CRC Report: ACES Phase 2

PHASE 2 OF THE ADVANCED COLLABORATIVE EMISSIONS STUDY

NOVEMBER 2013

COORDINATING RESEARCH COUNCIL, INC.
5755 NORTH POINT PARKWAY SUITE 265·ALPHARETTA, GA 30022

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Research described in this report was conducted under contract to the Heath Effects Institute (HEI), and was made possible, in part, through support provided by the United States Department of Energy (DOE), under the terms of Contract/Award Number DE-AC26-05NT42429, and certain motor vehicle and engine manufacturers. The opinions expressed herein are those of the author(s) and do not necessarily reflect the views of HEI, or its sponsors, nor do they necessarily reflect the views of DOE or motor vehicle and engine manufacturers.

PHASE 2 OF THE ADVANCED COLLABORATIVE EMISSIONS STUDY

FINAL REPORT

SwRI® Project No. 03.17124

Prepared for and Sponsored by:

Coordinating Research Council, Inc.
5755 North Point Parkway Suite 265
Alpharetta, GA 30022

Health Effects Institute
101 Federal Street, Suite 500
Boston, MA 02110

Funded by:

Department of Energy, Office of Vehicle Technologies
Environmental Protection Agency
Truck and Engine Manufacturers Association
California Air Resources Board
American Petroleum Institute

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November 2013

SOUTHWEST RESEARCH INSTITUTE®
SAN ANTONIO, TX ● HOUSTON, TX ● WASHINGTON, DC

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FOREWORD

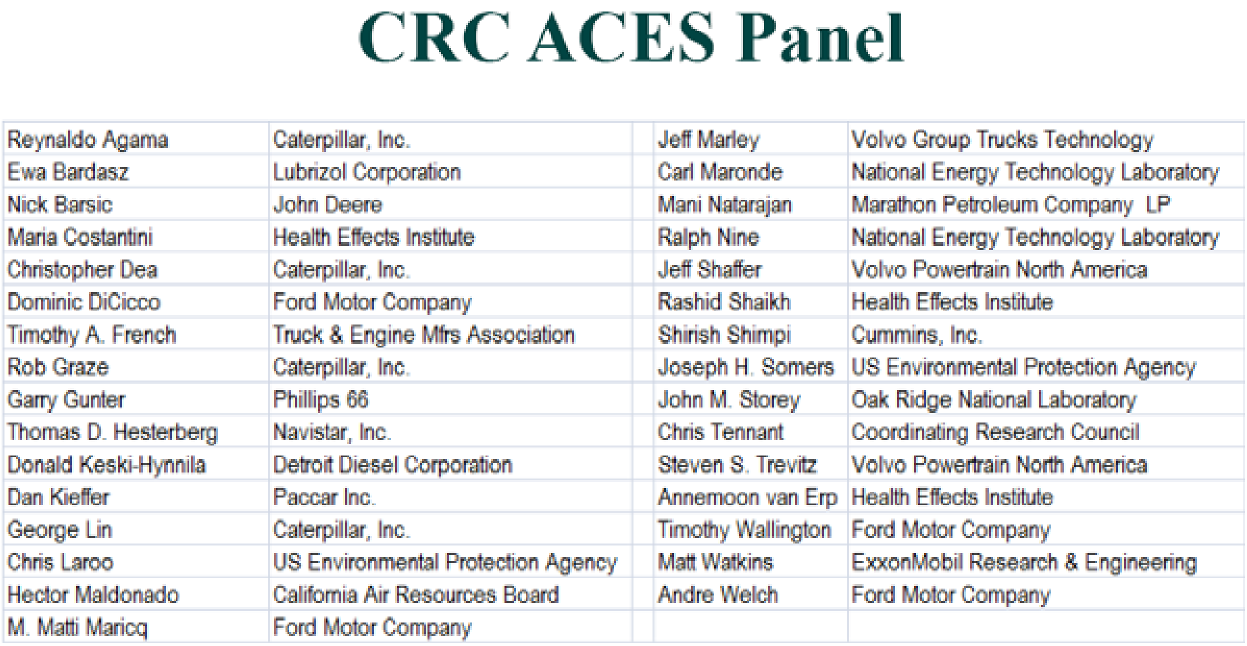
Phase 2 of the Advanced Collaborative Emissions Study (ACES Phase 2) was performed by the Department of Emissions R&D in the Engine, Emissions and Vehicle Research Division of Southwest Research Institute (SwRI).

SwRI's Principal Investigator and Project Manager was Dr. Imad Khalek (Senior Program Manager). Mr. Matt Blanks (Senior Research Engineer) was the Project Leader. Mr. Patrick Merritt (Principal Scientist) assisted in and coordinated the chemistry work. Mr. Vinay Premnath (Engineer), Mr. Richard Mechler (Senior Research Technologist), and Mr. Daniel Preece (Research Assistant) assisted in the particle measurement activities. Chemistry assistance was provided by Ms. Svitlana Kroll (Senior Research Scientist), Mr. Nolan Wright (Research Scientist), Ms. Yolanda Rodriguez (Staff Technician), Ms. Kelly Strate (Senior Technician), Mr. Chuan-Yi Tsai (Research Assistant), and Mr. Luis Sanchez (Assistant Supervisor). Additional assistance was provided by Mr. Chris Gourley (Senior Research Scientist), Ms. Shraddha Quarderer (Senior Research Scientist), and Ms. Jacqueline Ranger (Group Leader). Laboratory technical assistance was provided by Mr. Keith Echtle (Manager), Mr. David Elizondo (Supervisor), Mr. Tim Milligan (Staff Technician), Mr. Danny Terrazas (Supervisor), Mr. Joe Sosa (Principal Technician), and Mr. Rudy Guerra (Senior Technician).

The chemical analyses were performed by SwRI’s Department of Emissions R&D and SwRI’s Chemistry and Chemical Engineering Division. Additional chemical analyses such as PAHs, hopanes, steranes, alkanes, polar compounds, elements, and organic carbon/elemental carbon (OC/EC) were performed by Desert Research Institute (DRI), with Dr. Barbara Zielinska as the Principal Investigator. Urea related particle phase compounds were analyzed by Oak Ridge National Laboratory (ORNL), with Dr. John Storey as the Principal Investigator.

ACES Phase 2 was sponsored by the Coordinating Research Council and the Health Effects Institute (HEI), with funding from the DOE Office of Vehicle Technologies, Truck and Engine Manufacturers Association (EMA), Environmental Protection Agency (EPA), California Air Resources Board (CARB), and the American Petroleum Institute (API). The engines and engine support were provided by Cummins, Detroit Diesel, and Volvo Powertrain. Key contacts were Dr. Shirish Shimpi (Cummins), Mr. Don Keski-Hynnila (Detroit Diesel) and Mr. Jeff Shaffer (Volvo Powertrain). The lube oil was provided by Lubrizol, with Dr. Ewa Bardasz as a key contact.

The sponsors' project coordinators were Dr. Christopher Tennant from CRC, Dr. Maria Costantini and Dr. Rashid Shaikh from HEI. The CRC ACES Panel members included:



CRC ACES Panel

Reynaldo Agama	Caterpillar, Inc.	Jeff Marley	Volvo Group Trucks Technology
Ewa Bardasz	Lubrizol Corporation	Carl Maronde	National Energy Technology Laboratory
Nick Barsic	John Deere	Mani Natarajan	Marathon Petroleum Company LP
Maria Costantini	Health Effects Institute	Ralph Nine	National Energy Technology Laboratory
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Dominic DiCicco	Ford Motor Company	Rashid Shaikh	Health Effects Institute
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Garry Gunter	Phillips 66	John M. Storey	Oak Ridge National Laboratory
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M. Matti Maricq	Ford Motor Company		

EXECUTIVE SUMMARY

Introduction

Phase 2 of the Advanced Collaborative Emissions Study (ACES Phase 2) included detailed chemical characterization of exhaust species emitted from three 2011 model-year on-highway heavy heavy-duty diesel engines (HHDDE) in compliance with US Environmental Agency (EPA) 2010 emissions standards. The engines were supplied by Cummins, Detroit Diesel, and Volvo. They were randomly designated as Engine X, Engine Y, and Engine Z in this program to remain anonymous. Each engine had a total of 125 hours of manufacturer-run dynamometer operation prior to shipping to Southwest Research Institute® (SwRI®). Except for the urea-related compound analyses, the emissions characterizations performed under ACES Phase 2 were similar to those performed under ACES Phase 1 involving 2007 EPA-compliant on-highway HHDDE. According to the engine manufacturers, the 2011 ACES engines were obtained from the normal production supply, and are identical to those sold to customers during model year 2010. Throughout this report, the engines are referred to as 2010 engines to reflect the 2010 emissions compliance.

In 2010, EPA's stringent NO_X limit of 0.20 g/hp-hr became fully enforceable whereby the NO_X emissions limit decreased from an average level of 1.2 g/hp-hr between 2007 and 2009 to a level less than or equal to 0.20 g/hp-hr in 2010. To comply with the 2010 NO_X limit, on-highway heavy-duty engine manufacturers utilized a urea-based selective catalytic reduction (SCR) catalyst in engine exhaust placed downstream of a diesel oxidation catalyst (DOC) and a catalyzed diesel particulate filter (DPF) used for particulate matter (PM) emissions control. The engine manufacturers devoted substantial efforts to calibration of the urea dosing and mixing, SCR catalyst formulation, and engine control to achieve the desired NO_X reduction while maintaining a controlled level of ammonia slip using an ammonia oxidation (AMOX) catalyst downstream of the SCR catalyst. Improvements were also made in PM emissions control, eliminating the need for active regeneration (onboard cleaning via exhaust fuel injection upstream of DOC) of the DPF during ACES Phase 2 testing, compared to the several regeneration occurrences with the 2007 technology engines tested in ACES Phase 1.

In ACES Phase 1, we reported substantially lower regulated and unregulated emissions relative to the 2007 standard and to pre-2007 technology engines. With the anticipated changes in engine technology between 2009 and 2010, particularly the addition of the urea-based SCR catalyst in engine exhaust, the ACES Panel recognized earlier (before the launching of ACES Phase 1) the importance of documenting the emissions of 2010 technology engines through ACES Phase 2. With ACES Phase 1 and Phase 2 in place, one would have a more thorough and complete emissions characterization of modern heavy-duty on-highway diesel engines for the period between 2007 and 2009 (ACES Phase 1) and for post-2010 (ACES Phase 2).

Test Cycles and Emissions Measurements

We used the cold-start and hot-start Federal Test Procedures (FTP) transient cycle to determine if the engines met the applicable standard on regulated emissions species. We conducted three separate runs of the hot-start FTP and the 16-hour transient cycle (16-Hour), similar to ACES Phase 1, to characterize the regulated and unregulated emissions species in engine exhaust. Each 16-Hour ran over two 8-hour days with Day 1 as a hot-start and Day 2 as a cold-start. For each cycle, regulated emissions of carbon monoxide (CO), non-methane hydrocarbons (NMHC), oxides of nitrogen (NO_x) and particulate matter (PM) were measured. Unregulated emissions measurement included total hydrocarbons (THC), methane (CH_4), carbon dioxide (CO_2), nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), ammonia (NH_3), particle size distribution and number concentration, organic carbon (OC), elemental carbon (EC), metals and elements, inorganic ions, polynuclear aromatic hydrocarbons (PAH), nitroPAH, oxyPAH, polar compounds, alkanes, hopanes, steranes, cyanide ions, organic acids, gas phase acids, nitrosamines, detailed speciation of C_2 to C_{12} hydrocarbons, and carbonyls. Dioxins, furans and particle phase urea-related compounds were analyzed for the 16-Hour only.

Samples of the different exhaust species were taken either directly from the sample zone of the full-flow constant volume sampler (CVS) dilution tunnel (with a dilution ratio of 5 to 8) or from locations that were linked to the sample zone by a dilution step with a dilution ratio of approximately 2. Similar to ACES Phase 1, one sample location was an animal exposure chamber (unoccupied), provided by Lovelace Laboratory Research Institute (LRRI), to determine concentration levels that might be expected in future animal exposure such as those conducted in ACES Phase 3 on a 2007 technology engine. Real-time particle size distribution and number concentration, total PM, soot (as measured by MSS) and OC/EC measurements were taken from the exposure chamber. All measurements were performed with engine blow-by routed to the exhaust downstream of the urea SCR/AMOX catalysts.

Throughout this document, the emissions are reported on a work-specific basis (g/hp-hr) to represent the mass of emitted species over the brake-work produced by the engine during either the FTP or the 16-Hour. This is the official metric used in US EPA engine emissions regulations.

Reduction in Regulated Emissions for FTP Composite

Table ES-1 summarizes the average weighted brake-specific emissions for the FTP cold- and hot-start composite relative to the EPA 2010 standard. Brake-specific emission is a typical reported metric for engine emissions. Substantial reductions were observed for CO (97%), NMHC (>99.9%), PM (92%) and NO_X (61%). Figure ES-1 summarizes the emissions reduction relative to 2010, 2007, and 2004 standards. Relative to the 2004 standard, the reductions were 97% for CO, 97% for NO_X, >99.99% for NMHC, and 99% for PM.

TABLE ES-1. SUMMARY OF AVERAGE WEIGHTED REGULATED EMISSIONS BASED ON THE FTP COLD-START AND HOT-START COMPOSITE

	2010 EPA Standard (g/hp-hr)	[a]Weighted 2010 Engines Emissions (g/hp-hr)	Emissions % Reduction Relative to the 2010Standard
CO	15.5	0.50	97
NMHC	0.14	<0.001	>99
PM	0.01	0.0008	92
NO_X	0.20	0.08	61
[a](1/7×Cold-Start FTP) + (6/7×Hot-Start FTP)			

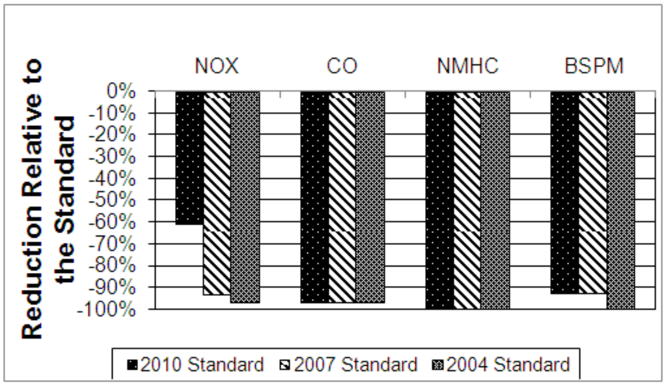

FIGURE ES-1. REGULATED EMISSIONS PERFORMANCE OF 2010 ENGINES RELATIVE TO 2010, 2007, AND 2004 EPA STANDARDS

Reduction in Regulated and Unregulated Average Emissions

Figure ES-2 summarizes the reductions in average emissions observed with the three 2010 technology engines relative to the average emissions of the four 2007 technology engines used in ACES Phase 1 for the 16-Hour. Substantial reductions in NO_X, NO_2, CO, NMHC, CH_4, PM, EC and OC mass, and particle number were observed. Greenhouse gas emissions based on CO_2, N_2O, and CH_4 led to no change in the 100-year global warming potential (GWP), as defined by the EPA. The reduction in CH_4 and the slight reduction in CO_2 observed with 2010 technology engines (Figure ES-2) were offset by the increase in N_2O (Figure ES-3) leading to no change in the GWP. Figure ES-3 shows that although N_2O emissions were higher with the 2010 technology engines compared to the 2007 technology engines, they were still below the EPA 2014 N_2O emissions limit of 0.1 g/hp-hr. The average N_2O emissions ranged from 0.052 g/hp-hr and 0.054 g/hp-hr for Engines X and Z to 0.11 g/hp-hr for Engine Y. The N_2O limit is a “cap” standard designed to prevent major increases in N_2O. The cap was set at approximately twice the level of N_2O emissions from 2008 heavy-duty diesel and gasoline engines[1].

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[1] CFR 76 179, page 1790, September 15, 2011

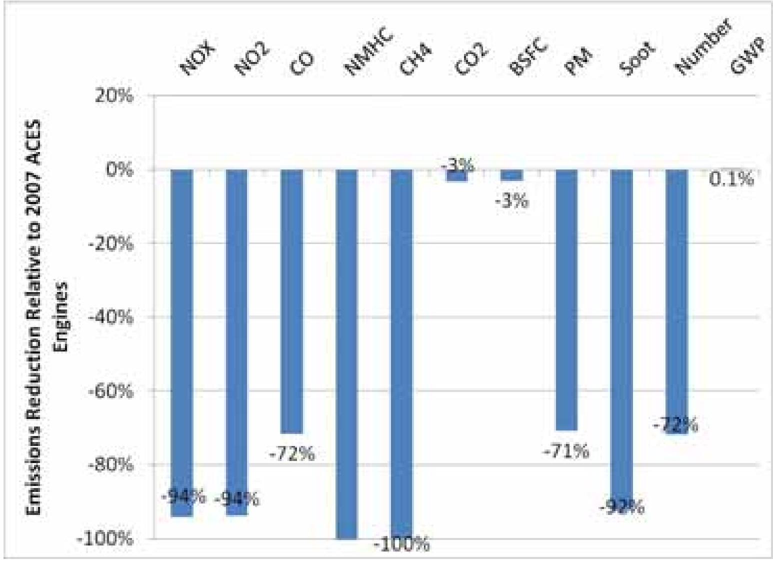

FIGURE ES-2. 2010 TECHNOLOGY ENGINES EMISSIONS REDUCTION RELATIVE TO 2007 TECHNOLOGY ENGINES FOR THE 16-HOUR

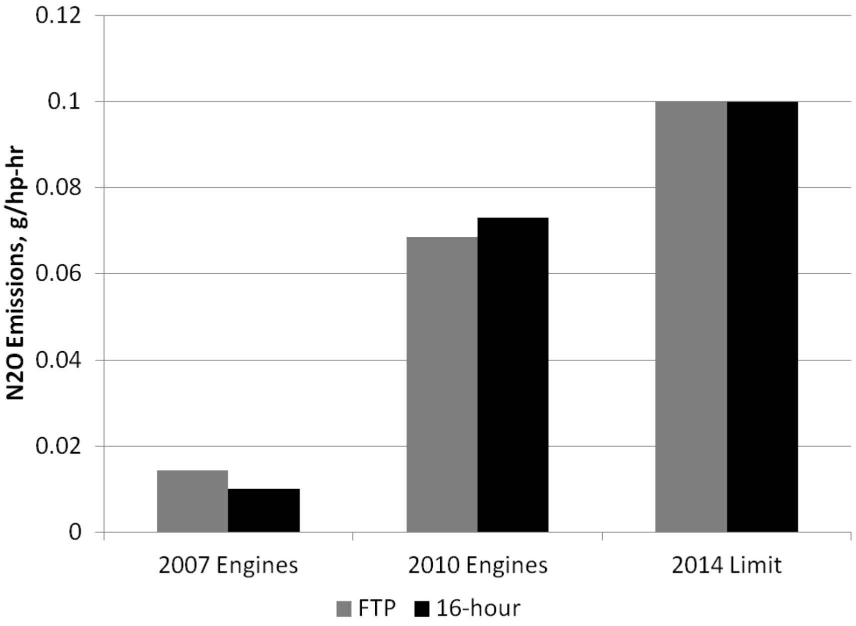

FIGURE ES-3. AVERAGE N_2O EMISSIONS COMPARISON FOR 2010 AND 2007 TECHNOLOGY ENGINES RELATIVE TO THE 2014 LIMIT

Table ES-2 shows the 2010 emissions reductions for several classes of unregulated emissions compounds relative to the 2007 technology engines used in ACES Phase 1, to a 2004 technology engine used in the CRC E55/59 study, and to a 1998 technology engine used for dioxins and furans. Very substantial reductions (91% to 100%) were observed relative to the 2004 technology engine. Substantial reductions (36% to 99%) were also observed relative to the 2007 technology engines.

TABLE ES-2. SUMMARY OF UNREGULATED EMISSIONS REDUCTION FOR 16-HOUR

	2010 % reduction relative to 2007 engines	2010 % reduction relative to 2004 engine
Single Ring Aromatics	50	91
PAH	97	99
NitroPAH	99	100
Alkanes	93	99
Polar	96	99
Hopanes & Steranes	89	100
Carbonyls	80	100
Inorganic Ions	87	92
Metals and Elements	81	100
Organic Carbon	36	97
Elemental Carbon	53	100
Dioxins and Furans[a]	88	100
[a]Relative to 1998 Technology Engine		

Urea-related Compounds

Out of six particle phase urea-related compounds for which we conducted analyses, only urea and cyanuric acid were detected. Even for those compounds, the emissions level was extremely low, with the highest cyanuric acid mass concentration level being just about 18 ppb in the undiluted engine exhaust, and the emissions in the range of 4.8 to 15.5 μg/hp-hr. The average exhaust concentration of ammonia (urea-related compound) due to ammonia slip ranged from 0.12 ppmv to 1.37 ppmv, depending on the engine and cycle used. This concentration range is much lower than the Euro VI limit of 10 ppm, and the potential US limit of 10 ppm to 15 ppm.

Particle Number Emissions

Interesting distinctions in particle number emissions and PM composition were observed between the 2010 and 2007 technology engines. Figure ES-4 (A) shows the total (solid + volatile) particle number emissions for the 2010, 2007, and 2004[2] technology engines for the FTP. Both the 2010 and 2007 had no active DPF regeneration events during the FTP. Substantial reduction (99%) in particle number was observed with the 2010 compared to the 2004 technology engine. Also, 2010 engines showed a 41% reduction in particle number relative to ACES Phase 1 2007 technology engines. Furthermore, a more substantial reduction of 72% was observed with the 2010 vs. 2007 engines when comparing the particle number emissions for the 16-Hour, shown in Figure ES-4 (B). For the 16-Hour, one distinction between the two technologies is that the 2010 engines DPF never actively regenerated during the entire ACES Phase 2 program, compared to 1 to 3 active regeneration events over one 16-Hour for the 2007 engines in ACES Phase 1. In ACES

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[2] SwRI Internal Data

Phase 1, active regeneration during 4-hour segments of the 16-Hour led to a one-order-of-magnitude increase in particle number emissions over 4-hour segments without active regeneration. Thus, it is not surprising that the particle number emissions reduction with the 2010 engines was higher for the 16-Hour, compared to the FTP, as shown in Figure ES-4.

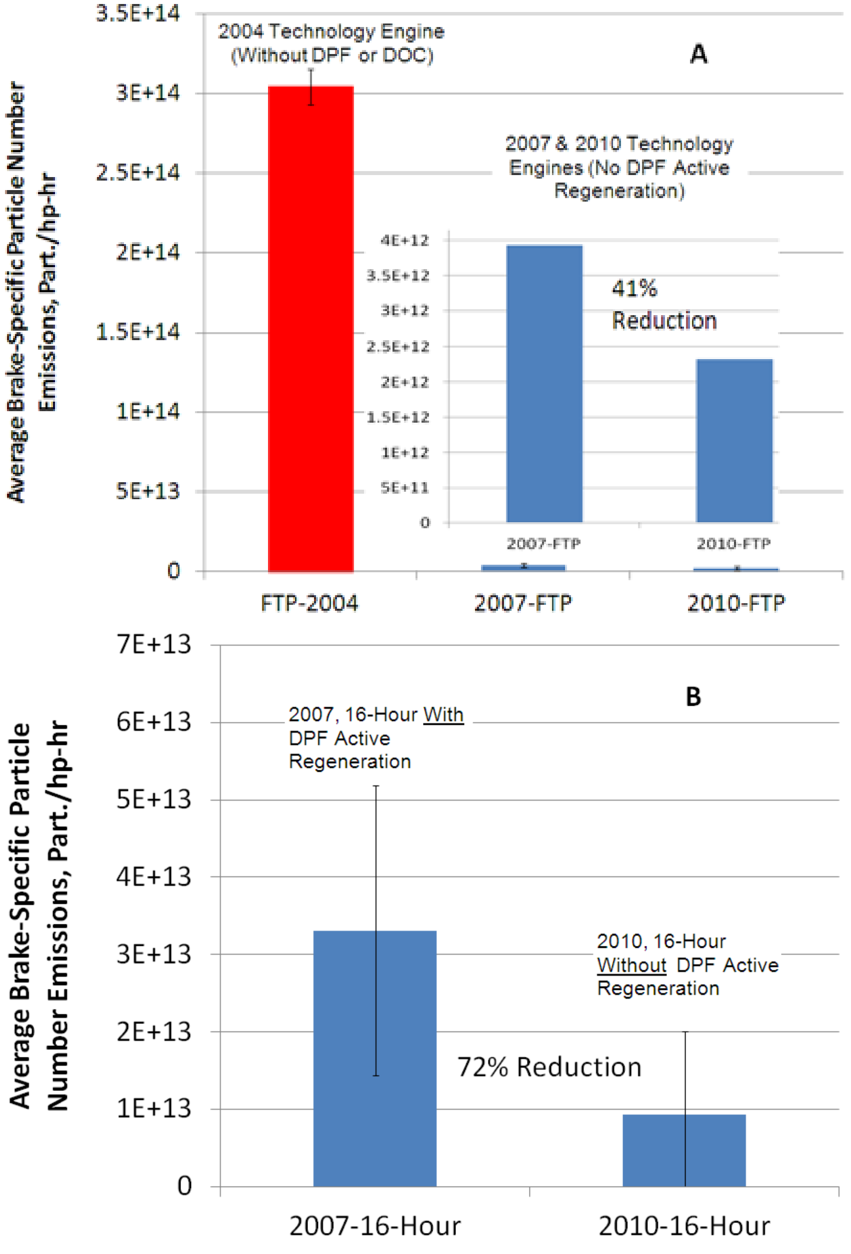

FIGURE ES-4. TOTAL (SOLID + VOLATILE) PARTICLE NUMBER EMISSIONS COMPARISON (A FOR FTP AND B FOR 16-HOUR)

PM Mass Emissions and Composition

Figure ES-5 and Table ES-3 show the main particle phase species contributing to PM emissions for the 2010 and 2007 technology engines. The reduction in PM mass in 2010 was mainly due to inorganic sulfate (SO_4^{2-}) ions, along with some elemental carbon (EC) and organic carbon (OC) reductions. PM composition in the 2010 technology engines also showed some levels of nitrate (NO_3^-) and ammonium ($NH4^+$) ions that were absent from the PM in 2007 technology engines. Nitrate and ammonium are likely to be derived products of the urea and SCR system interactions.

The substantial reduction in sulfate was intriguing. Since sulfur content in the fuel and lube oil was no different between 2007 and 2010, it is highly likely that the reduction in sulfate is due to sulfur adsorption by the various aftertreatment systems used in the engine exhaust, especially the DOC and DPF. Due to the lack of active DPF regeneration encountered with the 2010 engines, compared to 2007 technology engines, it is likely that the internal surfaces of the DOC and DPF never got hot enough for the adsorbed sulfur to be released in high concentration. This same phenomenon is also likely responsible for the additional reduction observed in particle number between 2010 and 2007 during the 16-Hour, where the additional reduction in particle number with the 2010 engines could be mainly due to the lack of sulfuric acid particle nucleation.

Figure ES-6 and Table ES-3 show the PM composition as a percent of total PM. For 2010 technology engines, the very low level of PM was dominated by OC (66%) followed by EC (16%) and nitrate (14%), compared to sulfate (53%) followed by OC (30%) and EC (13%) for the 2007 technology engines. Figures ES-5 and ES-6 also indicate that elements emissions were substantially lower with the 2010 vs. 2007 technology engines. The non-metallic elements were dominated by sulfur (fuel and oil derived) and metallic elements were dominated by calcium and zinc (lube oil derived) followed by iron and aluminum (engine wear).

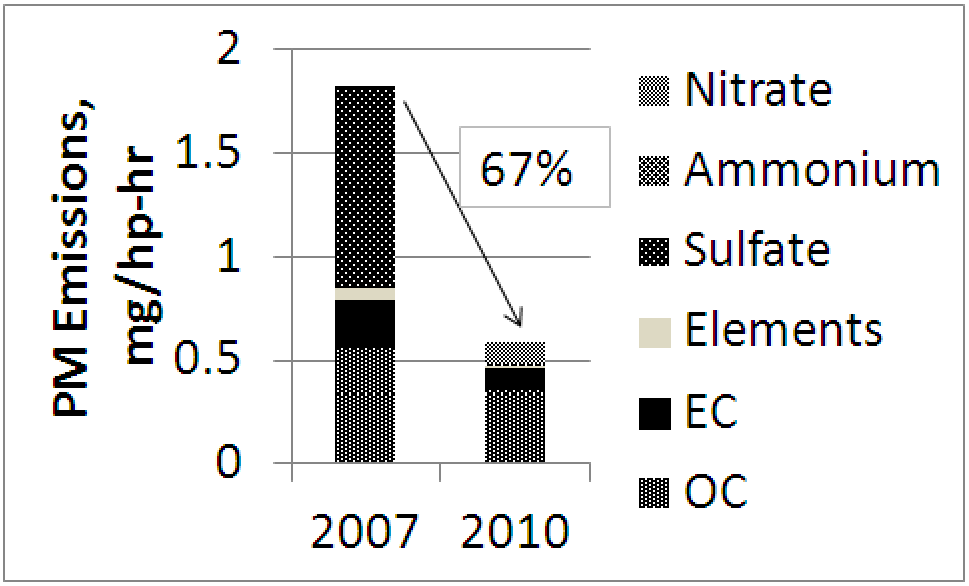

FIGURE ES-5. PM EMISSIONS COMPARISON BETWEEN 2010 AND 2007 TECHNOLOGY ENGINES (16-HOUR)

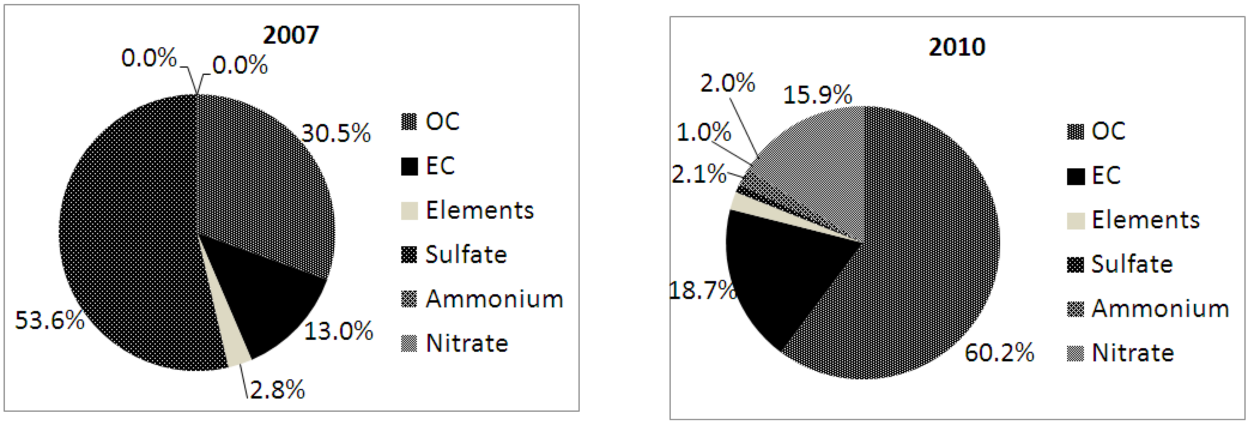

FIGURE ES-6. SUMMARY OF THE PM PERCENT COMPOSITION FOR 2010 AND 2007 TECHNOLOGY ENGINES

TABLE ES-3. SUMMARY OF PM EMISSIONS AND COMPOSITION FOR 2010 AND 2007 ENGINES

	OC	EC	Elements	Sulfate	Ammonium	Nitrate
	mg/hp-hr					
2007	0.556	0.238	0.052	0.978	0.000	0.000
2010	0.457	0.110	0.012	0.006	0.012	0.094
	% of total					
2007	30.5%	13.0%	2.8%	53.6%	0.0%	0.0%
2010	66.2%	15.9%	1.8%	0.8%	1.7%	13.6%

Summary

ACES Phase 2 demonstrates another large step in emissions reduction with 2010 EPA-compliant on-highway heavy heavy-duty diesel engines. The 2010-compliant engines showed substantially lower regulated emissions of NO_X, CO, NMHC, and PM relative to the 2010 standard. They also showed a substantial reduction in a very wide spectrum of particle and gas phase unregulated emissions species relative to pre-2007 and 2007 technology engines.

The observed reductions in PM (total mass, soot, and number) and unregulated emissions from 2007 to 2010 engines are likely due to differences in active DPF regeneration operation. The 2007 engines triggered multiple regeneration events during the 16-hour cycles, while the 2010 engines did not trigger any events. The improvement/reduction in regeneration was achieved through some combination of lower engine-out PM, increased passive regeneration and improved control strategies. PM emissions during regeneration events have been observed to be higher than normal operation for the 2007 engines used in ACES Phase 1. Unregulated emissions are believed to be higher during regeneration events. Thus, the results from the 2007 engines include emissions measured over both normal (no active regeneration) and regeneration operation, while the results from the 2010 engines only include emissions measured over normal operation. DPF active regeneration would have occurred had the 2010 engines been run for a much longer period of time (100 or more hours). The 2010 engines did not trigger a regeneration event even after three back-to-back 16-hour cycles (48 hours of operation).

According to the engine manufacturers, the process and length of time for DPF active regeneration is expected to be similar for 2010 and 2007 engines. Therefore, the emissions during regeneration events are expected to be similar except for any differences due to increased loading of certain species like sulfur and heavy molecular weight hydrocarbons that are not oxidized by the aftertreatment system. Since 2010 engines have fewer regeneration events, the PM and unregulated emissions averaged over both normal and active regeneration operation are expected to be lower than 2007 engines. While it is not known how much the average PM and unregulated emissions on the 2010 engines may have increased if the test were continued to include regeneration events, the consensus of this study's principal investigator and its sponsors is that the 2010 engines' PM and unregulated emissions averaged over both normal and active regeneration operation are somewhere between the results measured during normal operation and the results measured on the 2007 engines over both normal and active regeneration operation.

Finally, all analyzed species including second-by-second data will be posted on the publically accessible CRC website at http://www.crcao.org.

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ACRONYMS AND ABBREVIATIONS

ACES	Advanced Collaborative Emissions Study
API	American Petroleum Institute
AMOX	Ammonia Oxidation Catalyst
BG	Background (clean dilution air downstream of the HEPA filter of the full flow constant volume sampler tunnel)
BSE	Brake-Specific Emissions
BSFC	Brake Specific Fuel Consumption
CARB	California Air Resources Board
CFR	Code of Federal Regulations
CI	Chemical Ionization
CO	Carbon Monoxide
CRC	Coordinating Research Council
CVAAS	Cold Vapor Atomic Absorption Spectroscopy
CVS	Constant Volume Sampler
DCM	Dichloromethane
DMM	Dekati Mass Monitor
DNPH	Dinitrophenylhydrazine
DOE	Department of Energy
DOC	Diesel Oxidation Catalyst
DPF	Diesel Particulate Filter
DR	Dilution Ratio
DRI	Desert Research Institute
DFI/GC	Direct Filter Injection Gas Chromatography
EC	Elemental Carbon
ECM	Engine Control Module
EDXRF	Energy Dispersive X-Ray Fluorescence
EEPS	Engine Exhaust Particle Sizer
EGR	Exhaust Gas Recirculation
EI	Electron Impact
EMA	Truck and Engine Manufacturers Association
EPA	Environmental Protection Agency
ER&DD	Emissions Research and Development Department
FD	Fuel Density
FID	Flame Ionization Detector
FM	Fuel Mileage
FTIR	Fourier Transform Infrared Spectroscopy
FTP	Federal Test Procedure Transient Cycle
GC-ECD	Gas Chromatography-Electron Capture Detection
GC/MS	Gas Chromatograph/Mass Spectrometry
HDDE	Heavy-Duty Diesel Engine
HEI	Health Effects Institute
HEPA	High Efficiency Particulate Air
HHDDE	Heavy Heavy-Duty Diesel Engine
HPLC	High Performance Liquid Chromatography
HRGC	High Resolution Gas Chromatography
HRMS	High Resolution Mass Spectroscopy

IC	Ion Chromatography
ICPMS	Inductively Coupled Plasma/Mass Spectroscopy
LRRI	Lovelace Respiratory Research Institute
MID	Multiple Ion Detection
N/A	Not Available
MSS	Micro-Soot Sensor
NDIR	Non-Dispersed Infrared
NIST	National Institute of Standards and Technology
NitroPAH	Nitrated Polycyclic Aromatic Hydrocarbon
NMHC	Non-Methane Hydrocarbon
NO	Nitric oxide
NO_2	Nitrogen Dioxide
N_2O	Nitrous Oxide
NO_X	Oxides of Nitrogen
OC	Organic Carbon
ODS	Octadecasilane
ORNL	Oak Ridge National Laboratory
POC	Principle Organic Constituents
OxyPAH	Oxygenated Polycyclic Aromatic Hydrocarbon
PAH	Polycyclic Aromatic Hydrocarbon
PCDD	Polychlorinated Dibenzodioxins
PCDF	Polychlorinated Dibenzofurans
PM	Particulate Matter
PTFE	Polytetrafluoroethylene
PUF	Polyurethane Foam
SCFM	Standard Cubic Feet per Minute
SIS	Selective Ion Storage
SLPM	Standard Liters per Minute
S/N	Signal to Noise
SRM	Standard Reference Material
SVOC	Semivolatile Organic Compound
SwRI	Southwest Research Institute
TB	Tunnel Blank
TEF	Toxic Equivalency Factor
TEQ	Toxic Equivalent
THC	Total Hydrocarbon
TOR	Thermal Optical Reflectance
TOT	Thermal Optical Transmittance
ULSD	Ultra-low Sulfur Diesel
UV	Ultraviolet
VOC	Volatile Organic Compounds
VOST	Volatile Organic Sample Train
XAD^{TM}	“Polymeric Adsorbing Resins”
XRF	X-Ray Fluorescence

1.0 INTRODUCTION

Significant changes in on-highway, heavy-duty diesel engine technology took place between 1998 and 2010. While there were many improvements made in engine combustion, injection systems, turbochargers, and exhaust gas recirculation to reduce emissions, such improvements alone were not sufficient to meet EPA 2007 and 2010 emissions standards. Engine manufactures utilized four forms of aftertreatment technologies to assist in meeting the 2007 and 2010 emissions limits. As depicted in Figure 1, in 2007, due to a very stringent PM standard, diesel oxidation catalysts (DOC) followed by high efficiency catalyzed diesel particle filters (DPF) were introduced to diesel engine exhaust. A diesel injection system was also added upstream of the DOC to assist in regenerating or cleaning the DPF as needed. By injecting fuel upstream of a hot DOC, an exothermic reaction can take place raising the temperature upstream of the DPF to help oxidize the trapped EC and heavy molecular weight hydrocarbons. To meet the 2010 NO_X standards, a urea-based SCR system was also introduced to the exhaust downstream of the DPF for NO_X reduction. A separate urea dosing system upstream of the SCR along with a urea tank were also required. An ammonia oxidation (AMOX) catalyst was also added downstream of the SCR to minimize ammonia slip.

