West Virginia University

CHARACTERIZATION OF THE COMPOSITION AND TOXICITY OF PARTICULATE MATTER EMISSIONS FROM ADVANCED HEAVY-DUTY NATURAL GAS ENGINES

Arvind Thiruvengadam, Ph.D
Marc Besch
Daniel Carder
Mridul Gautam, Ph.D
Mechanical and Aerospace Department
West Virginia University, WV USA

John Collins, Ph.D
Yoon Seungju, Ph.D
California Air Resources Board
Sacramento, CA USA

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INTRODUCTION

- Heavy-duty ultrafine PM has been linked to adverse health effects
- Uncertainties related to contribution of different fractions of PM to health effects.
- Introduction of advanced after-treatment systems and alternative fuel technologies have brought a change in chemical and physical nature of PM.
- Lube oil contribution to PM could be a significant factor in a soot free tailpipe exhaust.
- No single bio-assay can characterize the toxicity potential of tailpipe PM emissions.
- Surface area could prove to be the appropriate metric for toxicity potential given the direct relationship between surface area and diffusion charger measurements.

PROBLEM STATEMENT

- Compositionally diverse heavy-duty engine PM emissions impart significant uncertainty to the relative contribution of different fractions to overall PM toxicity.
- Evaluation of toxicity of volatile and non-volatile fraction of PM is necessary to better understand the health effects over a simple broad classification of PM.

GLOBAL OBJECTIVE

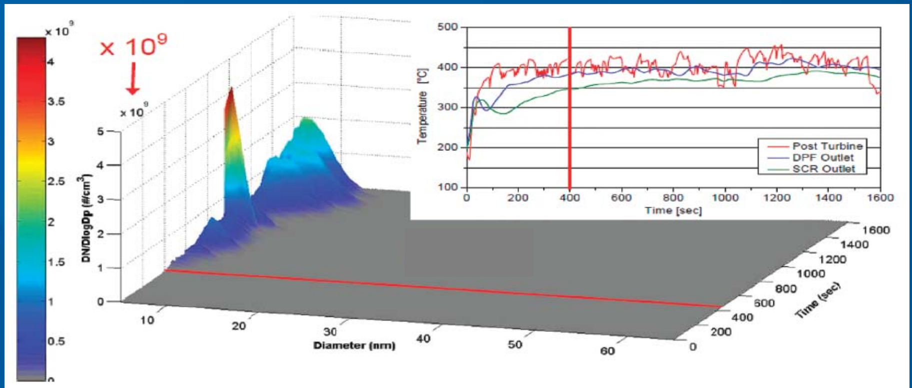
- Investigate the linkages between the different fractions of PM to their respective toxicity responses.

SPECIFIC OBJECTIVE

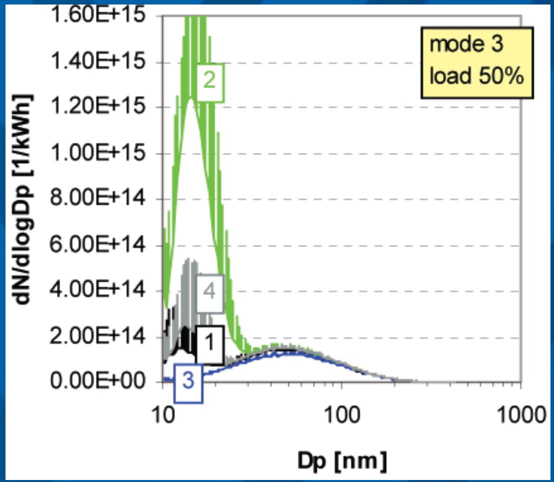
- To collect PM from a heavy-duty natural gas vehicle as a denuded (volatile fraction removed) and non-denuded (total particulate matter) composition to correlate the volatile and non-volatile fraction to its toxicity responses.
- To characterize volatile organic compounds (VOC), poly aromatic hydrocarbons (PAH), carbonyl compounds, elemental carbon, organic carbon, metals and ions emissions.
- Analysis of PM for three different bio assays namely, two cell free (chemical based) assays 1) DHBA assay, 2) DTT assay and 3) a cell based alveolar macrophage ROS assay (Reactive Oxidative Species).

BACKGROUND

- Diesel particulate filters are highly efficient in removing elemental carbon emissions.
- Catalyzed particulate filters and SCR after-treatment systems have been linked to sulfuric acid based particles.
- Relative contribution of fuel and lube oil sulfur not clearly understood.



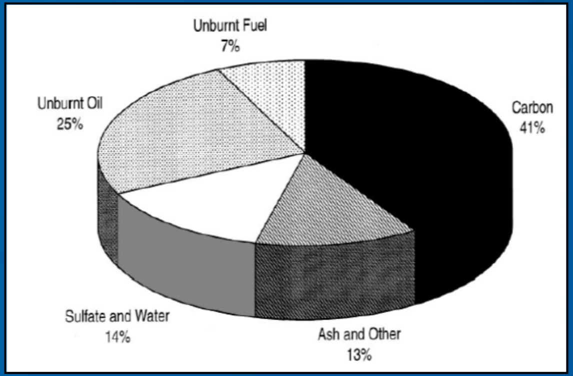
Thiruvengadam, A.; Besch, C. M.; Carder, D.; Oshinuga, A.; Gautam, M., Influence of Real-World Engine Load Conditions on Nanoparticle Emissions from a DPF and SCR Equipped Heavy-Duty Diesel Engine. Environmental Science and Technology ***2012,*** *46, 1907-1913.*



Vaaraslahti, K.; Keskinen, J.; Giechaskiel, B.; Solla, A.; Murtonen, T.; Vesala, H., Effect of Lubricant on the Formation of Heavy-Duty Diesel Exhaust Nanoparticles. Environmental Science and Technology ***2005,*** *39, 8497-8504.*

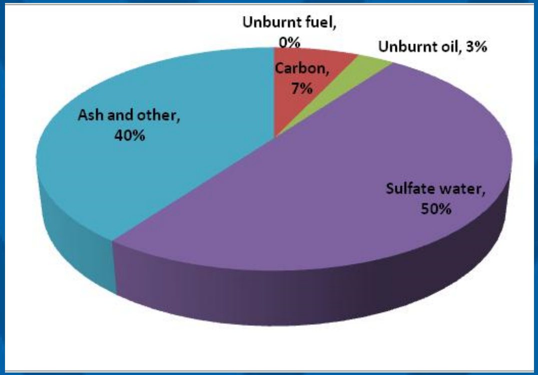
BACKGROUND Contd.

