

# A Risk Assessment Evaluation of New Technology Diesel Engine Exhaust Composition

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Diesel engine exhaust (DEE) has been demonstrated to cause several toxic effects in animals and humans. These effects include respiratory, cardiovascular and immune system toxicity. DEE has also been demonstrated to be genotoxic and carcinogenic. IARC and US EPA have respectively. The California Air Resources Board (CARB) listed developed diesel engines", or NTE) which (approximately 12-fold) for the CRT engine compared to the NT engine. the diesel exhaust particulate (DEP) TAC listing in 1998, diesel engine according to the engine type, fuel, type of emissions controls used, and engine. manufacturers have developed diesel engines ("new technology engines", engine test cycles used to evaluate engine emissions. It has been or NTE) which produce substantially lower exhaust levels of DEP and air suggested that the reductions in DEP and air toxics from NTE exhaust are Verbeek and Rabé (2007) used, and engine test cycles used to evaluate engine emissions. DEP and air toxics exhaust concentrations from NT engines and engines fitted with that the reductions of some air toxics such as polycyclic aromatic hydrocarbons, benzene and 1,3- butadiene in NTE exhaust (often 80 – 90%) are not as great as the corresponding reductions in DEP (often 95 – 99%). The resulting air toxics/DEP ratios for NTE exhaust may be greater than or equal to similar ratios found in exhaust from older diesel engines. As an example, an analysis of data from one published review indicated that the average 3-ring PAH, 1,3-butadiene and benzene/DEP ratios increased in NTE exhaust compared to older DEE by 2-, 10- and 4-fold, respectively. These data suggest that while the absolute amount of DEP (and thus estimated cancer risk) and air toxics is much reduced in NTE exhaust, the exhaust composition has not necessarily become less hazardous. Thus, the available data do not indicate that NTE exhaust should be considered to be fundamentally different in kind compared to older DEE for risk assessment purposes and suggests the TAC cancer unit risk value for DEP can continue to be applied to NTE exhaust risk

### Introduction

Diesel engine exhaust (DEE) is a complex mixture that contains thousands of inorganic and organic substances which occur in the form of gases and fine particles. The composition of this mixture varies depending on engine type, operating conditions, fuel, lubricating oil, and whether an emission control system is present.

DEP are mainly aggregates of spherical carbon particles coated with organic and inorganic substances, with the composition of the particles being predominantly organic and inorganic carbon. The organic fraction of DEP contains compounds such as aldehydes, alkanes and alkenes, aliphatic hydrocarbons, and polycyclic aromatic hydrocarbons (PAHs) and PAH-derivatives (ARB, 1998). The gas phase of DEE contains typical combustion gases such as  $N_2$ ,  $O_2$  and  $CO_2$ , and volatile hydrocarbon species, including classes of compounds such as aldehydes (e.g. formaldehyde, acetaldehyde), alkanes, alkenes, and aromatic compounds (e.g. benzene, toluene, 1,3-butadiene). Other gas phase components of DEE include lower molecular mass PAH and nitro-PAH derivatives (volatile 2- to 4-ring PAH and 2-ring nitro-PAH).

Emissions from diesel-fueled engines include over 40 substances that are listed by the U.S. Environmental Protection Agency (US EPA) as hazardous air pollutants (HAPs) and by the California Air Resources Board (ARB) as Toxic Air Contaminants (TACs). Toxic substances known to be present in diesel exhaust include the carcinogens benzene, 1,3 -butadiene, naphthalene and PAHs.

DEE has been demonstrated to cause several toxic effects in animals and humans. These effects include respiratory, cardiovascular and immune system toxicity. DEE has also been shown to induce genotoxicity and cancer in both animals and humans. The California Proposition 65 program identified DEE as a chemical known to cause cancer in 1990. ARB listed "Particulate Matter from Diesel-Fueled Engines" as a TAC in 1998. The TAC document included a cancer unit risk of  $3.0 \times 10^{-4}$  (µg/m<sup>3</sup>) for DEP. Additionally, the International Agency for Research on Cancer

(IARC) and the U.S. Environmental Protection Agency have described DEE as probably and likely to be carcinogenic to humans, respectively, and the National Toxicology Program (NTP) has listed diesel exhaust particulates as being "reasonably anticipated to be a human carcinogen".

exhaust composition exist between NTE and older diesel engines.