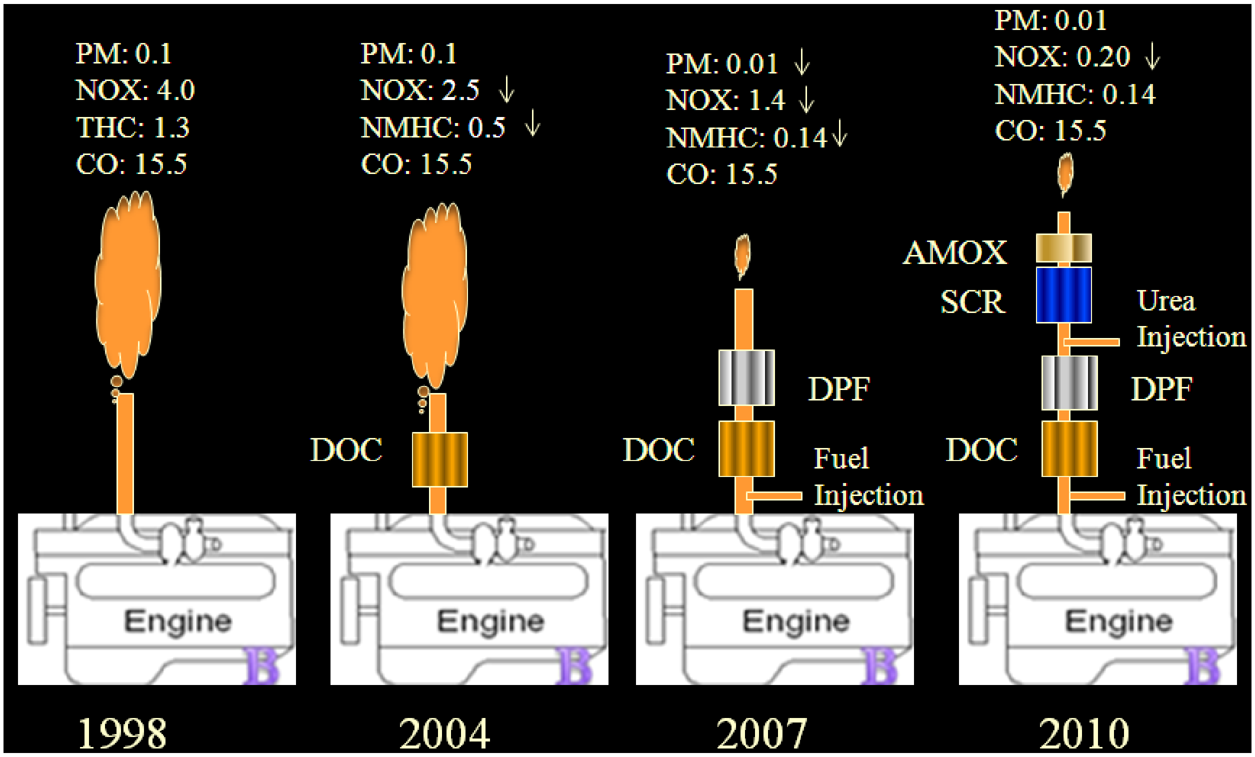

FIGURE 1. CHANGES IN THE EXHAUST OF ON-HIGHWAY HEAVY-DUTY DIESEL ENGINE TECHNOLOGY BETWEEN 1998 AND 2010

In anticipation of these technological changes in 2007 and later in 2010, there was a strong interest in thoroughly documenting the regulated and unregulated emissions impact of these engine technologies along with their impacts on potential health effects. In 2007, the ACES panel launched the ACES Phase 1 project[3,4], where we performed a detailed emissions

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[3] Khalek et al., CRC ACES Phase 1 Final Report, 2009,

characterization on four 2007 heavy-duty on-highway technology engines. One of the engines was selected for a detailed health study by the Lovelace Respiratory Research Institute (LRRI) as a part of the ACES Phase 3[5]. In 2010, the ACES panel launched ACES Phase 2 as a continuation of ACES Phase 1 to fully characterize the emissions from 2010 EPA-compliant heavy-duty, on-highway technology engines. In both ACES Phase 1 and ACES Phase 2, the engines were brand new with only 125 hours of engine operation prior to testing at SwRI.

Three diesel engine manufacturers (Cummins, Inc., Detroit Diesel Corporation (DDC) and Volvo Powertrain) provided engines and engine support for the ACES Phase 2 program. The engines were all 2011 model-year and included a Cummins ISX, Detroit Diesel DD15, and a Mack MP8. All three engines are considered to be heavy heavy-duty on-highway diesel engines that are currently being marketed in the United States (US). The engines were all brand new, but had 125 hours of a manufacturer-run break-in and degreening operation prior to shipping to SwRI for testing. Throughout the ACES Phase 2 project, all engines remained anonymous, and were randomly designated as Engine X, Engine Y, and Engine Z. It is understood that the identity of the engines will be revealed by CRC at a later time

The three engines (Engines X, Y, and Z) were tested for regulated and unregulated emissions using the hot-start Federal Test Procedure (FTP) and the 16-Hour[6] (16-Hour) that was used in ACES Phase 1. Prior to using the engines for official measurement of regulated and unregulated emissions, the engines were tested using a composite of a cold-start and a hot-start FTP to verify their compliance with the 2010 standard.

Regulated emissions measurements included carbon monoxide (CO), non-methane hydrocarbon (NMHC), oxides of nitrogen (NO_x), and particulate matter (PM). Unregulated emissions included total hydrocarbon (THC), methane (CH_4), carbon dioxide (CO_2), nitric oxide (NO), nitrogen dioxide (NO_2), ammonia (NH_3), particle size distribution and number concentration, organic carbon, elemental carbon, metals and elements, inorganic ions, polynuclear aromatic hydrocarbon (PAH), nitroPAH, oxyPAH, polar compounds, alkanes, hopanes, steranes, cyanide ion, organic acids, gas phase acids, nitrosamines, detailed speciation of $C_2 – C_{12}$ hydrocarbons, aldehydes and ketones, dioxins and furans, and six particle phase urea-related compounds.

All volumetric flows, volumes or concentrations shown in this report are based on a reference temperature of 20°C and a pressure of 101.3 kPa. All averages, standard deviations, and error bars are based on three repeats of the FTP and three repeats of the 16-Hour.

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http://www.crcao.org/reports/recentstudies2009/ACES%20Phase%201/ACES%20Phase1%20Final%20Report%2015JUN2009.pdf

[4] Khalek I, T. Bougher, P. Merritt, and B. Zielinska, “Regulated and Unregulated Emissions from Highway Heavy-Duty Diesel Engines Complying with U.S. Environmental Protection Agency 2007 Emissions Standards,” Submitted to *Journal of Air & Waste Management Association, March 2011*

[5] McDonald et al., “Advanced Collaborative Emissions Study (ACES) Subchronic Exposure Results: Biologic Responses in Rats and Mice and Assessment of Genotoxicity,” HEI Research Report No. 166 http://www1.eere.energy.gov/vehiclesandfuels/pdfs/deer_2010/thursday/presentations/deer10_greenbaum.pdf

[6] Clark, N.N., F. Zhen, C. Bedick, M. Gautam, W. Wayne, G. Thompson, and D. Lyons, “Creation of the 16-Hour Engine Test Schedule from the Heavy Heavy-Duty Diesel Engine Test Schedule,” CRC Report No. ACES-1-a, CRC Website at crcao.org, 2007

2.0 EXPERIMENTAL SETUP

2.1 Engines

Three 2011 model year (MY2011) on-highway, heavy-duty diesel engines, described in Table 1, were used in ACES Phase 2. They included a Cummins ISX (Cummins, Inc), Detroit Diesel DD15 (Detroit Diesel Corporation), and Mack MP8-415C (Volvo Powertrain). The power rating for the inline 6-cylinder engines ranged from 415 to 500 horsepower. The exhaust aftertreatment configuration included a DOC, DPF, SCR and an AMOX. Urea dosing was used for the SCR system, and diesel fuel injection was used when needed to actively regenerate the DPF. The exhaust system also included a turbocharger, a high-pressure loop exhaust gas recirculation (EGR) system with an EGR cooler, and NO_X sensors for active emissions control. The blow-by stream path included a separator before being vented to the atmosphere. The induction system was air to air cooled in a truck operation, but was water-cooled in the laboratory setting.

TABLE 1. ENGINE SPECIFICATIONS

Engine Series	ISX	DD15	MP8-415C
Manufacturer	Cummins	Detroit Diesel	Volvo Powertrain
Emissions Compliance	2010	2010	2010
Model year	2011	2011	2011
Displacement, liter	15	15	13
Rated Power, hp	500	455	415
Exhaust System	Turbocharged	Turbocharged	Turbocharged
Induction System	Compressed/Air to Air Cooled	Compressed/Air to Air Cooled	Compressed/Air to Air Cooled
Exhaust Configuration	(DOC+DPF)+SCR+AMOX	(DOC+DPF)+SCR+AMOX	(DOC+DPF)+SCR+AMOX
Exhaust NOX Sensors	Yes	Yes	Yes
Blow-By Configuration	Separator/Vented to Atmosphere	Separator/Vented to Atmosphere	Separator/Vented to Atmosphere
SCR Exhaust Fluid	Urea	Urea	Urea
DPF Active Regneration Exhaust Fluid	Diesel	Diesel	Diesel

2.2 Fuel, Urea, and Oil Properties

2.2.1 Fuel ASTM Properties and Elements

The ACES program fuel was provided by CRC through a commercial fuel supplier. It was a typical refinery commercial ultra-low sulfur diesel (ULSD) fuel that conformed to US EPA CFR Part 1065[7] ULSD fuel specifications. ASTM fuel properties are shown in Table 2. To ensure that no fuel contamination was introduced between the fuel tank and the engine, we changed all fuel sampling infrastructure into stainless steel tubing, similar to that done in ACES Phase 1. As shown in Table 2, no differences were observed in fuel properties between what was sampled directly from the fuel tank and what was sampled from the fuel system at the engine before the injection pump. The fuel has a sulfur level of 6.5 ppm, a cetane number of 48, and total aromatics of 32% (by volume). The cetane number was similar to that of the ACES Phase 1 fuel, but the sulfur level was 44% higher and the aromatics were 20% higher than those reported for ACES Phase 1 fuel. Higher initial and final boiling points of about 20°F to 30°F were also observed in ACES Phase 2 fuel, compared to ACES Phase 1 fuel.

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[7] http://www.ecfr.gov/cgi-bin/text-idx?c=ecfr&tpl=/ecfrbrowse/Title40/40cfr1065_main_02.tpl

TABLE 2. ASTM FUEL PROPERTIES

			Fuel Tank	Engine Pump
ASTM Method	**Test Property**	**Test Units**	**EM-8050-F**	
D86	**Distillation**		**Results**	**Results**
	IBP	deg F	346	342
	5% Evaporated	degF	384	378
	10% Evaporated	degF	403	402
	15% Evaporated	degF	421	419
	20% Evaporated	degF	436	435
	30% Evaporated	degF	465	463
	40% Evaporated	degF	490	488
	50% Evaporated	degF	512	511
	60% Evaporated	degF	533	533
	70% Evaporated	degF	555	555
	80% Evaporated	degF	578	578
	90% Evaporated	degF	607	608
	95% Evaporated	degF	632	633
	FBP	degF	655	657
	Vol% Recovered	mL	97.5	96.7
	Vol% Residue	mL	1.4	1.5
	Vol% Loss	mL	1.1	1.8
D130	Copper Corrosion Strip	rating	1A	1A
D1319	Aromatics	vol%	32.7	31.9
	Olefins	vol%	2.6	2.5
	Saturates	vol%	64.7	65.6
D1796	Water & Sediment	mL	0.0	0.0
D2500	Cloud Point	°C	-11	-12
D4052s	API Gravity		36.6	36.5
	Specific Gravity		0.8418	0.842
D445	Viscosity at 40°C	cSt	2.631	2.616
D482	Ash Content	mass%	<0.001	<0.001
D5291	Carbon Content	wt%	86.56	86.44
D5291	Hydrogen Content	wt%	13.35	13.3
D5453	Sulfur Content	ppm	6.5	6.5
D6079	Lubricity by HFRR			
	Major Axis	mm	0.473	0.483
	Minor Axes	mm	0.399	0.41
	Wear Scar Diameter	mm	0.436	0.447
	Wear Scar Description		evenly abraded oval	evenly abraded oval
	Fuel Temperature	degC	60	60
D613	Cetane Number		48	48.1
D93	Flash Point	degF	148	147
D93	Flash Point	degC	65	64
D976	Cetane Index	calculated	50.4	50.5

2.2.2 *Urea for SCR*

The urea was obtained from Brenntag, a major supplier of diesel exhaust fluid (DEF) in North America. It is a TerraCair Ultrapure DEF (32.5% aqueous urea solution) that meets ISO 22241-1:2006. TerraCair Ultrapure DEF is also certified by API and meets the quality standard set by the engine manufacturers' service warranties.

2.2.3 *Lube Oil ASTM Analyses and Elemental Composition*

The lube oil was provided by Lubrizol. It is an API CJ-4 lube oil, which is typically used in post 2007 technology on-highway diesel engines. Table 3 shows the ASTM analyses for the fresh lube oil, and for the used lube oil after 125 hours of break-in and degreening that was performed by the respective engine manufacturers. The dominant elements observed in the fresh lube oil were calcium (2233 ppm), phosphorus (1020 ppm), zinc (1157 ppm), and sulfur (4018 ppm). These were very similar to ACES Phase 1 lube oil, although sulfur was not measured in ACES Phase 1. The used lube oil had some higher levels of boron, copper, magnesium, iron, and silicon, compared to the fresh oil, implying that these elements were accumulated in the oil during normal lubrication. Sulfur in the used oil was about 10% lower for Engine X and Y, compared to fresh oil, and it was 22% lower for Engine Z. There is no clear understanding and/or explanation for the differences observed, nor how they impact emissions if any.

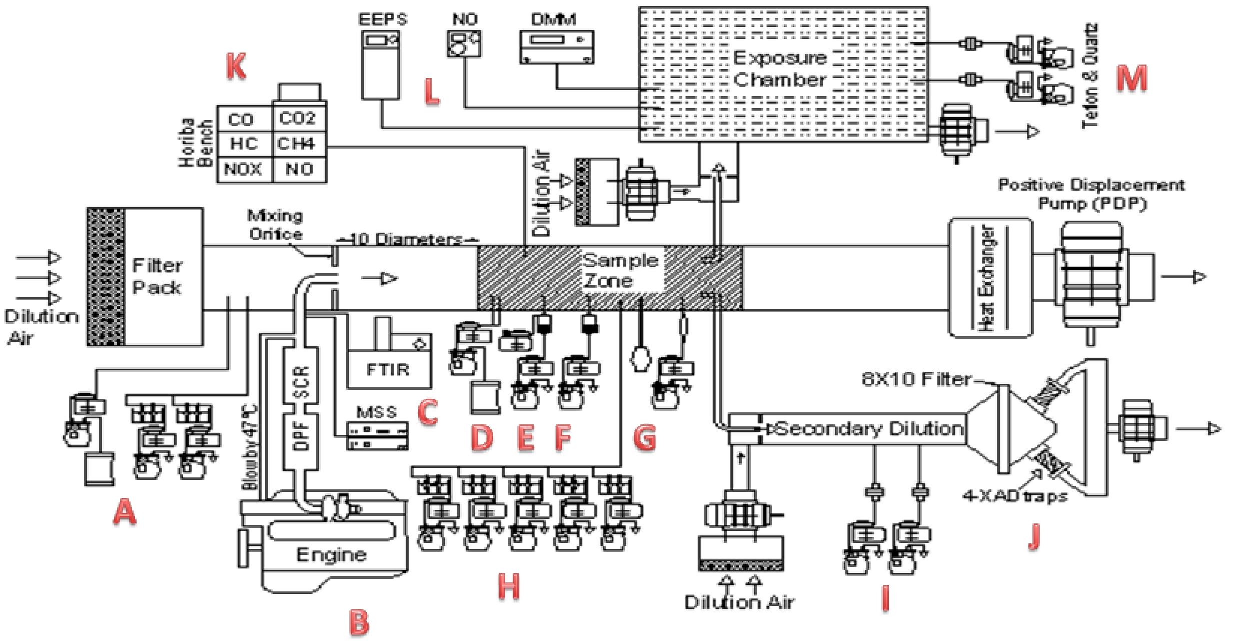
2.3 Sampling System

The sampling system for ACES Phase 2 is shown in Figure 2. It is similar to that used in Phase 1, with the exception of the additional 90 mm TX-40 filter collection for the urea-related particle phase compounds such as urea, melamine, cyanuric acid, ammelide, ammeline, and biuret which were analyzed by ORNL. In addition, the FTIR instrument was used for the measurement of ammonia and N_2O in the raw engine exhaust. Measurements and collection for different species from various locations along the sampling system are described below the schematic in Figure 1. Note that the filtered blow-by from the crankcase vent was routed to a location downstream of the SCR catalyst using a 47°C stainless steel sample line for all experiments conducted under ACES Phase 2. This is an EPA requirement to account for the filtered blow-by emissions contribution along with exhaust emissions since the filtered blow-by is routed to the atmosphere in heavy heavy-duty trucks.

The combustion intake air was humidity and temperature controlled in accordance with CFR Part 1065. The CVS air was a HEPA filtered air drawn from outside the airconditioned laboratory envrionment outside the test cell. The constant volume sampler (CVS) was maintained at a nominal flow rate of 1650 sfm for all three engines tested in this program. The relative humdity was in the range of 40% to 60%, but was uncontrolled. The minimum dilution ratio between the engine exhaust and the 47 mm filter (CVS dilution mutiplied by 47 mm filter dilution) was set between a dilution ratio of 5 and 7 at rated engine power operation, in accordance with the new requirement in 40 CFR Part 1065. The minimum dilution ratio in ACES Phase 2 was nearly a factor of 2 lower than that used in ACES Phase 1 to enhance the detection limit of the emissions measurements and to conform to the latest minimum dilution ratio requirement in CFR Part 1065 that was still under development during ACES Phase 1. The average dilution ratio between the engine exhaust and the CVS for the FTP and 16-Hours was between 5 and 8, depending on the engine used. The dilution ratio between the CVS tunnel and various filter locations such as the exposure chamber filters (M), auxiliary filters (I), 8 x 10 inch filter assembly (J) and 47 mm CFR Part 1065 filter (E) was set to a nominal dilution ratio of 2. For the urea collected compounds, a special sampling system was developed with no dilution ratio step between the CVS and the 90 mm filter (F). This was used to improve the detection limit of these compounds since they have high boiling point temperatures and the dilution ratio should have no effect on them. The dilution ratio DR is defined as: DR = (dilution air flow + sample flow)/(sample flow)

TABLE 3. LUBE OIL PROPERTIES FOR FRESH OIL AND AFTER 125 HOURS OF ENGINE AND DPF DEGREENING BY THE ENGINE MANUFACTURER

ASTM Test	Test Property / Description	Units	EM-3380-EO Fresh Lube Oil	EM-3382-EO Used Oil Engine X	EM-3381-EO Used Oil Engine Y	EM-3379-EO Used Oil Engine Z
D3524M	Fuel Dilution, Diesel	wt %		0.6	<0.3	<0.3
D4291	Glycol	ppm	<100	<100	<100	<100
D445	Viscosity @ 100 °C	cSt	15.38	13.37	14.18	13.56
D445	Viscosity @ 40 °C	cSt	116.8	97	103.8	101.4
D5185S	Sulfur by ICP	Wt. %	0.402	0.366	0.36	0.314
	Sulfur by ICP	ppm	4018	3660	3596	3144
D5185	Element Analysis					
	Aluminum	ppm	2	2	3	3
	Antimony	ppm	<1	<1	<1	2
	Barium	ppm	<1	<1	<1	3
	Boron	ppm	1	3	10	2
	Calcium	ppm	2233	2212	2022	2115
	Chromium	ppm	<1	<1	<1	<1
	Copper	ppm	<1	9	98	8
	Iron	ppm	2	13	17	15
	Lead	ppm	<1	2	<1	3
	Magnesium	ppm	6	71	190	112
	Manganese	ppm	<1	<1	2	6
	Molybdenum	ppm	<1	4	11	6
	Nickel	ppm	<1	3	1	<1
	Phosphorus	ppm	1020	981	969	964
	Silicon	ppm	4	30	4	30
	Silver	ppm	<1	<1	<1	<1
	Sodium	ppm	<5	5	5	8
	Tin	ppm	<1	<1	3	<1
	Zinc	ppm	1157	1187	1136	1168
	Potassium	ppm	6	<5	<5	<5
	Strontium	ppm	<1	<1	<1	<1
	Vanadium	ppm	<1	<1	<1	<1
	Titanium	ppm	<1	<1	<1	3
	Cadmium	ppm	<1	<1	<1	<1
D4739	Total Base Number					
	Inflection	mg KOH/g	7.74	6.18	6.78	6.62
	Buffer	mg KOH/g	7.62	4.91	5.5	5.83
D664	Total Acid Number					
	Inflection	mg KOH/g	N/A	N/A	N/A	N/A
	Buffer	mg KOH/g	1.25	1.94	1.94	1.85
E168	FTIR (Oxidation & Nitration)		0	2.83	2.37	0.67
	Diff. @ 5.8um	ABS/cm	0	0.09	0	0
	Diff. @ 6.1um	ABS/cm	0.7	0.7	0.8	0.7
TGA	Residue	wt %	0.109	0.41	0.473	0.339
	Volatiles	wt %	99.2	98.9	98.8	98.9
	Elemental Carbon	wt %		0.6	<0.3	<0.3



A Background bag sample of dilution air for CO, CO_2, NO_X, NO, NO_2, total hydrocarbon, CH_4, and C_2-C_{12} speciation. Impingers for Carbonyls & Alcohols

B 2010 Heavy-Duty Diesel Engine with DOC-DPF-SCR

C FTIR for NH_3 and N_2O measurements

D Proportional bag sample for hydrocarbon speciation of C_2-C_{12} compounds

E Regulated PM followed CFR Part 1065 using 47mm Teflon membrane filter (Whatman). The same filter is also used for elemental analysis using EDXRF and ICP-MS

F 90mm TX-40 filter system, which will be used for particle phase urea-related compounds (Urea, melamine, cyanuric acid, ammelide and ammeline

G Sorbent traps for nitrosamines and Summa canister for SVOC

H Impingers for carbonyls using DNPH, alcohols using de-ionized water, cyanide ions using KOH, SO_2 using H_2O_2, and NH_3+ using H_2SO_4

I Auxiliary PM samples on 47mm filters for inorganic ions (TX-40 filter), DFI GC/SOF (TX-40 filter)

J Filter (8"x10" Zefluor) for particulate-phase semi-volatile compounds: PAH, oxyPAH, nitroPAH, dioxins, furans, hopanes, steranes, carpanes, polar organics, high molecular weight alkines and cycloalkanes, dioxins, furans. Four XAD traps for gas phase semi-volatile compounds: PAH, oxyPAH, nitroPAH, hopanes, steranes, carpanes, polar organics, high molecular weight alkanes and cycloalkanes, dioxins, furans

K Horiba MEXA 7200 for total hydrocarbon, CH_4, CO, CO_2, Nox, and NO measurements

L PM mass size and number using EEPS, real time total PM using DMM-230, real time soot using MSS, NO Measurement using chemiluminescent analyzer

M PM mass using Teflon membrane filter (Whatman), OC/EC collection using a pair of quartz filters

FIGURE 2. ACES PHASE 2 OVERALL SAMPLING SYSTEM

3.0 TEST MATRIX

Table 4 shows the series of tests that were performed for each of the three ACES Phase 2 engines. The first series of regulated emissions testing is to confirm the engine emission levels with the engine manufacturer and to ensure that the engine compares well to the emissions produced or expected by the engine manufacturer. It also serves the purpose of conditioning the engine and emission control system prior to starting the official regulated and unregulated emissions testing. Table 5 shows the detailed breakdown of the test matrix for each engine tested, along with the length of each test cycle. Table 6 shows the measurements done for each test performed on each engine. Table 6 also shows the sample location for each of the measurement. The CFR Part 1065 filter, exposure chamber, auxiliary filters, and the 8" by 10" filter and XADs assembly had a similar dilution ratio of about 2 relative to the CVS. They also had a similar mixing time on the order of one second. Figures 3 and 4 show the percent normalized torque and speed profiles for the different cycles used in ACES Phase 2. Normalized engine torque is defined as the actual torque over the maximum torque produced by the engine at the designated speed. Normalized engine speed is defined as (actual speed – warm-idle speed)/(max speed – warm-idle speed).

TABLE 4. NUMBER OF REGULATED AND UNREGULATED EMISSIONS TESTS FOR EACH ENGINE

Cycle	Regulated Pollutants	Unregulated
Mode 1, rated speed, 100% load	3	[a, b]
Mode 3, rated speed, 50% load	3	[a, b]
Mode 5, peak torque speed, 100% load	3	[a, b]
One Cold-Start + three Hot-Start FTP	4	[a ,b]
Hot-Start FTP	3	3
16-Hour	3	3
Tunnel Blanks [c, d]	3 for Engine X and 2 for others	3 for Engine X and 2 for others
16-Hour for Dioxins/Furans [e]		1
16-Hour Tunnel Background for Dioxins/Furans[f]		1

[a] Only real time particle size, number, total mass, and soot mass were performed for these tests.

[b] Data to be shared with each engine manufacturer to make sure that the engine emissions performance complied with the manufacturer's expectation and to get approval to proceed with the program.

[c] Tunnel blank is a 20-minute test run exactly like an engine FTP test, except the engine is off.

[d] One tunnel blank after cleaning CVS tunnel but before running the engine. A second tunnel blank after finishing the three hot-start FTP runs. A third tunnel blank after finishing the three 16-Hours.

[e] Dioxins and furans were collected separately for 16 hours on Engines X, Y, and Z using 8 x 10 Zefluor filters followed by four XAD traps.

[f] Tunnel background is a 16-Hour test where samples are taken from the dilution air immediately downstream of the CVS HEPA filter.

TABLE 5. DETAILED MATRIX FOR EACH ACES ENGINE

Test	Regulated Pollutants (No. of Runs)	Unregulated (No. of Runs)	Cycle Length
Tunnel Blank No. 1	1	1	20 minutes
Mode 1	3	[a]	20 minutes
Mode 3	3	[a]	20 minutes
Mode 5	3	[a]	20 minutes
Cold-Start followed by three Hot-Start FTP	4	[a]	20 minutes
Tunnel Blank No. 2	1	1	20 minutes
Hot-Start FTP	3	3	20 minutes
16-Hour [b] Day 1&2 (Three Repeats)	1	1	16 hours
Day 3&4	1	1	16 hours
Day 5&6	1	1	16 hours
Tunnel Blank No. 3	1	1	20 minutes
16-Hour for Dioxins&Furans [c] Day 7&8		1	16 hours
Tunnel Background for Dioxins&Furans[c]	N/A	1	16 hours

[a] Only real time particle size, number, total mass, and soot mass were taken from exposure chamber.

[b] Each 16-Hour (four runs of 4-hour segments), accumulates over a two-day period (two 4-hour segments per day). Days 1, 3, 5, and 7 begins as a hot-start after warm-up, and Days 2, 4, 6, and 8 begins as a cold-start

[c] For each engine, one 16-Hour engine cycle and one 16-Hour background test were collected for dioxins & furans analysis.

TABLE 6. SAMPLING/ANALYSIS MATRIX FOR REGULATED AND UNREGULATED EMISSIONS ON EACH ENGINE

Parameter; Analytical Method(s)	Media	FTP Hot Start	16-Hr Transient Cycle	Tunnel Blank	16-Hr Tunnel Background	Background Corrected[a]?	Sample Location
Total Hydrocarbon (THC), CH_4	FID	3	3	3	0	Yes	CVS tunnel
Oxides of Nitrogen (NO_X)	Chemi-luminescent	3	3	3	0	Yes	CVS tunnel
Carbon Monoxide (CO)	NDIR	3	3	3	0	Yes	CVS tunnel
Particulate Matter (PM), elements and metals (XRF, ICPMS)	47 mm Teflon® membrane Whatman filter	3	3	3	0	No	CVS+dilution step of ~2 (CFR Part 1065, 47°C)
Particulate Matter	47 mm Teflon® membrane Whatman filter	3	3	3	0	No	Exposure Chamber[b] (~28°C)
Nitrogen Dioxide (NO_2)	Chemi-luminescent	3	3	3	0	Yes	CVS tunnel
N_2O, NH_3	FTIR	3	3	3	0	No	Engine Exhaust
OC/EC	47 mm Quartz filter	3	3	3	0	No	Exposure Chamber[b]
SOF/DFIGC	47 mm TX-40 Filter	3	3	3	0	No	
Particle Size and Number	EEPS	3	3	3	0	No	Exposure Chamber[b]
Real Time PM	DMM-230	3	3	3	0	No	Exposure Chamber[b]
Inorganic ions and acids; IC	47 mm TX-40® filter, DI Water Impinger	3	3	3	0	No	CVS+dilution step of ~2
NH_4^+; IC	47 mm TX-40 filter, H_2SO_4 impinger	3	3	3	0	No	CVS+dilution step of ~2
pH, H^+; pH, Titration	DI Water Impinger	3	3	3	0	No	CVS tunnel
Cyanide, Cr(VI) ; colorimetric	KOH Impinger	3	3	3	0	No	CVS tunnel
SO_2; IC	H_2O_2 Impinger	3	3	3	0	No	CVS tunnel
Gas phase hydrocarbons (C_2–C_{12});GC-FID	Tedlar® Bag	3	3	3	0	Yes	CVS tunnel
Carbonyl compounds; HPLC-UV	DNPH Impinger	3	3	3	0	Yes	CVS tunnel
Alcohols; GC-FID	DI Water Impinger	3	3	3	0	Yes	CVS tunnel
Dioxins and Furans; HRGC/HRMS	Zefluor® Filter + XAD® Cartridge	0	1	0	1	Yes	CVS+dilution step of 2
Selected VOCs; GC/MS	SUMMA® Canister	3	3	3	0	No	CVS tunnel
PAH; GC/MS	Zefluor® Filter + XAD® Cartridge	3	3	3	0	No	CVS+dilution step of 2
nitroPAH; GC/MS		3	3	3	0	No	CVS+dilution step of 2
Hopane/Steranes/Carpanes; GC/MS		3	3	3	0	No	CVS+dilution step of 2
Alkanes, Alkenes, Alkynes, Cyclo- and branched (C_{14}-C_{40}); GC/MS		3	3	3	0	No	CVS+dilution step of 2
Polar compounds, Oxygenated PAH, Organic Acids; GC/MS		3	3	3	0	No	CVS+dilution step of 2
Nitrosamines; GC/MS	Thermosorb®	3	3	3	0	No	CVS tunnel
Urea Compounds	90 mm TX-40 Filter	0	3	0	0	No	CVS tunnel

[a] Background corrected means that a sample of the background dilution air taken from downstream of the HEPA filter in the CVS tunnel is analyzed for the same species concentration measured in the dilute exhaust, and then subtracted from the dilute exhaust species concentration using the following equation: Xbgc=Xm –(1-1/DR)*Xbg, where Xbgc is the corrected concentration, Xm is the measured concentration, and Xbg is the background concentration of the species of interest.

[b] The dilution ratio between the CVS tunnel and exposure chamber was ~2.

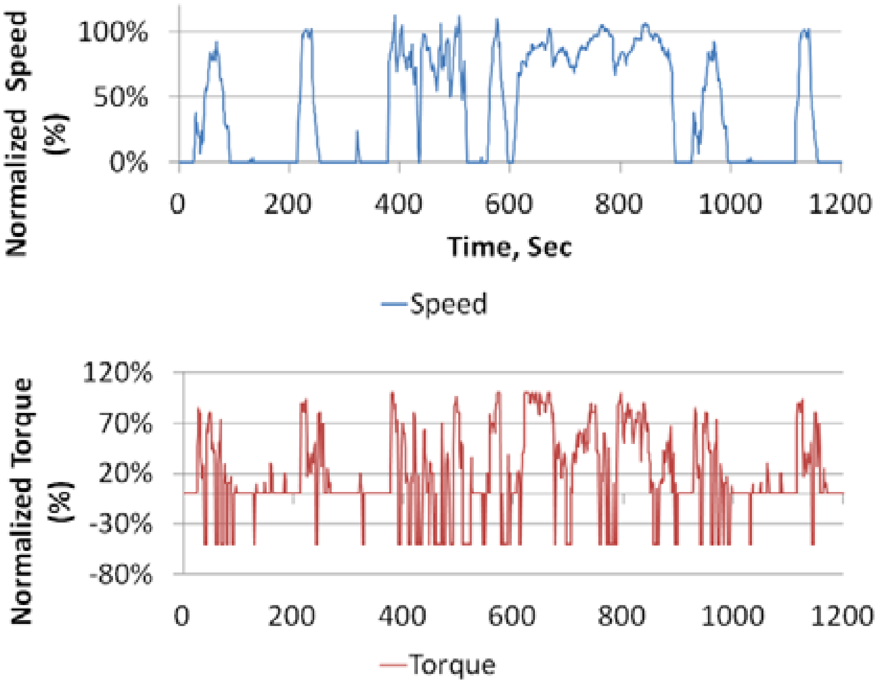


FIGURE 3. EXAMPLE OF FTP NORMALIZED SPEED AND TORQUE PROFILES

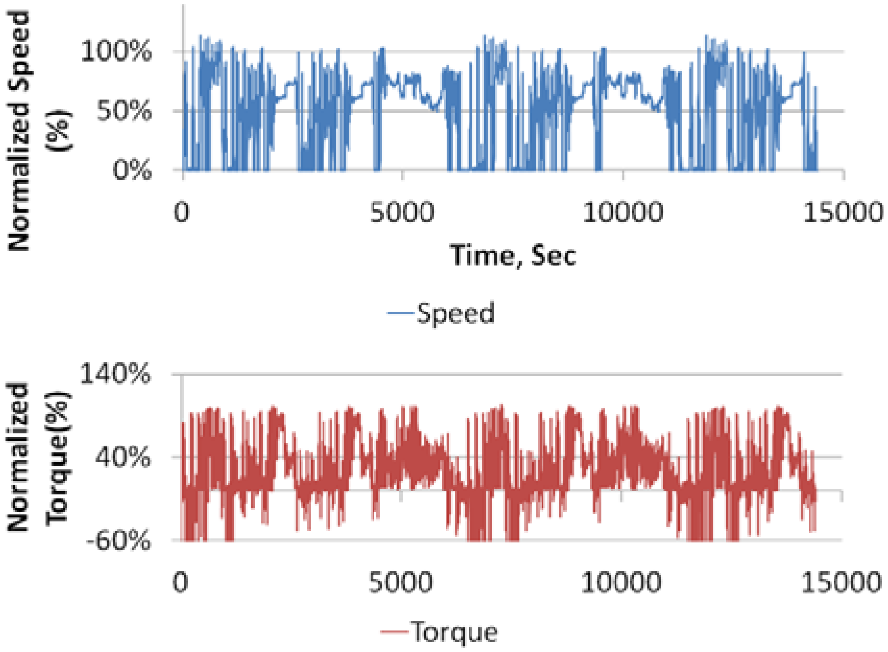


FIGURE 4. EXAMPLE OF FOUR-HOUR REPEATED SEGMENTS OF THE NORMALIZED SPEED AND TORQUE PROFILES FOR THE 16-HOUR

4.0 SPECIES AND ANALYTICAL TECHNIQUES

4.1 Regulated Emissions Measurements

Regulated emissions including NO_x, CO, and non-methane hydrocarbons (NMHC) were measured in the CVS in accordance with CFR Part 1065 using a Horiba MEXA-7200 emission bench. NO_x was measured using the chemiluminescent detection method. CO was measured using the non-dispersive infrared detection method, and NMHC was determined by taking the difference between CVS total hydrocarbons (THC) measurement and methane measurement using a non-methane cutter and the flame ionization detection method. For diesel engine test, heated sample line is required for NO_X and NMHC, and heated FID is required for NMHC.

