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

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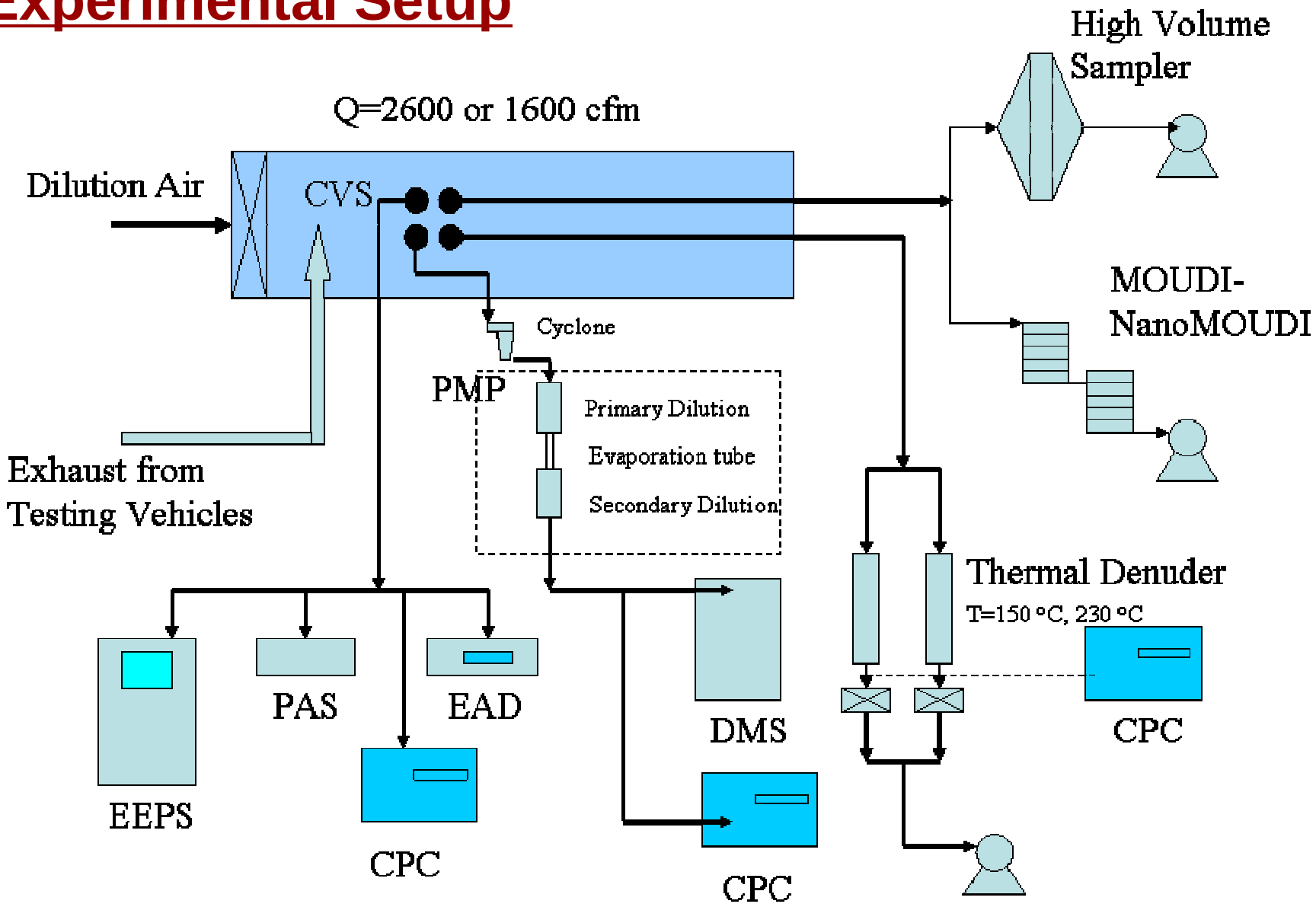
Background and Motivation

- 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 + Urea + Vanadium SCR, 50,000 mi + Oxid Cat	V-SCRT®*
	DOC + Uncatalyzed Filter, 50,000 mi + Urea + Zeolite SCR, 0 mi + Oxid Cat	Z-SCRT®*

1998 Cummins Diesel
11L, 360,000 miles,

BASELINE VEHICLE

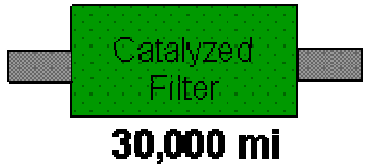
- **SCRT® systems used in this project are development prototypes, not commercial units.**

