Toxicity of Emissions from Heavy Duty Diesel Engines with and Without Retrofit Controls

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Executive Summary

1.1Background

The objective of this project was to enhance a planned ARB vehicle emissions study with a research component designed to determine the physicochemical and toxicological properties of particulate matter (PM) from heavy duty vehicles operating with and without emissions control technologies. The key objective of this comprehensive 4-year project was to determine the physicochemical and toxicological properties of the semi-volatile and non-volatile fractions of PM from heavy duty diesel vehicles operating with and without emissions control technologies.

1.2Methods

In this study, we assessed the PM-related oxidative activity from a wide variety of vehicles to represent the in-use fleet, including diesel vehicles with and without advanced PM emission control technologies. We investigated different driving cycles, since engine operation is known to affect the concentration, relative amounts and chemical composition of the nucleation and accumulation PM modes emitted. Experiments were carried out at the California Air Resources Board's (CARB) heavy-duty diesel emission testing laboratory (HDETL) in downtown Los Angeles. Ayala et al., (2002) described the dynamometer specifications in details. 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 fuel used to run the engines was CARB ultra-low sulfur diesel (ULSD) with sulfur content less than 15 ppm. Tunnel blank levels were measured and vehicles were conditioned (warmed up) every day before the start of official runs. The CVS was cleaned prior to starting the project. 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 SCRTs]. The other three test vehicles were a diesel hybrid electric bus, a school bus, and a Caltrans truck. Detailed physico-chemical and toxicological characteristics of PM were measured for each vehicle and driving cycle, including physical properties (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.

1.3Results

Substantial reduction in PM mass emissions (>90%) was accomplished for the HDDV operating with advanced emission control technologies. This reduction was not observed for particle number concentrations under cruise conditions, with the exceptions of the Hybrid-CCRT and EPF vehicles, which were efficient in controlling both - mass and number emissions. In general, significant nucleation mode particles (<50nm) were formed during cruise cycles in comparison with the UDDS cycles, which emit higher PM mass in the accumulation mode. The nucleation mode particles (<50nm) were mainly internally mixed, and evaporated considerably between 150 to 230^{o}C.

Significant reductions in the emission of major chemical constituents (TC, OC, EC, and organic compounds) were achieved by the introduction of retrofits. V-SCRT and Z-SCRT effectively reduced PAHs, hopanes and steranes, n-alkanes and acids by more than 99%, and often to levels below detection limits for both cruise and UDDS cycles. The CRT technology also showed similar reductions with SCRT for medium and high molecular weight PAHs, acids, but with slightly lower removal efficiencies for other organic compounds. Sulfate dominated the PM composition in vehicle configurations (V-SCRT-UDDS, Z-SCRT-Cruise, CRT, DPX) with considerable nucleation mode and TC was dominant for the configurations with less (ZSCRT-UDDS) or insignificant (CCRT, Horizon) nucleation.

Despite a noteable increase in the intrinsic activity (both DTT and ROS, per PM mass basis) of exhaust PM with use of most control technologies, the overall activity (expressed per km or per hr) was reduced for retrofitted configurations compared to the baseline vehicle. Significant reduction in DTT activity (by 50-100%) was observed for thermally-denuded PM from vehicles with retrofitted technologies (PM with significant semi-volatile fraction). On the other hand, Chelex treatment of undenuded PM samples removed a substantial (≥70 %) fraction of the ROS activity. Correlation analysis performed between measured activity and the chemical constituents showed that DTT activity is strongly associated (R=0.94) with the water soluble organic carbon (WSOC), while the ROS activity was mostly driven by Fe content of the PM samples.

1.4Conclusions

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 (e.g. elemental and organic carbon) are substantially reduced in the retrofitted vehicles compared to the baseline vehicle. However, sulfate emissions increase for the configurations with enhanced nucleation mode particles in their exhaust. 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 control devices, the individual ratios of speciated organic compounds to OC are reduced significantly for PAHs, while 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 PM mass basis) of exhaust PM with the use of control technologies for most configurations, the overall activity (expressed per km or per hr) 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 50-100%) 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.

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 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 vastly 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.

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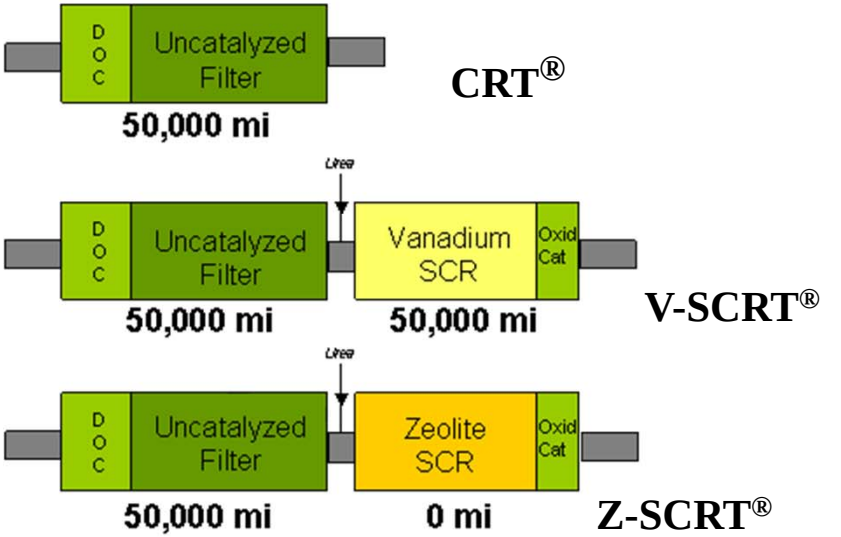
Test Matrix

