Physico-chemical and Toxicological Assessment of PM Emissions from Heavy-Duty Vehicles Operating With and Without Emission Control Technologies

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Outline and Study Objectives

- Conduct dynamometer experiments to collect diesel exhaust particles for physical, chemical and toxicological analysis, along with real-time data
- Conduct physical (e.g. PM mass and size distribution), chemical (EC, OC, organic compounds, trace elements, inorganic ions) and toxicological [dithiothreitol (DTT) and macrophage reactive oxygen species (ROS) assays] characterization of the collected PM samples.
- Perform data analysis, and prepare manuscripts for publication in the peer-reviewed literature.
- Prepare quarterly progress reports for CARB.
- Prepare and submit the final report to CARB

1. **Emission Sources of Air Pollutants**

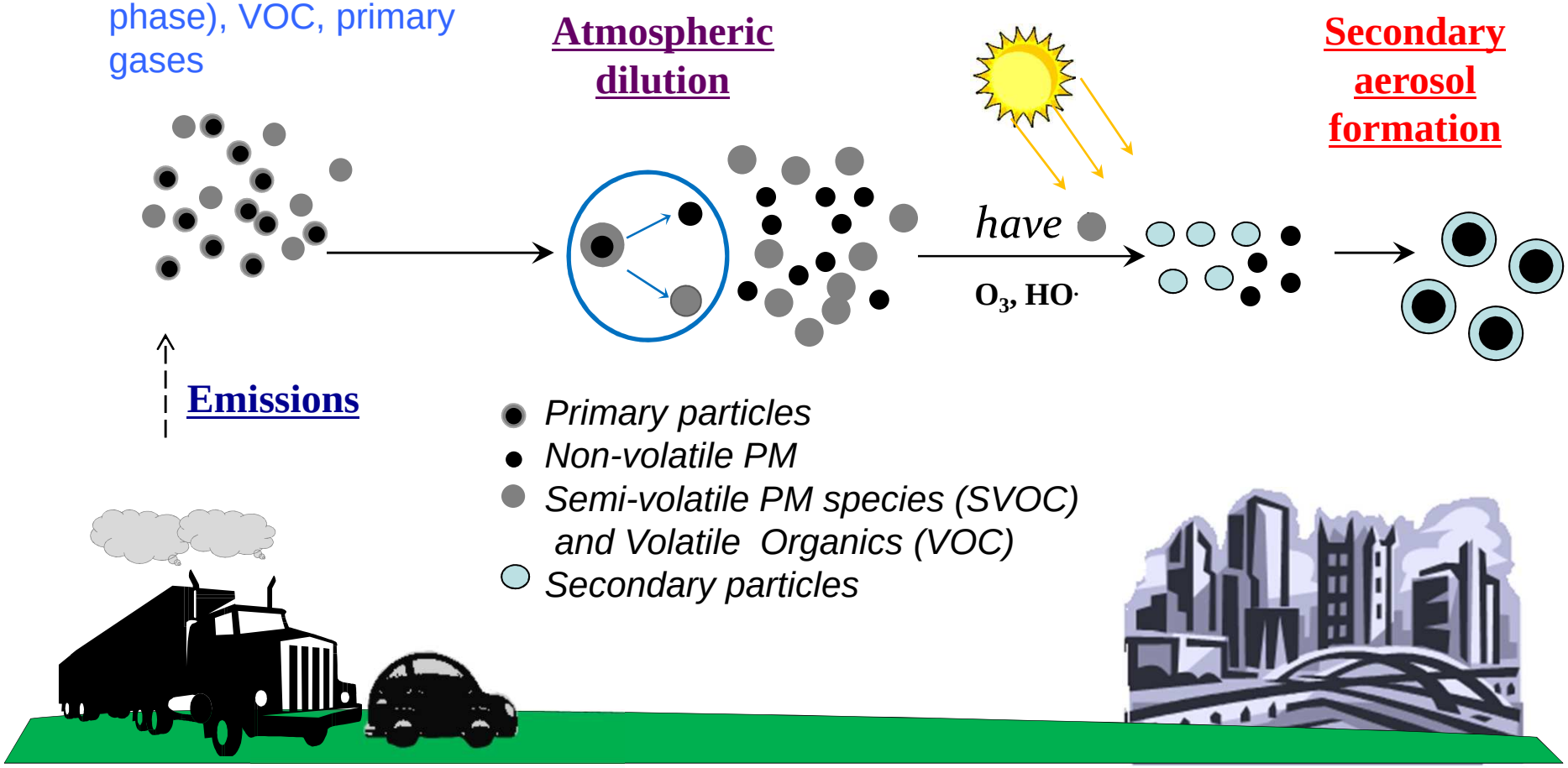
- **Traffic, Freeways, Ports, Power plants**
- Freshly emitted mixture of non-volatile PM, SVOC (PM and vapor phase), VOC, primary gases

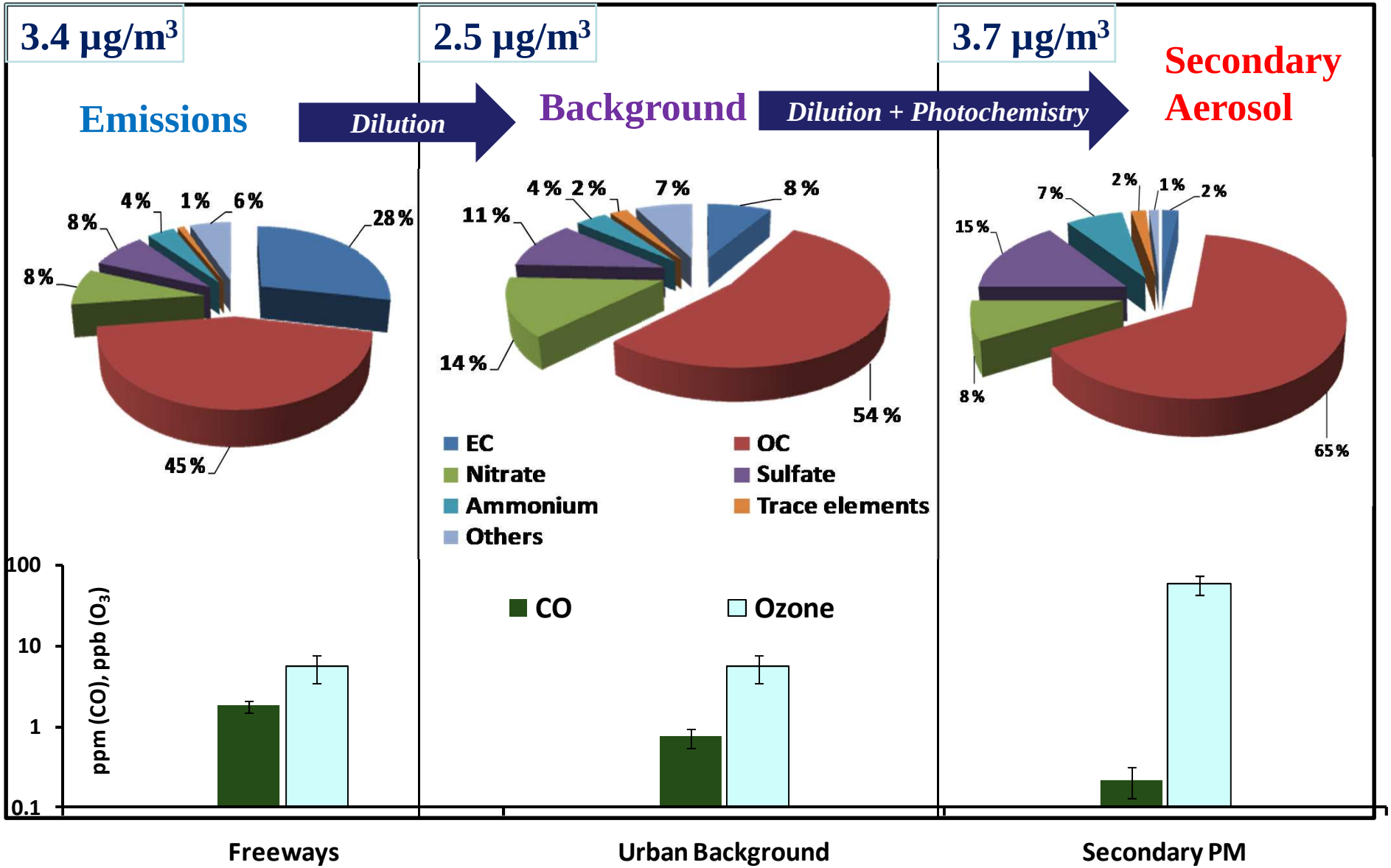
2. Atmospheric Dilution

- Phase transformation
- Volatilization of primary SVOC and partitioning from PM phase into gas phase

3. Atmospheric Aging and Photo-Chemical Reactions

- Photo-chemical reactions of gas phase SVOC with O3 and oxidant gases
- Formation of Secondary Organic Aerosol(SOA)





Ref.: Ntziachristos et al Atmos Environ 2007; Ning et al. ES&T 2007; Verma et al. Atmos Environ 2009, Sardar et al, JGR 2005

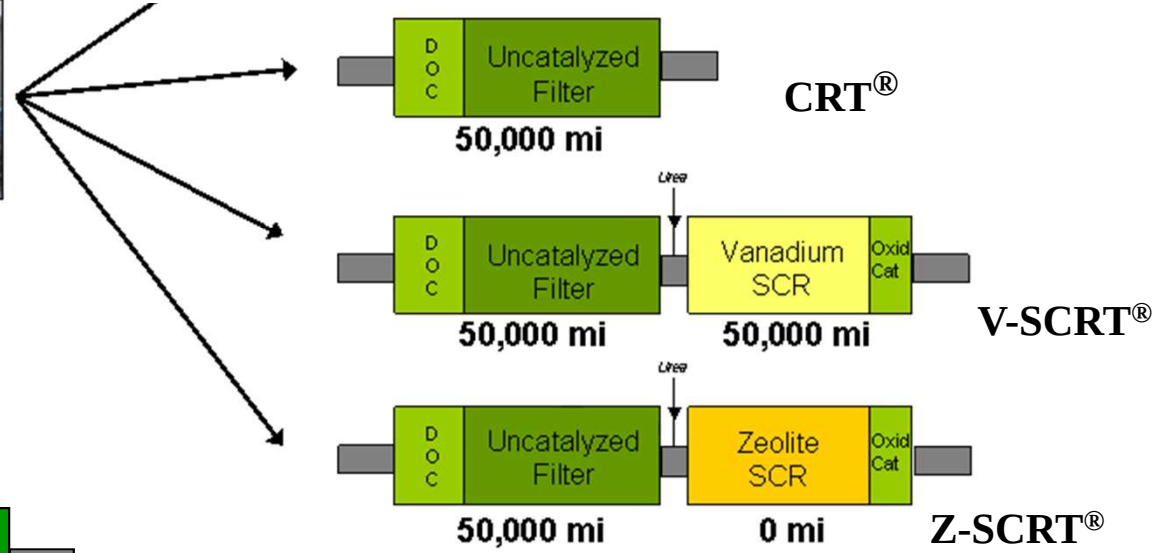
Test Matrix

4 vehicles, 7 configurations, 3 driving cycles (cruise, UDDS, Idle)

Baseline

Veh#1, 1998 Cummins

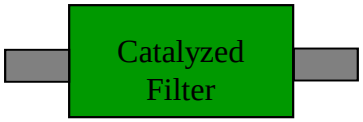
Diesel 11L, 360,000 miles



1,000 mi

CCRT®

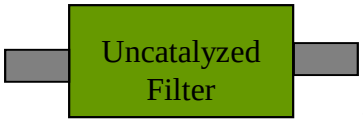
Veh#2 2006 Cummins Diesel w/ Allison Hybrid drive 5.9L, 1,000 miles



30,000 mi

DPX

Veh#3, 1999 International Diesel 7.6L, 40,000 miles



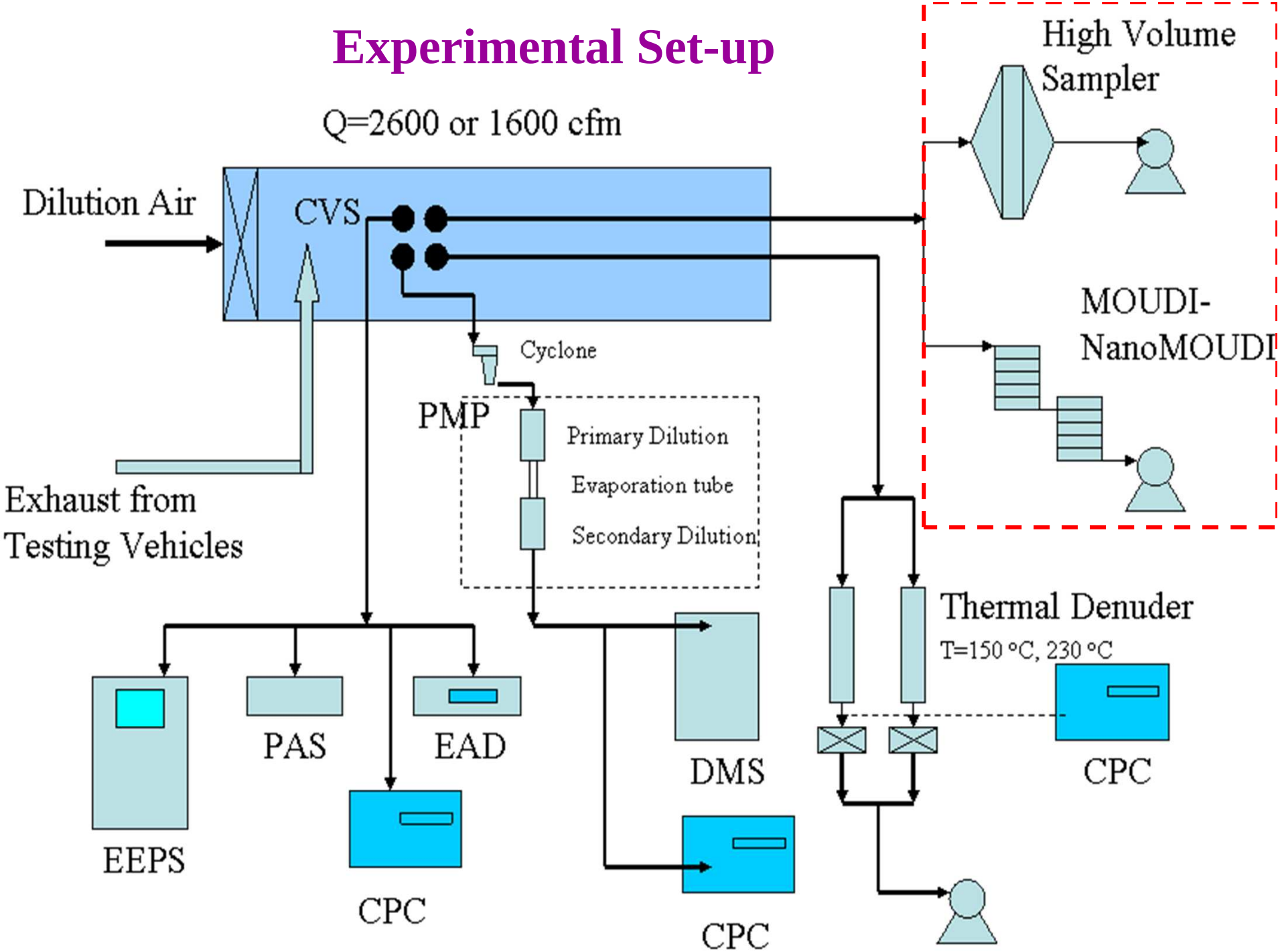
31,000 mi

Horizon

Veh#4 2003 Cummins Diesel, 5.9L, 50,000 miles

Source: Herner et al. 2007(AAAR)

Experimental Set-up



Chemical and Toxicity Assays

1. High volume sampler: Integrated PM samples collected on the Teflon coated glass-fiber filters

   (i) Redox activity of PM : Measured by consumption rate of dithiothreitol (DTT) and Reactive Oxygen species (ROS) assay

   (ii) Water soluble organic carbon (WSOC): organic speciation (GC/MS)

   (iii) Water Soluble Metals and Trace Elements

2. MOUDI-nano-MOUDI (10 nm – 10 μm)

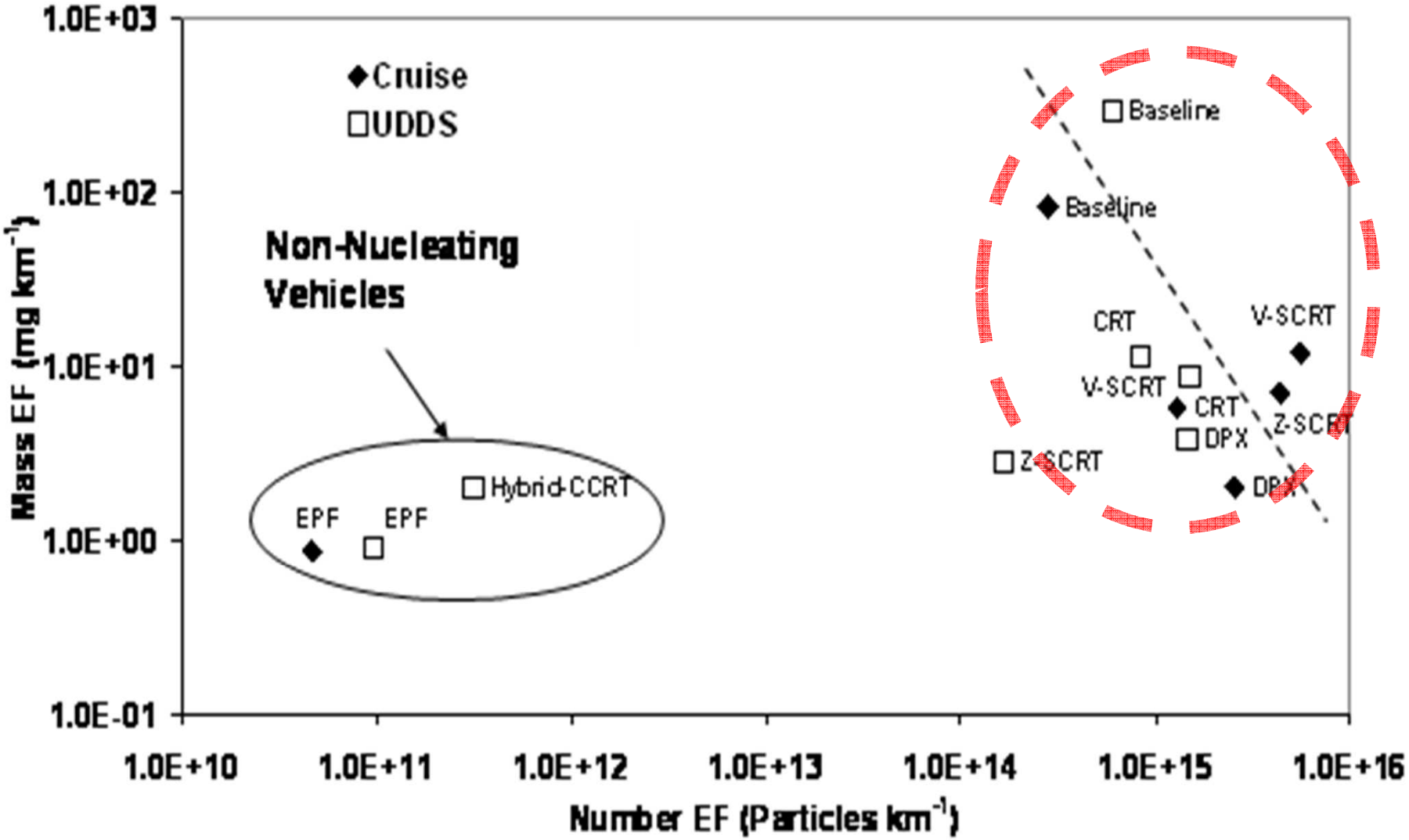
(i) Inorganic Ions (nitrate, sulfate, ammonium etc): Ion Chromatography