Test Matrix - 2/2

4 vehicles, 7 configurations, 3 driving cycles

Veh#2, 1999 International Diesel

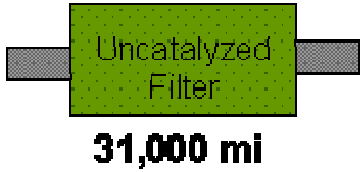
7.6L, 40,000 miles



DPX

Veh#3 2003 Cummins Diesel,

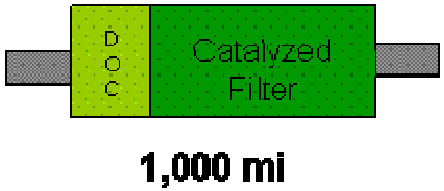
5.9L, 50,000 miles



EPF

Veh#4 2006 Cummins Diesel w/ Allison Hybrid drive

5.9L, 1,000 miles

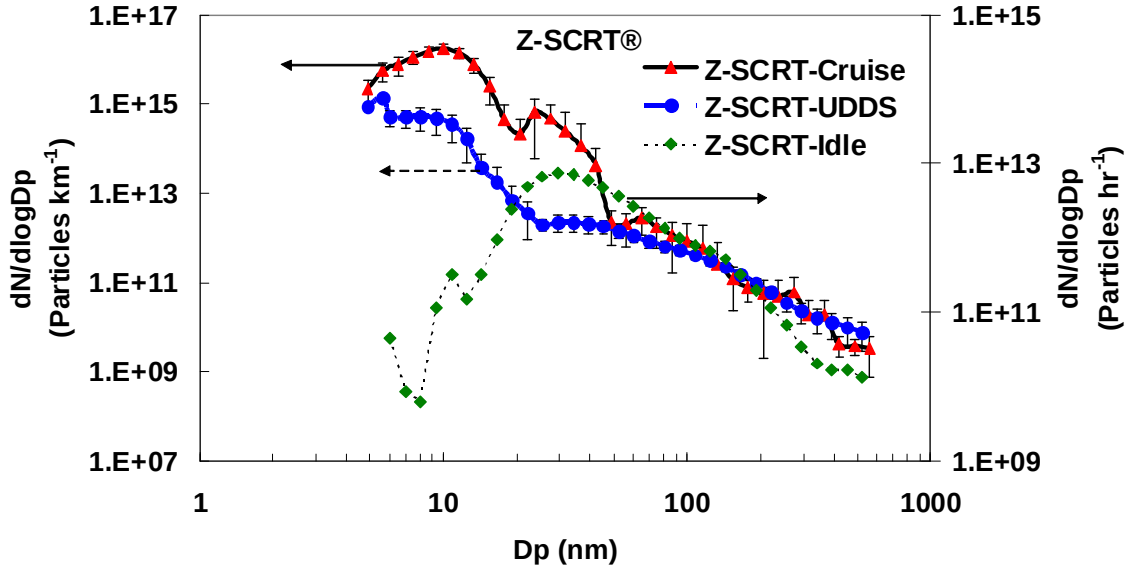


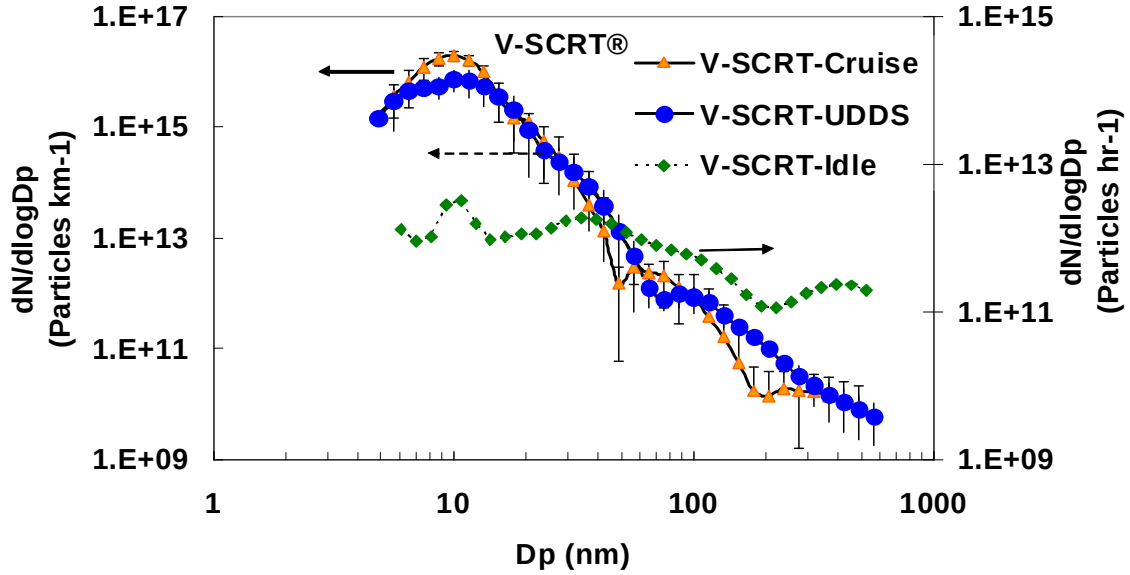
Hybrid-CCRT®

Chemical and Toxicological Analysis Plan

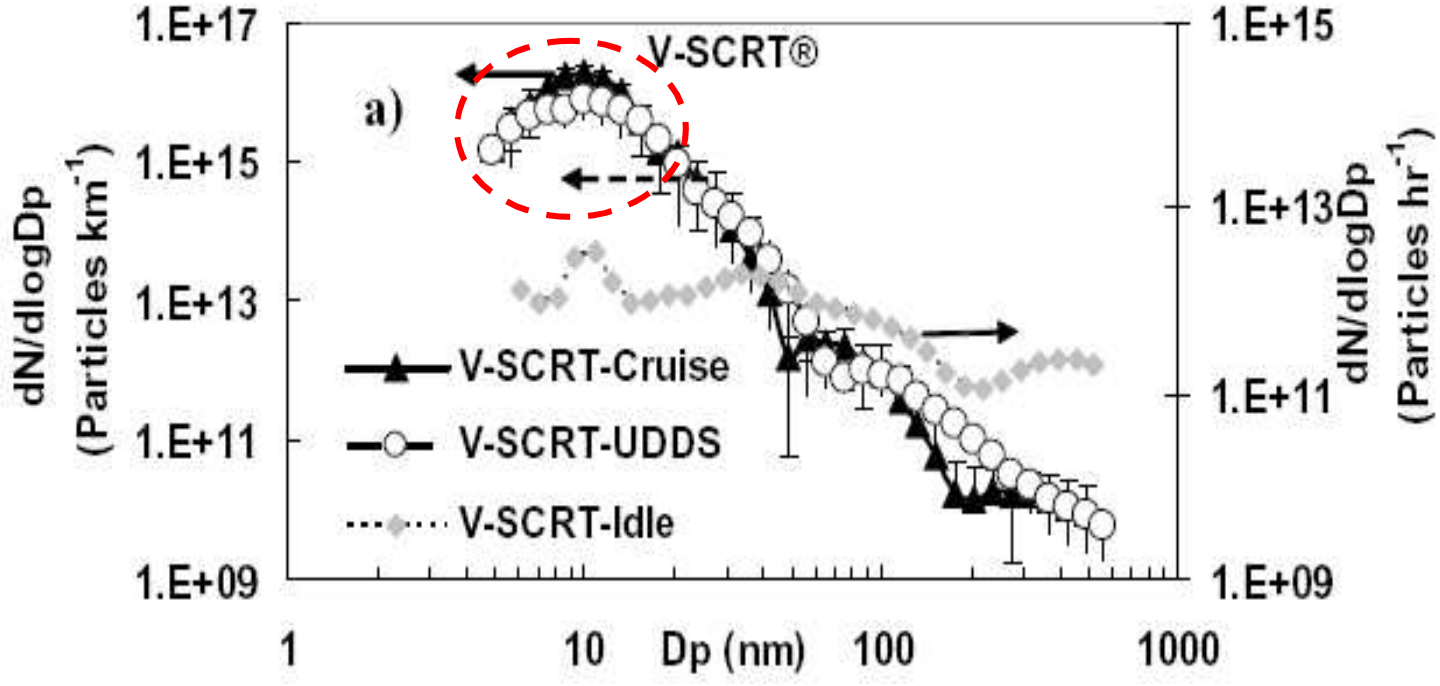
Samplers	U Wisconsin-Madison					UCLA-RIVM	
	IC	EC/OC	Organics	Metals	ROS	DTT	DHBA
NanoMOUDI	✓	✓			✓		
USC Hi-Vol	✓		✓	✓	✓	✓	✓
Thermo denuded filters	✓		✓	✓	✓	✓	✓

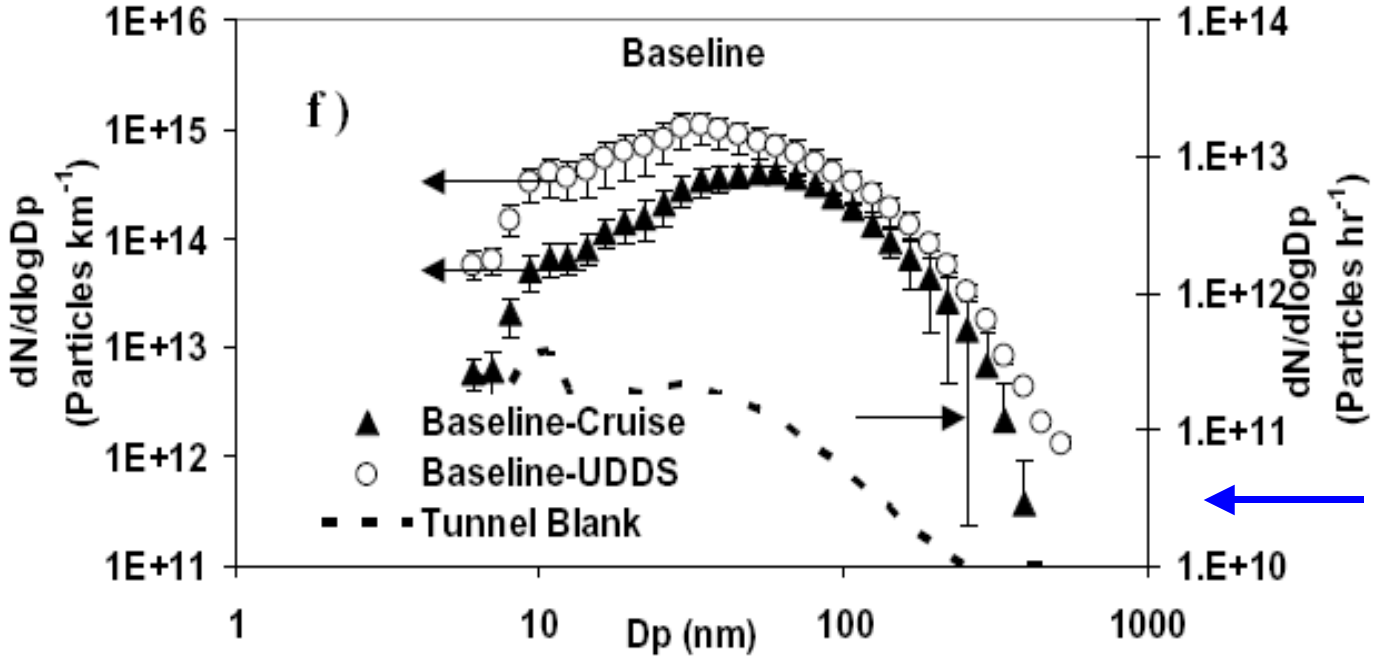
Particle Number Size Distribution (1)





