Chemical and Physical Properties of Nucleation Mode Diesel Exhaust Particles Sampled Downstream of a Catalyzed Filtration System

D. B. Kittelson, M. Fink, H. Sakurai, J. Savstrom, M. R. Stolzenburg, W. F. Watts, Jr., and P. H. McMurry
Center for Diesel Research
Department of Mechanical Engineering
University of Minnesota

C. G. Morgan, I. P. Murray, and M. V. Twigg
Johnson-Matthey, plc
Royston, England

10th ETH-Conference on Combustion Generated Nanoparticles

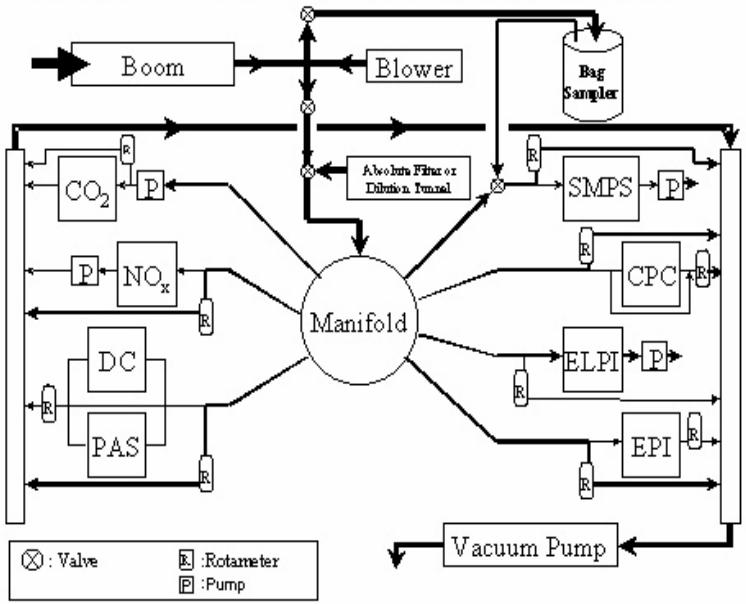
August 21st –23rd 2006

Outline

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

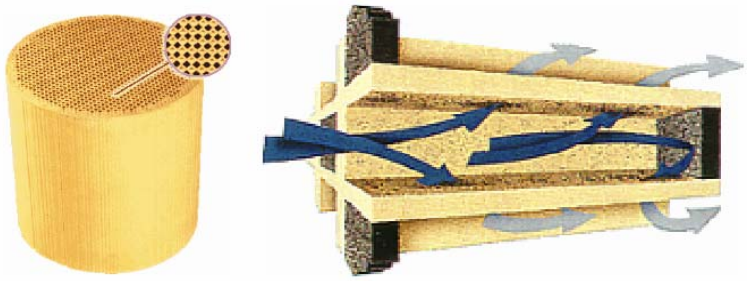
On-road exhaust filter evaluations the MEL

Mobile Emission Laboratory (MEL) Flow System Chart

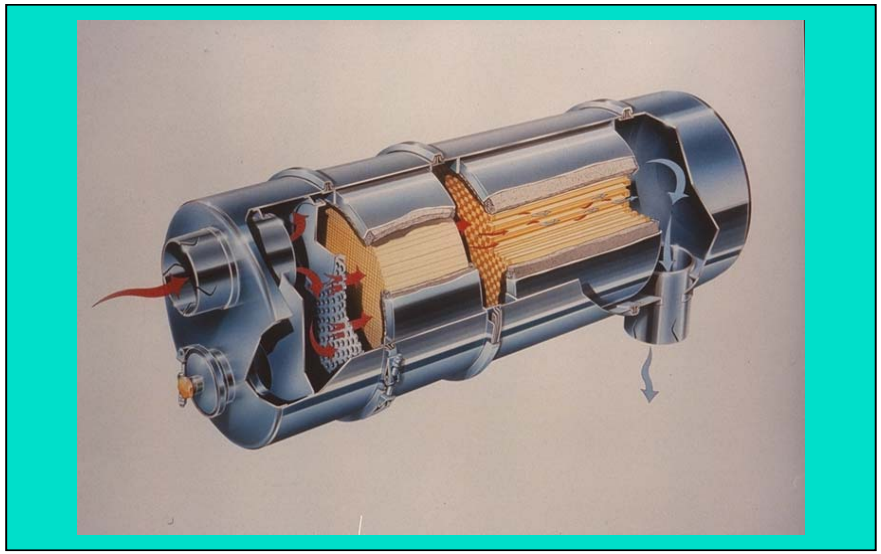


- Instruments (primary instruments in this work highlighted in blue)
  - SMPS to size particles in 9 to 300 nm size range, τ = 60 s
  - EEPS 3090 that sizes particles in the 5.6 to 560 nm range, τ < 1 s
  - 3025 CPC to count all particles larger than about 3 nm, τ ~ 1 s
  - Diffusion Charger to measure 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