Regulated PM was measured using a single Teflon® membrane filter (Whatman), 47 mm in diameter that is maintained at 47°C ± 5°C in accordance with CFR Part 1065. The nominal dilution ratio between the filter and the CVS tunnel was 2. The filter face velocity was maintained close to 100 cm/sec. The filter room used for filter conditioning and weighing was maintained in accordance with CFR Part 1065 requirements. The filter weighing procedure includes three filter pre and three filter post weights. The averages of the pre and post weights were used to determine the filter weight gain. In Project E-66, SwRI demonstrated a filter weighing variability of less than ±2.5 μg (one standard deviation) using Teflon® membrane filters. Since then, our typical variability is within less than ±1 μg for three repeated weighings.

4.2 Sampling and Analysis of Unregulated Emissions

Analysis of unregulated emissions was performed by SwRI, DRI, and ORNL. A summary of analytical responsibilities and notes on methodology are presented in Table 7.

Greenhouse gases of methane, CO_2, and N_2O were measured. They are unregulated for 2010 engines but subject to EPA emissions standards starting with 2014 model year engines. CO_2 was measured in the CVS using the non-dispersive infrared detection method. Methane was measured in the CVS using the FID method. N_2O was measured in engine exhaust using a Fourier Transform Infrared (FTIR) detector.

SwRI determined particle and gas phase ions by ion chromatography. Selected air pollutants were analyzed using gas chromatography/mass spectrometry (GC/MS). Speciation of C_1 through C_{12} hydrocarbons including alcohols, aldehydes, and ketones was performed using GC and high performance liquid chromatography (HPLC). Fourier transform infrared spectroscopy (FTIR) was used primarily for continuous monitoring of N_2O and NH_3. SwRI utilized dual chemiluminescent NO_x detectors, one operating in NO mode and one in NO_x mode, so an accurate determination of NO_2 could be made as the difference between NO_x and NO. Cyanide samples were collected in impingers and analyzed by an automated colorimetric procedure. Dioxins and furans samples were collected on an 8 by 10-inch Zefluor filter followed by four XAD traps, and were analyzed in accordance with EPA Method 8290 using high resolution gas chromatography (HRGC) and high resolution mass spectroscopy (HRMS).

For sampling in the animal exposure chamber, real-time particle size distribution was measured using the TSI engine exhaust particle sizer (EEPS); real time PM mass was measured with the Dekati DMM-230; and real time soot mass was measured with the AVL micro-soot sensor (MSS). OC and EC were collected from the exposure chamber on 47 mm quartz filters.

DRI provided analyses for hopanes, steranes, polar compounds, heavy alkanes ($>C_{12}$), polycyclic aromatic hydrocarbons (PAH), nitroPAH, oxyPAH, organic acids, and any unresolved complex mixtures, which were collected on an 8 by 10-inch Zefluor filter followed by four XAD traps. DRI provided analyses for OC/EC and nitrosamines, as well as metals and elements, which were analyzed by energy dispersive X-ray fluorescence (EDXRF) spectroscopy and induced coupled plasma mass spectroscopy (ICPMS).

ORNL provided analyses for particle phase urea related compounds that were collected on a 90 mm TX-40 filter during the 16-Hour. The nominal flow rate was 12 scfm targeting a filter face velocity of 100 cm/sec.

4.2.1 Filter and XAD Sample Collection for Chemical Analysis

For the collection of filter and XAD® samples for chemical analyses of semi-volatile compounds, SwRI used a large supplemental secondary dilution tunnel that permitted the use of an 8 by 10-inch (203 by 254 mm) Zefluor® filter followed by four 4-inch diameter XAD® cartridges that were sampled in parallel, downstream of the filter. The nominal flow rate through the filter and four XAD® cartridges was about 1700 slpm.

TABLE 7. SUMMARY OF ANALYSIS METHODOLOGY AND RESPONSIBILITY

Analyte Class	Notes	Method	Laboratory
Regulated Emissions	Dilute Exhaust	Various	SwRI
CO_2	Dilute Exhaust	NDIR	SwRI
CH_4	Dilute Exhaust	FID	SwRI
N_2O, NH_3	Raw Exhaust	FTIR	SwRI
Real Time PM	Size, Number, Soot mass, total mass	EEPS, DMM, MSS	SwRI
Sulfate, Nitrate, Ammonium ions	Water Impinger (4 slpm), 47 mm TX-40 filter (58 slpm)	IC	SwRI
Fuel/Oil PM Contribution (DFI/GC), and SOF	47 mm TX-40 filter, selected samples only, 58 slpm	DFI/GC	SwRI
Hydrogen Ion	H^+, water impinger, 4 slpm	Titration	SwRI
Cyanide Ion	KOH Impinger, 4 slpm	Colorimetry	SwRI
VOC (C_1 – C_{12})	Tedlar® bag	GC/FID	SwRI
Carbonyl compounds	DNPH impinger, 4 slpm	HPLC	SwRI
Alcohols	DI water impinger, 4 slpm	GC/FID	SwRI
SO_2	H_2O_2 impinger, 4 slpm	IC	SwRI
NH_4^+	H_2SO_4 impinger, 4 slpm	IC	SwRI
Other Ions	De-ionized water impinger, 4 slpm	IC	SwRI
Selected VOCs	SUMMA Canister	GC/MS	SwRI
Dioxins/Furans	8 x 10 inch Zefluor filter followed by four XAD traps. One sample and one tunnel background per engine, on 16-hr integrated sample, gas- and particle-phase extracts analyzed together, 1700 slpm	GC/MS	SwRI
Real Time Total PM	1Hz, 10 slpm	DMM-230	SwRI
Real Time Soot	1Hz, 2 slpm	MSS	SwRI
Real Time PM Size and Number	1Hz, 10 slpm	EEPS	SwRI
Metals and Elements	47 mm Teflo® filter, 28 slpm	EDXRF/ICPMS	DRI
PAH	Gas- and particle-phase extracts analyzed together, except 16-Hour integrated sample, 1700 slpm	GC/MS	DRI
NitroPAH	Gas- and particle-phase extracts analyzed together, except 16-Hour integrated sample, 1700 slpm	GC/MS	DRI
Hopanes, Steranes	Gas- and particle-phase extracts analyzed together, except 16-Hour integrated sample, 1700 slpm	GC/MS	DRI
Polar compounds	Gas- and particle-phase extracts analyzed together, except 16-Hour integrated sample, 1700 slpm	GC/MS	DRI
Other SVOC (C_{14}-C_{40}) and unresolved complex mixtures	Gas- and particle-phase extracts analyzed together, except 16-Hour integrated sample, 1700 slpm	GC/MS	DRI
Nitrosamines	Thermosorb N®, 1 slpm	GC/MS	DRI
OC/EC	Quartz filters, 58 slpm	TOR and TOT	DRI
Particle Phase Urea Compounds	90 mm Zefluor Filter, ~300 slpm	APCI-MS	ORNL

4.2.2 Ions and Inorganic Acids

Samples were collected in impingers containing a potassium hydroxide solution and analyzed for cyanide ion pursuant of a colorimetric procedure described in EPA Method 335.4, “Determination of Total Cyanide by Semi-Automated Colorimetry.”

Hexavalent chromium Cr(VI) was collected using a modified EPA Method 061 and analyzed by EPA 7199. Similar to cyanide, an impinger filled with a potassium hydroxide solution was used to collect the Cr(VI), and the impinger solution was subsequently analyzed by ion chromatography.

Anions and cations (NH_4^+, NO_2^-, NO_3^-, SO_4^{2-}), and inorganic acids (HNO_2, HNO_3, H_2SO_4) samples were collected on TX-40 filters, utilizing water and dilute sulfuric acid impingers. Filters were extracted to remove the analytes of interest, and the extract was analyzed using ion chromatography (IC). Impinger solutions were analyzed by IC as well; however, it is not possible to differentiate between anions and cations from ionic species versus inorganic acids. In addition, it should be noted that NO_2 passing through water may form HNO_2 and HNO_3. A titration to determine the H^+ concentration was performed, and the pH was measured.

4.2.3 Metals and Elements

Filter samples were analyzed with ICPMS and EDXRF to ensure that analyses for all required elements were covered with adequate detection limits. The CFR Part 1065 Teflon membrane filter was used for these analyses. The filter was sampling from the CVS with a dilution ratio of ~2 between the filter and the CVS tunnel.

The particulate filters for ICPMS metals analysis were digested with high purity acids. The majority of the metals were analyzed via ICPMS using EPA SW-846 Method 6020 to get the lowest possible detection limits. Blank filters were analyzed to assess any contribution from the media and the extraction/digestion solutions.

The ICPMS instrument was standardized using NIST traceable standard reference materials. Prior to analyzing any samples, the standardization was verified with a second NIST traceable reference material. This second standard was from a different lot or manufacturer than the first standardization material. Immediately after the second standard was run, a blank was run to verify the zero setting. The second standard was required to be within 90-110 percent recovery of the certified value. The absolute value of the check blank was required to be below the reporting limit for the analyte. If either condition was not met, the analysis would be terminated and the instrument re-standardized and re-checked. The standard and check blank were re-run after every 10 samples, and at the end of the run to ensure that the instrument remains in control throughout the entire run. If a standard falls out of the control limits, the analysis was terminated, the instrument re-standardized, and all samples since the last compliant standard were re-run. As an internal check, duplicate analyses were performed on approximately ten percent of samples, selected at random.

4.2.4 Selected Volatile Organic Compounds

Samples for the selected volatile organic compounds (nitromethane, nitropropane, hydrogen sulfide, carbonyl sulfide), were collected in sample bags and sorbent traps specific to the analytes. They were analyzed by GC/MS. SwRI Test and Analysis Procedures TAP 0404014 and 0404015 were utilized. TAP 0404014 is based upon EPA method TO-15, which uses a combination of multi-sorbent tubes and cryogenic focusing for sample concentration with subsequent analysis by GC/MS. TAP 0404015 is based upon SW-846 Method 5040 and covers the determination of volatile organic compounds (VOCs), collected on Tenax® and Tenax®/charcoal sorbent cartridges using a volatile organic sampling train (VOST). This method was utilized in conjunction with an appropriate analytical method, SW-846 8240, Volatile Analysis by GC/MS. Because a majority of gas streams sampled using VOST will contain a high concentration of water, the analytical method is based on the quantitative thermal desorption of volatile compounds from the Tenax® and Tenax®/charcoal traps with analysis by purge and trap GC/MS. The contents of the sorbent cartridges are spiked with an internal standard/surrogate solution and thermally desorbed with organic free nitrogen or helium, bubbled through organic-free water and trapped on an analytical absorbent trap. After the purge, the analytical trap is dry purged for two additional minutes, then heated rapidly to 240°C, with the carrier flow reversed so the effluent flow from the analytical trap is directed to the GC/MS. The VOCs are separated by temperature-programmed gas chromatography and detected by low-resolution mass spectrometry. The concentrations of VOCs are calculated using the internal standard technique. Tunnel blank samples were collected for each analyte as specified in Table 5.

4.2.5 Hydrocarbon Speciation of C_2 Through C_{12} Compounds

Vapor phase C_2 to C_{12} hydrocarbon species were sampled with Tedlar® bags from the CVS tunnel. Analyses of these samples were conducted within five to 10 minutes after collection to avoid degradation of the more reactive species, such as 1,3-butadiene. Carbonyls and alcohols were sampled from the CVS tunnel utilizing impingers. Alcohols were collected in impingers filled with deionized water, and carbonyls with a solution of dinitrophenylhydrazine (DNPH) in acetonitrile. To minimize degradation, aldehyde samples were analyzed as soon as the sampling was completed.

The analytical procedures used for conducting hydrocarbon speciation (C_2 to C_{12} hydrocarbons, aldehydes and ketones, and alcohols) were similar to the CRC Auto/Oil Phase II protocols. With these methods, exhaust emissions samples were analyzed for the presence of more than 200 different exhaust species. Four GC procedures and one HPLC procedure were used to identify and quantify compounds. A brief description of these procedures is given below.

The first GC procedure uses a 15 m x 0.53 mm I.D. DB-WAX (1μm film) pre-column and a 50 m x 0.53 mm I.D. (10 femtometer film) Alumina PLOT/KCI (Carbopack®) column to permit the separation and determination of exhaust concentrations of C_1-C_4 individual hydrocarbon species, including ethane, ethylene, acetylene, propane, propylene, propadiene, butane, trans-2-butene, 1-butyne, and cis-2-butene. Bag samples are analyzed using a gas chromatograph equipped with a flame ionization detector (FID). The gas chromatograph system utilizes two analytical columns. The carrier gas is helium. An external multiple component standard in zero air is used to quantify the results. Detection limits for the procedure are on the order of 5 ppbC in dilute exhaust for all compounds.

The second GC procedure uses a 60 m x 0.32 mm I.D. (10 µm film) DB-1 column to provide separation and exhaust concentrations for more than 100 C_5-C_{12} individual HC compounds. Bag samples are analyzed using a gas chromatograph equipped with a flame ionization detector (FID). The GC system utilizes a FID, a pneumatically operated and electrically controlled valve, and an analytical column. The carrier gas is helium. An external multiple component standard in zero air is used to quantify the results. Detection limits for the procedure are on the order of 10 ppbC in dilute exhaust for all compounds.

The third GC procedure uses a separate system configured similarly to the second GC method to determine individual concentrations of benzene and toluene according to CRC Auto/Oil Phase II Protocols. The third GC utilizes a 30 m x 0.25 mm I.D. (0.25 µm film) DB-5 column instead of a DB-1 column.

The fourth GC is used for alcohols. For alcohols, sample collection was performed by bubbling diluted exhaust through deionized water in a series of impingers. An aliquot of the solution was subsequently analyzed for alcohols using a gas chromatograph equipped with a flame ionization detector. External standards were used to quantify the results.

An HPLC with a Zorbax® octadecasilane (ODS) column was utilized for the analyses of aldehydes and ketones. Samples were collected in impingers with a solution of DNPH in acetonitrile. For analyses, a portion of the acetonitrile solution was injected into a liquid chromatograph equipped with an ultraviolet (UV) detector. External standards of the aldehyde and ketone DNPH derivatives were used to quantify the results.

4.2.6 Dioxins and Furans

As discussed above, sampling for dioxins and furans utilized an 8 by 10-inch Zefluor® filter followed by four 4 inch XAD cartridges. The dilution ratio between the CVS and the filter/XAD assembly was about 2. This approach is required to achieve the extremely low detection limits required for these analytes. The analytical protocol followed for analysis of dioxins and furans (PCDD or PCDF) is EPA Method 8290. The instruments include a Fisons AutoSpec Ultima high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS), a Micromass AutoSpec HRGC/HRMS, and a Micromass AutoSpec Premier HRGC/HRMS. The sample was spiked with a solution containing specified amounts of each of the nine isotopically ($^{13}C_{12}$) labeled PCDDs/PCDFs listed in the method. The sample was extracted according to a matrix-specific extraction procedure and analyzed. A tunnel background sample was collected as specified in Table 5.

4.2.7 Elemental Carbon/Organic Carbon

PM from the animal exposure chamber were collected on a primary and a backup quartz filter. Those filters were provided by DRI after being pre-fired at 900°C to remove organic contaminants. Quartz fiber filters absorb organic gases from ambient air and organic artifacts from the manufacturing process. By pre-firing the quartz filters before sampling, the absorbed gases and artifacts are reduced to constant insignificant levels. After collection, the filters were analyzed for OC/EC by DRI using the thermal optical reflectance (TOR) and the thermal optical transmittance (TOT) methods. This is a thermal desorption process subjecting the filters to temperatures between 25°C and 800°C. The results are reported using the primary filter only similar to what was done during ACES Phase 1.

4.2.8 Particulate- and Gas-Phase Organic Compounds

Among the many particulate and semi-volatile organic compounds (SVOC) are the following groups of compounds: PAH, oxyPAH, nitroPAH, hopanes/steranes, higher molecular weight alkanes, cycloalkanes, higher molecular weight aromatics, certain polar organic compounds, and unresolved complex mixtures. Sampling was performed with an 8 by 10 inch Zefluor PM filter followed by four, 4-inch traps containing XAD-4 resin. The dilution ratio between the CVS and the filter/XAD assembly was about 2.

Sampling materials were prepared by DRI and shipped to SwRI. Prior to shipping, XAD-4 resins were extracted with methanol followed by dichloromethane (CH_2Cl_2), using an Accelerated Solvent Extractor (Dionex 3000). The cleaned resin was dried in a vacuum oven heated to 40 ºC and stored in sealed glass containers in a clean freezer. The filters were cleaned by sonification in CH_2Cl_2 for 30 minutes, followed by another 30-minute sonification in methanol. The filters were then dried, placed in aluminum foil, and labeled. Each batch of pre-cleaned XAD-4 resin and approximately 10 percent of pre-cleaned filters were checked for purity by solvent extraction and GC/MS analysis of the extracts. The XAD-4 resins were assembled into glass cartridges (20 g of XAD) and stored in a clean freezer prior to shipment to SwRI.

All samples returned from SwRI to DRI were stored in a freezer prior to extraction. All samples were extracted within two weeks of being received at DRI.

Prior to extraction, the following deuterated internal standards were added to each filter and XAD sorbent: naphthalene-d8, biphenyl-d10, acenaphthene-d10, phenanthrene-d10, anthracene-d10, pyrene-d12, benz(a)anthracene-d12, chrysene-d12, benzo[e]pyrene-d12, benzo[a]pyrene-d12, benzo[g,h,i]perylene-d12, coronene-d12, cholestane-d6, hexadecane-d34, eicosane-d42, hexatriacontane-d74, 2-nitrodiphenyl-d9, 1-nitropyrne-d9, benzoic-d6 acid, phthalic 3,4,5,6-d4 acid, hexanoic-d11 acid, heptadecanoic-d33 acid, and myristic-d27 acid.

Filters and XAD-4 resins were extracted with dichloromethane using the Dionex ASE followed by acetone extraction under the same conditions. The dichloromethane extraction method has been reported to yield high recovery of PAH[8] and nitroPAH[9,10]. Dichloromethane extraction followed by acetone also gives good recovery for PAH, aliphatic hydrocarbons, cycloalkanes, hopanes, steranes, and polar organic compounds.

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[8] Chuang, J.C., M.R. Kuhlman, and N. Wilson, "Evaluation of methods for simultaneous collection and determination of nicotine and polynuclear aromatic hydrocarbons in indoor air," *Environ. Sci. Technol.,* **24**, 661-665, 2006.

[9] Atkinson, R., J. Arey, A.M. Winer and B. Zielinska, "A survey of ambient concentrations of selected polycyclic aromatic hydrocarbons (PAH) at various locations in California." Final Report, prepared under Contract No. A5-185-32, for the California Air Resources Board, Sacramento, CA, by Statewide Air Pollution Research Center, University of California, Riverside, CA, 1988.

[10] Zielinska, B., J. Arey, R. Atkinson, and A.M. Winer, "The nitroarenes of molecular weight 247 in ambient particulate samples collected in Southern California," *Atmos. Environ.,* **23,** 223-229, 1989.

All extracts were then concentrated by rotary evaporation at 35°C under gentle vacuum to approximately 1 mL and filtered through a 0.2 µm PTFE disposal filter device (Whatman Pura discTM 25TF), rinsing the flask 3 times with 1 mL dichloromethane and acetone (50/50 by volume) each time. The extract was split into two fractions (polar and non-polar analyses) and was solvent exchanged to acetonitrile under ultra-high purity nitrogen.

The extracts were analyzed first by GC/MS for higher molecular weight (C>15) aliphatic hydrocarbons and cycloalkanes. Subsequently, the extracts were pre-cleaned by the solid-phase extraction technique. Superclean LC-SI SPE cartridges (Supelco) were sequentially eluted with hexane, and hexane/benzene (1:1). The hexane fraction contains the non-polar aliphatic hydrocarbons (alkanes), and hopanes and steranes, and the hexane/benzene fraction contains PAH and nitroPAH. These two fractions are concentrated to approximately 100 µL and analyzed by GC/MS for hopanes, steranes, PAH and oxyPAH. For nitroPAH, the extracts are further pre-cleaned by the solid-phase extraction technique, using aminopropyl (NH2) SPE cartridges (Waters), with sequential elution with hexane/DCM, 98/2 v/v and hexane/DCM 80/20 v/v. For nitro- and dinitroPAH analysis, these fractions are further cleaned by semi-preparative normal-phase high performance liquid chromatography (HPLC) technique (Waters). The Chromegabond Amino Cyano 25 cm x 9.6 mm column (ES Industries, West Berlin, NJ) and isocratic elution with 20 percent DCM in hexane was used. The fraction corresponding to nitro- and dinitroPAH was collected and analyzed by negative ion chemical ionization GC/MS. The fraction for the polar analysis is derivatized using a mixture of bis(trimethylsilyl)trifluoroacetamide and pyridine to convert the polar compounds into their trimethylsilyl derivatives for analysis of organic acids, phenol and cresol.

The filters and XAD® extracts were analyzed by GC/MS, using a Varian CP-3800 GC equipped with a CP8400 auto sampler and interfaced to a Varian 4000 Ion Trap. Due to the high sensitivity of Ion Trap MS, it was used for analysis of all gas-phase and particulate phase organic compounds, with the exception of the nitroPAH compounds, which utilized the electron impact (EI) ionization method. Injections (1 µL) were made in the splitless mode onto a 30m 5 percent phenylmethylsilicone fused-silica capillary column (DB-5ms, J&W Scientific or equivalent). Quantification of the individual compounds was obtained by the selective ion storage (SIS) technique, monitoring the molecular (or the most characteristic) ion of each compound of interest and the corresponding deuterated internal standard. Calibration curves for the GC/MS quantification were made for the most abundant and characteristic ion peaks of the compounds of interest using the deuterated species most closely matched in volatility and retention characteristics as internal standards. National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1647 (certified PAH) with the addition of deuterated internal standards and of those compounds not present in the SRM (i.e., oxyPAH, nitroPAH, hopanes, steranes, carpanes, hydrocarbons, cycloalkanes) were used to make calibration solutions. A six- to eight-level calibration was performed for each compound of interest and the calibration check (using median calibration standards) was run every 10 samples to check for accuracy of analyses. If the relative accuracy of measurement (defined as a percentage difference from the standard value) was greater than 20 percent, the instrument was recalibrated.

NitroPAH compounds were analyzed using the Varian 1200 triple quadruple gas chromatograph/mass spectrometer (GC/MS/MS) system with a CP-8400 auto sampler. The tandem MS/MS system allows for structural elucidation of unknown compounds with precursor, product and neutral loss scan. The GC interface allows for sensitive analyses of complex mixtures in electron impact (EI) as well as positive and negative chemical ionization (CI) mode. Negative CI offers superior sensitivity for the analysis of nitroPAH (approximately 100 times higher than EI or positive CI) that could be emitted from combustion sources, including motor vehicle engines. The sensitivity of this instrument in full scan EI/MS mode was approximately 1 pg/µl with a 20:1 signal-to-noise ratio (S/N). In EI/MS SIM mode it reaches 50 fg/ul with a 10:1 S/N. For negative CI, 10 fg/ul of octafluoronaphthalene gives an S/N of 20:1. This superior sensitivity offers the advantage of analyzing small samples collected during a short sampling time.

4.2.9 Nitrosamines

Nitrosamines were collected on Thermosorb/N adsorbent cartridges using a Teflon® sample probe. Samples are quantified using modified EPA Method TO-7, which specifies analyses by GC/MS. The cartridge samples were collected from the CVS tunnel. The cartridges were eluted with a mixture of 25 percent methanol and 75 percent dichloromethane. The first 1.8 ml was collected for the GC/MS analyses, using negative CI mode. Injections (1 ul) are made in the splitless mode onto a CP WAX 51 capillary column (25 m long, 0.25 mm id). Quantification of the individual compounds was obtained by the multiple ion detection (MID) technique, monitoring the molecular ion of each compound of interest and the corresponding deuterated internal standard.

As to the modifications - the elution solvent was 25% methanol and 75% dichloromethane, instead of acetone and no dichloromethane pre-elution was used. Also, DRI used their new, very sensitive GC/MS – Scion TQ (triple quad) interfaced to 456 GC and fitted with Chrompack CPWAX 51 capillary column (25 m long, 0.25 mm id). They also used chemical ionization (CI) with methane and single ion monitoring (SIM) technique. Deuterated nitrosodiethylamine (d10) was used as internal standard for nitrosoamines quantification. The total volume was about 20 liter for the FTP, and 240 liter for the 16-Hour. The total volume was less than the maximum volume of 300 liter, recommended for the TO-7 method.

4.2.10 Particle Phase Urea-Related Compounds

Particle phase urea-related compounds such as urea, melamine, cyanuric acid, ammelide, ammeline, and biuret were analyzed by ORNL using atmospheric pressure chemical ionization mass spectroscopy (APCI-MS). The materials were extracted from a 90 mm TX-40 (Teflon coated borosilicate glass fiber filter) sample filter that was used to collect PM from the CVS tunnel during the 16-Hour. The nominal flow through the filter was set to 340 lpm, resulting in a filter face velocity close to a 100 cm/sec. This high flow increased the chance of detecting these compounds if they exist at a detection limit of 5 µg/filter.

Urea and its common decomposition products can be separated into acids and bases. Urea and melamine are bases and cyanuric acid, ammelide, and ammeline are acids. Urea and melamine are soluble in formic acid solutions and form $M\text{-}H^+$ ions by positive atmospheric pressure chemical ionization (APCI). Cyanuric acid, ammelide and ammeline are soluble in diethyl amine solutions and form M^- ions by negative APCI-MS. Below is a description of the extraction method:

- Extraction method:
  - Each filter was cut into two pieces.
  - Acid extraction
    - 1 ml of a 0.5% formic acid in 50:50 methanol:water
    - Sonicate 20 minutes
    - Extract is spiked with arginine (I.S.) and analyzed by APCI-MS
  - Base extraction
    - 1ml of a 0.5% diethyl amine in 50:50 methanol:water
    - Sonicate for 20 minutes
    - Extract is spiked with lactic acid (I.S.) and analyzed by APCI-MS

For the APCI-MS parameters, samples were infused urea and melamine were analyzed in positive ion mode and cyanuric acid, ammelide, and ammeline were analyzed in negative ion mode. Some of the characteristics of the APCI-MS used for the urea-related compounds by ORNL are shown below:

- Bruker Ion Trap MS-MS with electrospray ionization and APCI sources at FEERC
  - model year 2001; 2005 software update
- Direct infusion of solution
- Low fragmentation by ionization process
  - important because low end mass is 60 amu so fragments might be too small
- Discrimination between positive and negative ionization can identify functional groups
- Can switch between positive and negative ion mode without changing other mass spec parameters
- May be possible to identify size of complexes (i.e. number of melamine and cyanuric acid units)

4.2.11 Real Time PM Size, Number, Total and Soot Mass

Each of the instruments described below was cleaned and flow-calibrated prior to any engine testing. All instruments were set up to collect from the exposure chamber.

Particle size distribution and number concentration was measured using a TSI EEPS, as shown in Figure 5. The instrument covers a particle size range from 5.6 nm to 560 nm, and reports the full size distribution measurement on a 10 Hz basis. The principle of operation is to charge particles and mobilize them to deposit on a series of electrometers, each representing a narrow particle size range. The current reading from each electrometer is converted to number concentration.

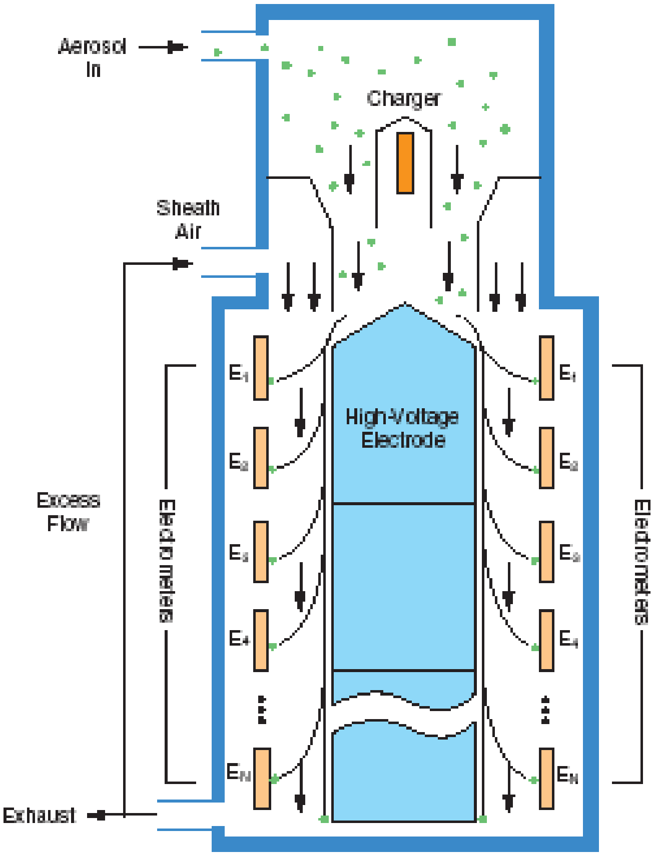

FIGURE 5. TSI ENGINE EXHAUST PARTICLE SIZER (EEPS)

The Dekati DMM-230, shown in Figure 6, was used for real time total particle mass emission measurement on a 1 Hz basis. The principle of operation is to charge particles and deposit the sub-30 nm particles on an electrometer by electric mobility and the rest of the particles on a series of electrometer stages by inertial impaction, with each electrometer representing a narrow aerodynamic size range. The current reading from each electrometer stage is converted into mass concentration using an average apparent density. The apparent density is determined by overlaying the calculated mobility diameter size distribution on top of the aerodynamic diameter size measured distribution.

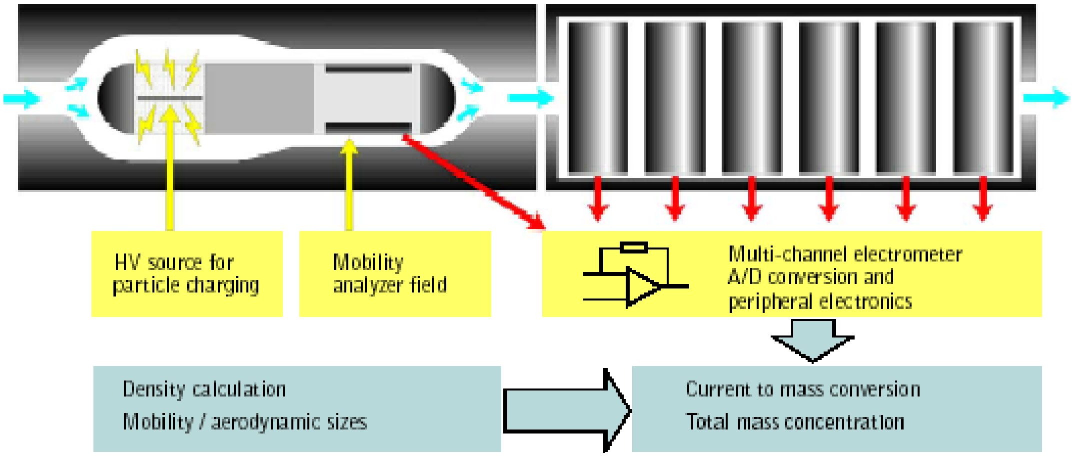

FIGURE 6. DEKATI MASS MONITOR (DMM-230)

An AVL micro-soot sensor (MSS), shown in Figure 7, was used for real time soot mass emission measurement on a 1 Hz basis. This instrument is widely used in engine emission activities focusing on the measurement of soot. The principle of operation is to slightly heat soot particles with a pulsed laser beam so the soot particles can heat the surrounding gas and generate a sound wave that can be detected by a sensitive microphone. The magnitude of the electric signal generated by the microphone is correlated with the mass concentration of soot.

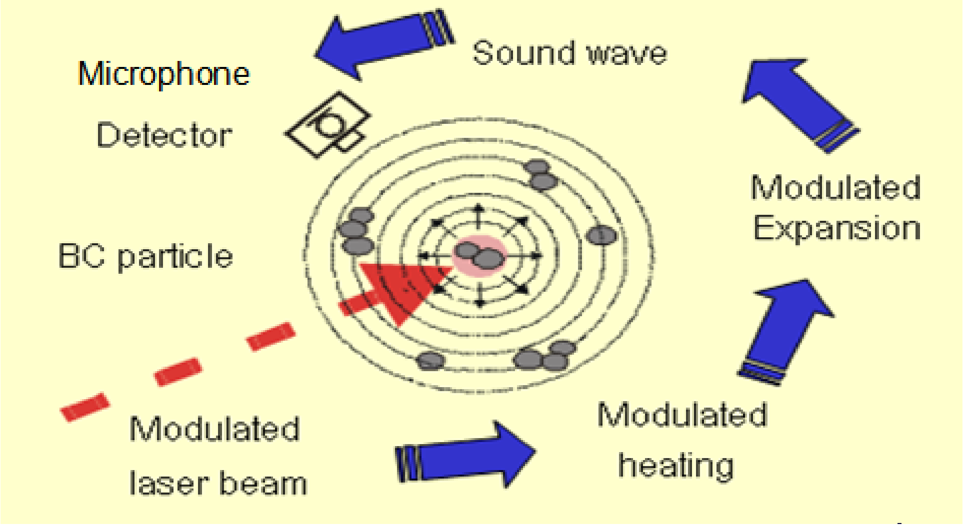

FIGURE 7. AVL MICRO-SOOT SENSOR (MSS)

5.0 PROCEDURES

5.1 Important Procedural Differences from ACES Phase 1

The following two sub-sections focus on important procedural differences between ACES Phase 2 and ACES Phase 1 that may have impact on emissions. Other procedural differences include the additional measurement of ammonia and urea-related compounds in ACES Phase 2. The potential presence of these compounds is derived from the use of urea-based SCR catalyst in the exhaust of 2010 technology engines. This is why their measurement was added to ACES Phase 2. One more difference was the CVS operation, where the average CVS dilution ratio in ACES Phase 2 was about half that of ACES Phase 1. This was done to adhere to CFR Part 1065 minimum dilution ratio requirement, as discussed in Section 2.3. This also helps improving the detection limit of various compounds. The dilution steps between the CVS and various other systems were kept at a nominal dilution ratio of 2, similar to that used in ACES Phase 1. Thus, with the reduced average CVS dilution ratio (5 to 8) by half, all other dilution ratios in exposure chamber, CFR Part 1065 filter, semivolatile filter assembly and auxiliary filter assembly was also reduced by half.

5.1.1 DPF Active Regeneration with 2010 Engines

In ACES Phase 1 testing of 2007 technology engines, the DPF actively regenerated on its own through a command from the engine control module (ECM) one to three times during the 16-Hour, depending on the engine used. To minimize variability in engine emissions and ensure consistency among engines using a common baseline, we performed a forced active regeneration on the DPF prior to starting a 16-Hour. Such a strategy did not prevent the capturing of emissions during a full cycle of DPF operation that included particle loading and active regeneration of at least once per 16-Hour.

