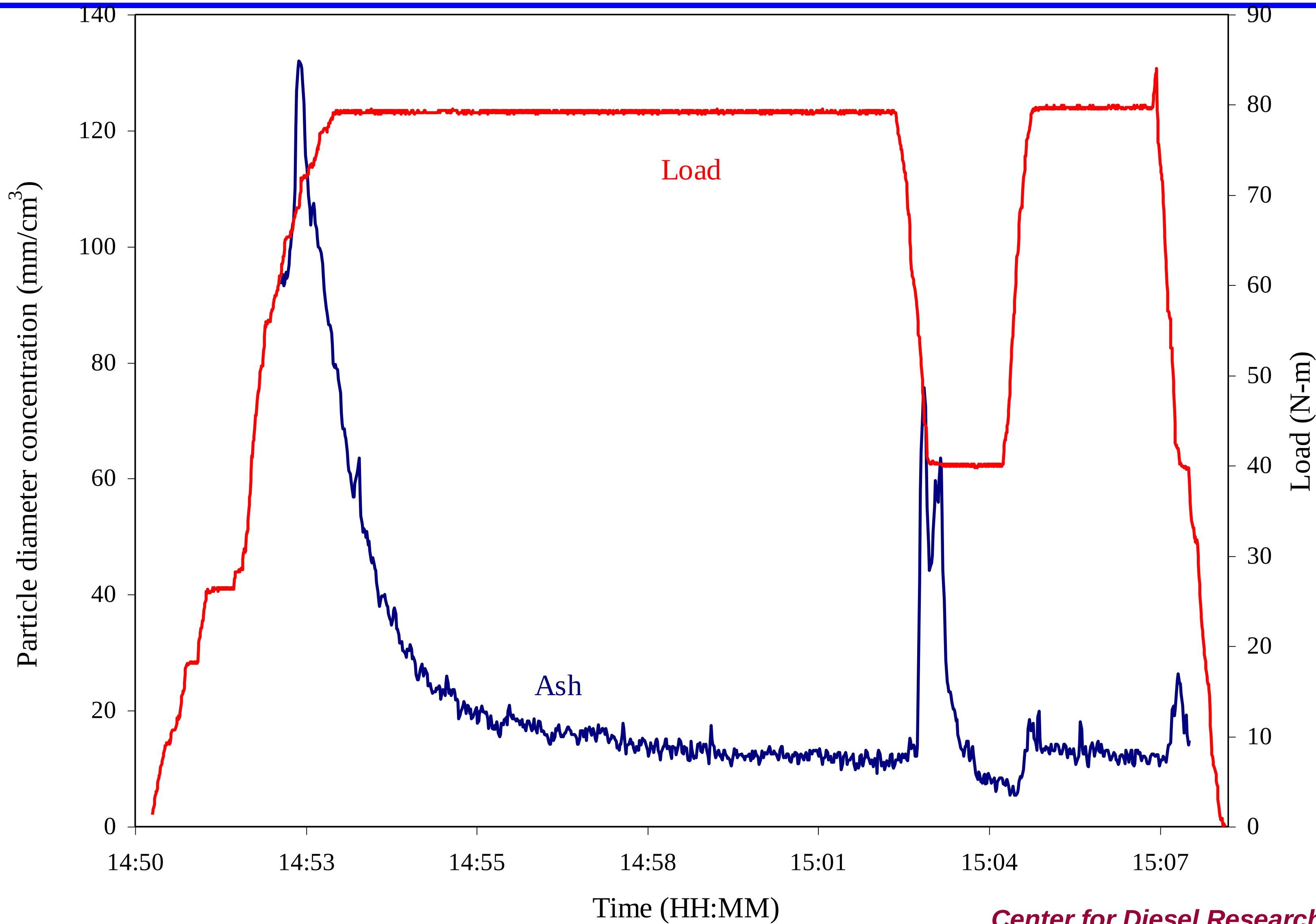


Engine exhaust measurements: volume weighted size distributions



Gladis, 2010

Transient ash emissions



Gladis, 2010

