12th ETH Conference on Combustion Generated Nanoparticles
The Swiss Federal Office for the Environment is Patron of this Conference
Zurich, 23rd – 25th June 2008

Physicochemical and Toxicological Assessment of Semi-volatile and Non-volatile Components of PM from Heavy-Duty Vehicles Operating with and without Advanced Emission Control Technologies*

C. Sioutas[1†], S. Biswas[1], V. Verma[1], S. Hu[1,2], J. Herner[2], A. Ayala[2], and A.K. Cho[3]

[1]Civil and Environmental Engineering Department, University of Southern California, 3620 South Vermont Avenue, Los Angeles, CA 90089

[2] California Air Resources Board, Research Division.
1001 "I" Street, P.O.Box 2815 Sacramento, CA 95812

[3]Department of Molecular and Medical Pharmacology, School of Medicine, University of California Los Angeles, Los Angeles, CA 90095, USA

* A paper on physical properties is accepted for publication in *Atmospheric Environment* and a Paper on chemical properties is submitted in *Atmospheric Environment.* A paper on toxicological properties is under preparation. This summary is part of an extended abstract submitted to annual AWMA conference (2008).

[†]Corresponding author
Email: sioutas@usc.edu, fax (213)744-1426

1. BACKGROUND

The US EPA 2007 emission standard aims to reduce diesel PM mass emission from heavy duty engines by ten fold (from the old 0.1g/bhp-hr PM limit to 0.01g/bhp-hr). To effectively meet such stringent emission standards, various advanced engine design and control technologies are being considered and rigorously evaluated for the newer fleet of heavy duty trucks. While these aftertreatment devices (such as diesel particulate filters [DPF]) have been remarkably efficient in removing refractory solid particles (>50nm), some of the potentially harmful volatile and semi volatile species (such as PAHs), originally emitted in the vapor phase at high plume temperature, may penetrate through. As the exhaust temperature decreases drastically at the tail pipe exit, these vapor phase species condense and form fresh nucleation mode particles.

The primary objective of this collaborative study between the California Air Resources Board (CARB) and the University of Southern California is to estimate physicochemical and toxicological characteristics of the volatile and non-volatile fractions of particles emitted from a variety of different engines, fuels and emissions control, each operating under different driving conditions using a dynamometer set-up. In this paper we will focus on the PM physical properties such as size distribution, volatility, surface characteristics and chemical speciation for diesel vehicles retrofitted with state-of-the-art aftertreatment devices. Comparisons within HD vehicle types and driving cycles and also with respect to a baseline vehicle (without any control technology) will be discussed. Details of PM chemical and toxicological characteristics from these vehicles will follow in subsequent publications.

2. METHODS

Experiments were carried out at the California Air Resources Board's (CARB) heavy-duty diesel emission testing laboratory (HDETL) in downtown Los Angeles. The sampling train includes heavy-duty chassis dynamometer, constant volume sampling (CVS) dilution tunnel and aerosol samplers. Diesel vehicle exhausts were transported by a stainless steel hose pipe and diluted with filtered air through the CVS. Three driving cycles, i.e. steady state cruise (50mph), transient [EPA urban dynamometer driving schedule (UDDS)] and idle were tested to simulate various real-world driving conditions.

The test fleet comprised of four heavy-duty diesel vehicles in seven configurations. A 1998 Kenworth truck served as a baseline vehicle, without any emission control technology. The same Kenworth truck was also tested with three different control technologies: a Continuously Regenerating Technology [CRT®], consisting of a diesel oxidation catalyst (DOC) followed by an uncatalyzed trap; CRT® in combination with a selective catalytic reduction system [Zeolite or vanadium based SCRT®s]. The other three test vehicles were a diesel hybrid electric bus with catalyzed continuously regenerating trap (CCRT®), a school bus with electric particulate filter (EPF, Horizon), and a Caltrans truck with DPX® filter. Realtime data were obtained by various instruments (EEPS, DMS, EAD and PAS). The chemical speciation data is based on nano-MOUDI substrates. Toxicity (redox activity) was determined by the consumption rate of dithiothreito (DTT) on PM collected on undendued highvolume filters and thermodenuded Teflon filters.

3. RESULTS AND DISCUSSION (SUMMARY)

3.1 Physical Properties

Remarkable reductions in PM mass emissions (>90%) were found for the test fleet compared to the baseline vehicle However, enhanced nucleation mode particles were observed for some of the vehicles especially during cruise cycles. Comparing to cruise cycles, the UDDS cycles emit higher particle mass in the accumulation mode (Particle size>50nm). Idle cycles are characterized with remarkably low particle number emission rates, coupled with fairly broad size distributions. The Hybrid-CCRT® and EPF vehicles were efficient in controlling both mass and number emissions.

The majority of particles by number evaporated by heating the aerosol to 150 - 230 ^{o}C, suggesting the nucleation mode particles are predominantly internally mixed and consist of semi-volatile compounds. Particles from the test fleet (except Hybrid-CCRT®) have shown about 100-fold higher active surface area per unit mass than the baseline vehicle.

3.2 Chemical Characteristics

The V-SCRT-UDDS, Z-SCRT cruise, CRT and DPX displayed the highest content of sulfates. This finding is consistent with the conclusions of recent emission studies that nuclei mode particles from DPF equipped vehicles are predominantly sulfates. However, measurable fraction of TC was also present in these vehicles. During the analysis of physical data, we observed that nucleation is suppressed for Hybrid-CCRT, EPF vehicles. These vehicles have shown higher content of total carbon concentration in all size ranges and less sulfate in nucleation mode PM. Unlike other SCRT cycles, UDDS cycles for Z-SCRT are unique in the sense that TC dominates over sulfate concentrations. Due to higher activation temperature of Zeolite catalysts, the conversion of SO_2 to sulfate is hindered during transient cycles, where the exhaust temperature fluctuates. Total carbon concentration (>90% of total concentration) outweighs other species for the Baseline vehicle. The baseline vehicle without any after treatment device is emits significant amount of elemental and organic carbon.

3.3 Toxicological Characteristics

The consumption rate of dithiothreitol (DTT), a surrogate measure of redox PM activity, is determined for PM samples collected at ambient temperatures as well as samples collected after they pass a thermo-denuder, where they are heated to 150^{o}C. Significant reduction in toxicity (by 50-100%) was observed as PM is heated to 150^{o}C for vehicles with retrofitted technologies while particles generated by the baseline vehicle (highly non-volatile) did not demonstrate any changes in toxicity with heating. The toxic potential (per unit mass of PM) was highest for EPF (DTT-0.14-0.19 nano-mole min^{-1} μg^{-1}) followed by CRT, DPX-Idle, SCRTs, Baseline. The introduction of SCRTs catalysts to CRT has reduced DTT consumption by approximately four-fold. In terms of PM redox activity expressed per vehicle distance traveled, control devices reduced the net burden of toxicity by 60-90%. Correlation analysis was performed between DTT consumption and various chemical constituents such as metals and trace elements, Elemental Carbon (EC), Organic carbon (OC), ions and organic species Analysis suggests that water soluble fraction of OC is strongly correlated (R=0.94) with DTT activity, while a lower but also significant association was observed for total OC (R=0.4).

Physicochemical and Toxicological Assessment of Semi-volatile and Non-volatile PM from Heavy-Duty Vehicles Operating with and without Advanced Emission Control Technologies

Constantinos Sioutas
Department of Civil and Environmental Engineering
University of Southern California
Los Angeles, CA 90089

Co-Investigators:
Subhasis Biswas, Vishal Verma, USC,
Shaohua Hu, Alberto Ayala, Jorn Herner, CARB
Arthur Cho, John R Froines, UCLA
Jamie Schauer, U Wisconsin
Flemming Cassee, RIVM

12th ETH Conference on Combustion Generated Nanoparticles
Zurich, 23rd – 25th June 2008

Acknowledgements

USC

- Michael Geller
- Harish Phuleria
- Zhi Ning
- Payam Pakbin
- Mohammad Arhami

CARB

- Ralph Rodas
- George Gatt
- Paul Rieger
- Oliver Chang
- Christine Maddox
- Keshav Sahay
- Jim Shears