Due to improvement in engine and aftertreatment emissions control, 2010 engines self-trigger much less frequent active DPF regenerations, compared to 2007 technology engines. As a result, no active DPF regeneration was expected to take place in a 16-Hour. Since there was a high degree of interest in capturing emissions on cycles with and without DPF active regenerations, the ACES panel endorsed the idea of removing any forced active regeneration between the three 16-Hour runs used in official testing to increase the probability of encountering an active DPF regeneration in one of them. While this approach did not guarantee the occurrence of an active regeneration, it was the best approach to implement on this program without changing the original scope of work. But, even with this approach, no active regeneration was encountered during the 16-Hour testing of the 2010-compliant engines. This was a distinct difference between ACES Phase 1 and ACES Phase 2.

5.1.2 Engine Preconditioning Prior to Official Testing

In ACES Phase 1, we performed forced active regeneration of the DPF followed by an overnight soak, prior to official testing of the cold-start/hot-start FTP. This was done for consistency among engines and to avoid active regeneration from occurring during an official FTP. For engines equipped with SCR catalysts, ammonia storage by the SCR catalyst at low temperature is a key in reducing cold-start NO_X emissions. Thus, the history of the SCR catalyst prior to a cold-start FTP or a hot-start FTP can affect NO_X emissions substantially. A forced active regeneration of the DPF prior to official testing, similar to that done in ACES Phase 1, may deprive the SCR catalyst from stored ammonia due to high exhaust temperature. If the SCR catalyst has no stored ammonia prior to a cold-start FTP, the engine might fail the standard on NO_X. To avoid such issue that was under discussion between EMA and EPA, under the Emission Measurement and Testing Committee (EMTC), we used an approach where we conditioned the aftertreatment system using a forced active regeneration followed by three runs of the FTP. This strategy was intended to equilibrate the catalyst with some ammonia storage prior to official testing to avoid failing NO_X emissions. So, in ACES Phase 2 work, the engine and emission control system were conditioned prior to any official cold-start and hot-start FTP testing using the following conditioning strategy:

1. Perform a forced DPF active regeneration to clean the DPF
2. Run three back-to-back hot-start FTP to condition the SCR Catalyst with ammonia storage
3. Shut down the engine for an overnight soak
4. Run a cold-start followed by a hot-start FTP for official emission reporting

The forced active regeneration was triggered by the engine ECM using the manufacturer proprietary software. A set of instructions were given by each manufacturer to SwRI for the forced active regeneration procedure. The time for forced active regeneration took between 20 to 40 minutes, depending on the engine being tested. The end of regeneration was dictated by the engine ECM. The procedures for forced active regeneration were similar to those used in ACES Phase 1. The time it took to complete an active regeneration was also similar.

For the hot-start FTP for regulated and unregulated emissions measurement, we ran Step 1 and Step 2 above, and then started official testing. For the 16-Hour, Day 1 was run as a hot-start after conditioning using Step 1 and Step 2 above and Day 2 continued as a cold-start after an overnight soak. For the second and third 16-Hour runs (Day 3, 4, 5, and 6), Step 1 and Step 2 were omitted to increase the probability of active DPF regeneration as discussed in Section 5.1.1.

For dioxins and furans (Day 7 and 8) Steps 1 and 2 were performed prior to starting the 16-Hour. Since only one 16-Hour is run per engine for dioxins and furans, the ACES panel agreed to perform a forced DPF active regeneration prior to any testing for to ensure better consistency among engines.

5.2 Full Flow Constant Volume Sampler Tunnel Cleanup and Conditioning

Similar to what was done in ACES Phase 1 project prior to test cell engine installation, a thorough full flow CVS tunnel cleaning was performed in ACES Phase 2. Due to the very low PM and unregulated emission levels expected from the 2010 engines, it was important to clean the internal surface of the tunnel to remove any adsorbed material that could interfere with PM and unregulated emissions measurements. Volatile and semi-volatile materials that may have adsorbed onto the internal surface of the tunnel or the surface of particles could desorb during an engine run or when sampling a tunnel blank. The tunnel was completely removed from the test cell and cleaned using a small amount of Simple Green detergent and power washed and rinsed using water. According to the manufacturer's Material Safety Data Sheet(MSDS)[11], it is

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[11]

composed of water (≥78%), 2-butoxyethanol (≤5%), ethoxylate alcohol (≤5%), tetrapotassium pyrophosphate (≤5%), sodium citrate (≤5%), fragrance (≤1%), colorant (≤1%).

5.3 Step-By-Step Procedure for Testing

In ACES Phase 2, we adhered to a specific test procedure for all engines and cycles tested. This is to make sure that all engines and cycles were run in a similar manner for a particular engine and among all three engines. All testing was done with engine blow-by routed to a location downstream of the SCR catalyst, in accordance with CFR Part 1065. Similar to ACES Phase 1, three hot-start FTP and three 16-Hour were run for regulated and unregulated emissions, and one 16-Hour was run for dioxins and furans collection. The reason for the separate 16-Hour for dioxins and furans is because the extraction and analyses for dioxins and furans were done at SwRI and the rest of the semi-volatile extraction and analyses were done at DRI.

Table 8 shows the step-by-step procedure for conducting the official regulated and unregulated testing for each 2010-compliant engine. This is similar to what was used in ACES Phase 1, except for the differences discussed above.

TABLE 8. STEP-BY-STEP PROCEDURES

Steps	Action Items
1	Clean CVS tunnel (done only once before the first engine)
2	Set CVS flows as required by CFR Part 1065
3	Perform all necessary calibration required under CFR Part 1065
4	*Generate a tunnel blank with a sampling time of 20 minutes before any engine exhaust run through the tunnel*
5	Install engine in test cell
6	Power validate engine and compare the performance with that declared by the manufacturer
7	If Step 6 is acceptable, proceed to Step 8, otherwise resolve the performance issues with the engine manufacturer
8	Generate an engine torque map at wide open throttle in accordance with CFR Part 1065
9	Run practice FTP, and perform the necessary tuning to pass cycle statistics
10	Perform “forced” active DPF regeneration followed by three back-to-back hot-start FTP to condition the engine and emission control system
11	Perform three repeats of Mode 1, Mode 3, and Mode 5 taking regulated emissions with selected real time particle measurement in exposure chamber (EEPS, DMM-230, MSS)
12	Repeat Step 10 and soak the engine overnight. Perform a cold-start FTP followed by three hot-start transient cycles and measure regulated emissions along with EEPS, DMM-230, and MSS measurements in exposure chamber. Shut down the engine for 20 minutes in between cycles
13	Compare all regulated brake specific emissions with those determined by the manufacturer
14	Resolve the differences, if any, between SwRI and the manufacturer results and proceed with the emission characterization
15	Condition engine and sampling system by performing a “forced” active DPF regeneration followed by three back-to-back hot-start FTPs
16	Perform three hot-start FTP cycles with 20 minutes engine-off soak between cycles. Sample for all regulated and unregulated emission species on each run.
18	*Generate a tunnel blank with a sampling time of 20 minutes similar to that in Step 4*
19	Condition engine and sampling system by performing a “forced” active DPF regeneration followed by three hot-start FTP
20	Perform one 16-Hour over a period of two days. Sample for all regulated and unregulated emissions. On day 1, warm up engine and bring it to idle for 15 minutes then run two 4-hour hot-start segments of the 16-Hour with 15 minutes idle time in between segments, followed by an overnight shut-down. On day 2, run a cold-start for the first 4-hour segment, bring the engine to low idle for 15 minutes, and then run another 4-hour segment, and shut down engine
21	Repeat Step 20 twice for Day 3&4 and for Day 5&6 , but without Step 19
22	Repeat Step 19, and then Repeat Step 20 one more time and collect for dioxins/furans analysis only using Day 7 and Day 8
23	*Generate a tunnel blank with a sampling time of 20 minutes similar to that in Step 4*
24	*Generate a tunnel background for 16 hours while sampling as in Step 22 only*
26	*Repeats Steps 5 through 24 for Engine Y*
27	*Repeats Steps 5 through 24 for Engine Z*
Warm-Up Procedure*: Start-up engine and run it at intermediate speed, 50% load, until the coolant thermostat open. Run engine at rated power for 5 minutes, then bring it down to idle, before you start a test.*	

6.0 RESULTS

Because the power rating, displacement volume, and the engine model are known, we excluded from this report any information on cycle work and other related variables so the engines designated as Engine X, Y, and Z can remain anonymous. All detailed regulated and unregulated emissions species will be accessed through a CRC database that is available to the public along with this report.

This results section includes information on the regulated and unregulated emissions from each of the engines tested. Also, we include emissions comparisons between 2010 technology engines used in ACES Phase 2 and 2007 technology engines used in ACES Phase 1, where applicable. The main focus will be on the three repeats of the hot-start FTP and the three repeats of the 16-Hour performed on each engine. However, prior to proceeding with the results section, it is important to show that the engines are in full compliance with the respective EPA standards based on the FTP cold-start and hot-start composite that is typically used for engine certification in the laboratory.

Table 9 and Figure 8 summarize the FTP composite results for regulated emissions for Engines X, Y, and Z, along with % reduction relative to the 2010 standards. All of the engines' emissions were well below the 2010 standard. NO_X reduction ranged from 24% for Engine Y to 67% and 76% for Engine X and Z, respectively. The reduction in CO ranged from 91% for Engine X to 99% and 100% for Engines Y and Z, respectively. The reduction in NMHC was a 100% and the reduction in PM ranged from 84% for Engine Z to 97% for Engines Y and Z. Using Table 9 to determine the average emissions from all three engines, the emissions reductions relative to the 2010 standard were 61%, 97%, 100%, and 92% for NO_X, CO, NMHC, and PM, respectively. This demonstrates that there is a very good margin of compliance relative to the 2010 standards.

TABLE 9. SUMMARY OF FTP COMPOSITE REGULATED EMISSIONS

Engine X, g/hp-hr

	Cold FTP	Hot FTP	Composite	2010	% Reduction
	102_C1	103_H1	1/7C+6/7 hot	Standard	Rel. 2010 Std.
NOX	0.301	0.026	0.065	0.200	67%
CO	2.84	1.07	1.32	15.50	91%
NMHC	0.000	0.000	0.000	0.140	100%
BSPM	0.0001	0.0003	0.0003	0.0100	97%

Engine Y, g/hp-hr

	Cold FTP	Hot FTP	Composite	2010	% Reduction
	Y_259_C1	Y_260_H1	1/7C+6/7 hot	Standard	Rel. 2010 Std.
NOX	0.490	0.096	0.153	0.200	24%
CO	0.62	0.06	0.143	15.50	99%
NMHC	0.002	0.000	0.000	0.140	100%
BSPM	0.0004	0.0003	0.000	0.0100	97%

Engine Z, g/hp-hr

	Cold FTP	Hot FTP	Composite	2010	% Reduction
	Z_283_C1	Z_284_H1	1/7C+6/7 hot	Standard	Rel. 2010 Std.
NOX	0.268	0.012	0.049	0.200	76%
CO	0.16	0.03	0.05	15.50	100%
NMHC	0.000	0.000	0.000	0.140	100%
BSPM	0.0066	0.0008	0.0016	0.0100	84%

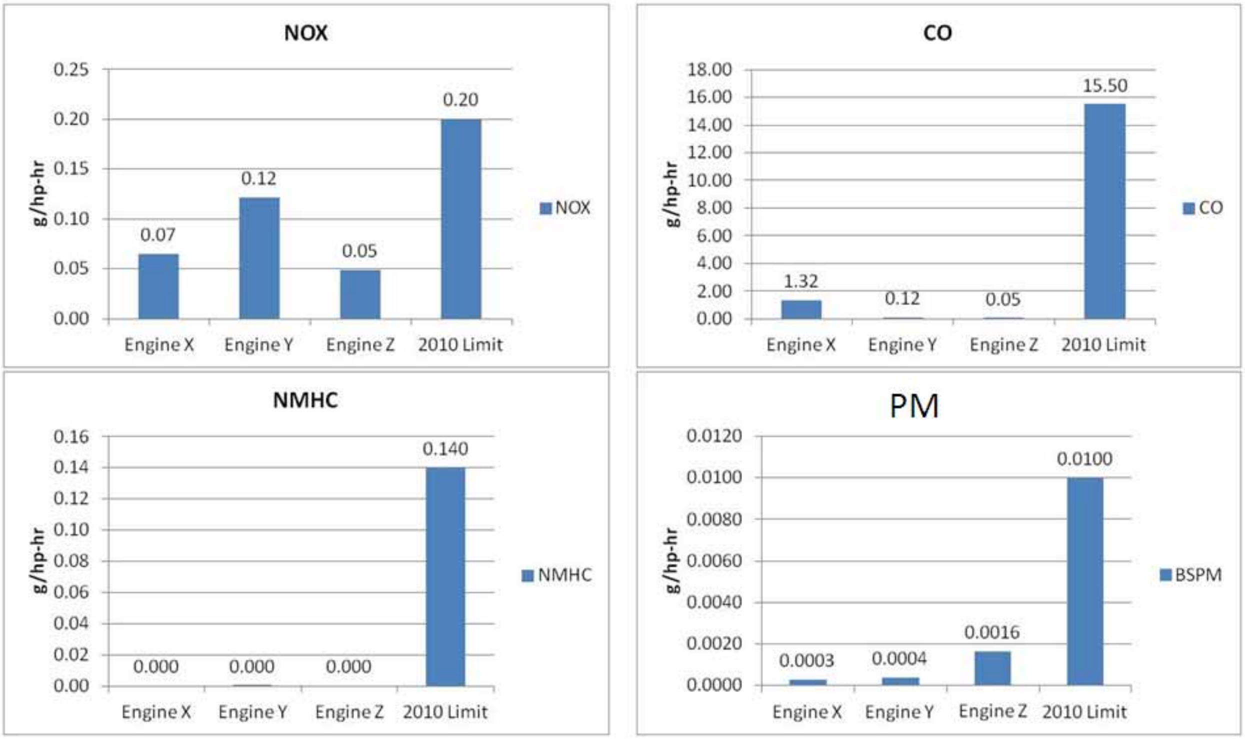

FIGURE 8. REGULATED EMISSIONS FOR FTP COLD- AND HOT-START COMPOSITE

6.1 Nitrogen Oxides (NO_X), Nitrogen Dioxide (NO_2), Nitrous Oxide (N_2O), and Ammonia (NH_3) Emissions

Figures 9 and 10 show a summary of the results for NO_X and NO_2 during the hot-start FTP and the 16-Hour. NO_X is a regulated emissions species that includes NO and NO_2. The 2010 emissions limit for NO_X is 0.20 g/hp-hr for the cold/hot start FTP composite. As can be seen from Figure 9, the NO_X emissions for the hot-start FTP were substantially below the 2010 standard, demonstrating the strong effectiveness of the SCR system in reducing NO_X under hot-start conditions. The 16-Hour resulted in higher NO_X emissions compared to the FTP, most likely due to the low temperature segments of the cycle (Idle and Creep) and the fact that the cycle had a cold-start portion, during which the SCR catalyst may not be very effective in reducing NO_X. As we saw with the 2007 technology engines, the majority of NO_X was in the form of NO_2 due to NO oxidation over the DOC. NO_2 is desirable downstream of the DOC since it acts as a low temperature EC oxidant in the DPF leading to passive DPF regeneration. NO_2 is also the desired species to have at the inlet of the SCR since SCR catalysts favor the reduction of NO_2 over NO. As can be seen from Figure 10, NO_2 was absent for Engine X and Engine Z for the FTP, while constituting a high percentage (60%) of the NO_X level for Engine Y during the FTP and for all engines during the 16-Hour ranging from 33% to 69%.

Another byproduct of SCR/AMOX NO_X control is N_2O emissions species (Figure 11), which is a strong greenhouse gas. Some of the NO_X reduction over the SCR or NH_3 reduction over the AMOX may lead to N_2O formation. N_2O as a percent of NO_X was higher than that of NO_2. N_2O will be regulated in 2014 with an emission limit of 0.1 g/hp-hr based on the FTP cold/hot start composite. The N_2O limit is a "cap" standard designed to prevent major increases in N_2O. It is also required for up to an EPA specified engine useful life[12]. It was set at approximately twice the level of N_2O emissions from 2008 heavy-duty diesel and gasoline engines. The Engine X and Engine Z N_2O emissions were well below the 2014 limit based on the hot-start FTP, and Engine Y was about 12 percent above the limit. The average emissions ranged from 0.052 g/hp-hr and 0.054 g/hp-hr for Engines X and Z to 0.11 g/hp-hr for Engine Y. Figure 12 shows the average N_2O emissions for ACES Phase 2 (2010 Technology) and ACES Phase 1 (2007 Technology) engines relative to the 2014 limit. It can be observed from Figure 12 that the 2010 technology engines on average had a much higher N_2O emissions than the 2007 technology engines, but the emissions are still 26% to 31% below the 2014 standard of 0.1 g/hp-hr.

NH_3 is another important byproduct of the urea-SCR NO_X control strategy. NH_3 is the ultimate required urea decomposition product needed to reduce NO_X. Without ammonia production, NO_X reduction will not take place. Some of the NH_3 that is produced slips past the SCR catalyst and makes it to engine exhaust. To reduce ammonia slip, an ammonia slip catalyst (AMOX) was used downstream of the SCR with all 2010 technology engines tested in ACES Phase 2. Figure 13 shows the NH_3 emissions on a brake-specific emissions basis during the hot-start FTP and the 16-Hour, although there is no regulation for ammonia comparison. In the EU and perhaps later in the US, there are discussions underway to limit average exhaust ammonia slip to no more than 10 ppm to 15 ppm. Table 10 summarizes the NH_3 concentration in engine exhaust. The average NH_3 concentration ranged from 0.124 ppm for Engine X to 0.465 ppm and 0.647 ppm for Engine Y and Z, respectively. Similar trends were observed for the 16-Hour but

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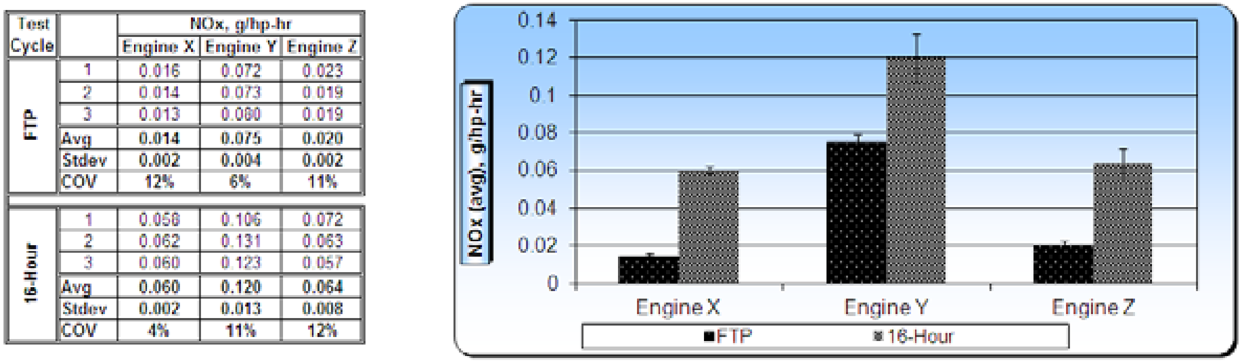
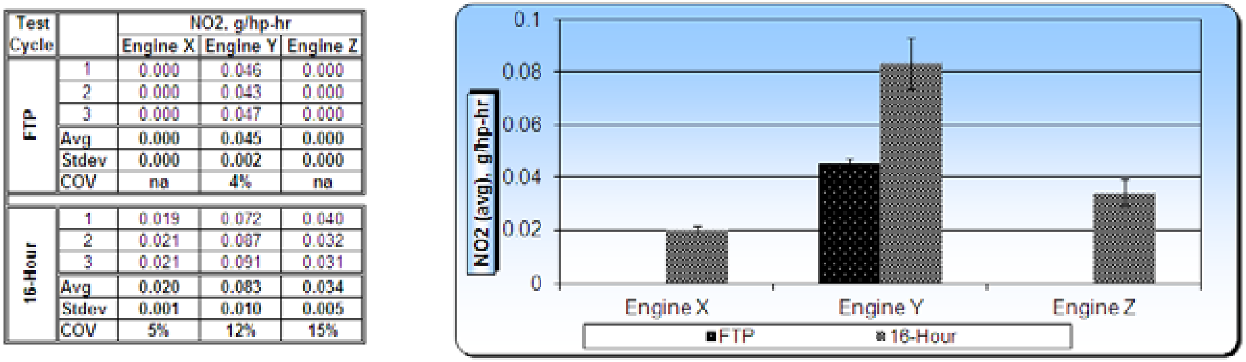
[12] CFR 76, 179 page 57176, September 15, 2011

the level was higher in the range from 0.422 ppm to 1.369 ppm. Regardless of the cycle used, the NH_3 concentrations were well below a potential standard at 10 ppm or 15 ppm level.



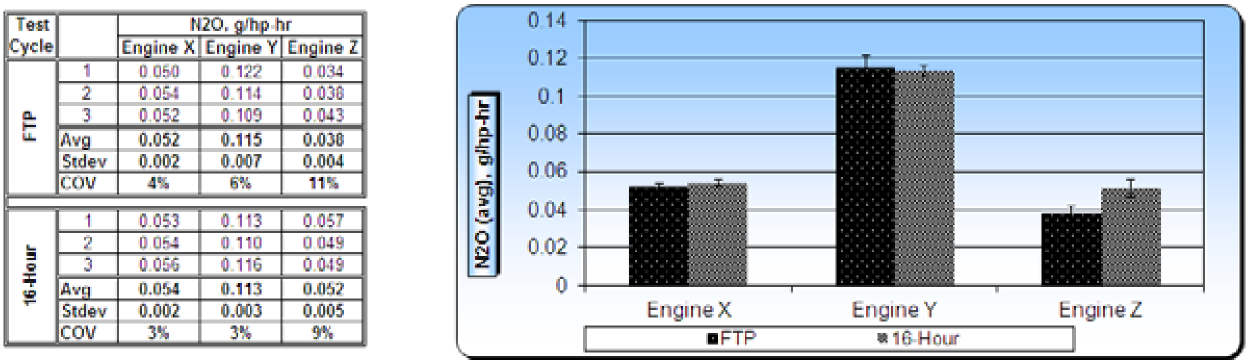
Test Cycle		NOx, g/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.016	0.072	0.023
	2	0.014	0.073	0.019
	3	0.013	0.080	0.019
	Avg	**0.014**	**0.075**	**0.020**
	Stdev	**0.002**	**0.004**	**0.002**
	COV	12%	6%	11%
16-Hour	1	0.058	0.106	0.072
	2	0.062	0.131	0.063
	3	0.060	0.123	0.057
	Avg	**0.060**	**0.120**	**0.064**
	Stdev	**0.002**	**0.013**	**0.008**
	COV	4%	11%	12%

FIGURE 9. NO_X EMISSIONS FOR THE HOT-START FTP AND 16-HOUR



Test Cycle		NO2, g/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.000	0.046	0.000
	2	0.000	0.043	0.000
	3	0.000	0.047	0.000
	Avg	**0.000**	**0.045**	**0.000**
	Stdev	**0.000**	**0.002**	**0.000**
	COV	na	4%	na
16-Hour	1	0.019	0.072	0.040
	2	0.021	0.087	0.032
	3	0.021	0.091	0.031
	Avg	**0.020**	**0.083**	**0.034**
	Stdev	**0.001**	**0.010**	**0.005**
	COV	5%	12%	15%

FIGURE 10. NO_2 EMISSIONS FOR THE HOT-START FTP AND 16-HOUR



Test Cycle		N2O, g/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.050	0.122	0.034
	2	0.054	0.114	0.038
	3	0.052	0.109	0.043
	Avg	**0.052**	**0.115**	**0.038**
	Stdev	**0.002**	**0.007**	**0.004**
	COV	4%	6%	11%
16-Hour	1	0.053	0.113	0.057
	2	0.054	0.110	0.049
	3	0.056	0.116	0.049
	Avg	**0.054**	**0.113**	**0.052**
	Stdev	**0.002**	**0.003**	**0.005**
	COV	3%	3%	9%

FIGURE 11. N_2O EMISSIONS FOR THE HOT-START FTP AND 16-HOUR

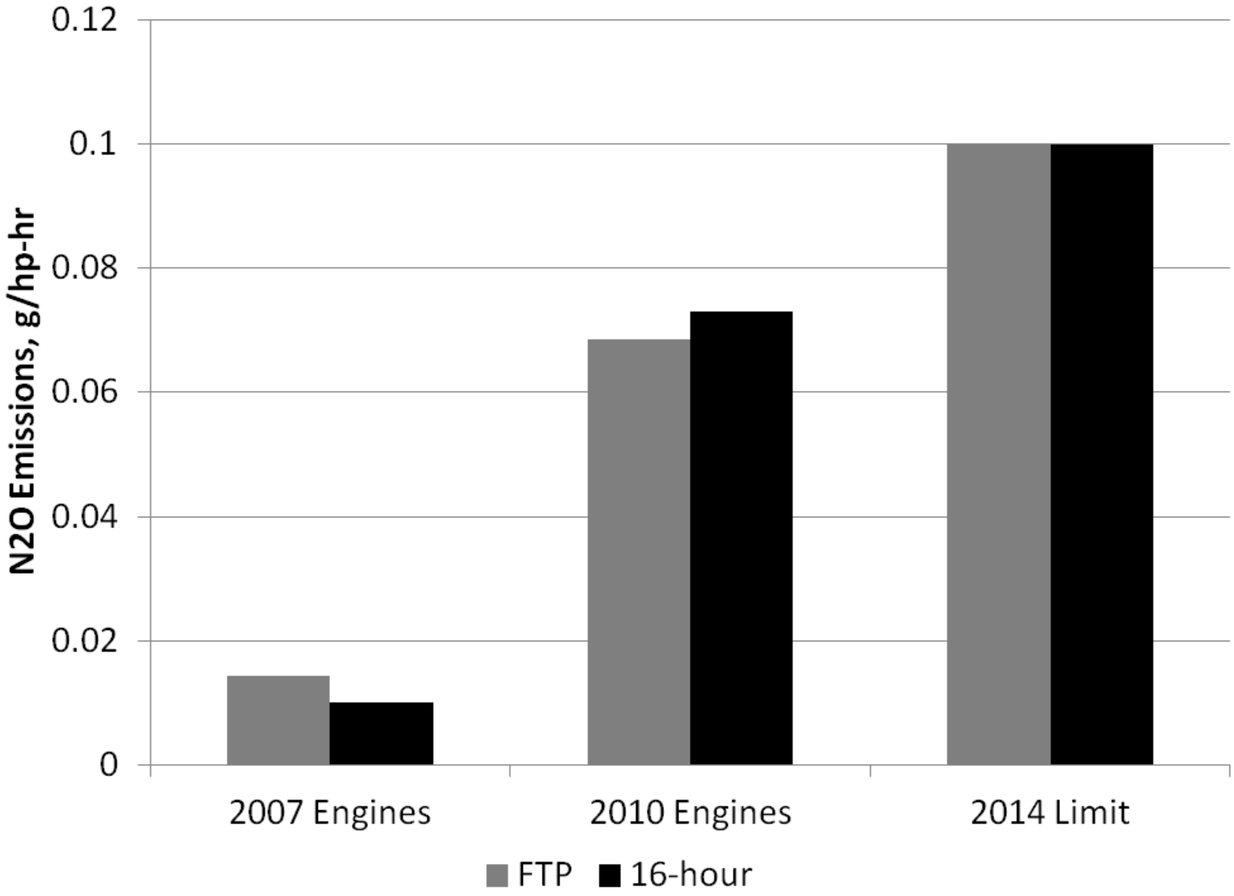
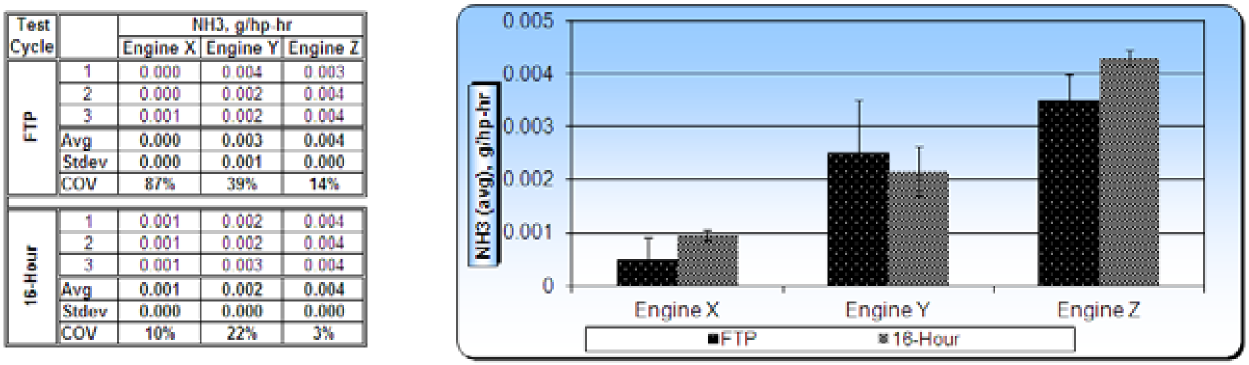


FIGURE 12. COMPARISON BETWEEN 2007 AND 2010 N_2O EMISSIONS AND THE 2014 LIMIT (LIMIT APPLIES ONLY TO COLD/HOT COMPOSITE OF THE FTP)



Test Cycle		NH3, g/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.000	0.004	0.003
	2	0.000	0.002	0.004
	3	0.001	0.002	0.004
	Avg	0.000	0.003	0.004
	Stdev	0.000	0.001	0.000
	COV	87%	39%	14%
16-Hour	1	0.001	0.002	0.004
	2	0.001	0.002	0.004
	3	0.001	0.003	0.004
	Avg	0.001	0.002	0.004
	Stdev	0.000	0.000	0.000
	COV	10%	22%	3%

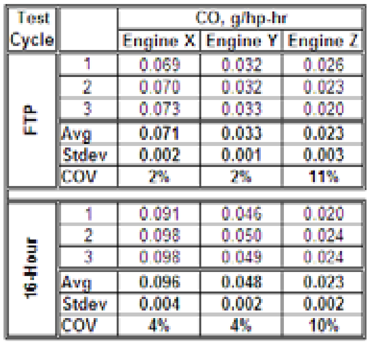
FIGURE 13. NH_3 EMISSIONS FOR THE HOT-START FTP AND 16-HOUR

TABLE 10. NH_3 CONCENTRATION IN ENGINE EXHAUST

Test Cycle		NH3, ppmv		
		Engine X	Engine Y	Engine Z
FTP	1	0.021	0.672	0.549
	2	0.116	0.398	0.668
	3	0.235	0.325	0.724
	Avg	**0.124**	**0.465**	**0.647**
	Stdev	**0.107**	**0.183**	**0.090**
	COV	**87%**	**39%**	**14%**
16-Hour	1	0.396	0.613	1.415
	2	0.396	0.588	1.368
	3	0.473	0.824	1.323
	Avg	**0.422**	**0.675**	**1.369**
	Stdev	**0.044**	**0.130**	**0.046**
	COV	**11%**	**19%**	**3%**

6.2 Carbon Monoxide (CO) Emissions

The 2010 CO emission standard is 15.5 g/hp-hr. Figure 14 shows the brake-specific CO emissions for all three engines. Overall, CO emissions were much lower than the standard for all engines under both cycles. In diesel engines, CO engine-out emissions are typically very low. The aftertreatment systems, especially the DOC and DPF, oxidize CO into CO_2 and bring it further down to a very low level. Although the emissions are low, there is still variation among the different engines tested.



Test Cycle		CO, g/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.069	0.032	0.026
	2	0.070	0.032	0.023
	3	0.073	0.033	0.020
	Avg	0.071	0.033	0.023
	Stdev	0.002	0.001	0.003
	COV	2%	2%	11%
16-Hour	1	0.091	0.046	0.020
	2	0.098	0.050	0.024
	3	0.098	0.049	0.024
	Avg	0.096	0.048	0.023
	Stdev	0.004	0.002	0.002
	COV	4%	4%	10%

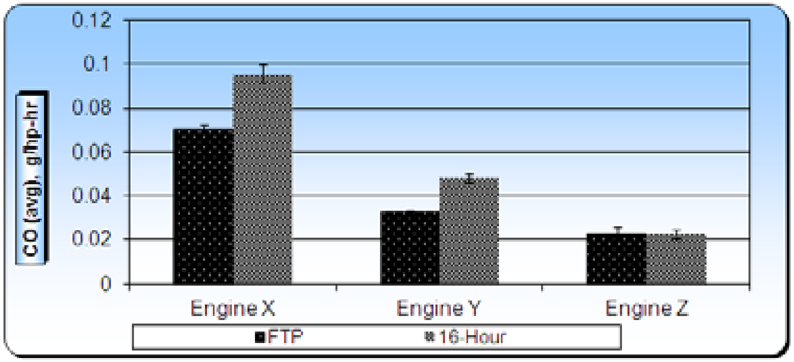
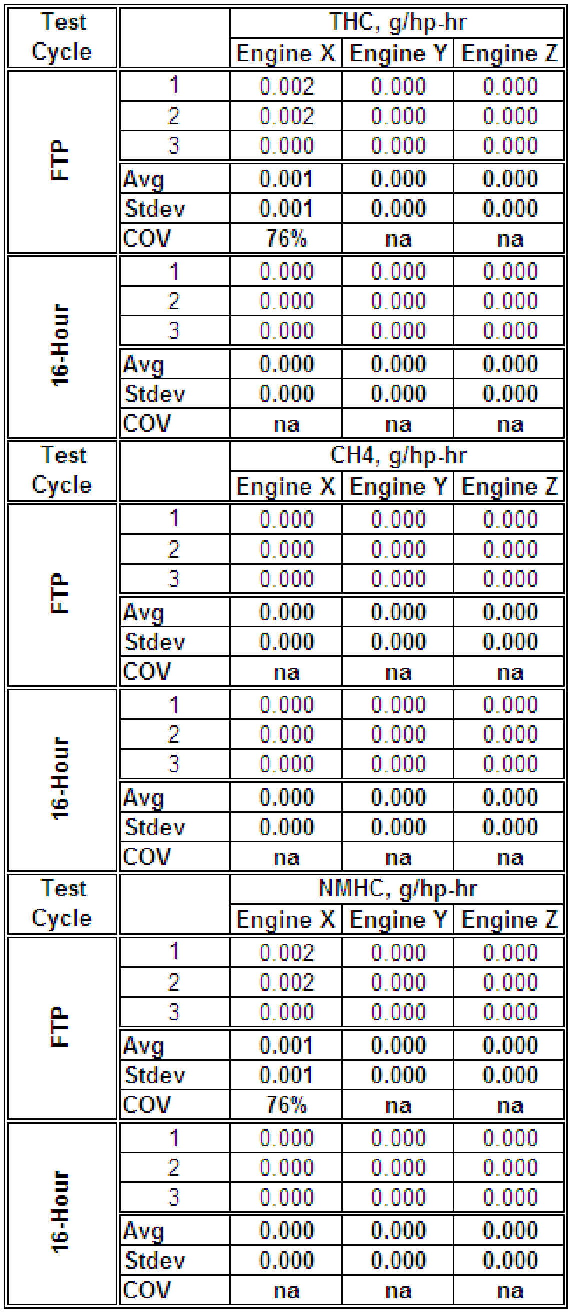


FIGURE 14. CO EMISSIONS FOR THE HOT-START FTP AND 16-HOUR

6.3 Total Hydrocarbon (THC), Methane (CH_4), and Non-Methane Hydrocarbon (NMHC) Emissions

The NMHC emission standard for 2010 is 0.14 g/hp-hr. NMHC was determined by taking the difference between the measurement of THC and CH_4. Table 11 shows the brake-specific emissions for THC, CH_4, and NMHC, respectively. Except for the very low emissions of THC and NMHC with Engine X for the FTP, hydrocarbon emissions measured in accordance with EPA CFR Part 1065 were effectively zero or less than the detection limit of 0.001 g/hp-hr.