(ii) EC, OC: Thermal optical method

3. Thermodenuder: Teflon filters : Non-volatile PM

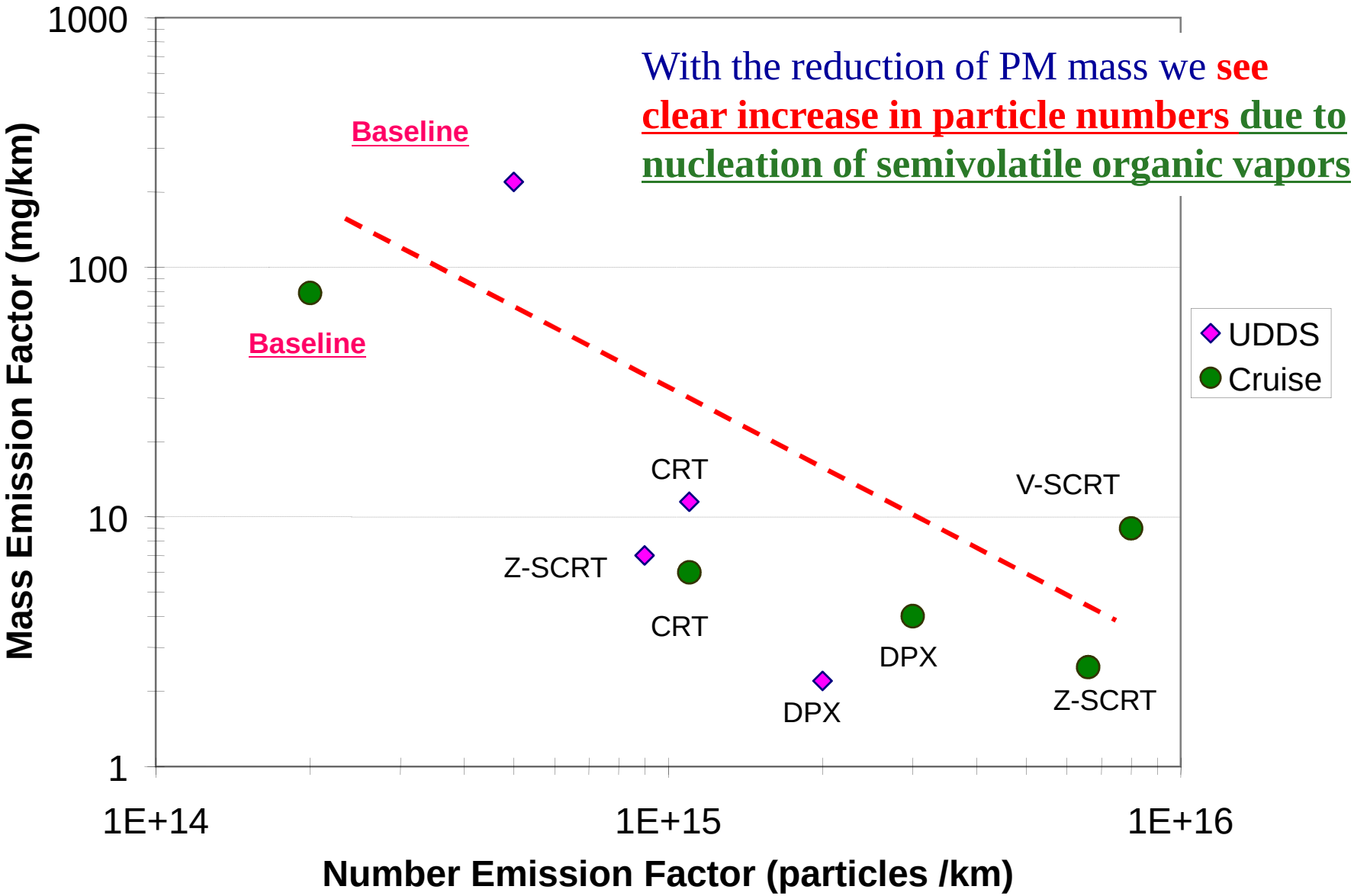
   i) Redox activity (DTT)

   ii) WSOC , GC/MS, inorganic ions



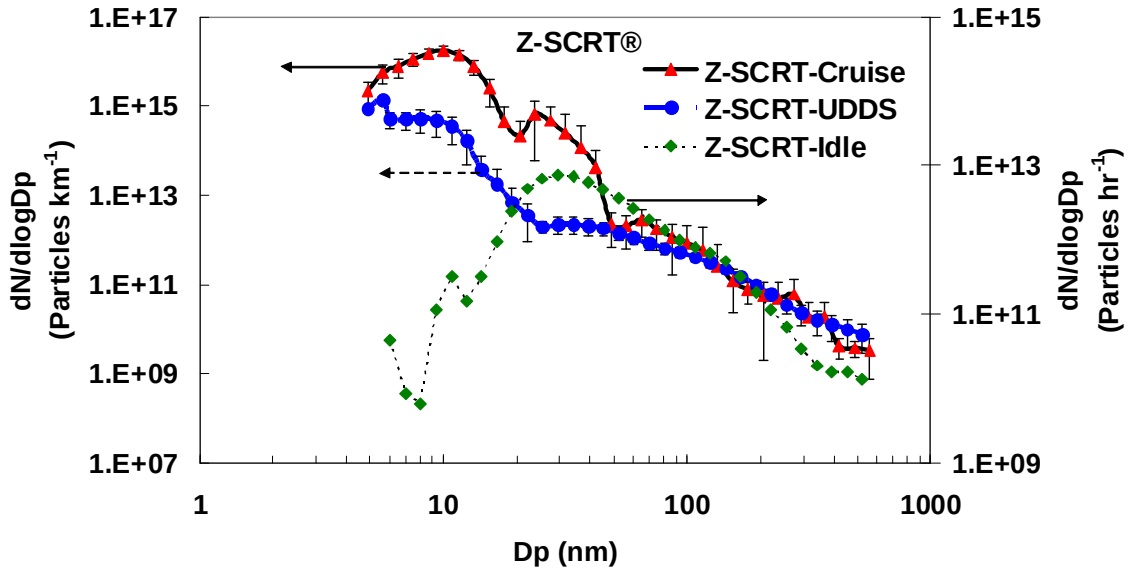
Biswas et al Atmos Environ 2008

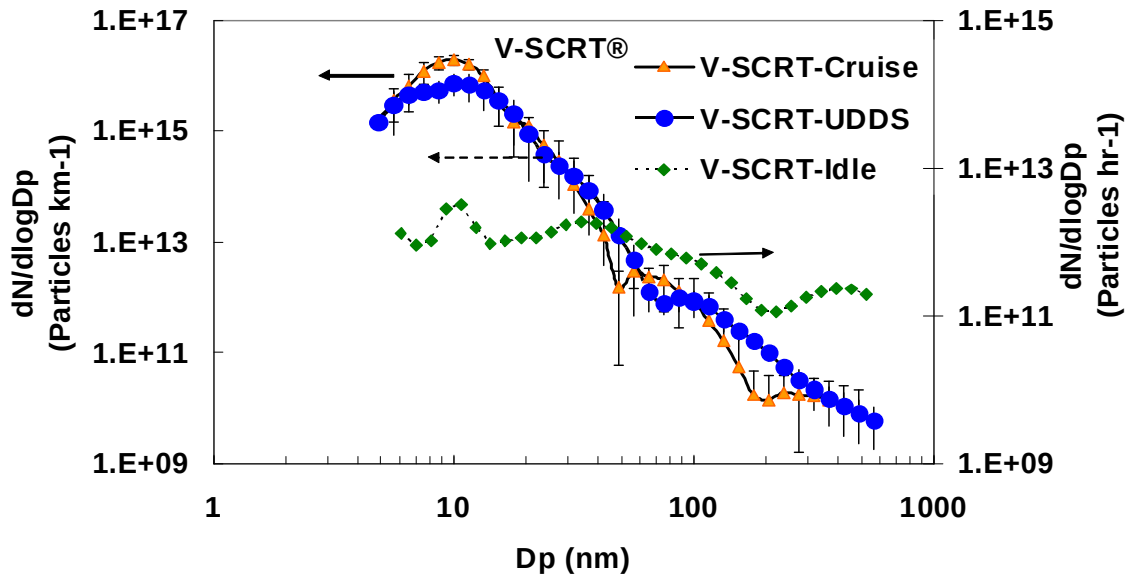
Particle Number vs Mass Emission Factors (EF) from Older and Newer Diesel Trucks



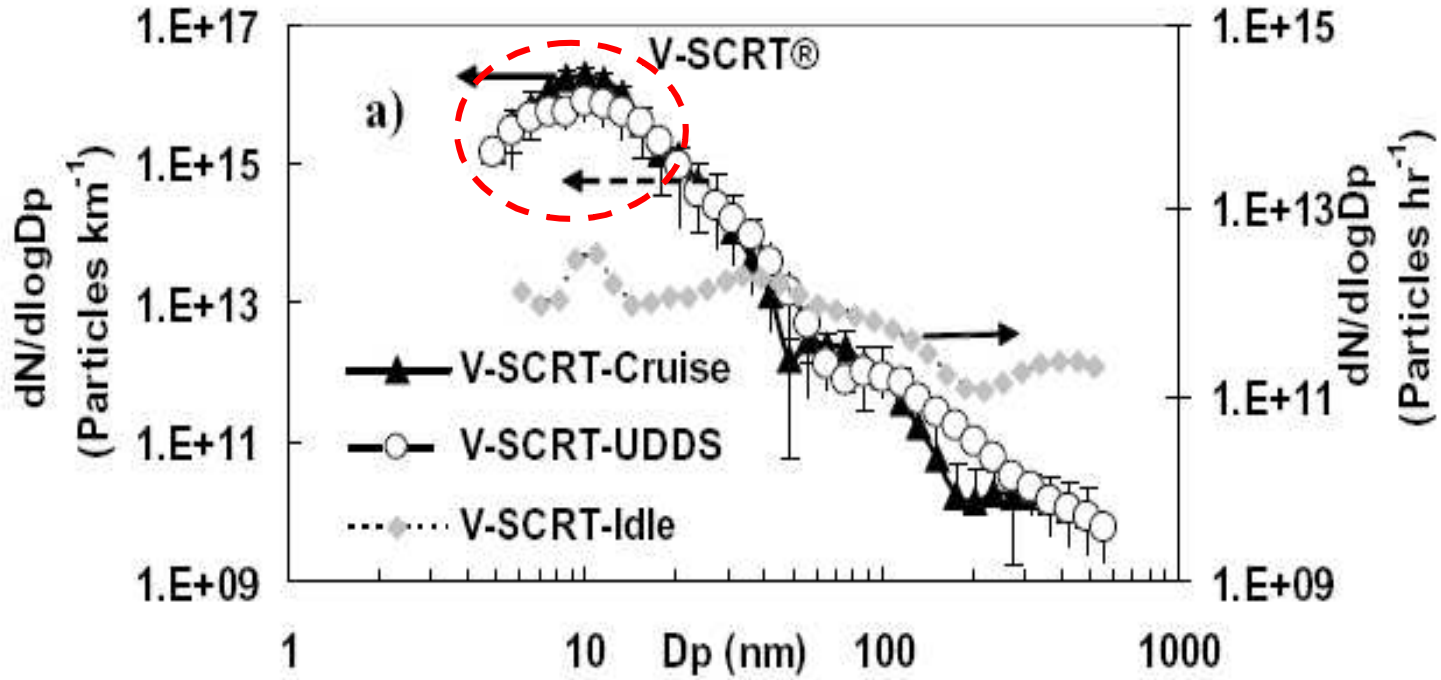
Biswas et al. Atmos. Environ, 2008

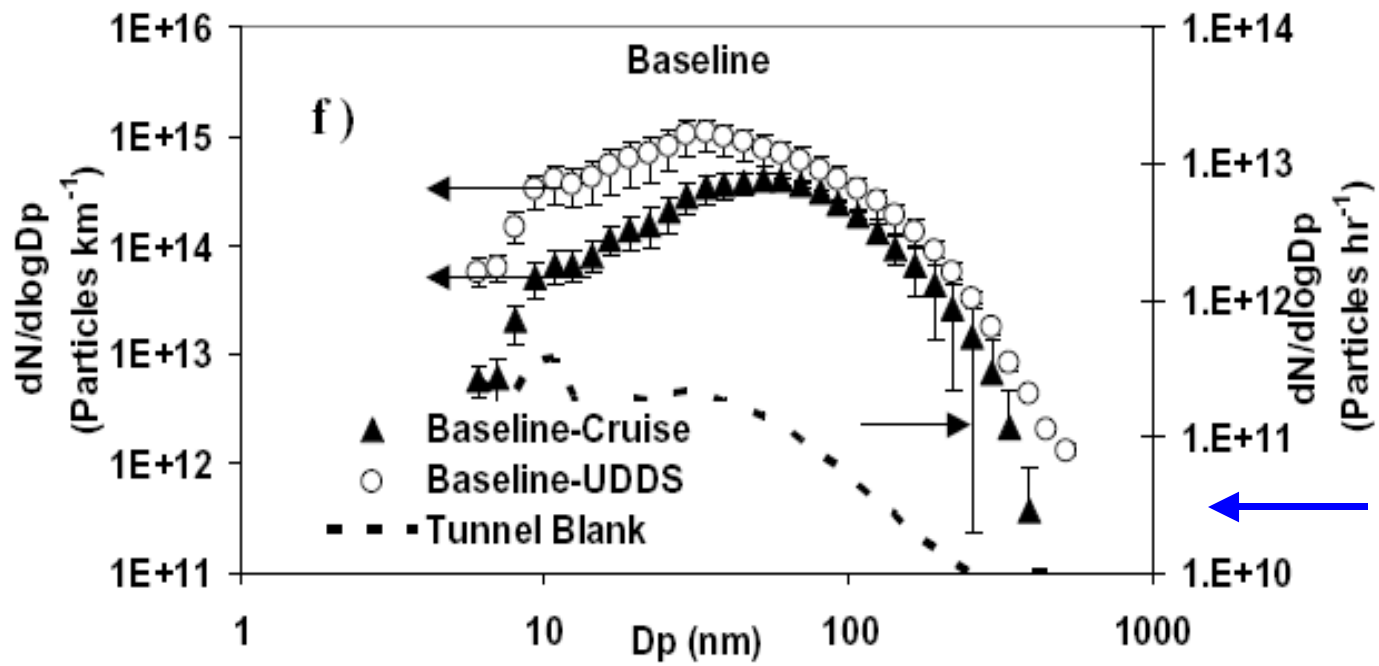
Particle Number Size Distribution (1)





- 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

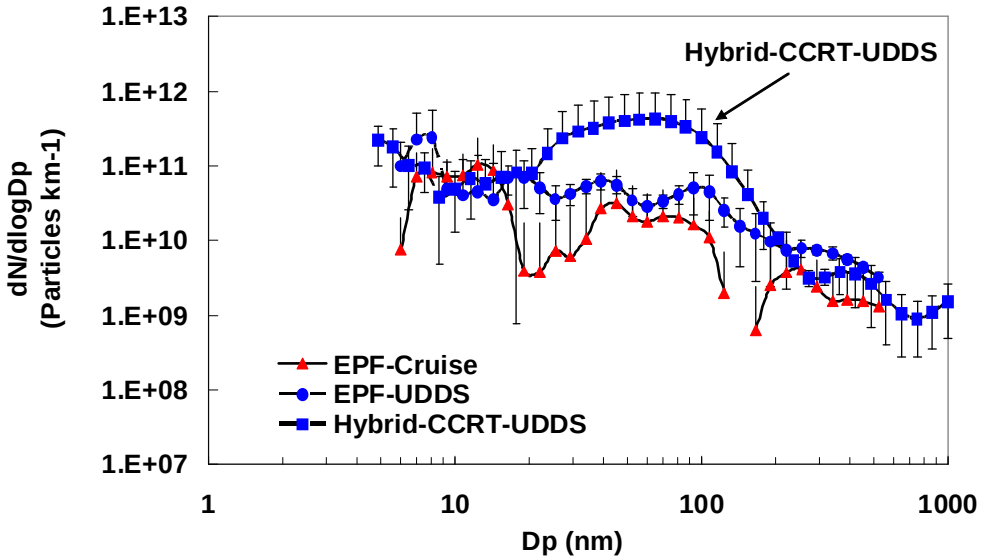
Note difference in y-axis scales

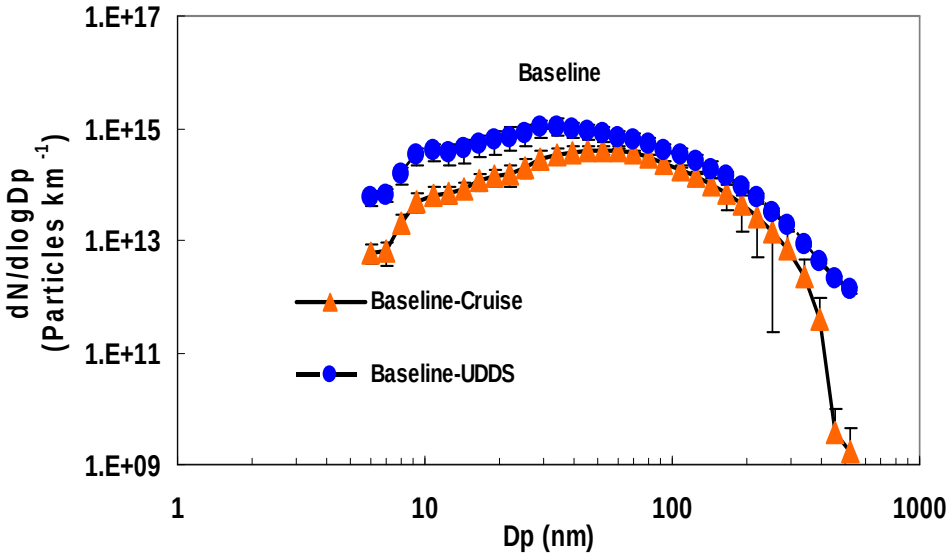
Nucleation seen in V-SCRT but not in baseline truck