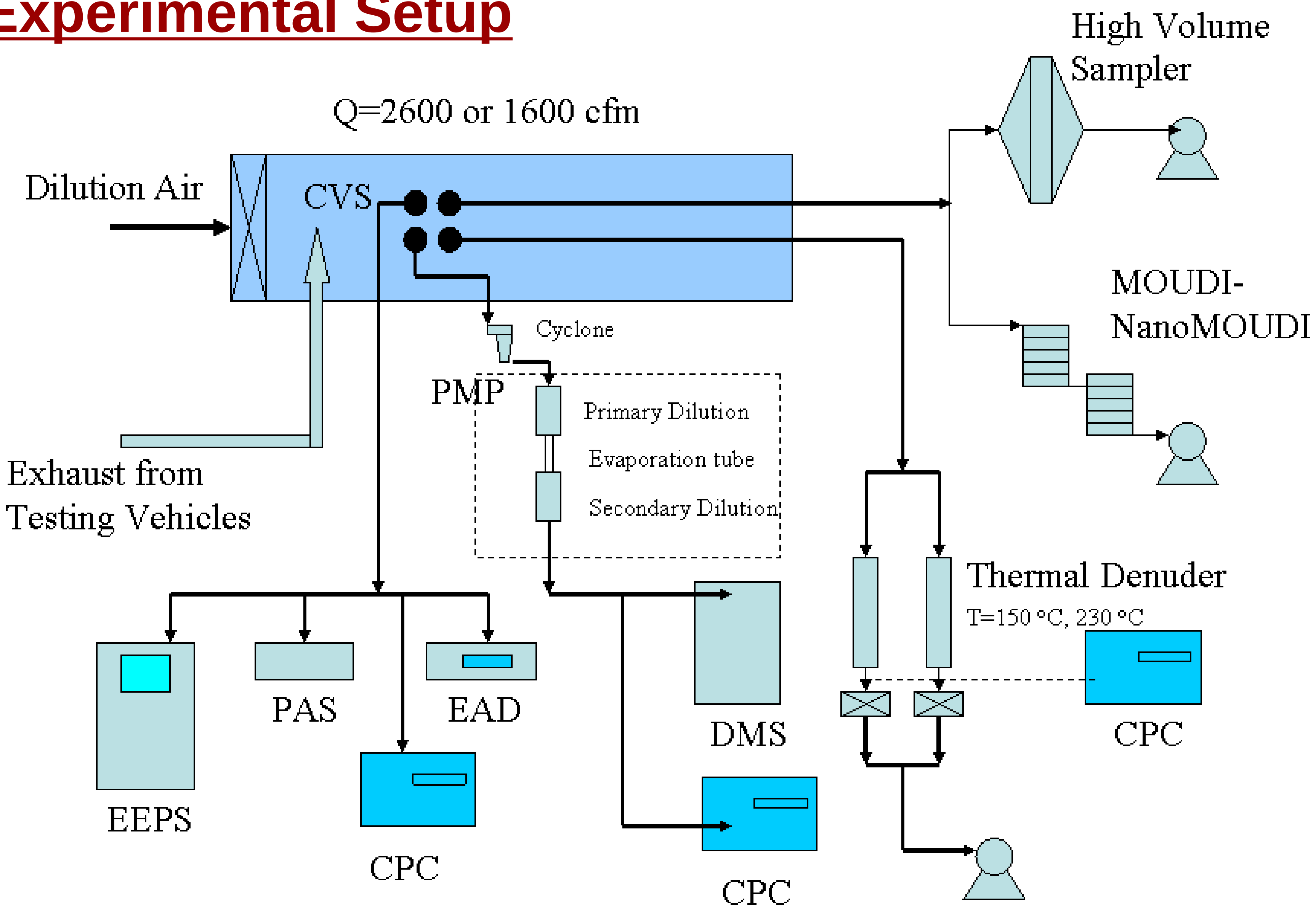
Sponsors

- California Air Resource Board (CARB)
- California Energy Commission (CEC)
- South Coast Air Quality Management District (AQMD)

Background and Motivation

- An increasing epidemiological and toxicological evidence links cardio-respiratory health effects and exposures to ultrafine particles (Peters et al., 1997; Li et al., 2002 and 2003; Xia et al., 2004)
- Emission inventories suggest that motor vehicles may be the primary emission sources of ultrafine particles to the atmosphere in urban areas (Hitchins et al., 2000; Zhu et al, 2002)
- Newer after treatment technologies have been developed to capture non-volatile fraction of exhaust emissions.
- However, their effectiveness in removing the semi-volatile fraction of PM remains unclear
- This is a multi-year collaborative project to investigate the physicochemical and toxicity of the volatile fraction of emissions from newer diesel vehicles
- This presentation summarizes the physical properties of PM emissions from test heavy-duty diesel trucks comparing to a baseline vehicle and preliminary chemical and toxicological results

Experimental Setup



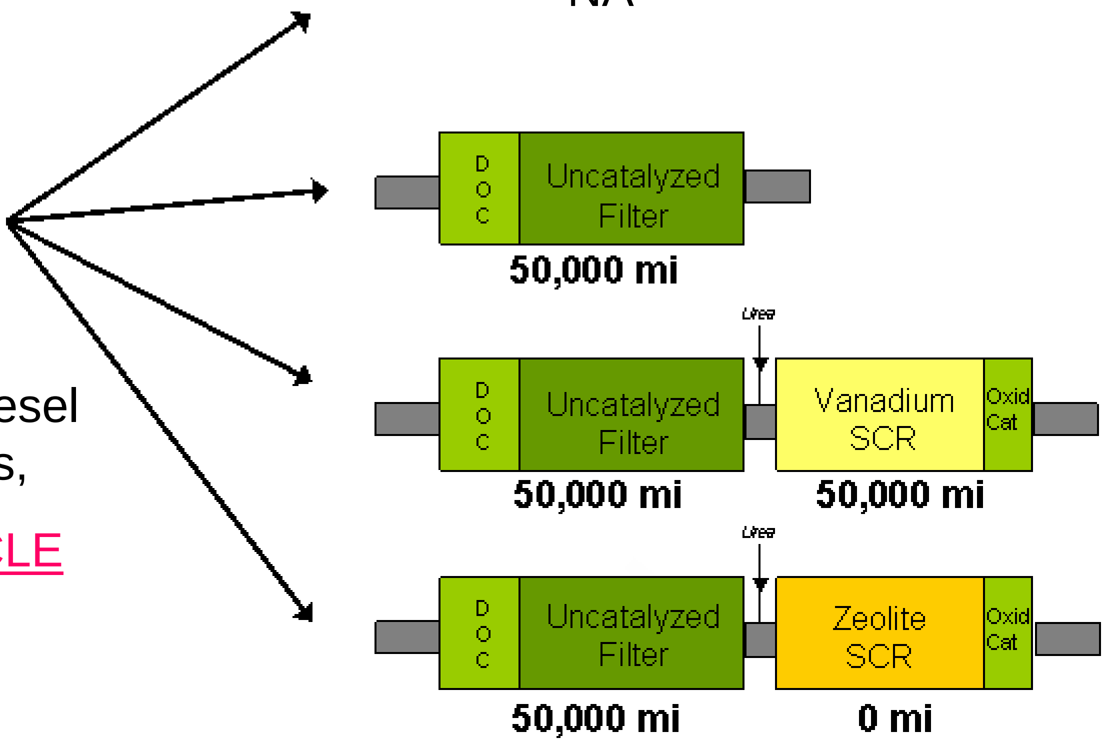
Test Matrix – 1/2

4 vehicles, 7 configurations, 3 driving cycles

Vehicle	After-treatment	Abbreviation
Veh#1	NA	Baseline
	DOC + Uncatalyzed Filter (50,000 mi)	CRT®
	DOC + Uncatalyzed Filter (50,000 mi) + Vanadium SCR / Oxid Cat (50,000 mi)	V-SCRT®*
	DOC + Uncatalyzed Filter (50,000 mi) + Zeolite SCR / Oxid Cat (0 mi)	Z-SCRT®*

1998 Cummins Diesel 11L, 360,000 miles,

BASELINE VEHICLE



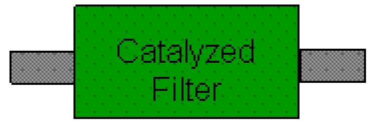
•SCRT® systems used in this project are development prototypes, not commercial units.