TABLE 11. THC, CH_4, AND NMHC EMISSIONS



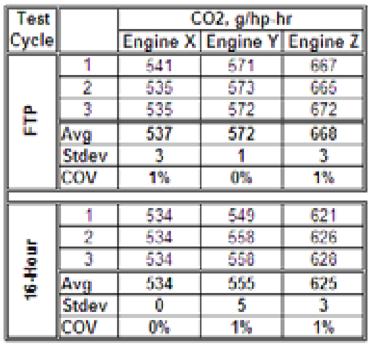
Test Cycle		THC, g/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.002	0.000	0.000
	2	0.002	0.000	0.000
	3	0.000	0.000	0.000
	Avg	0.001	0.000	0.000
	Stdev	0.001	0.000	0.000
	COV	76%	na	na
16-Hour	1	0.000	0.000	0.000
	2	0.000	0.000	0.000
	3	0.000	0.000	0.000
	Avg	0.000	0.000	0.000
	Stdev	0.000	0.000	0.000
	COV	na	na	na

Test Cycle		CH4, g/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.000	0.000	0.000
	2	0.000	0.000	0.000
	3	0.000	0.000	0.000
	Avg	0.000	0.000	0.000
	Stdev	0.000	0.000	0.000
	COV	na	na	na
16-Hour	1	0.000	0.000	0.000
	2	0.000	0.000	0.000
	3	0.000	0.000	0.000
	Avg	0.000	0.000	0.000
	Stdev	0.000	0.000	0.000
	COV	na	na	na

Test Cycle		NMHC, g/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.002	0.000	0.000
	2	0.002	0.000	0.000
	3	0.000	0.000	0.000
	Avg	0.001	0.000	0.000
	Stdev	0.001	0.000	0.000
	COV	76%	na	na
16-Hour	1	0.000	0.000	0.000
	2	0.000	0.000	0.000
	3	0.000	0.000	0.000
	Avg	0.000	0.000	0.000
	Stdev	0.000	0.000	0.000
	COV	na	na	na

6.4 Carbon Dioxide (CO_2) Emissions and BSFC

CO_2 emissions have become a very important emission species because CO_2 is major greenhouse gas. The first greenhouse gas regulation pertaining to heavy-duty on-highway diesel engines will take effect in 2014, when the CO_2 emissions limit (based on the FTP cold and hot-start composite) will be 567 g/hp-hr. Since CO_2 is a major byproduct of complete fuel combustion, CO_2 emissions will also be impacted by regulations requiring improved fuel economy. Figure 15 shows the CO_2 emissions for the FTP and 16-Hour for all three engines. Relative to the 2014 standard (not applicable but used as a reference only), Engine X met the standard on both the FTP and the 16-Hour while Engine Y was borderline with Engine Z exceeding the standard. As mentioned before, CO_2 emission is a major component of fuel economy, which is expressed in brake-specific fuel consumption (BSFC). BSFC is calculated in accordance to CFR Part 1065 for the diesel fuel using gaseous emissions species such as CH_4, NMHC, CO, and CO_2. Figure 16 shows the BSFC for all three engines. Similar trends were observed in BSFC to that of CO_2. BSFC calculation does not take into account urea consumption. Urea can be considered a fuel that adds to the overall fuel consumption. Based on our internal calculation, the urea consumption from all three engines was 2% to 3% of the diesel fuel consumed. Thus, urea consumptions should not impact the trends observed below in BSFC among the three engines.



Test Cycle		CO2, g/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	541	571	667
	2	535	573	665
	3	535	572	672
	Avg	537	572	668
	Stdev	3	1	3
	COV	1%	0%	1%
16-Hour	1	534	549	621
	2	534	558	626
	3	534	558	628
	Avg	534	555	625
	Stdev	0	5	3
	COV	0%	1%	1%

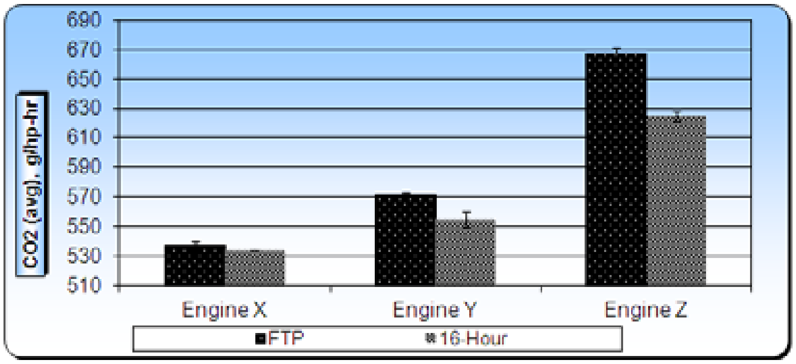
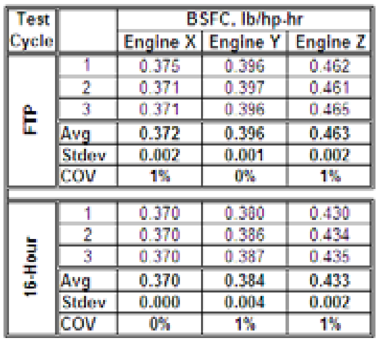


FIGURE 15. CO_2 EMISSIONS FOR THE HOT-START FTP AND 16-HOUR



Test Cycle		BSFC, lb/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.375	0.396	0.462
	2	0.371	0.397	0.461
	3	0.371	0.396	0.465
	Avg	0.372	0.396	0.463
	Stdev	0.002	0.001	0.002
	COV	1%	0%	1%
16-Hour	1	0.370	0.380	0.430
	2	0.370	0.386	0.434
	3	0.370	0.387	0.435
	Avg	0.370	0.384	0.433
	Stdev	0.000	0.004	0.002
	COV	0%	1%	1%

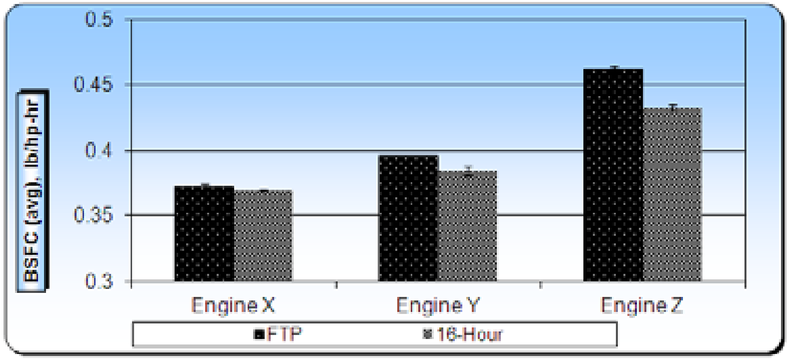


FIGURE 16. BSFC FOR THE HOT-START FTP AND 16-HOUR

6.4.1 *Greenhouse Gas and Global Warming Potential*

It is important to note that the greenhouse gas regulations do not apply to the 2010 technology engines that we test. Those regulations initially take effect in 2014. Nonetheless, in Figures 11, 12, Table 11 and Figure 15, we reported results on the three greenhouse gas emissions species (N_2O, CH_4, and CO_2) emitted from the tested engines, although CH_4 emissions were essentially zero. Using CO_2, N_2O, and CH_4 data as applicable, we compared the 100 year global warming potential (GWP), as defined by EPA greenhouse gas rulemaking for medium and heavy-duty engines[13], between the 2010 and 2007 technology engines. GWP is a relative measure of the amount of heat trapped from the instantaneous release of one kilogram of a trace substance relative to that of one kilogram of a reference gas. For the purpose of our calculation, we used CO_2 as the reference and we multiplied CH_4 by 25 and N_2O by 298 to get the 100 year GWP[14]. Based on our calculation, the 100 year GWP of the two engine technologies was very similar leading only to a 0.1% increase with the 2010 technology engines.

6.4.2 *Sulfur Dioxide (SO_2) Emissions*

SO_2 emissions are combustion byproducts of sulfur in the fuel and the lube oil. Figure 17 shows SO_2 emissions for FTP and 16-Hour using all three ACES engines. The 16-Hour data in this case are much more reliable because the levels measured are well above the detection limit of 0.03 mg/hp-hr for the 16-Hour. To give a better perspective on SO_2 emissions, we assumed that all sulfur in the fuel is converted to SO_2 to predict SO_2 emissions. We also assumed an oil sulfur contribution to SO_2 emissions using a measured oil sulfur content of 4,000 ppm and an oil consumption of 0.06% of fuel consumption. The oil to fuel consumption was derived from a 2007 medium duty technology vehicle with a DOC in the exhaust, using calcium as a tracer for oil consumption[15]. Table 12 shows the estimated SO_2 emissions calculation. The calculated SO_2 emissions were significantly higher than the measured SO_2 emissions, suggesting significant sulfur storage in the aftertreatment system, particularly the DPF due to the lack of DPF active regeneration, where internal surfaces of the DPF increase in temperature causing a release of the stored sulfur. To investigate this point further, we compared measured and calculated SO_2 emissions between 2010 (no occurrence of DPF active regeneration) and 2007 technology engines used in ACES Phase 1, where DPF active regeneration occurred one to three times during the 16-Hour. For the 2007 technology engines (Figure 18), the calculated SO_2 emissions based on the assumptions made above were a factor of 2 of the measured SO_2 emissions, while the calculated SO_2 emissions for the 2010 engines were nearly a factor of 10 higher. This storage of sulfur in the aftertreatment system is not permanent and will likely be cleared through an active DPF regeneration that we did not observe during ACES Phase 2 tests. So far, in the above analysis, we did not include the contribution of sulfur from the particle-phase sulfate for the overall sulfur mass balance. For the 2010 engines, the total sulfur mass in measured particle-phase sulfate (Figure 36) is insignificant, representing less than 1 percent of the sulfur mass in measured SO_2. So, it can be ignored in the sulfur mass balance. However, sulfur mass in particle-phase sulfate for the 2007 technology engines is equal to 70% of the sulfur mass in measured

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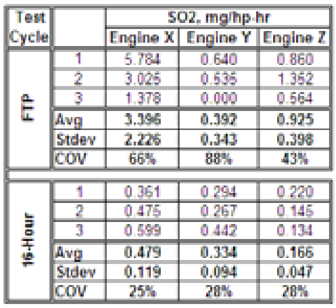
[13] (http://www.epa.gov/otaq/climate/documents/420r11901.pdf)

[14] Intergovernmental Panel on Climate Change. Chapter 2. Changes in Atmospheric Constituents and in Radiative Forcing. September 2007. http://www.ipcc.ch/pdf/assessment-report/ar4/wg1/ar4-wg1-chapter2.pdf Docket ID: EPA-HQ-OAR-2009-0472-0117

[15] Carroll J, I Khalek, L. Smith, E. Fujita, and B. Zielinska, "Collaborative Lubricating Oil Study on Emissions," http://www.nrel.gov/docs/fy12osti/52668.pdf

SO_2. For the 2007 engines, the sulfur level in sulfate combined with the sulfur level in SO_2 led to total sulfur mass that is similar to that calculated based on fuel and oil consumption.



Test Cycle		SO2, mg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	5.784	0.640	0.860
	2	3.025	0.535	1.352
	3	1.378	0.000	0.564
	Avg	3.396	0.392	0.925
	Stdev	2.226	0.343	0.398
	COV	66%	88%	43%
16-Hour	1	0.361	0.294	0.220
	2	0.475	0.267	0.145
	3	0.599	0.442	0.134
	Avg	0.479	0.334	0.166
	Stdev	0.119	0.094	0.047
	COV	25%	28%	28%

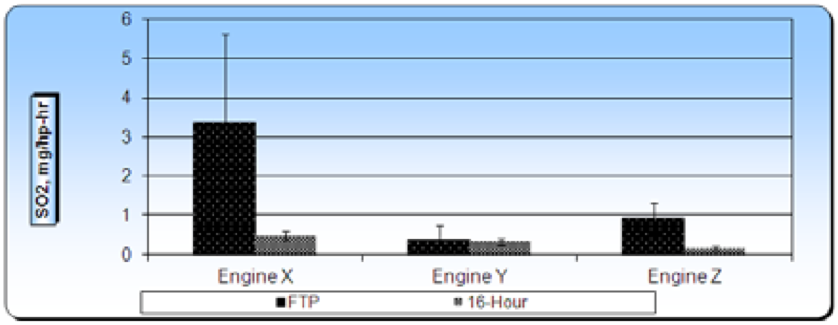


FIGURE 17. MEASURED SO_2 EMISSIONS FOR THE HOT-START FTP AND 16-HOUR

TABLE 12. 2010 ENGINES PREDICTED SO_2 EMISSIONS USING FUEL AND OIL SULFUR CONTRIBUTION

Test Cycle		SO2, mg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	3.03	3.20	3.74
	2	3.00	3.21	3.73
	3	3.00	3.20	3.77
	Avg	**3.01**	**3.21**	**3.75**
	Stdev	**0.019**	**0.005**	**0.019**
	COV	**1%**	**0%**	**1%**
16-Hour	1	2.99	3.08	3.48
	2	2.99	3.13	3.51
	3	3.00	3.13	3.52
	Avg	**2.99**	**3.11**	**3.51**
	Stdev	**0.001**	**0.030**	**0.019**
	COV	**0%**	**1%**	**1%**

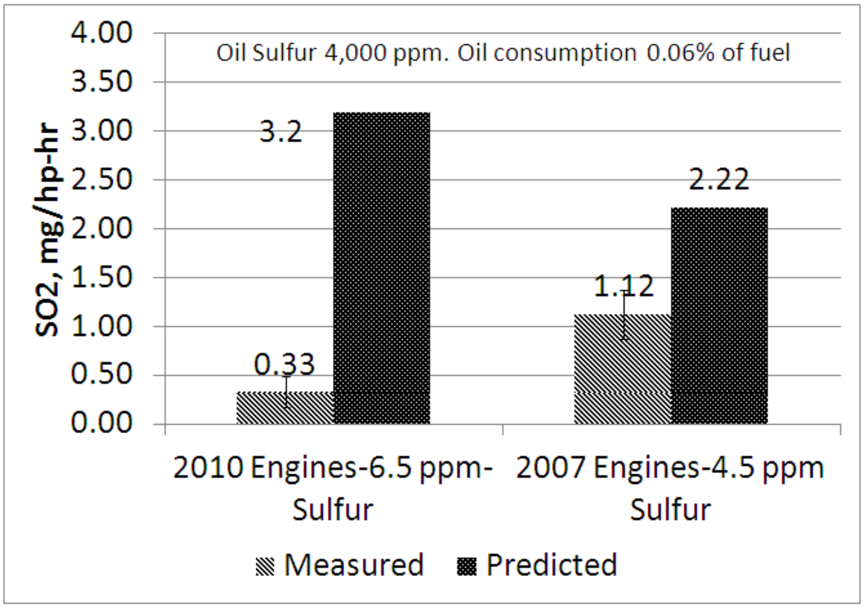


FIGURE 18. COMPARISON BETWEEN PREDICTED AND MEASURED SO_2 EMISSIONS FOR 2010 AND 2007 TECHNOLOGY ENGINES

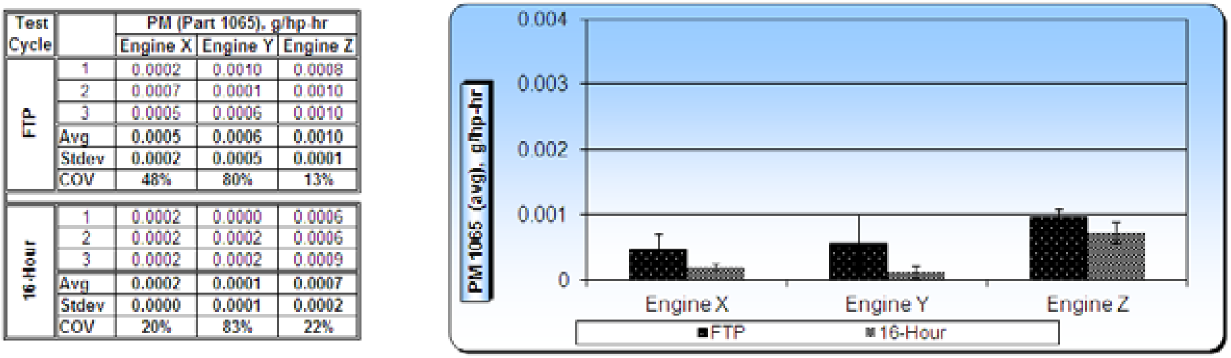
6.5 Particulate Matter Emissions

Several metrics and methods were used to characterize PM. This section includes information on Teflon® membrane filter-based PM measurements, quartz filter-based OC/EC analysis, filter-based elemental EDXRF and ICPMS analysis, real time total PM using the DMM-230, real time soot using the MSS, and real time number and size distribution measurements using the EEPS.

6.5.1 Filter-Based PM Mass-CVS Tunnel and Exposure Chamber

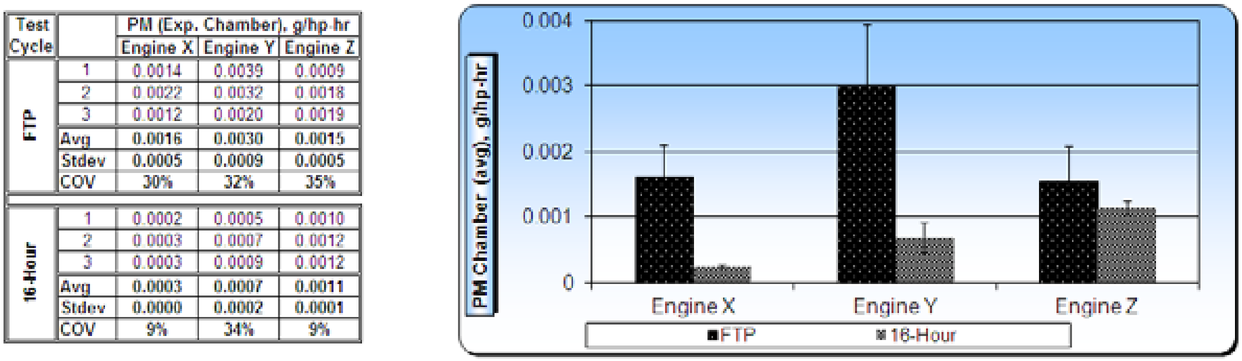
Filter-based PM was collected from two locations. The first location was from the CVS tunnel sample zone, in accordance with CFR Part 1065, where the filter face temperature was maintained at 47°C ±5°C, and total residence time (CVS plus secondary tunnel) was on the order of 3 to 5 seconds. The second location was from the exposure chamber, where the dilution ratio from the CVS tunnel was about 2, the filter face temperature was about 28°C, and the residence time was on the order of 4 to 5 minutes to purge 90 percent of the volume entering the chamber. It takes an additional 15 minutes for the remaining 10 percent volume to be fully purged. The temperature of the exposure chamber filter was not actively controlled and was dictated by the temperature inside the exposure chamber. The total flow through each of the 47 mm filters was approximately 57 slpm, resulting in a filter face velocity near 100 cm/s.

Figures 19 and 20 show the brake-specific PM emissions from the CFR Part 1065 method and the exposure chamber, respectively. Generally, PM emissions were very low, more than 90% below the 2010 PM standard of 0.01 g/hp-hr. However, the PM reported based on exposure chamber collection was much higher, especially for the FTP. This observation is not surprising since the filter face temperature (47°C vs. 28°C) and residence time (3 seconds vs. 4 minutes) between the two sampling locations are different. Lower temperature and particle growth in the chamber are likely contributing to the higher emissions. Also note that the FTP PM emissions based on the chamber collection were higher than those for the 16-Hour. During the short FTP, the PM is typically dominated by gas phase artifact collection by the filter at these low emissions levels. During the 16-Hour, due to the long duration of sampling, the filter saturates and minimizes the contribution of artifacts, thus leading to lower PM emissions that better reflects the true particle phase.



Test Cycle		PM (Part 1065), g/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.0002	0.0010	0.0008
	2	0.0007	0.0001	0.0010
	3	0.0005	0.0006	0.0010
	Avg	0.0005	0.0006	0.0010
	Stdev	0.0002	0.0005	0.0001
	COV	48%	80%	13%
16-Hour	1	0.0002	0.0000	0.0006
	2	0.0002	0.0002	0.0006
	3	0.0002	0.0002	0.0009
	Avg	0.0002	0.0001	0.0007
	Stdev	0.0000	0.0001	0.0002
	COV	20%	83%	22%

FIGURE 19. PM EMISSIONS FOR THE HOT-START FTP AND 16-HOUR BASED ON CVS TUNNEL CFR PART 1065 COLLECTION METHOD



Test Cycle		PM (Exp. Chamber), g/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.0014	0.0039	0.0009
	2	0.0022	0.0032	0.0018
	3	0.0012	0.0020	0.0019
	Avg	0.0016	0.0030	0.0015
	Stdev	0.0005	0.0009	0.0005
	COV	30%	32%	35%
16-Hour	1	0.0002	0.0005	0.0010
	2	0.0003	0.0007	0.0012
	3	0.0003	0.0009	0.0012
	Avg	0.0003	0.0007	0.0011
	Stdev	0.0000	0.0002	0.0001
	COV	9%	34%	9%

FIGURE 20. PM EMISSIONS FOR THE HOT-START FTP AND 16-HOUR BASED ON EXPOSURE CHAMBER COLLECTION

Figure 21 shows the average ratio of exposure chamber-based PM and CVS-based PM for all engines. The PM emissions based on exposure chamber filter collection were a factor of three higher for the FTP and a factor of 2 higher for the 16-Hour than those using CFR Part 1065 method. The reason for the higher PM in the chamber relative to the PM measured in accordance with CFR Part 1065 can be attributed to temperature and residence time. The filter face temperature in the chamber was at 28°C, compared to a temperature of 47°C using the CFR Part 1065 method. The residence time in the chamber was on the order of 5 minutes compared to the 5 seconds in CVS and secondary dilution system for the CFR Part 1065 PM collection method. The lower temperature and the longer residence time in the chamber may have enhanced gas phase adsorption onto existing particles and promote particle nucleation and growth resulting in higher PM emissions, compared to those based on the CFR Part 1065 method.

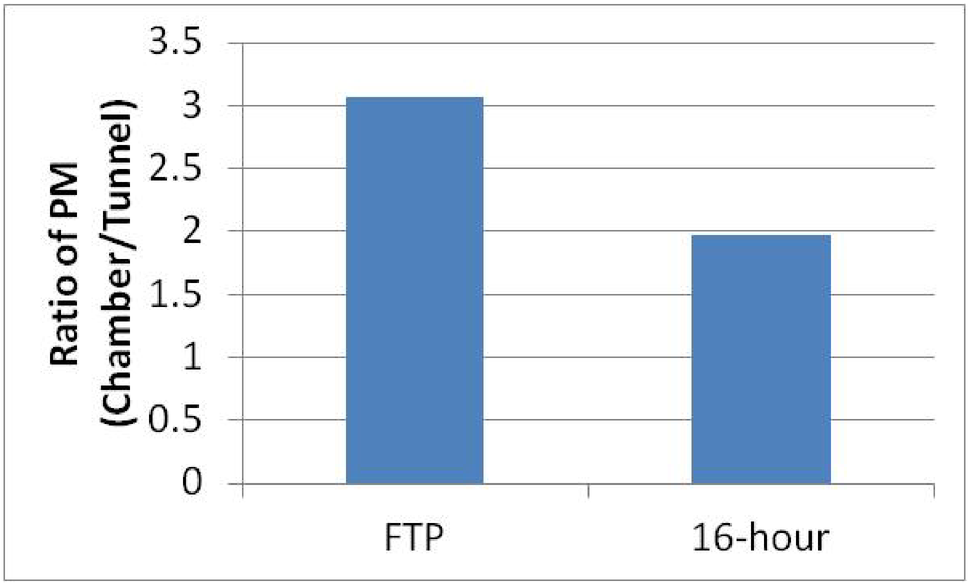
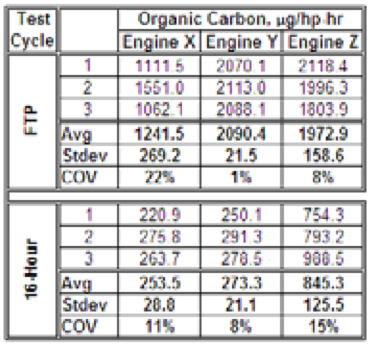


FIGURE 21. RATIO OF PM BASED ON EXPOSURE CHAMBER OVER PM BASED ON CVS USING CFR PART 1065

6.5.2 Quartz Filter-Based OC and EC-Exposure Chamber

PM was collected on quartz filters from the exposure chamber, and the filters were analyzed using the OC/EC reflectance method by DRI. Similar to what was done in ACES Phase 1, we report OC based on the primary filter used for PM collection with no subtraction of the back-up filter. For the 16-Hour, due to the long sampling time, it is not clear whether the back-up filter should be subtracted or added to the primary filter. So, we used the primary filter only as measured. Figures 22 and 23 show the brake-specific OC and EC emissions for the FTP and 16-Hour. OC emissions were substantially higher for the short FTP, compared to the 16-Hour. This observation is consistent with the PM filter measurement shown in Figure 20. Essentially, for the short cycle, the filter was likely dominated by gas phase artifact collection, compared to the 16-Hour filter. By sampling for a longer time with the 16-Hour, the filter saturates and the artifact contribution to filter measurement is minimized. The EC emissions were extremely low, to the point where they were not detected during the FTP that has an EC detection limit of 90 µg/hp-hr. For the 16-Hour, the EC levels were also extremely low between 59 and 170 µg/hp-hr, but well above the detection limit of 2 µg/hp-hr. The highest EC emission levels represent only 2% of the 2010 PM standard. The highest average EC emissions represent an EC chamber concentration of 3.5 µg/m^3.

Figures 24 and 25 show the average reduction in OC and EC for the 16-Hour relative to the 2007 technology engines. The OC reduction was 36%, while the EC was 53%. The OC reduction was likely due to the lack of active DPF regeneration and some probable additional oxidation and/or adsorption of heavy-molecular hydrocarbon by the SCR catalyst. The reduction in EC is likely due to a higher efficiency DPF operation due to the lack of active regeneration. We know from our previous work that a partially loaded DPF has a higher efficiency than a clean DPF.



Test Cycle		Organic Carbon, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	1111.5	2070.1	2118.4
	2	1551.0	2113.0	1996.3
	3	1062.1	2088.1	1803.9
	Avg	1241.5	2090.4	1972.9
	Stdev	269.2	21.5	158.6
	COV	22%	1%	8%
16-Hour	1	220.9	250.1	754.3
	2	275.8	291.3	793.2
	3	263.7	278.5	988.5
	Avg	253.5	273.3	845.3
	Stdev	28.8	21.1	125.5
	COV	11%	8%	15%

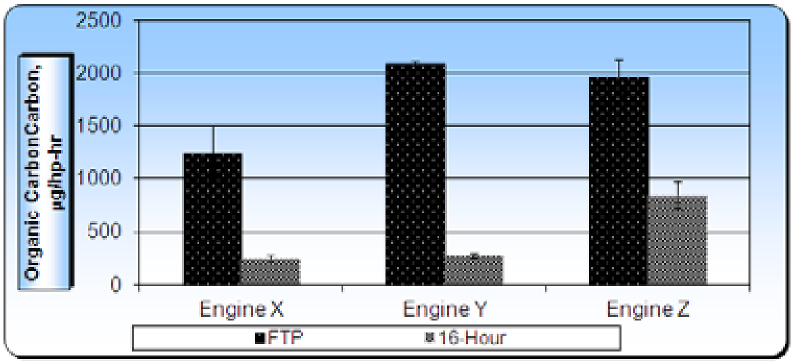
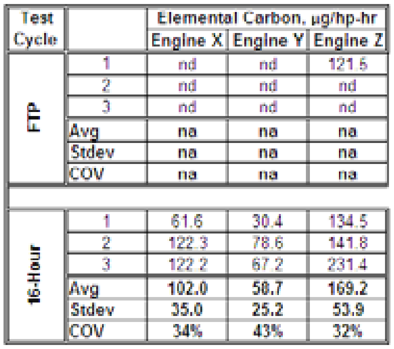


FIGURE 22. ORGANIC CARBON EMISSIONS FOR THE HOT-START FTP AND 16-HOUR



Test Cycle		Elemental Carbon, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	nd	nd	121.5
	2	nd	nd	nd
	3	nd	nd	nd
	Avg	na	na	na
	Stdev	na	na	na
	COV	na	na	na
16-Hour	1	61.6	30.4	134.5
	2	122.3	78.6	141.8
	3	122.2	67.2	231.4
	Avg	102.0	58.7	169.2
	Stdev	35.0	25.2	53.9
	COV	34%	43%	32%

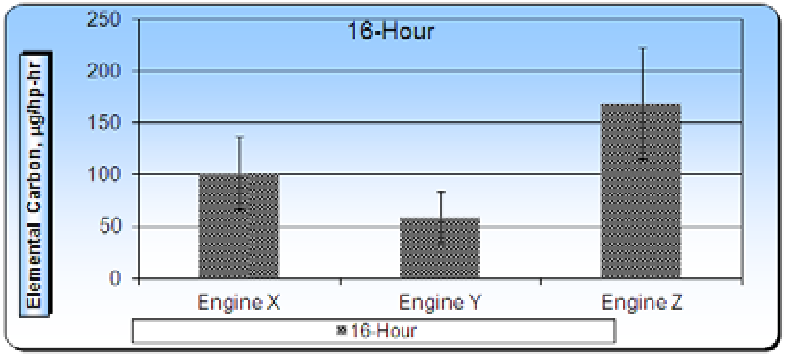


FIGURE 23. ELEMENTAL CARBON EMISSIONS FOR THE HOT-START FTP AND 16-HOUR

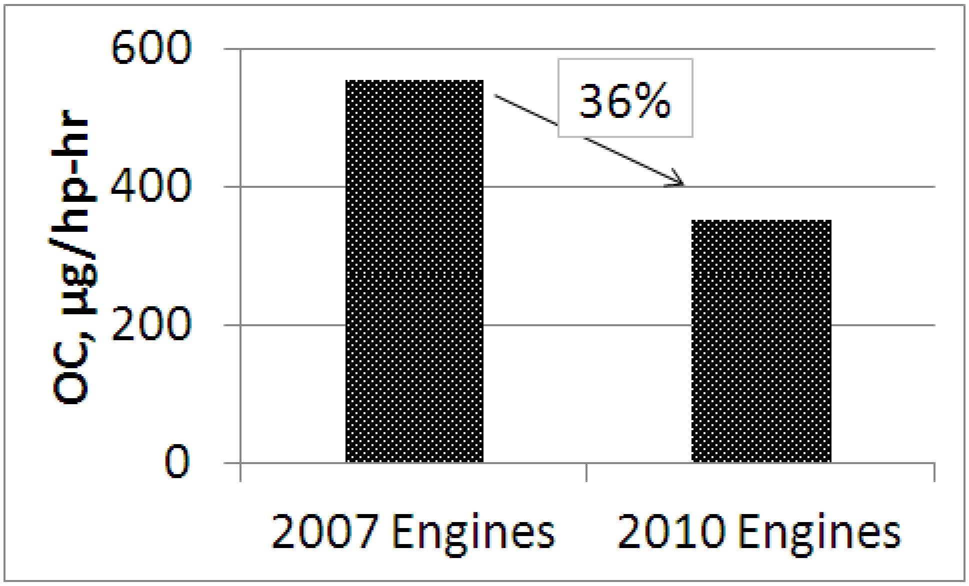


FIGURE 24. ORGANIC CARBON REDUCTION WITH 2010 VS. 2007 TECHNOLOGY ENGINES (16-HOUR)

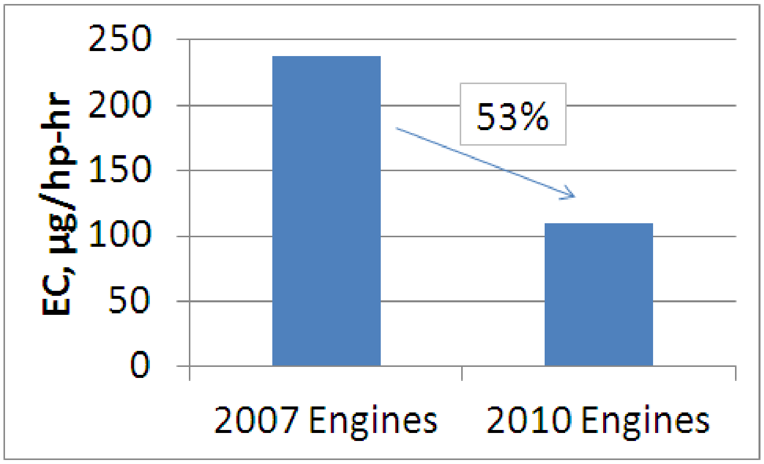


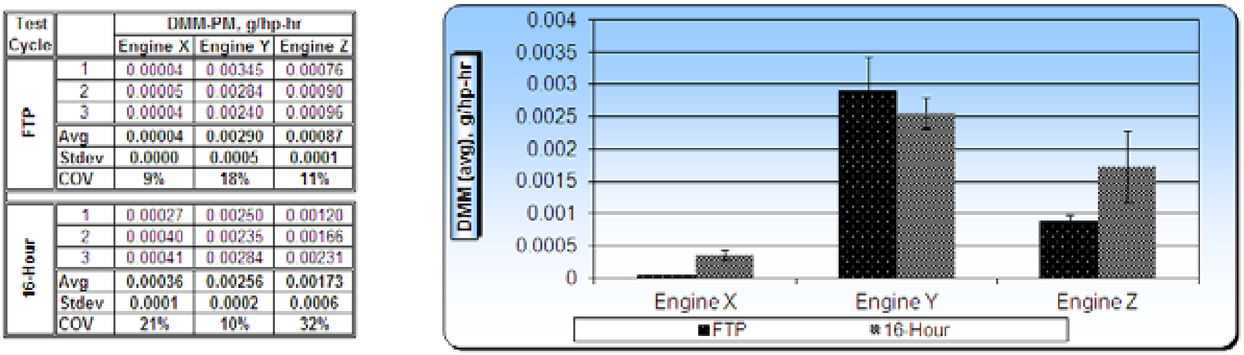
FIGURE 25. ELEMENTAL CARBON REDUCTION WITH 2010 VS. 2007 TECHNOLOGY ENGINES (16-HOUR)

6.5.3 MSS-Based Soot Mass-Exposure Chamber

Overall, the soot measurement from the exposure chamber was below the detection limit of the instrument at 5 µg/m³. At this very low level of PM, the instrument showed sensitivity to exhaust gas composition where negative values were observed. For example, the reading went slightly negative when switching from HEPA-filtered zero air reading to sampling from the chamber. There was not enough soot in the chamber to overcome the negative readings, so some of the average emission levels were negative. The EC reported in Figure 25 and 23 for the 16-Hour gives a more representative reading of the soot or elemental carbon emitted.

6.5.4 DMM-Based Total PM Mass-Exposure Chamber

Figure 26 summarizes the DMM-based PM emissions for the FTP and 16-Hours. Overall, the DMM gave a relatively similar PM emissions trend to that reported by the PM collection from the exposure chamber (Figure 20). At this low level of PM, and due to the virtual absence of EC particles in the exhaust, this instrument can only be used to give qualitative information on PM.



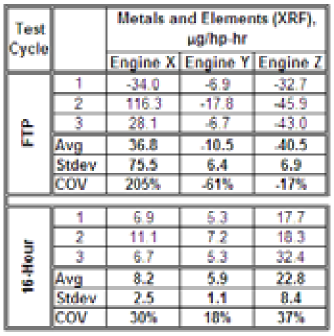
Test Cycle		DMM-PM, g/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.00004	0.00345	0.00076
	2	0.00005	0.00284	0.00090
	3	0.00004	0.00240	0.00096
	Avg	0.00004	0.00290	0.00087
	Stdev	0.0000	0.0005	0.0001
	COV	9%	18%	11%
16-Hour	1	0.00027	0.00250	0.00120
	2	0.00040	0.00235	0.00166
	3	0.00041	0.00284	0.00231
	Avg	0.00036	0.00256	0.00173
	Stdev	0.0001	0.0002	0.0006
	COV	21%	10%	32%

FIGURE 26. PM EMISSIONS FOR THE HOT-START FTP AND 16-HOUR BASED ON DMM MEASUREMENT FROM THE EXPOSURE CHAMBER

6.5.5 Metals and Other Elements

Figure 27 shows the sum of the elements emitted over the FTP and the 16-Hour using the XRF detection method. These elements were dominated by a non-metallic element such as sulfur and metallic elements such as Ca, Zn, Fe, and Al. The total elements collected on a sample filter over the FTP were similar in levels to those detected in a filter blank. As a result, we have some negative data for the FTP due to sample filter correction with the filter blank. The mass of total elements collected on a sample filter over the 16-Hour was much higher than that measured for a filter blank. Thus, we should only use the emissions data for the 16-Hour. Still, the elements mass emitted over the 16-Hour was extremely low, representing only about 2% of the very low PM. The emissions vary among engines with a range between 6 µg/hp-hr and 23 µg/hp-hr. The dominant non-metallic element in the particle phase is sulfur. Sulfur represents 23% (1.91 µg/hp-hr ± 0.24) of the total elements emitted for Engine X, 23% (1.34 µg/hp-hr ± 0.31) for Engine Y and 41% (4.38 µg/hp-hr ± 1.96) for Engine Z. Figure 28 shows a substantial reduction in emissions from elements relative to the 2007 technology engines used in ACES Phase 1. The reduction in the emissions from elements may be partially attributed to the lack of DPF regeneration. When active regeneration occurs, sulfur is expected to be released and the DPF is expected to become less efficient after the EC is burned. Both factors may elevate the emissions of sulfur as well as metallic ash.