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

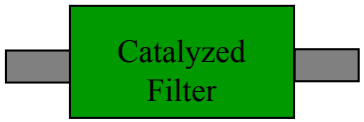
Baseline

Veh#1, 1998 Cummins

Diesel 11L, 360,000 miles



1,000 mi **CCRT®**



30,000 mi **DPX**

31,000 mi **Horizon**

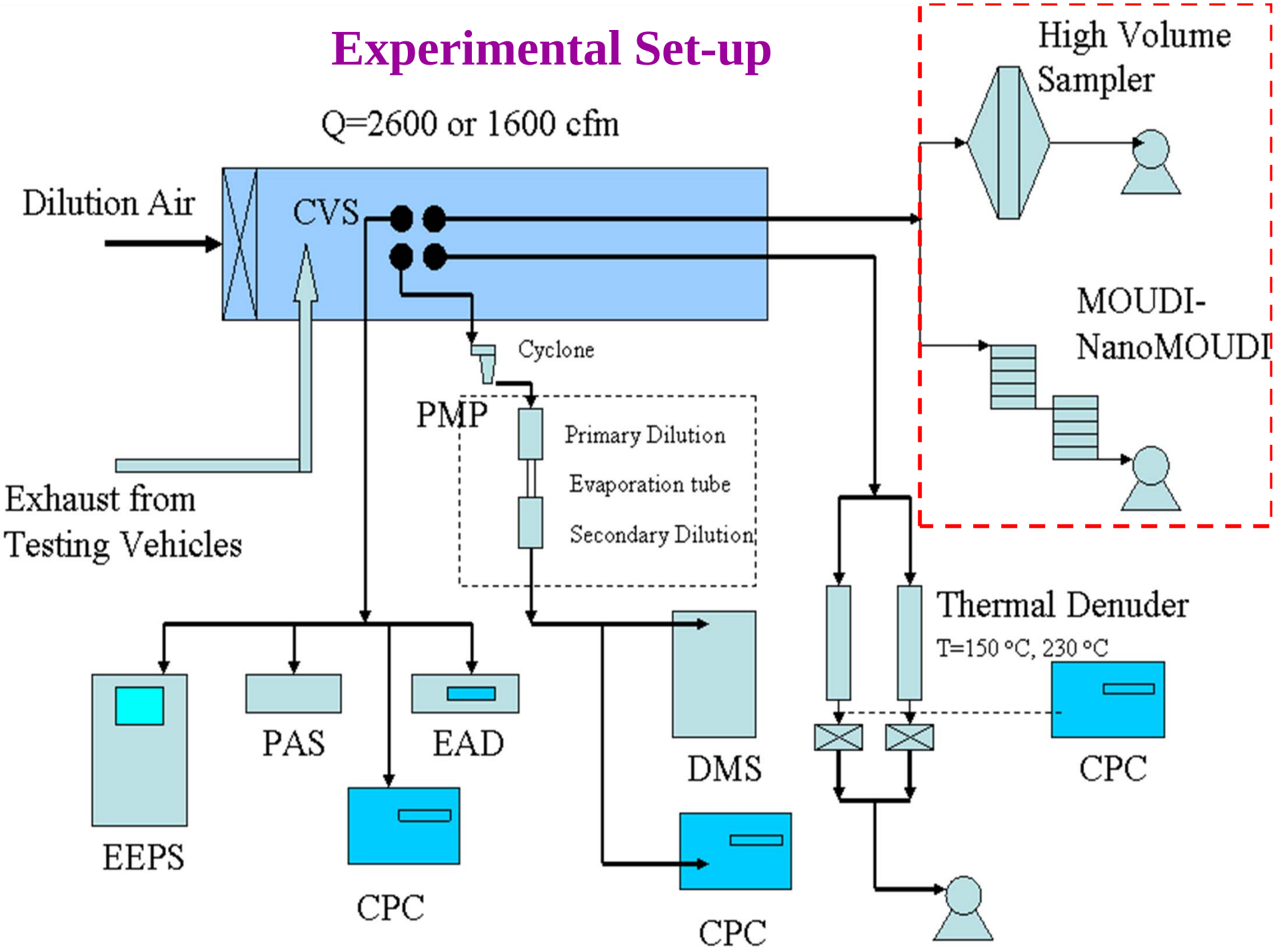
Veh#2 2006 Cummins Diesel w/ Allison Hybrid drive 5.9L, 1,000 miles