Test Matrix - 2/2

4 vehicles, 7 configurations, 3 driving cycles

Veh#2, 1999 International Diesel

7.6L, 40,000 miles

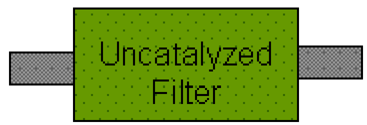


30,000 mi

DPX

Veh#3 2003 Cummins Diesel,

5.9L, 50,000 miles

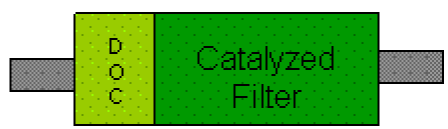


31,000 mi

EPF

Veh#4 2006 Cummins Diesel w/ Allison Hybrid drive

5.9L, 1,000 miles



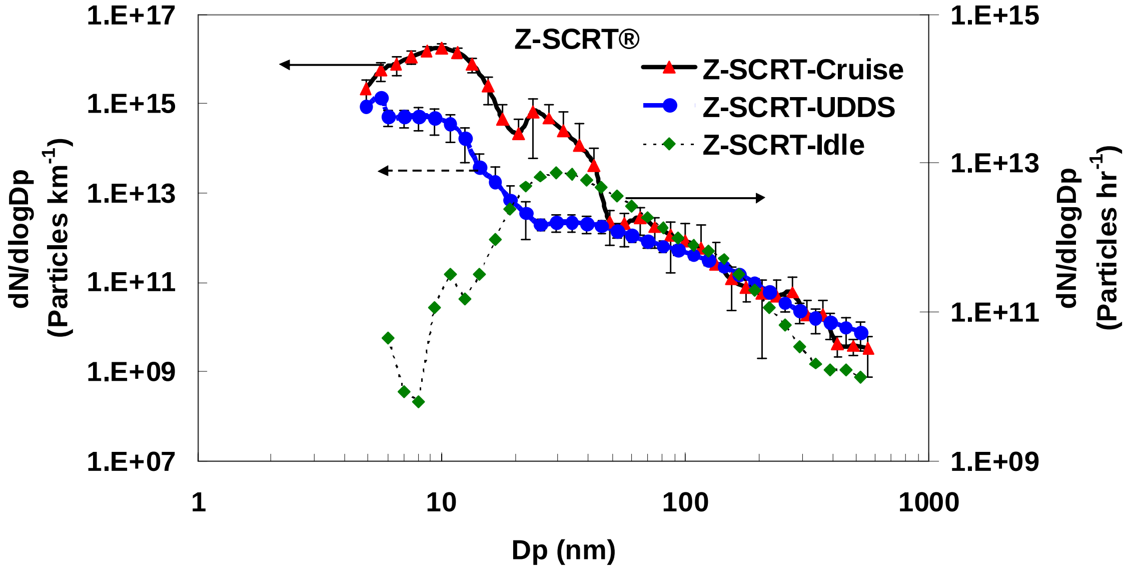
1,000 mi

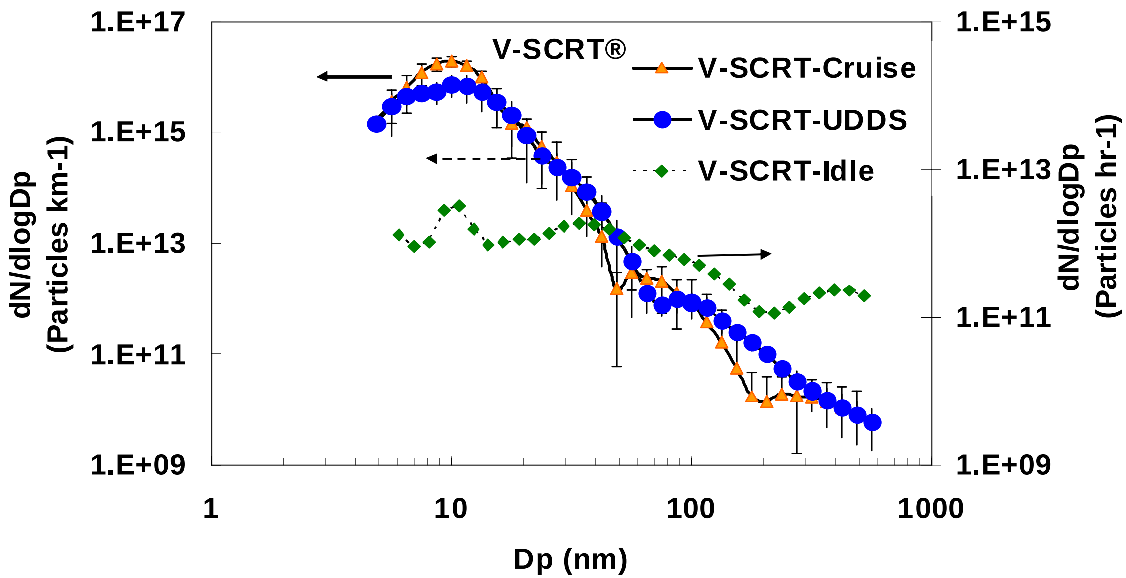
Hybrid-CCRT®

Chemical and Toxicological Analysis Plan

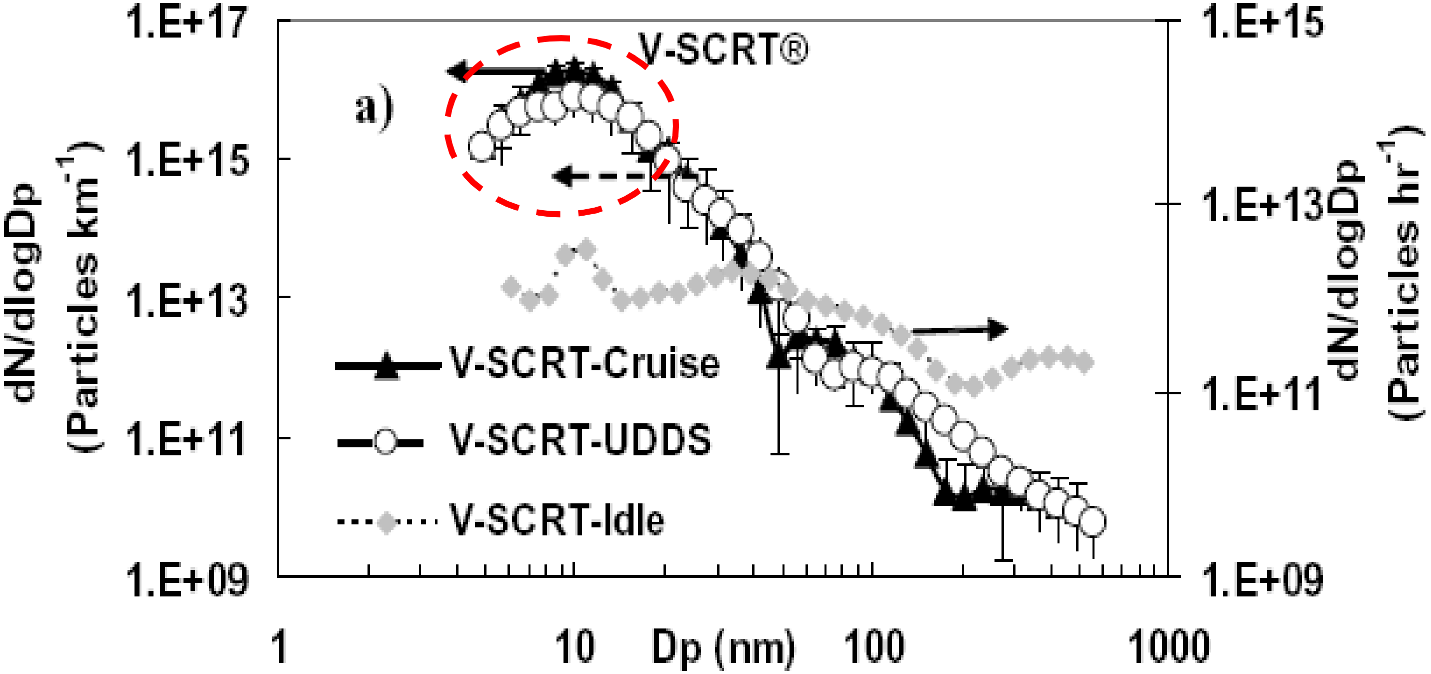
Samplers	U Wisconsin-Madison					UCLA-RIVM	
	IC	EC/OC	Organics	Metals	ROS	DTT	DHBA
NanoMOUDI	✓	✓			✓		
USC Hi-Vol	✓		✓	✓	✓	✓	✓
Thermo denuded filters	✓		✓	✓	✓	✓	✓

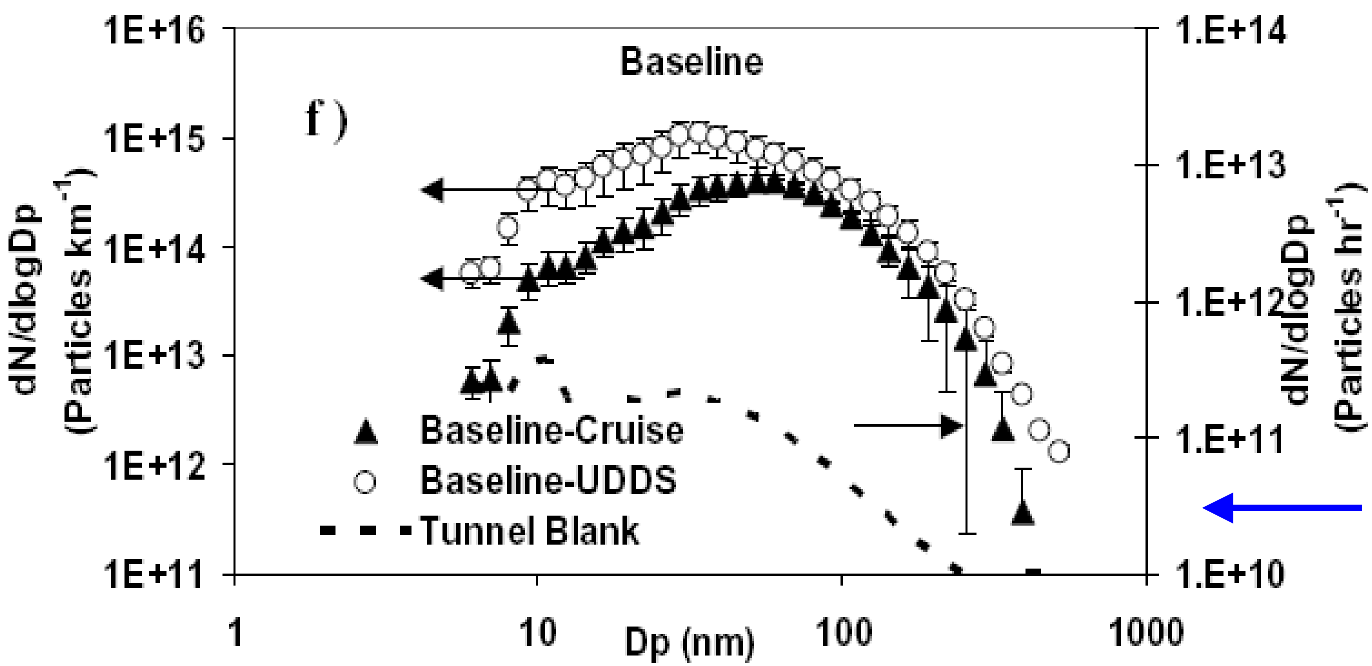
Particle Number Size Distribution (1)