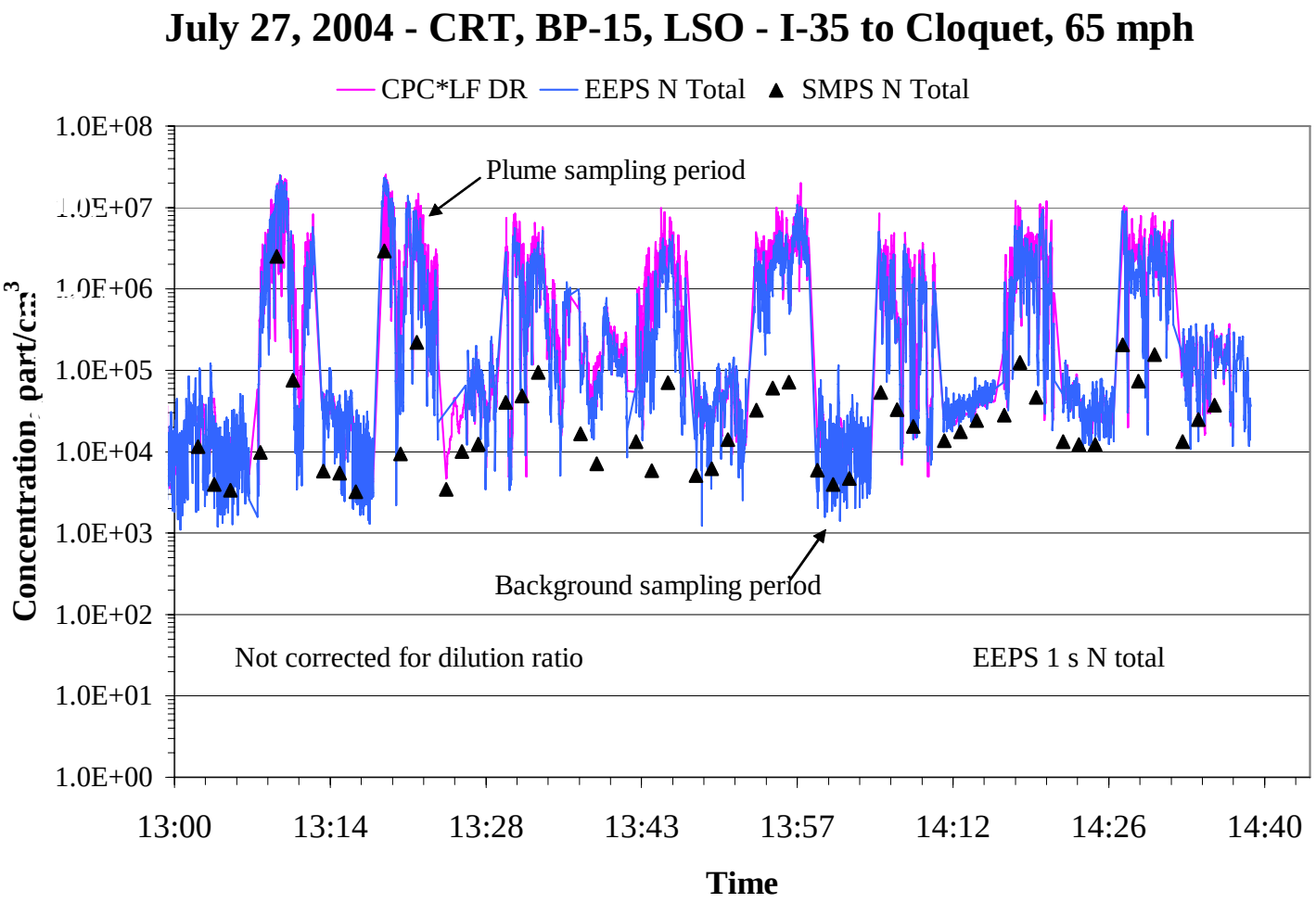
- Most PM filtration systems being considered for 2007 are the wall flow type shown on the left. Without regeneration to oxidize soot these devices quickly plug.
- Catalyzed filtration systems like the J-M CRT® shown on the right reduce regeneration temperature by producing NO_2 from exhaust NO in an 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