## Nylund *et al.* (2004)

This study examined the emission characteristics of diesel-fueled and compressed natural gas-fueled (CNG) transit buses. The diesel buses studied were model year 2003 vehicles, employing Euro 3 technology with electronically controlled injection and run on ultra-low sulfur diesel fuel. The exhaust after-treatment options were 1) no exhaust aftertreatment (NT); 2) oxidation catalyst (OC); 3) continuously regenerating particulate filter (CRT). The test cycles used were the European Braunschweig and the US Orange County cycles.

Table 1 lists the benzene, total PAH and particle phase Ames bacterial

NT: no retrofit emission controls; OC: oxidative catalyst; CRT: diesel particulate filter mutagenicity (without metabolic activation) emissions data using the Braunschweig cycle from all three engine types. Ames bacterial Hesterberg et al. (2008) mutagenicity data was generated using test strain TA98 in the absence of This study combined emissions data from 25 reports on transit buses, metabolic activation for all three engine types, but in the presence of S9 school buses, refuse trucks, and passenger cars in order to conduct a metabolic activation only for the NT and OC engines due to sample size comparison of emissions from vehicles fueled with diesel or compressed constraints. Mutagenicity values in the presence and absence of metabolic natural gas (CNG). Seventeen studies examined transit buses, three activation were similar for both the NT and OC engines. studies each examined refuse trucks and passenger cars and two examined

Diesel particulate matter and total PAH content and Ames diesel particulate matter mutagenicity of diesel exhaust from Nylund *et al.*, 2004 (Table 10).

		Benzene	total PAH	Ames mutagenicity
Engine	PM (mg/km)	(mg/km)	(mg/km)	(krev/km)
NT	170	3000	0.0613	59
OC	120	1000	0.0427	85
CRT	20	1000	0.094	23

Figure 1 Benzene, total PAH and Ames mutagenicity/PM ratios in diesel exhaust (adapted from Nylund et al., 2004)