Figure 29 shows the total metallic elements emissions using the ICPMS method. Metallic elements detected during the FTP are on the same order of those detected in a filter blank. Thus, negative values are reported for the FTP due to filter blank subtraction. Similar to the conclusion we made with the XRF method, only data for the 16-Hour should be used. The emissions for the 16-Hour vary among engines with a range between 3.2 to 4.0 µg/hp-hr for Engine X and Y to 11.6 µg/hp-hr for Engine Z. A linear regression between the XRF method and the ICPMS is shown in Figure 30 using the exact same species. A reasonable agreement between the two methods was obtained, where the ICPMS method reported about 20% lower metallic emissions than those reported by the XRF. In principle, the ICPMS method has a lower detection limit and can be considered more accurate. Figure 31 shows individual metal elements detected using the ICPMS method (A) and the XRF method (B). Figure 31 includes all the metal elements that we analyzed using the XRF and ICPMS methods. Both methods showed a similar trend. The emissions were dominated by calcium and zinc (oil additives) followed by engine wear elements such as iron and aluminum. Other traces of engine wear elements such as chromium, nickel and copper were observed. This is in addition to traces of lube oil elements such as magnesium and manganese.



Test Cycle		Metals and Elements (XRF), µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	-34.0	-6.9	-32.7
	2	116.3	-17.8	-45.9
	3	28.1	-6.7	-43.0
	Avg	36.8	-10.5	-40.5
	Stdev	75.5	6.4	6.9
	COV	205%	-61%	-17%
16-Hour	1	6.9	5.3	17.7
	2	11.1	7.2	18.3
	3	6.7	5.3	32.4
	Avg	8.2	5.9	22.8
	Stdev	2.5	1.1	8.4
	COV	30%	18%	37%

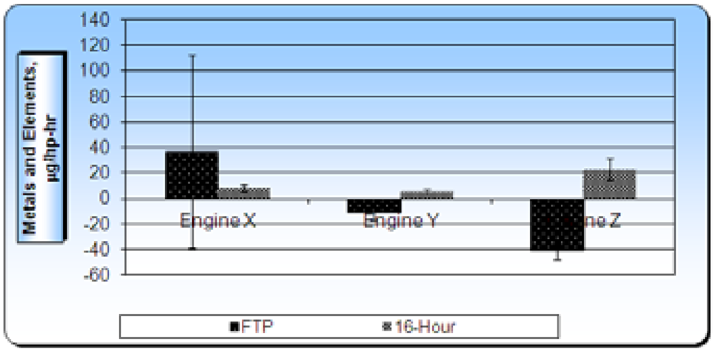


FIGURE 27. TOTAL ELEMENTS EMISSIONS USING THE XRF METHOD

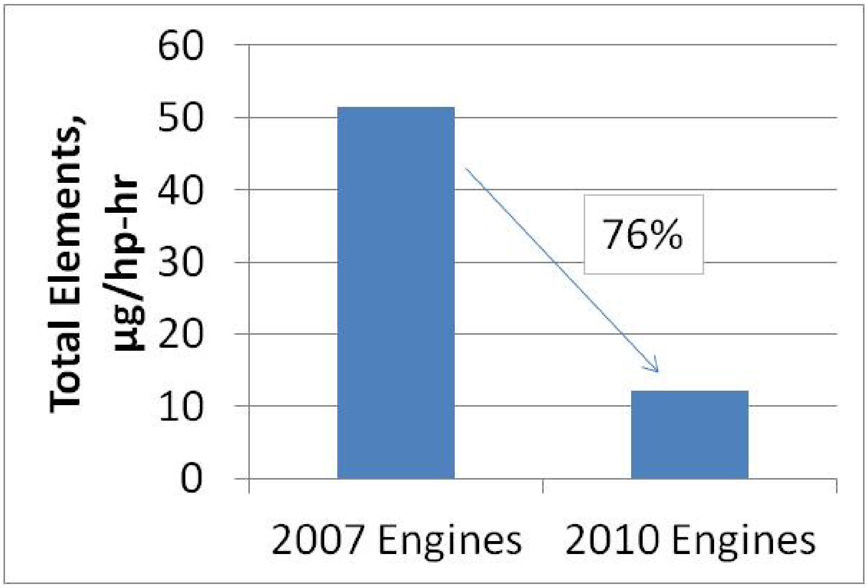
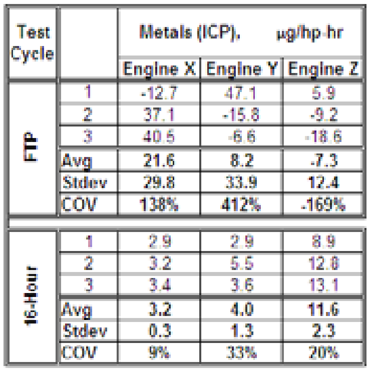


FIGURE 28. TOTAL ELEMENTS EMISSIONS COMPARISON bETWEEN 2010 AND 2007 TECHNOLOGY ENGINES



Test Cycle		Metals (ICP), µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	-12.7	47.1	5.9
	2	37.1	-15.8	-9.2
	3	40.5	-6.6	-18.6
	Avg	21.6	8.2	-7.3
	Stdev	29.8	33.9	12.4
	COV	138%	412%	-169%
16-Hour	1	2.9	2.9	8.9
	2	3.2	5.5	12.8
	3	3.4	3.6	13.1
	Avg	3.2	4.0	11.6
	Stdev	0.3	1.3	2.3
	COV	9%	33%	20%

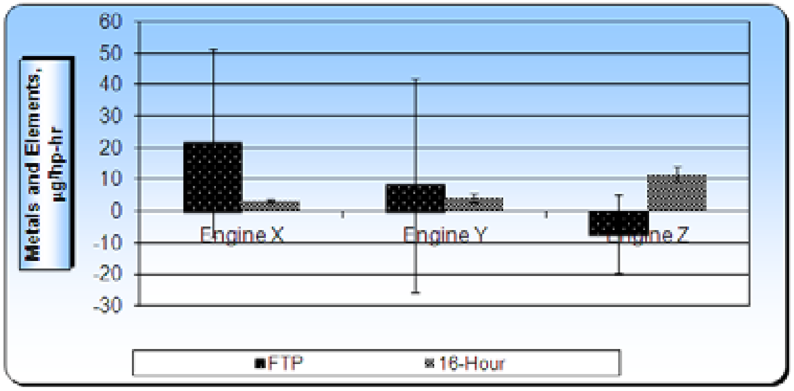


FIGURE 29. METALLIC ELEMENTS EMISSIONS USING THE ICPMS METHOD

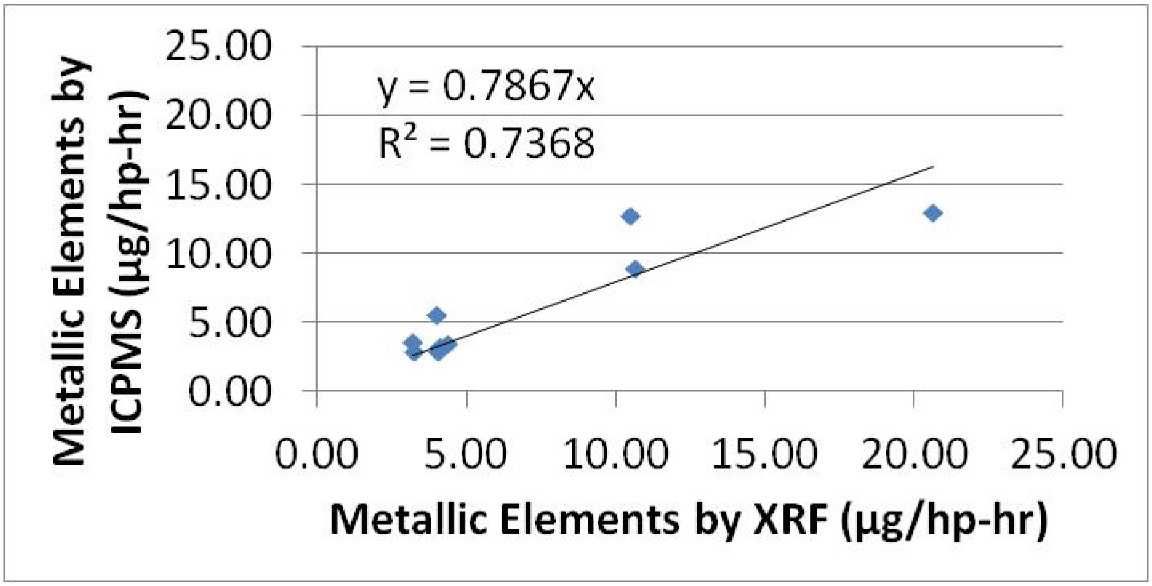


FIGURE 30. CORRELATION FOR METALLIC ELEMENTS USING XRF AND ICPMS (16-HOUR)

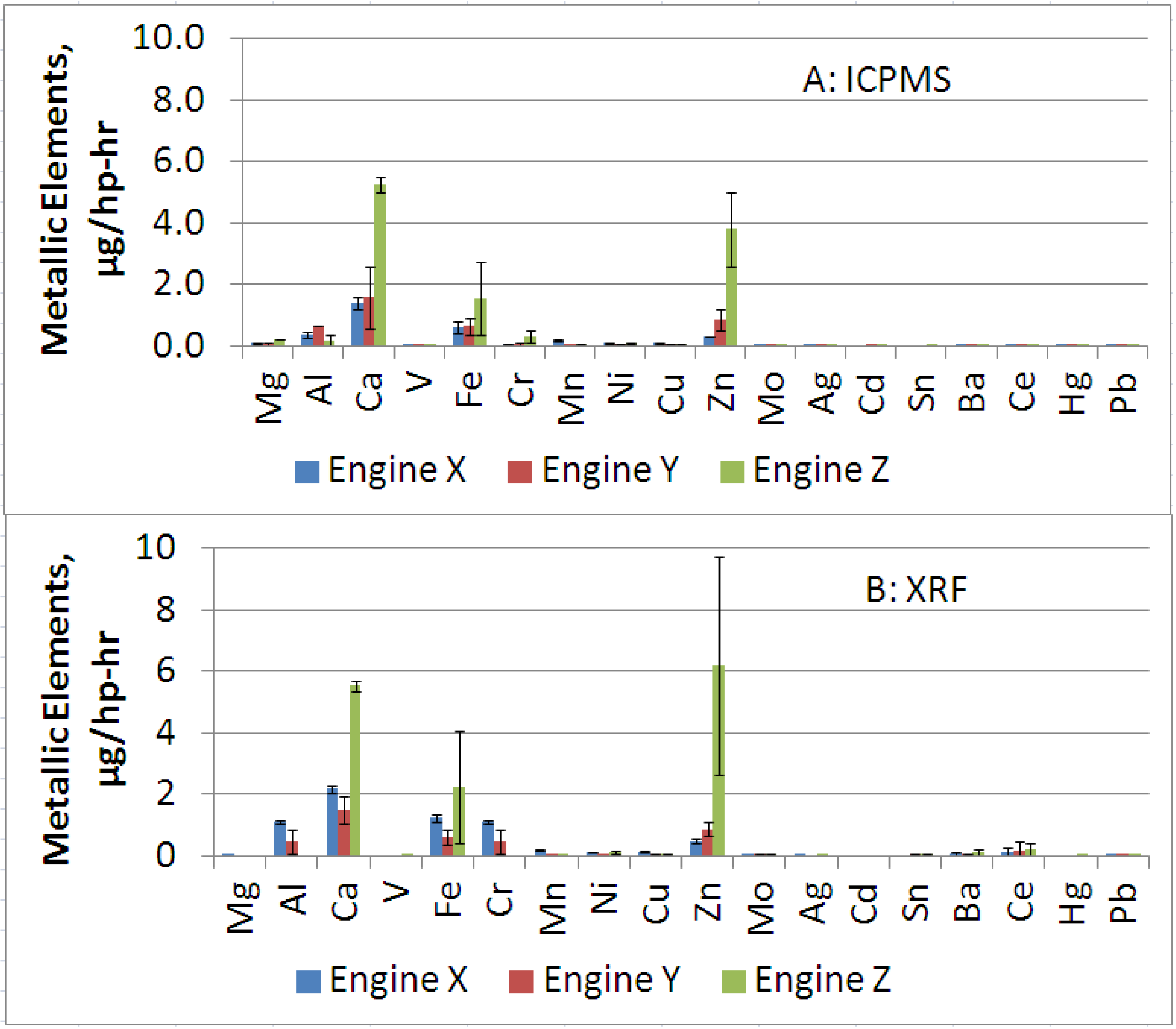
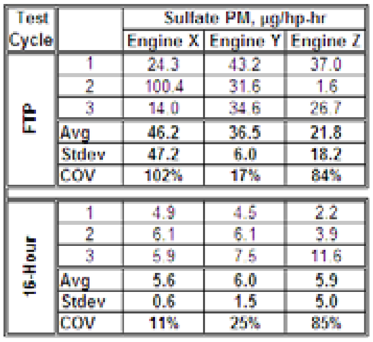


FIGURE 31. METALLIC ELEMENTS EMISSIONS USING ICPMS AND XRF (16-HOUR)

6.6 Inorganic Ions Emissions

Figures 32 through 35 show sulfate, ammonium, and nitrate emissions for the FTP and 16-Hour. Sulfate is typically derived from sulfur in the fuel and lube oil. We did not observe ammonium and nitrate emissions with the 2007 technology engines. They are likely present here because of the urea-SCR system interaction. Although the emissions data are above the detection limit for both the FTP and the 16-Hour, unless otherwise noted, the ion detection for the 16-Hour is more reliable. For example, the average emissions for the FTP were 2 to 4 times higher than the detection limit, while they were 30 times higher for the 16-Hour. Also, some of the nitrate emissions for the FTP exceeded the total PM emissions, suggesting unreliable measurements for nitrate during the FTP. Thus, the focus will be on the 16-Hour. Sulfate emissions represent a very small fraction of total PM on the order of 1%, followed by 2% for ammonium, and 14% for nitrate. Also, sulfate emissions were substantially lower than those observed with 2007 technology engines in ACES Phase 1, as shown in Figure 35. The reduced level of sulfate is likely due to sulfur adsorption by the aftertreatment system. This is also consistent with the reduced level of SO_2 emissions (Figure 18) observed with the 2010 engine technology. As discussed before, the lack of active regeneration was one of the key differences between the two engine technologies that suppressed the release of sulfate. Another reason for the continued adsorption of sulfate could be the fact that the DPF did not have sufficiently long hours of engine operation to be saturated with sulfur. At some point in the engine operation, the aftertreatment system will be saturated with sulfur and stop adsorbing. We hypothesize that this phenomenon occurred with Engine Z during the 3rd 16-Hour. We noted that sulfate emissions went up between the 1st and 2nd 16-Hour and drastically increased for the 3rd 16-Hour, as shown in the table in Figure 32. Furthermore, we will show in the next section on particle number and size that the number emissions of nuclei mode nanoparticles increased drastically during the 3rd 16-Hour with Engine Z.



Test Cycle		Sulfate PM, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	24.3	43.2	37.0
	2	100.4	31.6	1.6
	3	14.0	34.6	26.7
	Avg	46.2	36.5	21.8
	Stdev	47.2	6.0	18.2
	COV	102%	17%	84%
16-Hour	1	4.9	4.5	2.2
	2	6.1	6.1	3.9
	3	5.9	7.5	11.6
	Avg	5.6	6.0	5.9
	Stdev	0.6	1.5	5.0
	COV	11%	25%	85%

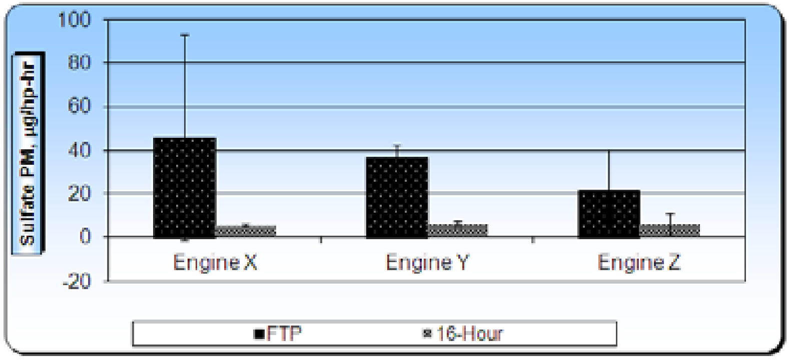
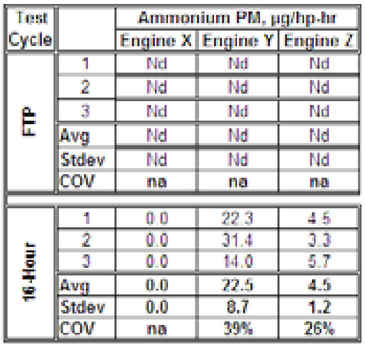


FIGURE 32. SULFATE EMISSIONS FOR THE HOT-START FTP AND 16-HOUR



Test Cycle		Ammonium PM, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	Nd	Nd	Nd
	2	Nd	Nd	Nd
	3	Nd	Nd	Nd
	Avg	Nd	Nd	Nd
	Stdev	Nd	Nd	Nd
	COV	na	na	na
16-Hour	1	0.0	22.3	4.5
	2	0.0	31.4	3.3
	3	0.0	14.0	5.7
	Avg	0.0	22.5	4.5
	Stdev	0.0	8.7	1.2
	COV	na	39%	26%

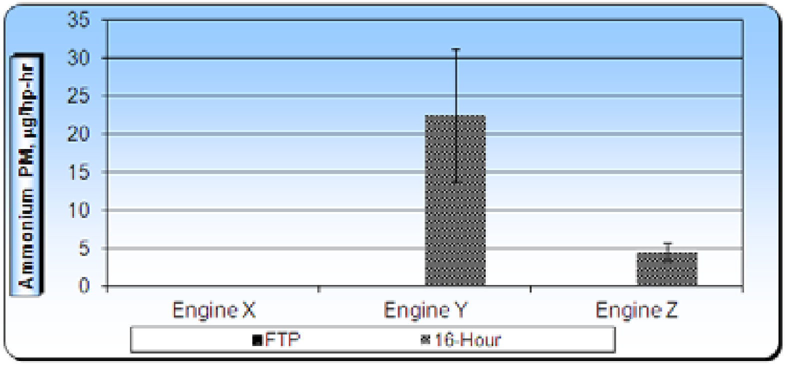
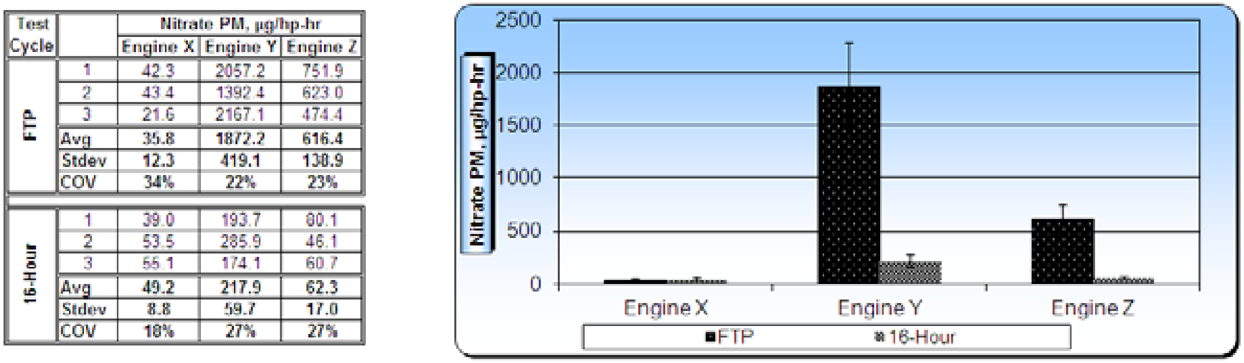


FIGURE 33. AMMONIUM EMISSIONS FOR THE HOT-START FTP AND 16-HOUR



Test Cycle		Nitrate PM, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	42.3	2057.2	751.9
	2	43.4	1392.4	623.0
	3	21.6	2167.1	474.4
	Avg	35.8	1872.2	616.4
	Stdev	12.3	419.1	138.9
	COV	34%	22%	23%
16-Hour	1	39.0	193.7	80.1
	2	53.5	285.9	46.1
	3	55.1	174.1	60.7
	Avg	49.2	217.9	62.3
	Stdev	8.8	59.7	17.0
	COV	18%	27%	27%

FIGURE 34. NITRATE EMISSIONS FOR THE HOT-START FTP AND 16-HOUR

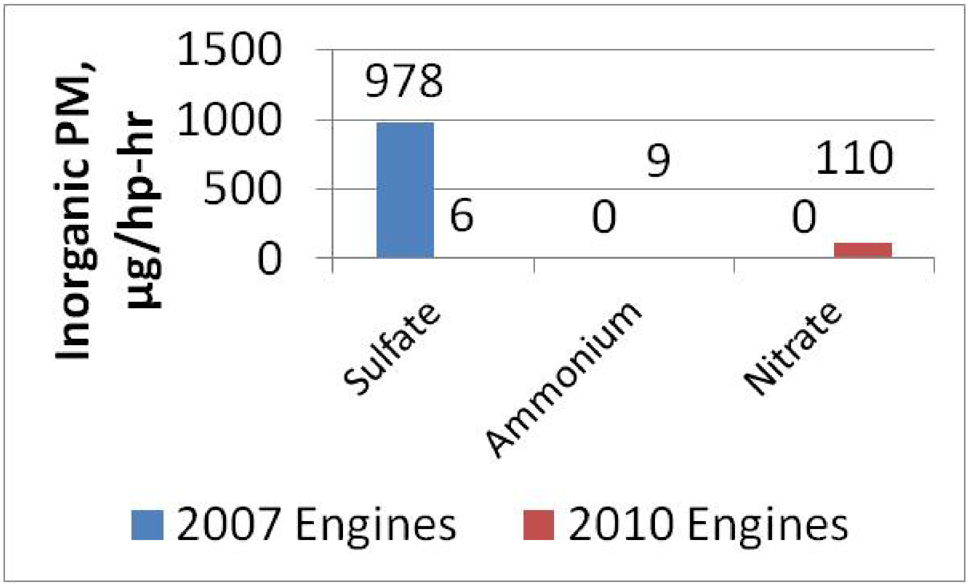


FIGURE 35. INORGANIC ION EMISSIONS COMPARISON BETWEEN 2010 AND 2007 ENGINES (16-HOUR)

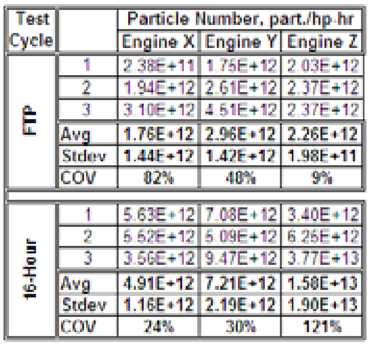
6.7 EEPS-Based Particle Number and Size-Exposure Chamber

It is important to note here that we measured total (solid + volatile) particle number in the size range from 5.6 nm to 560 nm. Thus, our measurements cannot be directly compared with the EU regulations. However, since volatile particle formation dominates the range below 23 nm, one can determine the number emissions for particles larger than 23 nm to give an indication of particle emissions relative to the EU standard at 0.45 x 10^{12} part./hp-hr (6 x10^{11} part./kW-hr), based on the World Harmonized Transient Cycle (WHTC), a different cycle than those used in ACES Phase 2.

Figure 36 shows the particle number emissions for particles in the size range from 5.6 nm to 560 nm. The number emissions for the FTP were lower than that observed for the 16-Hour. For the FTP, the number ranged from 1.8×10^{12} part./hp-hr for Engine X to 3 $\times10^{12}$ part./hp-hr for Engine Y. Engine Z was in between at 2.3×10^{12}part./hp-hr. For the 16-Hour, the number ranged from 5×10^{12} part./hp-hr for Engine X to 7×10^{12} part./hp-hr for Engine Y and 1.6×10^{13}

part./hp-hr for Engine Z. Note that although the average number emissions were on the same order for the FTP, the size distribution characteristics were different among the three engines. For example, Figure 37 shows that Engine X and Y number emissions were dominated by nuclei mode nanoparticles with a mean diameter of 10 nm to 14 nm, while Engine Z emissions were dominated by particles with a mean diameter of 41 nm with no nuclei mode particles. We determined that Engine Z had 80% of the particles emitted larger than 23 nm while they constituted only 22% for Engine X and Y.

For the 16-Hour, the geometric number mean diameter (GNMD) of the size distribution for Engine X and Y was similar to that of the FTP, as shown in Figure 38, but that was not the case for Engine Z. For Engine Z, more nuclei mode particles were produced during the 16-Hour, resulting in a GNMD shift from 41 nm for the FTP to 21 nm for the 16-Hour. Furthermore, Engine Z average number emissions data had a large standard deviation, suggesting a difference in number emissions among the three 16-Hour runs. To look further into this issue, Figure 39 shows the average size distribution for each of the three 16-Hour tested with Engine Z. The average and standard deviation were based on the four 4-hour repeated segments that make up each 16-Hour. As shown in Figure 39, there was a progressive shift in the GNMD toward smaller particles among the 16-Hour runs. The GNMD shifted from 39 nm for the first 16-Hour run to 31 nm for the second run to an 18 nm for the third run. This was accompanied by a large increase in particle number. The reason for the increase in particle number with Engine Z is not known, but we have seen some evidence (Figures 22 and 23) of increased OC and especially EC as we progressed from the first 16-Hour to the third one for Engine Z. Based on our recent work with OC[16], it is very difficult to have any nucleation of OC at these low levels. Also, the increase in EC cannot account for the strong rise in nuclei mode particles observed for Engine Z in Figure 40. The most likely cause for the rise in nanoparticle emissions with Engine Z is sulfuric acid nucleation and growth. This can be corroborated by the large increase observed in Engine Z sulfate emissions (Figure 32) between the second 16-Hour run (3.9 µg/hp-hr) and the third (11.6 µg/hp-hr) 16-Hour run.



Test Cycle		Particle Number, part./hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	2.38E+11	1.75E+12	2.03E+12
	2	1.94E+12	2.61E+12	2.37E+12
	3	3.10E+12	4.51E+12	2.37E+12
	Avg	1.76E+12	2.96E+12	2.26E+12
	Stdev	1.44E+12	1.42E+12	1.98E+11
	COV	82%	48%	9%
16-Hour	1	5.63E+12	7.08E+12	3.40E+12
	2	5.52E+12	5.09E+12	6.26E+12
	3	3.56E+12	9.47E+12	3.77E+13
	Avg	4.91E+12	7.21E+12	1.58E+13
	Stdev	1.16E+12	2.19E+12	1.90E+13
	COV	24%	30%	121%

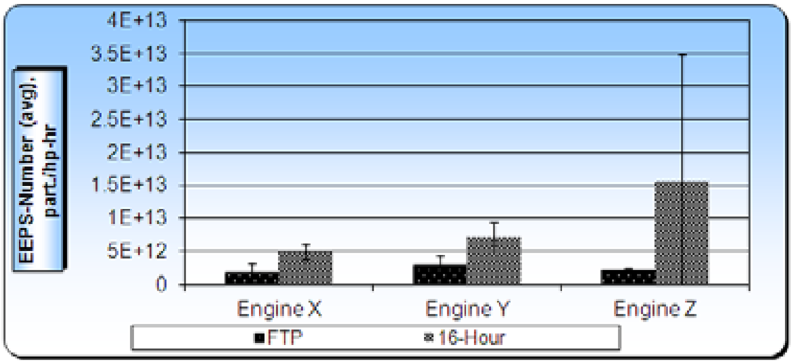


FIGURE 36. PARTICLE NUMBER EMISSIONS FOR THE HOT-START FTP AND 16-HOUR

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[16] Khalek, I., A. Mamakos, V. Premnath, R. Mechler, D. Preece, R. Giannelli, and M. Spears, "Particle Generator For Engine Exhaust Simulation: 2012-2013 Progress, 23rd CRC Real World Emissions Workshop, April, 2013

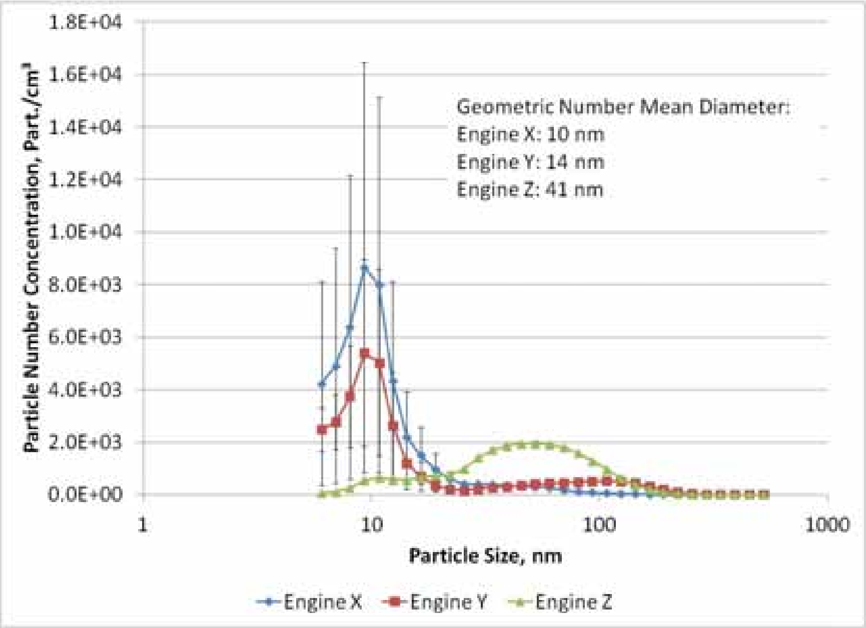


FIGURE 37. AVERAGE PARTICLE NUMBER-WEIGHTED SIZE DISTRIBUTION FOR THE FTP CYCLE (EXPOSURE CHAMBER, STANDARD DEVIATION BASED ON THREE REPEATS OF THE FTP)

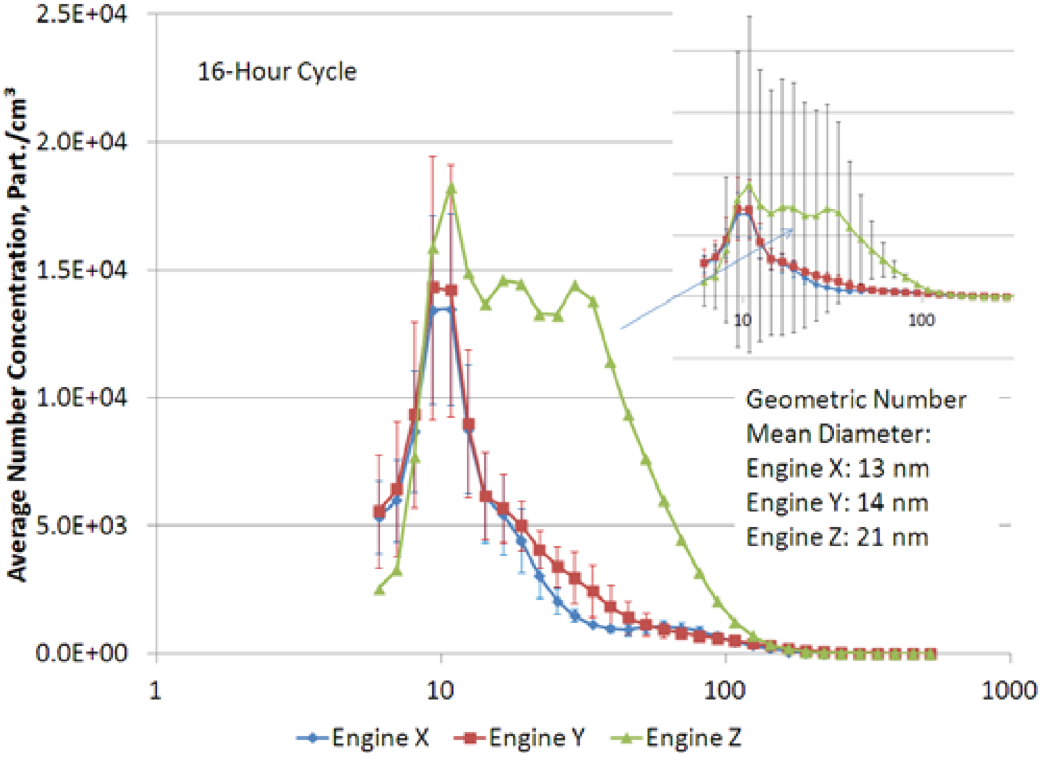


FIGURE 38. AVERAGE PARTICLE NUMBER-WEIGHTED SIZE DISTRIBUTION FOR THE 16-HOUR (EXPOSURE CHAMBER, STANDARD DEVIATION BASED ON THREE REPEATS OF 16-HOUR)

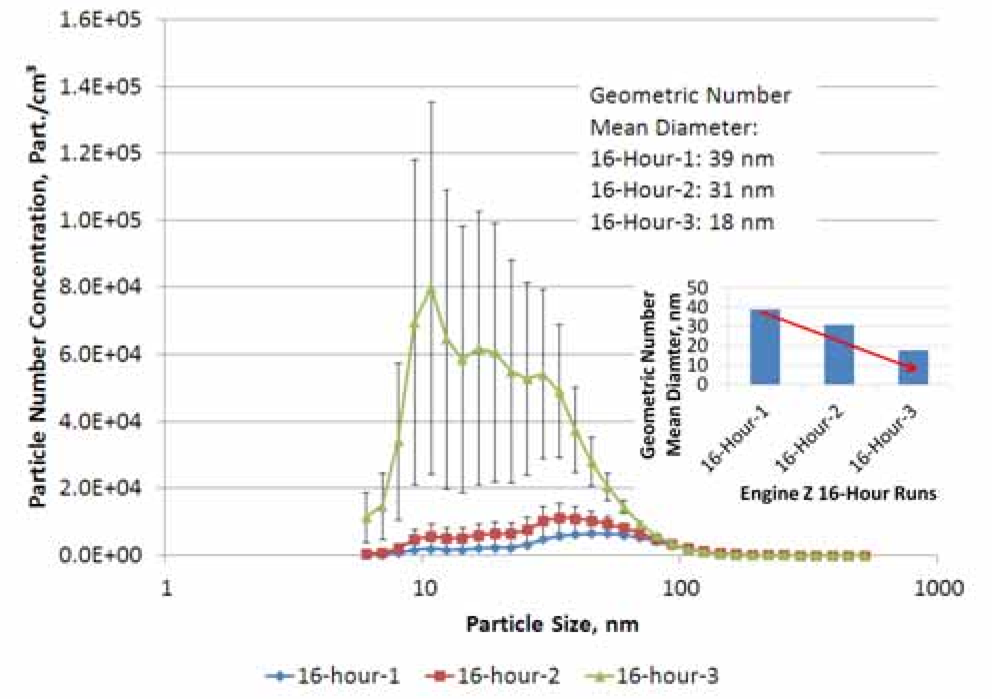


FIGURE 39. AVERAGE PARTICLE NUMBER-WEIGHTED SIZE DISTRIBUTION FOR THE 16-HOUR USING ENGINE Z (EXPOSURE CHAMBER, STANDARD DEVIATION BASED ON FOUR 4-HOUR SEGMENTS OF EACH 16-HOUR)

Figure 40 shows the average (based on three repeats) particle number concentration in exposure chamber for the FTP. Based on a dilution ratio of 16 between the exhaust and the chamber, the average number concentration was between 20,000 part./cm³ and 40,000 part./cm³. That is a very low concentration (close to the ambient background concentration), considering that the dilution ratio was only 16. Figure 41 summarizes the average particle number concentration expected in the exposure chamber during the 16-Hour operation. The average concentration ranged from about a 100,000 part./cm³ for Engine X and Engine Y to 200,000 part./cm³ for Engine Z.