- 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

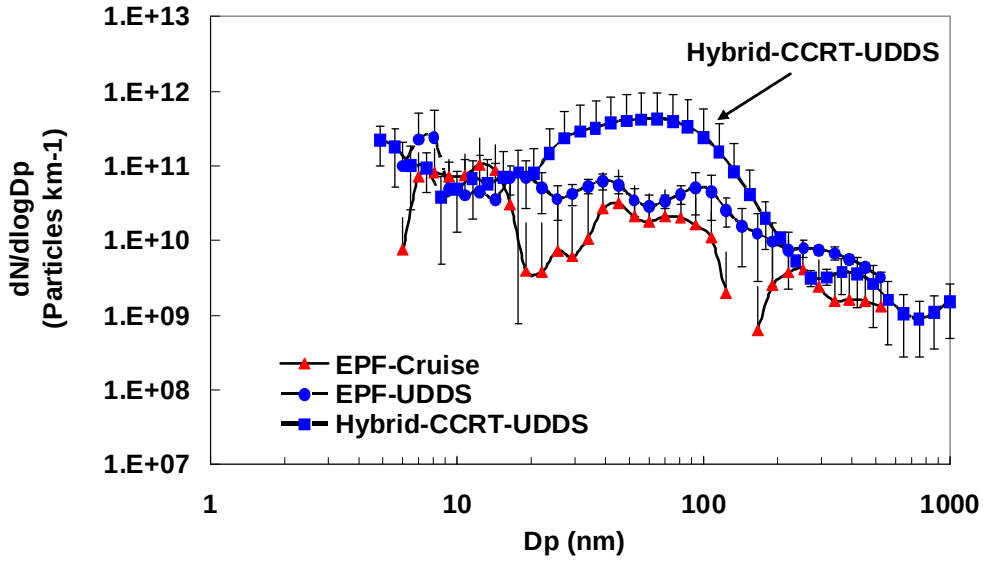
Note difference in y-axis scales

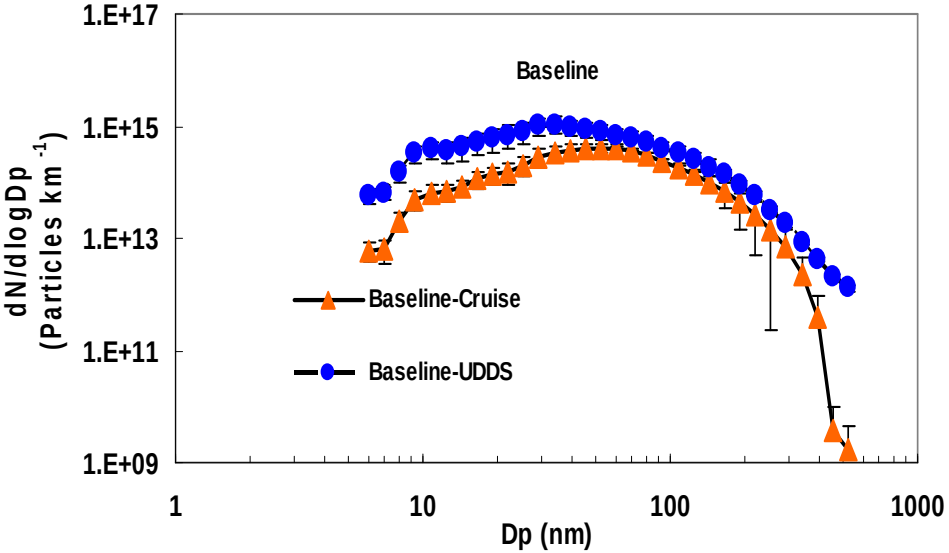
Nucleation seen in V-SCRT but not in baseline truck

Baseline Truck

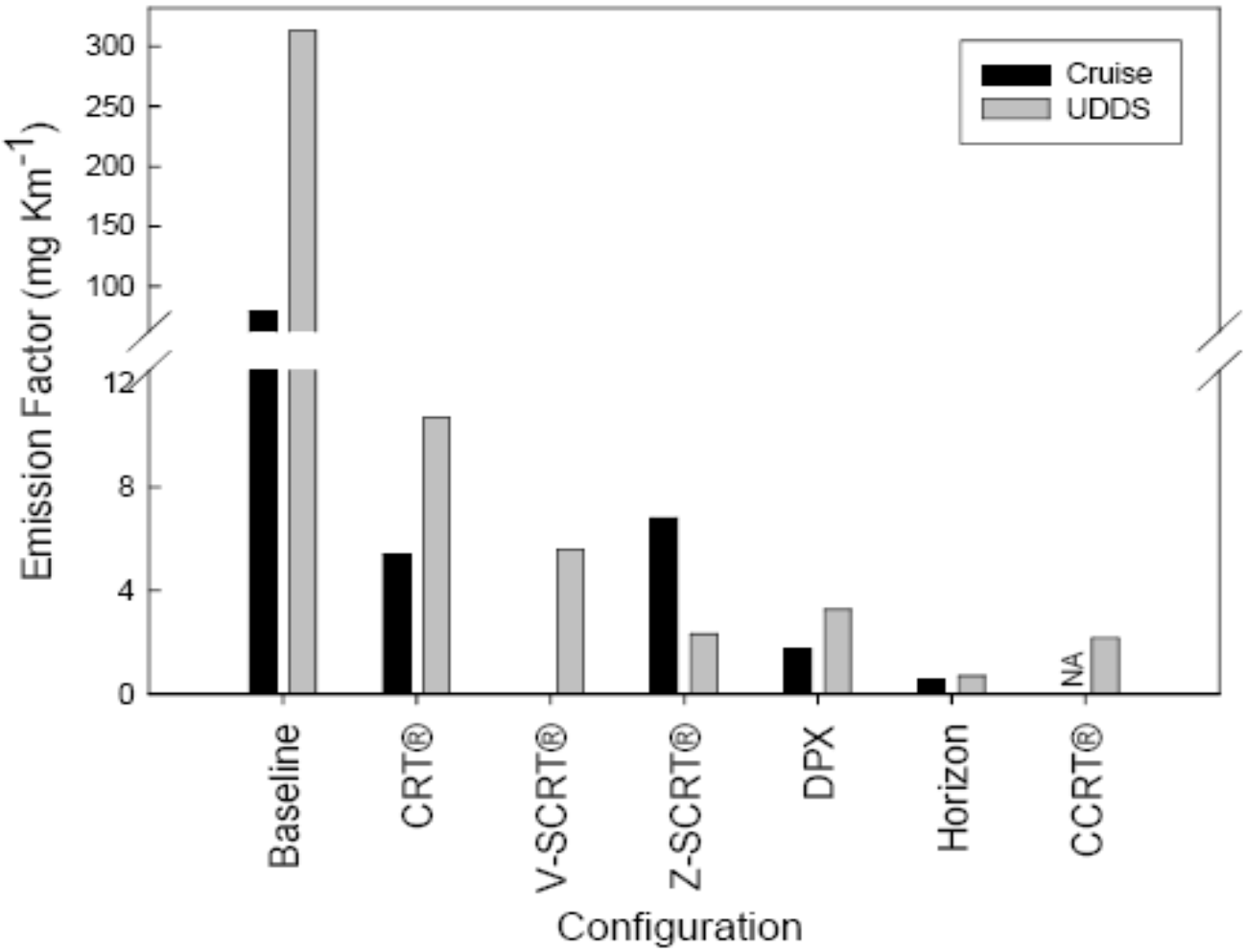
Particle Number Size Distribution (3)