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

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

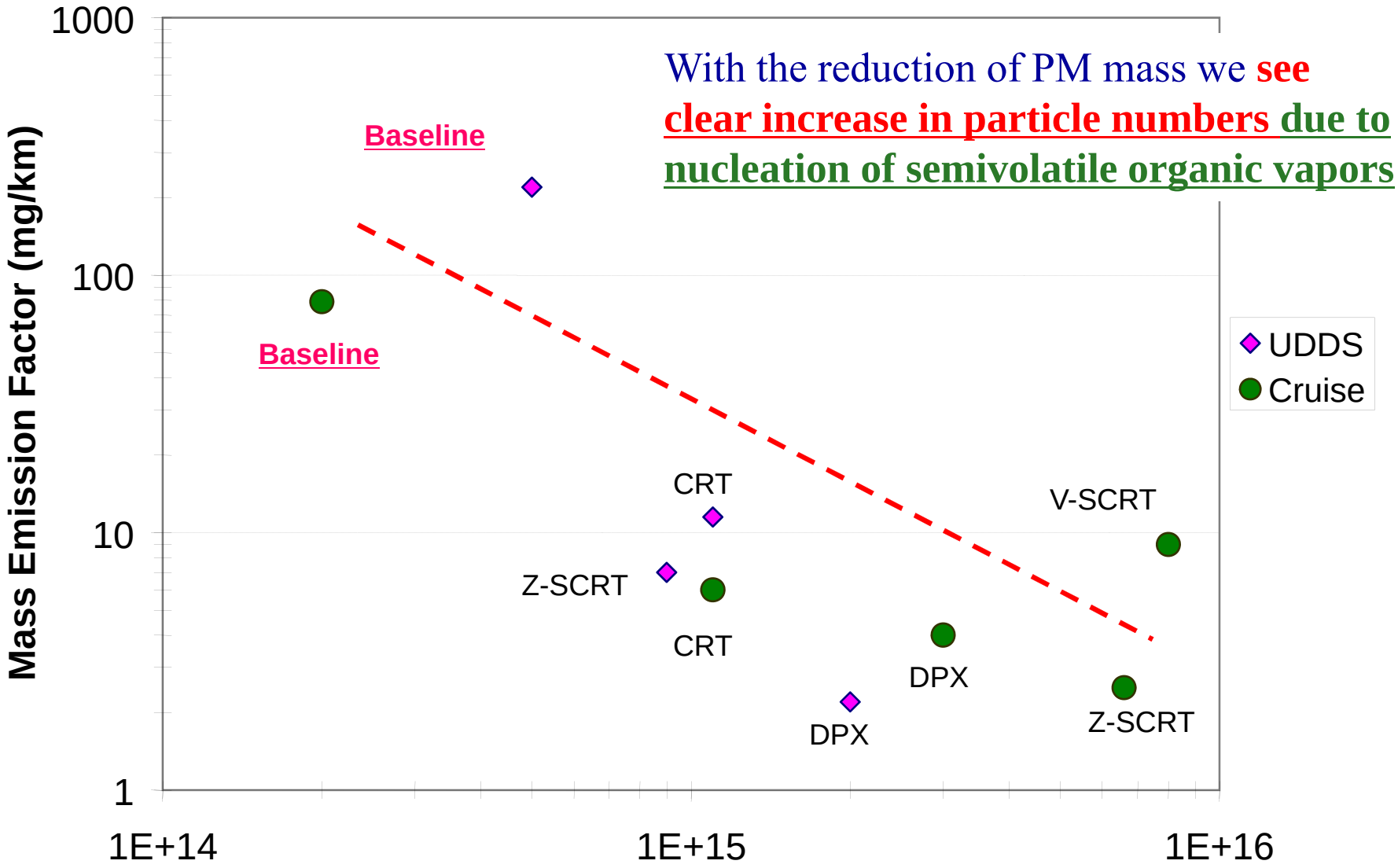
(ii) EC, OC: Thermal optical method

3. Thermodenuder: Teflon filters : Non-volatile PM

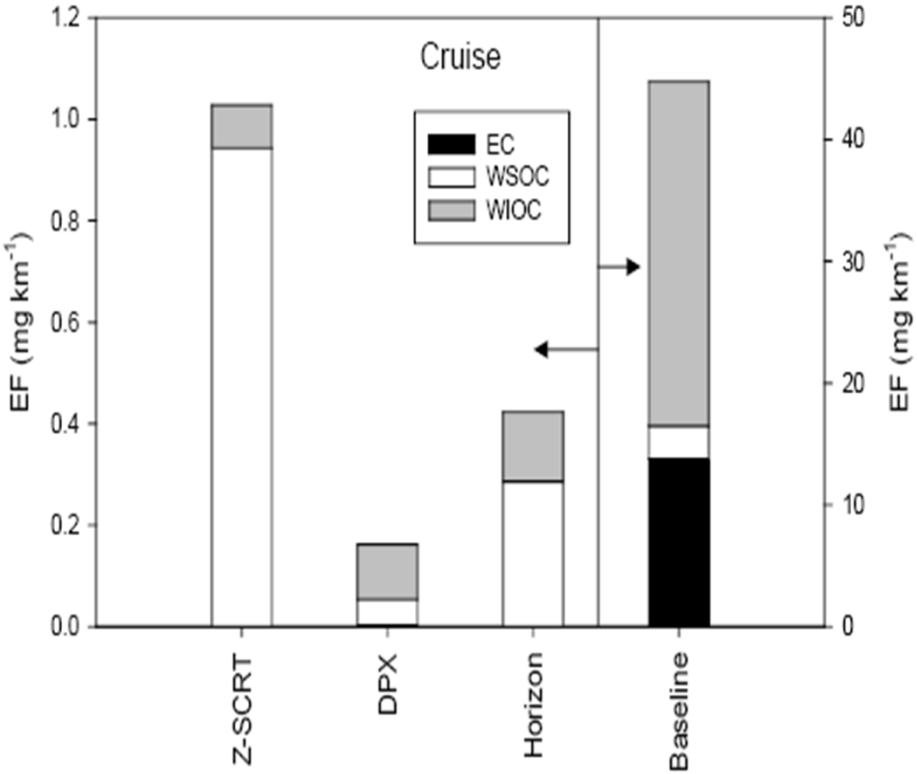
   i) Redox activity (DTT)