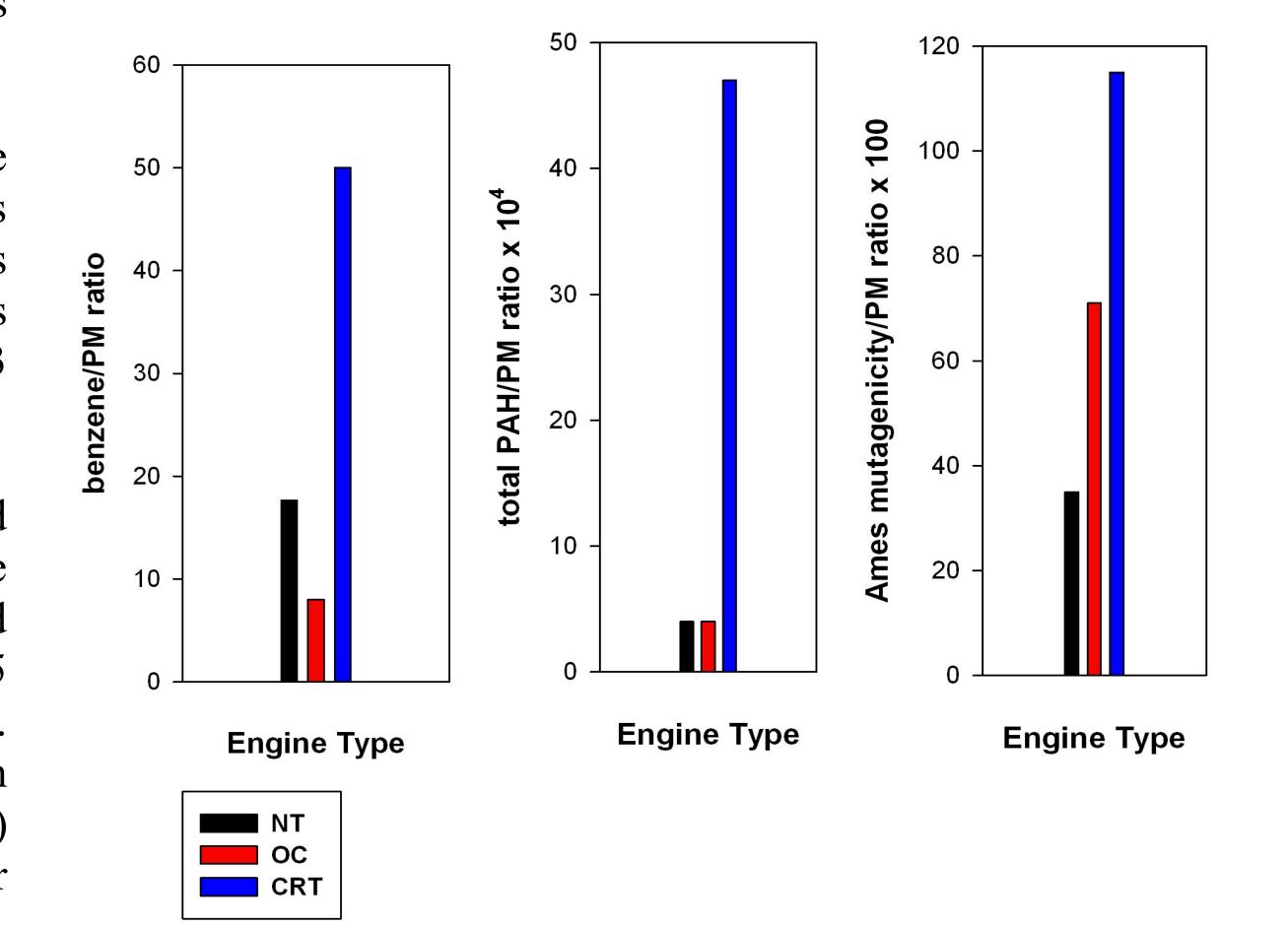


Figure 1 illustrates the ratios of benzene and total PAH engine output and particulate Ames mutagenicity to PM output for all three engine types. The benzene/PM ratio was decreased for the OC engine (approximately 50% less) and increased for the CRT engine (approximately 2.7-fold greater) compared to the NT engine. The total PAH/PM ratio was not described DEE as probably and likely to be carcinogenic to humans, Since the DEE TAC listing in 1998, diesel engine manufacturers have increased for the OC engine, but was increased substantially particulate matter from diesel-fueled engines as a Toxic Air Contaminant produce substantially lower exhaust levels of DEP and air toxics Ames mutagenicity was increased for both the OC engine (approximately (TAC) in 1998, with a cancer unit risk factor of  $3 \times 10^{-4}$  (µg/m<sup>3</sup>)<sup>-1</sup>. Since compared to older engines. Reported reductions in DEP and air toxics vary 2-fold) and the CRT engine (approximately 3-fold) compared to the NT

toxics compared to older engines. Reported reductions in DEP and air large enough that the regulatory determinations made for DEE from older. The authors listed data from a Swedish transit bus study using the toxics vary according to the engine type, fuel, type of emissions controls—engines should not apply to NTE exhaust. Several studies have compared—Braunschweig transient cycle which determined regulated and unregulated Experimental data from several NTE engine emissions studies indicate older engines equipped with comparable retro-fit emissions controls. Data either an OC or CRT. Total PAH/PM ratios were decreased for OC from these studies can be used to determine if fundamental differences in engines, but increased for CRT engines. These data are listed in Table 2.