- Typical composition of PM has changed significantly from its traditional definition which was based on emissions from legacy diesel engines.



KITTELSON, D. B. 1998b. Engines and Nanoparticles: A Review. Journal of Aerosol Science, 29, 575-588.

Current estimate of PM composition for a DPF equipped diesel and natural gas fueled heavy-duty vehicles



- Tailpipe PM size distribution of heavy-duty diesel and natural gas engines are quite similar. Compositional differences exist.
- Advancements in natural gas engine technology have resulted in NOx emissions well below certification limits and organic and elemental PM close to detection limits of the analytical method.
- Verma et al. (USC-LA) have identified metals to be a major fraction of PM from heavy-duty diesel engines.

METHODOLOGY

- Two transit buses fueled with natural gas engines were tested using the WVU transportable heavy-duty laboratory and the TEMS.
- The vehicles were powered by USEPA 2010 compliant, stoichiometric fueled natural gas engine with cooled EGR and a three-way catalyst (details tabulated below).

Engine Manufacturer	Engine Model	Engine Model Year	Displacement/Power (L/HP)	fuelling	NOx/PM (gm/bhp-hr) *
Cummins	ISLG 280	2007	8.9/280	CNG Stoichiometric	0.2/0.01

TEST MATRIX

	UDDS (40 min duration Cycle)	45 MPH steady state (60 min duration cycle)	Idle (60 min duration)
Two Buses **(Odometer: 84994 and 77538 miles)**	Unregulated Emissions - 3 runs Toxicity w/ & w/o thermodenuder	Unregulated Emissions - 3 runs Toxicity w/ & w/o thermodenuder	Unregulated Emissions - 3 runs Toxicity w/ & w/o thermodenuder

SAMPLE MEDIA AND ANALYSIS

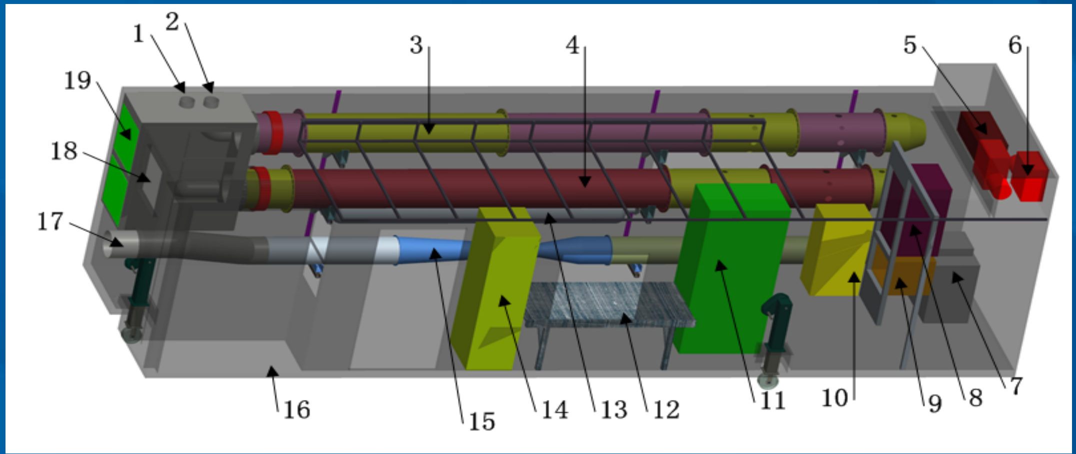
Sample	Sample Media	Flow rate
PM10	T60A20	16.7 lpm
PM2.5	T60A20	16.7 lpm
PM1.0	T60A20	16.7 lpm
Methane	Horiba Non-Methane Cutter	
EC/OC	Pre-fired Quartz (CARB MLD)	2.5 SCFM
VOC	Steel Canister (CARB MLD)	
Carbonyls	DNPH Cartridge (CARB MLD)	2 lpm
Metals/Ions	Teflo Filters (Univ of Wisconsin)	16.7 lpm
PAH	PUF/XAD (SWRI)	200 lpm
Particle Size and Concentration	TSI EEPS/EAD	

Sample	Sample Media	Flow rate
DHBA and DTT assays Denuded Stream	T60A20	50X4 lpm
DHBA and DTT Non-Denuded Stream	T60A20	200lpm
Mutagenicity Denuded	T60A20 (UC Davis)	50X4 lpm
Mutagenicity Non-Denuded	T60A20 (UC Davis)	200 lpm
ROS Toxicity Denuded	T60A20 (Univ Wisconsin)	50X4 lpm
ROS Toxicity Non-Denuded	T60A20 (Univ Wisconsin)	200lpm

SAMPLING SETUP

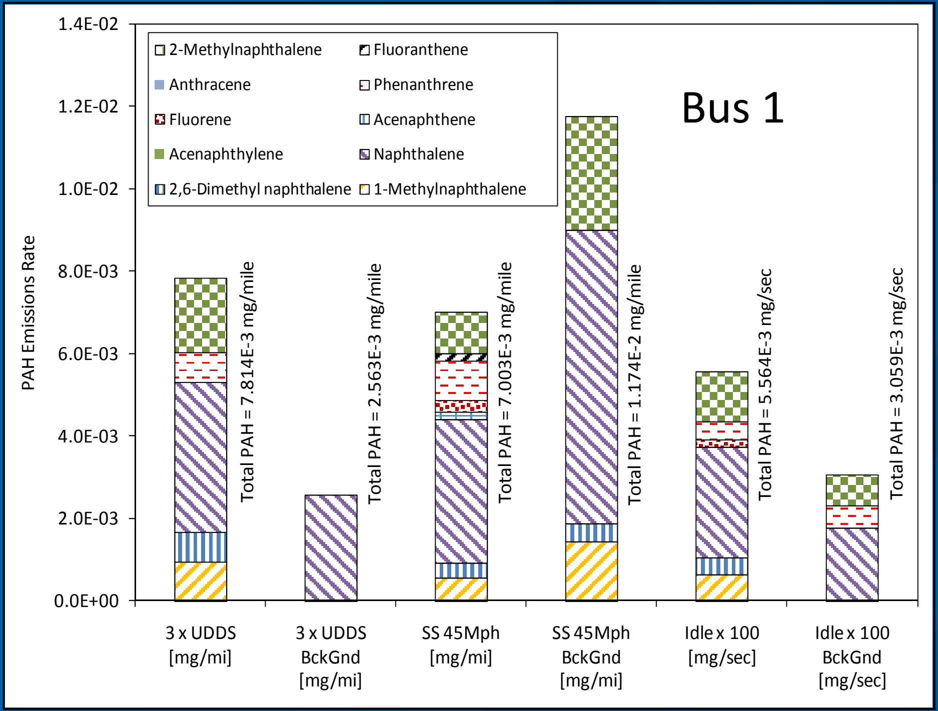
WVU Hi-Vol Thermodenuder Sampling System (WVU-HVTSS)