Non-Nucleating Vehicles



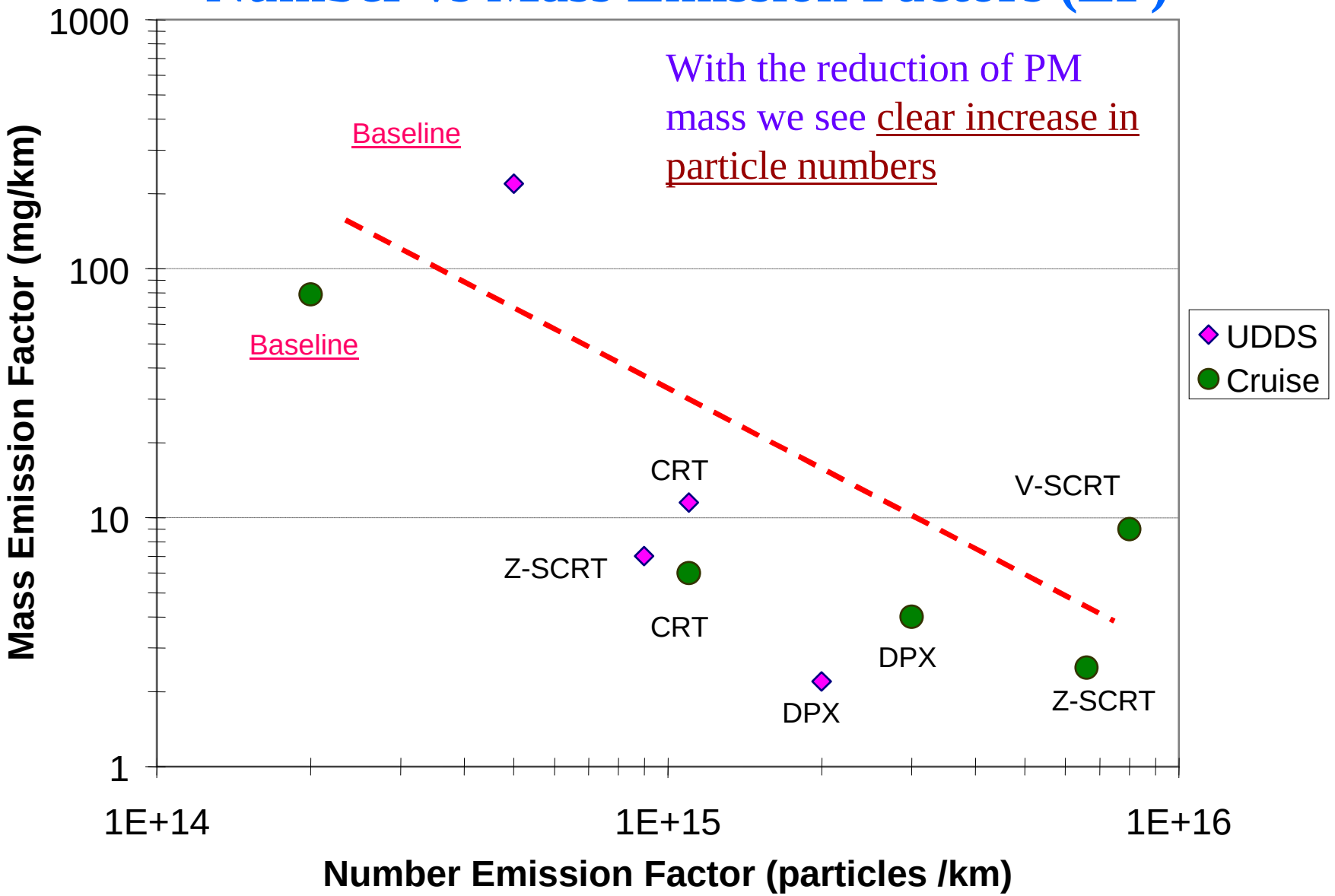


- Accumulation mode particles formed at high engine load mode (Cruise and high speed of UDDS)
- Also note the much lower number emission factors of the Hybrid and EPF vehicles compared to other test vehicles
- Baseline truck high concentrations and peak in accumulation mode



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

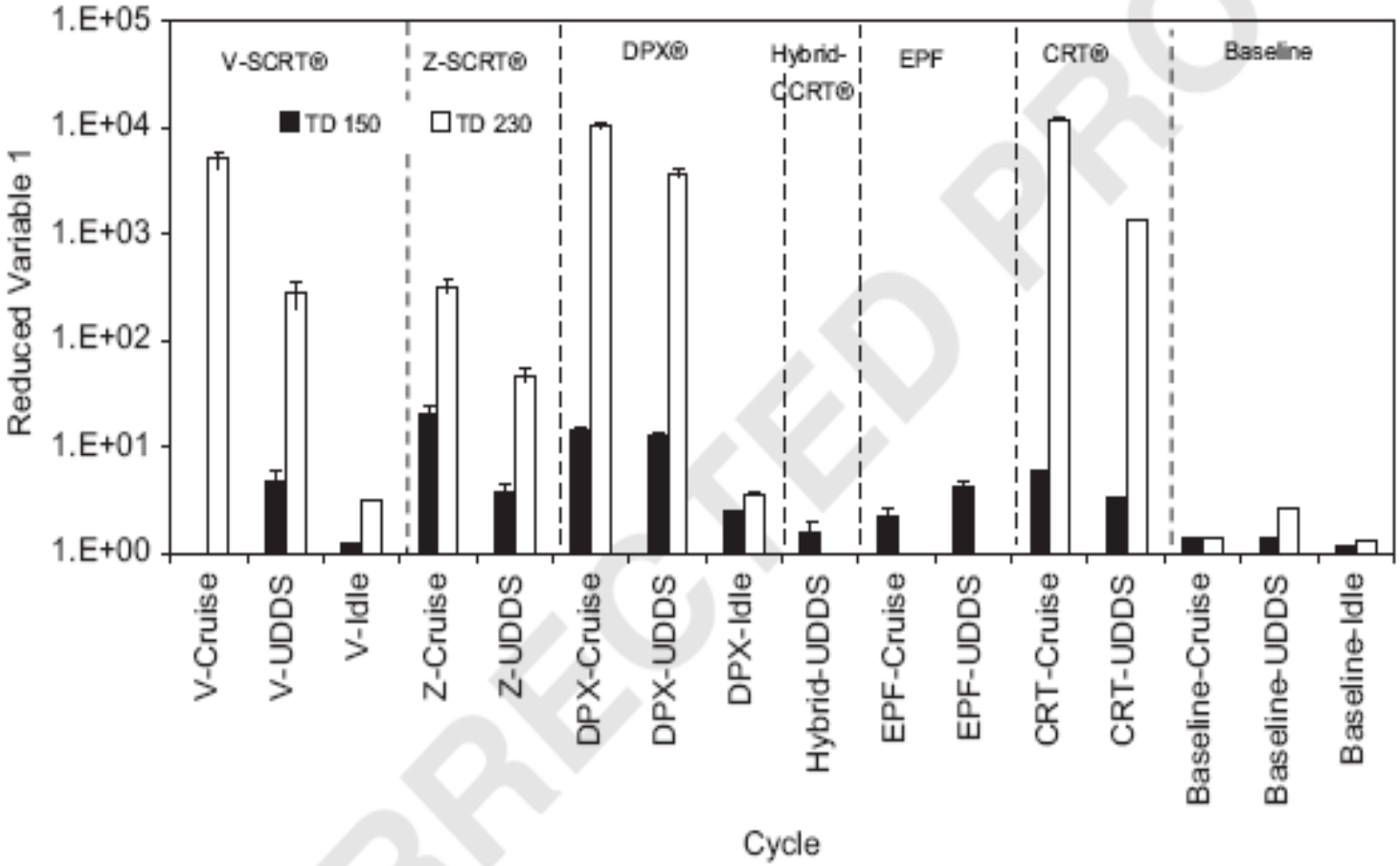
Number vs Mass Emission Factors (EF)