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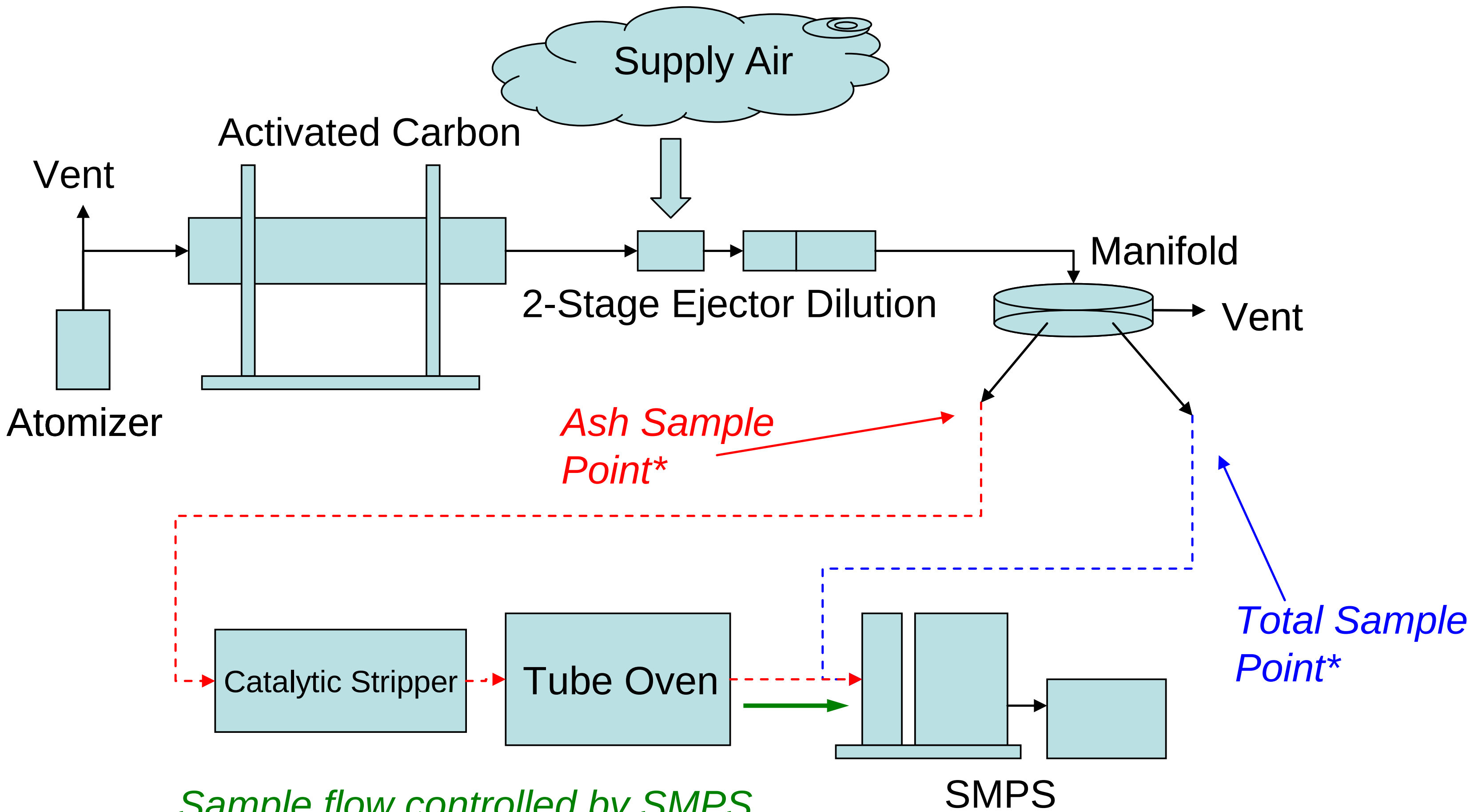
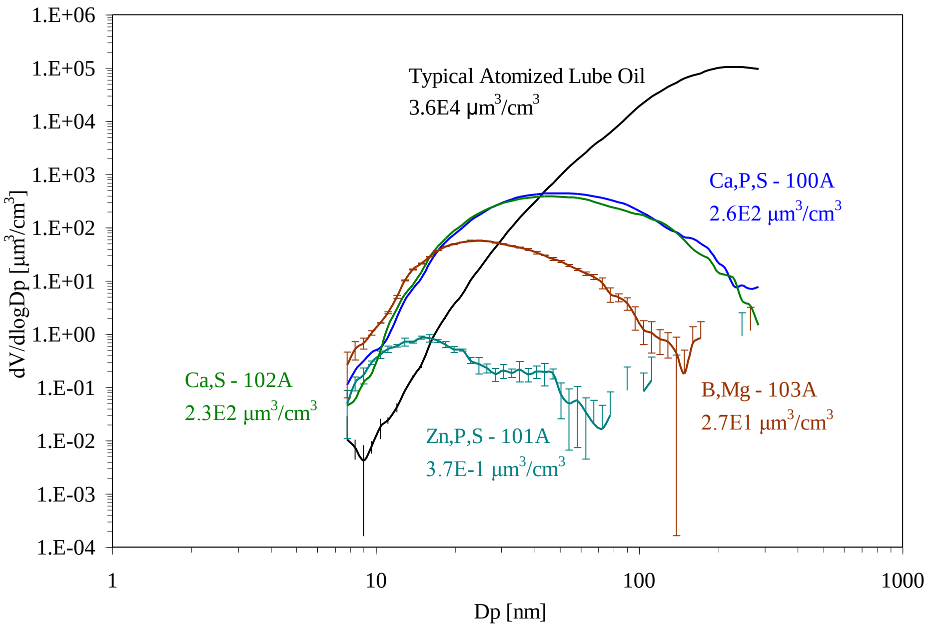
Lube oil spray apparatus