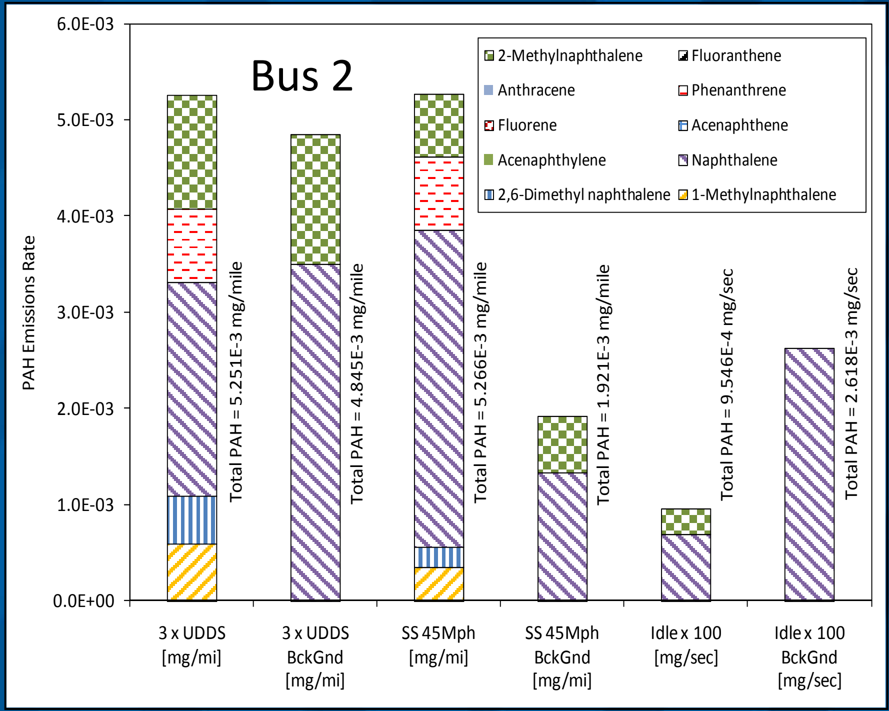
Clean tunnel CVS sampling plane



1- Exhaust inlet of dirty tunnel; 2- Exhaust inlet of clean tunnel; 3- Clean tunnel; 4- Dirty tunnel; 5- Air compressor; 6- Vacuum pumps; 7- Oven; 8- PM sampling box; 9- Glove box; 10- Zero air generator; 11- MEXA-7200D motor exhaust gas analyzer; 12- Computer table; 13- Air tank; 14- DAQ rack; 15- Subsonic venturi; 16- Air conditioner deck; 17- Outlet to blower; 18- Ventilation fan; 19- HEPA filters

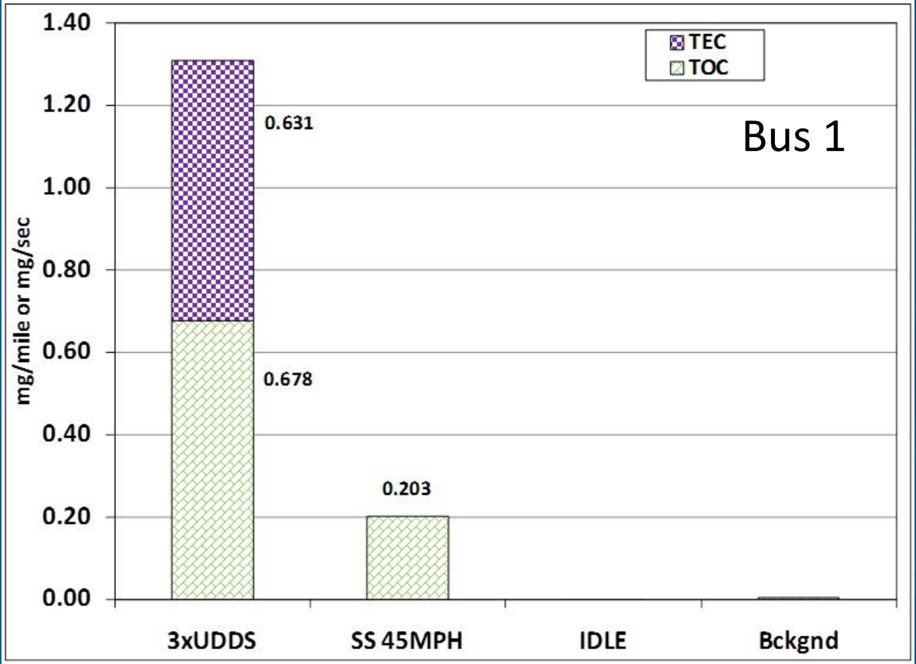
PAH EMISSIONS RESULTS

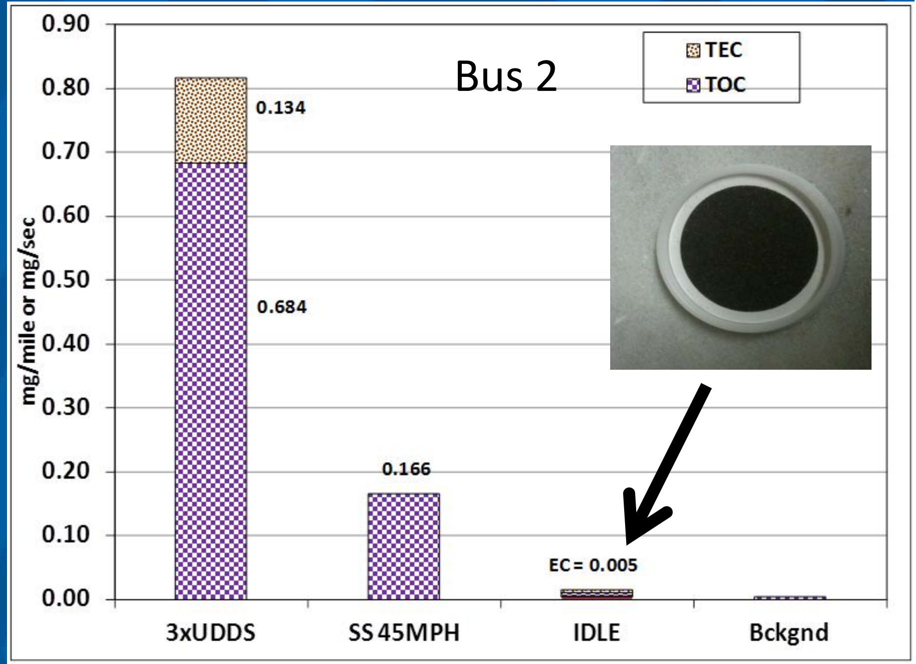




- PAH compounds are precursors to soot formation.
- Absence of aromatic compounds in the fuel resulted in PAH emissions close to levels found in the background.
- Phenanthrene and 2-Methylnaphthalene were observed to be greater than levels found in background.
- Lube oil may be the sources for the observed emissions.

