

Monitoring of PM-bound Polycyclic Aromatic Hydrocarbons from Diesel Vehicles by Photoelectric Aerosol Sensor (PAS)

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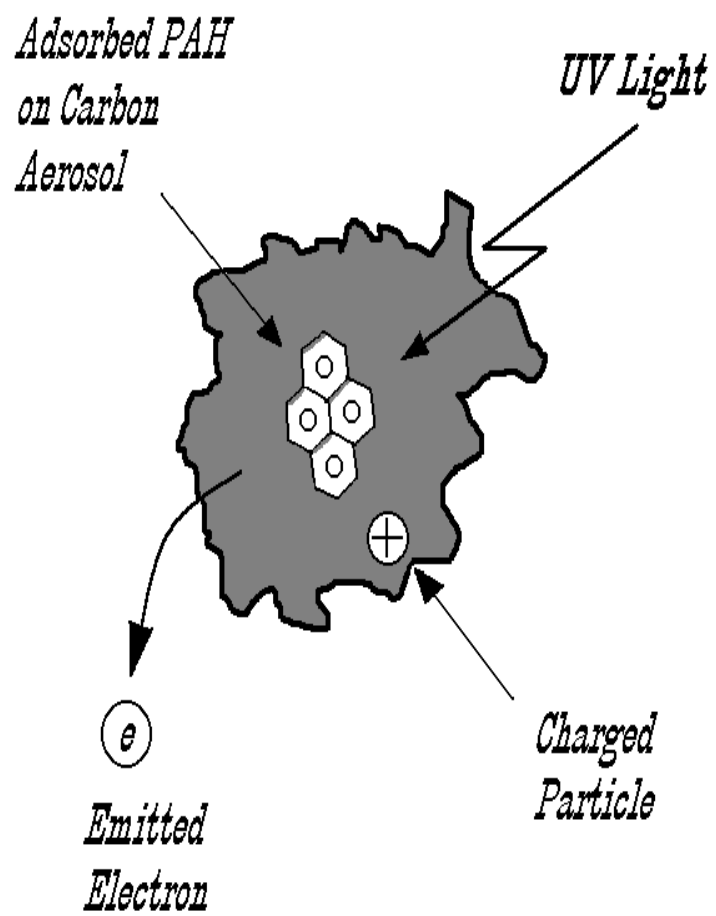
BACKGROUND

The public is increasingly concerned about the health impact of particulate matter (PM) in the air, especially PM from diesel combustion. A recent HEI study¹ using PM₁₀ data from ninety cities has shown, in general, an association between the daily changes in concentration of ambient PM and daily number of deaths (mortality) as well as increased hospitalization (morbidity) among the elderly for specific causes. Analysis by state and local clean air regulators estimates that diesel PM is responsible for more than 125,000 cancers in the United States.² Furthermore, the percentage of U.S. population suffering from asthma, especially in low income urban areas, has increased during recent years. The principal causes of elevated asthma rates are currently debated, but diesel exhaust emissions, even if not a primary causal factor, appear to at least exacerbate asthmatic symptoms.³

The mechanism of the toxic effect by PM is not clear. However, diesel PM contains polycyclic aromatic hydrocarbons (PAHs), an organic class that includes many potential mutagenic and carcinogenic species. Conventionally, these PM-bound PAHs are measured by a complicated chemical analysis⁴ involving collection of PM on a filter material followed by solvent extraction, clean-up, pre-concentration, and final instrumental analysis by gas chromatography-mass spectrometry (GC-MS) or liquid chromatography-mass spectrometry (LC-MS).

As the chemical analysis of PAHs is such a complicated, time consuming, and expensive process, a sensor technique has been studied for this purpose and the possibility of continuous monitoring of PM-bound PAHs. A photoelectric aerosol sensor (PAS) for the detection of total PM-bound PAHs has been developed by EcoChem Me\$technik GmbH of Uberlingen, Germany and, is available from EcoChem Analytics of West Hills, CA. The operational principle of PAS is described in detail by Burtscher⁵ and is depicted in Figure 1. Briefly, PAS employs UV radiation (222 nm) produced by the KrBr excimer lamp to ionize PM-bound PAHs. Only PM with PAH coated on the surfaces is ionized because of the PAH's low ionization potentials. Following ionization, the photoelectron attaches to the oxygen to form a negative ion in the carrier gas if it contains oxygen. The negative ion diffuses back to the particle if it is about 1 μm or larger in