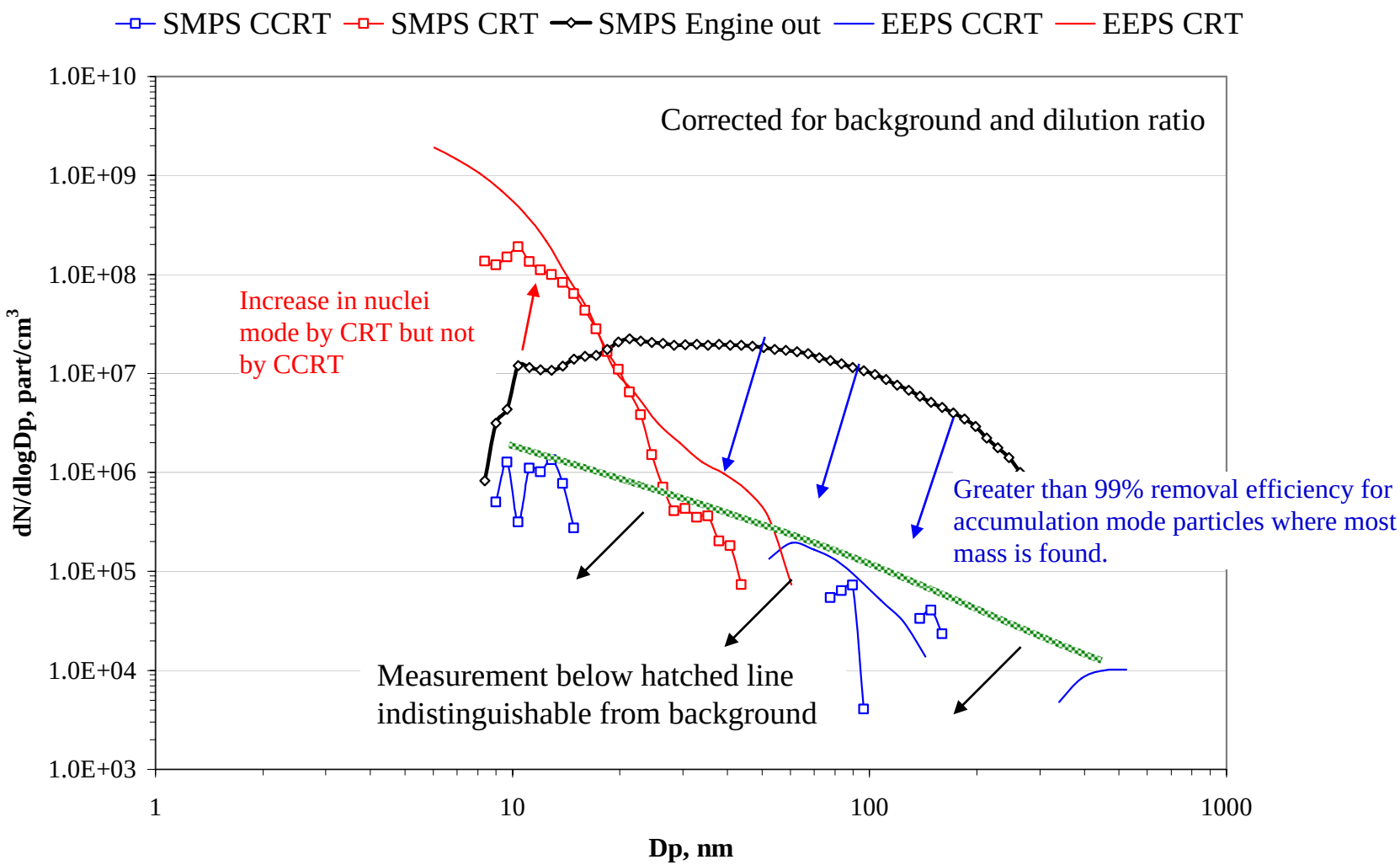
Kittelson, D. B., W. F. Watts, J. P. Johnson, C. Rowntree, M. Payne, S. Goodier, C. Warrens, H. Preston, U. Zink, M. Ortiz, C. Goersmann, M. V. Twigg, A. P. Walker, and R. Caldow. 2006. On-Road Evaluation of Two Diesel Exhaust Aftertreatment Devices, Journal of Aerosol Science, in press.

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

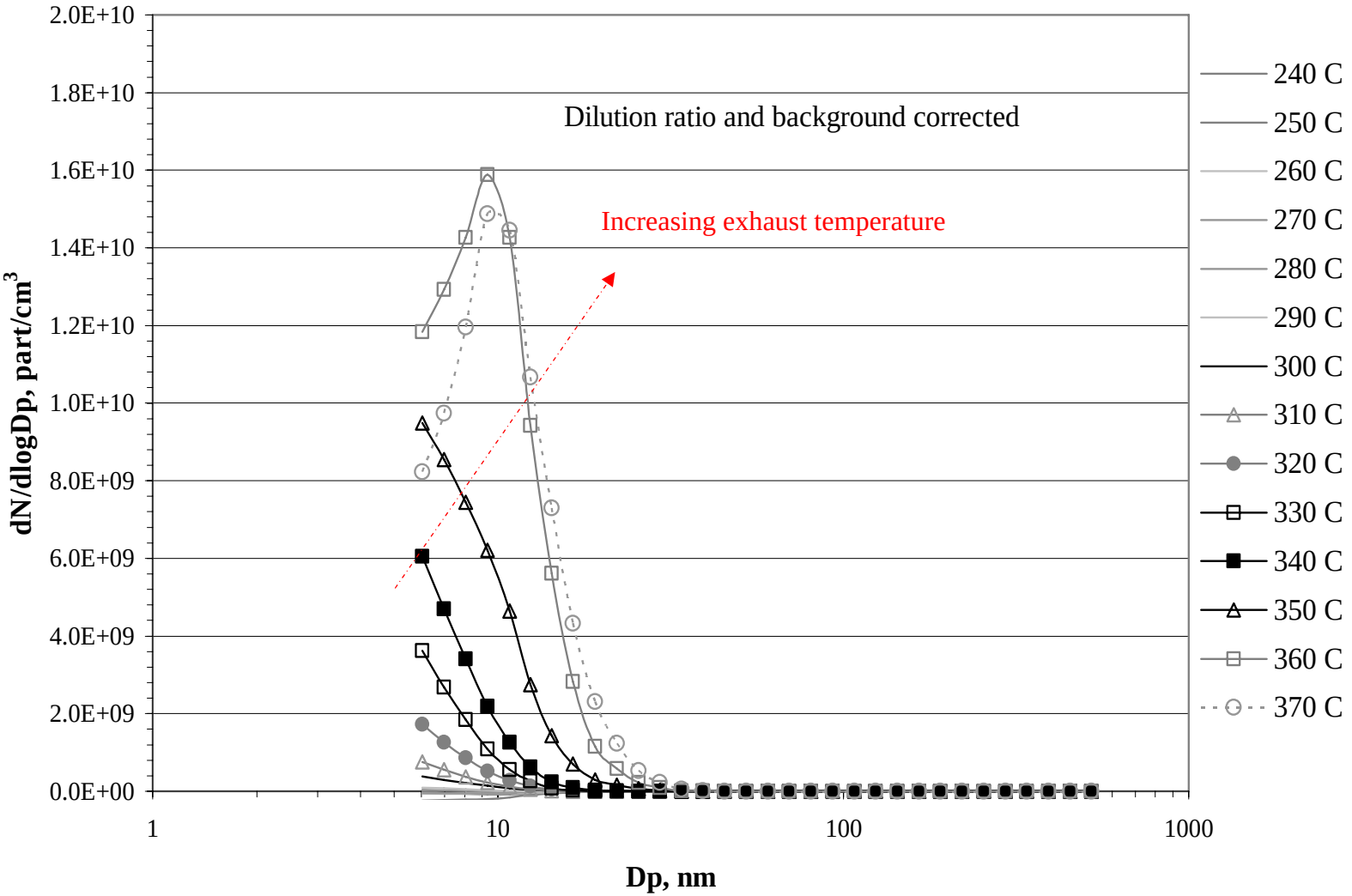
Sampling pattern – background, plume, background



