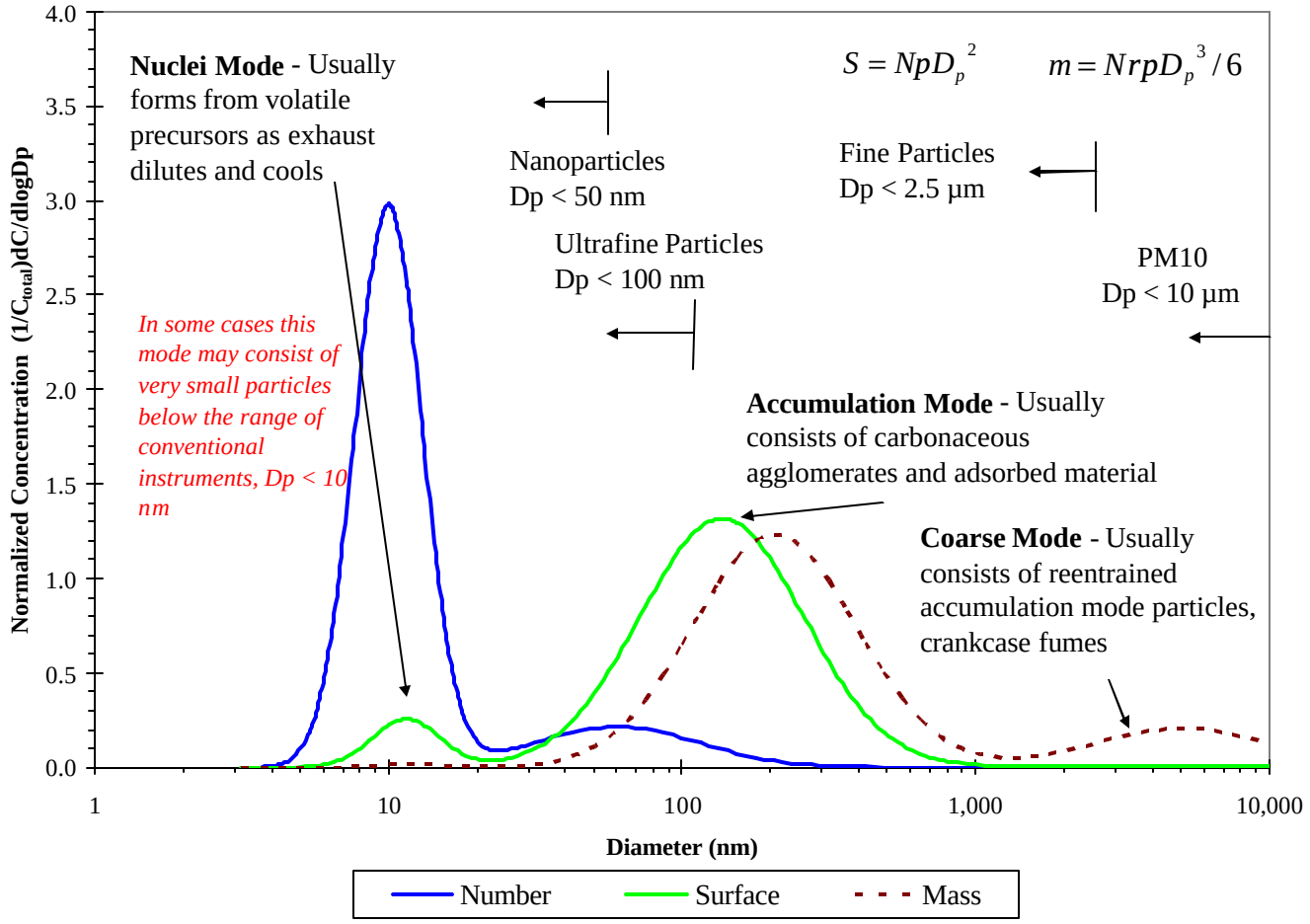
Recent engine nanoparticle measurements at the University of Minnesota

This work was supported by generous donations from BP, Castrol, Corning, Johnson-Matthey, TSI, and Volvo

Outline

- Introduction
- Review of recent on-road measurements
- Lab measurements of nucleation mode composition
- Some comparisons

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



Kittelson, D.B. 1998. "Engines and Nanoparticles: A Review," J. Aerosol Sci., Vol. 29, No. 5/6, pp. 575-588, 1998

Nucleation mode and engine technology

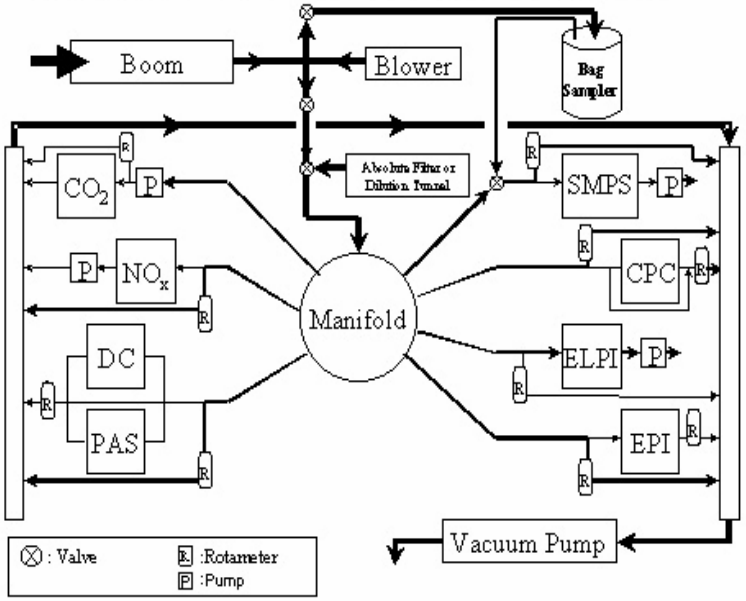
- The earliest roadside measurements made in the 1960s showed a large nucleation mode
- Early SI engines – large concentrations of lead compounds from leaded fuel
- SI with oxicat – sulfate, ash
- Traditional diesel – HC and ash (light load), HC and sulfate (higher load)
- Diesel with oxicat – HC and ash (light load), sulfate and ash (heavy load)
- Diesel with catalyzed DPF – sulfate (higher loads), HC (transients)
- CNG, LPG, H_2 – HC and ash

PM emissions for post 2007 Diesel with DPF

- The accumulation mode (ultrafine soot and adsorbed material) eliminated
- Coarse exhaust mode eliminated
- Coarse crankcase mode eliminated by PCV - maybe
- Ash particles in nucleation mode eliminated
- **Volatile nuclei mode particles that form downstream of filter are only PM emissions – all the number, surface, and mass**

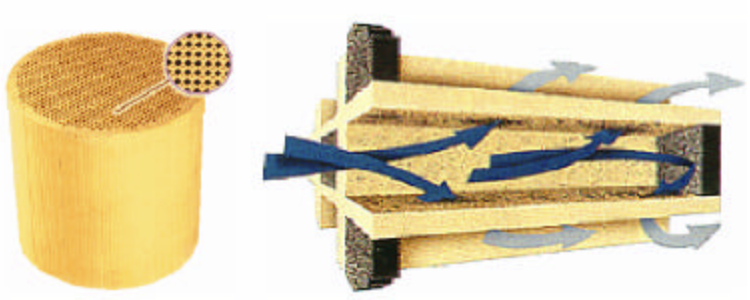
On-road exhaust filter evaluations the MEL

Mobile Emission Laboratory (MEL) Flow System Chart

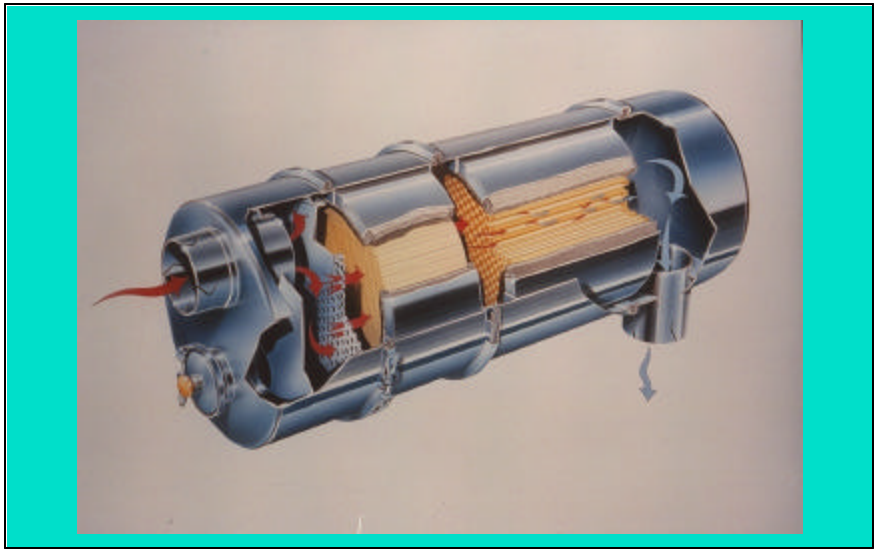


- Instruments (primary instruments in this work highlighted in blue)
  - SMPS to size particles in 9 to 300 nm size range, τ = 60 s
  - EEPS 3090 that sizes particles in the 5.6 to 560 nm range, τ < 1 s
  - 3025 CPC to count all particles larger than about 3 nm, τ ~ 1 s
  - Diffusion Charger to measure total submicron particle surface area
  - PAS to measure total submicron surface bound PAH equivalent
  - CO_2 , CO, NO and NO_2 analyzers for gas and dilution ratio determinations

Particle removal by exhaust filters – On road evaluations of CRT® and CCRT®



Figures courtesy Corning and Johnson-Matthey



- Most PM filtration systems being considered for 2007 are the wall flow type shown on the left. Without regeneration to oxidize soot these devices quickly plug.
- Catalyzed filtration systems like the J-M CRT® shown on the right reduce regeneration temperature by producing NO_2 from exhaust NO in an oxidizing catalyst upstream of filter
- The J-M CCRT® has a catalyzed washcoat on the filter as well to further reduce regeneration temperature
- NO_2 in the exhaust is an issue
- In most applications active regeneration is also required

On-road evaluations of exhaust particle filters – plume sniffing of MEL with CRT, CCRT

Kittelson, D. B., W. F. Watts, J. P. Johnson, C. Rowntree, M. Payne, S. Goodier, C. Warrens, H. Preston, U. Zink, M. Ortiz, C. Goersmann, M. V. Twigg, A. P. Walker, and R. Caldow. 2006. On-Road Evaluation of Two Diesel Exhaust Aftertreatment Devices, Journal of Aerosol Science, in press.