- Significant nucleation mode particles formed at high engine load mode (Cruise and high speed of UDDS)
- Nucleation pronounced for vehicles with catalytic reduction technologies used as after-treatment devices
- Nucleation not seen during idling





Baseline Truck with V-SCRT trap

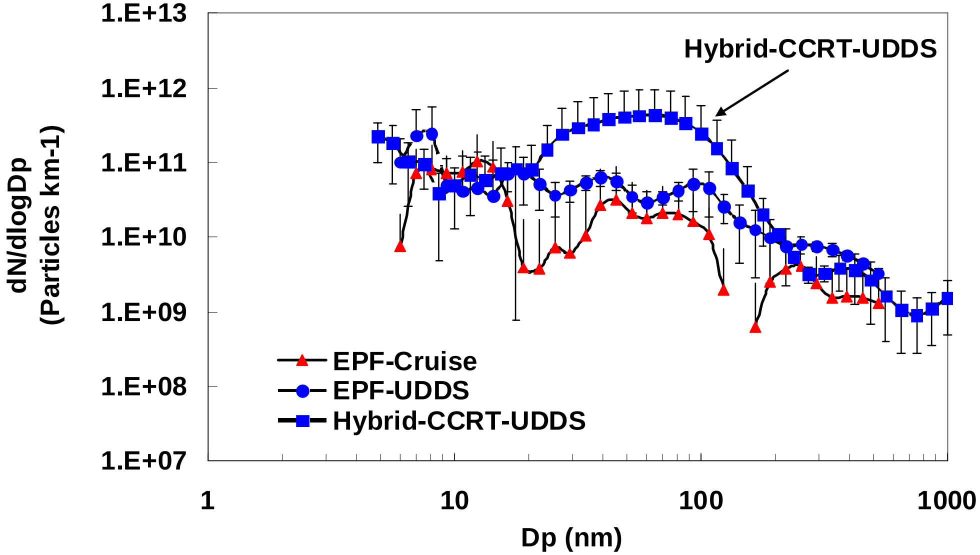
Note difference in y-axis scales

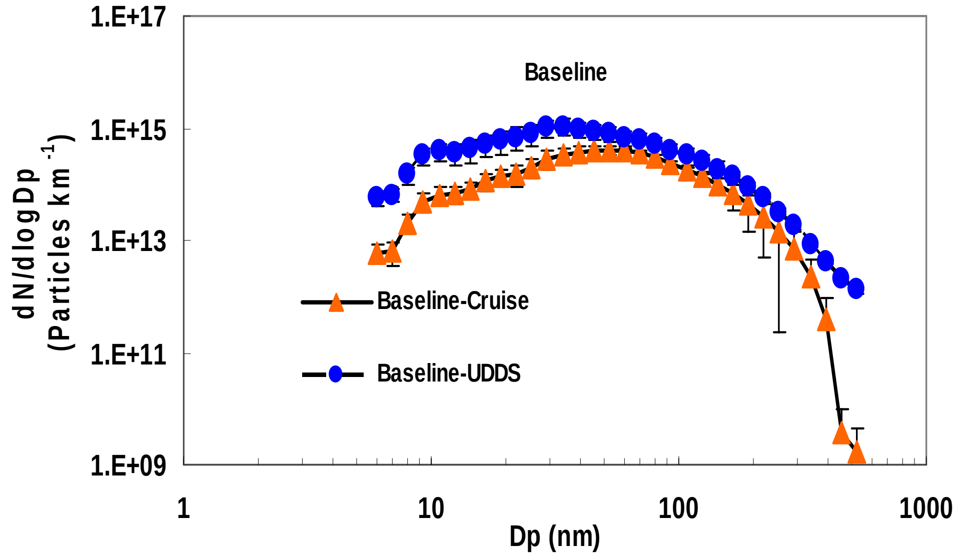
Nucleation seen in V-SCRT but not in baseline truck

Baseline Truck

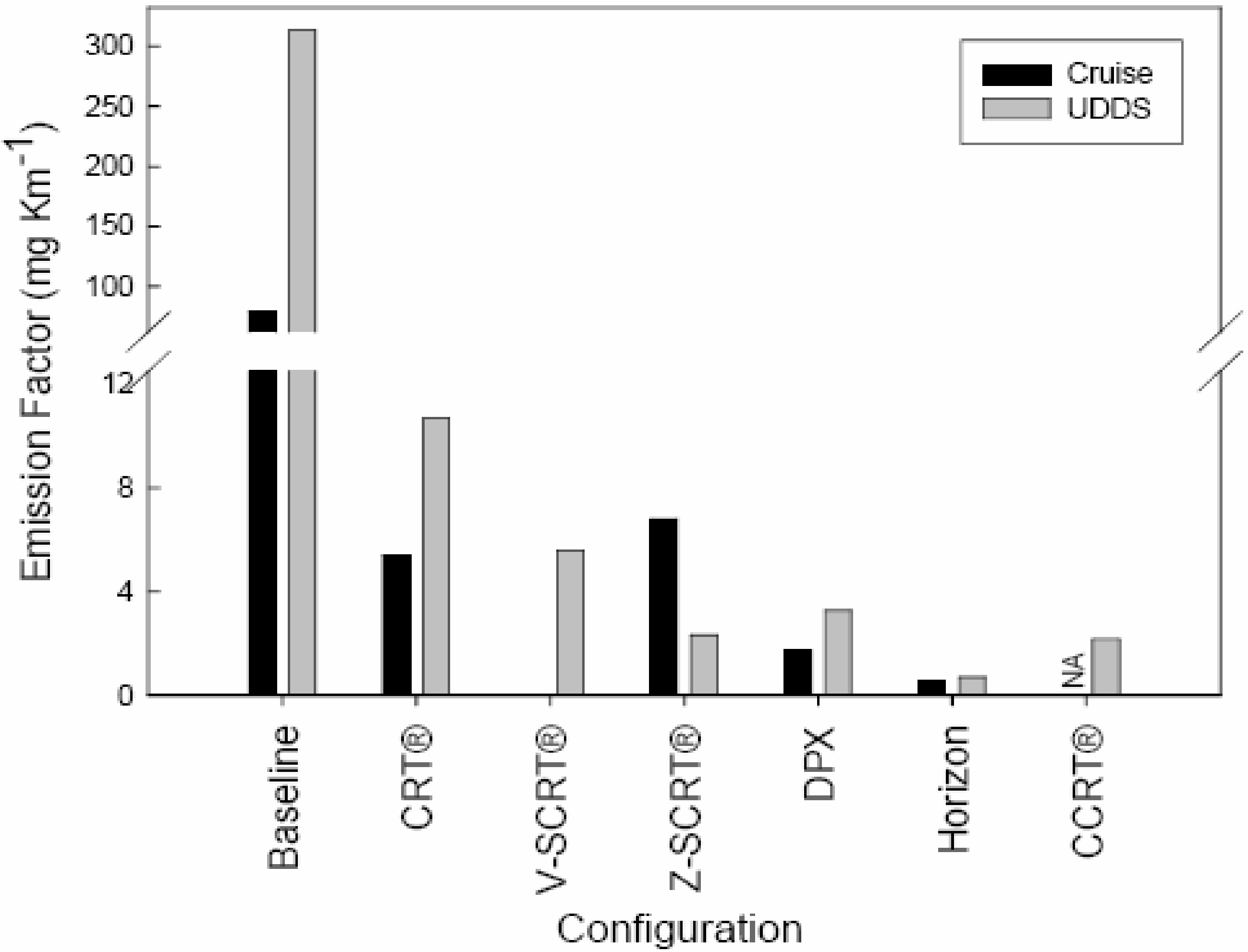
Particle Number Size Distribution (3)