   ii) WSOC , GC/MS, inorganic ions

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



Biswas et al. Atmos. Environ, 2008

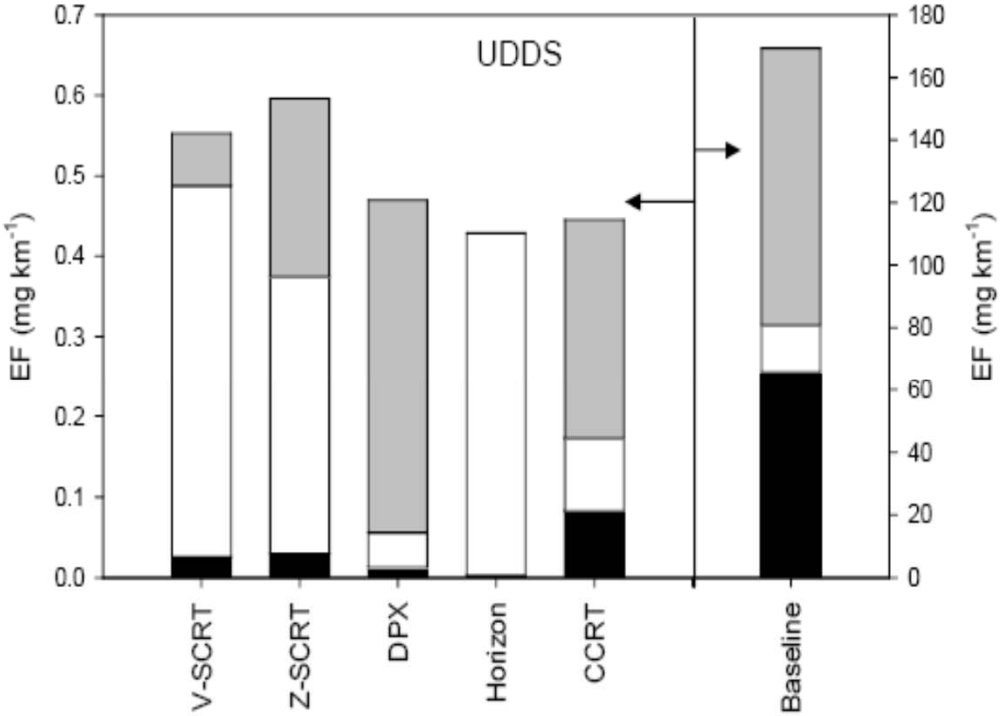


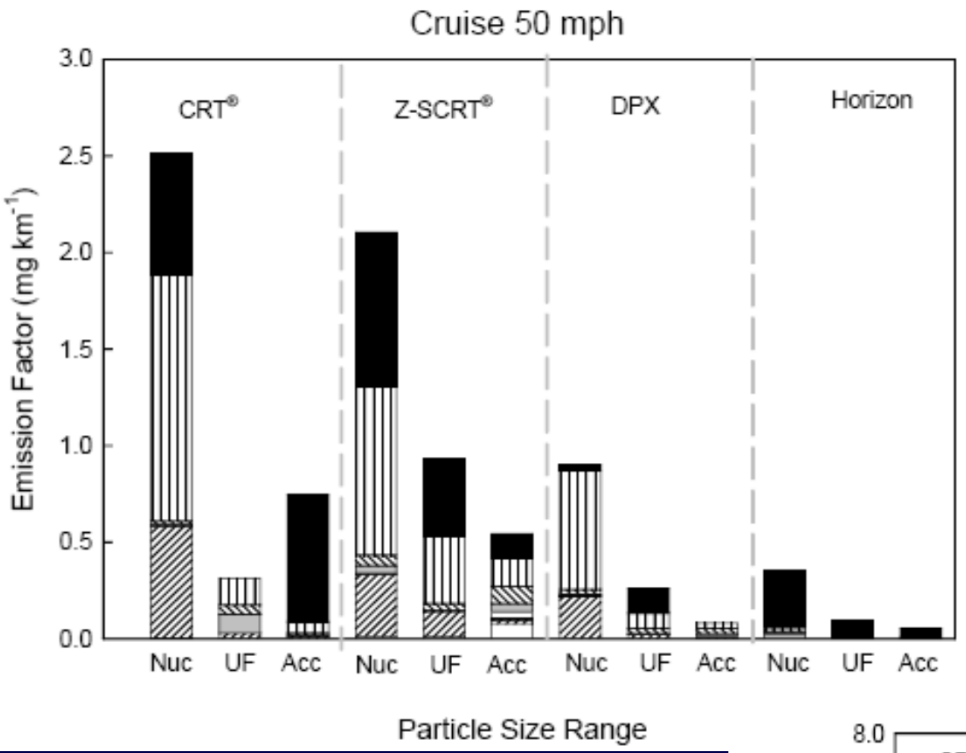
- **High EC content of baseline vehicle**

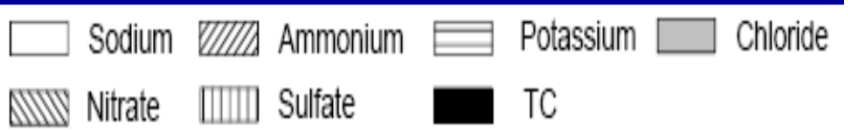
- **Noticeable increases in the mass fraction of water soluble OC in newer vehicles**