Kittelson, D. B., W. F. Watts, J. P. Johnson, C. J. Rowntree, S. P. Goodier, M. J. Payne, W. H. Preston, C. P. Warrens, M. Ortiz, U. Zink, C. Goersmann, M. V. Twigg and A. P. Walker, 2006. "Driving Down On-Highway Particulate Emissions," SAE paper number 2006-01-0916

Test conditions for on-road filter evaluations

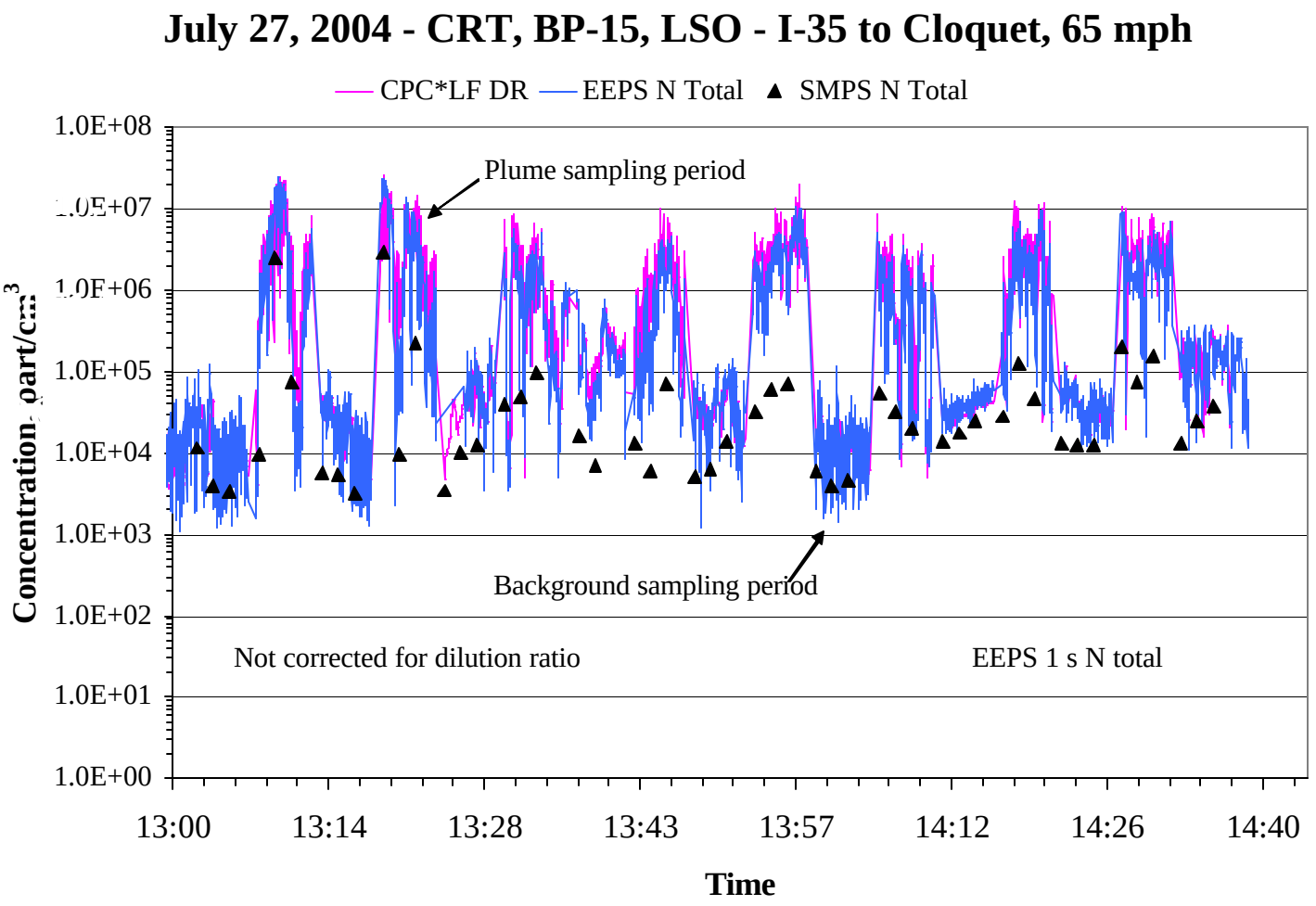
- Tests run with J-M CRT and CCRT
  - CRT consist of oxidizing catalyst plus wall flow filter
  - CCRT consist of oxidizing catalyst plus catalyzed wall flow filter
- BP15 fuel (2007 compliant)
- Castrol low S lube oil (~1500 ppm)
- 65 mph cruise on Minnesota rural freeway
- Load and exhaust temperature varied with grade, headwind, tailwind

Date[a]	Source	N[b]	CO_2, ppm		Exhaust CO_2, %		Exhaust temp, C		Ambient temp, C		Speed, km/hr	
			Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std
7/27/2004	Background	5730	371	9	6.4	1.1	317	27	25.6	1.4	107	2
7/27/2004	Plume	5182	527	88	6.4	1.1	318	27	25.6	1.3	108	2
7/29/2004	Background	5580	386	13	6.4	1.1	312	33	21.4	2.2	107	2
7/29/2004	Plume	4963	494	100	6.4	1.1	312	29	21.2	2.2	107	2
8/5/2004	Background	5924	395	12	6.3	1.1	312	19	22.8	1.6	106	2
8/5/2004	Plume	5272	625	99	6.3	1.1	311	20	22.8	1.6	106	2
8/11/2004	Background	3980	380	11	6.5	1.0	313	24	16.1	0.9	107	2
8/11/2004	Plume	3290	520	102	6.3	1.2	312	28	16.2	0.9	107	3
8/12/2004	Background	6134	386	9	6.3	0.9	317	19	19.6	1.5	109	2
8/12/2004	Plume	5274	588	95	6.3	0.9	317	19	19.6	1.5	109	4

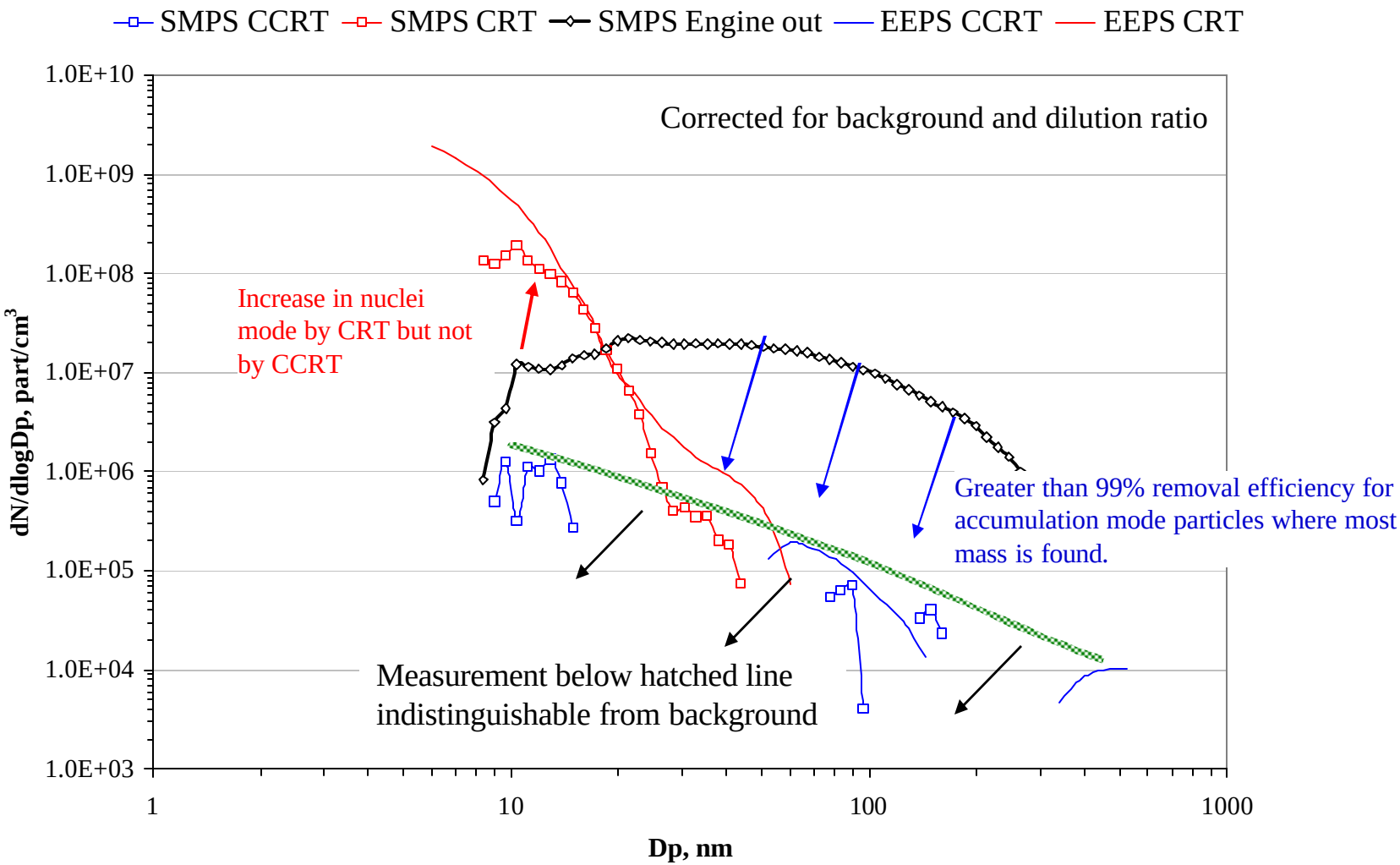
[a] 7/27 and 7/29 a CRT was used; 8/5, 8/11,8/12 a CCRT was used