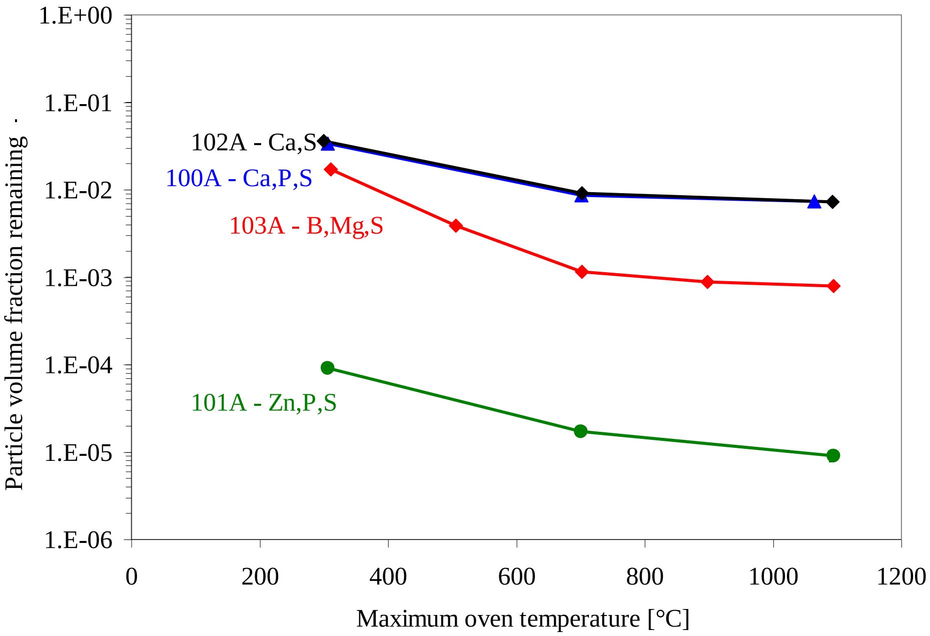


Sample flow controlled by SMPS sample flow, 1 lpm

**Sample Location Manually Switched*

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





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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	$CaCO_3$	3946	2.9E-03	7.3E-03	2.51
101A	Zn	$ZnSO_4$	1008	5.9E-04	9.6E-06	0.02
102A	Ca	$CaSO_4$	3724	3.4E-03	7.2E-03	2.10
103A	Mg	$MgCO_3$	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?