Higher EC and OC emission in UDDS than cruise cycle

Biswas et al Atmos Environ, 2009





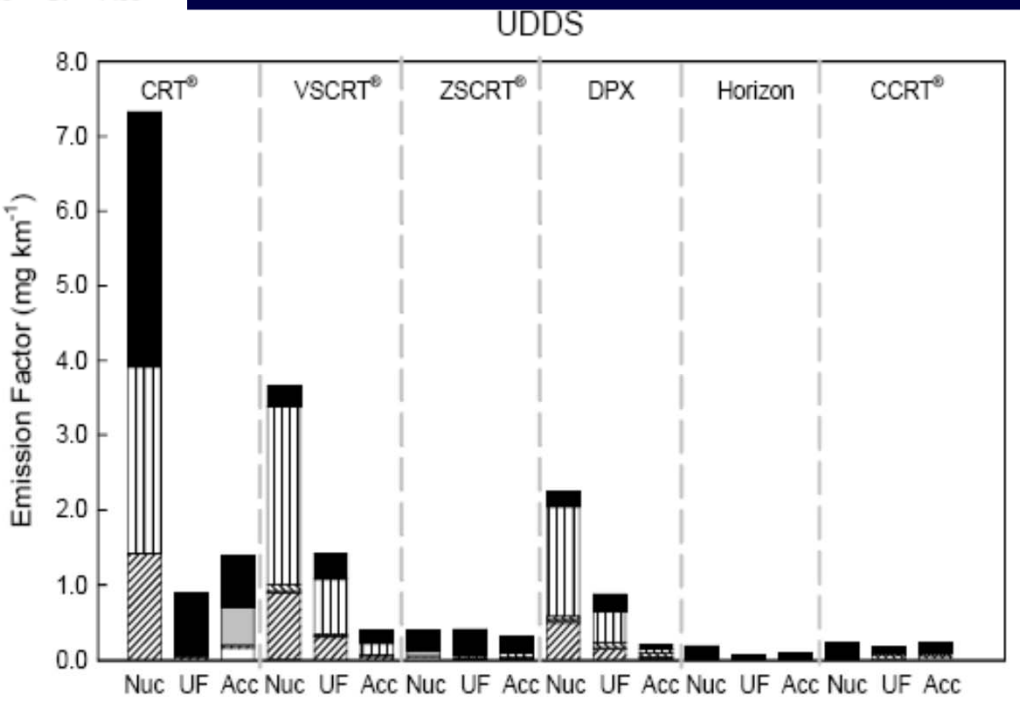


Nuc: 0.01 – 0.056 μm

UF: 0.056- 0.18 μm

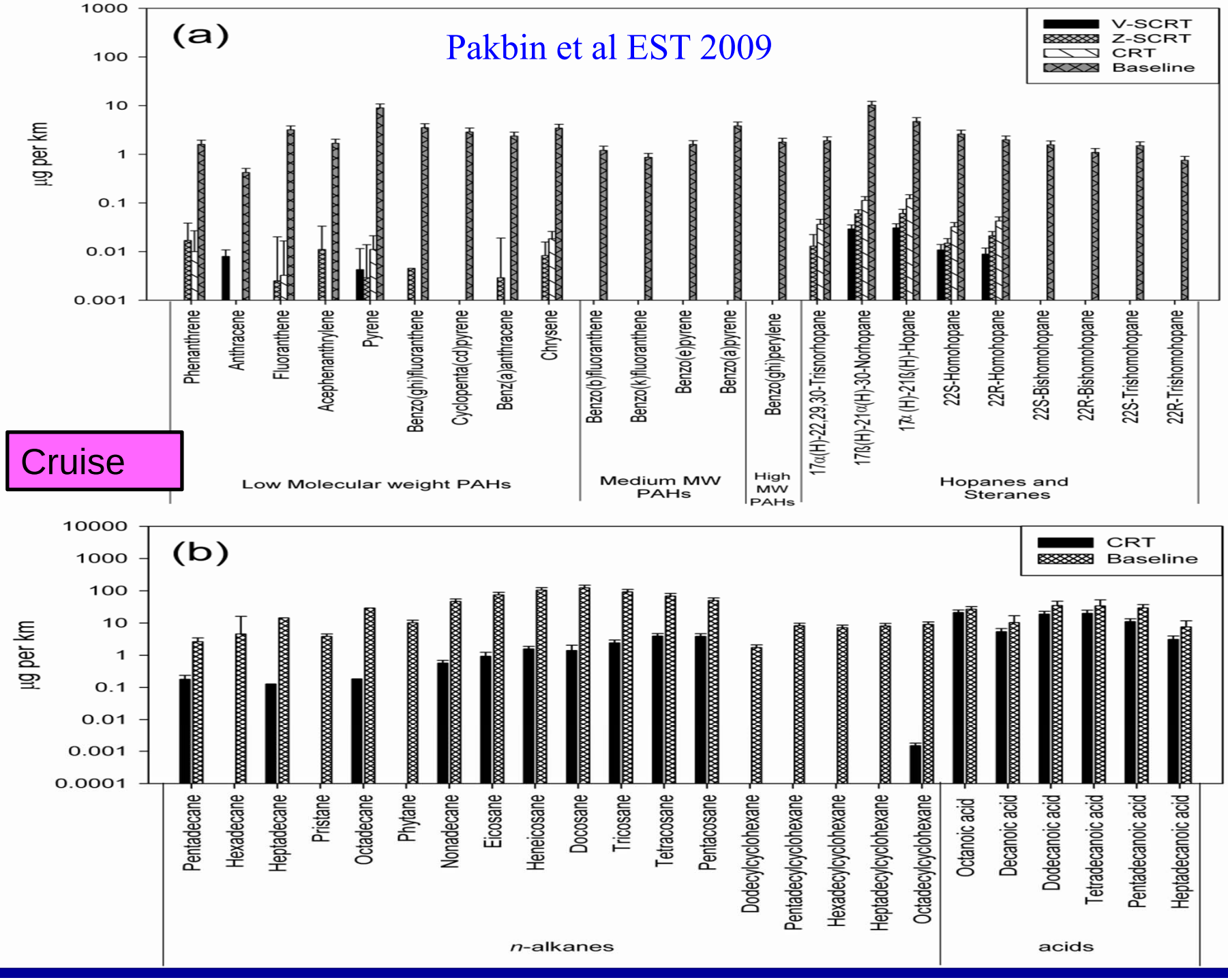
Acc: 0.18- 2.5 μm