[b] N is the number of measurements recorded by the data logger at approximately 1 second intervals

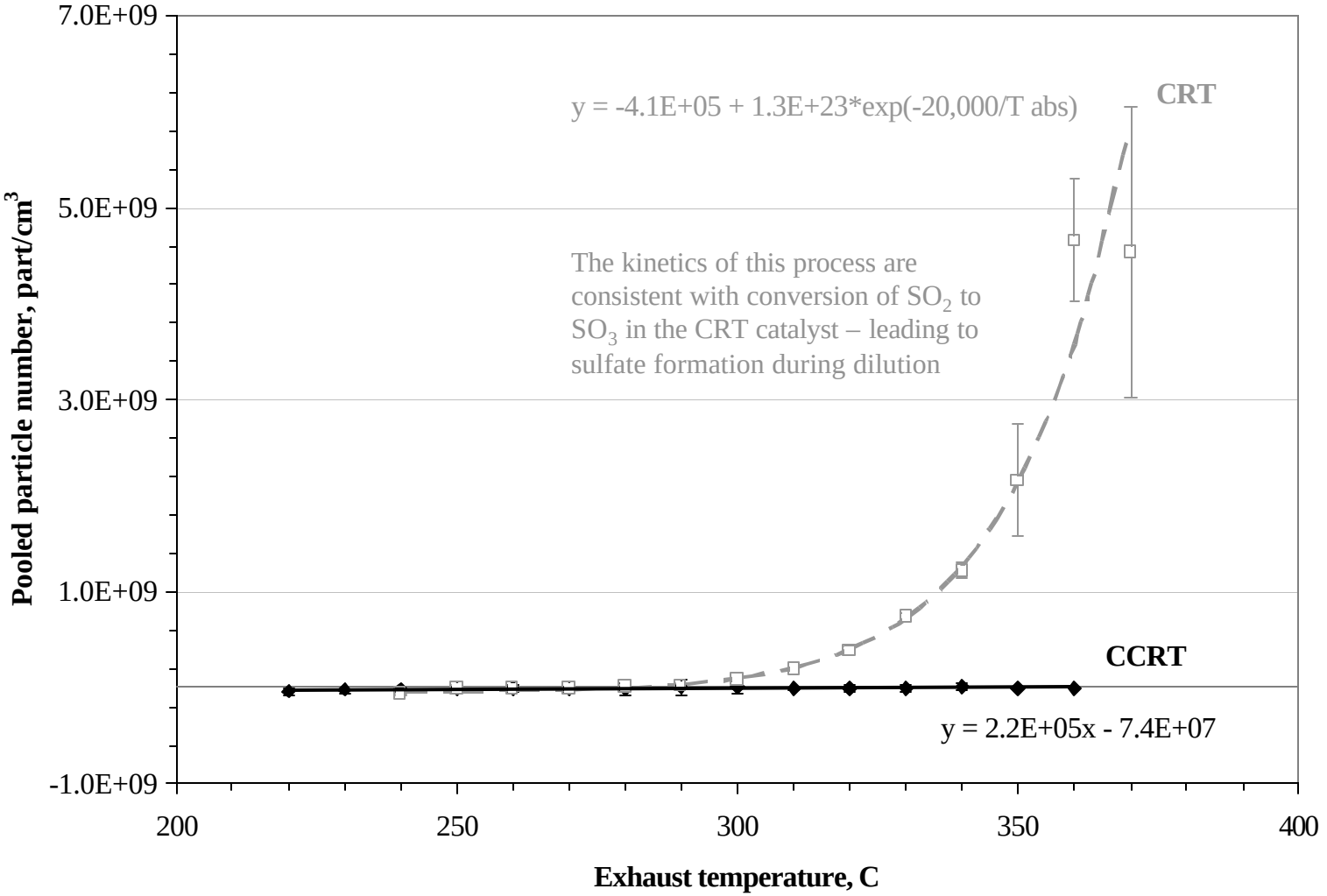
Sampling pattern – background, plume, background



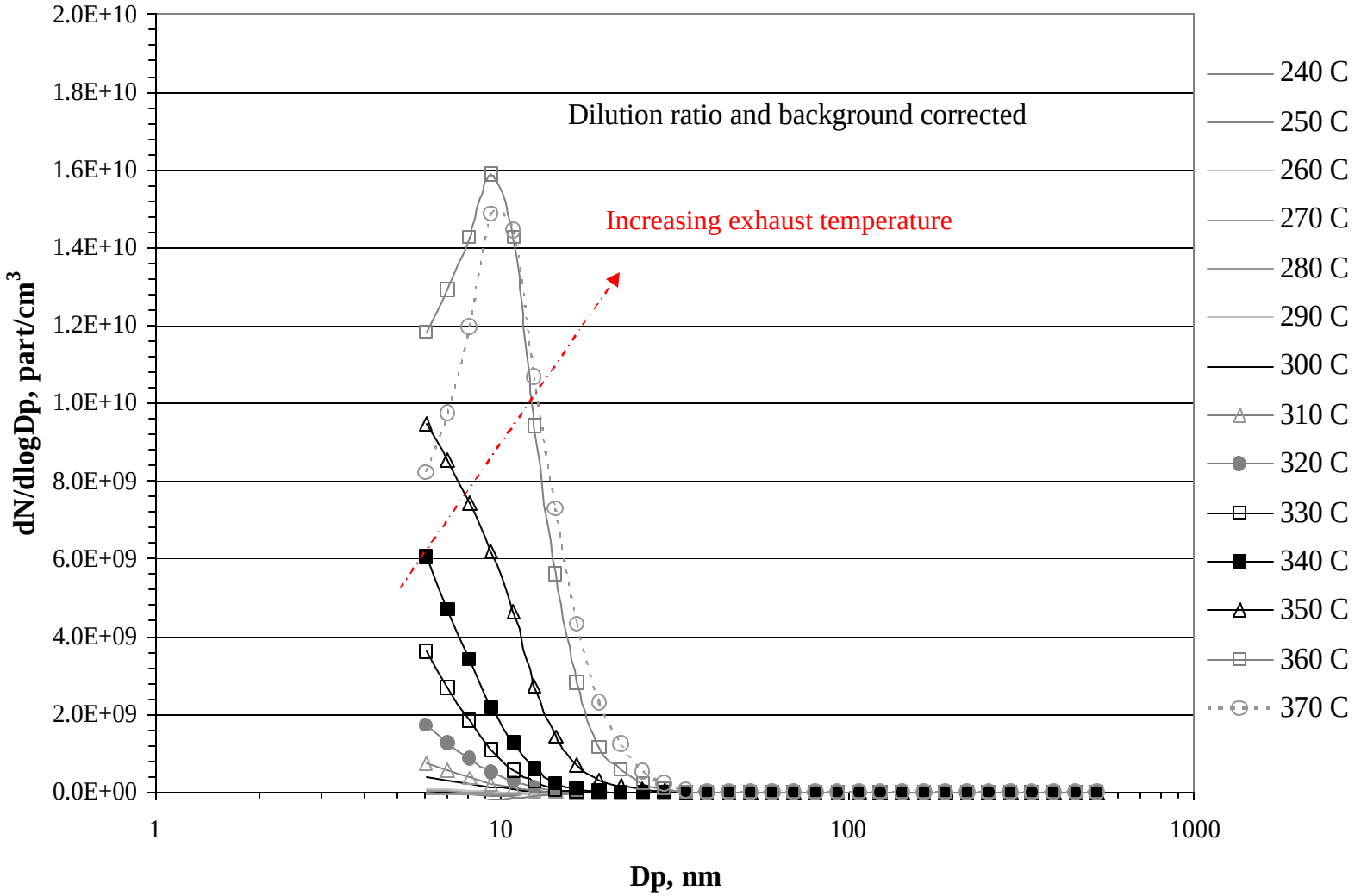
Plume – background size distributions corrected for dilution ratio - BP15 fuel and LSO



The CRT showed strongly temperature dependent number emissions but the CCRT showed no detectable emissions