PM and PAH exhaust concentrations and PAH/PM ratios for NT, OC and CRT-equipped diesel engines. Adapted from Verbeek and Rabé, 2007

	NT	OC	CRT
PM (mg/mile)	398	364	30
% decrease PM		85	92
total PAH (mg/mile)	0.195	0.036	0.027
% decrease PAH		82	86
PAH/PM ratio	5E-04	1E-04	9E-04
% ratio change		-80	86

school buses. All but two studies operated the test vehicles on chassis dynamometers to generate emissions. Those two studies (one transit bus and one refuse truck study) measured emissions while being driven in

Table 3 lists the PM, butadiene, benzene, 2-ring, 3-ring and 4-ring PAH emissions data, % reductions in measured air toxics, TAC/PM ratios and % change in those ratios for older diesel engines ("traditional diesel engines", or TDE) and NTE fitted with OCs. Ethyl benzene- and 2-ring PAH/PM ratios were slightly decreased for NTE-OC engines compared to TDE engines. 3-ring- and 4-ring PAH/PM ratios were increased, and butadiene- and benzene/PM ratios were substantially increased for NTE-OC engines compared to TDE engines.

PM and air toxics emissions concentrations and TAC/PM emissions ratios in NTE-OC and TDE exhaust (adapted from Hesterberg et al., 2008).

		TAC/PM		TAC/PM	%TAC	% ratio
(mg/mile)	OC	ratio	TDE	ratio	decrease	change
PM	38		630		94	
butadiene	1.45	0.038	4.3	0.007	66	459%
benzene	2.01	0.053	1.8	0.003	-12	1751%
ethyl benzene	0.1	0.003	2.1	0.003	95	-21%
2 ring PAH	0.34	0.009	7.2	0.011	95	-22%
3 ring PAH	0.09	0.002	0.65	0.001	86	132%
4 ring PAH	0.06	0.001	0.36	0.0005	85	156%

Figure 2 illustrates the TAC/PM ratios for TDE and NTE-OC engines.