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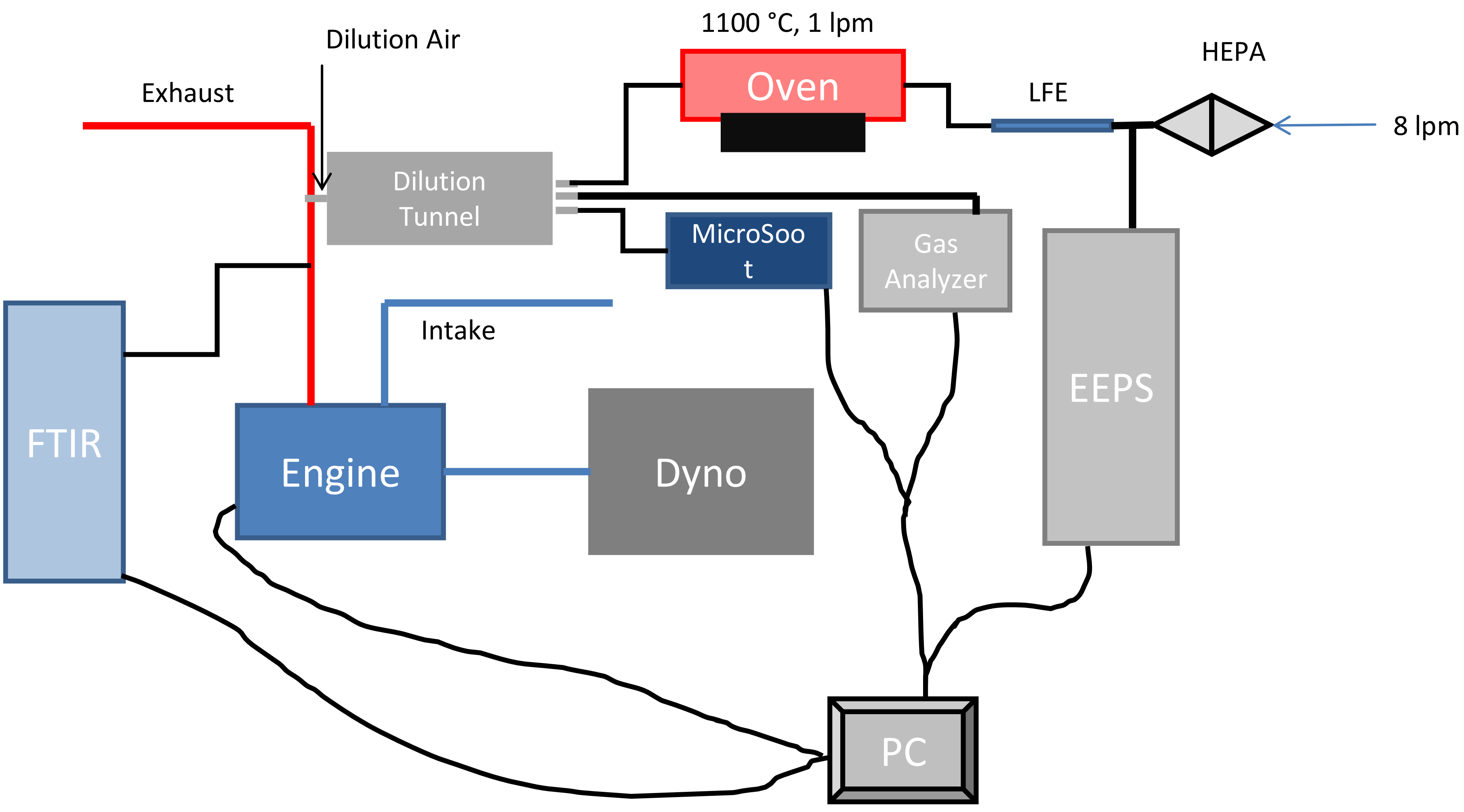