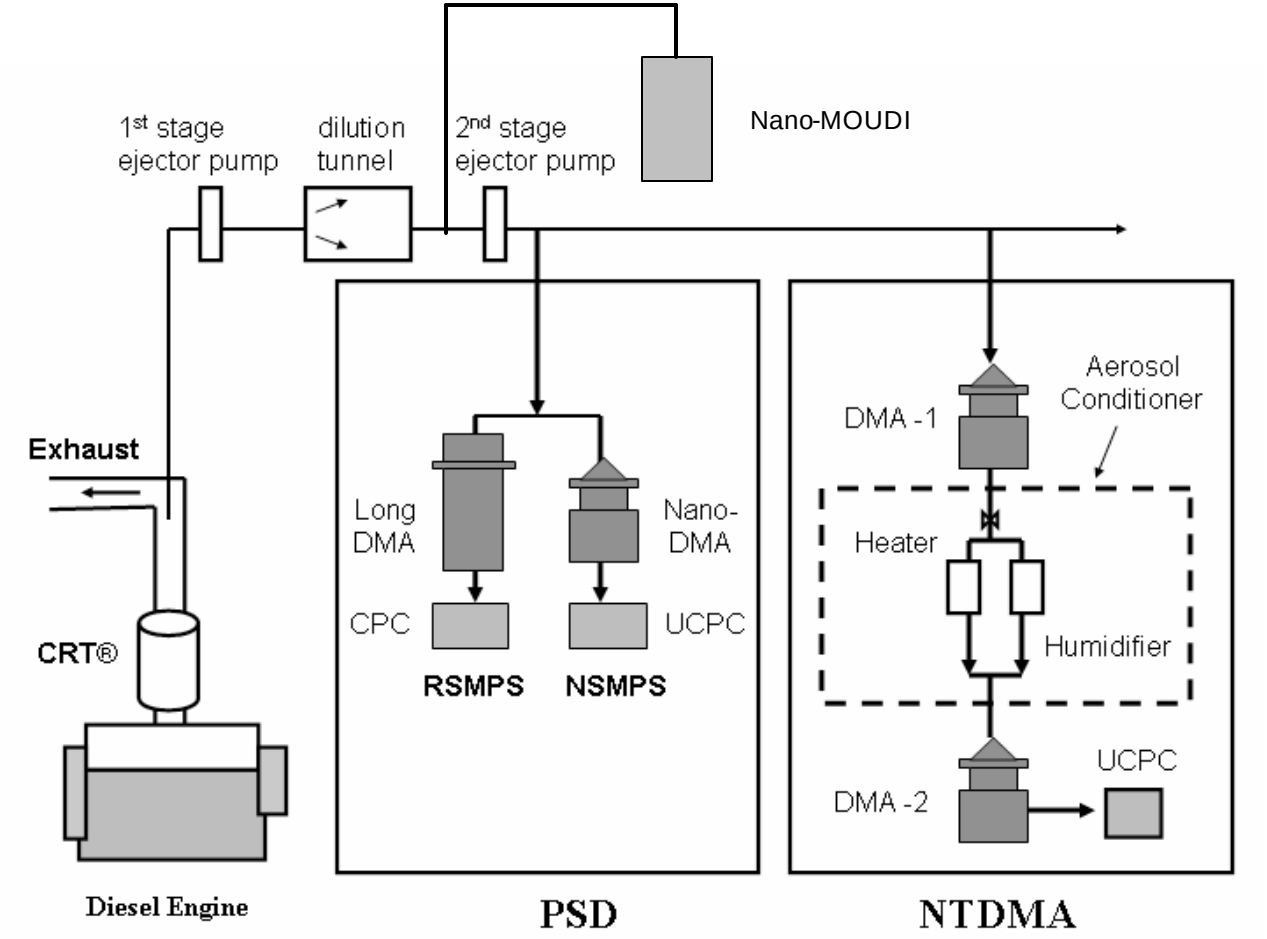
Nearly all particles downstream of CRT were in nucleation mode and strongly temperature dependent



Conclusions - On-road CRT and CCRT measurements

- CRTs and CCRTs tested on-road under relatively light load conditions
- In the accumulation mode size range where most of the mass is found:
  - Neither the CRT nor the CCRT emitted concentrations significantly above background ambient air.
  - This corresponds to > 99% removal efficiency
- Significant number emissions were observed with the CRT
  - The particles are extremely small nucleation mode particles
  - These particles represent nearly no mass
  - Number emissions are extremely exhaust temperature dependent
  - The particles are believed to be mainly sulfuric acid
- CCRT number emissions could not be distinguished from ambient air
  - This effect is not fully understood
  - Apparently particle precursors are stored in catalyzed filter section

Composition of volatile nucleation mode particles downstream catalyzed exhaust filtration system



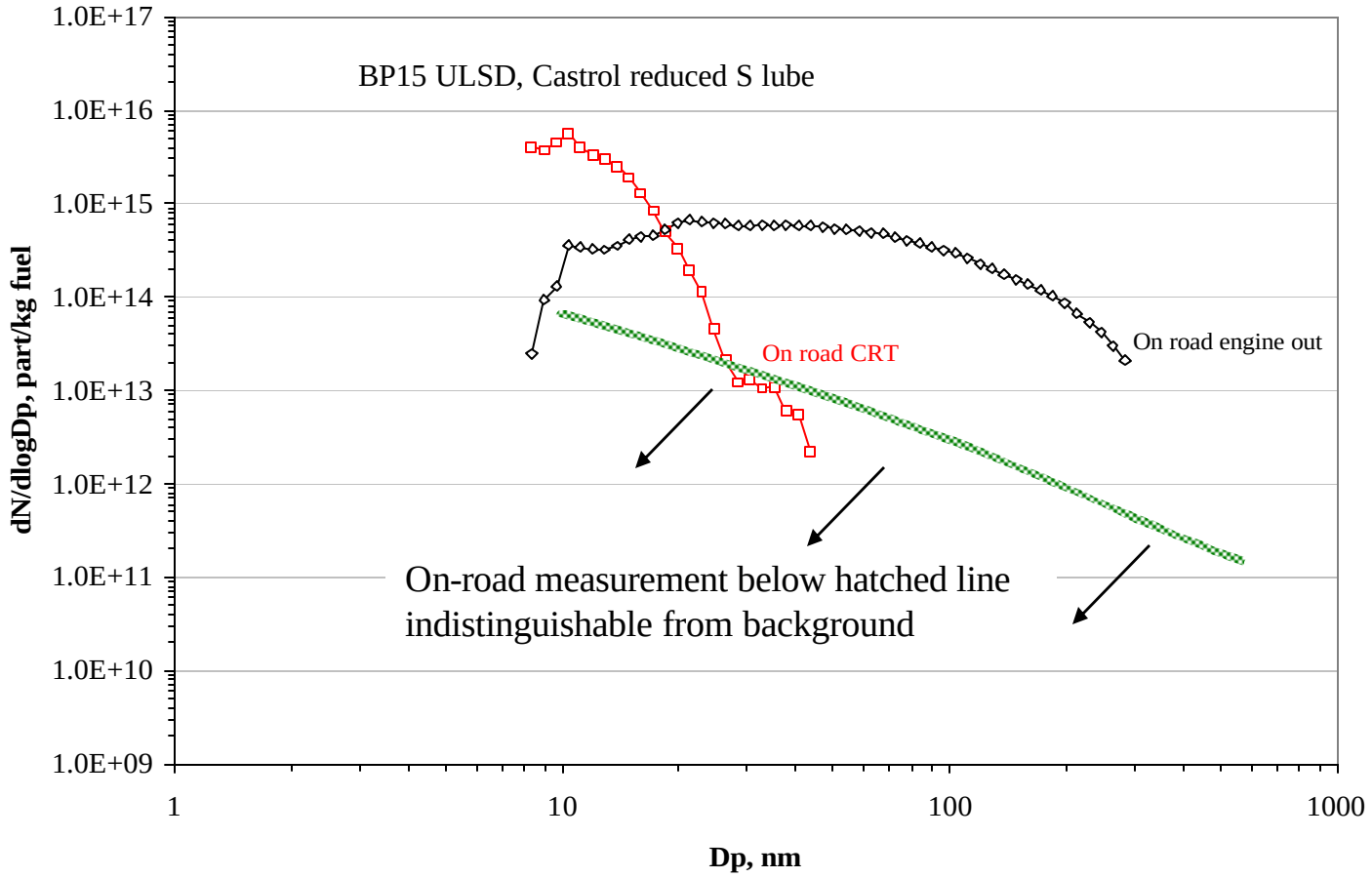
Fink, M., H. Sakurai, J. Savstrom, M. R. Stolzenburg, W. F. Watts, Jr., C. G. Morgan, I. P. Murray, M. V. Twigg, D. B. Kittelson, and P. H. McMurry, 2006. "Chemical and Physical Properties of Ultrafine Diesel Exhaust Particles Sampled Downstream of a Catalytic Trap," Environmental Science and Technology, in review.

Summary – Lab measurements of composition of nucleation mode particles formed after CRT