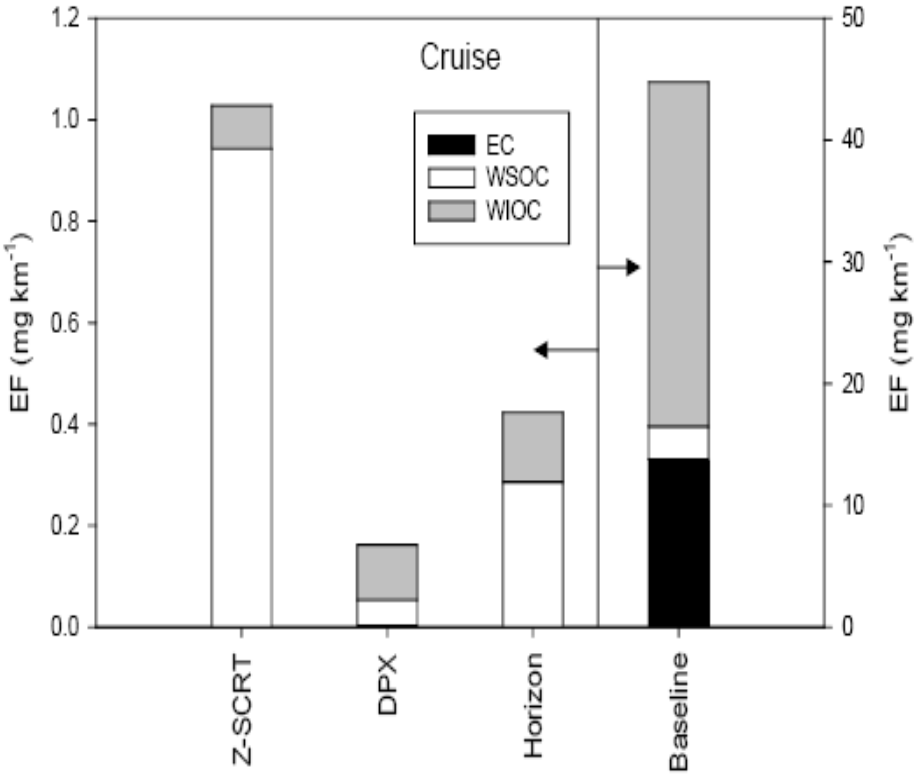
Biswas et al. Atmos. Environ, 2008

$R = N_{Exhaust} / N_{TD}$ = 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.

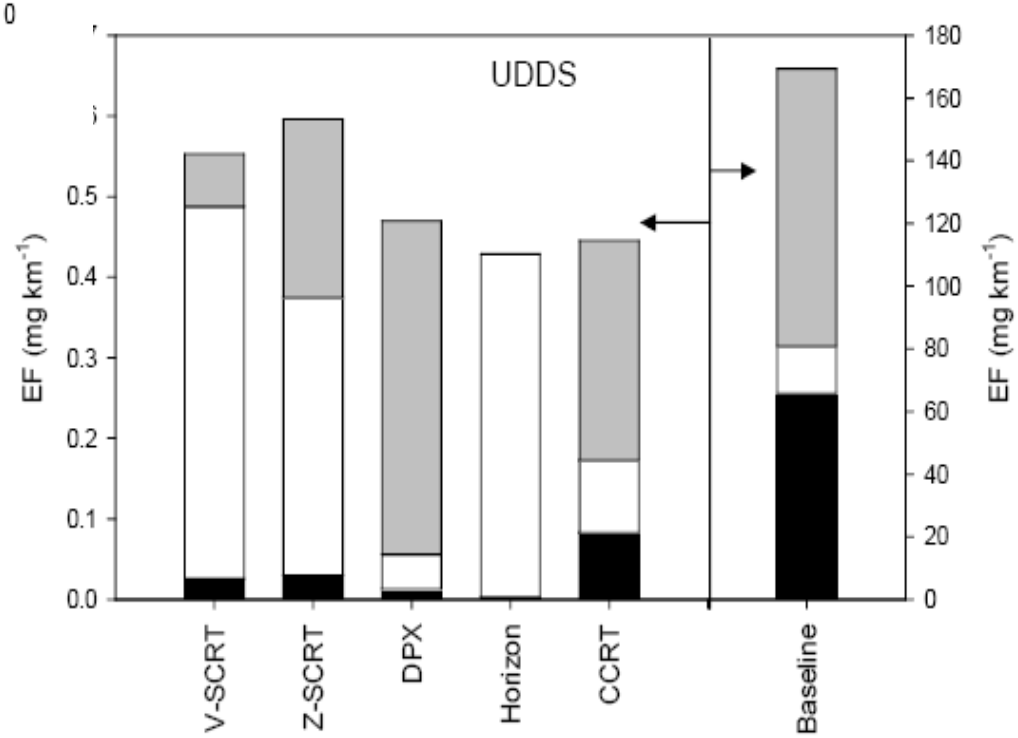


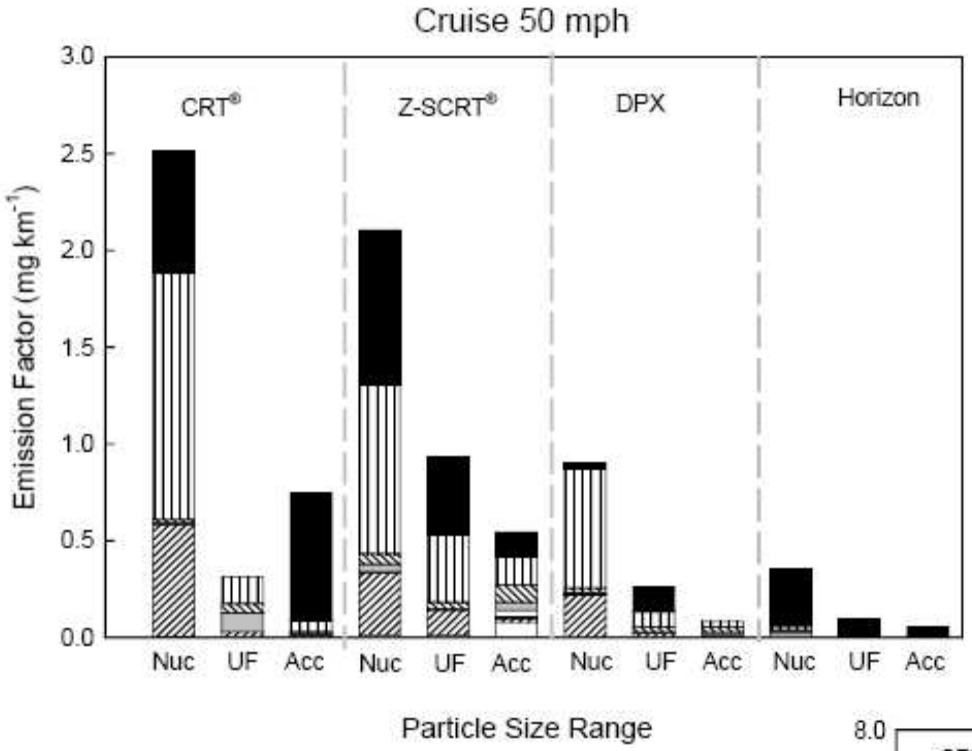
Particle Volatility (by Number) of Various Vehicles and Driving Cycles