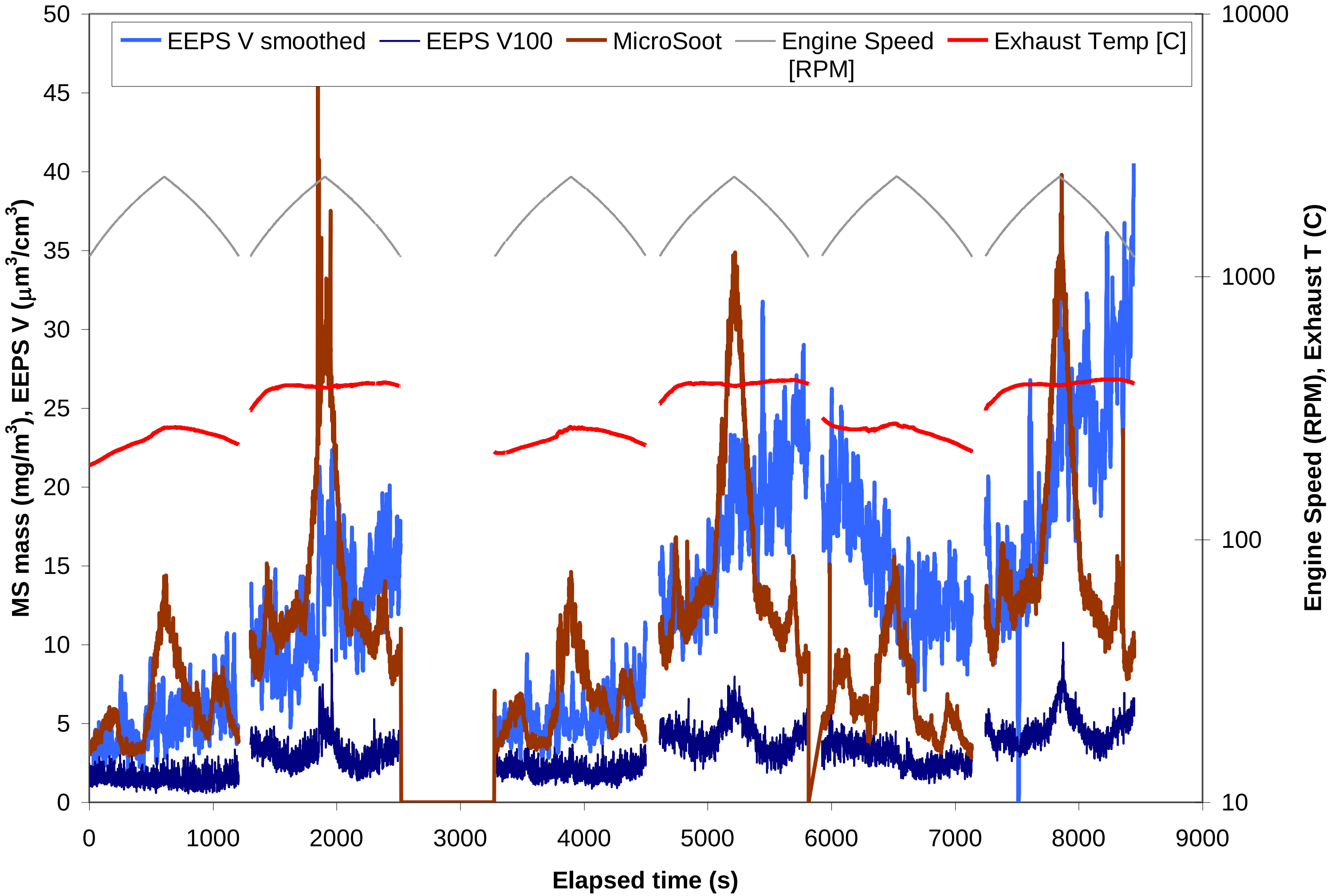
New setup for transient ash measurements