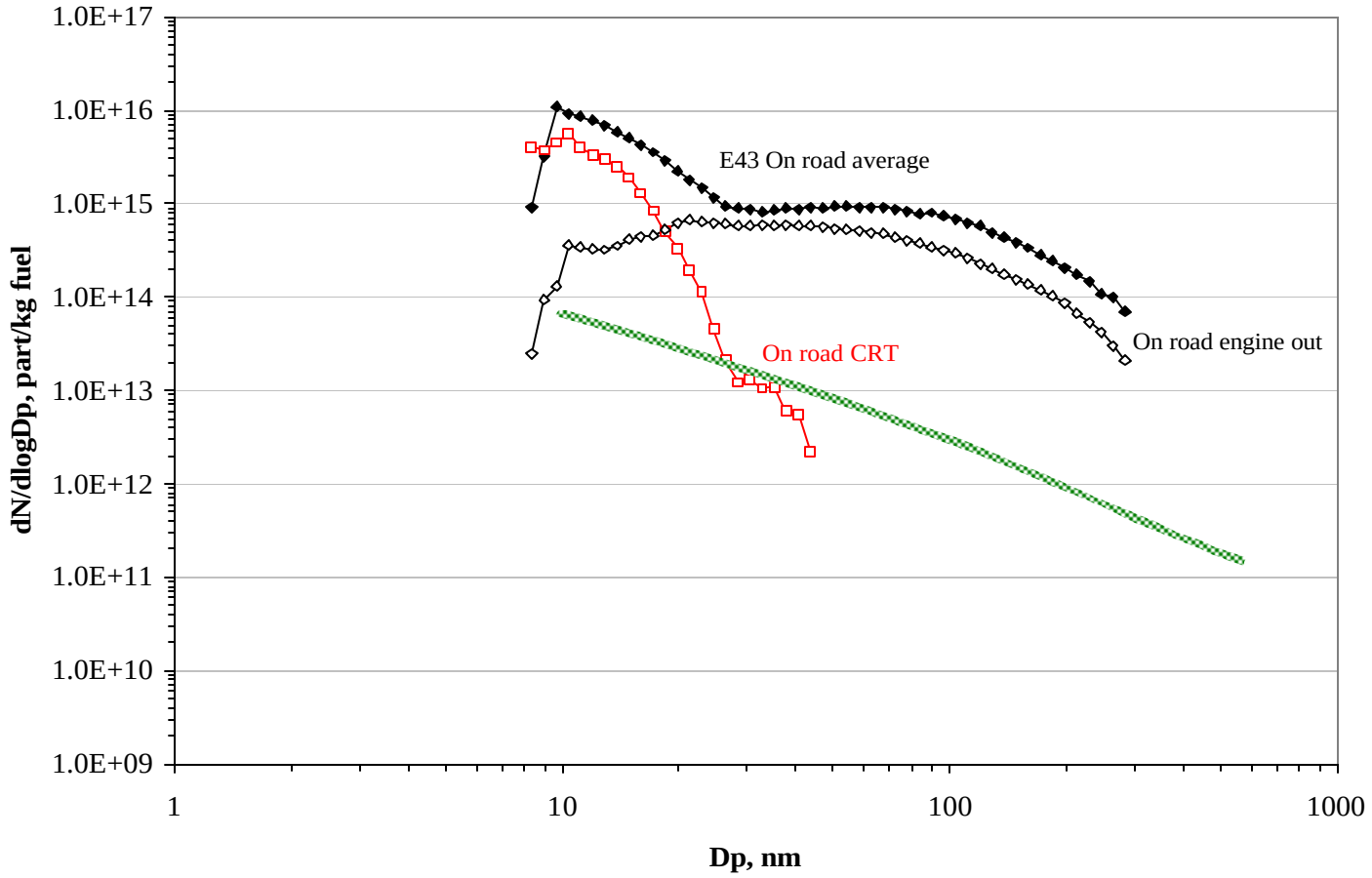
- The amount of material in the nucleation mode was very sensitive to the sulfur content of the fuel - the nucleation mode volume with BP15 was only 7% of that with BP50
- Nano-TDMA measurements
  - Particles evaporate like ammonium sulfate
  - Particles are hygroscopic and grow like ammonium sulfate
  - The behavior of these particles is very different from nucleation mode particles formed by heavy-duty engines without aftertreatment which are mainly heavy hydrocarbons
- Nano-MOUDI measurements
  - Very little organic carbon found
  - The only ion found in significant concentration was sulfate – suggesting mainly sulfuric acid
- Apparently sulfuric acid is neutralized by ambient ammonia in nano-TDMA
- This neutralization will also occur under on-road conditions, characteristic time ~ 10 s
- Details of these measurements will appear in the paper listed below

Fink, M., H. Sakurai, J. Savstrom, M. R. Stolzenburg, W. F. Watts, Jr., C. G. Morgan, I. P. Murray, M. V. Twigg, D. B. Kittelson, and P. H. McMurry, 2006. "Chemical and Physical Properties of Ultrafine Diesel Exhaust Particles Sampled Downstream of a Catalytic Trap," Environmental Science and Technology, in review.

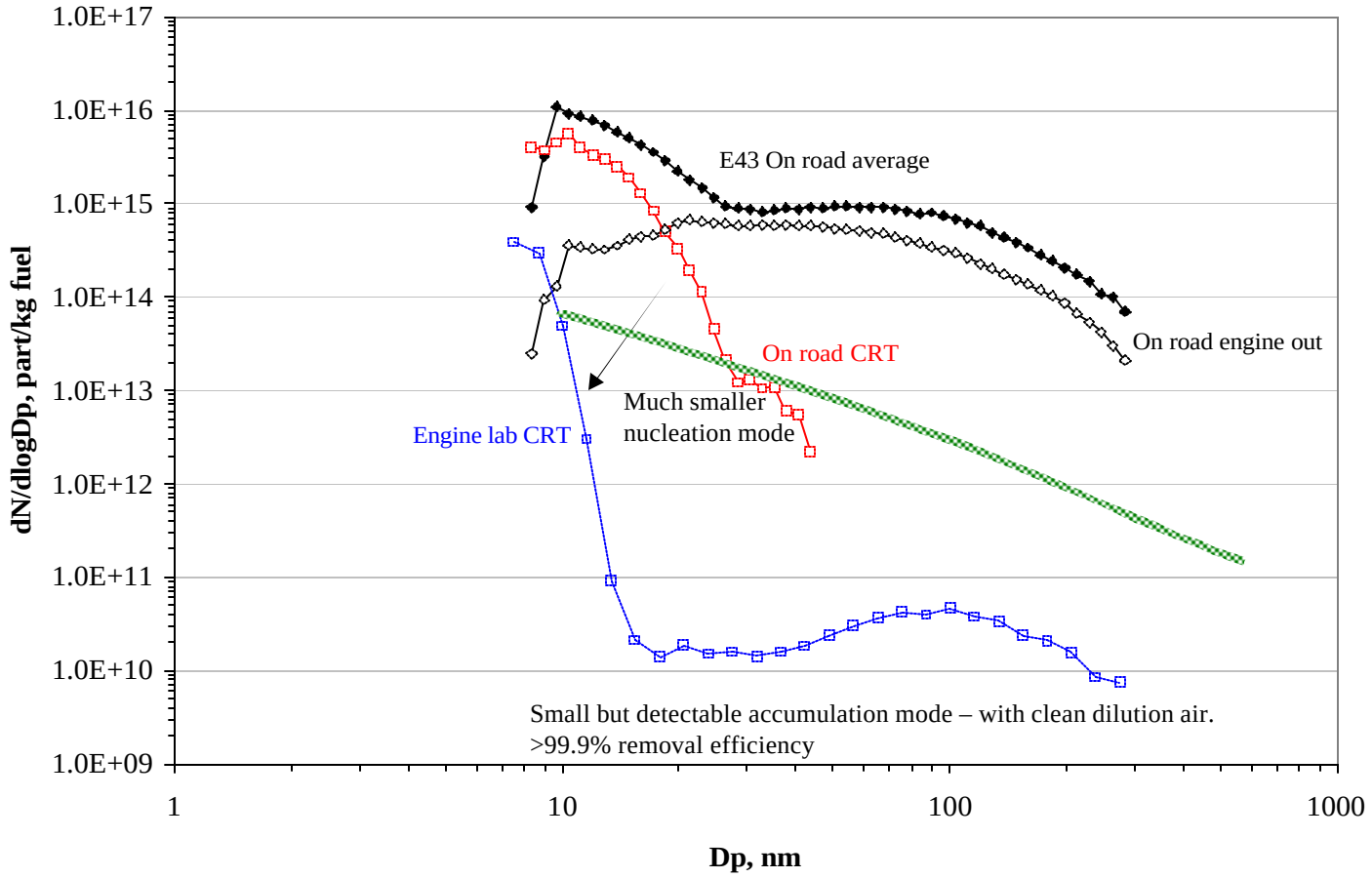
Here the results are put into a fuel specific form so that they may be compared with other studies



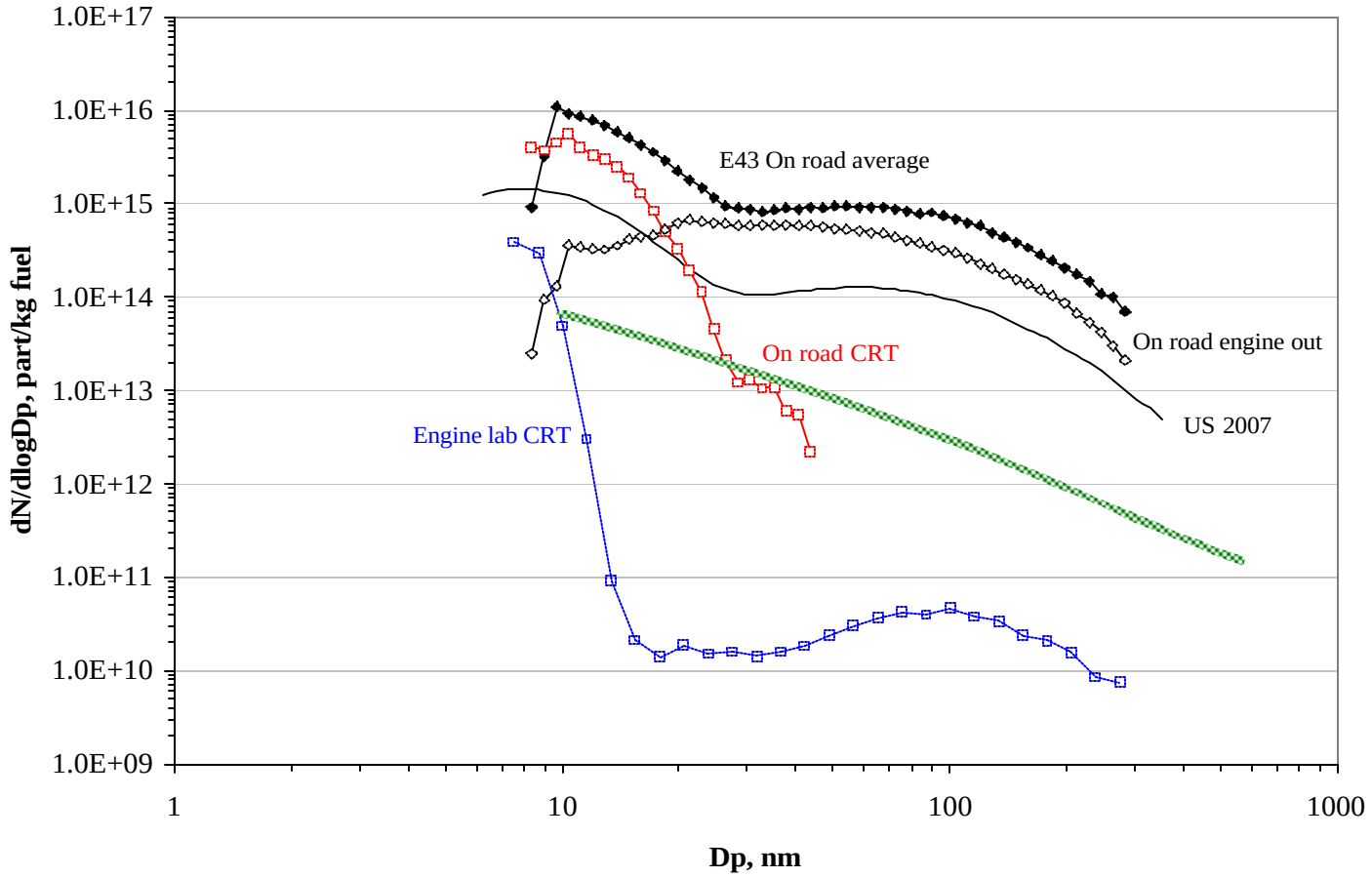
Here we compare with the on road fleet tested in the E43 program – engine out ~350 ppm S fuel