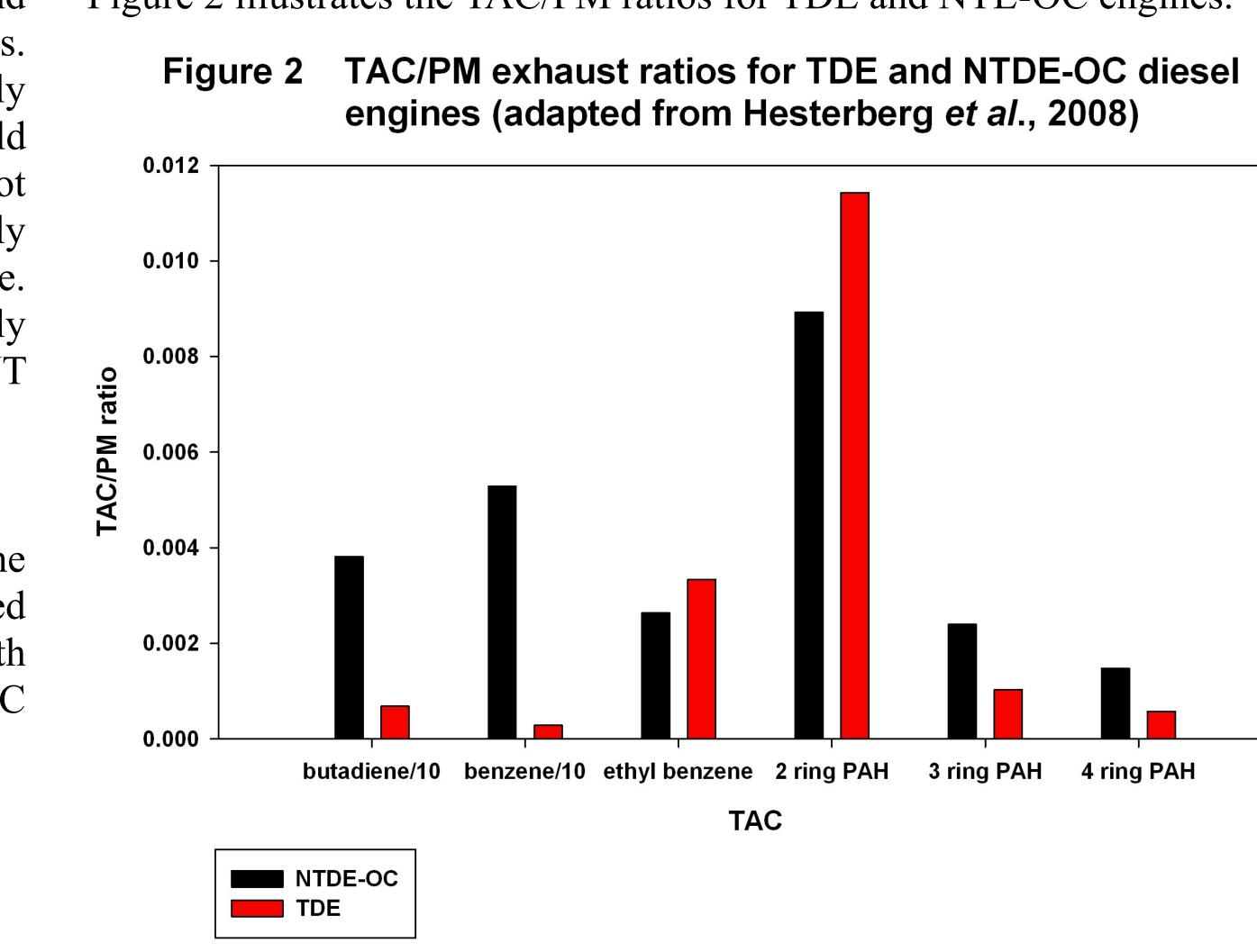


Table 4 lists the PM, butadiene, benzene, 2-ring, 3-ring and 4-ring PAH emissions data, % reductions in measured air toxics, TAC/PM ratios and Emissions (regulated and unregulated) characterization of the four engines NTE-CRT engines compared to TDE engines.

Table 4 PM and air toxics emissions concentrations and TAC/PM emissions ratios in NTE-CRT and TDE exhaust (adapted from Hesterberg et al., 2008).

(mg/mile)	NTDE	TAC/PM ratio	TDE	TAC/PM ratio	%TAC decrease	% ratio change
PM	30		630		95	
butadiene	2.3	0.077	4.3	0.007	47	1023
benzene	0.4	0.013	1.8	0.003	78	367
ethyl benzene	0.1	0.003	2.1	0.003	95	0
2 ring PAH	0.216	0.0072	7.2	0.011	97	-37%
3 ring PAH	0.098	0.003	0.65	0.001	85	217%
4 ring PAH	0.016	0.00053	0.362	0.00057	96	-7%