Baseline Truck

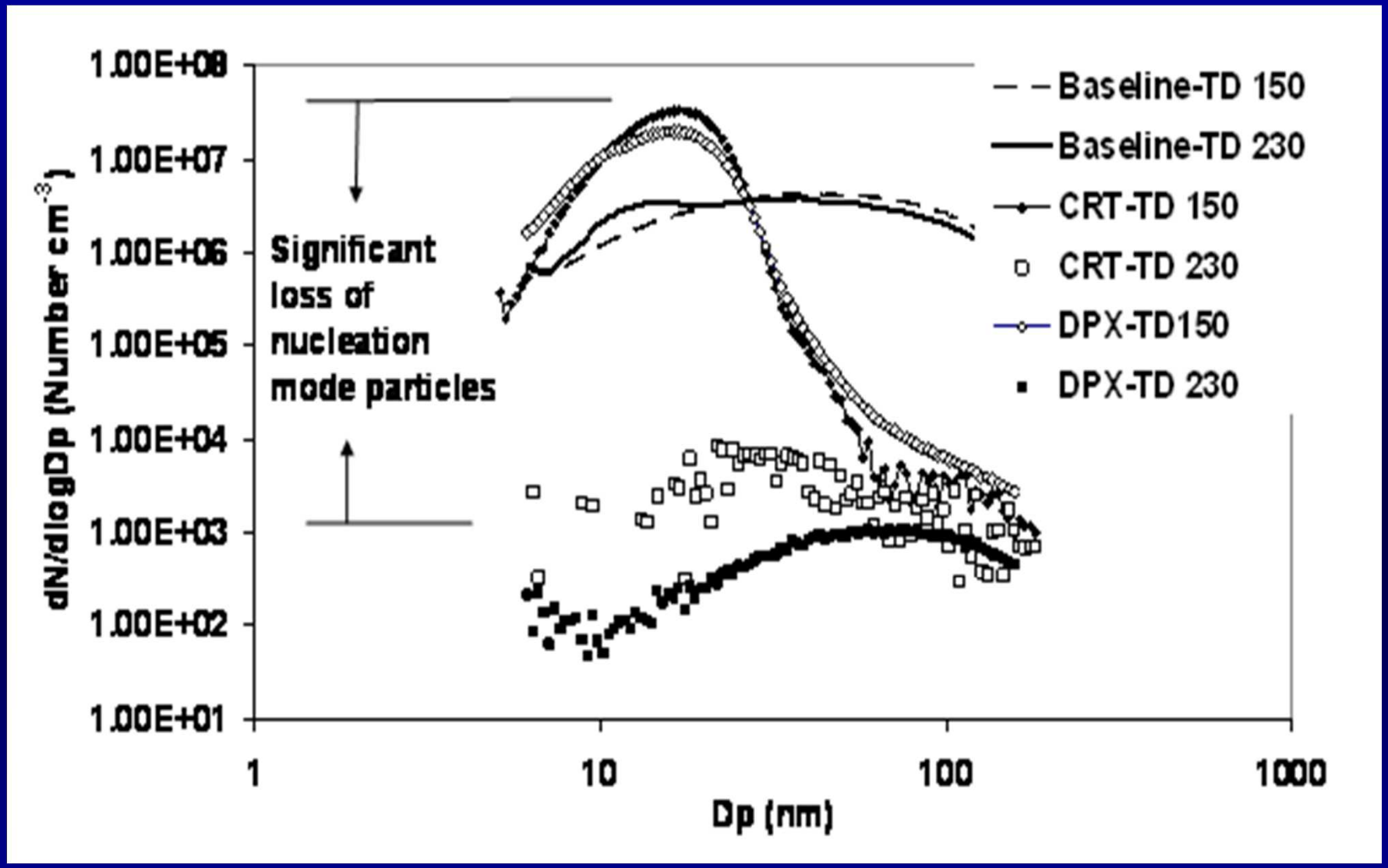
Particle Number Size Distribution (3)

Non-Nucleating Vehicles

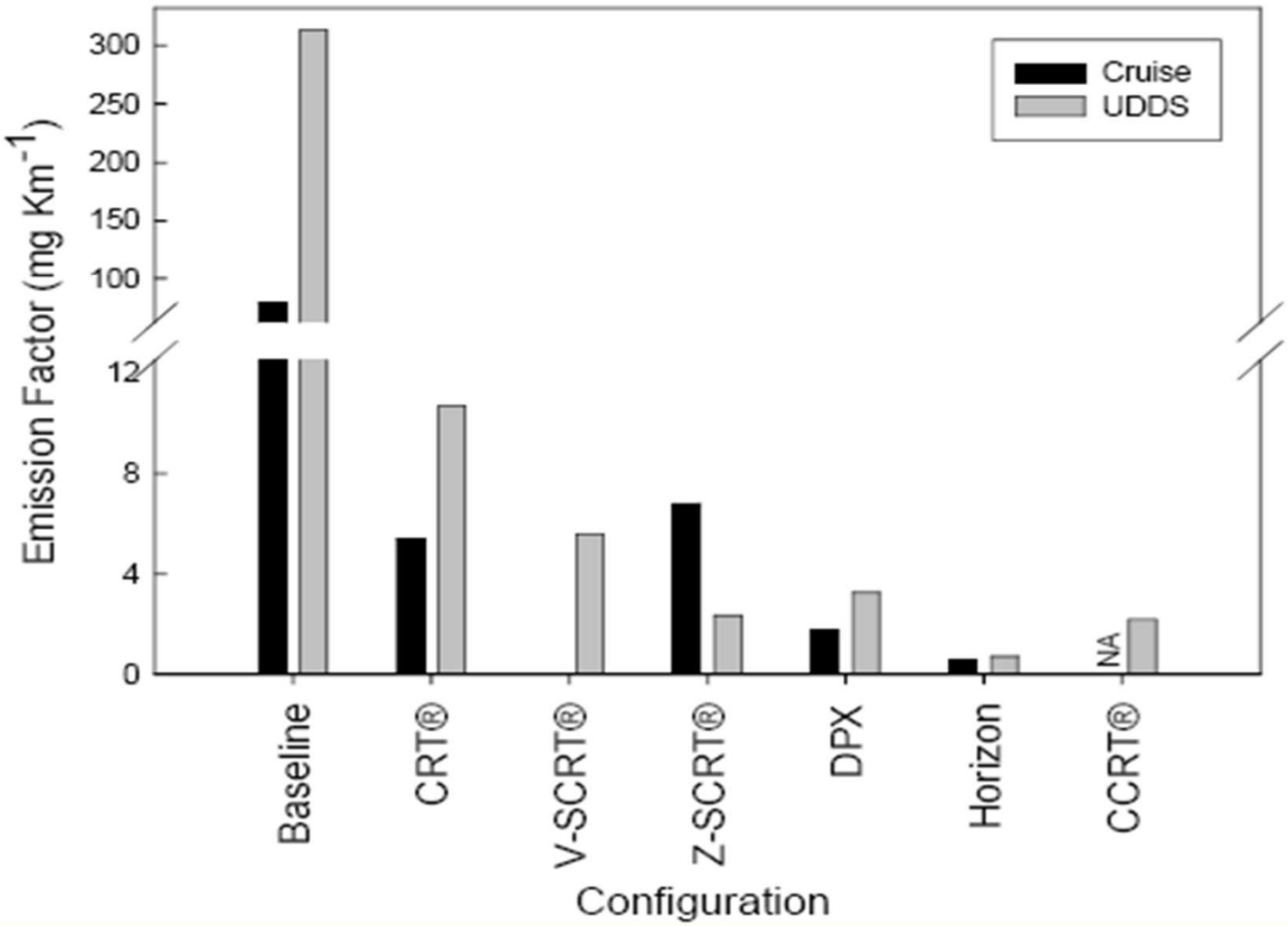




- Accumulation mode particles formed at high engine load mode (Cruise and high speed of UDDS)
- Also note the much lower number emission factors of the Hybrid and EPF vehicles compared to other test vehicles
- Baseline truck high concentrations and peak in accumulation mode



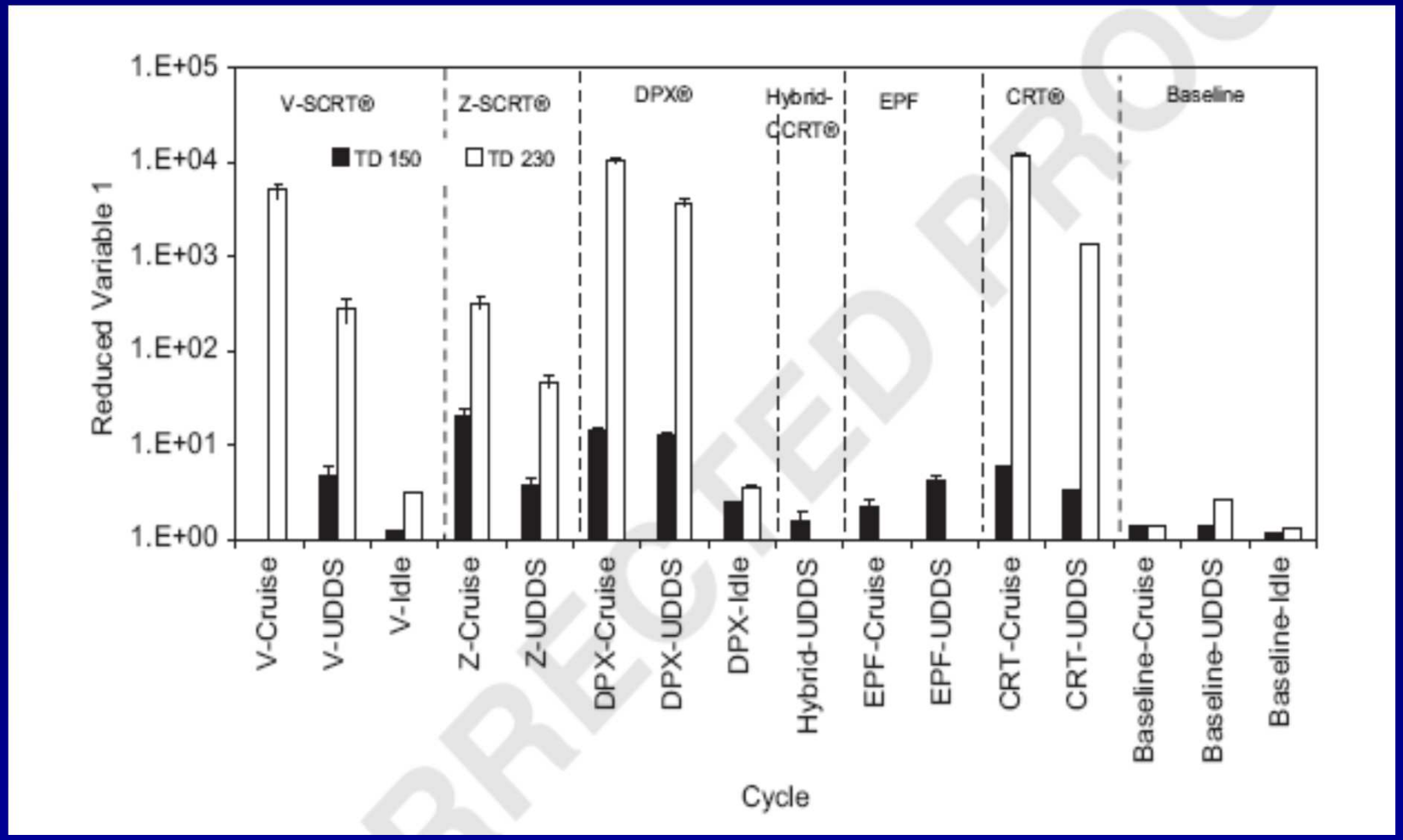
Nucleation mode particles are **semivolatile**



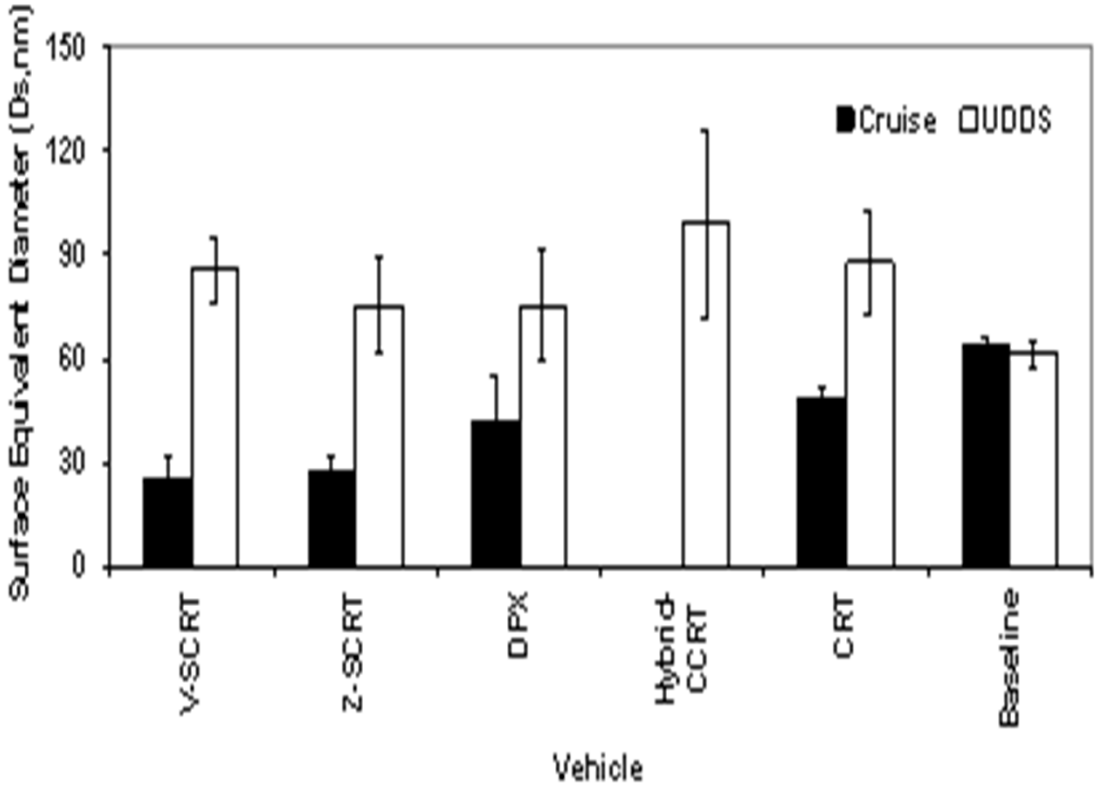
Mass PM emission rates for baseline vehicle are 25- 100 times higher than those of the rest of the tested fleet

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



Surface-rated Diameter

The EAD electrometer current is given by

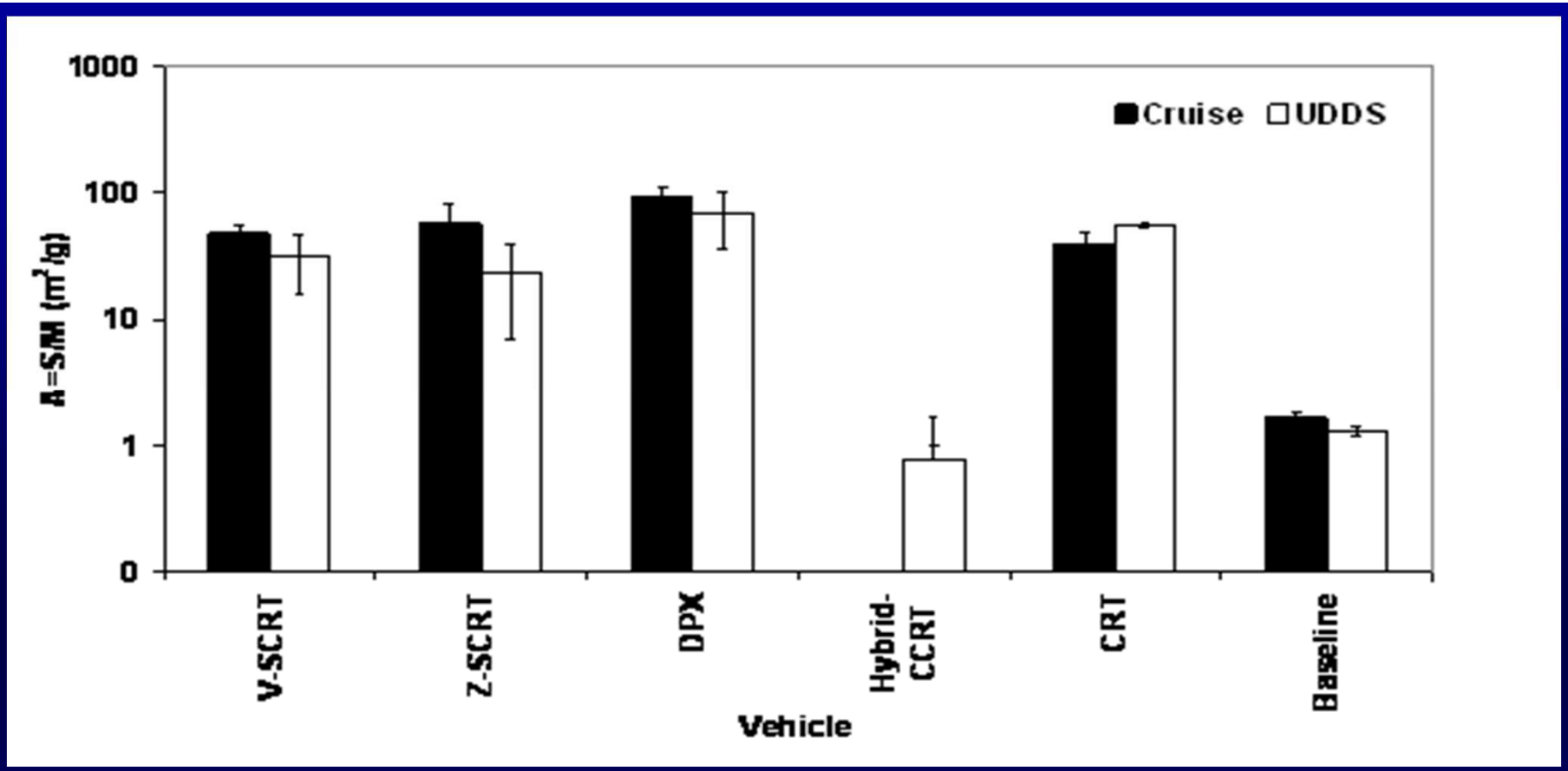
$$I = Np * Nt * Q * e$$

I= Total current measured by EAD (fA)

Np = Charge (charge/particle) attachment = **$0.0181 * Ds^{1.13}$**
(Jung and Kittelson, 2005)

e = Elementary charge, 1.6×10^{-19} coulomb
Q = Aerosol flow rate through EAD, 1.5 lpm
Nt = Total exhaust particle number, 10-1000nm from DMS; 10-523nm for EEPS.
Note: Particle number in the size range of 523-1000nm is insignificant.