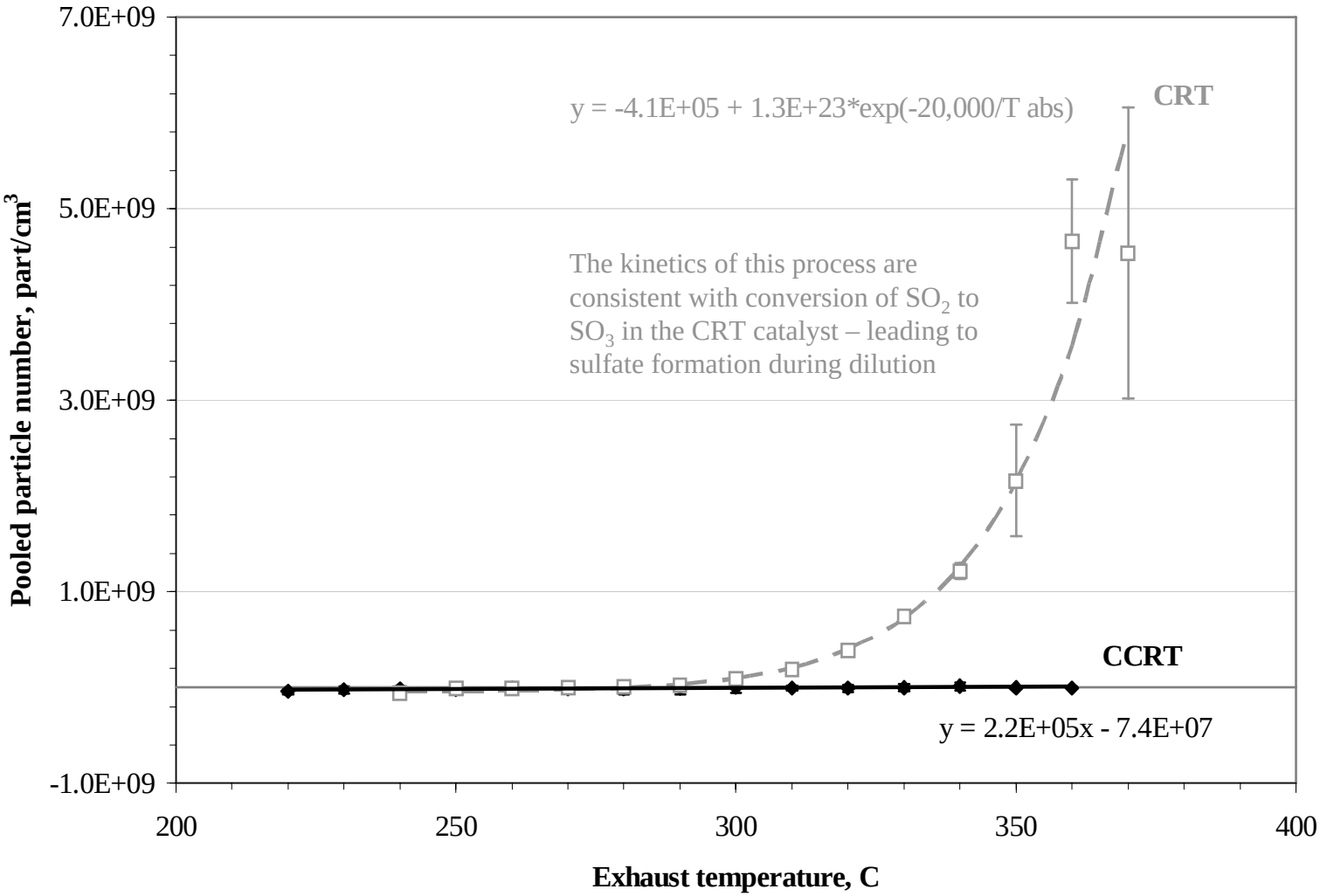
Plume – background size distributions corrected for dilution ratio - BP15 fuel and LSO