- **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

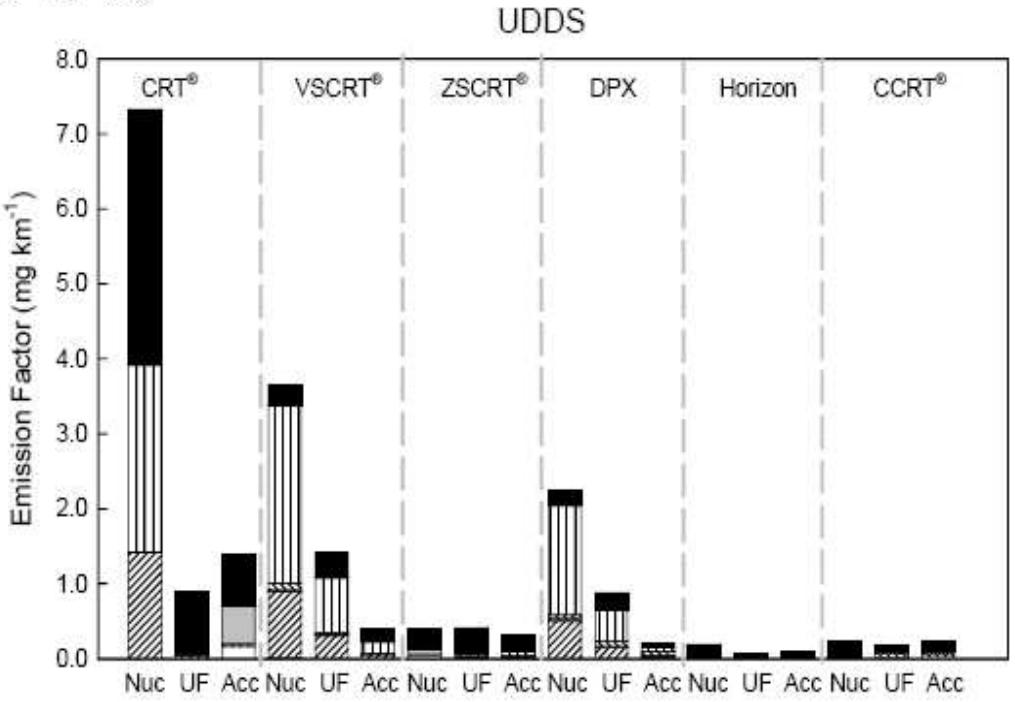




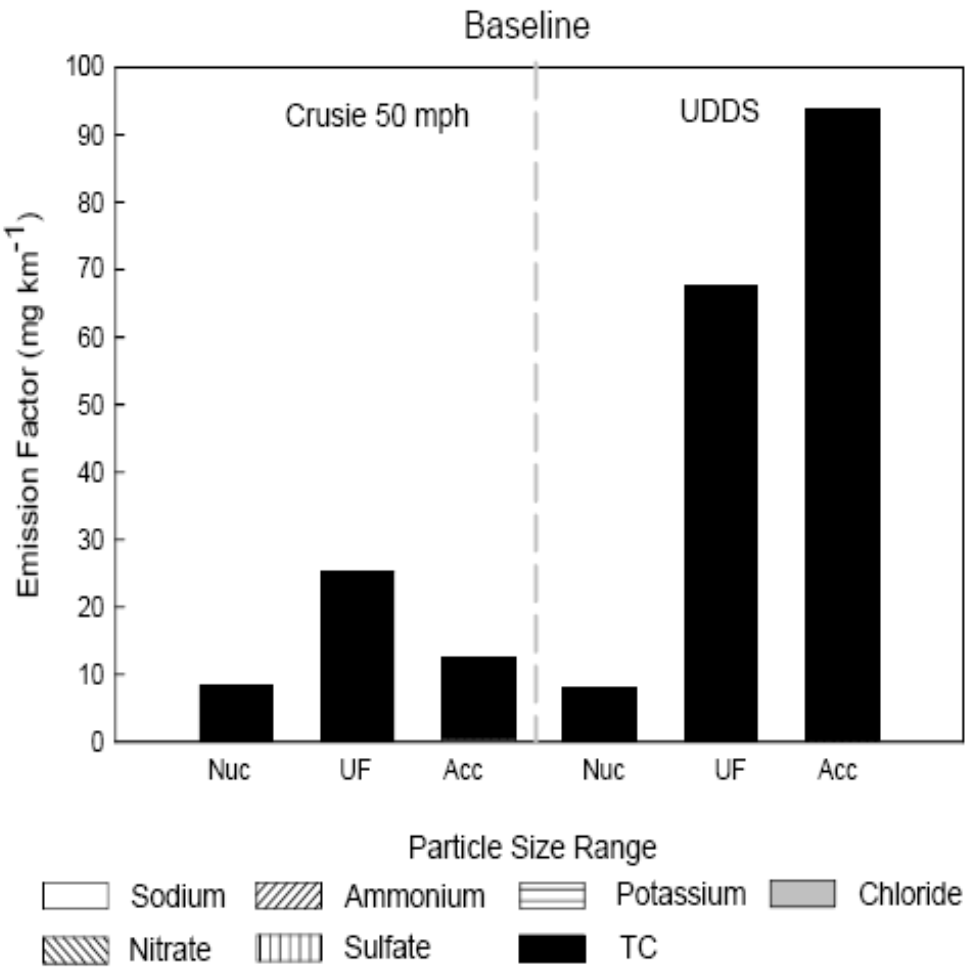
Nuc: 0.01 – 0.056 μm

UF: 0.056- 0.18 μm

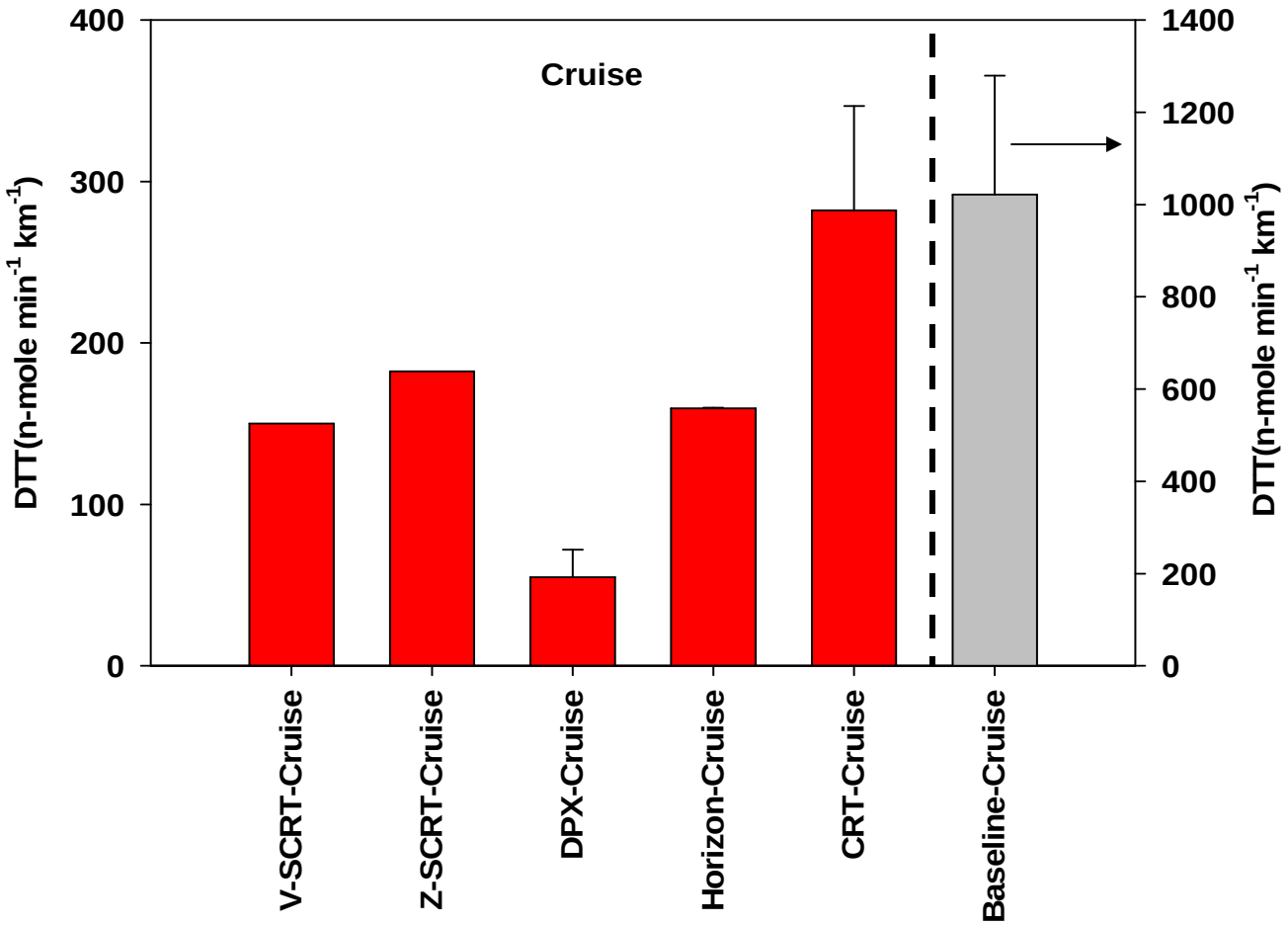
Acc: 0.18- 2.5 μm