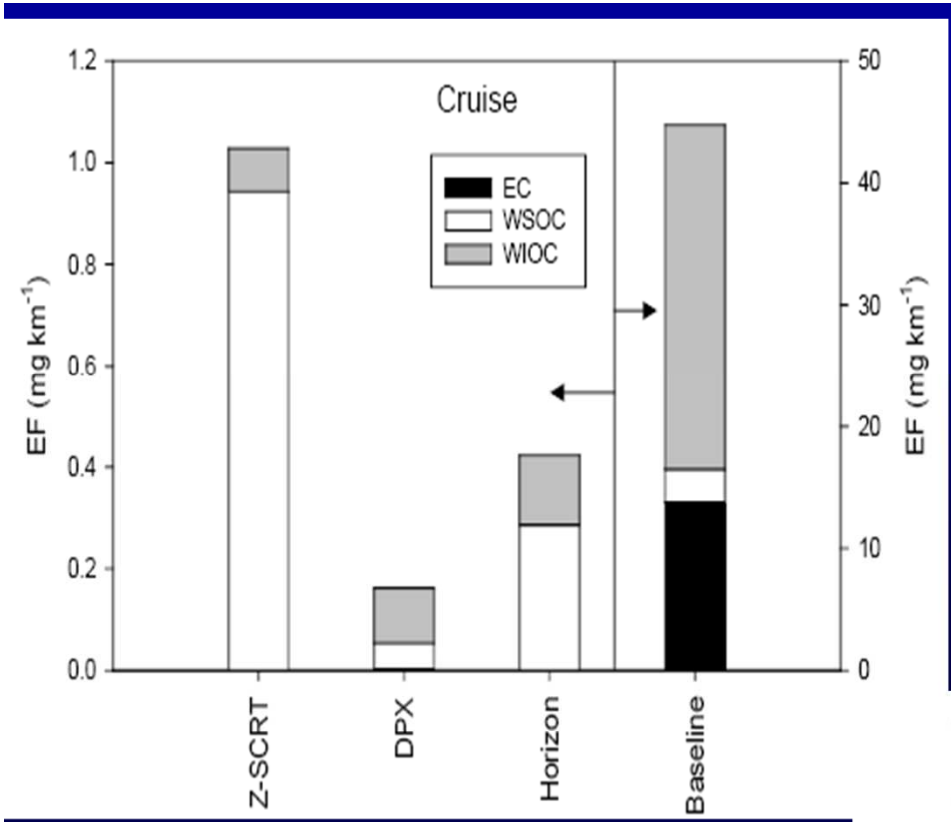
$$D_s = \left(\frac{I}{0.0181 N_t e Q}\right)^{1/1.13}$$



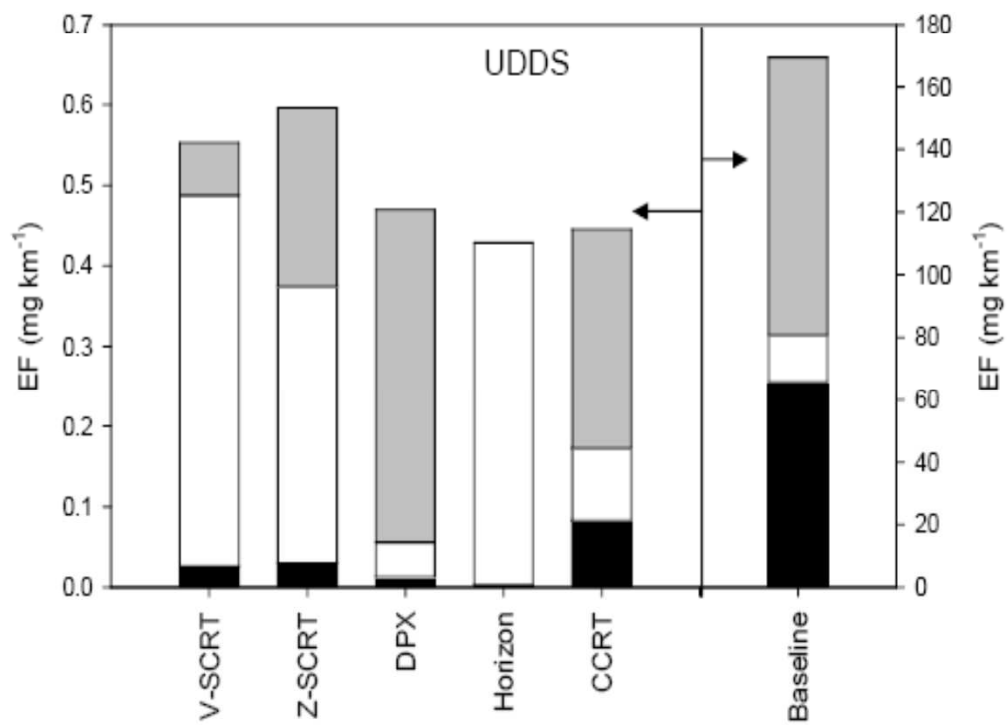
Mass Specific Surface Area : S/M (indicator of PM agglomeration)

A = Mass specific surface area ($m^2\ g^{-1}$)
S= Surface concentration, in $m^2\ km^{-1}$
(EAD current was converted to particle surface area using the conversion factor of 65 $\mu m^2/pA$ (R^2= 0.9, Wilson et al., (2007).

M = Total particle mass between 10nm-2.5µm Nano MOUDI stages, in mg km^{-1}.

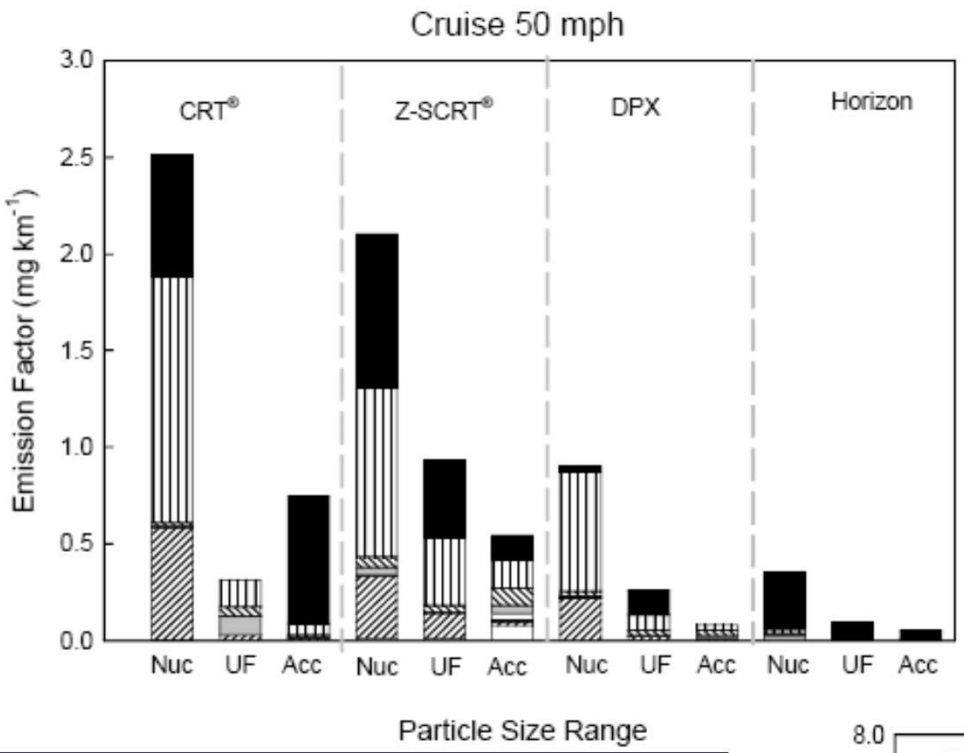


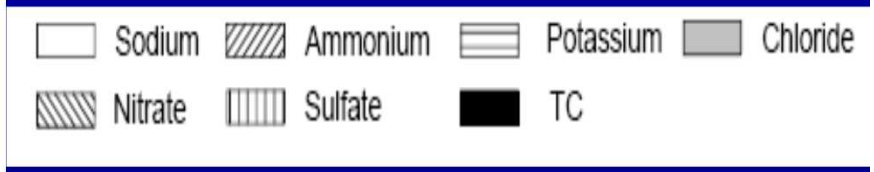
- **High EC content of baseline vehicle**
- **Noticeable increases in the mass fraction of water soluble OC in newer vehicles**