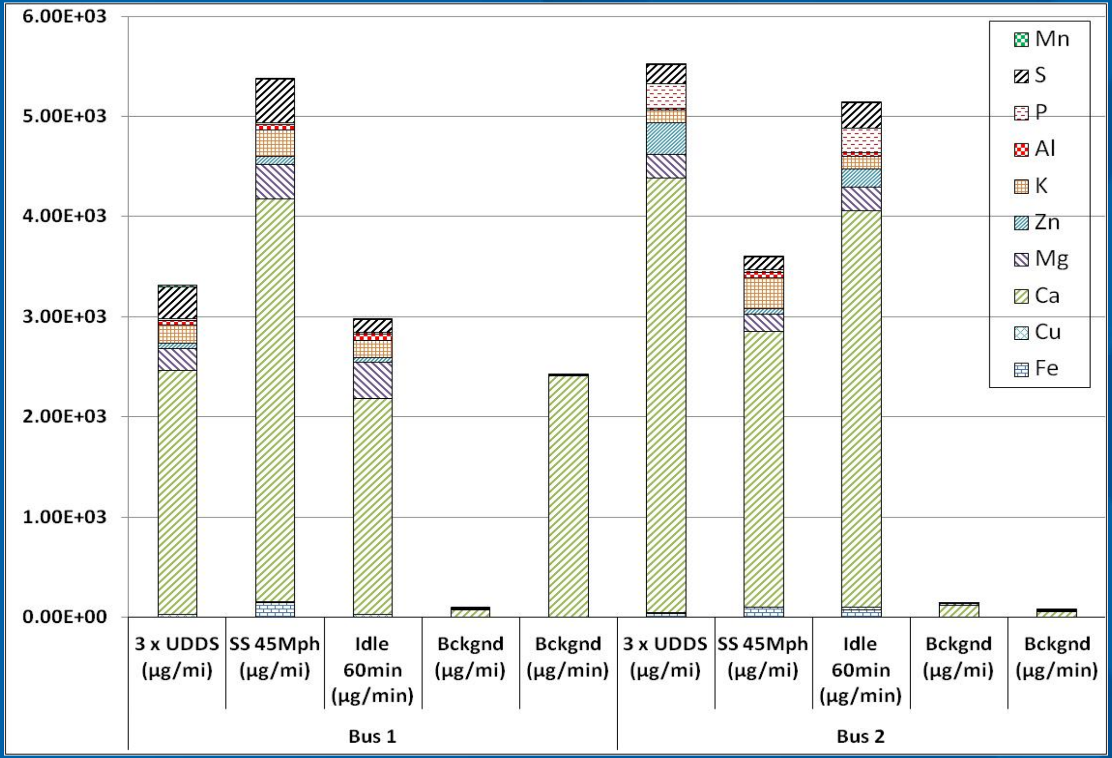
EC/OC EMISSIONS RESULTS





- Results indicate significant OC emissions.
- Possibility of bias in results due to gas phase adsorption on to pre-fired quartz filters.
- Bus 2 idle operation resulted 162 mg of EC emissions over 9 hrs of idle compared to 148 mg of thermally denuded PM mass.
- Higher EC emissions over the idle cycle may be attributed to excessive lube oil consumption.

ION EMISSIONS

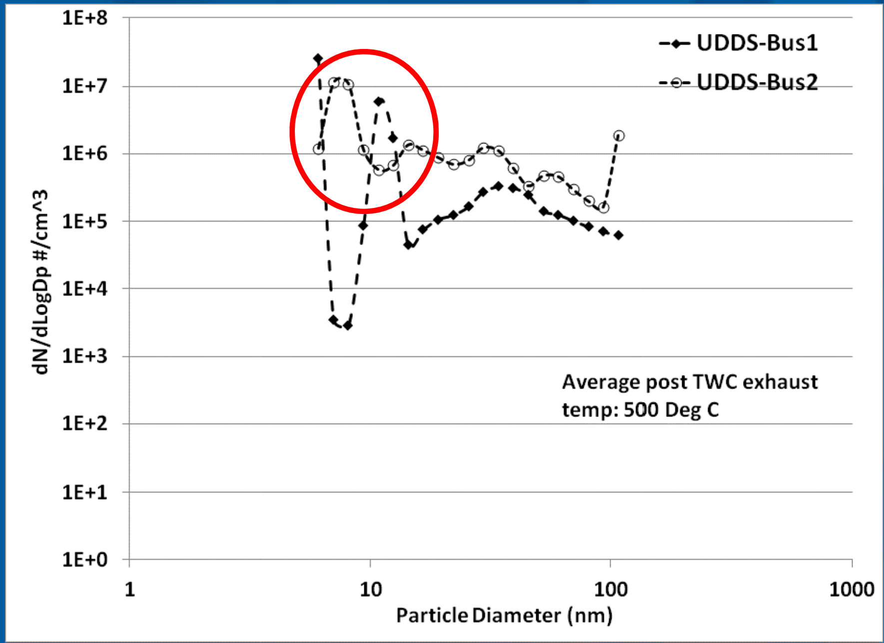


OIL ANALYSIS RESULTS

	(ppm)	Bus 1	Bus 2
Wear Metals	**Fe**	19	9
	Cu	188	168
	Cr	2	2
Additive Metals	**Ca**	1393	1391
	Mg	54	6
	Zn	971	927
	P	640	514
Contaminant Metals	**Si**	46	4
	Na	16	16
	K	8	1

- Calcium was observed to be the dominant contributor to elemental emissions.
- Elemental sulfur was observed in all test samples.
- Phosphorus, magnesium, zinc, potassium are other elemental emissions observed in the sample.
- All elemental fractions observed in sample are lube oil derived.
- Elemental emissions observed in samples could be byproducts of decomposition of zinc dialkyldithiophosphates (ZDDP), a popular lube oil additive formulated by Castrol.