TDE: no retrofit emission controls; CRT: diesel particulate filter

TDE

TAC/PM exhaust ratios for TDE and NTDE-CRT diesel

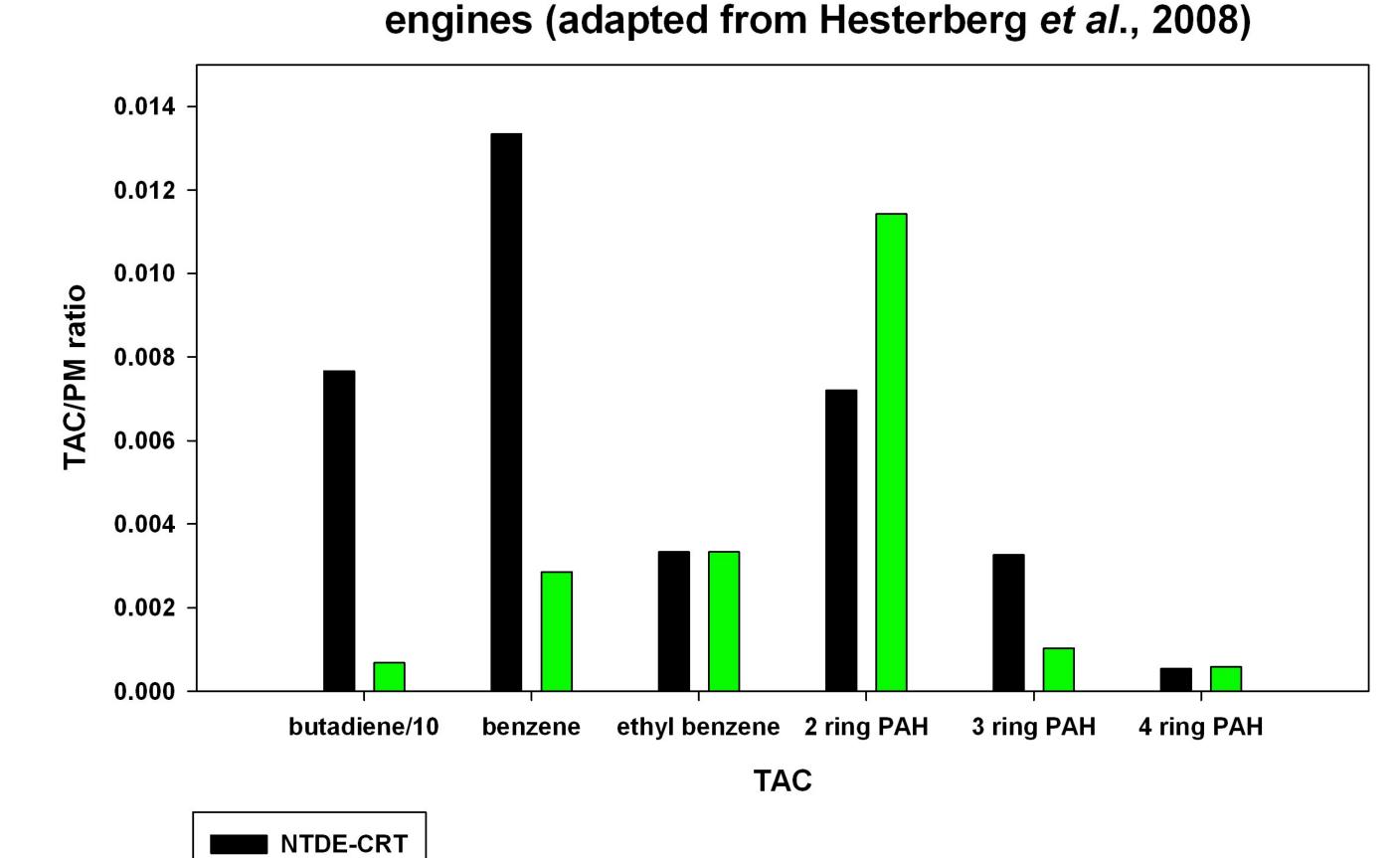


Figure 3 illustrates the TAC/PM ratios for TDE and NTE-CRT engines.