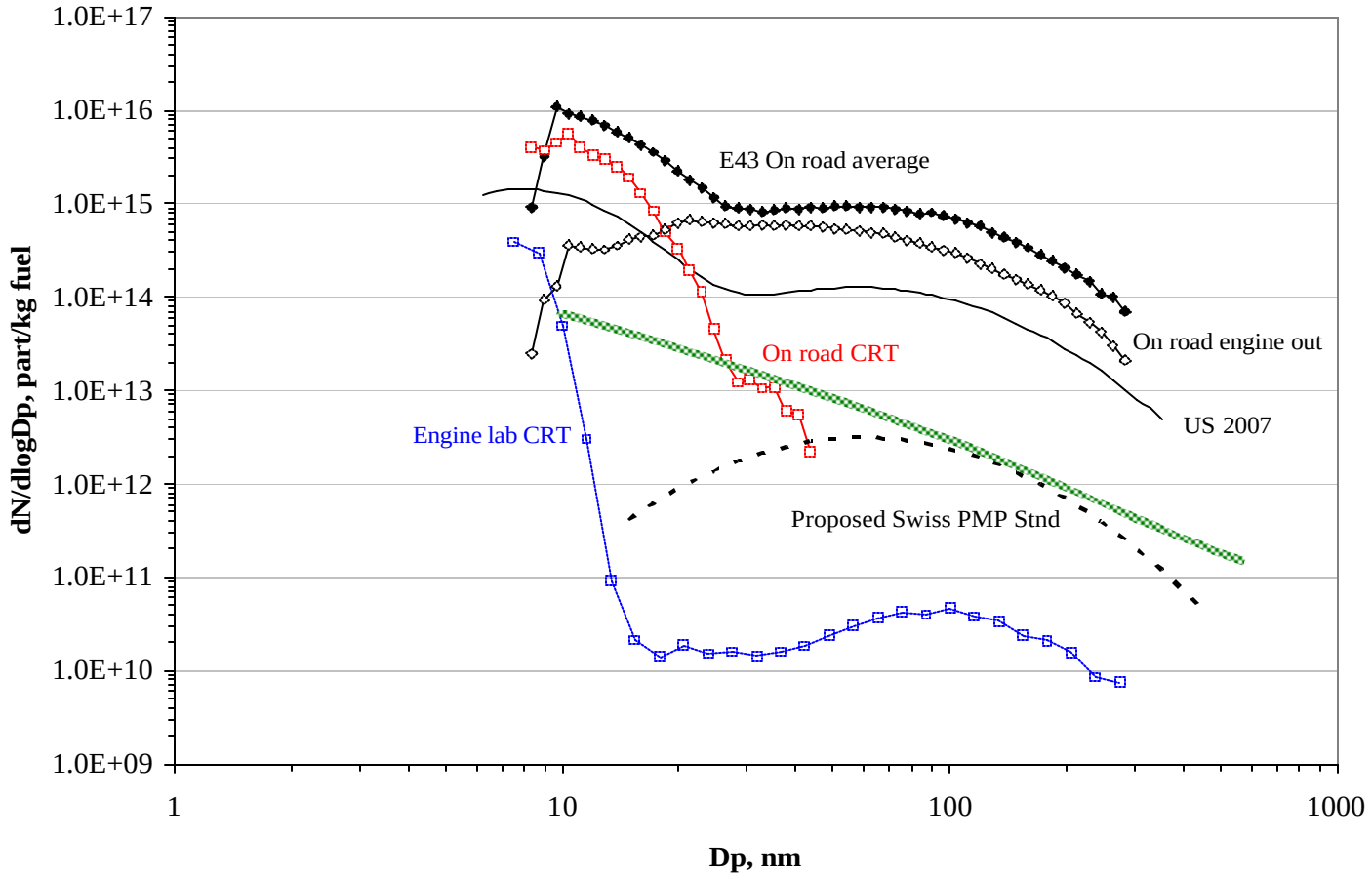
What if we test the CRT in the lab – same BP15 fuel and operating condition



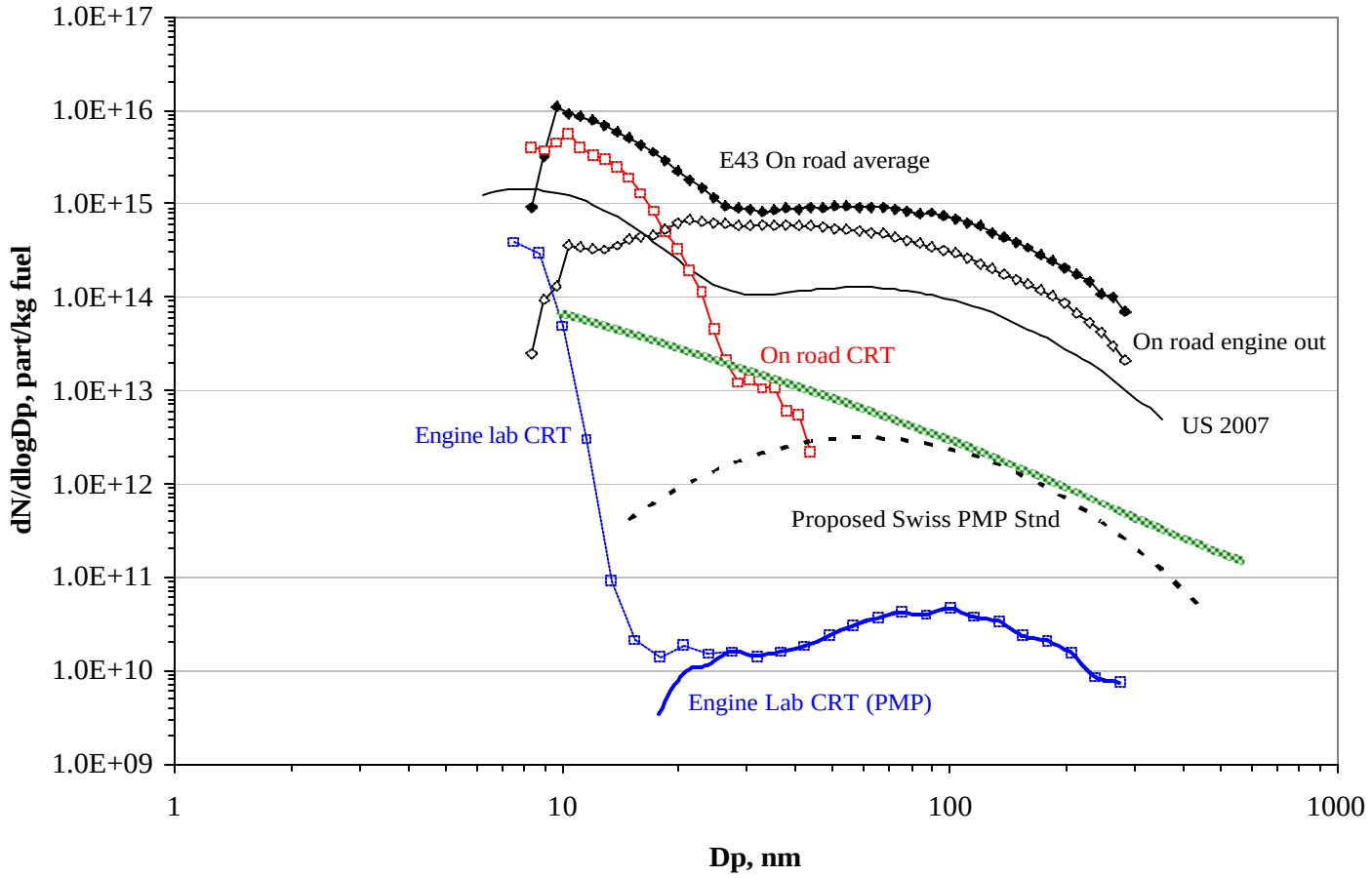
CRT accumulation mode well below the US 2007 standard (mass converted to equivalent number)