- **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**

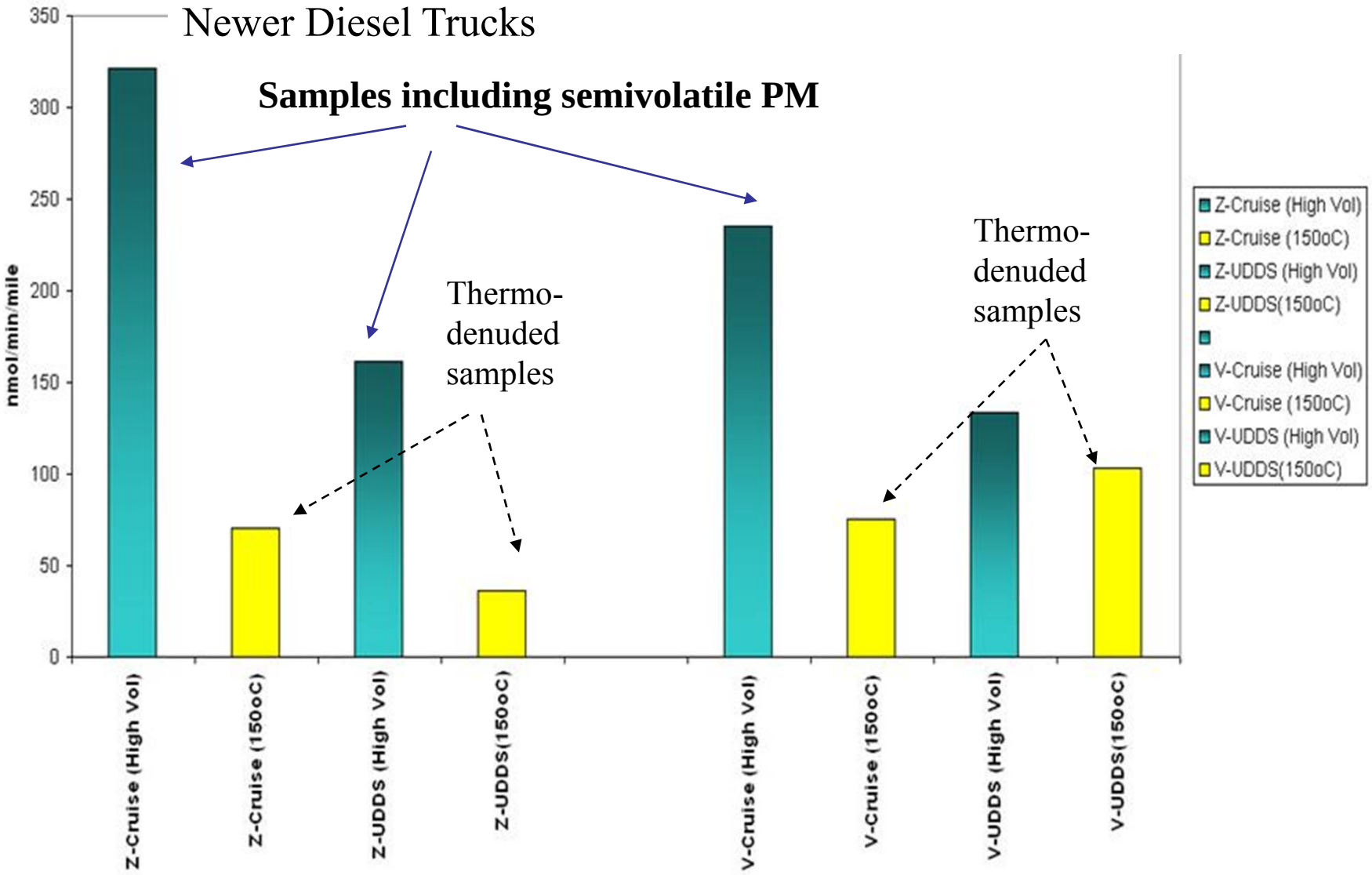


Pakbin et al EST 2009

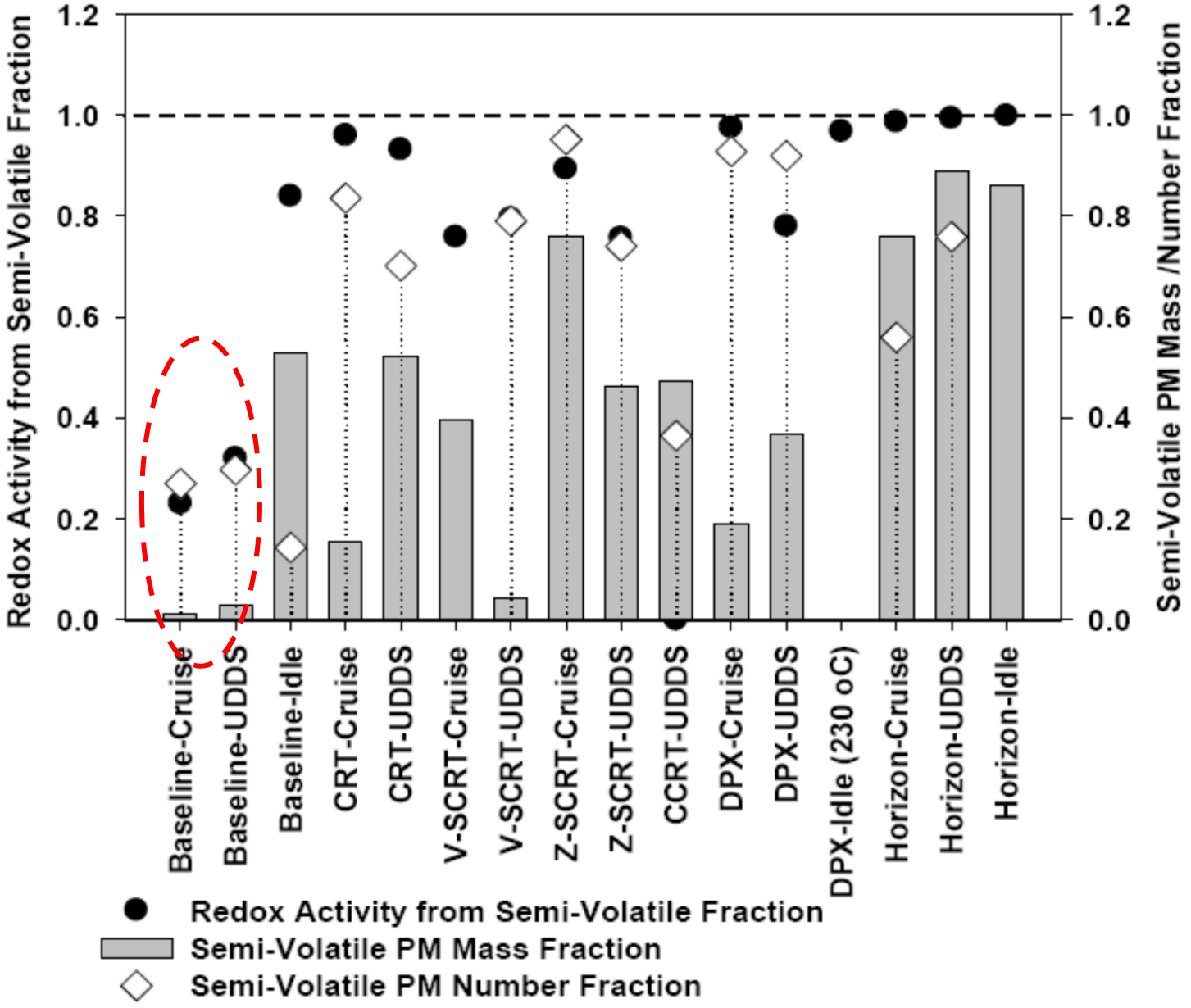
Cruise



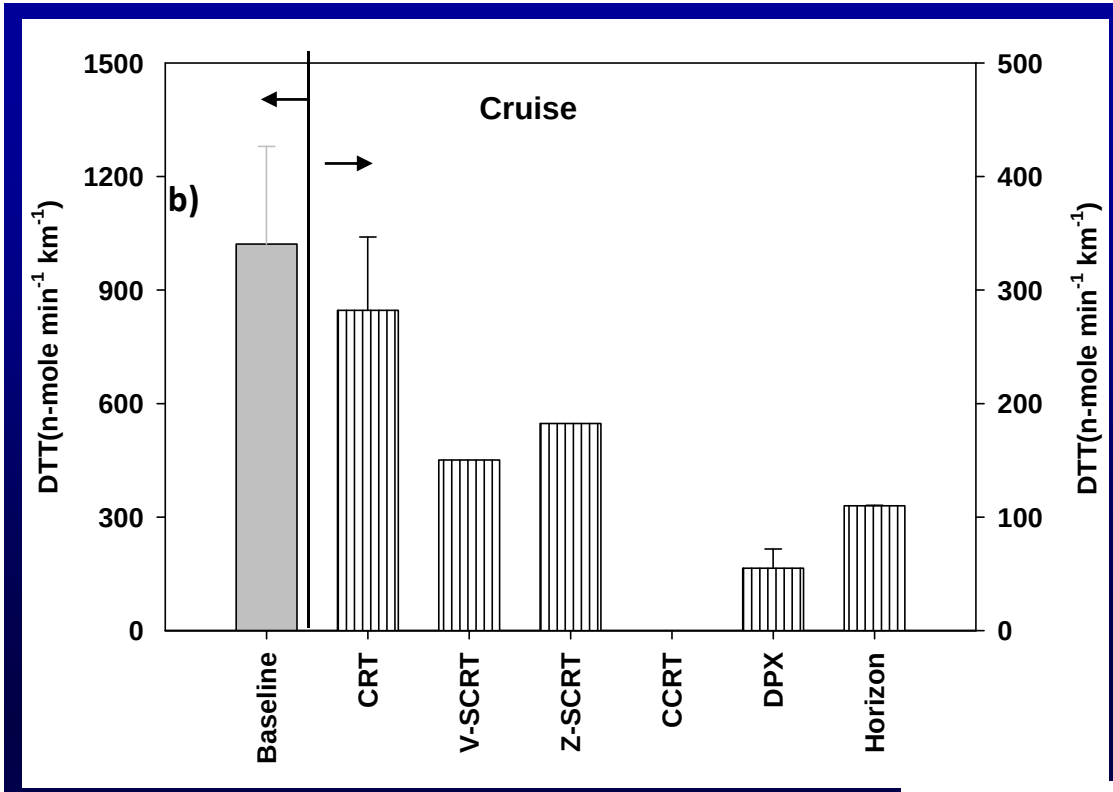
Redox Activity (DTT assay) of Semivolatile