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



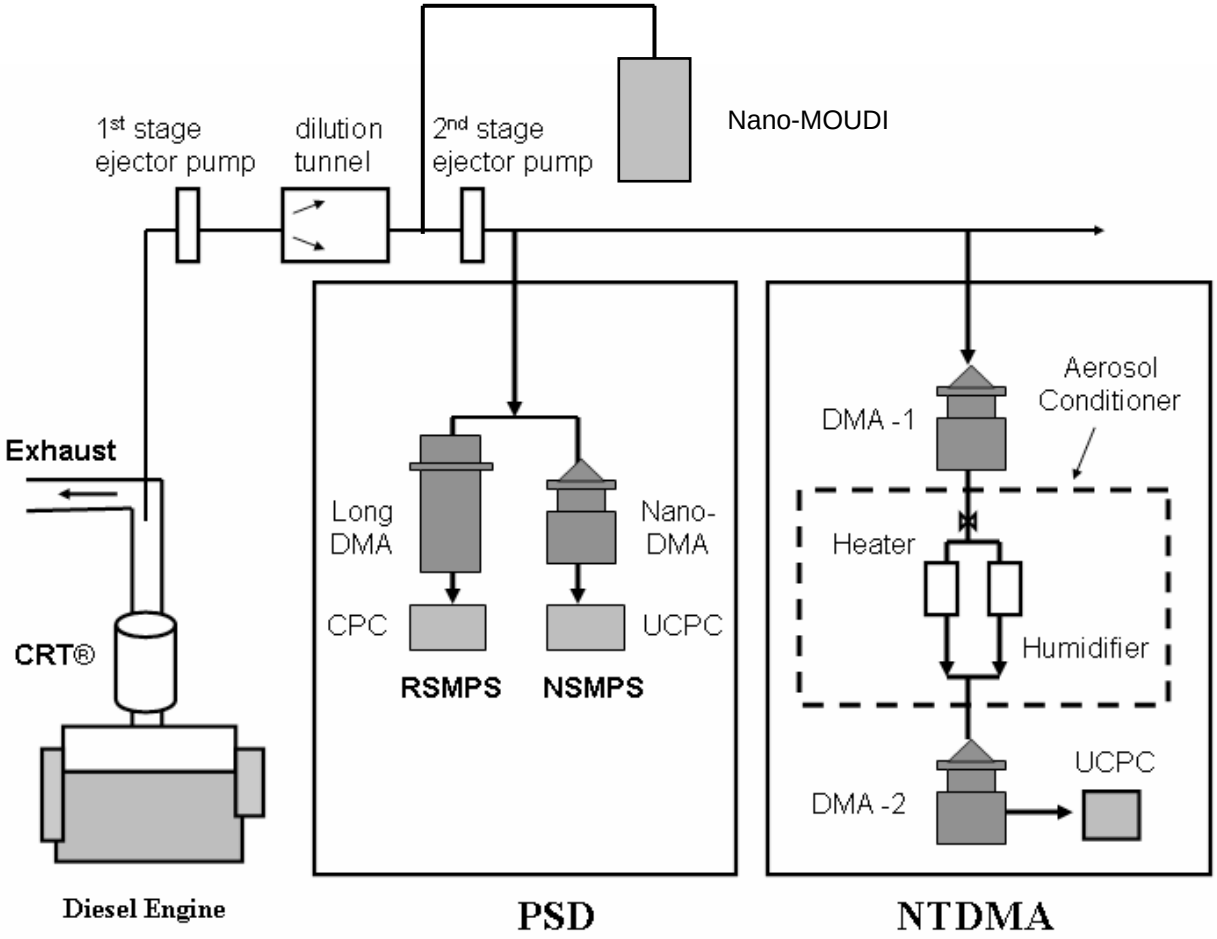
The CRT showed strongly temperature dependent number emissions but the CCRT showed no detectable emissions