### Southwest Research Institute (SwRI) (2009)

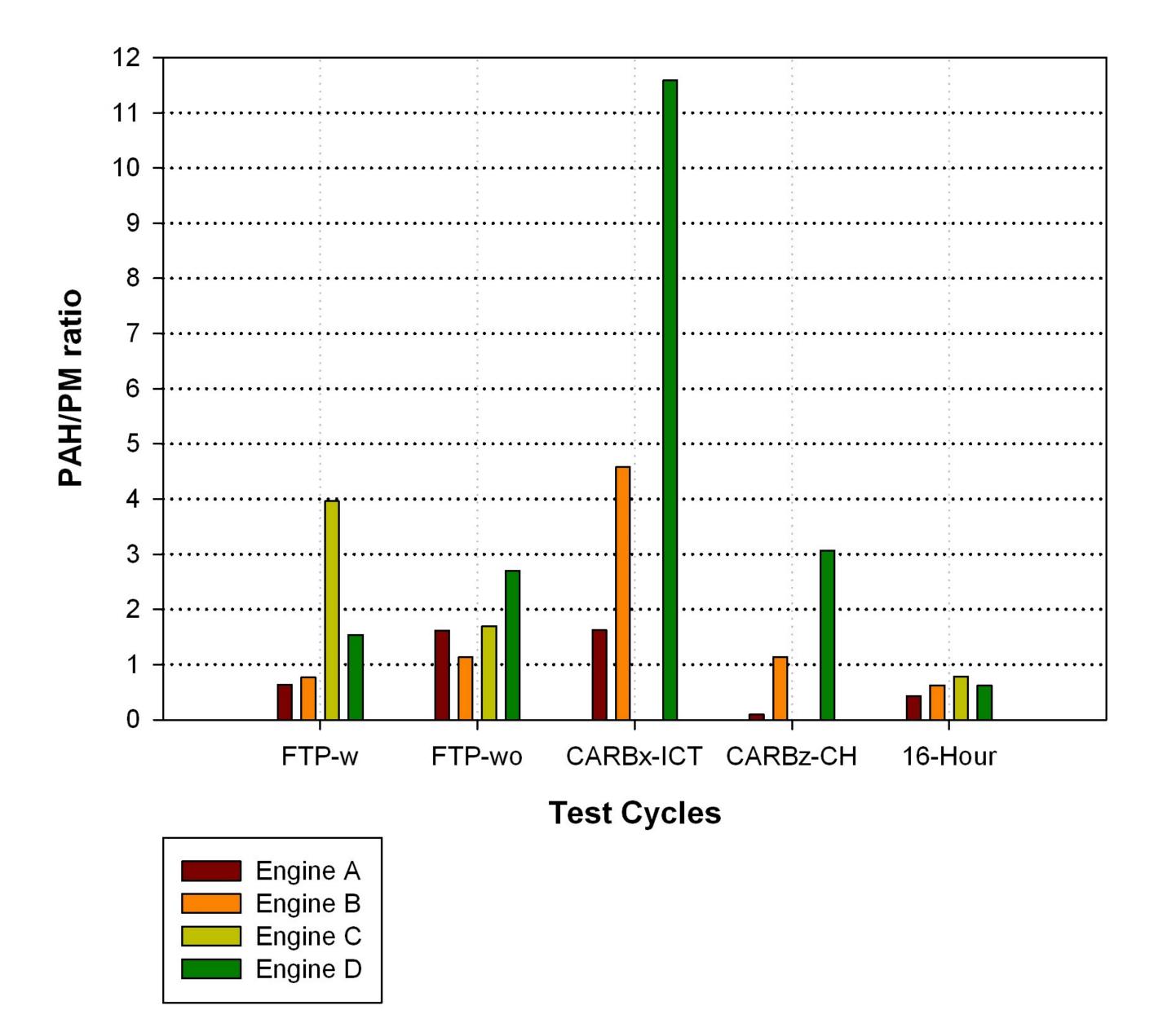
The Advanced Collaborative Emissions Study (ACES) is a multi-party developed retrofit emissions controls for older diesel engines and NTE effort to characterize the emissions and assess possible health effects—engines with advanced emissions control techniques included as part of caused by the emissions of heavy-duty diesel (HDD) truck engines the engine design which produce substantially lower exhaust levels of designed to meet the new Federal emissions requirements for such engines DEP and air toxics compared to older engines. Reported reductions in which took effect in model years 2007 and 2010. The project involves DEP and air toxics vary according to the engine type, fuel, type of emission characterization, selected toxicological studies and results emissions controls used, and engine test cycles used to evaluate engine interpretation from selected prototype engines and control technology emissions. The reduction of PM exhaust concentrations suggests that a combinations. The overall research design and development, calculation of cancer risk using the CARB diesel exhaust cancer unit risk implementation and overall reporting of results for ACES are being value will result in a much reduced cancer risk per engine, since the metric performed by the Health Effects Institute (HEI).