and Total PM from Newer Diesel Trucks



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



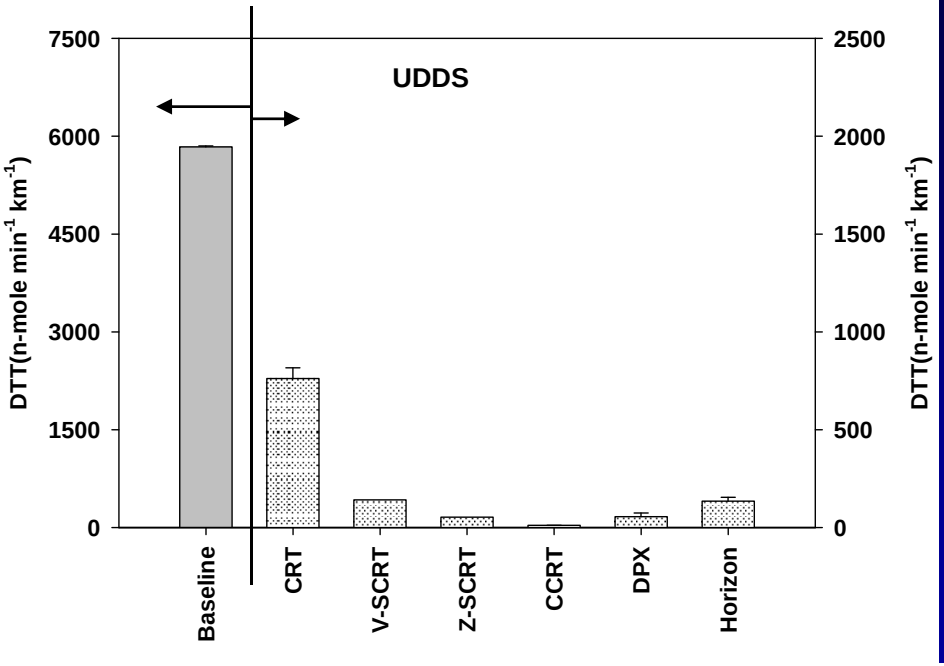
Semi-volatile PM faction accounts for over 80- 90% of the per PM mass toxicity (Biswas et al, ES&T, 2009)