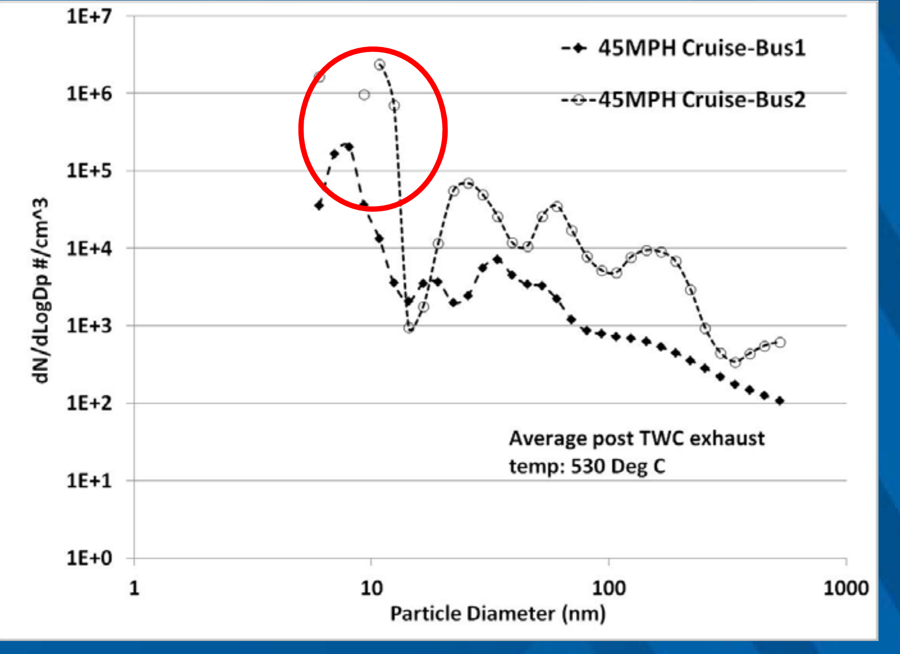
PARTICLE SIZE DISTRIBUTION-UDDS



- Dilution corrected average particle concentrations

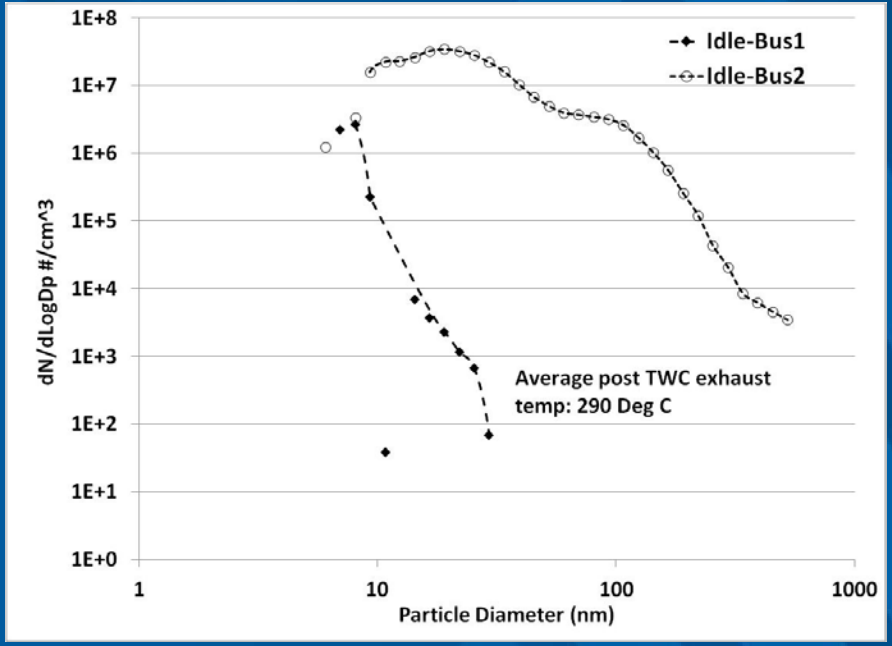
- UDDS operation resulted in a highly variable particle size distribution.
- A consistent nucleation mode distribution is observed for all test runs.
- Accumulation mode distribution shows high variability in size distribution and number concentrations.
- It is to be noted EC emissions from Bus 1 and Bus 2 were 0.631 mg/mi and 0.134 mg/mile respectively.
- Particle size concentration over 120 nm has been omitted due to extensive noise in TSI EEPS electrometer channels.

PARTICLE SIZE DISTRIBUTION-SS 45 MPH



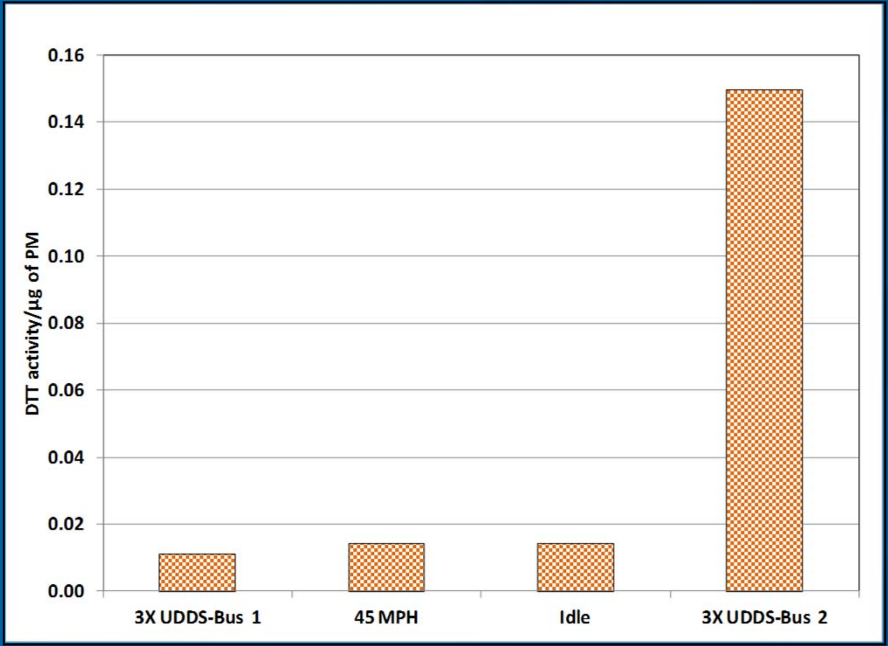
- Steady-state 45 MPH operation resulted in particle concentration in the accumulation mode to be below levels found in background.
- The presence of the nucleation mode on a high exhaust temperature cycle, indicates the possibility of a non-volatile particle formation mechanism.
- The decrease in accumulation mode particle concentration between each successive run, indicates the possibility of tunnel artifacts as a result of ammonia emissions from three-way catalyst.