Non-Nucleating Vehicles



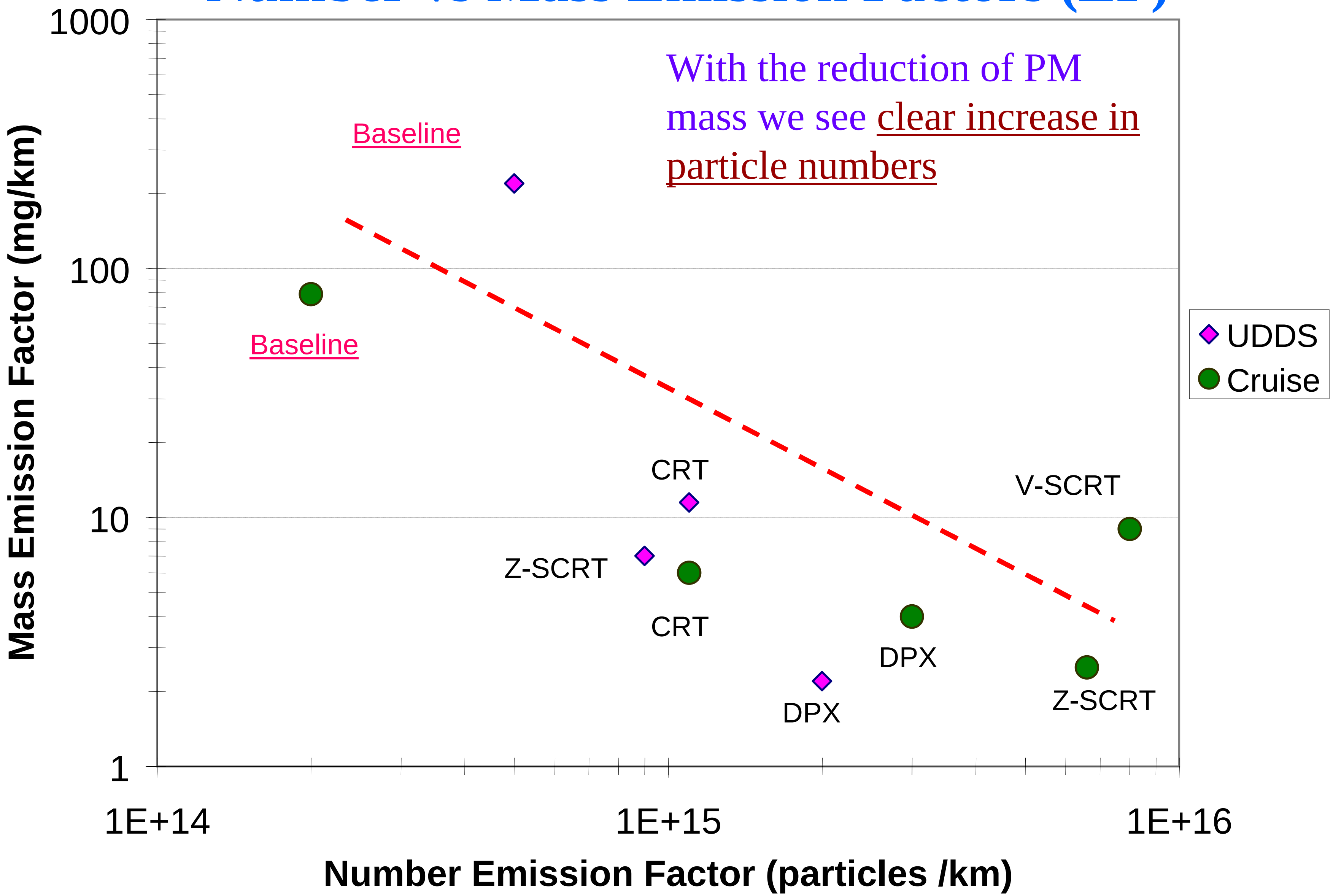


- Accumulation mode particles formed at high engine load mode (Cruise and high speed of UDDS)
- Also note the much lower number emission factors of the Hybrid and EPF vehicles compared to other test vehicles
- Baseline truck high concentrations and peak in accumulation mode



Mass PM emission rates for baseline vehicle are 20- 100 times higher than those of the rest of the tested fleet

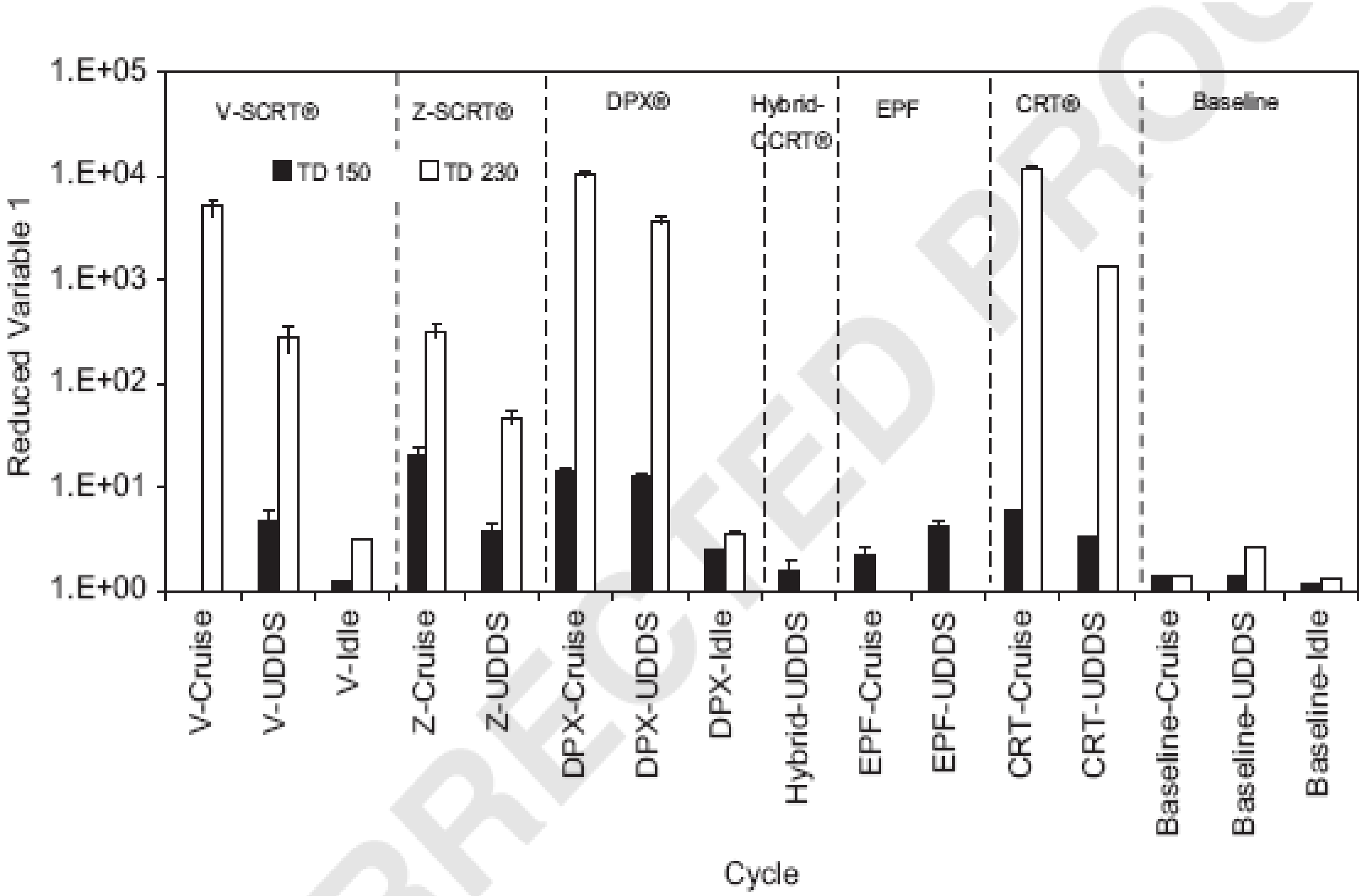
Number vs Mass Emission Factors (EF)



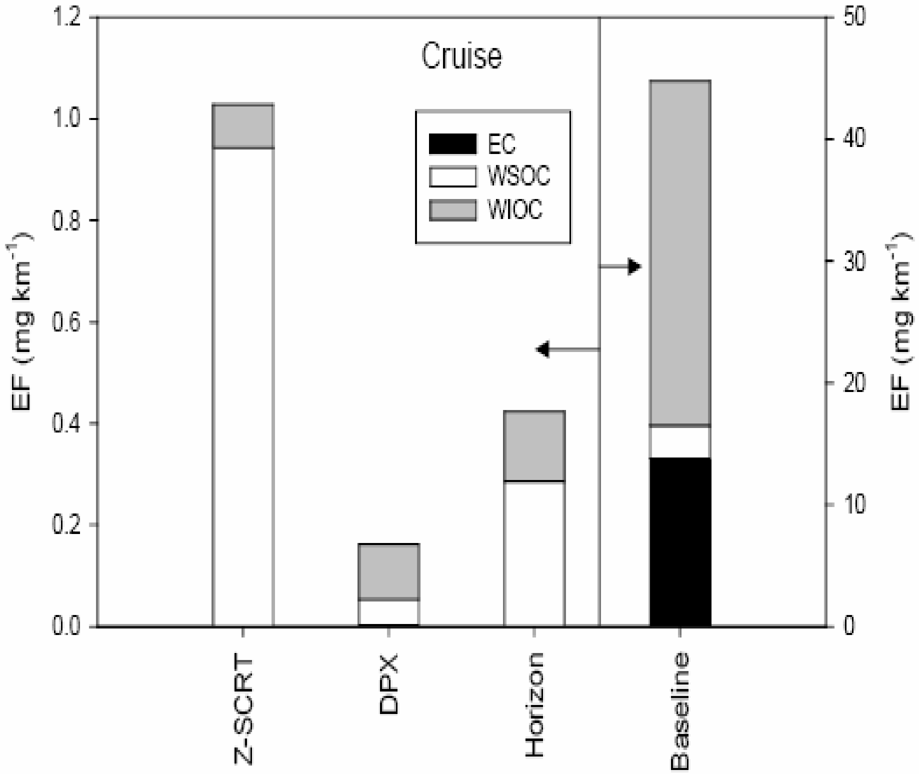
Biswas et al. Atmos. Environ, 2008

$R = N_{Exhaust} / N_{TD}$ = Ratio of volatile/ non volatile number of particles

- $N_{Exhaust}$ = Total dilution corrected particle concentration
- N_{TD} = number concentration measured by CPC after the thermo-denuders.