Higher EC and OC emission in UDDS than cruise cycle

Biswas et al Atmos Environ, 2009



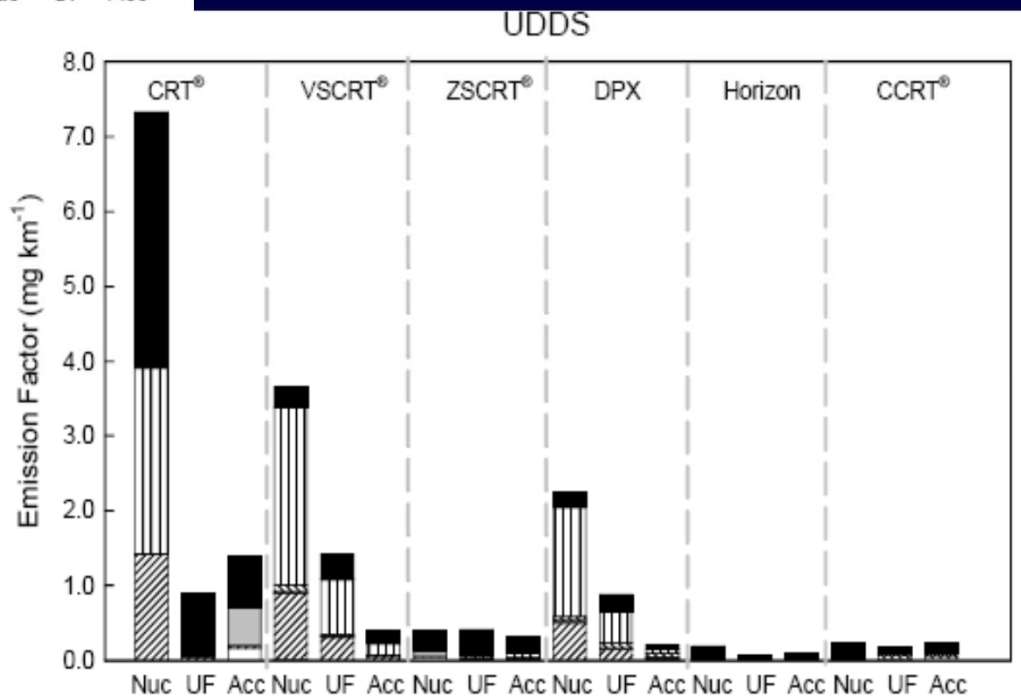


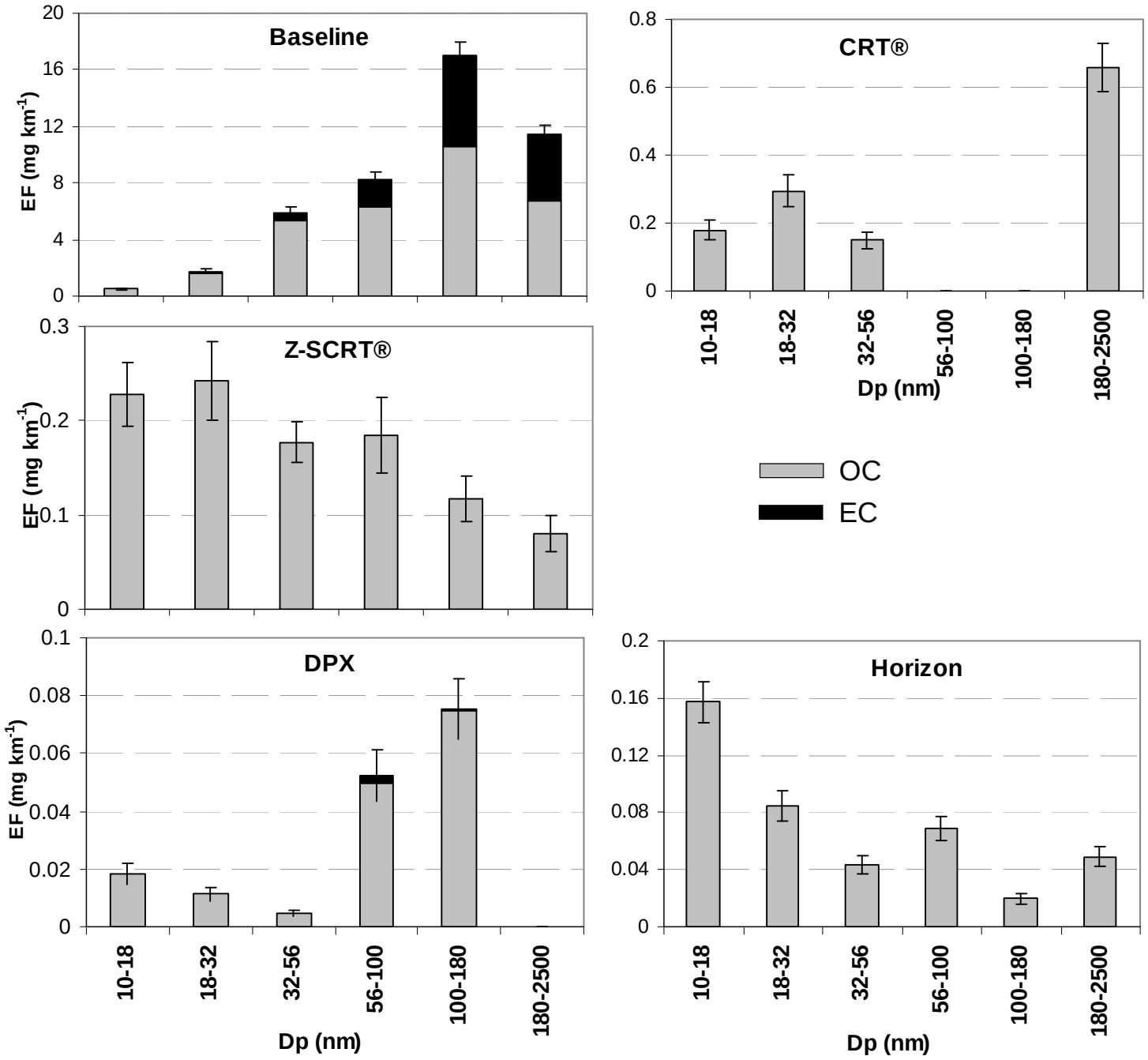
Nuc: 0.01 – 0.056 μm

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**

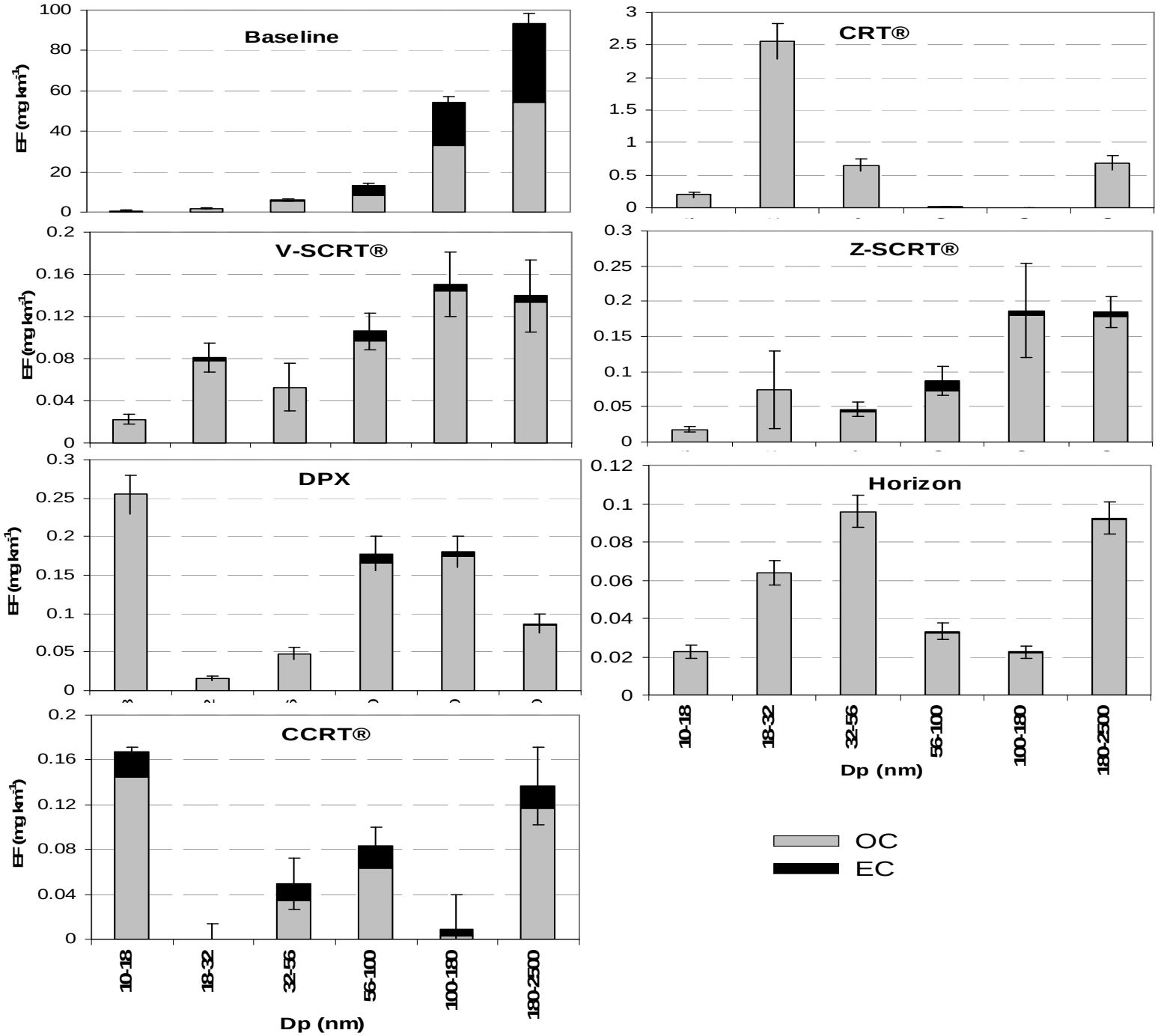




EC/OC Size Distribution

Cruise

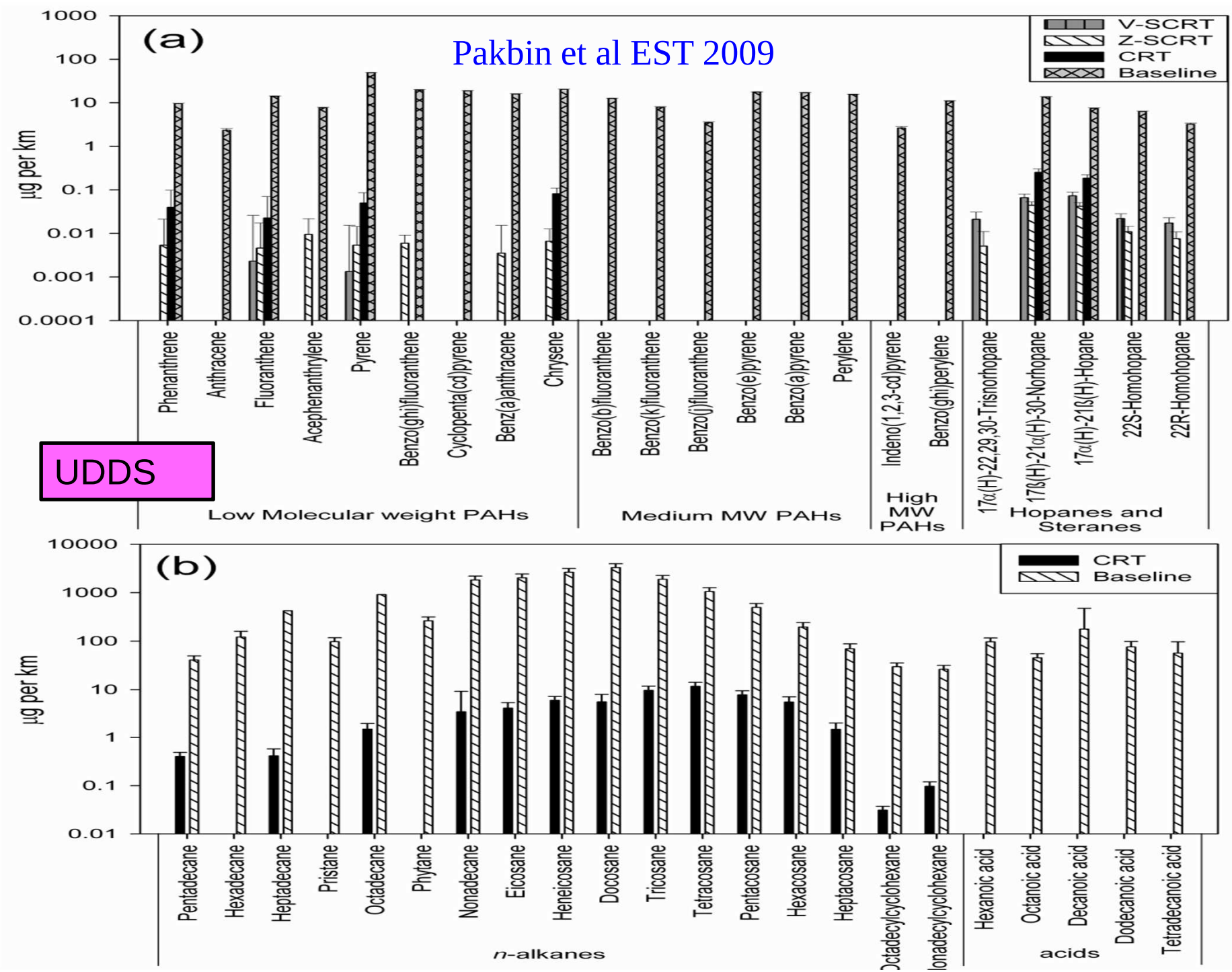
Biswas et al Atmos Environ, 2009



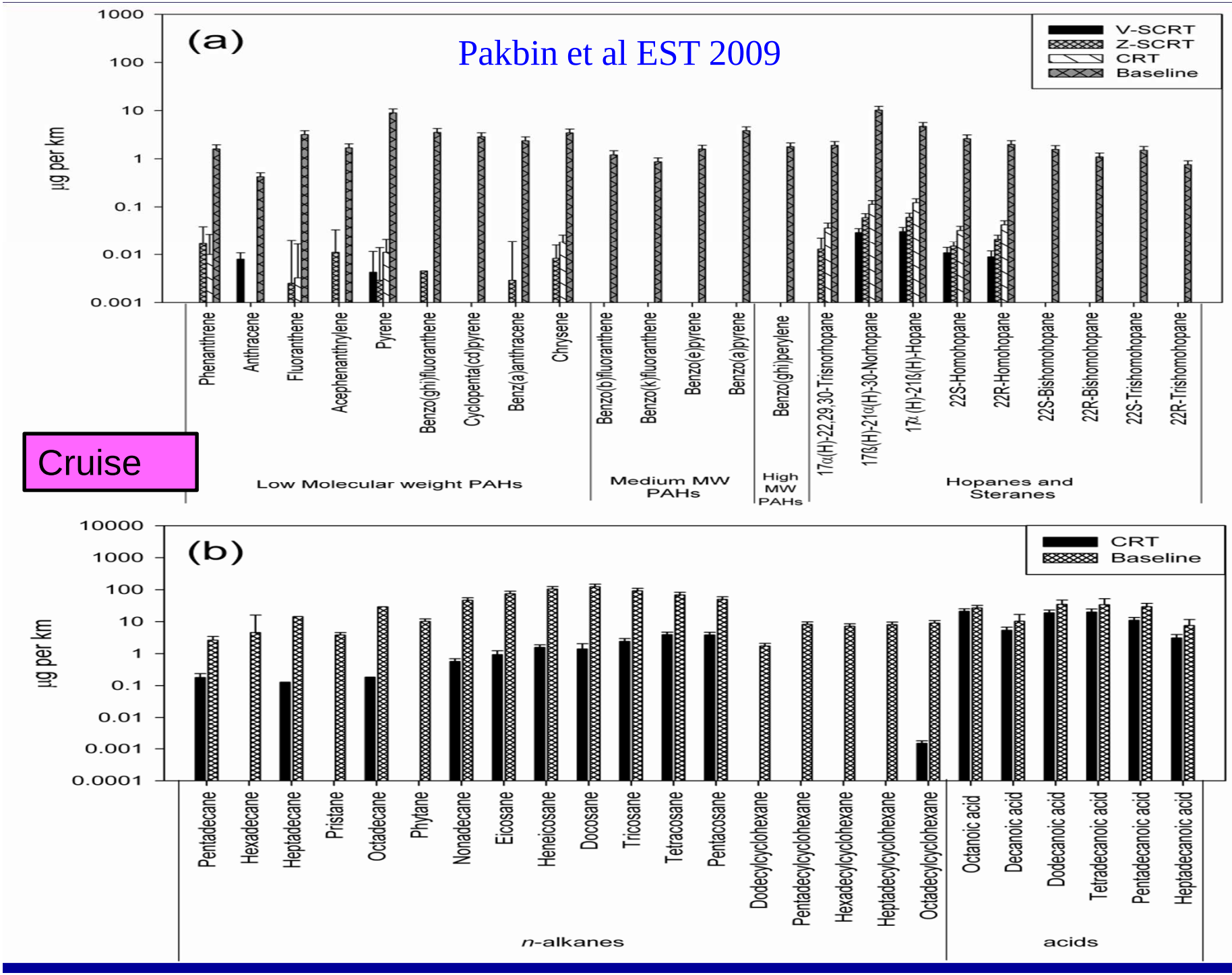
EC/OC Size Distribution

UDDS

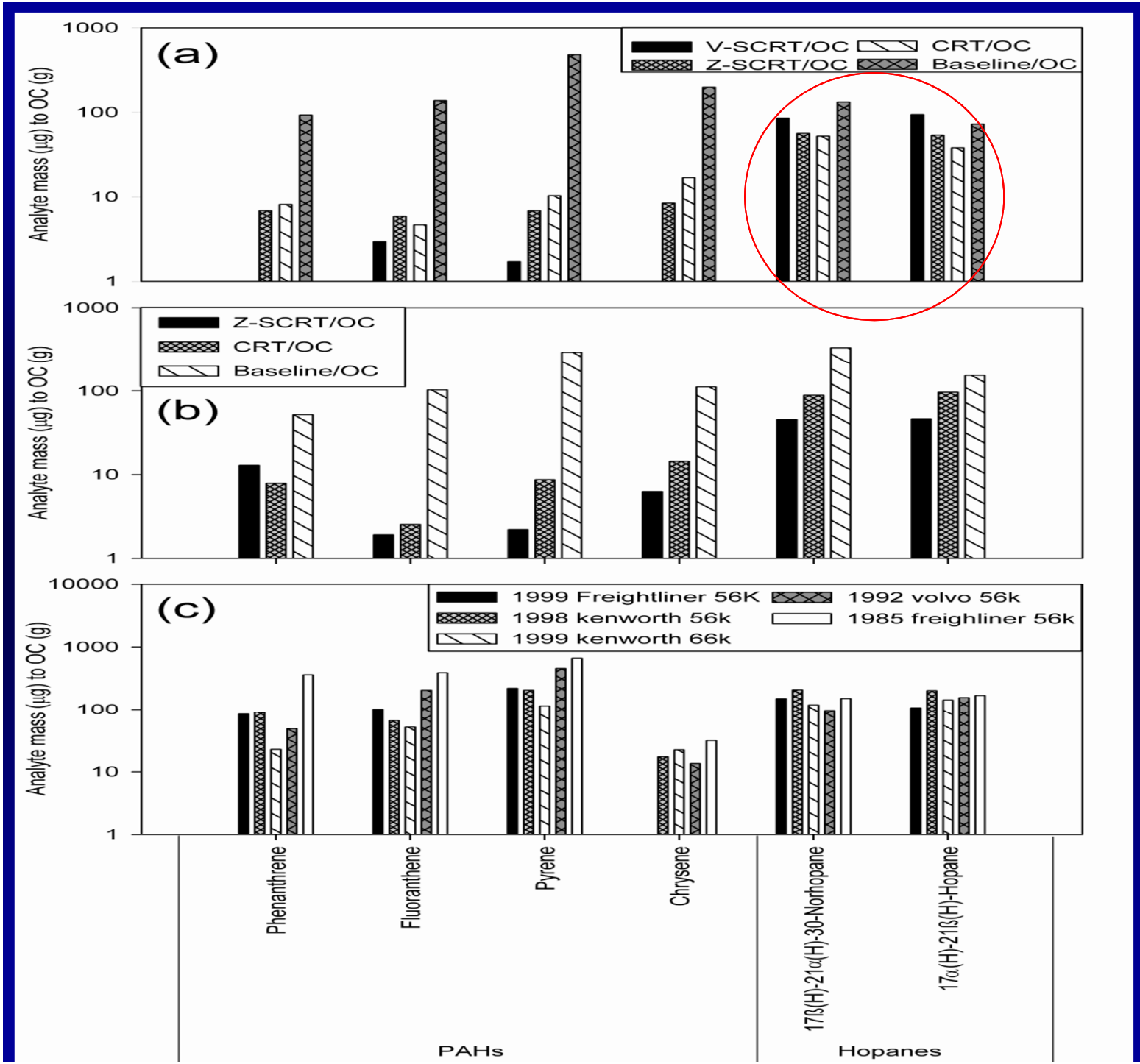
Biswas et al Atmos Environ, 2009


Pakbin et al EST 2009
(a)
V-SCRT
Z-SCRT
CRT
Baseline
µg per km
1000
100
10
1
0.1
0.01
0.001
0.0001
Phenanthrene
Anthracene
Fluoranthene
Acephenanthrylene
Pyrene
Benzo(ghi)fluoranthene
Cyclopenta(cd)pyrene
Benz(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(j)fluoranthene
Benzo(e)pyrene
Benzo(a)pyrene
Perylene
Indeno(1,2,3-cd)pyrene
Benzo(ghi)perylene
17α(H)-22,29,30-Trisnorhopane
17ß(H)-21α(H)-30-Norhopane
17α(H)-21ß(H)-Hopane
22S-Homohopane
22R-Homohopane
UDDS
Low Molecular weight PAHs
Medium MW PAHs
High MW PAHs
Hopanes and Steranes
(b)
CRT
Baseline
µg per km
10000
1000
100
10
1
0.1
0.01
Pentadecane
Hexadecane
Heptadecane
Pristane
Octadecane
Phytane
Nonadecane
Eicosane
Heneicosane
Docosane
Tricosane
Tetracosane
Pentacosane
Hexacosane
Heptacosane
Octadecylcyclohexane
Nonadecylcyclohexane
Hexanoic acid
Octanoic acid
Decanoic acid
Dodecanoic acid
Tetradecanoic acid
n-alkanes
acids