PARTICLE SIZE DISTRIBUTION-IDLE



- Idle operation from bus 1 resulted in low particle number concentrations; however a significant nucleation mode was observed.
- Bus 2 particle size distribution indicates a very repeatable distribution with particles detected over the nucleation mode and accumulation mode.
- Filter mass and EC mass correlate well; hence indicate a dominant elemental carbon composition.
- EC mass could be a result of excessive entry of lube oil in the combustion chamber, potential combustion; subsequently, manifesting itself as soot and lube oil ash.

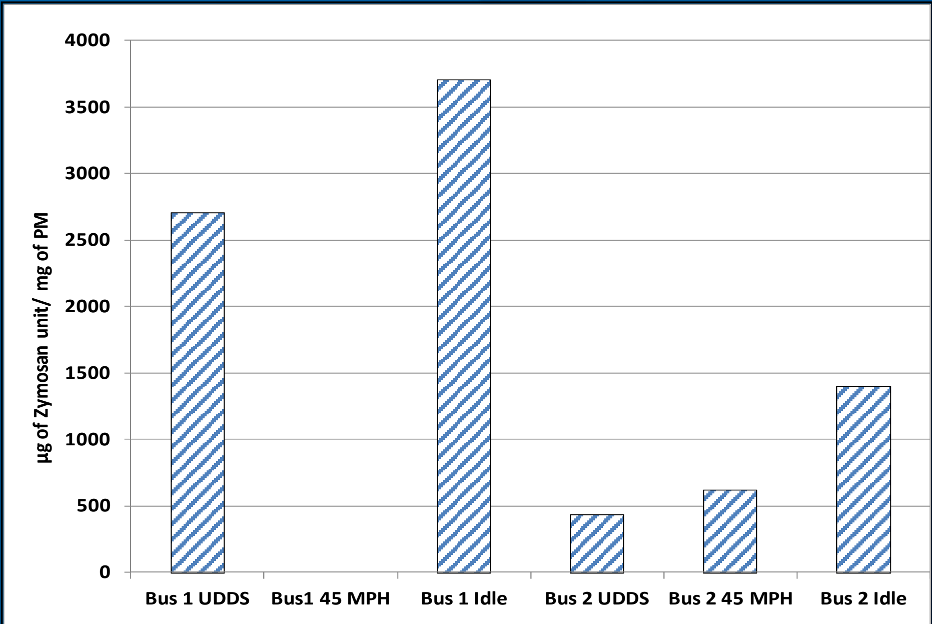
DTT TOXICITY RESULTS (UCLA)

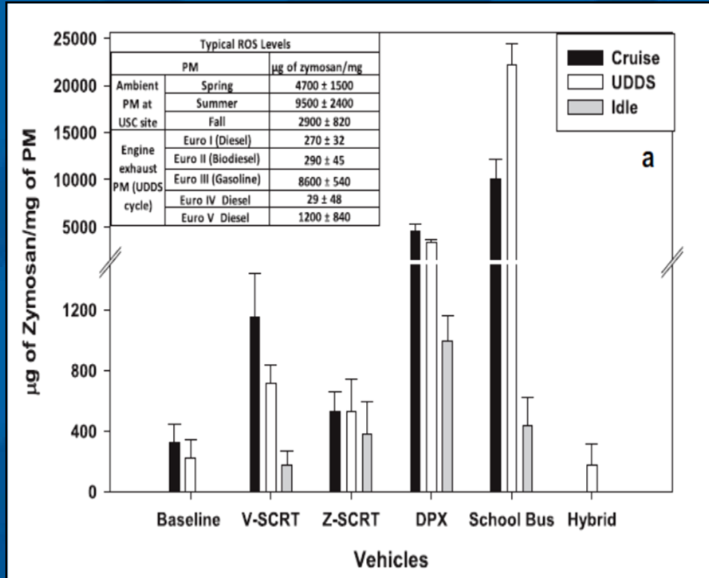


Species	R	p
Cu	**0.99**	**0.01**
Mg	0.84	0.16
Al	0.79	0.21
P	**0.99**	**0.01**
S	0.57	0.43
K	0.43	0.57
Ca	0.73	0.26
V	0.57	0.43
Cr	0.81	0.19
Mn	0.70	0.30
Fe	0.28	0.72
Co	-0.24	0.76
Zn*	**0.93***	**0.07***

- Results show that copper (R=0.99) and phosphorus (R=0.98) exhibit a significant correlation ($p<0.05$) towards DTT activity
- Both copper and phosphorus show significant correlation in the 95% confidence interval whereas zinc (R=0.93) falls within the 90% confidence interval
- DTT consumption is approximately 300 times faster in comparison to other elements
- Metal removal process from the sample resulted in very low DTT activity.

ALVEOLAR MACROPHAGE TOXICITY RESULTS (Univ Wisconsin Madison)





VERMA, V., SHAFER, M. M., SCHAUER, J. J. & SIOUTAS, C. 2010. Contribution of transition metals in the reactive oxygen species activity of PM emissions from retrofitted heavy-duty vehicles. Atmospheric Environment, 44, 5165-5173.