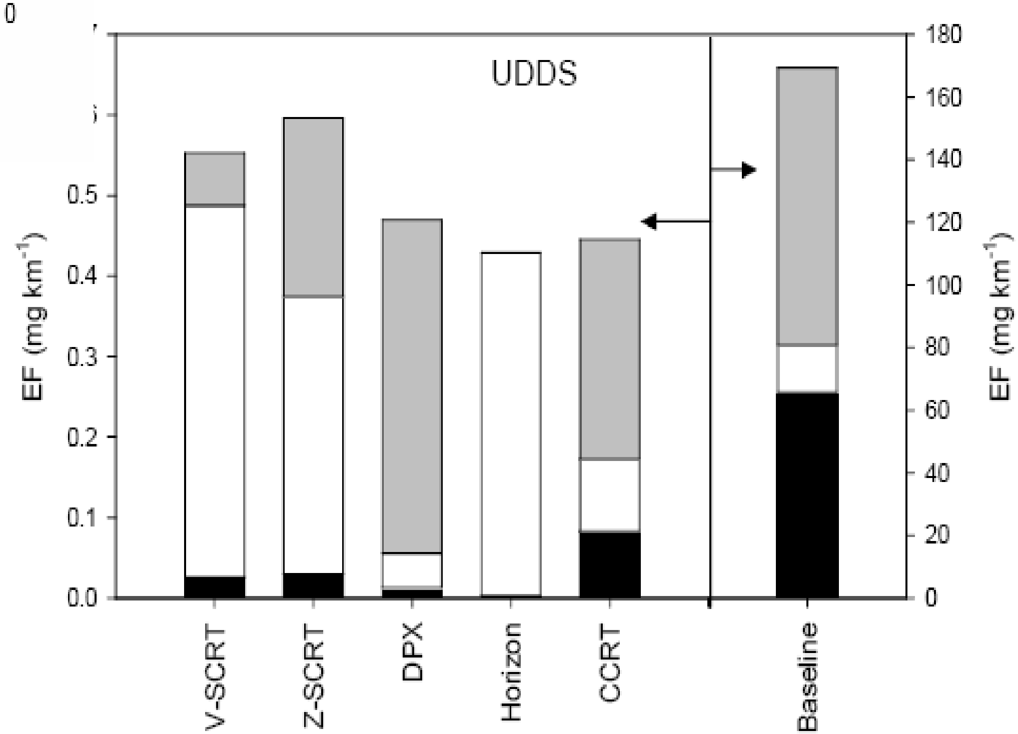


Particle Volatility (by Number) of Various Vehicles and Driving Cycles

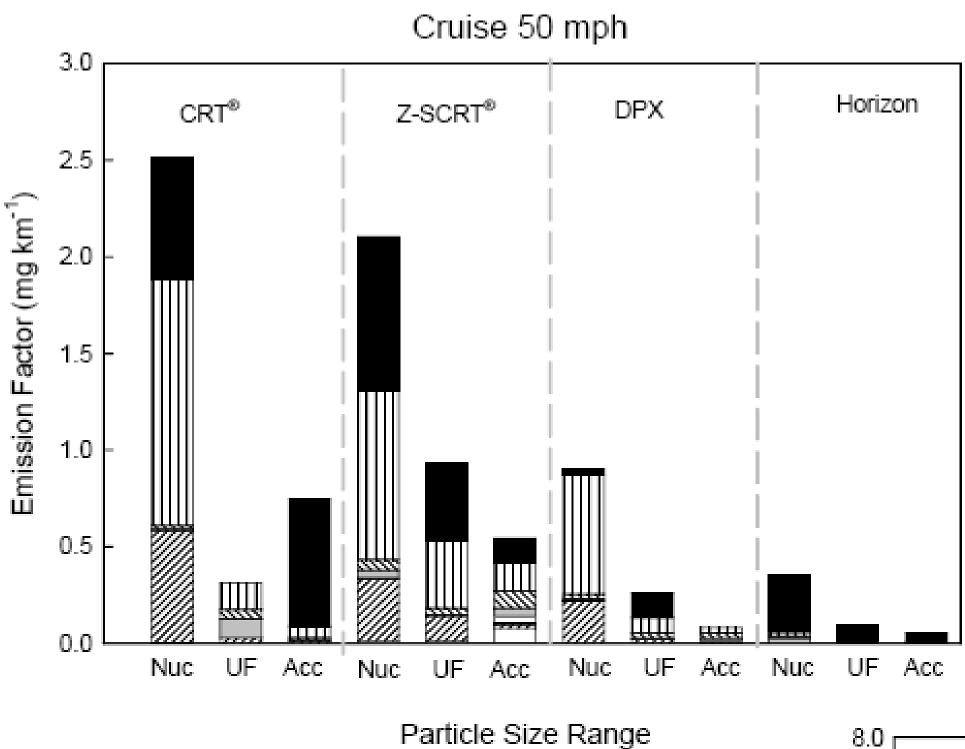


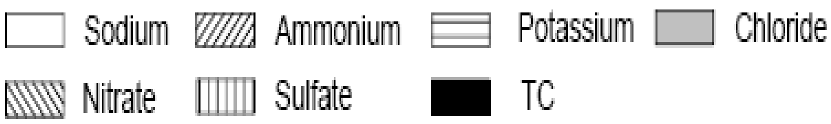
- High EC content of baseline vehicle

- Noticeable increases in the mass fraction of water soluble OC in newer vehicles