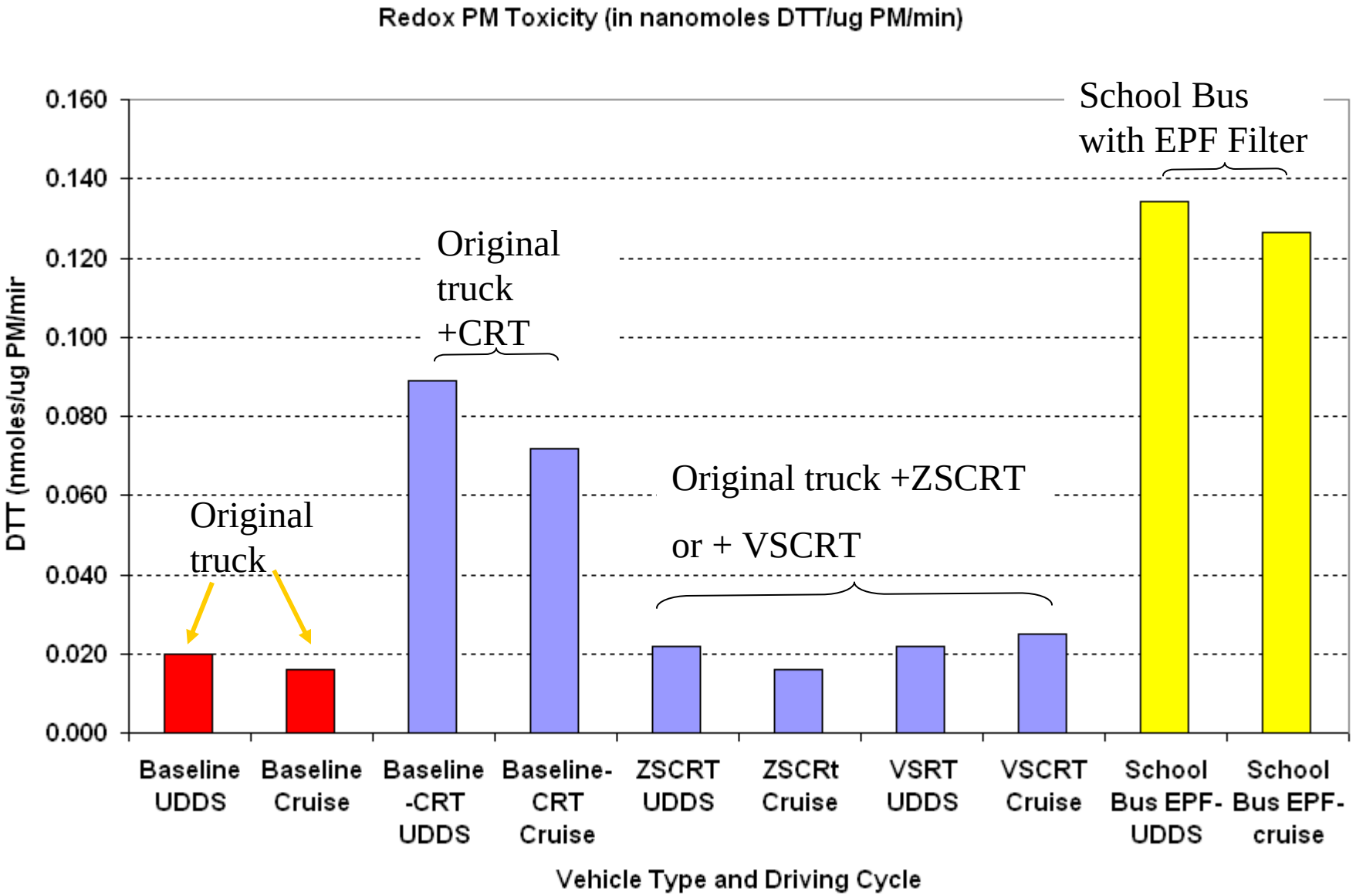
- **Nucleation mode PM from vehicles with catalytic reduction mostly ammonium sulfate and TC (to a lesser degree)**
- **Higher emissions in UDDS, except:**
- **Higher emissions in cruise mode of nucleation mode PM for SCRT vehicles**