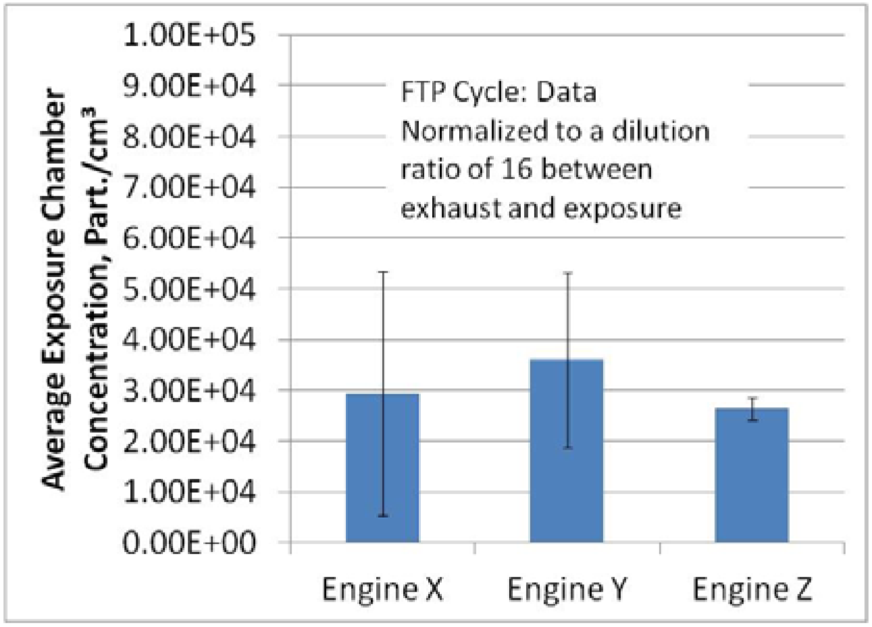


FIGURE 40. AVERAGE PARTICLE NUMBER CONCENTRATION IN EXPOSURE CHAMBER (FTP)

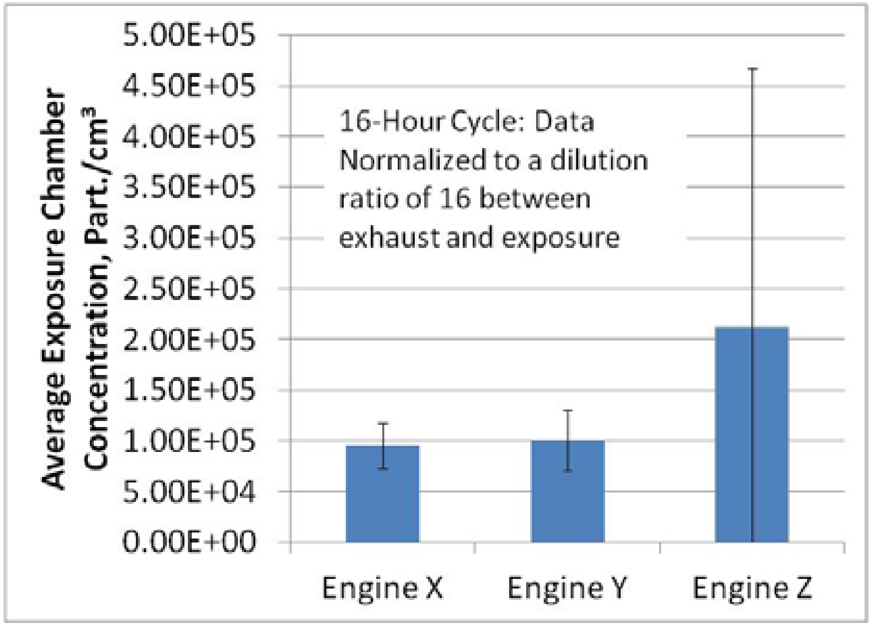


FIGURE 41. AVERAGE PARTICLE NUMBER CONCENTRATION IN EXPOSURE CHAMBER (16-HOUR)

6.8 Carbonyl Emissions

Figure 42 shows the carbonyl emissions species for the 16-Hour. Carbonyl emissions were dominated by formaldehyde and acetaldehyde. Figure 43 summarizes the emissions of total carbonyl emissions for all engines and cycles. We also compared (Figure 44) the emissions of carbonyls with those emitted from 2007 technology engines. We observed an 80% reduction with the 2010 technology engines, compared to the 2007 technology engines used in ACES Phase 1.

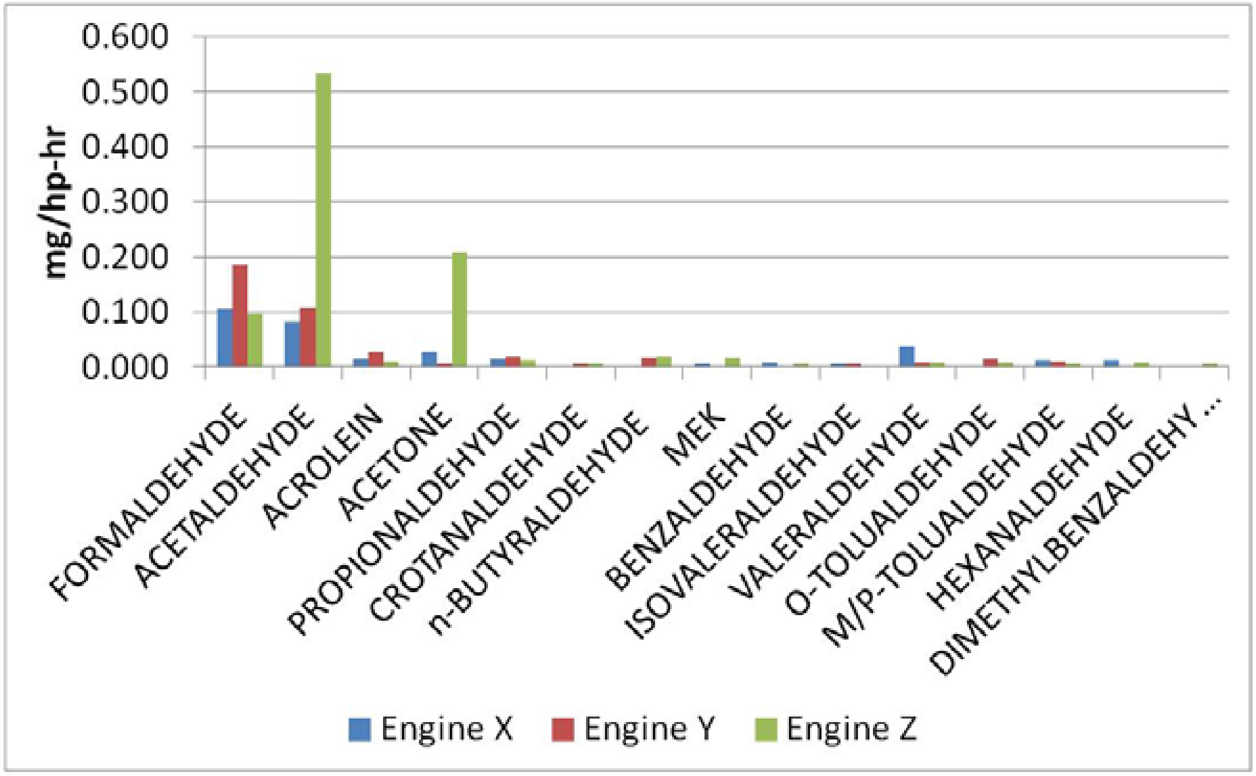
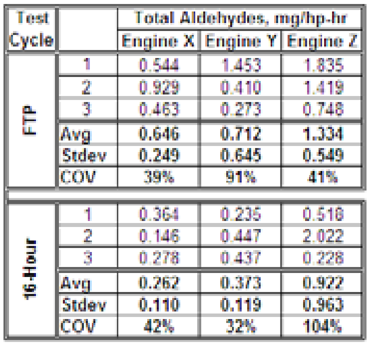


FIGURE 42. CARBONYLS SPECIES EMISSIONS FOR THE 16-HOUR



Test Cycle		Total Aldehydes, mg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.544	1.453	1.835
	2	0.929	0.410	1.419
	3	0.463	0.273	0.748
	Avg	0.646	0.712	1.334
	Stdev	0.249	0.645	0.549
	COV	39%	91%	41%
16-Hour	1	0.364	0.235	0.518
	2	0.146	0.447	2.022
	3	0.278	0.437	0.228
	Avg	0.262	0.373	0.922
	Stdev	0.110	0.119	0.963
	COV	42%	32%	104%

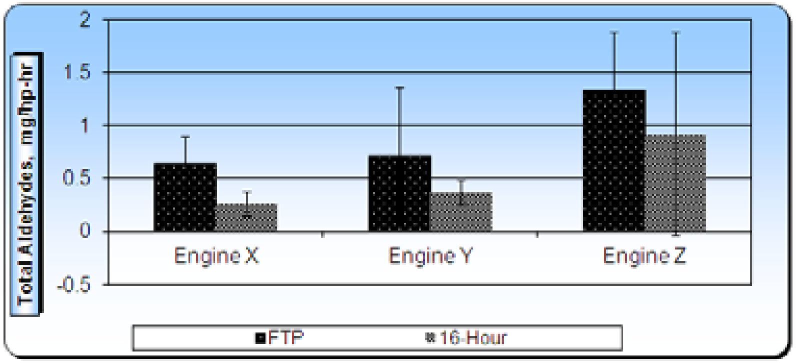


FIGURE 43. CARBONYLS EMISSIONS FOR THE FTP AND 16-HOUR

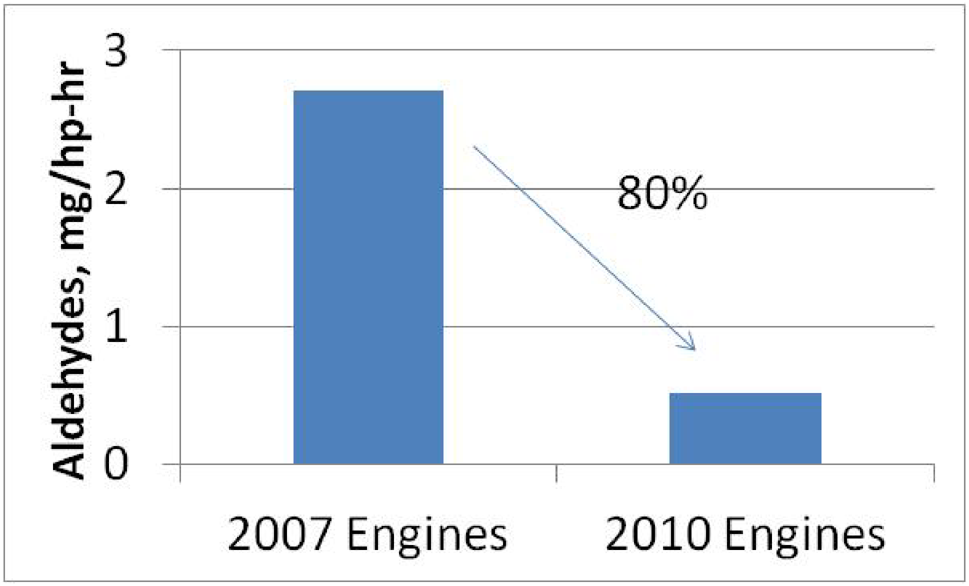


FIGURE 44. CARBONYLS EMISSIONS REDUCTION BETWEEN 2007 AND 2010 TECHNOLOGY ENGINES (16-HOUR)

6.9 Volatile Organic Compounds (VOC) Speciation-C_1-C_{12}

Figure 45 summarizes the emissions of benzene, toluene, ethylbenzene, and mixed xylenes (BTEX) for the different engines using the 16-Hour. The rise in ethylbenzene and mixed xylenes with Engine Z occurred only during the third 16-Hour run, where we observed the rise of in other emissions such as OC and sulfate. It is worth noting here that BTEX was below detection for the FTP. Figure 46 summarizes the BTEX emissions, and Figure 47 shows that the BTEX emissions for the 2010 technology engines were 50% lower than those emitted from 2007 technology engines.

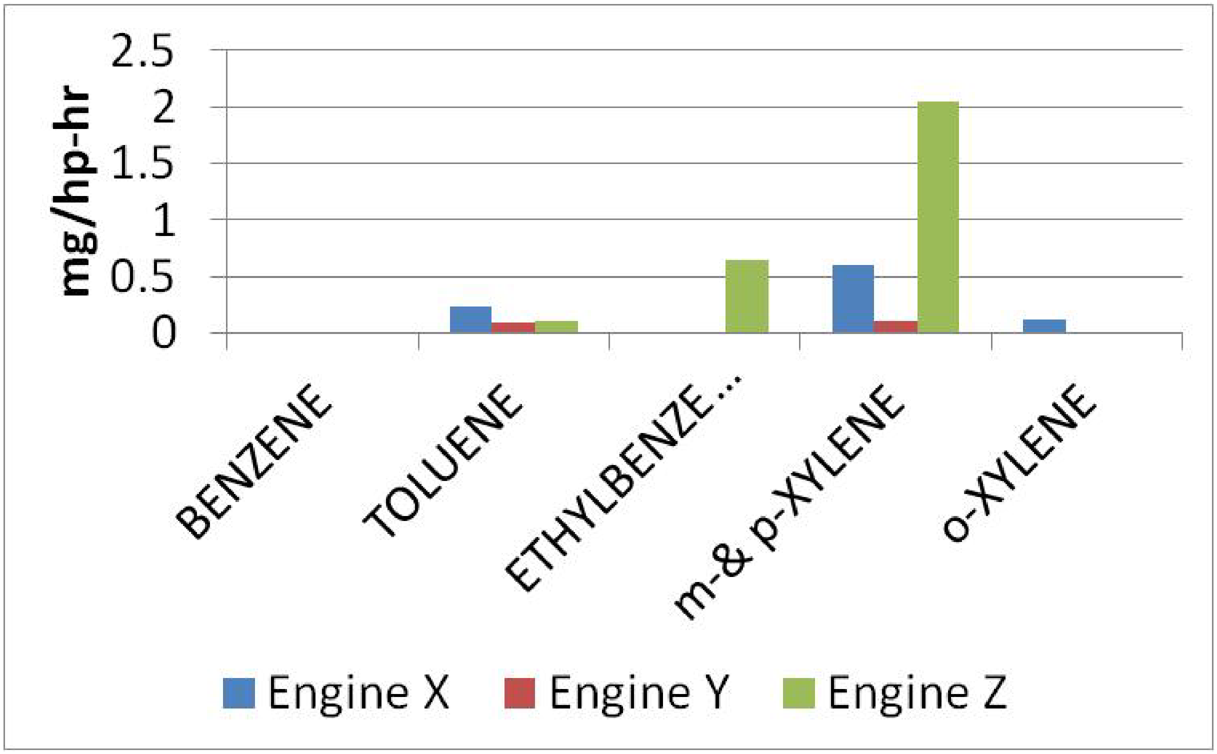
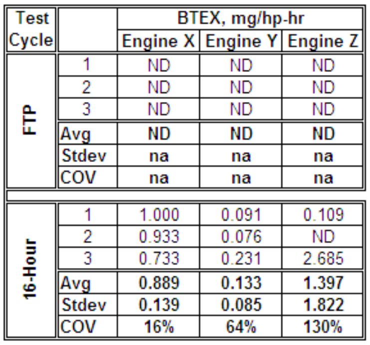


FIGURE 45. BTEX SPECIES EMISSIONS FOR THE 16-HOUR



Test Cycle		BTEX, mg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	ND	ND	ND
	2	ND	ND	ND
	3	ND	ND	ND
	Avg	ND	ND	ND
	Stdev	na	na	na
	COV	na	na	na
16-Hour	1	1.000	0.091	0.109
	2	0.933	0.076	ND
	3	0.733	0.231	2.685
	Avg	0.889	0.133	1.397
	Stdev	0.139	0.085	1.822
	COV	16%	64%	130%

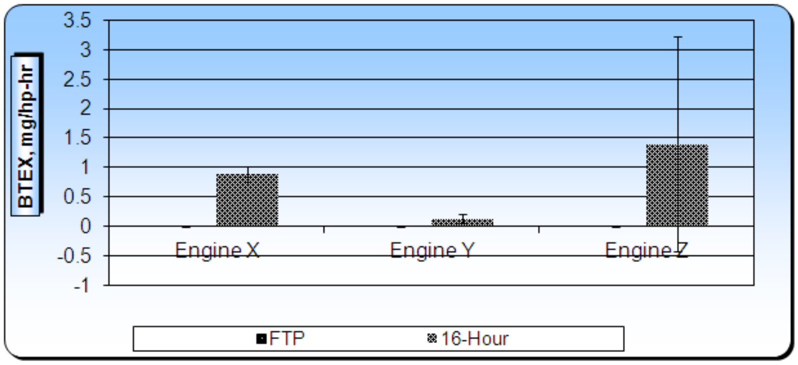


FIGURE 46. BTEX EMISSIONS FOR THE 16-HOUR

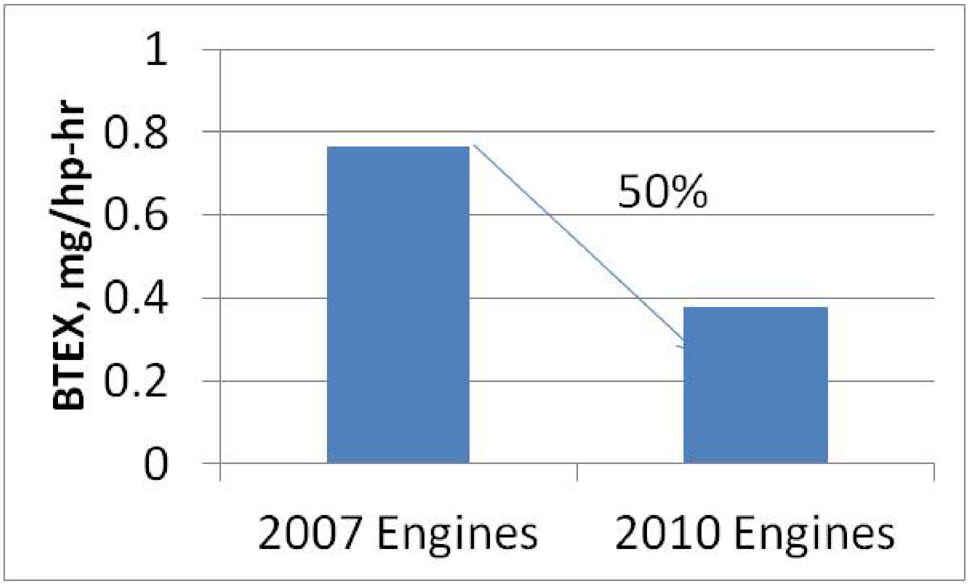


FIGURE 47. BTEX EMISSIONS REDUCTION BETWEEN 2007 AND 2010 TECHNOLOGY ENGINES (16-HOUR)

6.10 Alkanes

As shown in Figure 48, alkanes are mainly found in the fuel at a much higher percentage than in the lube oil. Figure 49 shows total alkane emissions. The emissions were comparable between the FTP and 16-Hour ranging from 76 to 137 µg/hp-hr. Substantial emission reductions of alkanes (92% reductions) was observed when the emissions were compared to those emitted from 2007 technology engines, as shown in Figure 50.

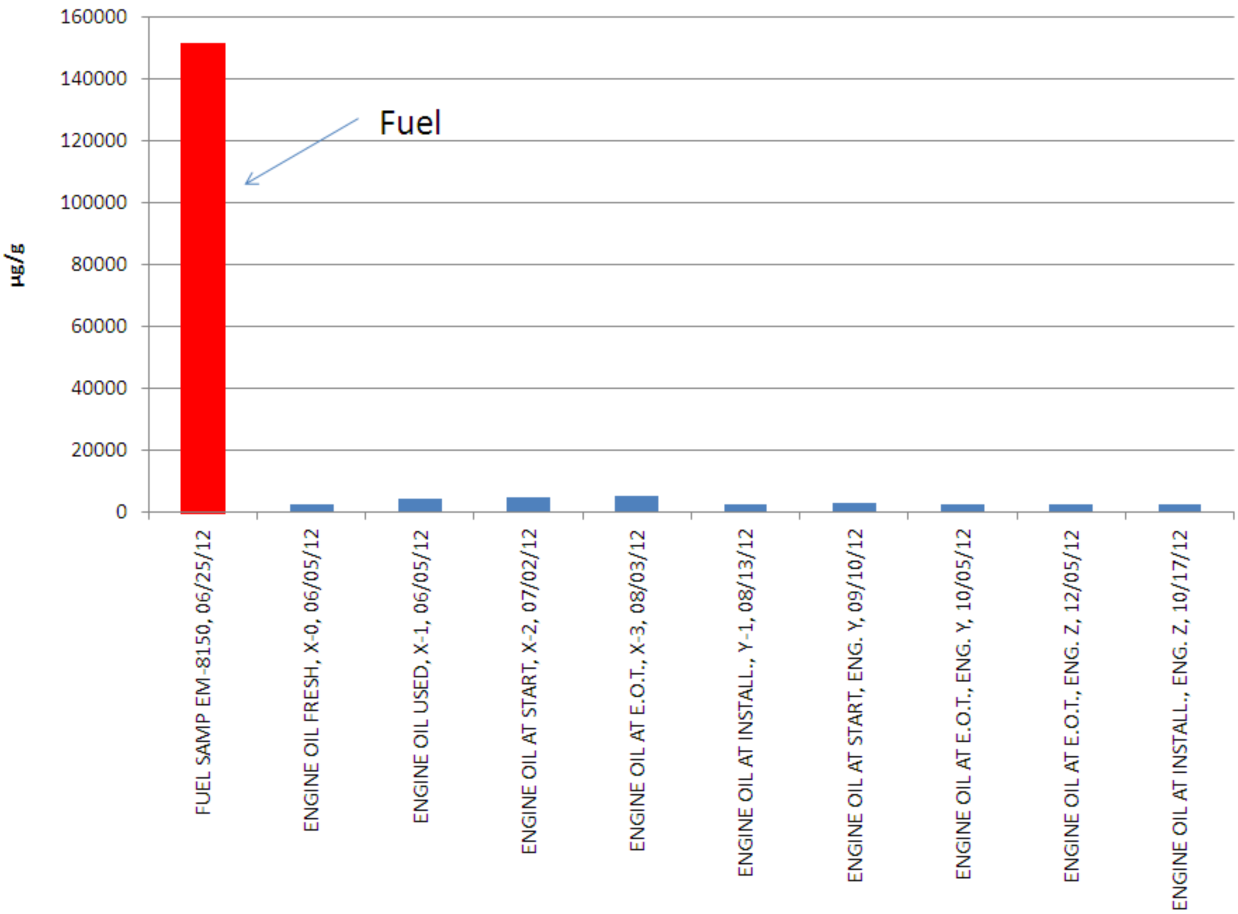
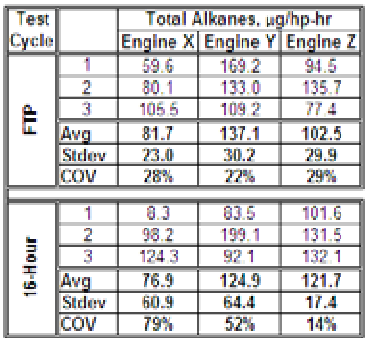


FIGURE 48. TOTAL ALKANES IN DIESEL FUEL AND LUBE OIL



Test Cycle		Total Alkanes, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	59.6	169.2	94.5
	2	80.1	133.0	135.7
	3	105.5	109.2	77.4
	Avg	81.7	137.1	102.5
	Stdev	23.0	30.2	29.9
	COV	28%	22%	29%
16-Hour	1	8.3	83.5	101.6
	2	98.2	199.1	131.5
	3	124.3	92.1	132.1
	Avg	76.9	124.9	121.7
	Stdev	60.9	64.4	17.4
	COV	79%	52%	14%

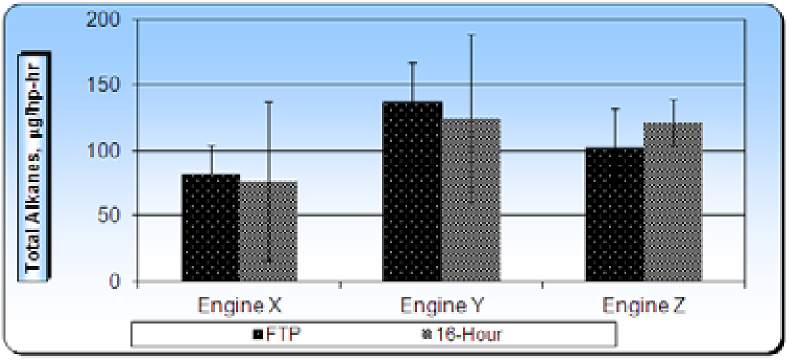


FIGURE 49. ALKANES EMISSIONS FOR THE FTP AND 16-HOUR

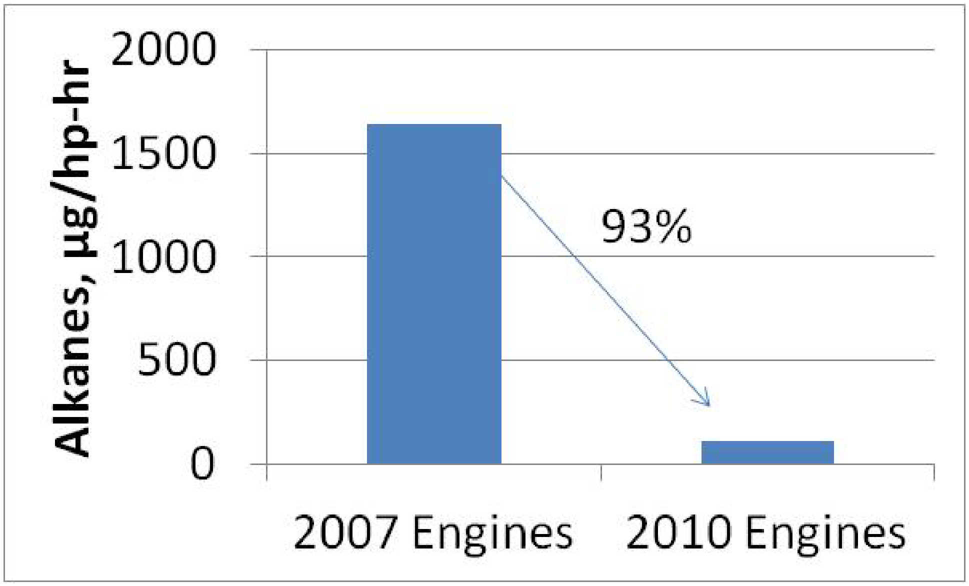
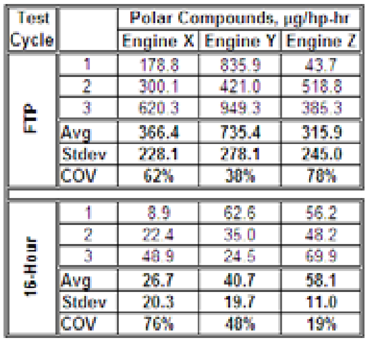


FIGURE 50. ALKANES EMISSIONS REDUCTION BETWEEN 2007 AND 2010 TECHNOLOGY ENGINES (16-HOUR)

6.11 Alcohol and Organic Acid

Figure 51 shows a summary of the alcohol and organic acid compounds reported as brake-specific emissions. The emissions ranged between 26 and 58 µg/hp-hr for the 16-Hour, and were higher for the FTP. The same trend was observed with 2007 technology engines. However, 2010 technology engines reduced the emissions as shown in Figure 52. 2010 technology engines reduced the emissions of alcohols and organic acid by 96% relative to 2007 technology engines.



Test Cycle		Polar Compounds, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	178.8	835.9	43.7
	2	300.1	421.0	518.8
	3	620.3	949.3	385.3
	Avg	366.4	735.4	315.9
	Stdev	228.1	278.1	245.0
	COV	62%	38%	78%
16-Hour	1	8.9	62.6	56.2
	2	22.4	35.0	48.2
	3	48.9	24.5	69.9
	Avg	26.7	40.7	58.1
	Stdev	20.3	19.7	11.0
	COV	76%	48%	19%

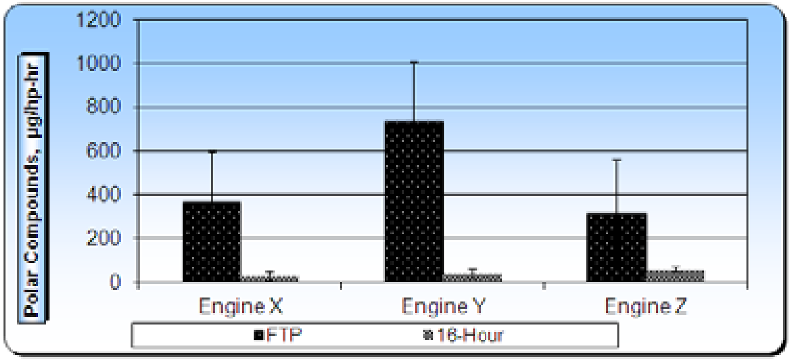


FIGURE 51. ALCOHOLS AND ORGANIC ACID EMISSIONS FOR THE FTP AND 16-HOUR

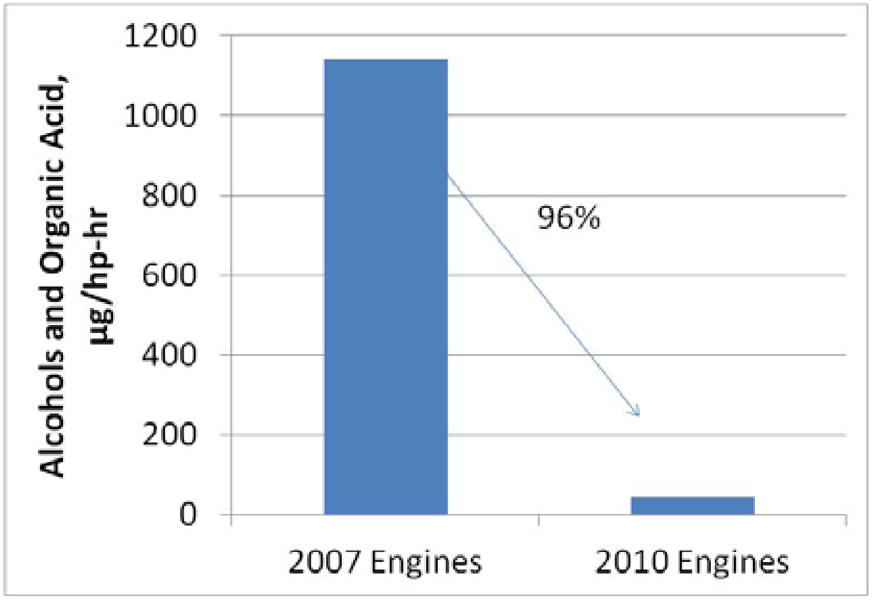


FIGURE 52. ALCOHOLS AND ORGANIC ACID EMISSIONS REDUCTION BETWEEN 2007 AND 2010 TECHNOLOGY ENGINES (16-HOUR)

6.12 Polynuclear Aromatic Hydrocarbon (PAH) Compounds

As shown in Figure 53, PAH compounds are mainly found in the fuel at a much higher percentage than in lube oil. Summaries of the emissions of PAH, nitro-PAH and oxy-PAH for the 16-Hour are shown in Figures 54, 55, and 56, respectively. Figure 57 shows the reduction of those compounds compared to 2007 technology engines. The reductions were 96% for total PAH, 97% for oxyPAH and 99% for nitroPAH.

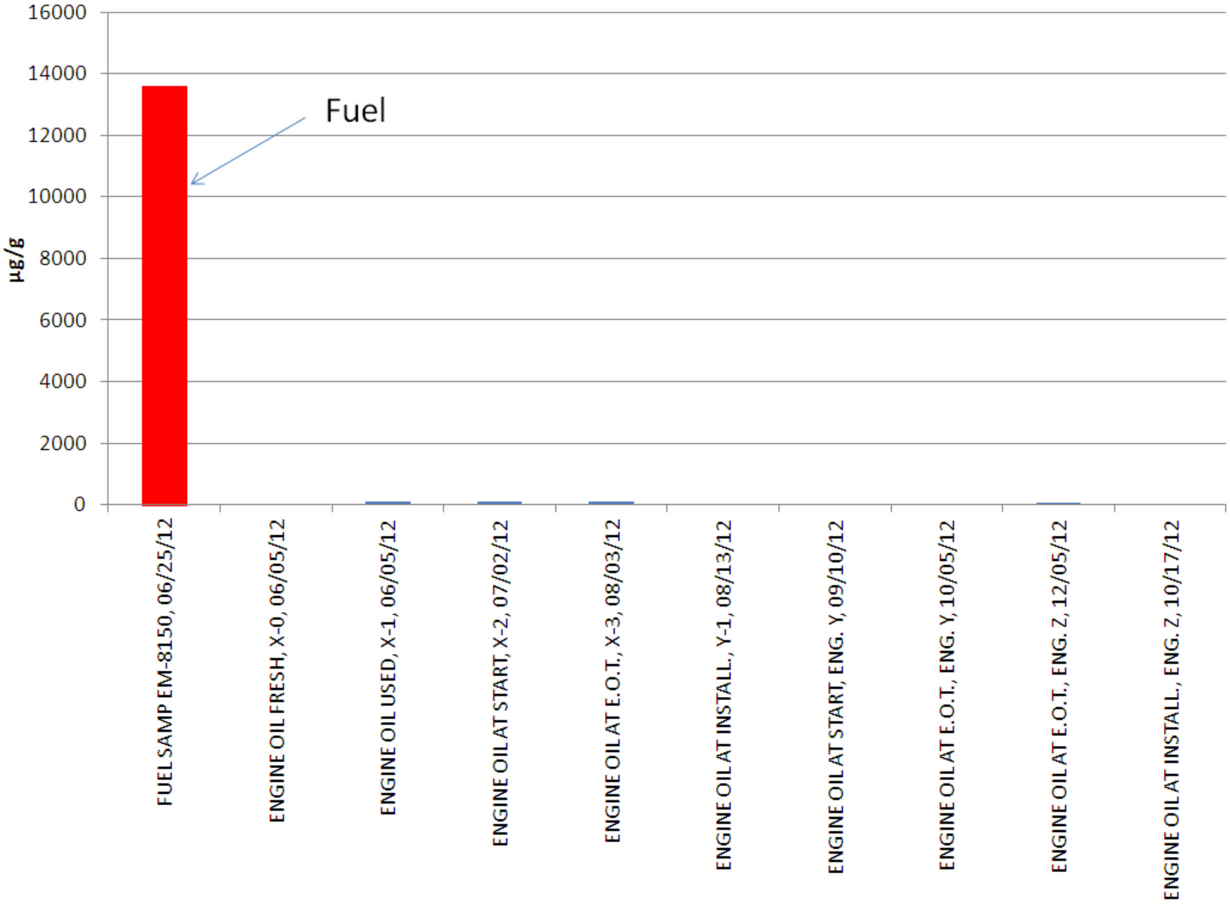
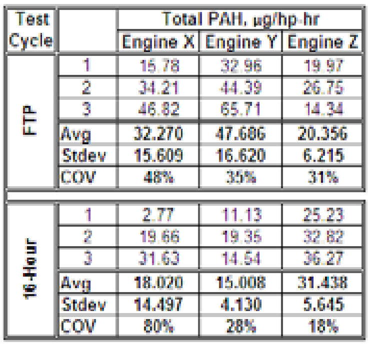


FIGURE 53. TOTAL PAH COMPOUNDS IN DIESEL FUEL AND LUBE OIL



Test Cycle		Total PAH, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	15.78	32.96	19.97
	2	34.21	44.39	26.75
	3	46.82	65.71	14.34
	Avg	32.270	47.686	20.356
	Stdev	15.609	16.620	6.215
	COV	48%	35%	31%
16-Hour	1	2.77	11.13	25.23
	2	19.66	19.36	32.82
	3	31.63	14.54	36.27
	Avg	18.020	15.008	31.438
	Stdev	14.497	4.130	5.645
	COV	80%	28%	18%

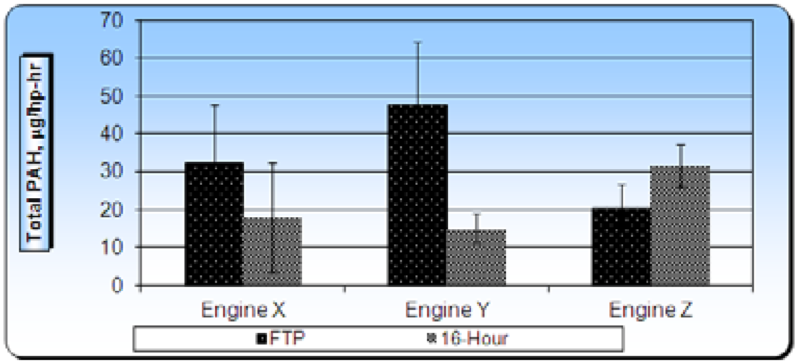


FIGURE 54. PAH EMISSIONS FOR THE FTP AND 16-HOUR

Test Cycle		Nitro PAH, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.18	0.02	0.03
	2	0.12	0.07	0.05
	3	0.33	0.19	0.01
	Avg	0.209	0.095	0.029
	Stdev	0.111	0.083	0.016
	COV	53%	88%	54%
16-Hour	1	0.00	0.01	0.01
	2	0.01	0.02	0.01
	3	0.01	0.02	0.01
	Avg	0.005	0.015	0.010
	Stdev	0.003	0.005	0.001
	COV	56%	31%	14%

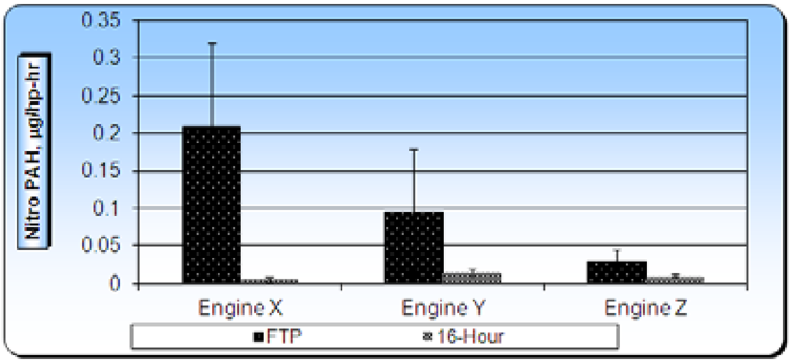


FIGURE 55. NITRO-PAH EMISSIONS FOR THE FTP AND 16-HOUR

Test Cycle		Oxy PAH, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.05	0.06	0.04
	2	0.50	0.14	0.07
	3	0.95	0.31	0.01
	Avg	0.498	0.171	0.040
	Stdev	0.451	0.127	0.032
	COV	91%	75%	80%
16-Hour	1	0.01	0.11	0.11
	2	0.09	0.19	0.14
	3	0.14	0.16	0.14
	Avg	0.081	0.152	0.130
	Stdev	0.068	0.041	0.014
	COV	83%	27%	11%

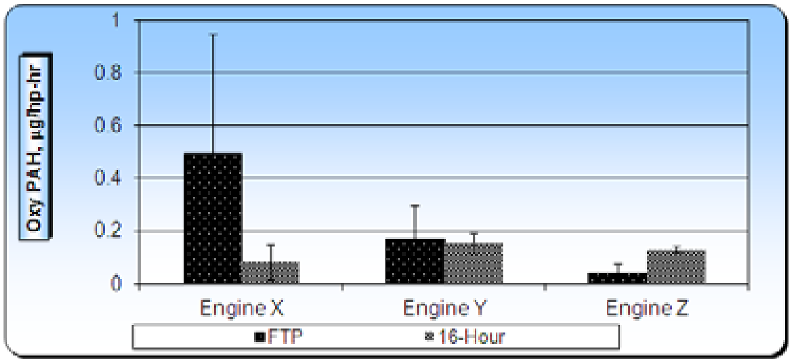


FIGURE 56. OXY-PAH EMISSIONS FOR THE FTP AND 16-HOUR

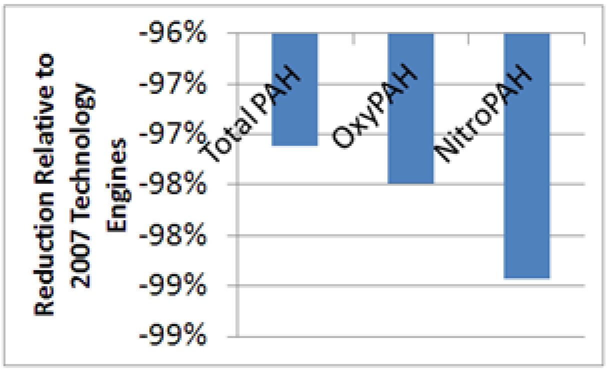


FIGURE 57. PAH EMISSIONS REDUCTION BETWEEN 2007 AND 2010 TECHNOLOGY ENGINES (16-HOUR)

6.13 Hopanes and Steranes

As shown in Figure 58, hopanes and steranes are mainly lube oil components with virtually no detection in the fuel. Figure 59 and 60 summarize the results for hopanes and steranes for the FTP and 16-Hour. Figure 61 shows the substantial reduction observed in hopanes

(83%) and steranes (95%) with the 2010 technology engines, compared to the 2007 technology engines used in ACES Phase 1.