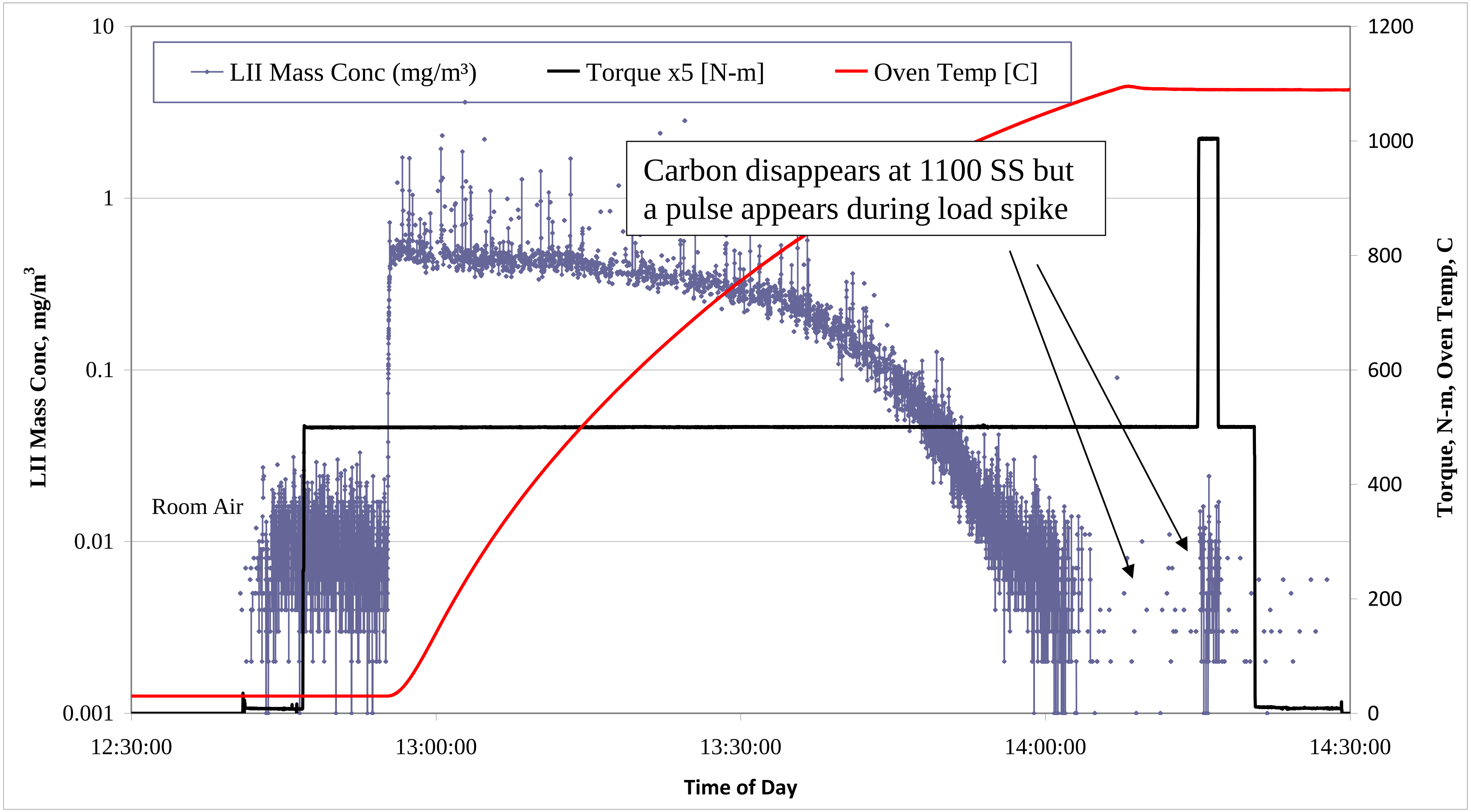
Transient ash measurements during speed ramps at heavy and light loads