Higher EC and OC emission in UDDS than cruise cycle

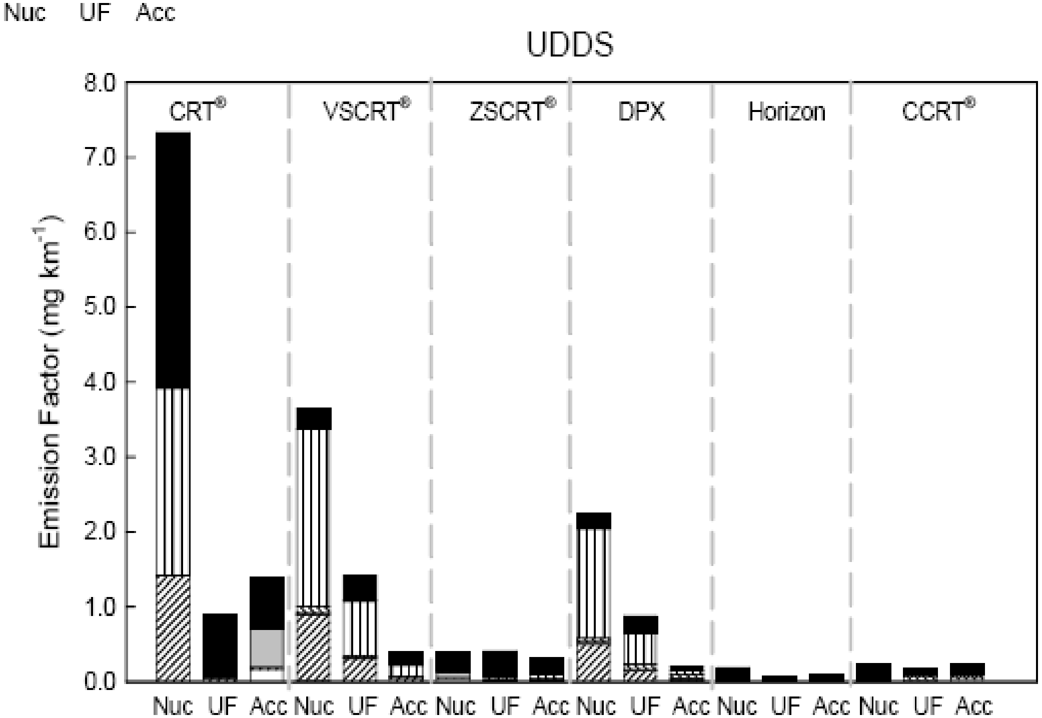




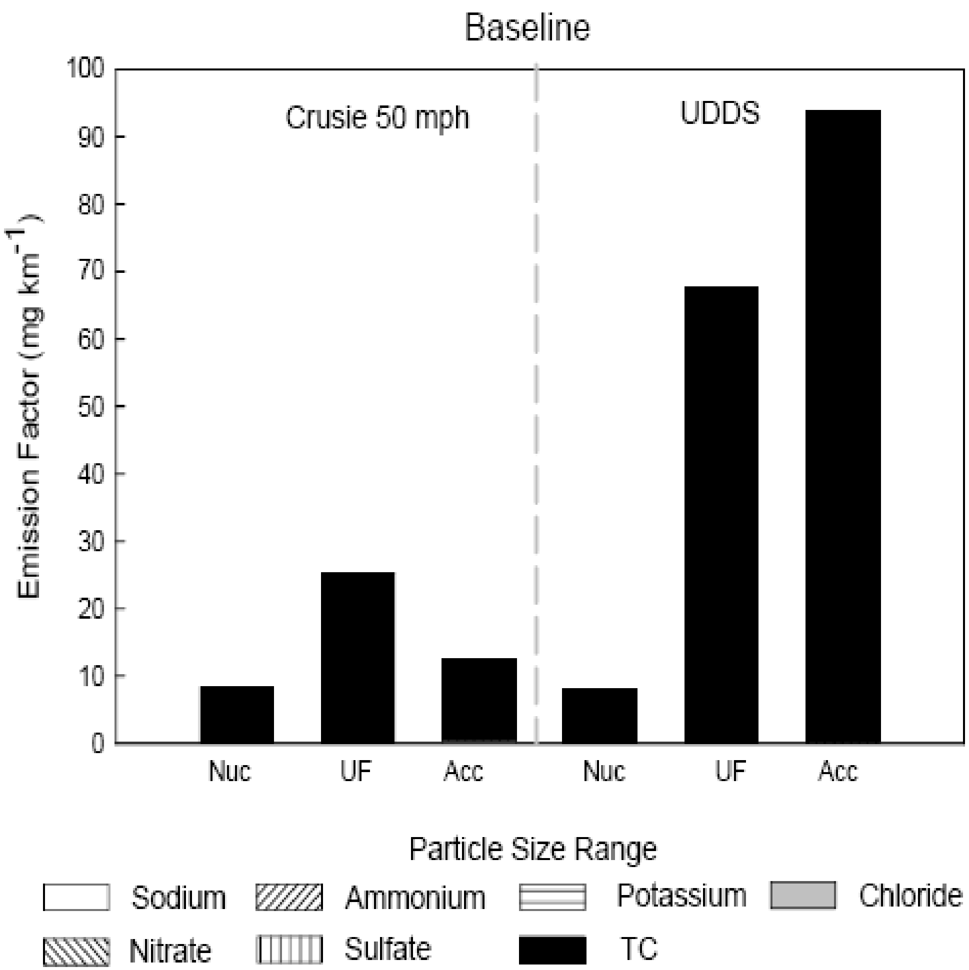
Nuc: 0.01 – 0.056 μm

UF: 0.056- 0.18 μm

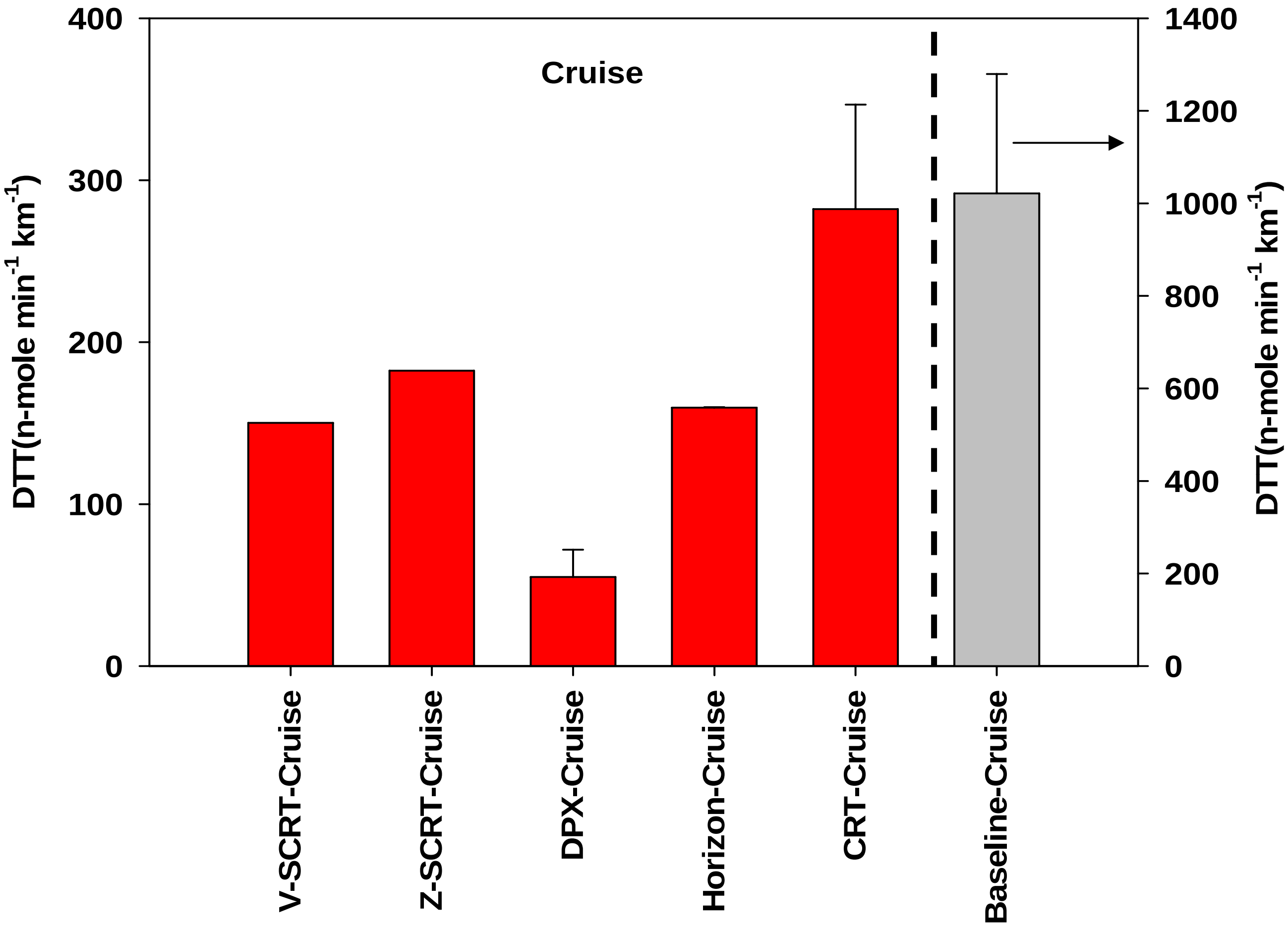
Acc: 0.18- 2.5 μm



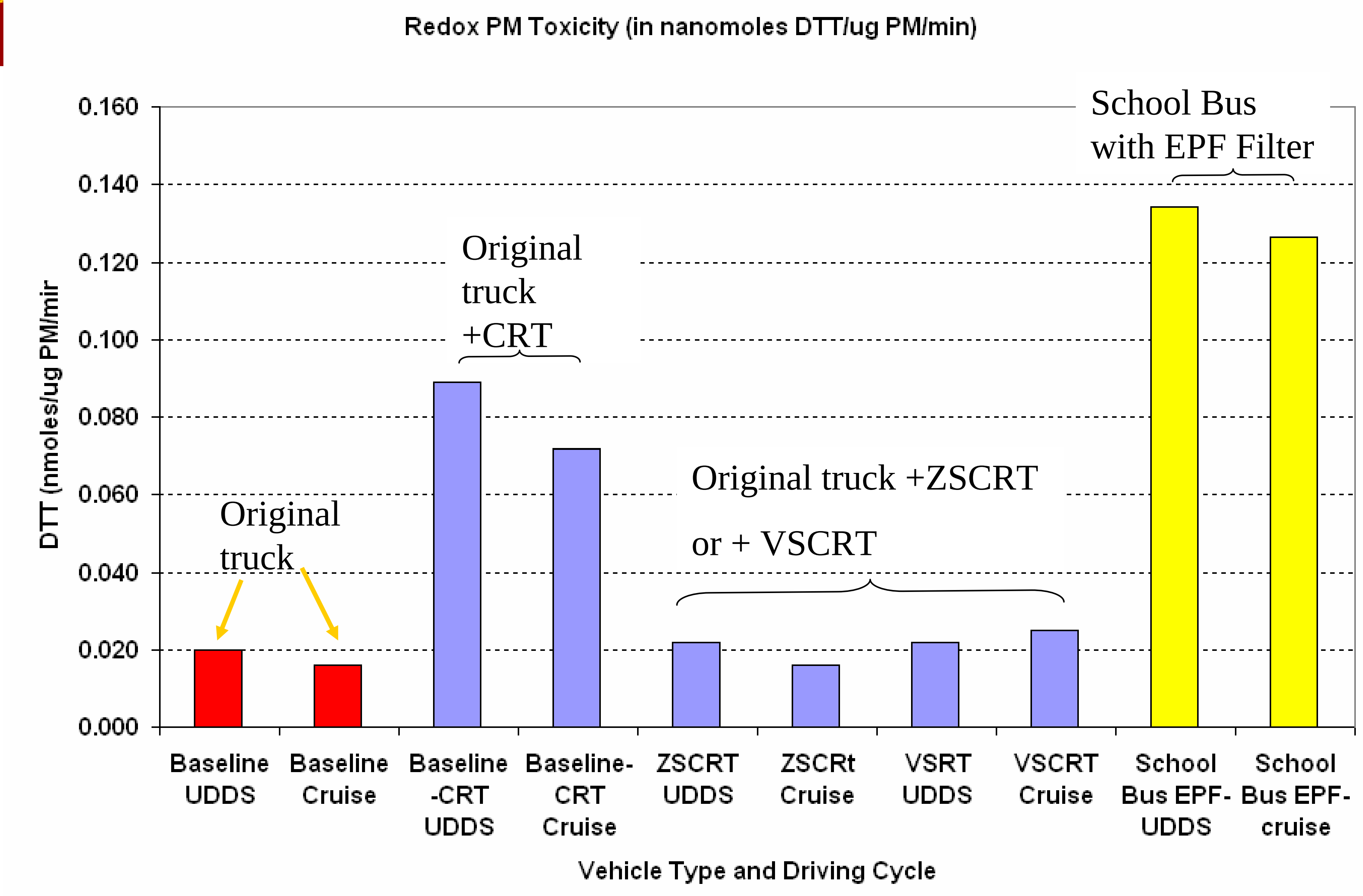
- **Nucleation mode PM from vehicles with catalytic reduction mostly ammonium sulfate and TC (to a lesser degree)**
- **Higher emissions in UDDS, <u>except</u>:**
- **Higher emissions in <u>cruise mode</u> of nucleation mode PM for <u>SCRT vehicles</u>**