ACES is planned to take place in four Phases. Phase 1 involves the engine exhaust. Data from the studies described above indicate that the emission characterization of a group of 2007 model year HDD engines reductions of some air toxics such as PAHs, benzene and 1,3- butadiene in with associated aftertreatment systems in order to select one HDD engine NTE exhaust (often 80 - 90%) are often not as great as the corresponding to be used in health effects studies. The engines provided for use in ACES reductions in DEP (often 95 - 99%). The resulting air toxics/DEP ratios Phase I were a Caterpillar C13, Cummins ISX, Detroit Diesel Corporation for NTE exhaust may be greater than or equal to similar ratios found in Series 60, and a Volvo Powertrain Mack MP7. The identities of the exhaust from older diesel engines. These data suggest that while the engines were made anonymous for ACES Phase 1, and were designated as absolute amount of DEP and air toxics is much reduced in NTE exhaust, Engine A, Engine B, Engine C and Engine D.

% change in those ratios for older diesel engines ("traditional diesel was performed at the SwRI San Antonio TX facility using ultra-low sulfur is not known, it is entirely plausible that genotoxic carcinogens such as engines", or TDE) and NTE fitted with CRTs. Two-ring PAH/PM ratios diesel fuel and the hot-start Federal Test Procedure transient cycle (FTP- PAHs, benzene and 1,3-butadiene found in DEE contribute to that were decreased and 4-ring PAH/PM ratios were slightly decreased for TC) with and without crankcase blow-by, two composites of the CARB carcinogenic process. Thus, the available data do not indicate that NTE NTE-CRT engines compared to TDE engines. Ethyl benzene/PM ratios Heavy-Duty Diesel Engines (HHDDE) 5-Modes cycle (CARB 5- exhaust should be considered to be fundamentally different in kind were unchanged for NTE-CRT engines compared to TDE engines. Three- Modes), and a 16-hour transient cycle composed of the FTP-TC and the compared to older DEE for risk assessment purposes and suggest that the ring-, butadiene- and benzene/PM ratios were substantially increased for CARB 5-Modes. The two CARB composite cycles were CARBx-ICT TAC cancer unit risk value for DEP can continue to be applied to NTE (idle, creep and a transient portion of the CARB HHDDE-5 Modes), and exhaust risk assessments. CARBx-CH (cruise and high speed cruise of the CARB 5-Modes). Engine C had a diesel particulate filter (DPF) crack failure during emissions characterizations involving the CARBx-ICT and CARBz-CH References cycles. SwRI excluded these data from the emission comparison results.

> Figure 4 provides a graphic representation of the average dilution tunnel total PAH/PM ratios (data from Tables 24 and 32 of the report) for all Nylund N-O, Erkkilä K, Lappi M and & Ikonen M. (2004) Transit Bus available engine and test cycle combinations. In general, the majority of Emission Study: Comparison of Emissions from Diesel and Natural Gas the total PAH/PM ratios were greater than or equal to one, indicating that Buses. VTT Processes Research Report PRO3/P5150/04. VTT Technical the dilution tunnel exhaust contained more PAHs (particle-bound and semi Research Centre of Finland, Espoo, Finland. -volatile phase) than PM.

Figure 4: ACES Phase 1 emissions data PAH/PM ratios



### **Discussion and Conclusions**

for risk in this calculation is µg DEP/m<sup>3</sup>. However, it is not clear that the composition of NTE exhaust is fundamentally different from older diesel and thus the estimated cancer risk using the OEHHA URF is much lower, the exhaust composition has not necessarily become less hazardous. Additionally, while the exact mechanism of DEE-induced carcinogenesis

Since the DEP TAC listing in 1998, diesel engine manufacturers have

California Air Resources Board (CARB) (1998) Proposed Identification of Diesel Exhaust as a Toxic Air Contaminant. Sacramento, CA.

Verbeek R and Rabé E. (2007) Pre-study of exhaust gases of diesel engines with "open" and "wall-flow" diesel particulate filters and their toxicity. TNO report MON-RPT-033-DTS-2007-01072. TNO Science and Industry. Delft, the Netherlands.

Hesterberg et al. (2008) A comparison of emissions from vehicles fueled with diesel or compressed natural gas. Environmental Science & Technology, 42(17): 6437-6445.

Southwest Research Institute (SwRI) (2009) Phase 1 Of The Advanced Collaborative Emissions Study. Revised Final Report, Revision 6. SwRI Project No. 03.13062.