Conclusions - On-road CRT and CCRT measurements

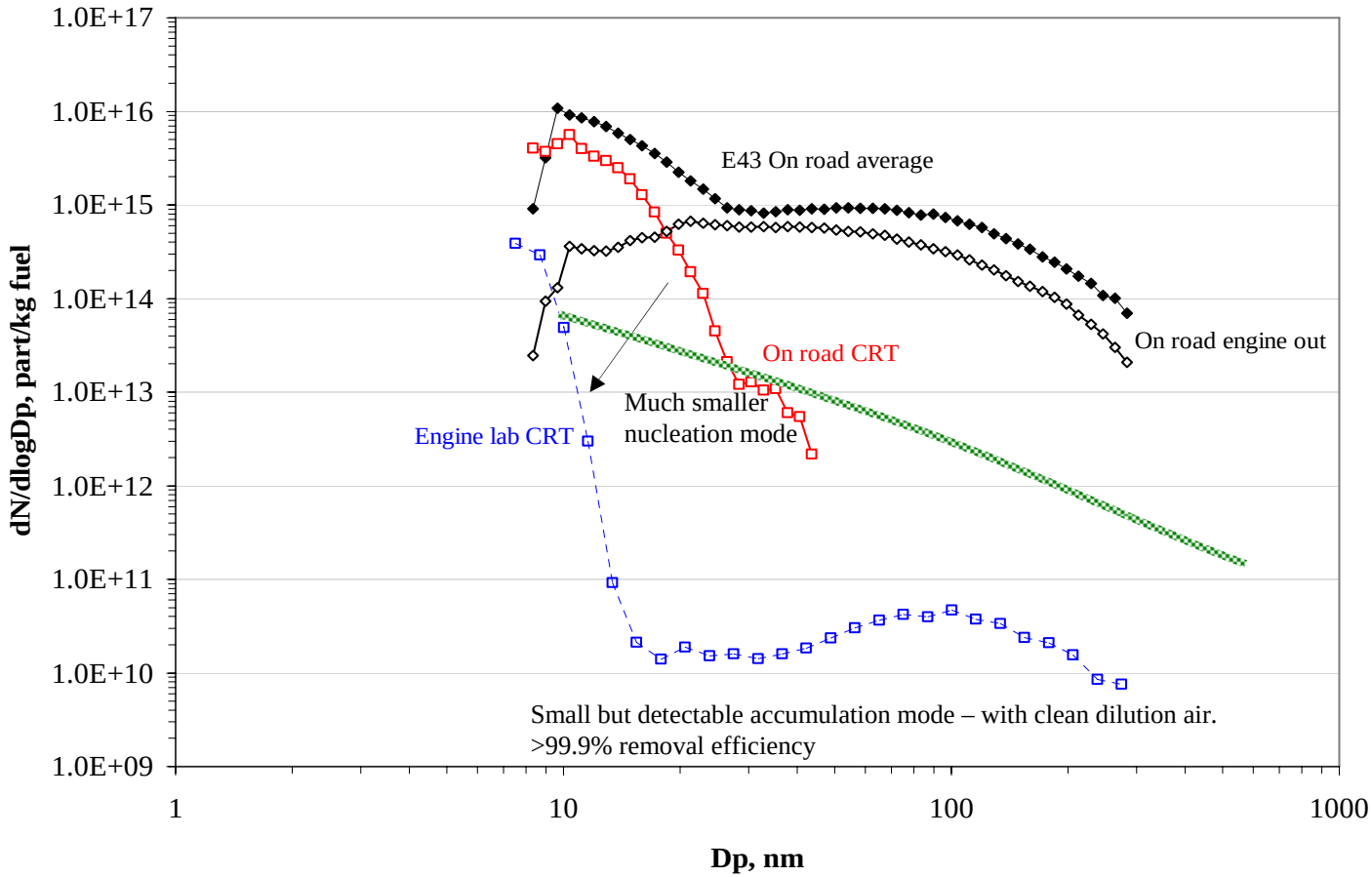
- CRTs and CCRTs tested on-road under relatively light load conditions
- In the accumulation mode size range where most of the mass is found:
  - Neither the CRT nor the CCRT emitted concentrations significantly above background ambient air.
  - This corresponds to > 99% removal efficiency
- Significant 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