Baseline vehicle PM emissions comprise almost entirely of carbonaceous material

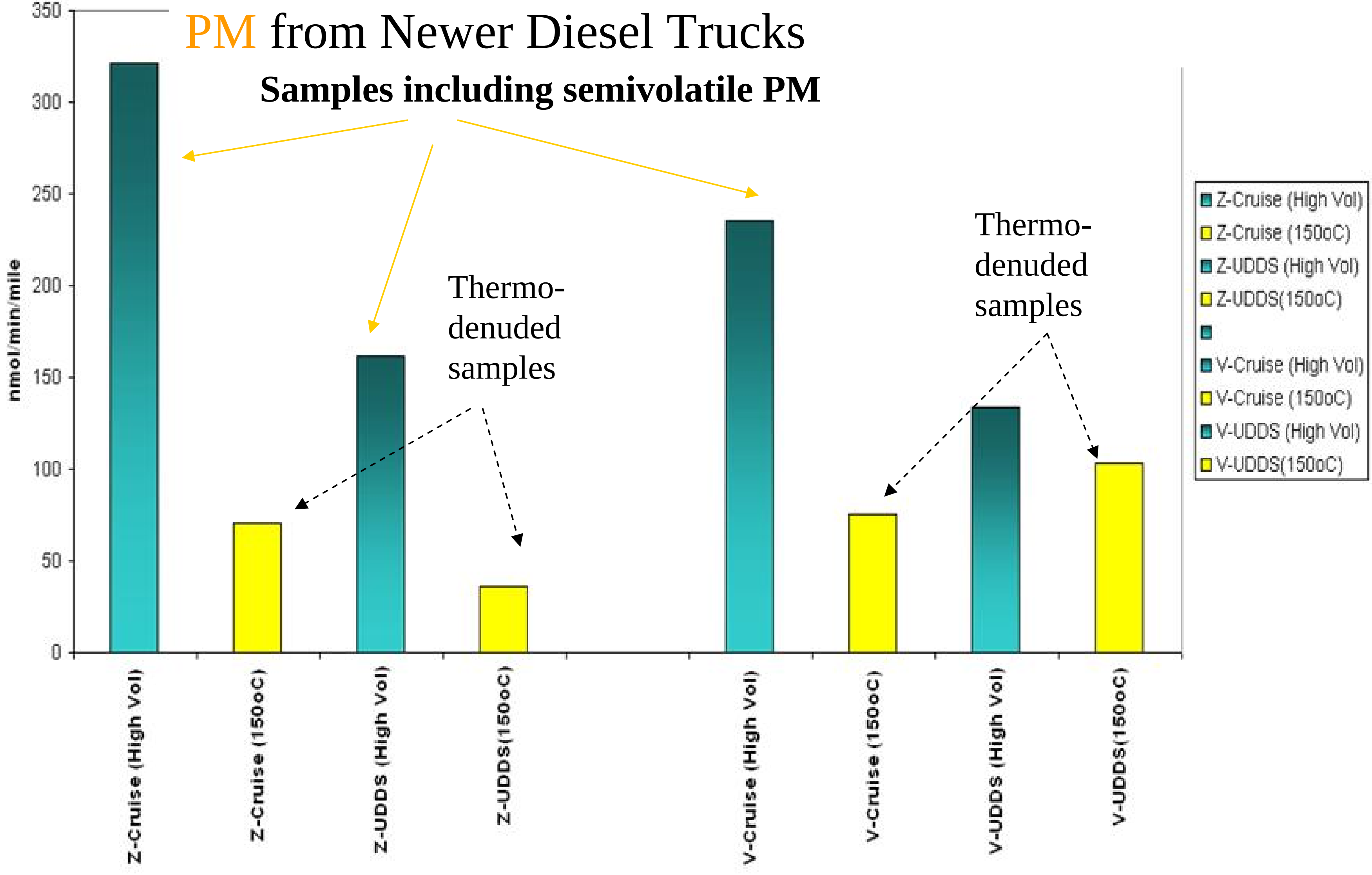


- **On a per km basis, the baseline vehicle has the highest PM redox activity;**
- **However, the redox activity reduction by after-treatment technologies is <u>highly non linear</u> with respect to their PM mass emission rates**



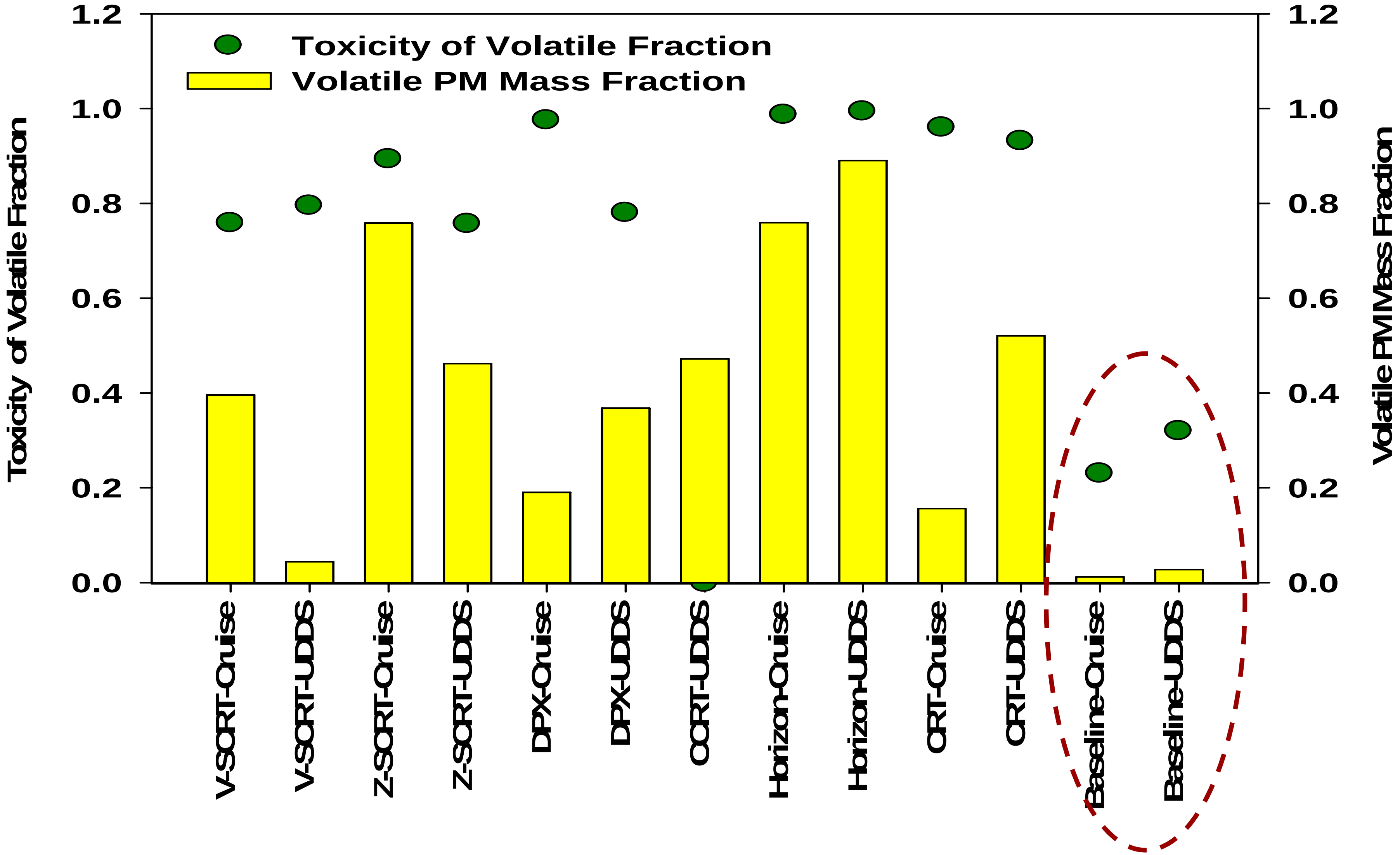
DTT activity expressed per PM mass; note the very high activity of some of the reduced mass emission trucks, especially with non-catalyzed silicon carbide (CRT) substrate for PM control

Redox Activity (DTT assay) of Semivolatile and Total PM from Newer Diesel Trucks



DTT rate of consumption per PM mass (nmoles/µg PM/min) is **<u>much higher when the semi-volatile fraction is included</u>**

Relationship between toxicity and volatile PM fraction



Toxicity of volatile fraction= [(DTT,Undenuded, n-mole/km/min) - (DTT at150oC, n-mole/km/min)] / [DTT ,Undenuded, n-mole/km/min)]

SUMMARY AND CONCLUSIONS

- Substantial reductions in the emission rates of PM mass were achieved with newer vehicles or those operating with after treatment technologies
- Increase in the emission rates of particle numbers by almost every vehicle operating with after treatment
- PM produced by enhanced nucleation are a mixture of partially or fully neutralized ammonium sulfate and organic carbon
- Substantial reduction in the overall redox activity of PM was achieved with newer vehicles on a per km driven basis
- Nonetheless, several newer vehicles had a higher redox activity on a PM mass basis
- The semi volatile fraction of PM (with the exception of baseline vehicle) was responsible for over 80% of the total redox activity of the exhaust
- In addition to the in vitro evaluations, in vivo studies to semi volatile and non volatile PM are necessary (issue of inhaled dose), and are currently under way