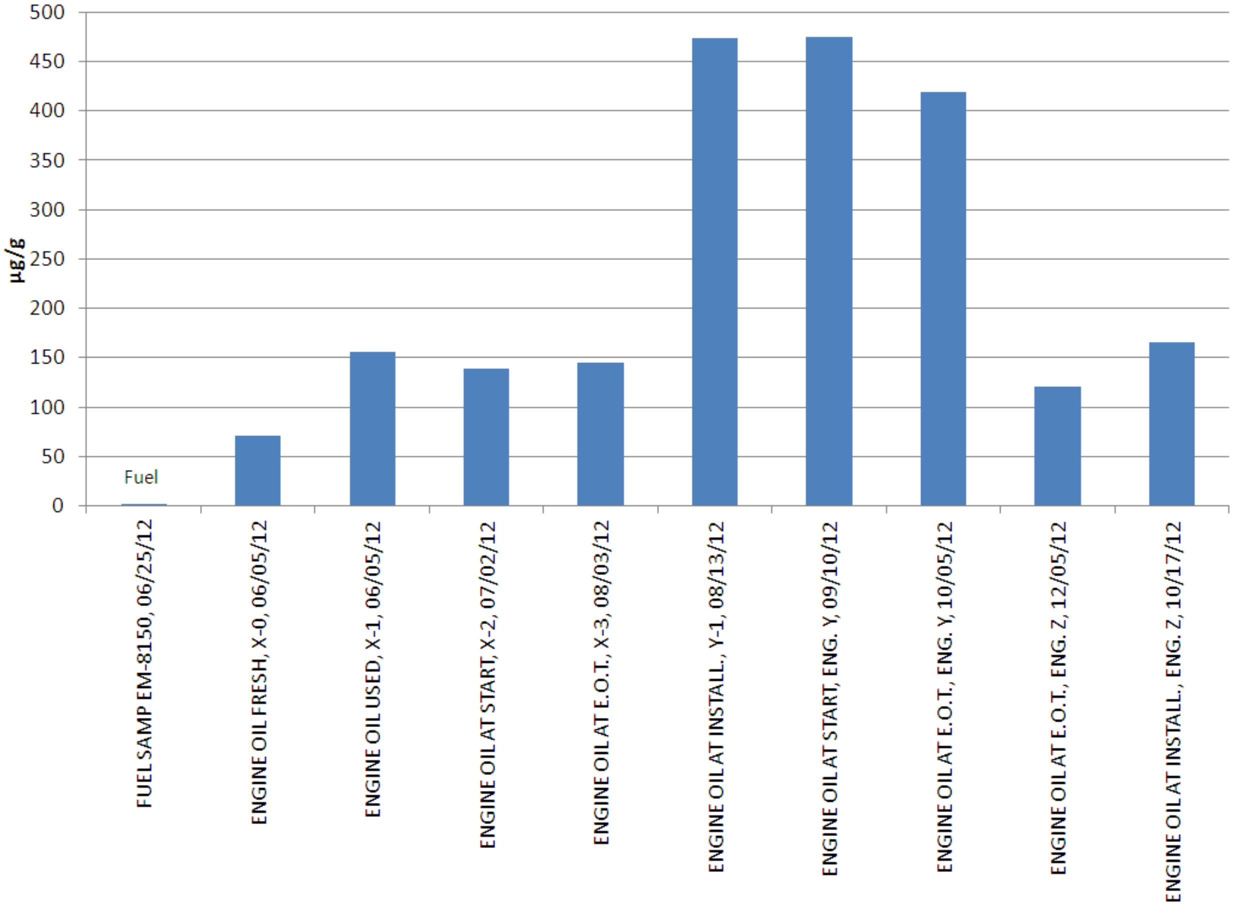
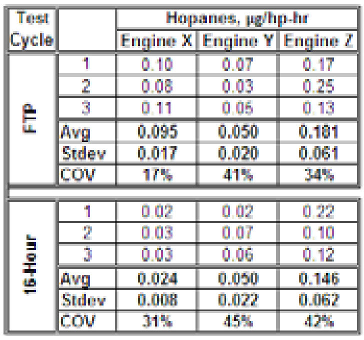


FIGURE 58. TOTAL HOPANES AND STERANES IN DIESEL FUEL AND LUBE OIL



Test Cycle		Hopanes, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.10	0.07	0.17
	2	0.08	0.03	0.25
	3	0.11	0.05	0.13
	Avg	0.095	0.050	0.181
	Stdev	0.017	0.020	0.061
	COV	17%	41%	34%
16-Hour	1	0.02	0.02	0.22
	2	0.03	0.07	0.10
	3	0.03	0.06	0.12
	Avg	0.024	0.050	0.146
	Stdev	0.008	0.022	0.062
	COV	31%	45%	42%

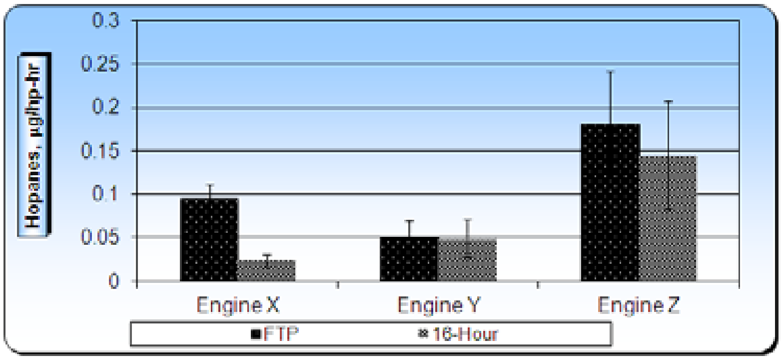
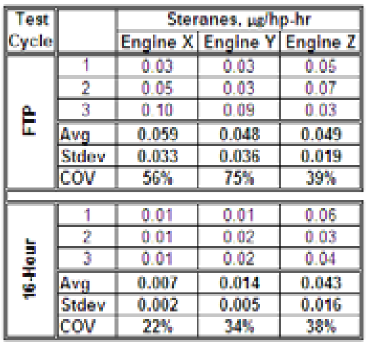


FIGURE 59. HOPANES EMISSIONS FOR THE FTP AND 16-HOUR



Test Cycle		Steranes, μg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	0.03	0.03	0.05
	2	0.05	0.03	0.07
	3	0.10	0.09	0.03
	Avg	0.059	0.048	0.049
	Stdev	0.033	0.036	0.019
	COV	56%	75%	39%
16-Hour	1	0.01	0.01	0.06
	2	0.01	0.02	0.03
	3	0.01	0.02	0.04
	Avg	0.007	0.014	0.043
	Stdev	0.002	0.005	0.016
	COV	22%	34%	38%

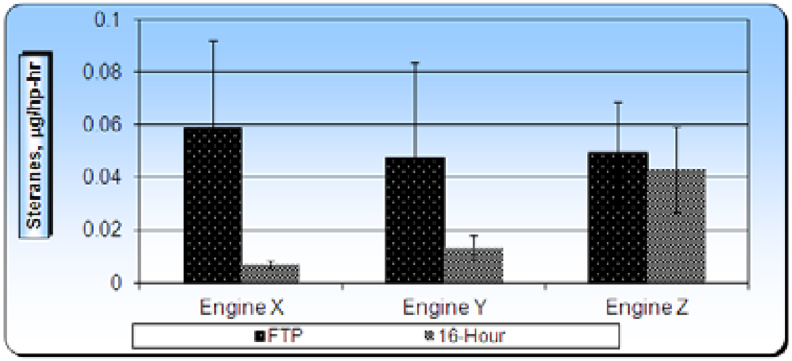


FIGURE 60. STERANES EMISSIONS FOR THE FTP AND 16-HOUR

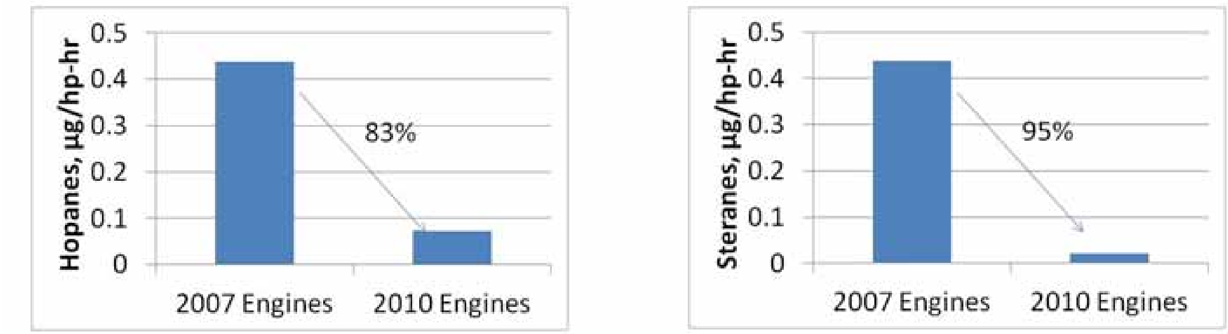


FIGURE 61. HOPANES AND STERANES EMISSIONS REDUCTION BETWEEN 2007 AND 2010 TECHNOLOGY ENGINES (16-HOUR)

6.14 Dioxins and Furans

Figure 62 shows the toxic equivalent (TEQ) brake-specific emissions of 17 dioxin and furan compounds, for Engines X, Y, and Z, respectively. Out of the 17 compounds, 14 were detected with Engine Z, 8 with Engine Y, and 4 with Engine X. The majority of the species detected were in the gas phase rather than in the particle phase. Figure 63 shows the total brake-specific emissions that ranged from 0.004 pg/hp-hr for Engine X, to 0.032 pg/hp-hr for Engine Y, and 0.196 pg/hp-hr for Engine Z. The emissions were extremely low, representing an 88% reduction relative to 2007 technology engines, as shown in Figure 64. In ACES Phase 1, we already showed that dioxins and furans emissions were substantially lower than 1998 technology engines. The 2010 technology engines showed even more reduction, thus minimizing any potential concerns associated with SCR catalyst promotion of dioxins and furans.

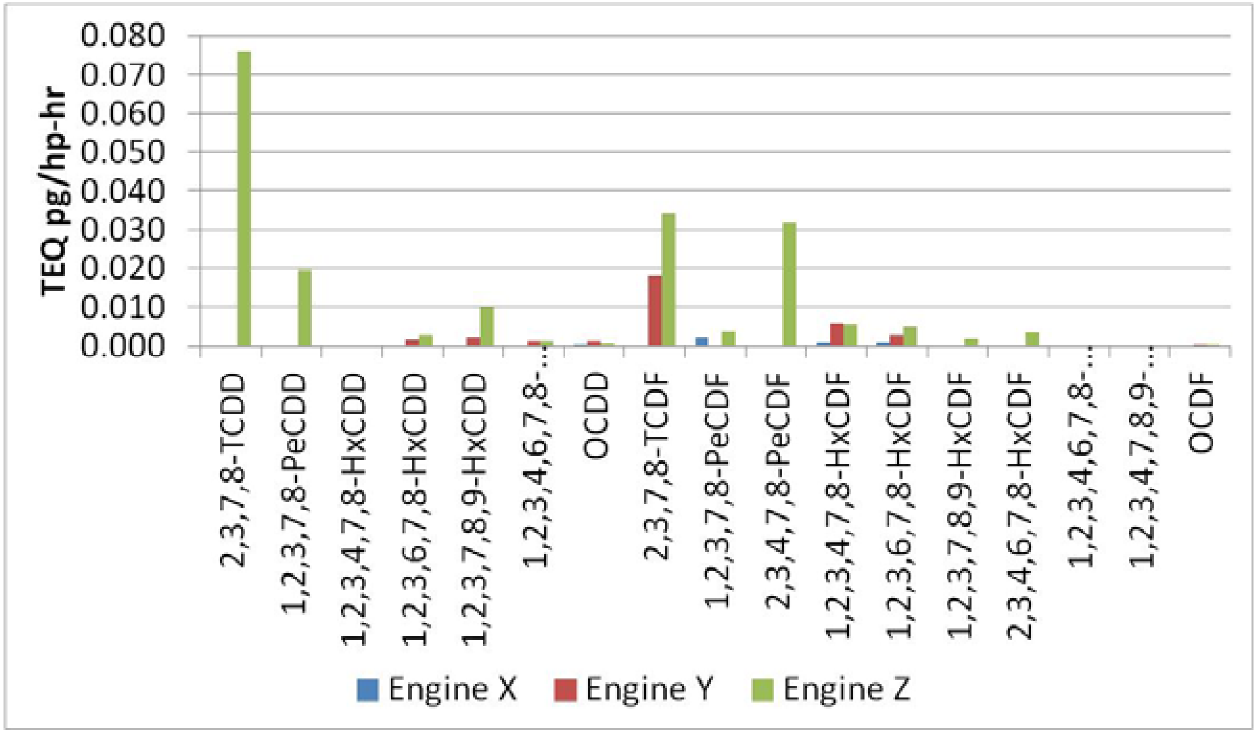
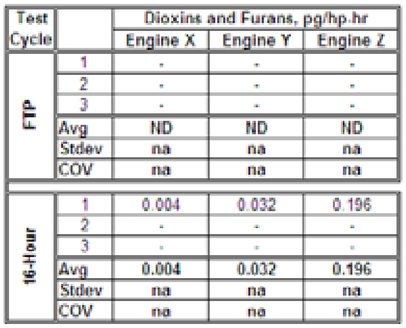


FIGURE 62. DIOXINS AND FURANS EMISSIONS SPECIES (16-HOUR)



Test Cycle		Dioxins and Furans, pg/hp.hr		
		Engine X	Engine Y	Engine Z
FTP	1	-	-	-
	2	-	-	-
	3	-	-	-
	Avg	ND	ND	ND
	Stdev	na	na	na
	COV	na	na	na
16-Hour	1	0.004	0.032	0.196
	2	-	-	-
	3	-	-	-
	Avg	0.004	0.032	0.196
	Stdev	na	na	na
	COV	na	na	na

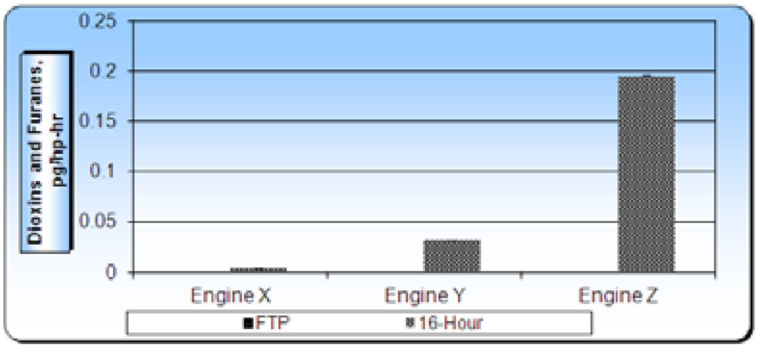


FIGURE 63. DIOXINS AND FURANS EMISSIONS FOR THE 16-HOUR

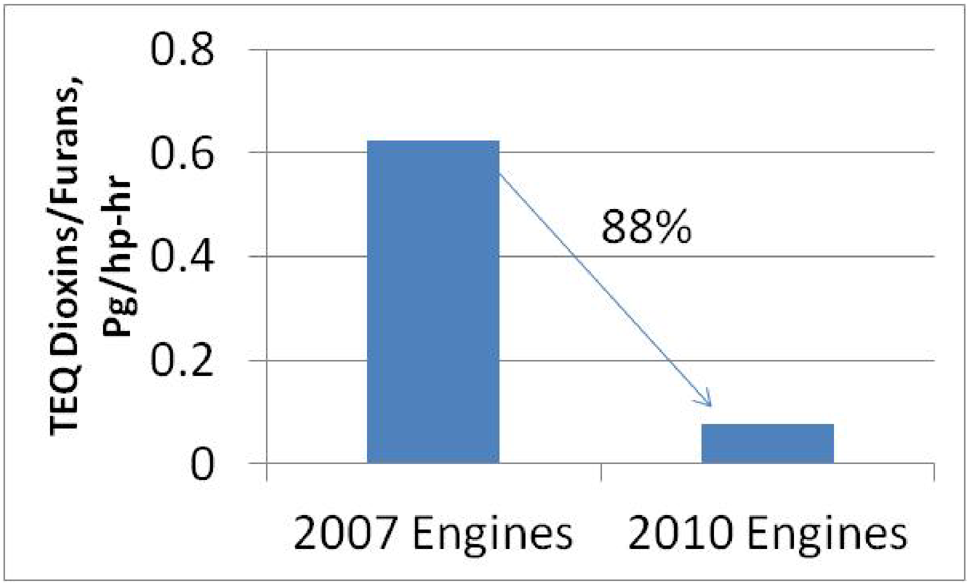


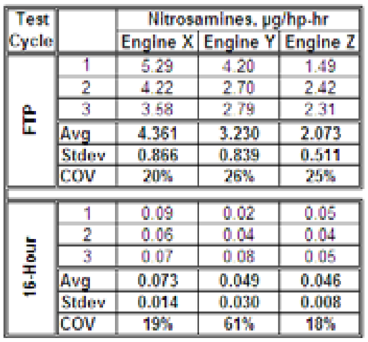
FIGURE 64. DIOXINS AND FURANS EMISSIONS REDUCTION BETWEEN 2007 AND 2010 TECHNOLOGY ENGINES (16-HOUR)

6.15 Cyanide, Sulfide, and Hexavalent Chromium

The emissions for cyanide, sulfide, and hexavalent chromium were all below the lowest detection limits, which were about 45, 90, and 9 µg/hp-hr, respectively, for the 16-Hour.

6.16 Nitrosamines

Figure 65 shows a summary of total nitrosamines and Figure 66 shows that nitrosamines are emitted at much lower levels than those emitted from 2007 technology engines. 2010 technology engines reduced nitrosamines by more than 99%, relative to 2007 technology engines.



Test Cycle		Nitrosamines, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	5.29	4.20	1.49
	2	4.22	2.70	2.42
	3	3.58	2.79	2.31
	Avg	4.361	3.230	2.073
	Stdev	0.866	0.839	0.511
	COV	20%	26%	25%
16-Hour	1	0.09	0.02	0.05
	2	0.06	0.04	0.04
	3	0.07	0.08	0.05
	Avg	0.073	0.049	0.046
	Stdev	0.014	0.030	0.008
	COV	19%	61%	18%

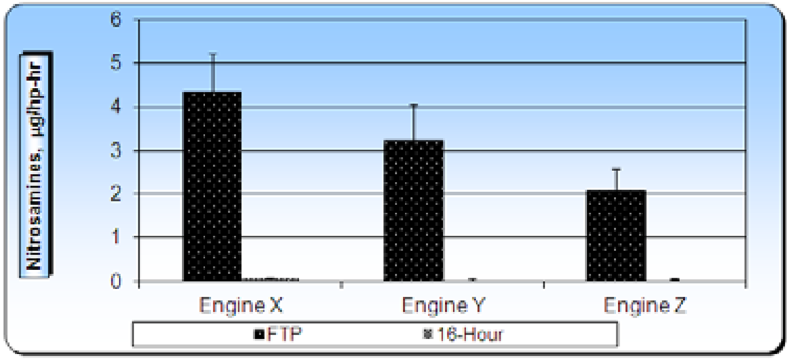


FIGURE 65. NITROSAMINES EMISSIONS FOR THE 16-HOUR

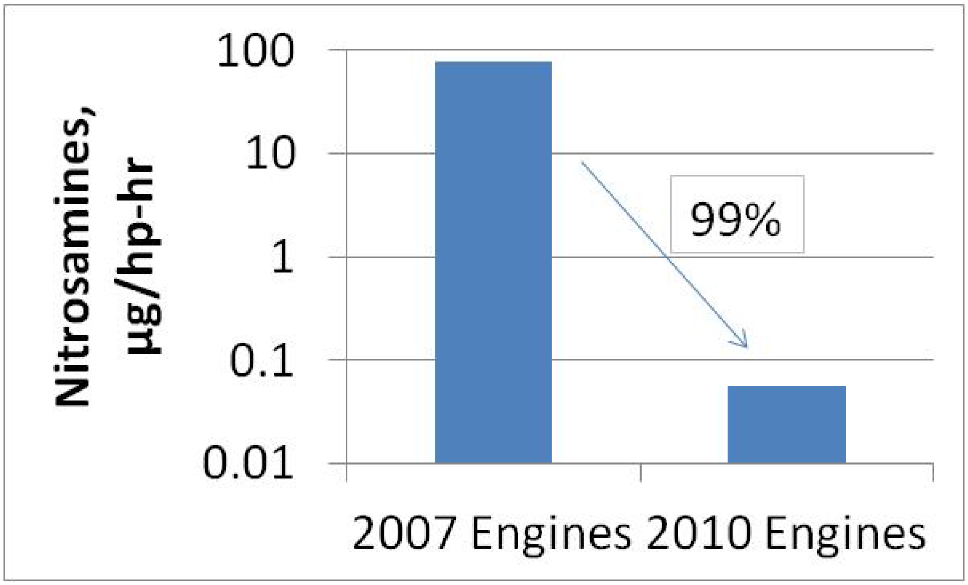
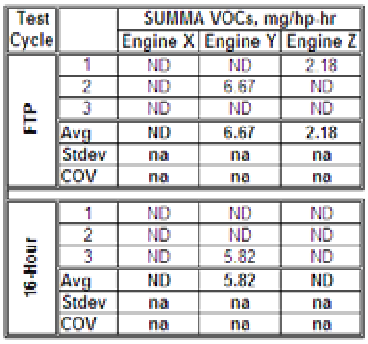


FIGURE 66. NITROSAMINES EMISSIONS REDUCTION BETWEEN 2007 AND 2010 TECHNOLOGY ENGINES (16-HOUR)

6.17 Selected Volatile Organic Compounds

Figure 67 shows the brake-specific emissions of selected VOCs. These included carbonyl sulfide (COS), nitromethane, nitroethane, 2-nitropropane, and 1-nitropropane. In general these compounds were below the limit of detection of 1 to 4 ppb.



Test Cycle		SUMMA VOCs, mg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	ND	ND	2.18
	2	ND	6.67	ND
	3	ND	ND	ND
	Avg	ND	6.67	2.18
	Stdev	na	na	na
	COV	na	na	na
16-Hour	1	ND	ND	ND
	2	ND	ND	ND
	3	ND	5.82	ND
	Avg	ND	5.82	ND
	Stdev	na	na	na
	COV	na	na	na

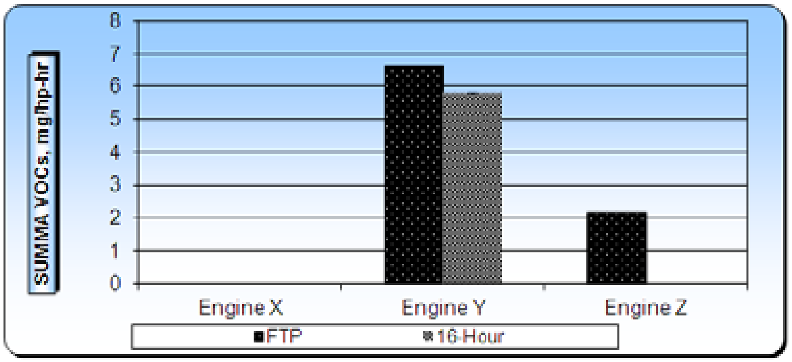
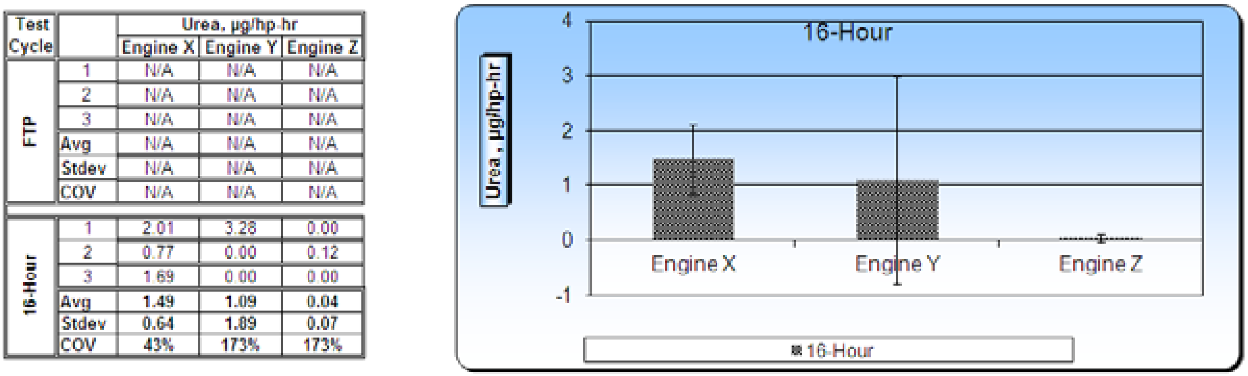


FIGURE 67. SELECTED VOC EMISSIONS

6.18 Particle Phase Urea-Related Compounds

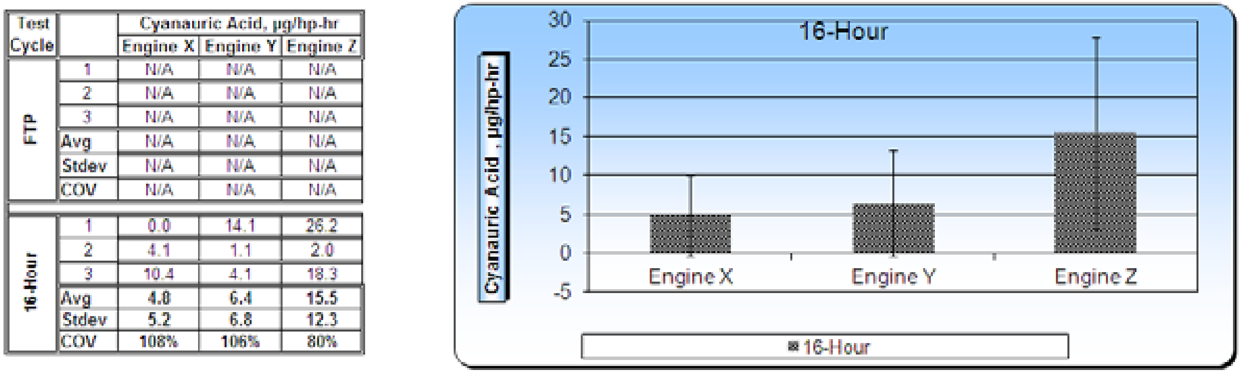
Particle phase urea compounds were analyzed by ORNL. Those compounds were not analyzed in ACES Phase 1 because they are derived from 2010 technology engines equipped with SCR. Out of the six urea-related compounds that included urea, melamine, cyanuric acid, ammelide, ammeline, and biuret, only urea and cyanuric acid were detected for the 16-Hour, but the emissions were very low. As shown in Figures 68 and 69, urea emissions ranged from 0.04 µg/hp-hr for Engine Z to 1.49 µg/hp-hr for Engine X. Engine Y emissions were 1.09 µg/hp-hr. Cyanuric acid emissions ranged from 4.8 µg/hp-hr with Engine X to 15.5 µg/hp-hr for Engine Z.

Engine Y emissions were 6.4 µg/hp-hr. The highest exhaust concentration of cyanuric acid calculated based on this work is about 18 ppb by mass.



Test Cycle		Urea, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	N/A	N/A	N/A
	2	N/A	N/A	N/A
	3	N/A	N/A	N/A
	Avg	N/A	N/A	N/A
	Stdev	N/A	N/A	N/A
	COV	N/A	N/A	N/A
16-Hour	1	2.01	3.28	0.00
	2	0.77	0.00	0.12
	3	1.69	0.00	0.00
	Avg	1.49	1.09	0.04
	Stdev	0.64	1.89	0.07
	COV	43%	173%	173%

FIGURE 68. UREA EMISSIONS FOR (16-HOUR)



Test Cycle		Cyanauric Acid, µg/hp-hr		
		Engine X	Engine Y	Engine Z
FTP	1	N/A	N/A	N/A
	2	N/A	N/A	N/A
	3	N/A	N/A	N/A
	Avg	N/A	N/A	N/A
	Stdev	N/A	N/A	N/A
	COV	N/A	N/A	N/A
16-Hour	1	0.0	14.1	26.2
	2	4.1	1.1	2.0
	3	10.4	4.1	18.3
	Avg	4.8	6.4	15.5
	Stdev	5.2	6.8	12.3
	COV	108%	106%	80%

FIGURE 69. CYANURIC ACID EMISSIONS (16-HOUR)

7.0 SUMMARY

ACES Phase 2 engine testing started in March, 2012. Three model year 2011 heavy-duty on-highway diesel engines were characterized for regulated and unregulated emissions using the FTP and the 16-Hour. Each of the engines complied with EPA 2010 standards, and was equipped with a DOC+DPF+SCR+AMOX in the exhaust system. One batch of refinery ULSD fuel (6.5 ppm sulfur content) was used throughout this program along with one batch of CJ-4 15W40 lube oil provided by Lubrizol. Also, one batch of commercial grade urea was used for urea injection upstream of the SCR catalysts. In general, 2010 technology engines showed substantial reductions in regulated and unregulated emissions species versus the emission standards, 2007-compliant engines, and pre-2007 technology engines. Below is a summary of the key results:

- Regulated emissions of NO_X, NMHC, CO, and PM were 61%, 100%, 97%, and 92% below the 2010 emission standards, respectively.
- Greenhouse gas emissions resulted in no increase in global warming potential, when compared to 2007 technology engines. The improved fuel economy and lower average CO_2 emission with the 2010 technology engines were offset by a rise in N_2O emissions. However, N_2O remained 30% below the EPA 2014 emissions limit.
- Unregulated emissions that included single ring aromatics, PAH, oxyPAH, nitroPAH, alkanes, alcohol and organic acids, hopanes/steranes, carbonyls, metals and elements, organic carbon, elemental carbon, dioxins and furans were 50% to 99% percent lower than those emitted from 2007 technology engines tested in ACES Phase 1.
- In contrast to 2007 technology engines, no active DPF regenerations were encountered throughout this work, including the 16-Hour. This resulted in a PM composition that is virtually sulfate-free, with some levels of elemental carbon, organic carbon, nitrate and ammonium, with the latter two compounds being urea-SCR derived species.
- Average particle number emissions were 41% to 72% lower than those observed with the 2007 technology engines used in ACES Phase 1, and one to two orders of magnitude lower than those emitted from typical 2004 technology engines.
- Only two out of six particle-phase urea-related compounds were detected. But, even the ones that were detected such as urea and cyanuric acid had an extremely low emissions level.

The observed reductions in PM (total mass, soot, and number) and unregulated emissions from 2007 to 2010 engines are likely due to differences in active DPF regeneration operation. The 2007 engines triggered multiple regeneration events during the 16-hour cycles, while the 2010 engines did not trigger any events. The improvement/reduction in regeneration was achieved through some combination of lower engine-out PM, increased passive regeneration and improved control strategies. PM emissions during regeneration events have been observed to be higher than normal operation for the 2007 engines used in ACES Phase 1. Unregulated emissions are believed to be higher during regeneration events. Thus, the results from the 2007 engines include emissions measured over both normal (no active regeneration) and regeneration operation, while the results from the 2010 engines only include emissions measured over normal operation. DPF active regeneration would have occurred had the 2010 engines been run for a much longer period of time (100 or more hours). The 2010 engines did not trigger a regeneration event even after three back-to-back 16-hour cycles (48 hours of operation).

According to the engine manufacturers, the process and length of time for DPF active regeneration is expected to be similar for 2010 and 2007 engines. Therefore, the emissions during regeneration events are expected to be similar except for any differences due to increased loading of certain species like sulfur and heavy molecular weight hydrocarbons that are not oxidized by the aftertreatment system. Since 2010 engines have fewer regeneration events, the PM and unregulated emissions averaged over both normal and active regeneration operation are expected to be lower than 2007 engines. While it is not known how much the average PM and unregulated emissions on the 2010 engines may have increased if the test were continued to include regeneration events, the consensus of this study's principal investigator and its sponsors is that the 2010 engines' PM and unregulated emissions averaged over both normal and active regeneration operation are somewhere between the results measured during normal operation and the results measured on the 2007 engines over both normal and active regeneration operation.

Finally, all analyzed species including second-by-second data will be posted on the publically accessible CRC website at http://www.crcao.org.