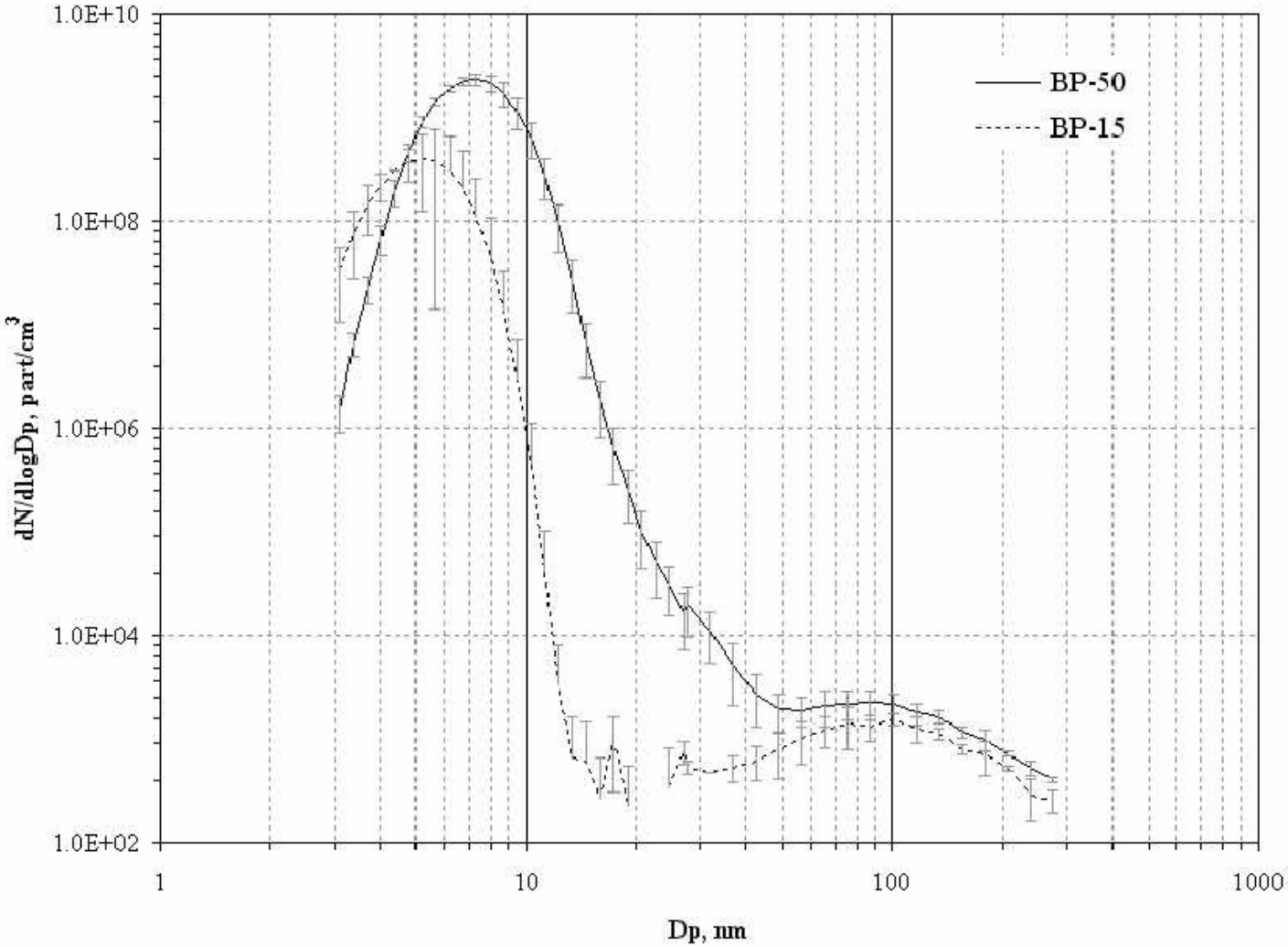


Fink, M., H. Sakurai, J. Savstrom, M. R. Stolzenburg, W. F. Watts, Jr., C. G. Morgan, I. P. Murray, M. V. Twigg, D. B. Kittelson, and P. H. McMurry, 2006. "Chemical and Physical Properties of Ultrafine Diesel Exhaust Particles Sampled Downstream of a Catalytic Trap," Environmental Science and Technology,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

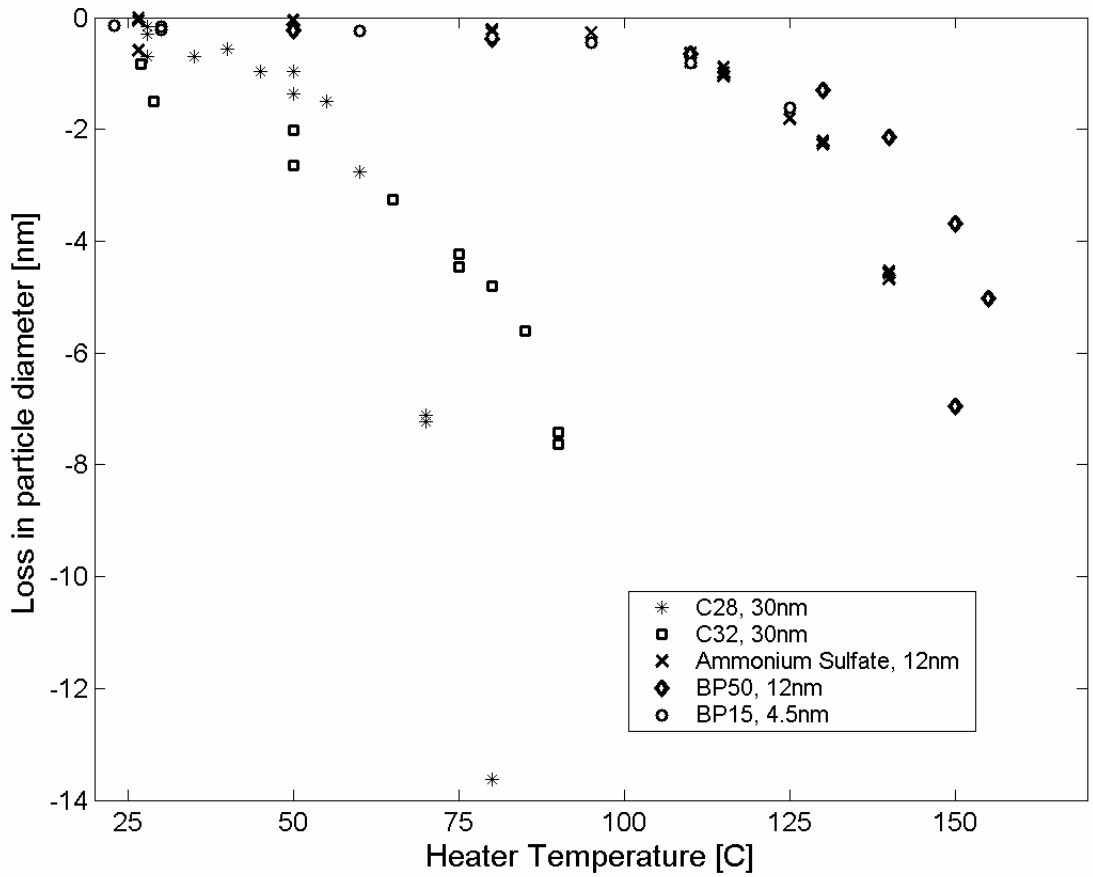
Lab tests of the CRT – same BP15 fuel and operating condition