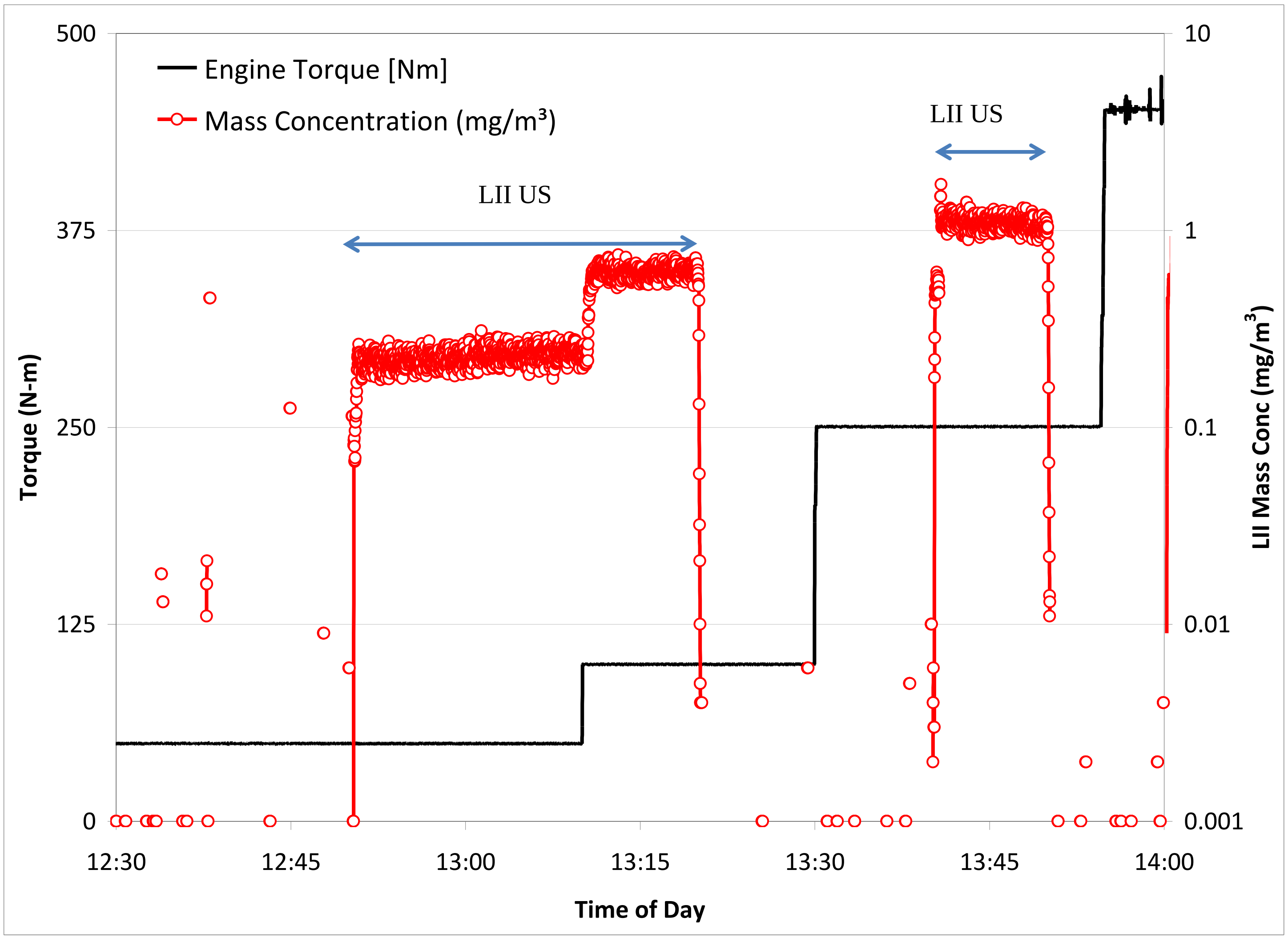
Real time black carbon and real time ash show similar time response