Species	R	P
EC	0.94	0.004
OC	0.55	0.25
PAH (MW<200)	-0.50	0.30

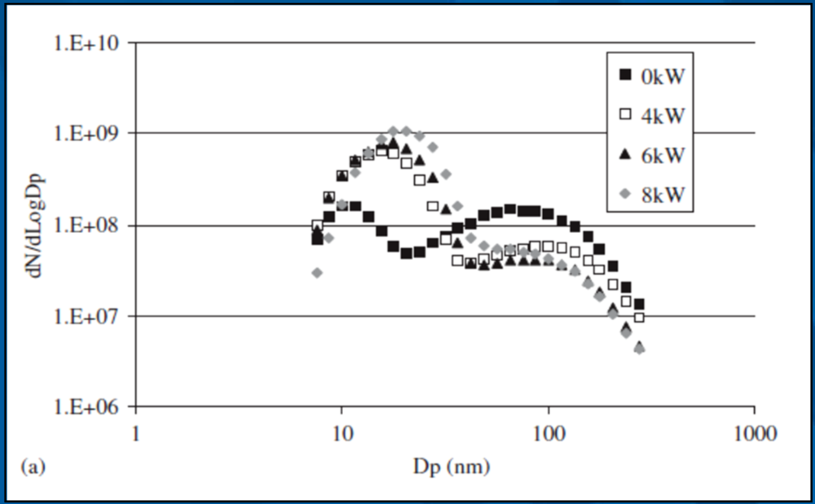
	Denuded PM		Non-Denuded PM	
Species	R	P	R	P
Cu	**0.97**	**0.00**	**0.52**	**0.28**
Mg	0.28	0.59	0.06	0.90
Al	0.27	0.59	0.06	0.90
P	**0.99**	**0.00**	**0.56**	**0.25**
S	**0.73**	**0.09**	**0.34**	**0.50**
K	0.30	0.55	0.07	0.88
Ca	0.33	0.52	0.72	0.11
V	0.83	0.04	0.40	0.43
Cr	**0.99**	**0.00**	**0.55**	**0.26**
Mn	0.49	0.32	0.20	0.69
Fe	**0.95**	**0.00**	**0.47**	**0.33**
Co	0.68	0.13	0.27	0.60
Zn	**0.94**	**0.00**	**0.49**	**0.32**

- Denuded PM exhibited better correlation with elemental fraction than non-denuded PM
- The observed trend could be due to a possible coating of adsorbed gas phase compounds on the filter material.
- Alveolar macrophage assay was carried out by washing the filter in an aqueous solution.

PARTICLE MASS CORRELATION RESULTS

Metals (Zn, P, Cr, Fe)		
Size Bin	R	P
NP	0.96	0.002
UFP	0.25	0.636
FP	-0.09	0.864

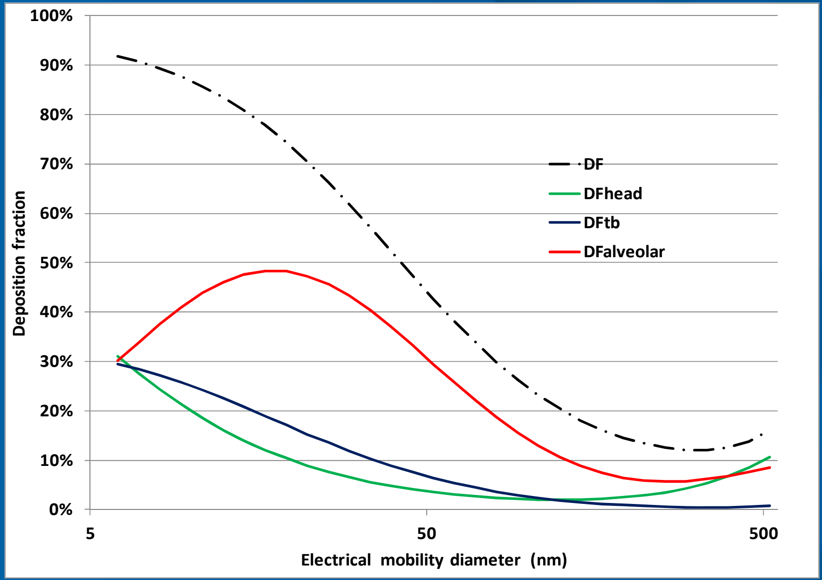
a) Nanoparticle (NP) with size ranges between 6.04 and 25.5 nm b) Ultrafine particle (UFP) with size ranges between 29.4 and 107 nm and c) Fine particle (FP) with size ranges between 124 and 523.3 nm



- Figure shows the iron based nucleation mode for diesel fuel doped with 60 ppm iron.
- LEE, D., MILLER, A., KITTELSON, D. B. & ZACHARIAH, M. R. 2006. Charcaterization of metal-bearing diesel nanoparticles using single-particle mass spectrometry. *Journal of Aerosol Science,* 37**,** 88-110.

- Mass of the nanoparticle size bin shows statistically significant correlation with mass of zinc, phosphorus, chromium and iron.
- The correlations indicate that non-volatile nucleation mode particles are possibly metallic in nature.
- Lee's work with metallic additives in fuel provides a similar insight in to this particle formation mechanism.
- The referenced work indicated the possibility that metals enter the combustion chamber via fuel additives, lubrication oil and wear. The metallic compounds go through the combustion process and possibly re-nucleate during cooling of exhaust stream.
- Their results have been corroborated with SEM images of such metallic 10 nm particles.

DEPOSITION FRACTION RESULTS

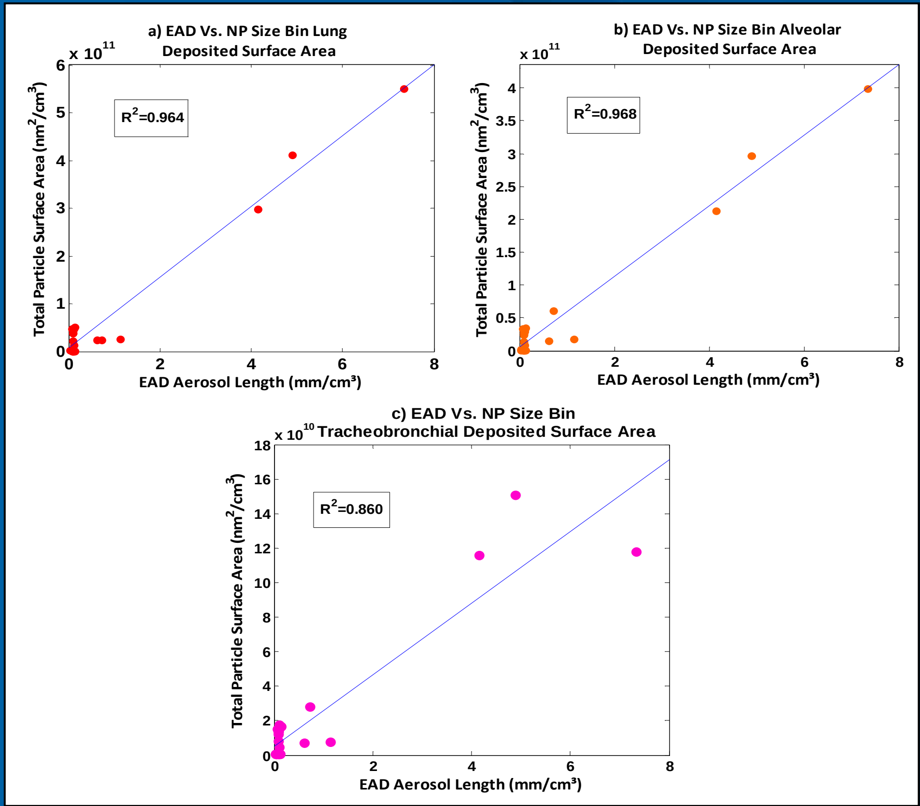


Bus 1 UDDS					
NP size Bin					
	CMD (nm)	**DF**	**DF_{head}**	**DF_{tb}**	**$DF_{alveolar}$**
Average	6.11	0.917	0.309	0.293	0.304
Std Dev	0.501	0.006	0.014	0.005	0.016
UFP size Bin					
	CMD (nm)	**DF**	**DF_{head}**	**DF_{tb}**	**$DF_{alveolar}$**
Average	36.84	0.552	0.054	0.099	0.388
Std Dev	8.792	0.065	0.010	0.018	0.048
FP size Bin					
	CMD (nm)	**DF**	**DF_{head}**	**DF_{tb}**	**$DF_{alveolar}$**
Average	173.44	0.163	0.024	0.012	0.077
Std Dev	45.020	0.022	0.008	0.004	0.014