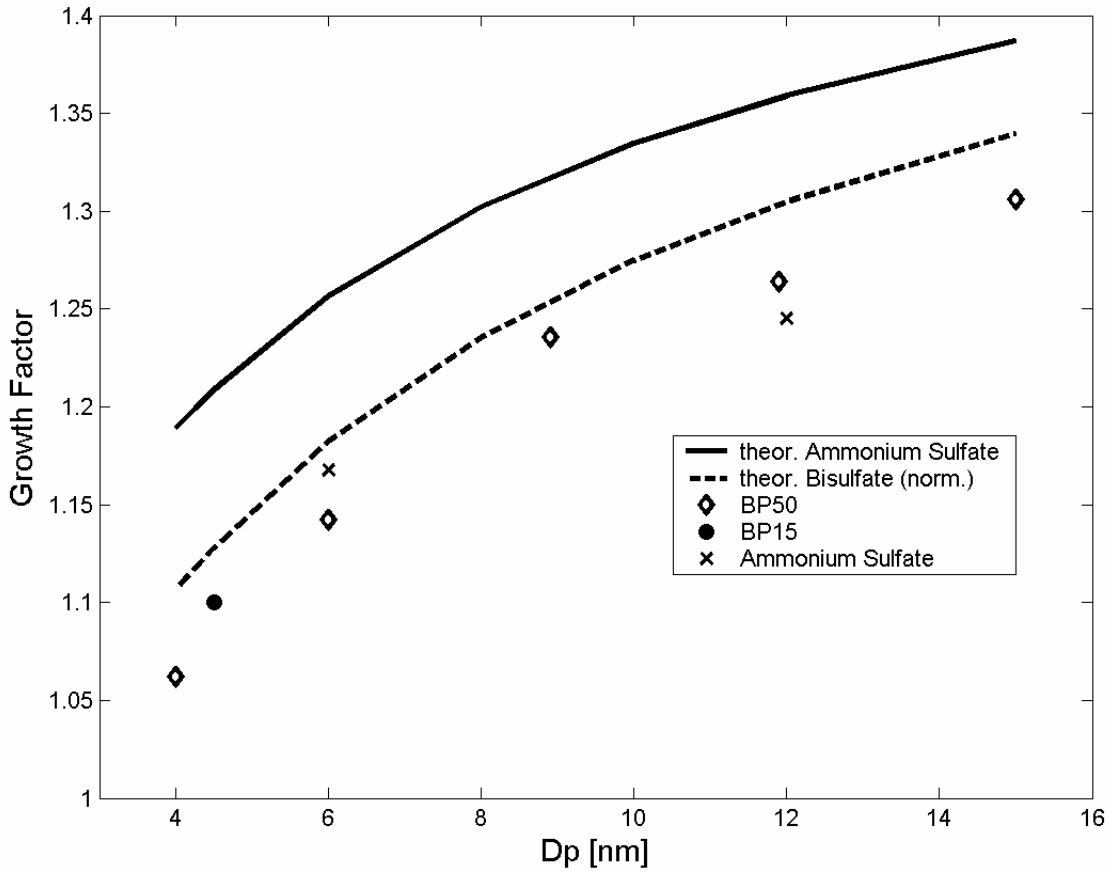
Lab tests - Average size distributions downstream of CRT – fuel effects



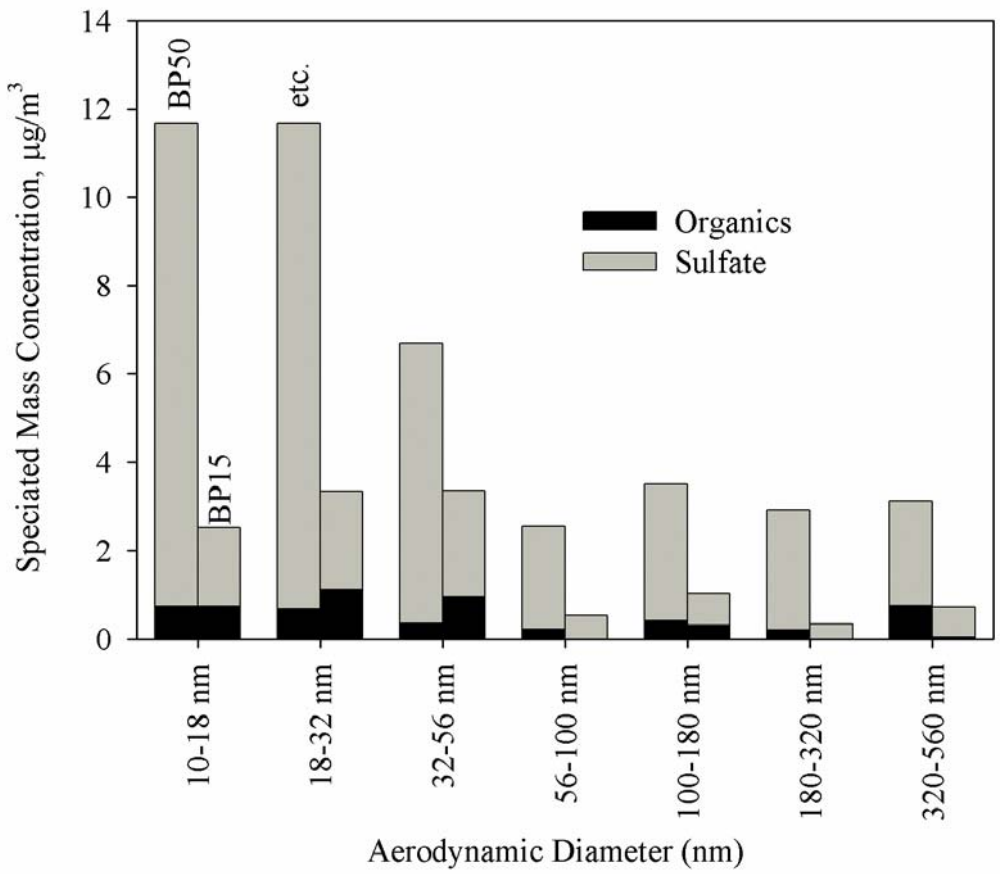
Volatility measurements suggests that nucleation mode particles formed by CRT behave like ammonium sulfate



Hygroscopic growth shows CRT nucleation mode particles behave like ammonium bisulfate



Nano-MOUDI measurements indicate emissions from CRT mainly sulfuric acid



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 press.