Pakbin et al EST 2009

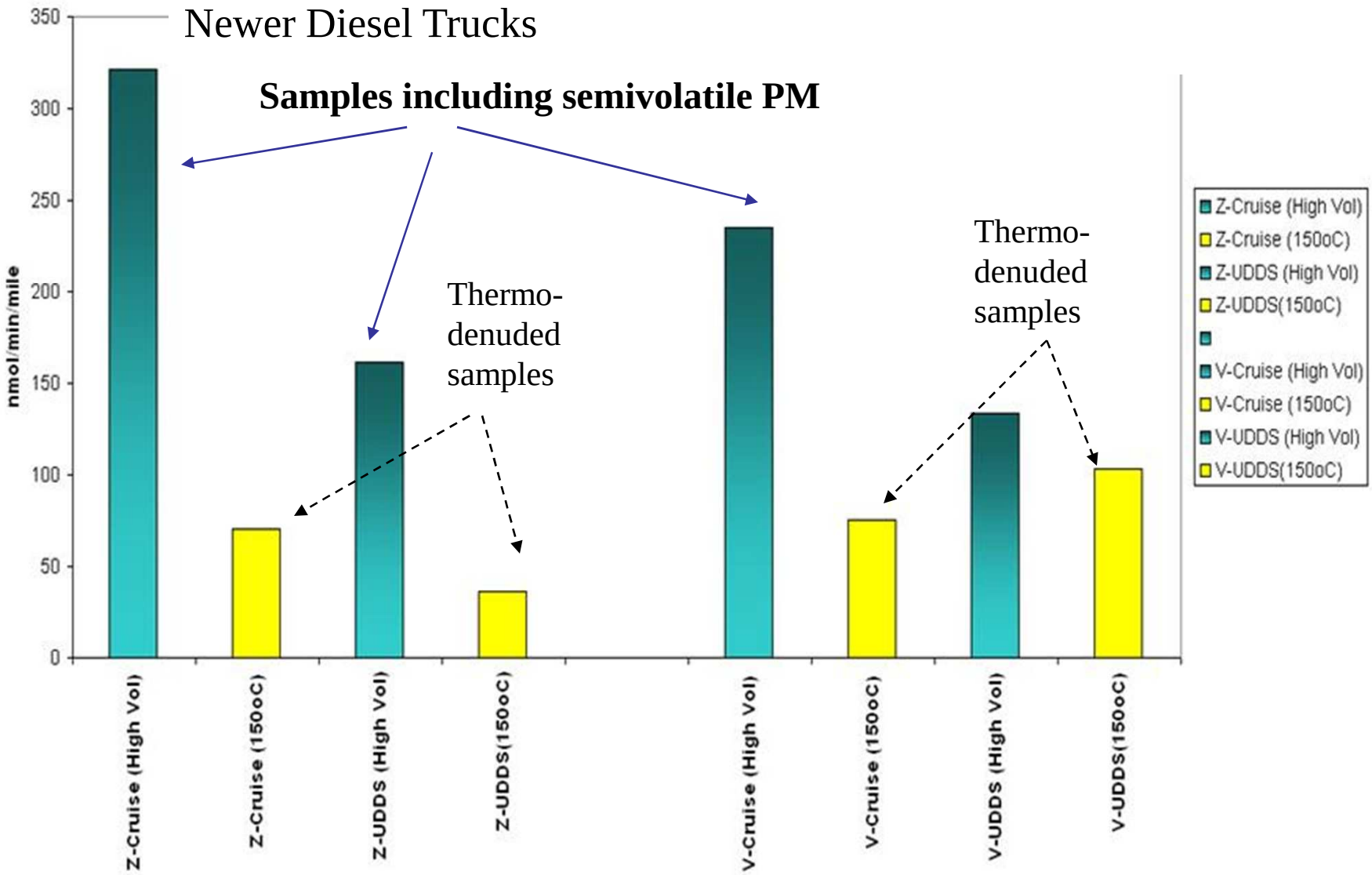


Cruise

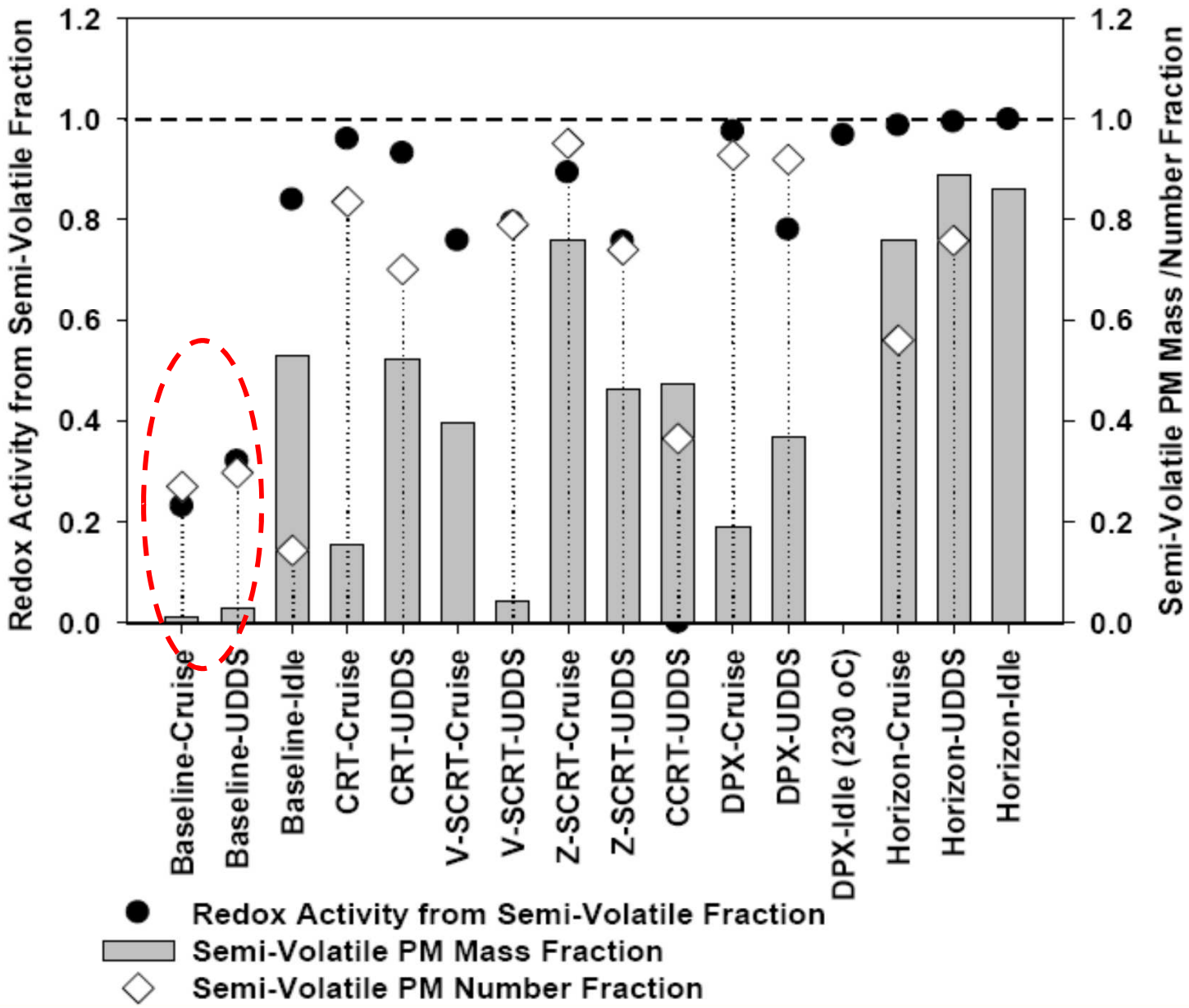


PAH/OC and hopanes/steranes to OC ratios for various vehicles in:
(a) cruise
(b) UDDS
and
(c)comparison with other dyno studies

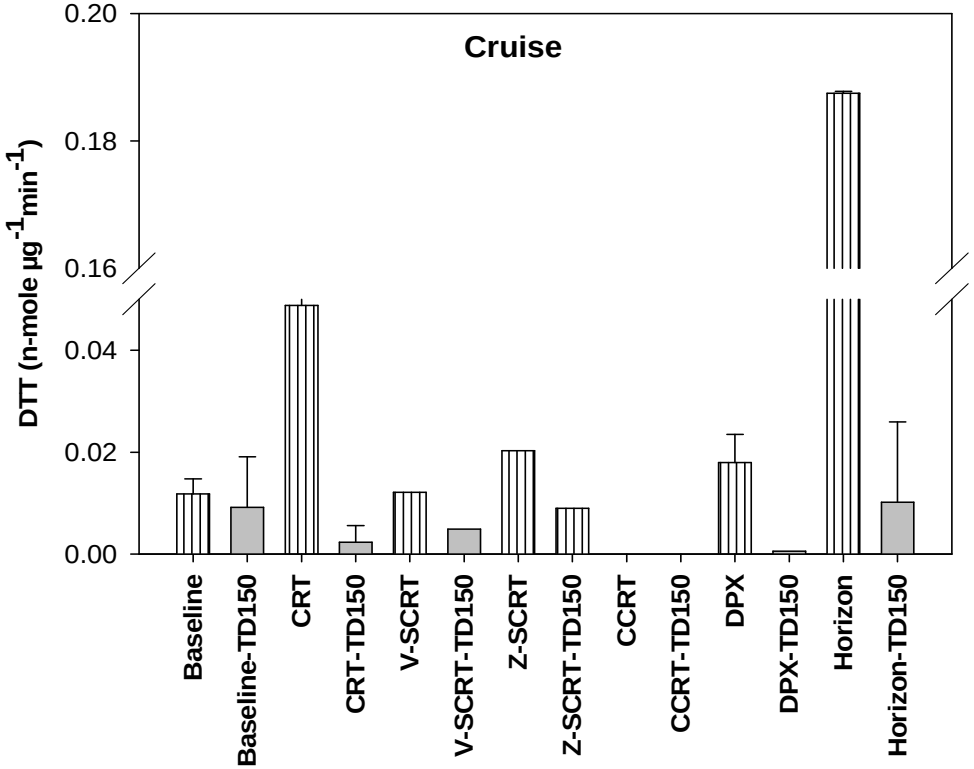
Redox Activity (DTT assay) of Semivolatile and Total PM from Newer Diesel Trucks



DTT rate of consumption per PM mass (nmoles/μg PM/min) is **<u>much higher when the semi-volatile fraction is included (</u>**Biswas et al, ES&T, 2009)

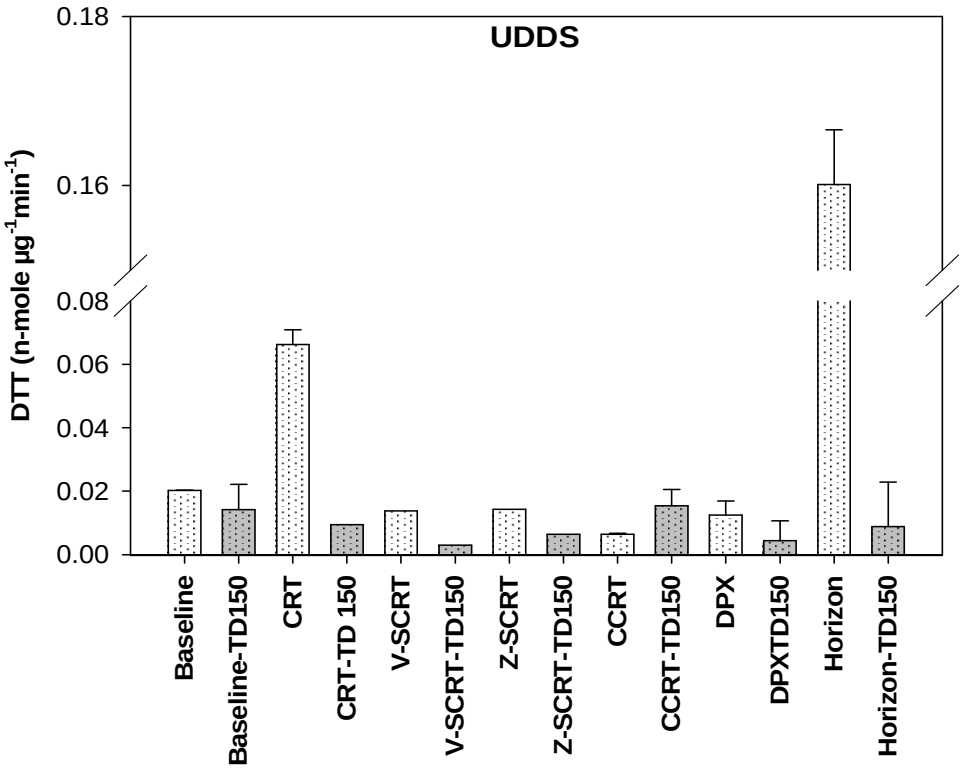


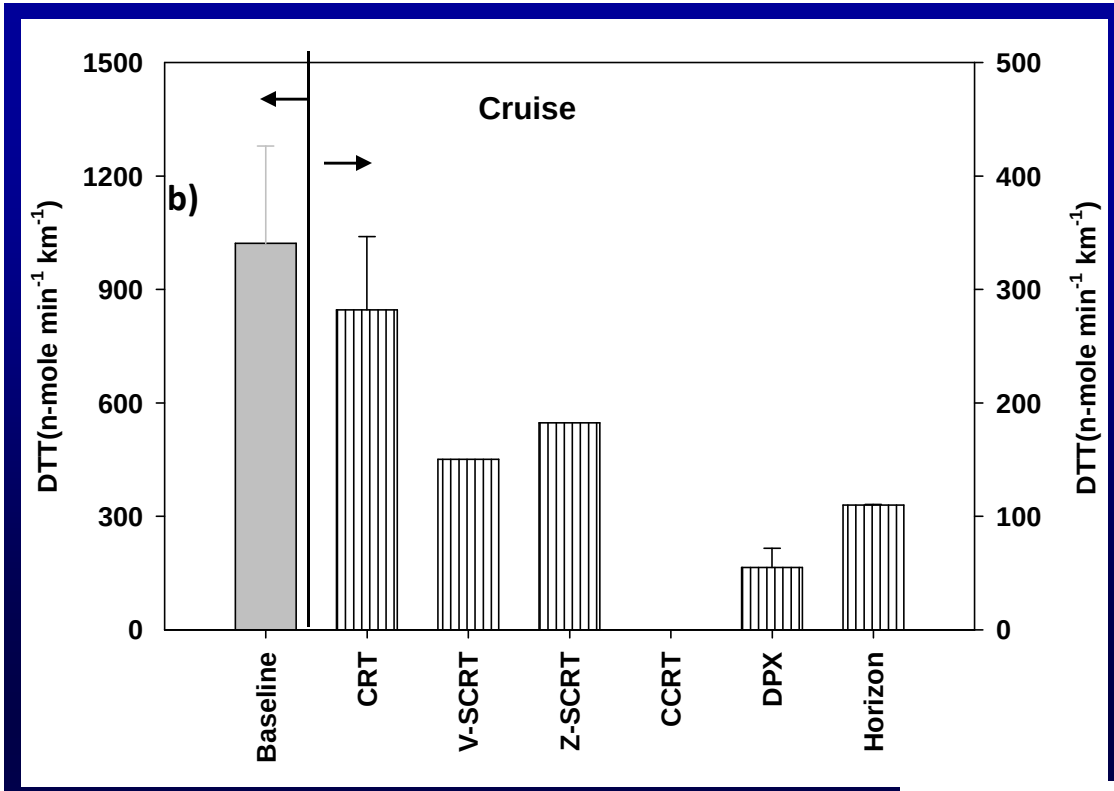
Semi-volatile PM faction accounts for over 80- 90% of the per PM mass toxicity (Biswas et al, ES&T, 2009)