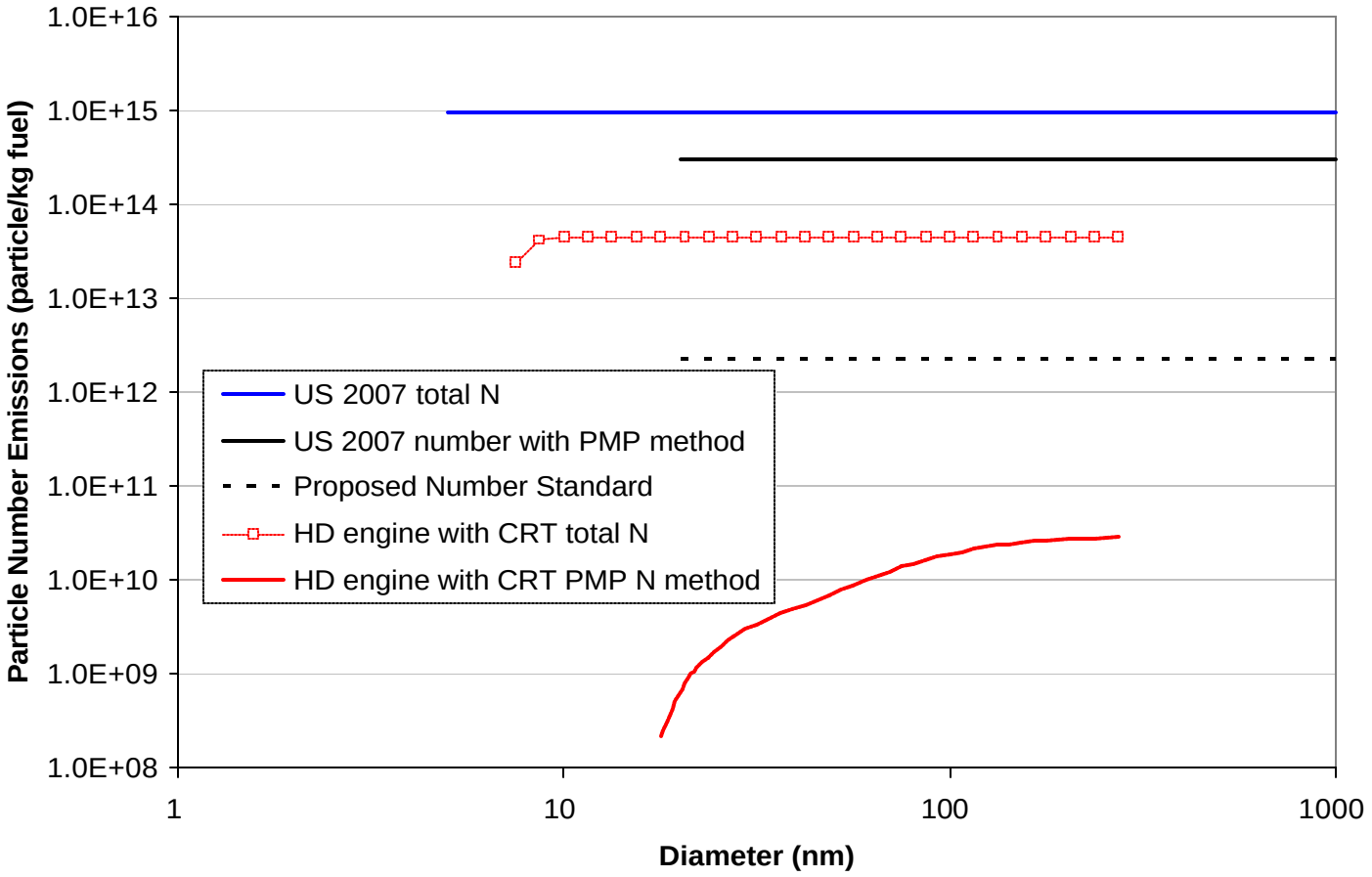
Here the an estimate of the proposed Swiss and EU number standard is added



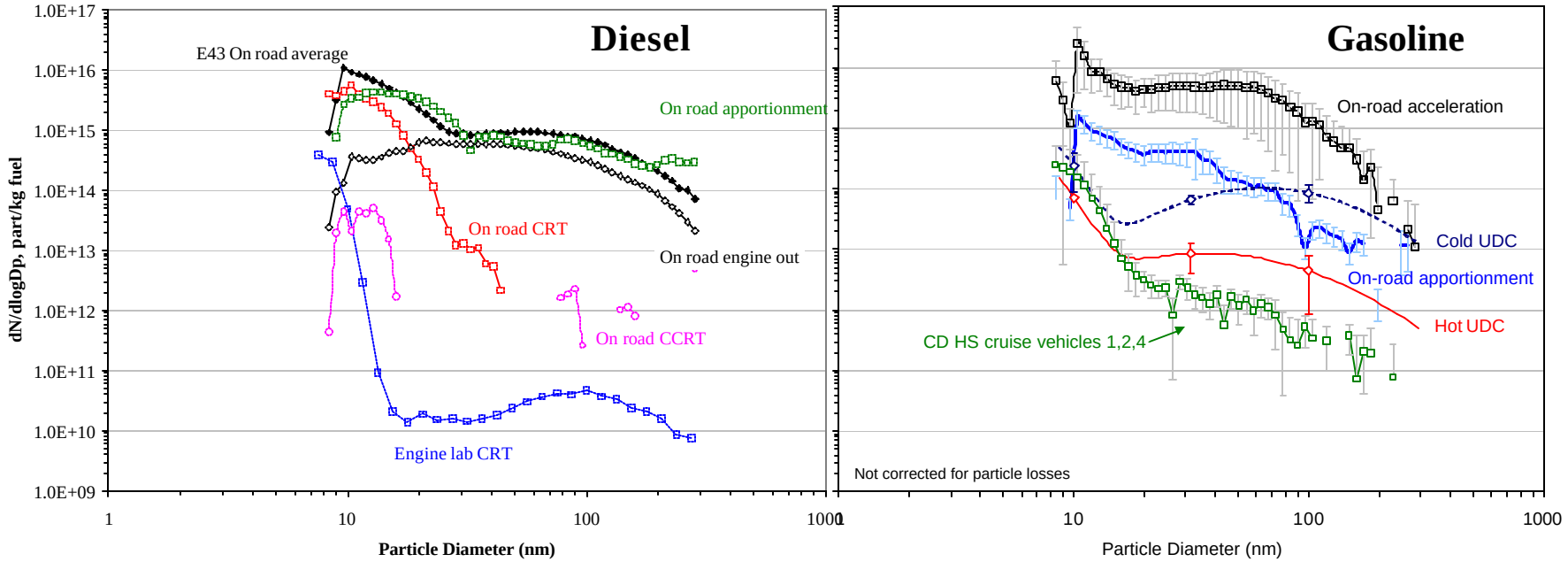
Here the lab measurement has been treated in the manner of the PMP program removing nuclei mode



Lab measurements of similar system compared to standards – cumulative number emissions



On-road and lab experiments – comparison of Diesel and gasoline SI emission



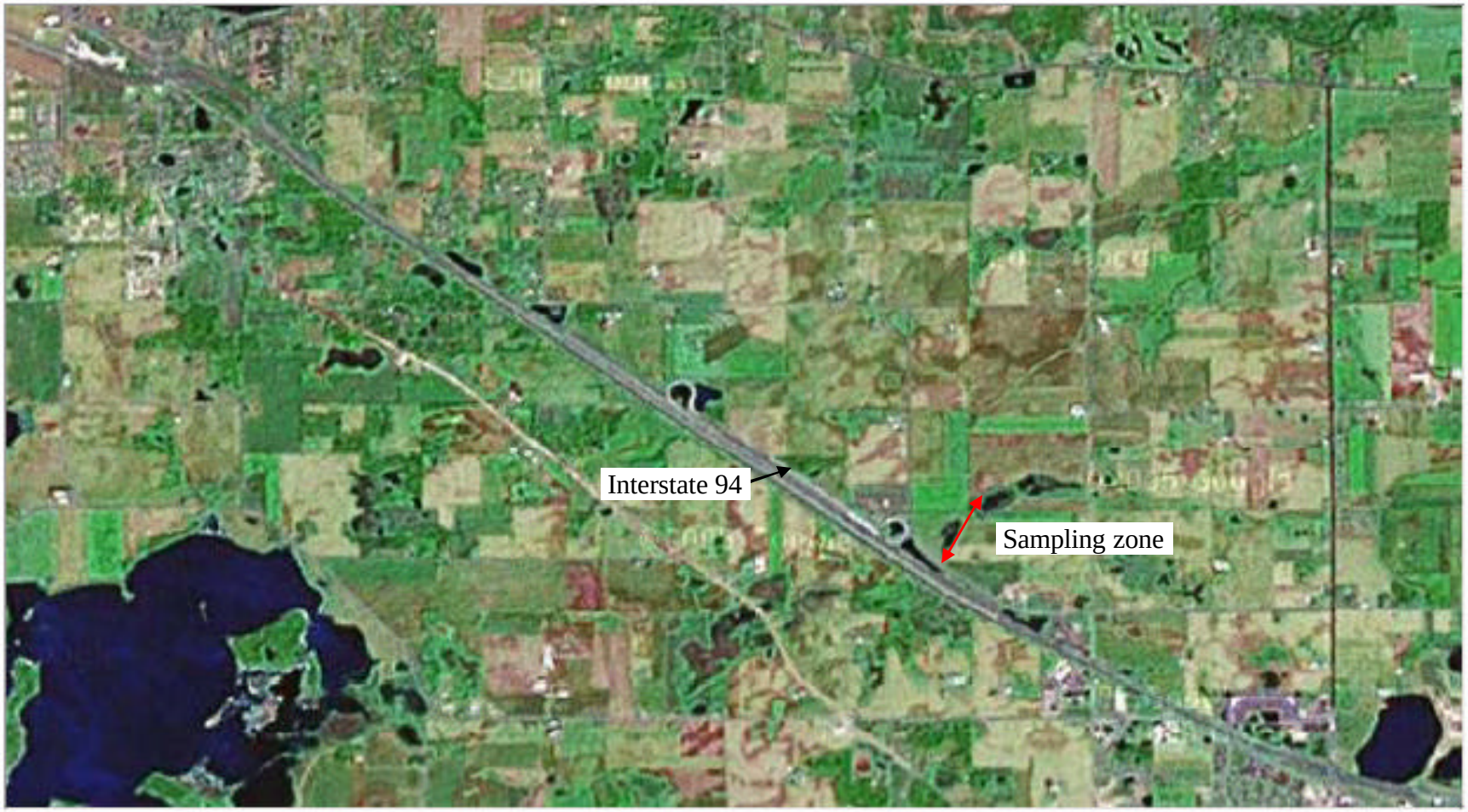
- SI emissions are much more load dependent than Diesel
- During highway cruise SI emissions are significantly lower than Diesel
- However, during hard accelerations, size distributions for gasoline light-duty vehicles were surprisingly similar to modern heavy-duty Diesel vehicles
- Diesel with CRT or CCRT has lowest emissions

Johnson, Jason P., David B. Kittelson, Winthrop F. Watts, 2005. "Source Apportionment of Diesel and Spark Ignition Exhaust Aerosol Using On-Road Data from the Minneapolis Metropolitan Area," Atmospheric Environment 39, 2111–2121.