- 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
- Decided to borrow LII instrument to make these measurements

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



Raising the oven temperature to 1150 C eliminates nearly all of the carbon breakthrough



Ongoing issues

- Need additional metal survival calibration, ICPMS
- What is happening to the zinc?
- Carbon breakthrough, interference
  - Appears to be solved using 1150 C
  - Likely associated with larger particles with insufficient time to fully oxidize
  - Raise oven temperature
    - Material limitations
    - Ash volatilization and losses
  - Remove coarse PM upstream of oven
    - How much ash is carried by these particles?
    - May be especially important on transients

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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
- Concerns
  - Lack of response to zinc
  - Carbon breakthrough

Questions

References

- Heibel A, Bhargava R. Advanced Diesel particulate filter design for lifetime pressure drop solution in light duty applications. *Fuels and Emissions Conference*. 2007.
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- Kittelson D. Engines and nanoparticles: A review. *J Aerosol Sci*. 1998;29(5):575-588.
- Sappok A, Wong V. Detailed chemical and physical characterization of ash species in Diesel exhaust entering aftertreatment systems. *SAE World Congress*. 2007.

Lube oil consumption pathways

- Piston rings
  - Atomization
  - Ring collapse
- Leaky valve seals
- Crank case ventilation and exhaust gas recirculation (EGR)

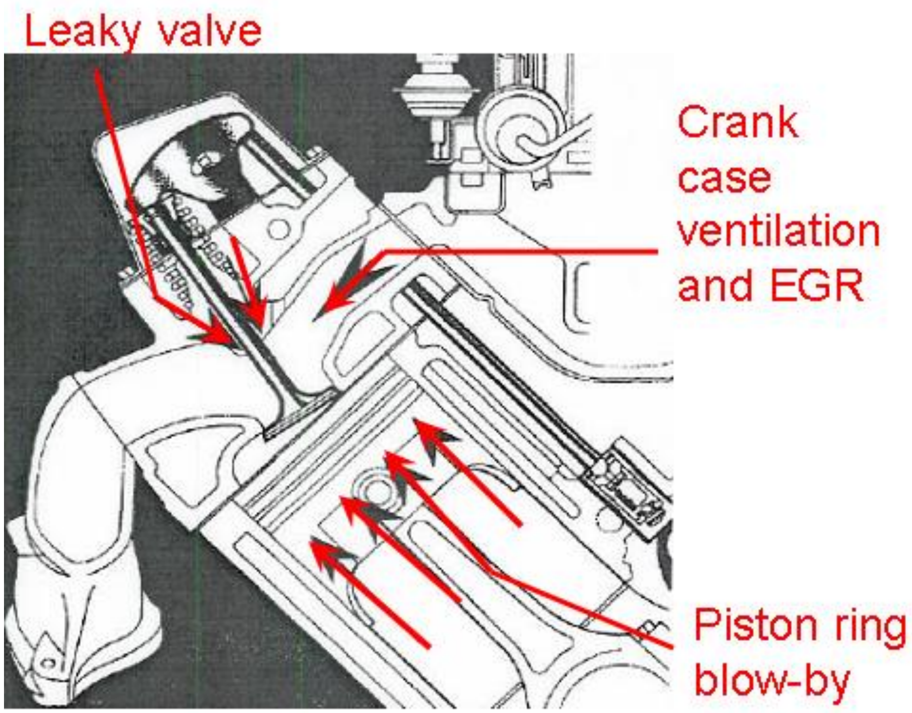

Diagram of lube oil pathways on a typical engine (modified from Hill and Systasma, 1991)

Typical engine result, VW TDI, light load cruise, stable ash residue at 1100 – 1150 C