Per PM mass DTT for Cruise and UDDS cycles

Biswas et al ES&T 2009

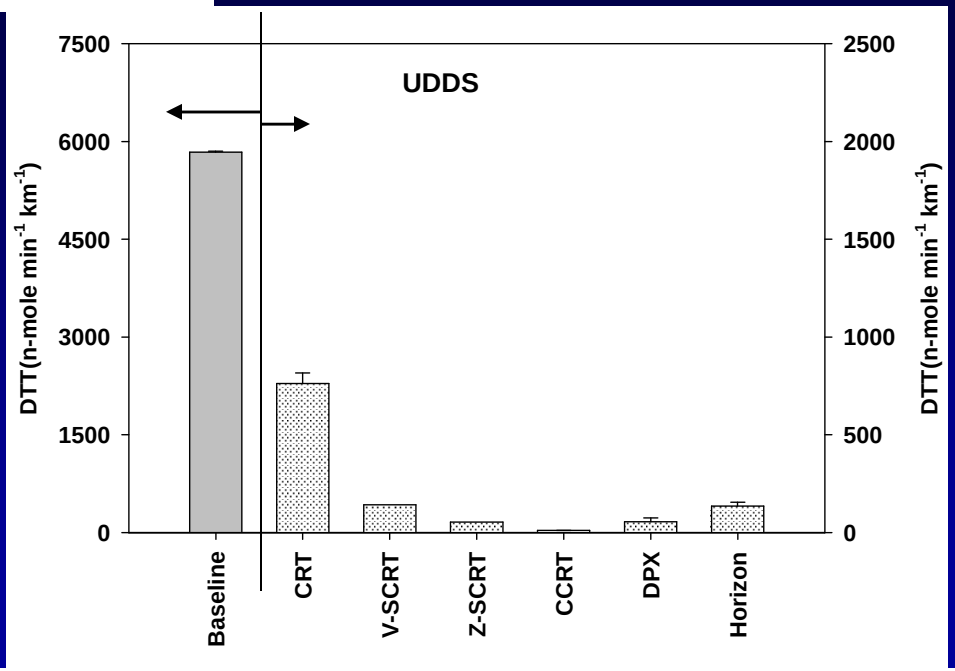


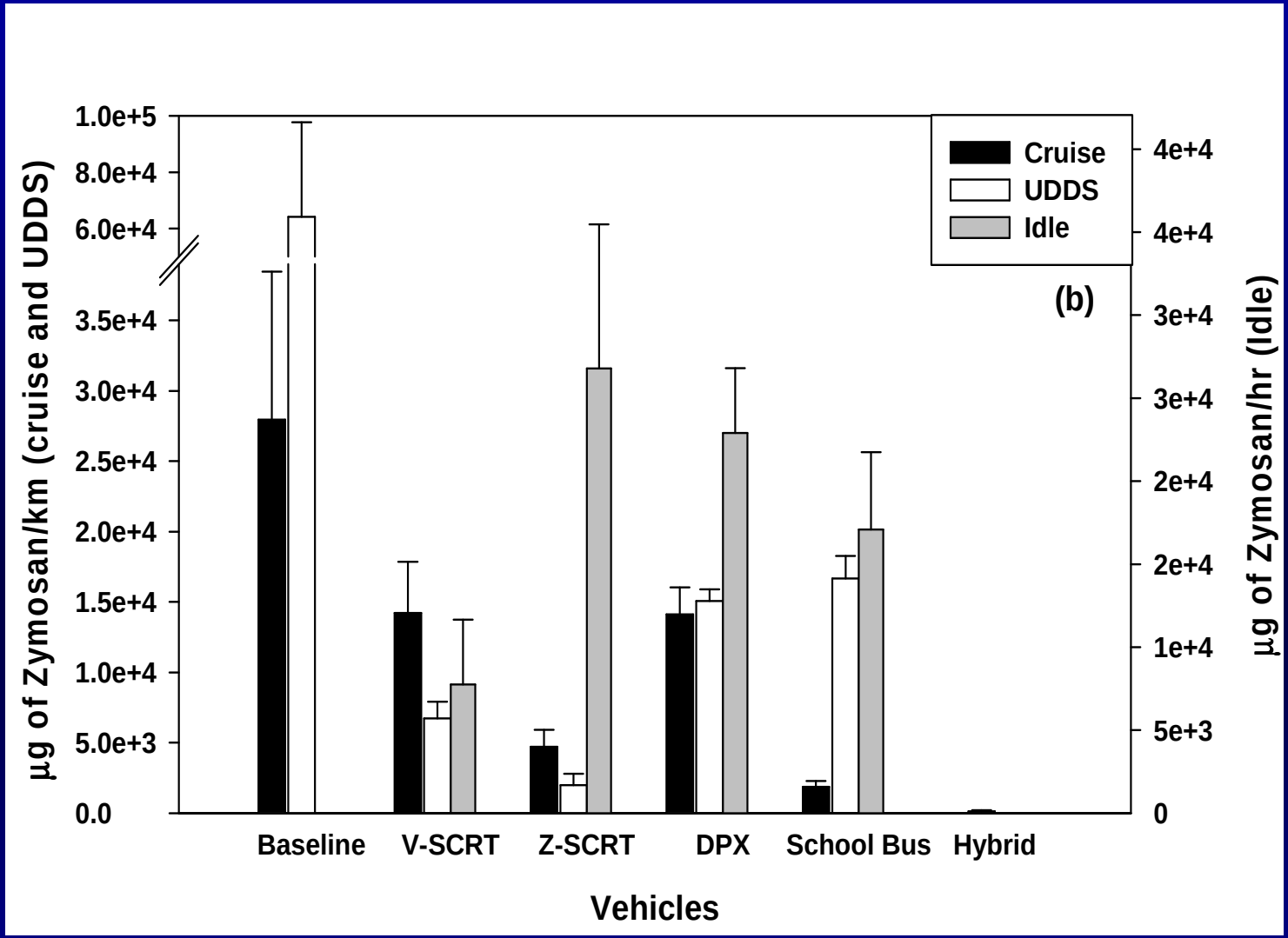


Per km driven DTT for Cruise and UDDS cycles

Biswas et al ES&T 2009

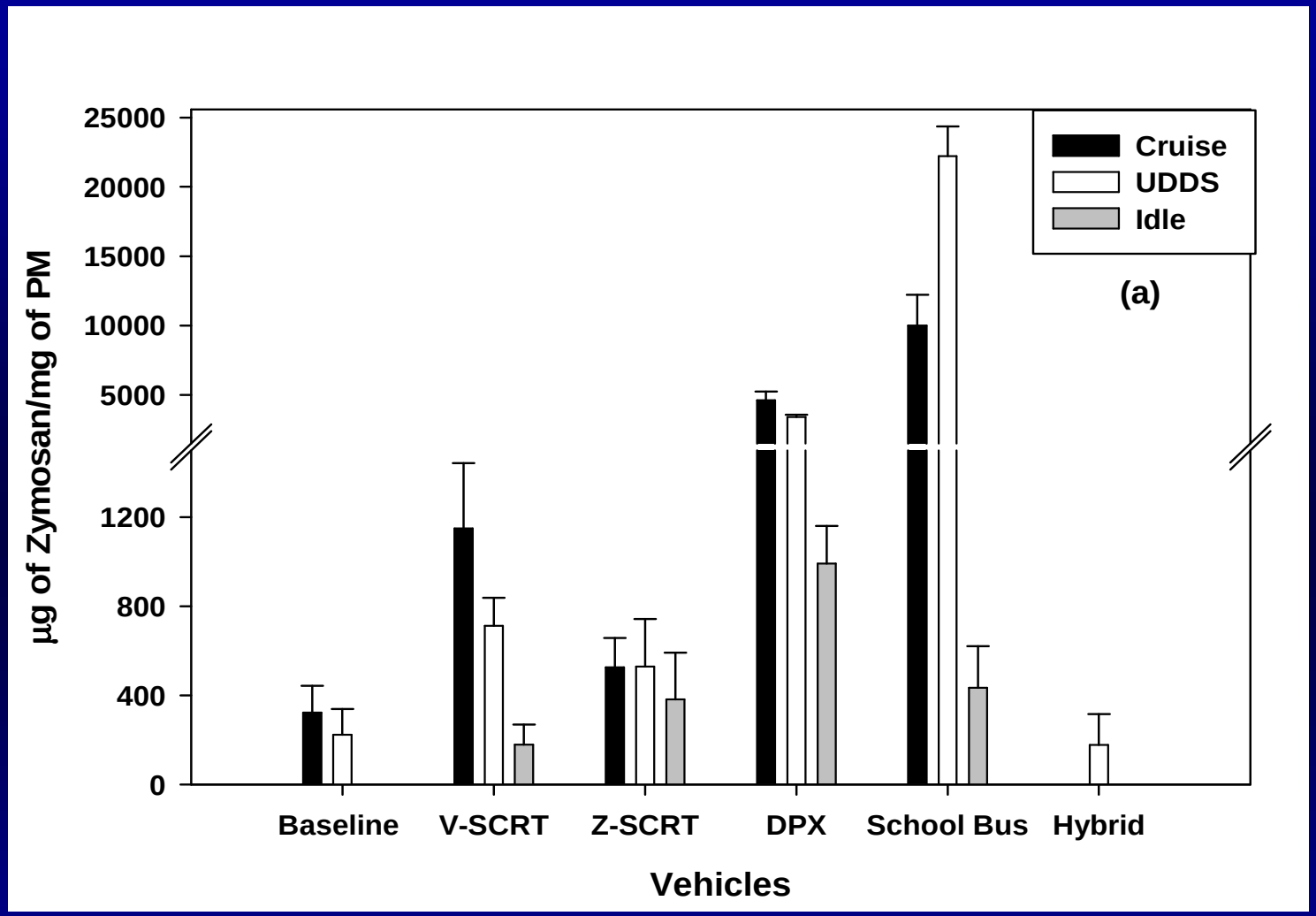
Substantial reduction on overall per km redox activity but non-linearly related to PM mass reductions





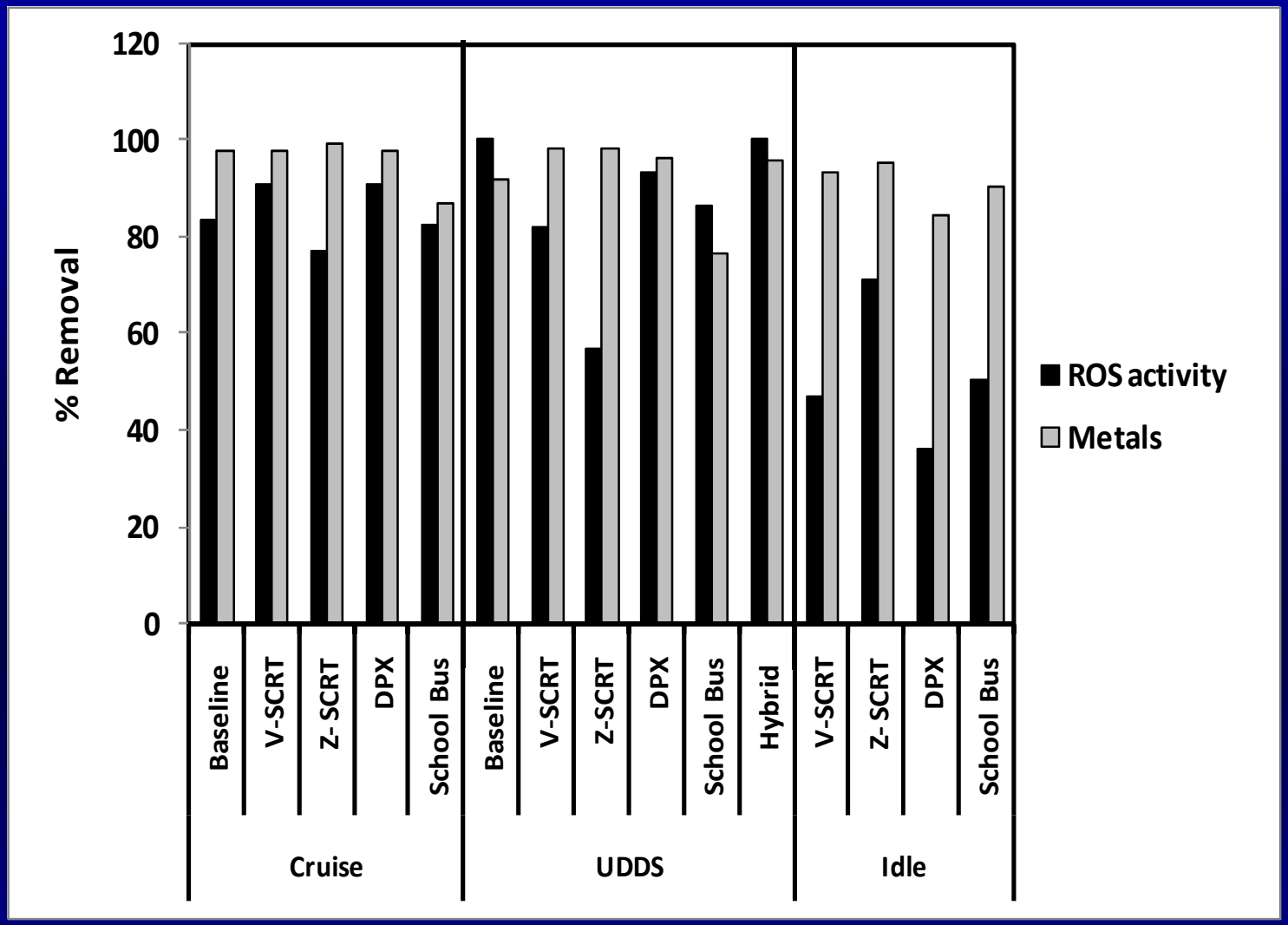
Per km ROS activity (per hr for idle)

Verma et al , Atmos Environ, 2010



Per PM mass ROS activity

Verma et al , Atmos Environ, 2010

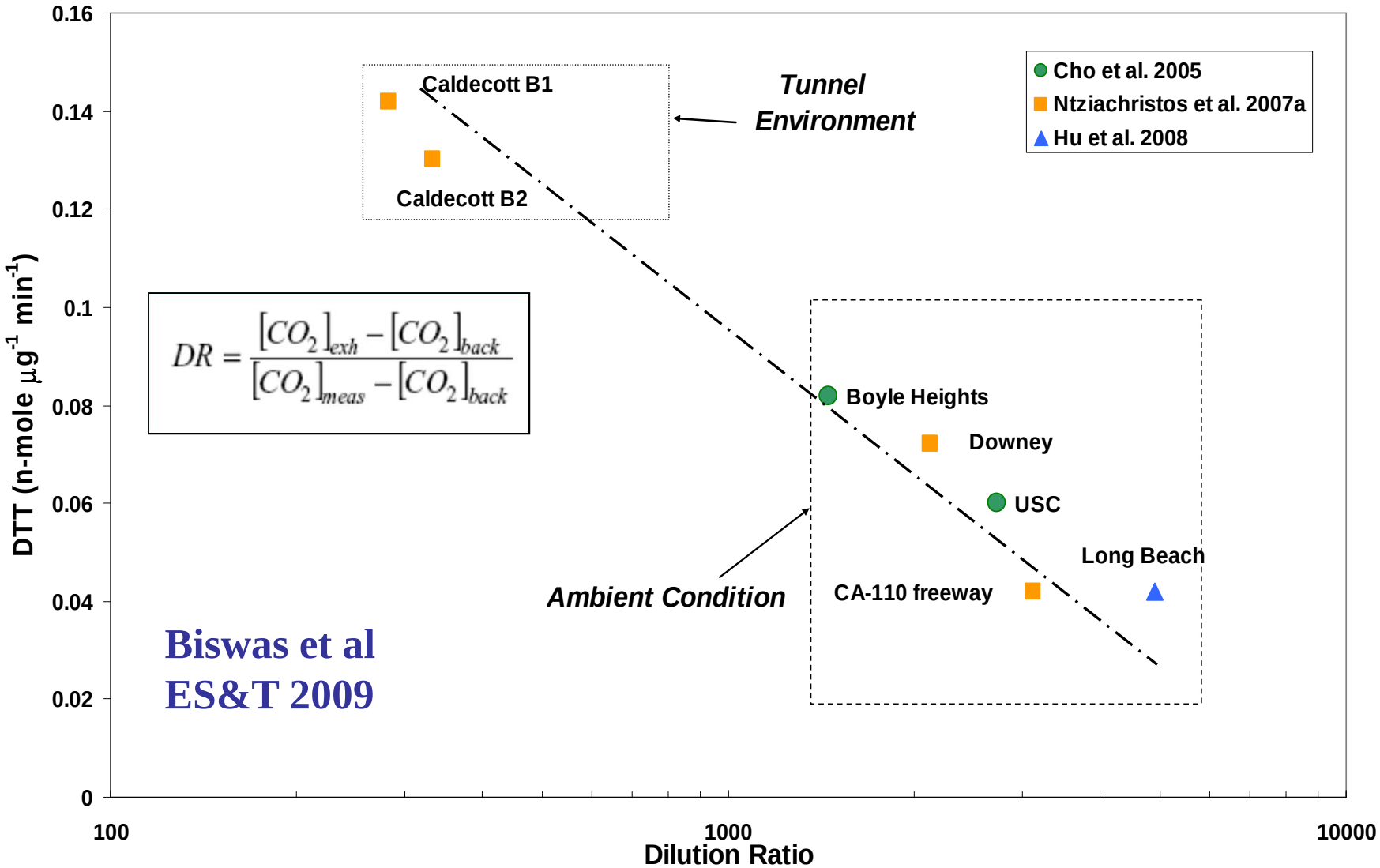


Percent removal of ROS activity in relation to that of aggregate water soluble metals after Chelex treatment of the exhaust PM samples from test vehicle-configurations under different driving cycles.

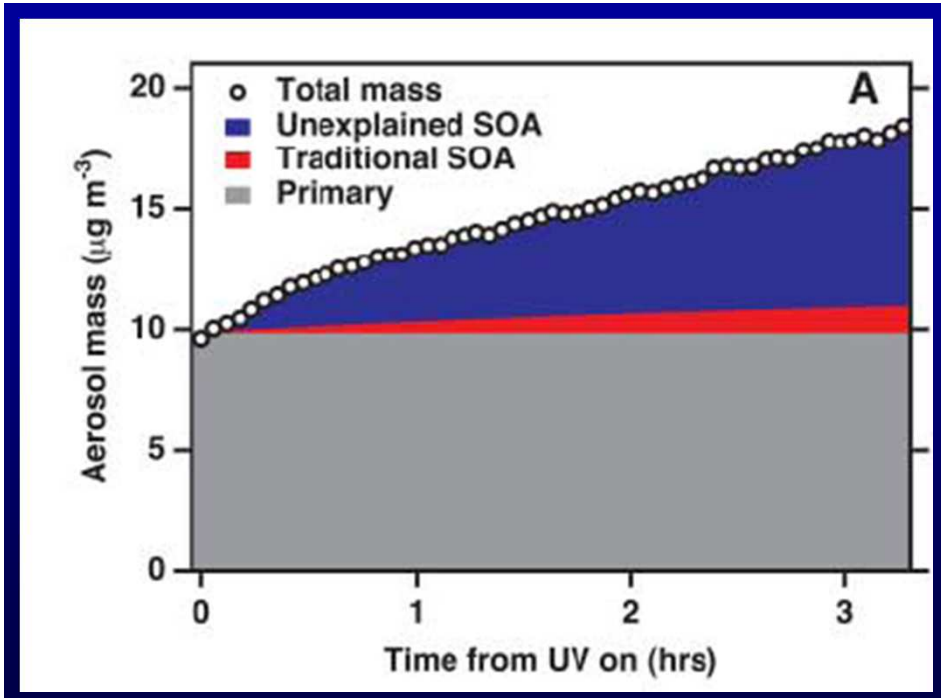
Species	Correlation with DTT	
	R	*P*
EC	-0.35	0.37
OC	0.76	0.02
NO_3^-	-0.09	0.77
SO_4^{2-}	-0.32	0.27
NH_4^-	-0.25	0.26
K^+	0.43	0.20
Cl^-	0.34	0.15
WSOC	0.94	<0.01
Alkanes (Alk.)	0.03	0.54
PAHs	-0.26	0.75
Organic Acids (OA)	0.91	<0.01

Elements	Correlation with ROS	
	R	*P*
Mg	-0.19	0.36
Al	0.38	0.07
P	0.27	0.21
S	0.13	0.53
Ca	-0.01	0.95
V	-0.02	0.92
Cr	0.67	0.00
Mn	0.62	0.01
Fe	0.93	0.00
Co	0.61	0.04
Ni	0.22	0.31
Cu	0.47	0.02
Zn	0.46	0.02
As	0.03	0.89
Cd	0.50	0.01
Ba	0.31	0.15
Pb	0.47	0.02

Redox Activity per PM Mass Decreases with Atmospheric Dilution

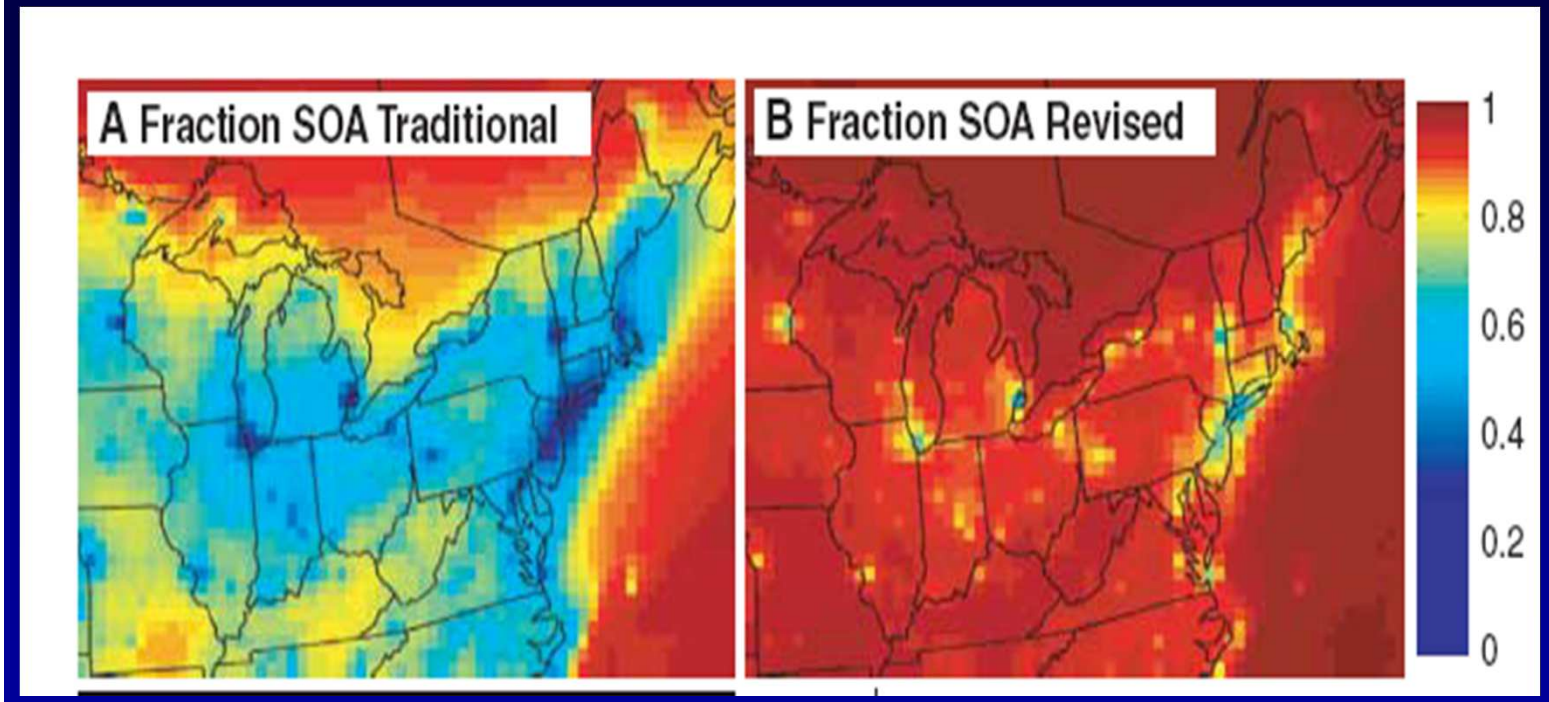


- Dilution ratio affects PM content of semi-volatile species
- Redox activity (DTT consumption) decreases with higher dilution
- Semi-volatile fraction are more redox active