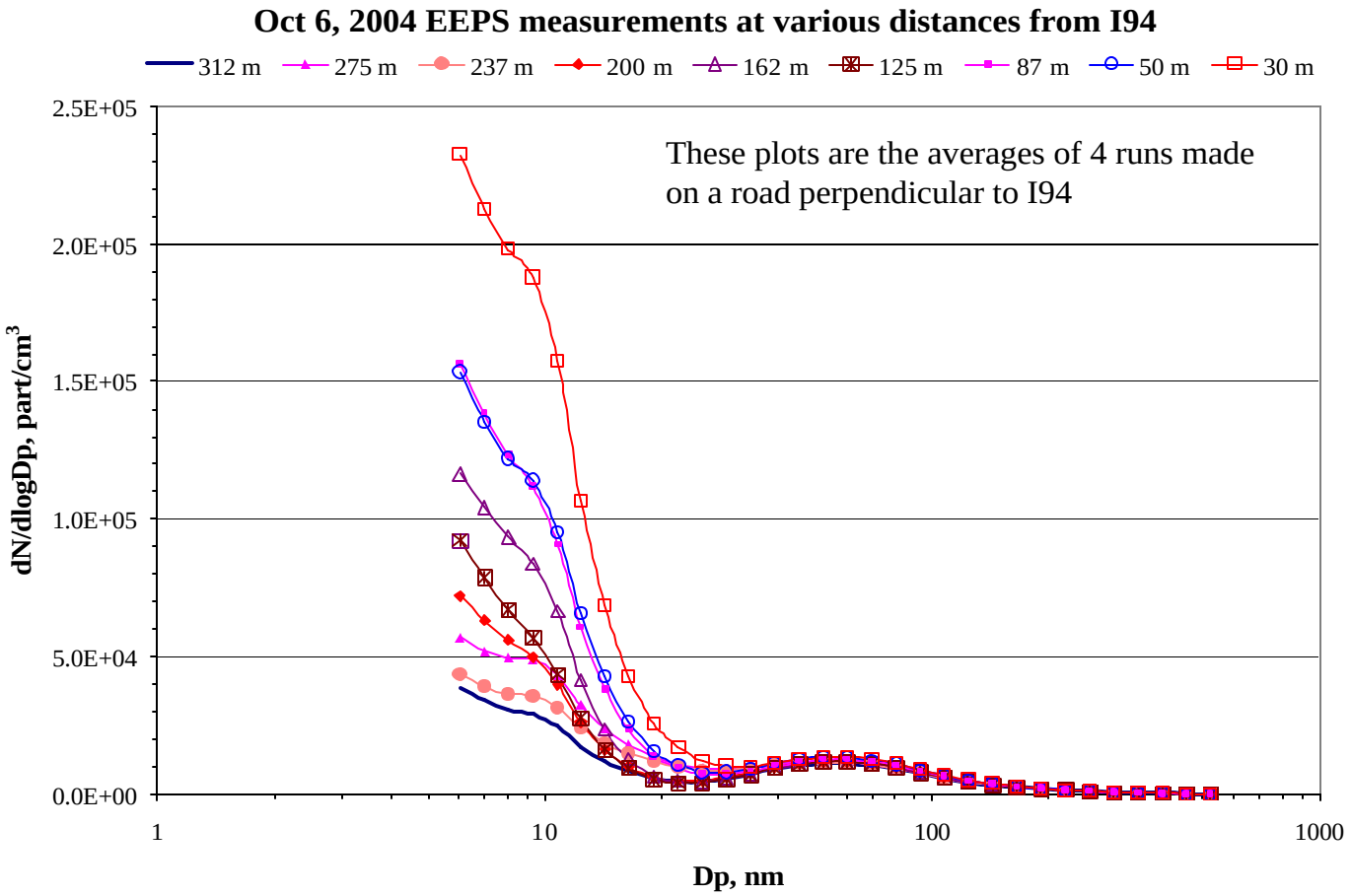
Kittelson, D. B., W. F. Watts, J. P. Johnson, J. Schauer, and D. R. Lawson 2006. "On-road and Laboratory Evaluation of Combustion Aerosols Part 2: Summary of Spark Ignition Engine Results," Journal of Aerosol Science, in press.

Kittelson, D. B., W. F. Watts, J. P. Johnson, C. J. Rowntree, S. P. Goodier, M. J. Payne, W. H. Preston, C. P. Warrens, M. Ortiz, U. Zink, C. Goersmann, M. V. Twigg and A. P. Walker, 2006. "Driving Down On-Highway Particulate Emissions," SAE paper number 2006-01-0916

Measurements of the decay of nanoparticles downwind of a major rural roadway

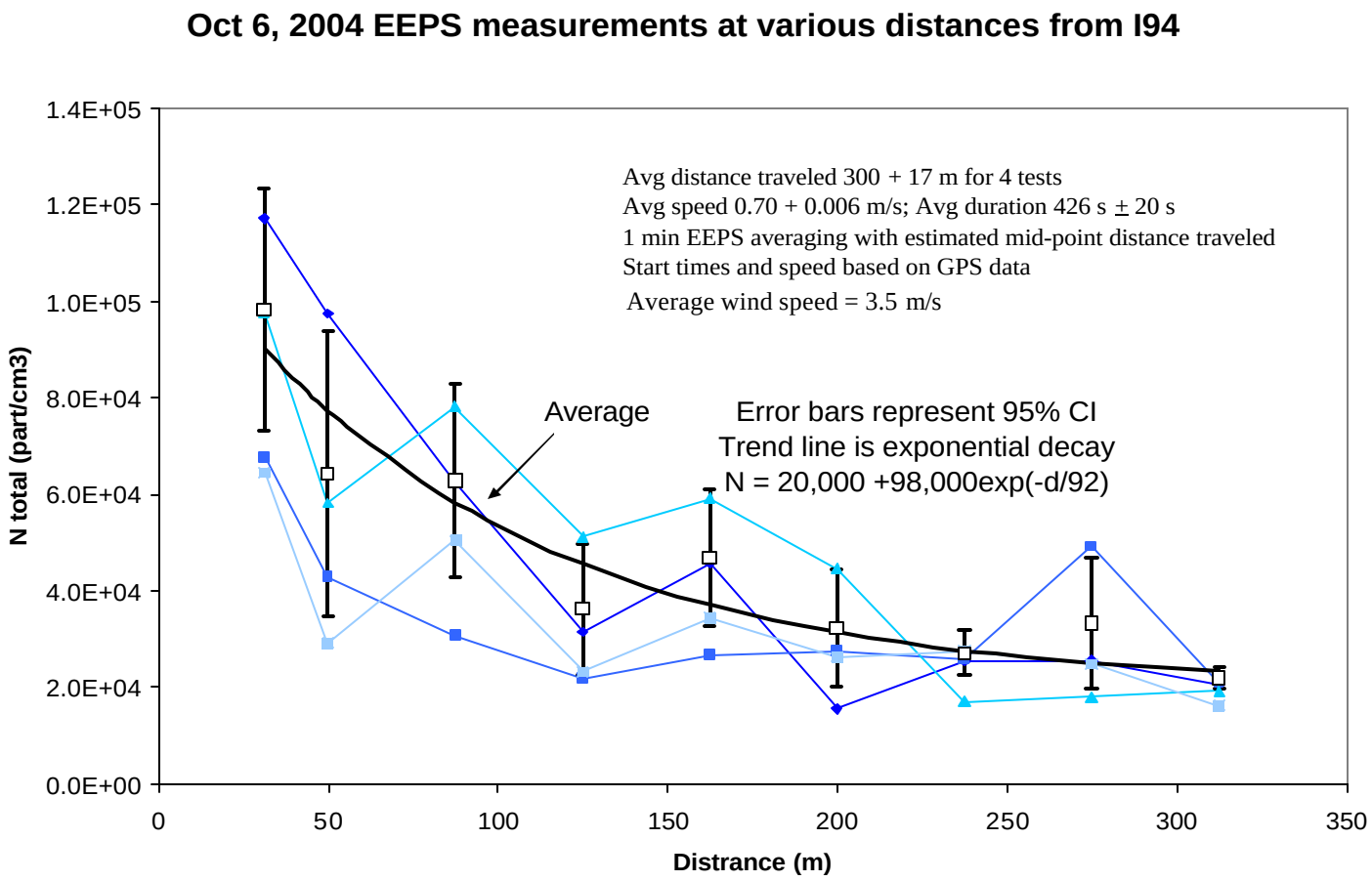


EEPS measurements show nuclei mode decays quickly downwind of rural roadway



These measurement are described and modeled in: Jacobson, M. Z., D. B. Kittelson, and W. F. Watts. 2005. "Enhanced Coagulation Due to Evaporation and its Effect on Nanoparticle Evolution," Environmental Science and Technology, v 39, n 24, p 9486-9492

Integrated EEPS number measurements downwind of rural freeway show rapid decay



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