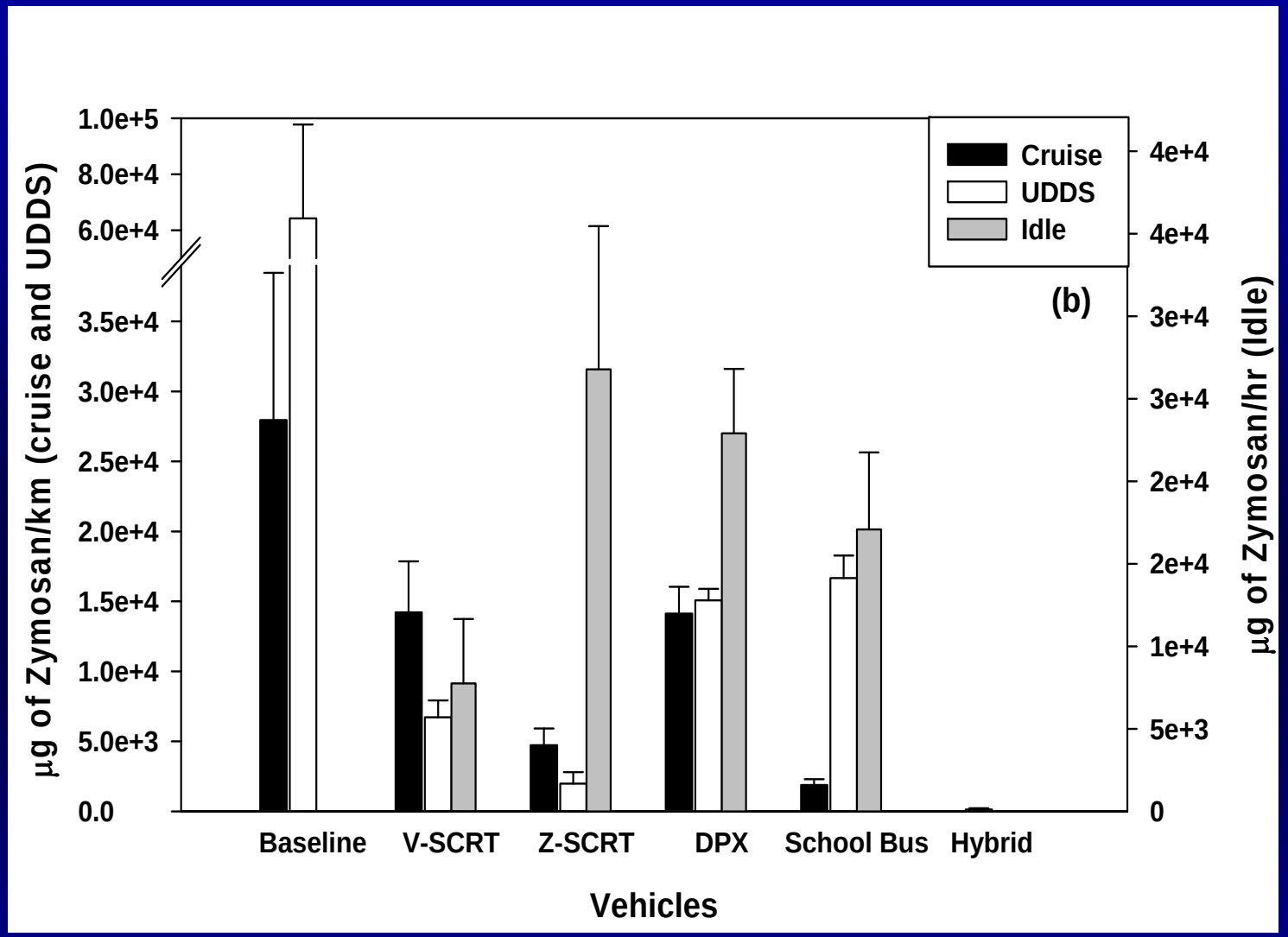


Per km driven DTT for Cruise and UDDS cycles

Biswas et al ES&T 2009

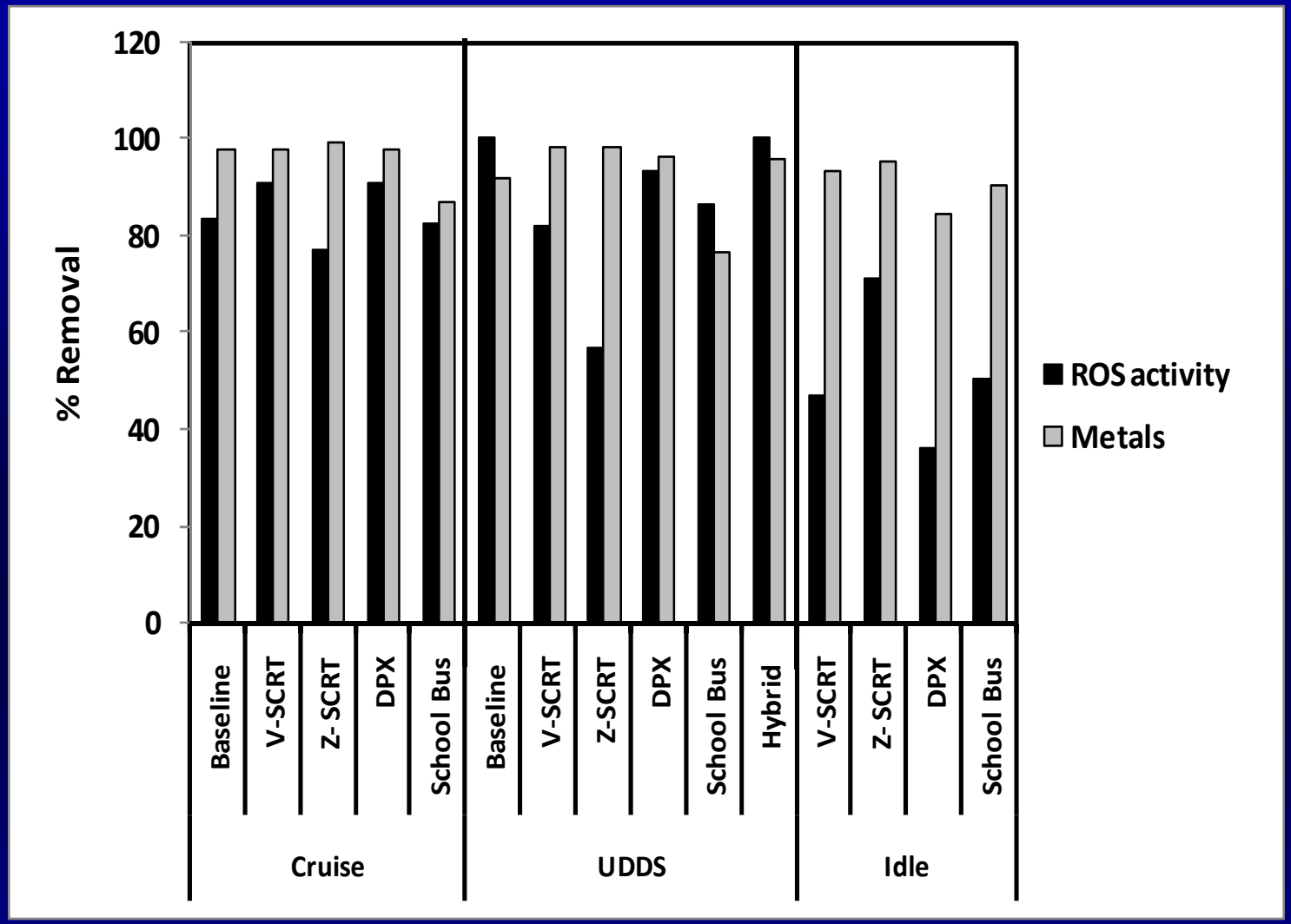
Substantial reduction on overall per km redox activity but non-linearly related to PM mass reductions





Per km ROS activity (per hr for idle)

Verma et al , Atmos Environ, 2010



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

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 some retrofitted configurations. The vast majority of these nucleation mode particles are semi-volatile in nature.

- The total emissions of the major chemical species (except of sulfate) are substantially reduced in the retrofitted vehicles

- 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

•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.

• An important caveat of the toxicological findings of this study is that they are all based on molecular or cellular assays that examine toxicity of 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.

•Such important investigations can only be addressed by in vivo inhalation exposure studies

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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