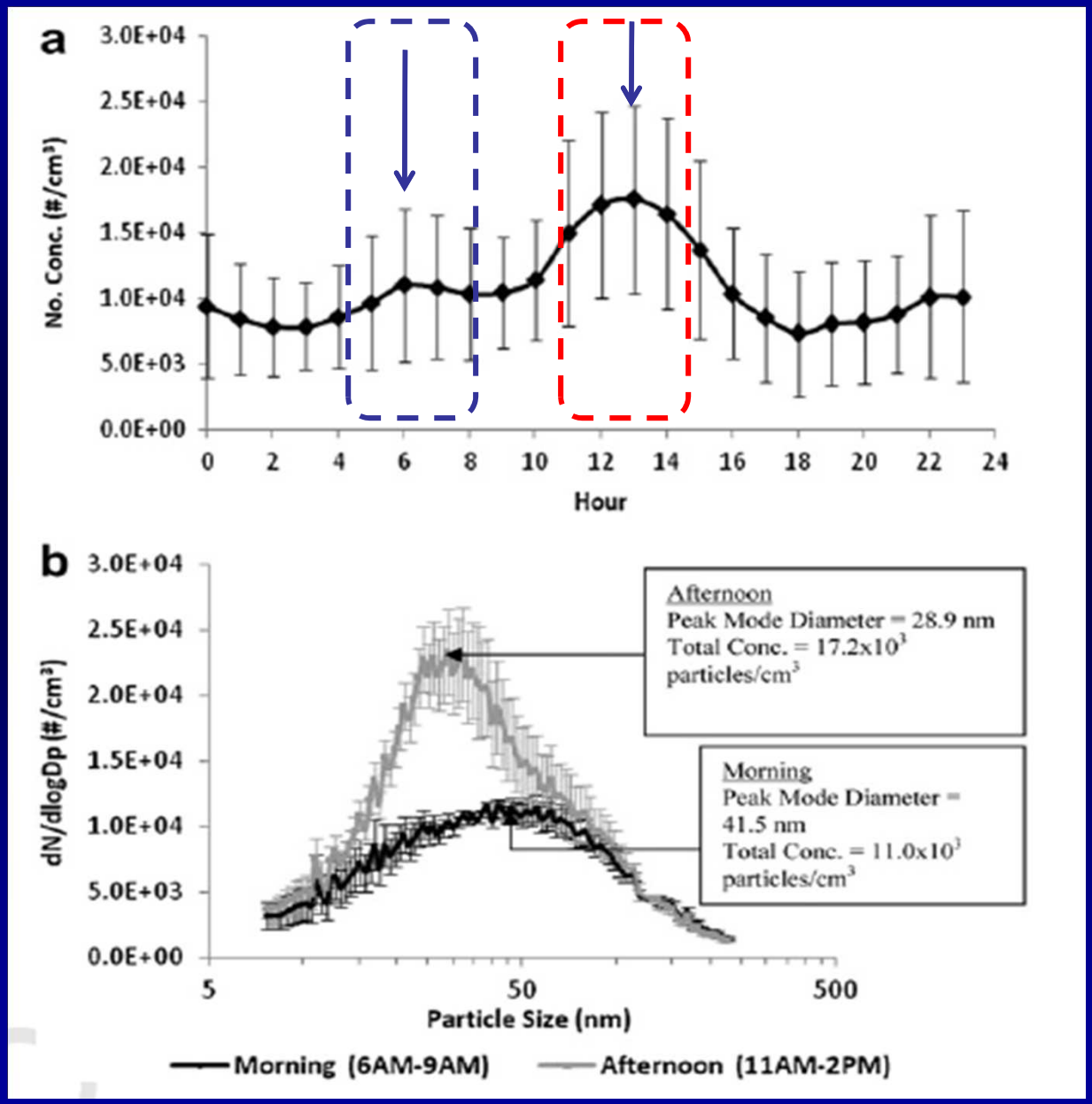
Robinson et al. [Science 2007]

- Oxidation of primary diesel exhaust
- Secondary Organic Aerosol (SOA) from Traditional gas phase precursors accounts only for 15-20% of total measured SOA
- The rest is a result of oxidation of semivolatile organic species (SVOC)



Revised model taking into account SVOC oxidation increases overall SOA/POA ratio in urban areas

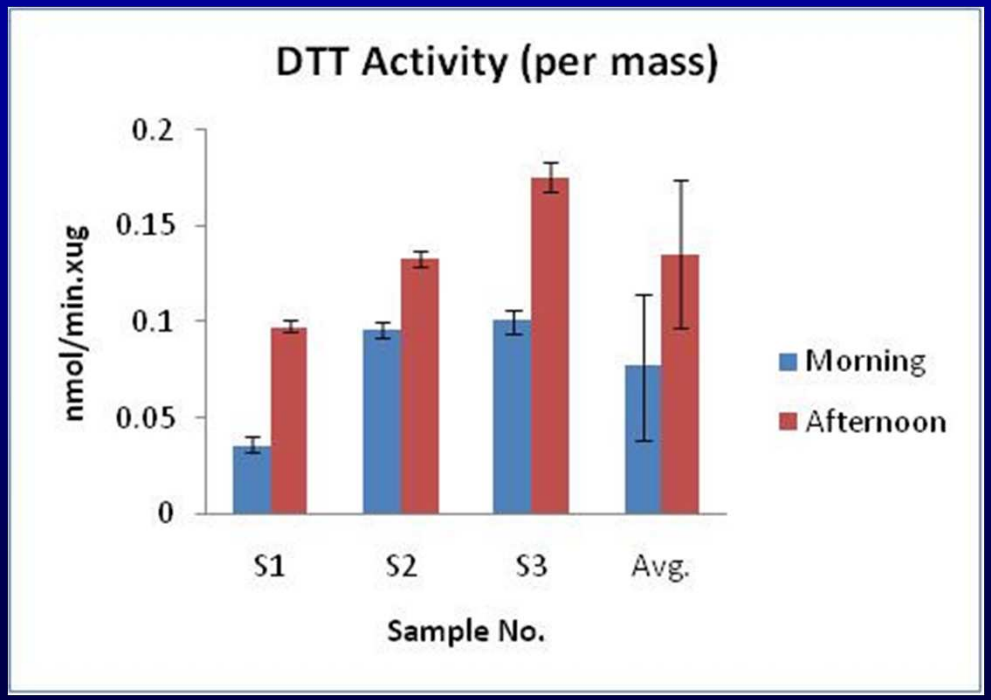
The Role of Atmospheric Aging and Photochemical Processing

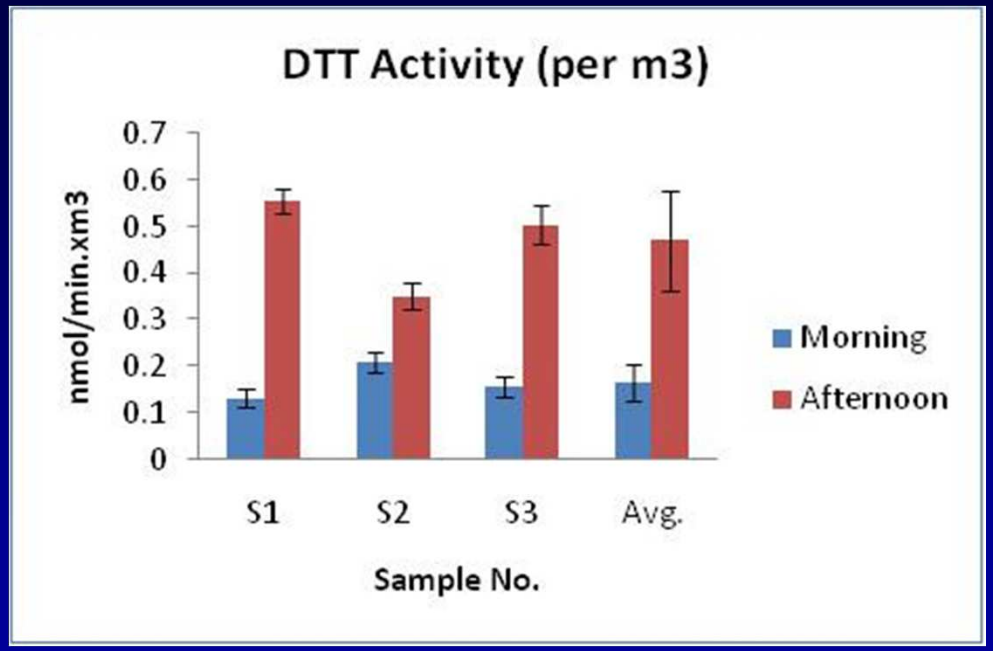


Samples in summer period during photochemical periods to distinguish effects from those of PM mostly emitted from mobile traffic sources

Collections from 6-9 am (traffic) and noon- 4 pm (photochemistry)

Verma et al, Atmos. Environ, 2009





In vitro studies :

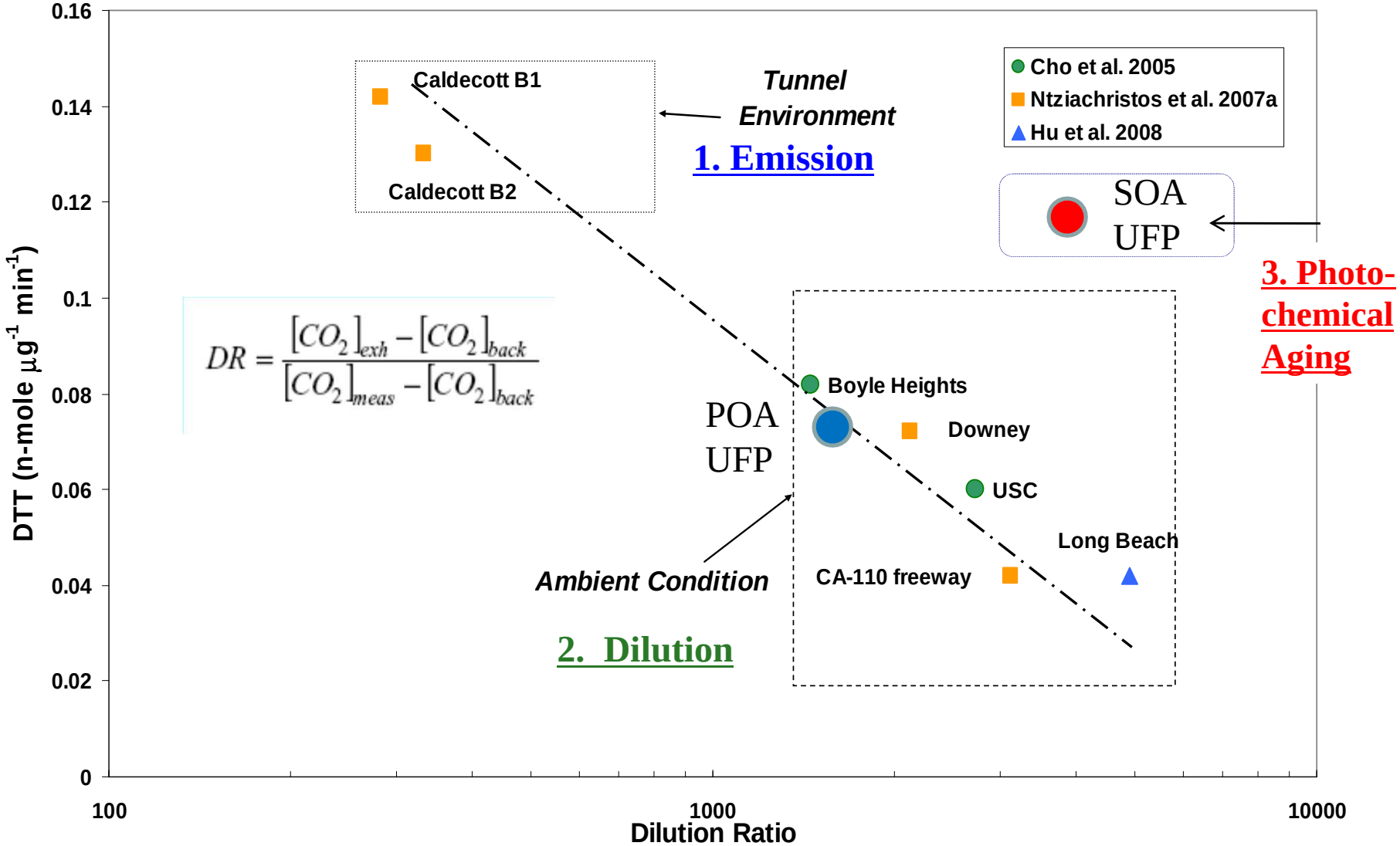
Much higher DTT activity (a measure or redox activity of UFP) in the afternoon than AM (traffic) period expressed both in terms of :

per PM mass

and per m3 of air volume

Verma et al,
Atmos. Environ, 2010

Photochemical Aging Modifies Relationship Between Redox Activity and atmospheric dilution (*Verma et al, Atmos Environ 2010*)



DTT vs Dilution for Primary Organic Aerosols with agreement with other data

DTT vs Dilution for Secondary Organic Aerosols much higher, comparable to tunnel data

Major Conclusions

- The newer diesel engines with emission control devices are very efficient in reducing the mass emission of particulate matter

- However, enhanced formation of nucleation mode particles is observed in the exhausts of some retrofitted configurations. The vast majority of these nucleation mode particles are semi-volatile in nature.

- The total emissions (per distance of vehicle traveled) of the major chemical species (except of sulfate) are substantially reduced in the retrofitted vehicles compared to the baseline vehicle .

- Although the retrofitted vehicles emit less water soluble organic carbon (WSOC) per mile of vehicle driven, the per PM mass water soluble fraction of the organic carbon (WSOC/OC) is increased for most configurations

- With the introduction of retrofit control devices, the individual ratios of speciated organic compounds to OC are reduced significantly for PAHs

- The reduction was more modest for hopanes and steranes, implying that fuel and lubricating oil have substantially different contributions to the OC emitted by vehicles operating with control devices compared to the baseline vehicle.

- We hypothesize that PAHs can form in combustion processes and/or originate from diesel fuel, whereas hopanes and steranes come from lubricating oils.

- Despite an increase in the intrinsic oxidative activity (both DTT and ROS) per mass basis of exhaust PM with the use of control technologies for most configurations, the overall activity expressed per km or per hr- (arguably a more relevant metric for public policy) was substantially reduced for retrofitted configurations compared to the baseline vehicle.

- The semi-volatile fraction of the exhaust particles was observed to be highly oxidative in nature as demonstrated by a significant reduction in DTT activity (by 80-100%) observed for thermally-denuded PM.

- However, non-volatile species – particularly transition metals, are also responsible in cellular oxidative stress, as indicated by a substantial removal (≥70 %) of the ROS activity after Chelex treatment of the PM samples.

- The correlation analysis showed that DTT activity is strongly associated (R=0.94) with the water soluble organic carbon (WSOC), while Fe is responsible for most of the variability (R=0.93) in ROS levels.

- An important caveat of the toxicological findings of this study is that they are all based on molecular or cellular assays that examine the toxicity of the PM suspension collected from a given vehicle and driving configuration based on bulk PM mass.

- By their nature and design, these investigations did not take into account important parameters determining the toxicity and overall health effects attributable to the inhalation of an aerosol , such as particle size.

- The substantial reduction in the overall particle size distribution of newer vehicles creates an aerosol with a much higher lung deposition fraction than the baseline vehicle, and with considerably different toxicokinetics inside the human body once inhaled.

- Such important investigations can only be addressed by in vivo inhalation exposure studies to these aerosols, whether using animal models or human volunteers (or both), and are greatly needed in order to provide a more complete perspective to the results of this study

List of Publications from this Study

•Biswas, S., Hu, S.H., Verma, V., Herner, J.D., Robertson, W.H., Ayala, A., Sioutas, C. Physical properties of particulate matter (PM) from late model heavy-duty diesel vehicles operating with advanced PM and NOx emission control technologies. Atmospheric Environment 42 (22), 5622-5634,2008

•Biswas, S., Verma, V., Schauer, J.J., Sioutas, C.. Chemical speciation of PM emissions from heavy-duty diesel vehicles equipped with diesel particulate filter (DPF) and selective catalytic reduction (SCR) retrofits. Atmospheric Environment 43 (11), 1917-1925, 2009.

•Pakbin, P., Ning, Z., Schauer J. J., Sioutas, C. Characterization of particle bound organic carbon from diesel vehicles equipped with advanced emission control technologies, Environmental Science and Technology 43 (13), 4679–4686, 2009

•Biswas, S., Verma, V., Schauer, J.J., Cassee, F.R., Cho, A.K., Sioutas, C. Oxidative potential of semi-volatile and non volatile particulate matter (PM) from heavy-duty vehicles retrofitted with emission control technologies. Environmental Science & Technology 43 (10), 3905-3912, 2009.

•Verma, V., Shafer, M.M., Schauer, J.J. and Sioutas, C., Contribution of transition metals in the reactive oxygen species activity of PM emissions from retrofitted heavy-duty vehicles. Atmospheric Environment, 44 (39), 5165-5173, 2010.

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