Baseline vehicle PM emissions comprise almost entirely of carbonaceous material

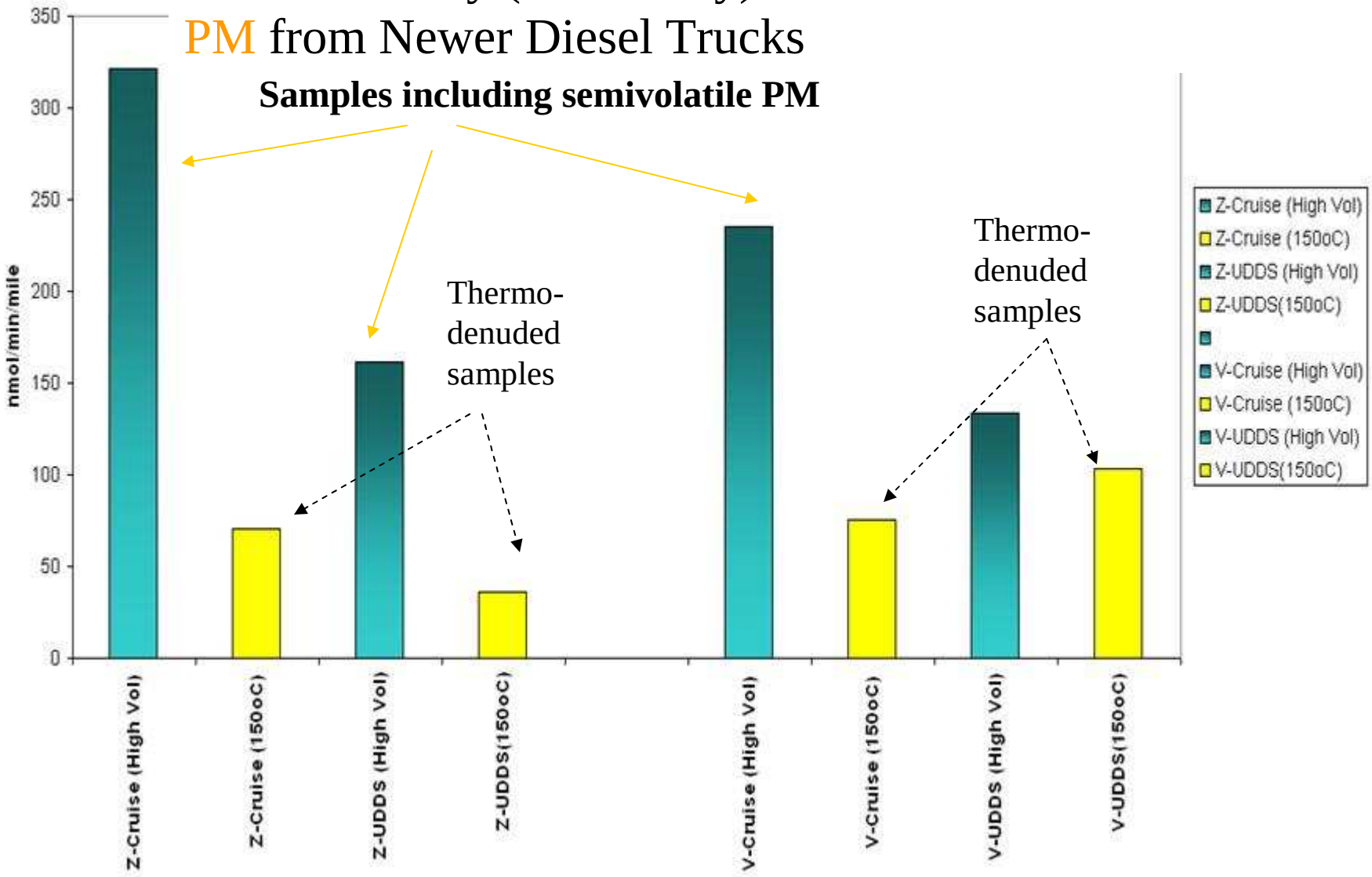


- **On a per km basis, the baseline vehicle has the highest PM redox activity;**
- **However, the redox activity reduction by after-treatment technologies is highly non linear with respect to their PM mass emission rates**



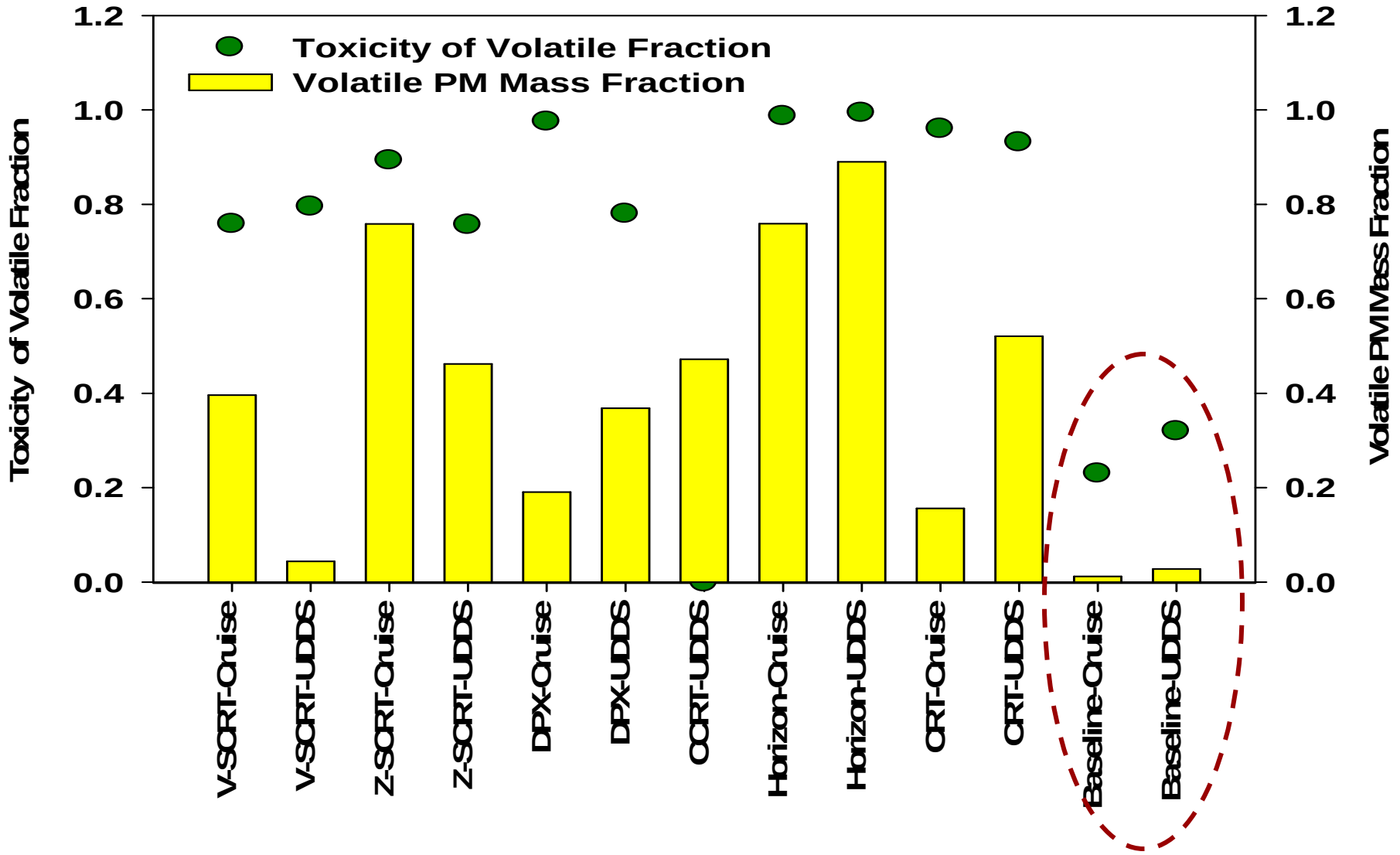
DTT activity expressed per PM mass; note the very high activity of some of the reduced mass emission trucks, especially with non-catalyzed silicon carbide (CRT) substrate for PM control

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 **much higher when the semi-volatile fraction is included**

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