Bus 2 Idle					
NP size Bin					
	CMD (nm)	**DF**	**DF_{head}**	**DF_{tb}**	**$DF_{alveolar}$**
Average	8.06	0.831	0.164	0.225	0.452
Std Dev	0.000	0.038	0.030	0.025	0.020
UFP size Bin					
	CMD (nm)	**DF**	**DF_{head}**	**DF_{tb}**	**$DF_{alveolar}$**
Average	30.13	0.618	0.065	0.119	0.433
Std Dev	5.803	0.000	0.000	0.000	0.000
FP size Bin					
	CMD (nm)	**DF**	**DF_{head}**	**DF_{tb}**	**$DF_{alveolar}$**
Average	127.16	0.204	0.020	0.019	0.106
Std Dev	29.448	0.000	0.000	0.000	0.000

- Deposition fraction calculations for UDDS cycle indicate that about 60% of particles in the nanoparticle size bin penetrate into the tracheobronchial and alveolar region.
- Similarly the idle mode operation from bus 2 showed a similar deposition trend for the nucleation mode size bin.
- The possible link between nanoparticle size bin, elemental fraction and toxicity responses illustrated in this study, may contribute to adverse health effects in the gas exchange and tracheobronchial regions of the airways.

EAD Vs. LDSA



EAD Aerosol Length		
	R	**p**
NP size bin lung deposited surface area	**0.980**	**0.000**
NP size bin alveolar deposited surface area	**0.980**	**0.000**
NP size bin Tracheobronchial deposited surface area	**0.920**	**0.000**
UFP size bin lung deposited surface area	**0.754**	**0.000**
UFP size bin alveolar deposited surface area	0.579	0.003
UFP size bin Tracheobronchial deposited surface area	0.625	0.001
NP size bin total particle number	0.690	0.000
UFP size bin total particle number	0.481	0.010

- The results show high correlation coefficient with high statistical significance between EAD response and lung and regional deposited surface area of particles of the NP size bin
- However, the particle surface area in the UFP size bin showed only reasonable correlation for lung deposited surface area and tracheobronchial deposited surface area and poor correlation with alveolar deposited surface area

CONCLUSIONS

- Elements and metals such as Ca, P, K, Zn, S and Mg were found in significant concentration in the PM samples. The findings of the study directly relate lubrication oil as the single most dominant source to non-volatile fraction PM emissions in the tailpipe.
- Both DHBA and DTT assay correlated highly with mass of elements and metals such as Zn, Fe and Co. The DTT assay resulted in high correlation with mass of Cu, Zn, P.
- Results link the source of the elemental and metal emissions to the lubrication oil additives that could gain entry into the exhaust system through various oil transport mechanisms such as piston rings and valve covers or through crankcase ventilation ducted into the intake of the engine.
- The possible existence of non-volatile particles in the size range of 10 nm emphasizes the need to further conduct a size segregated PM sampling to correlate the emission rates of elemental and metallic species from non-DPF equipped engines to its toxicity.

FUTURE WORK

- Scanning Electron Microscope (SEM) analysis of such nucleation mode particles could shed light on the metallic nature and physical morphology of the particles.
- Links between diffusion charging particle sensor output and toxicity could contribute to improved metrics for future PM regulations.
- Improved volatile removal processes such as a catalytic strippers could decrease the effects of sampling artifacts.

PUBLICATIONS

Journal Papers

1. **THIRUVENGADAM, A.**, BESCH, C. M., CARDER, D., OSHINUGA, A. & GAUTAM, M. 2011. Influence of Real-World Engine Load Conditions on Nanoparticle Emissions from a DPF and SCR Equipped Heavy-Duty Diesel Engine. *Environmental Science and Technology,* 46**,** 1907-1913.
2. **Thiruvengadam, A**.; Carder, D. K.; Krishnamurthy, M.; Oshinuga, A.; Gautam, M., Effect of an economical oxidation catalyst formulation on regulated and unregulated pollutants from natural gas fueled heavy duty transit buses. *Transportation Research Part D: Transport and Environment* ***2011, 16 (6), 469-473.***
3. Ardanese, R., Ardanese, M., Besch, M. C., Adams, T. R., **Thiruvengadam, A.**, Shade, B. C., et al. (2009). PM Concentration and Size Distributions from a Heavy-duty Diesel Engine Programmed with Different Engine-out Calibrations to meet the 2010 Emission Limits. *SAE* , 2009-01-1183.

Conference Presentation

1. **Thiruvengadam, A.** (Speaker),, Carder, D., Krishnamurthy, M., & Gautam, M. (2010). Comparison Of Regulated And Unregulated Exhaust Emissions From Twelve Multi-Fuel Solid Resource Collection Vehicles From The City Of Los Angeles. 20th CRC ON-ROAD VEHICLE EMISSIONS WORKSHOP. San Diego, CA.
2. **Thiruvengadam, A.** (Speaker),, Gautam, M., Besch, M., Ardanese, M., Ardanese, R., Thiagarajan, M., et al. (2009). PM Size Distributions from a DPF-SCR Equipped 2010 Compliant Heavy-Duty Diesel Engine during NTE zone operation. 18th CRC ON-ROAD VEHICLE EMISSIONS WORKSHOP. San Diego, CA.
3. **Thiruvengadam, A.** (Speaker),, Krishnamurthy, M., & Gautam, M. (2008). Reduction Of Regulated And Unregulated Emissions From Natural Gas Fueled Heavy Duty Transit Bus Equipped With An "Alternative" Oxidation Catalyst . 18th CRC ON-ROAD VEHICLE EMISSIONS WORKSHOP. San Diego, CA.