Figure 1. Photoionization of PM-Bound PAHs



size.⁶ However, particles with smaller size remain positive while the negative ions diffuse to the wall or are removed by an alternating electric field. The positively charged particles are collected on a filter element and the electric current generated is monitored by an electrometer.⁷ The electrometer provides an output signal that is theoretically proportional to the PAH mass collected by the filter. Note that the PAS instrument can measure only “total PM-bound PAHs” and cannot provide PAH speciation which will require techniques such as GC-MS or LC-MS. PAHs in the vapor phase are not detected by PAS.⁸ Furthermore, the excimer lamp is operated in a pulsed mode to eliminate interference from naturally-occurring particles presented in the sample stream and to suppress zero drift.

Thorough laboratory studies on PAS have been carried out by Siegmann’s group^{5,9} at Swiss Federal Institute of Technology and by Niessner and his colleagues at University of Dortmund, Germany.^{10,11,12,13} EPA and the California Air Resources Board have conducted PAS evaluation studies and reported positively on PAS performance.^{8,14} A correlation between PM-bound PAHs in airborne PM and their bacterial genotoxicity has been demonstrated indicating that the PAS detects biologically relevant PM-bound PAHs.¹⁵ Some applications of PAS have been reported and a bibliography of publications on PAS is available from EcoChem Analytics. PAS is, however, a developing technology and problematic in some aspects, particularly regarding instrument calibration and potential response variability vs. PAH composition. Although photoelectric responses from different PAH species were found to be additive in a laboratory study,¹² PAS calibration may still be both difficult and uncertain because different PAH species exhibit somewhat different ionization potentials and the PAH composition of the targeted PM may not be known. Therefore, a source specific calibration — using matrix matched PM with known PAH mass adsorbed on the PM surface and PAH composition representative of the emission source — would seem desirable. Although it can’t be considered as a calibration procedure, credibility of PAS will be definitely gained by favorable comparison between PAS and standard chemical analysis. However, results from the very limited comparison studies have been contradictory.^{16,17}

In this study, the capability of PAS as a PM-bound PAH monitoring device is evaluated for

heavy duty diesel vehicles (trucks and buses) transient testing over different driving cycles. Comparison study between PAS and standard chemical analysis of PAHs is performed for a limited number of diesel and CNG buses. We also report the PAS analysis of diesel particulate standard reference material SRM1650a with certified PAHs values from National Institute of Standards & Technology (NIST).

EXPERIMENTAL

Instruments - Instruments employed in this study are listed in the Table 1 below.

Field testing: Although emissions from new diesel engines are routinely measured in EPA engine certification testing, emissions from in-use diesel fleets are not well studied and, consequently, poorly characterized. To aid in the development of in-use diesel emission inventories for the New York City metropolitan area (NYMA), the New York State Department of Environmental Conservation (DEC) conducted a heavy duty diesel (HDD) truck emissions testing project in the summer of 1999. Project funding was obtained through the federal Congestion Mitigation and Air Quality Improvement (CMAQ) program, with additional support from the EPA Office of Mobile Sources. The project is referred to herein as the CMAQ project.

West Virginia University (WVU) was contracted to perform CMAQ-HDD emissions testing for HC, CO, NO_x, and PM. Thirty five NYMA in-use HDD trucks were procured for testing over the WVU 5-mile and the TEST-D route driving cycles (see Figure 2a for cycle speed vs. time profiles). The DEC Automotive Emissions Laboratory (AEL) supplemented WVU emissions measurement with specialized particulate monitoring instrumentation: a tapered element oscillating microbalance (TEOM) for realtime mass measurement; a diesel particulate analyzer (5100); and a photoelectric aerosol sensor (PAS) to measure PM-bound PAHs. In the CMAQ project, both PAS and TEOM were set up down stream of the main dilution tunnel (CVS) for sampling the diluted diesel exhausts similar to the set-up schematic for CRT shown in Figure 3.

Comparison with off-line chemical analysis - In February 2000, a “Clean Diesel Demonstration Program” project was initiated by New York City Metropolitan Transit Authority (MTA) under the supervision of NY State Department of Environmental Conservation. Johnson Matthey, Corning Inc., Equilon Enterprises, Environment Canada and Rad Energy have actively participated in this project by providing the continuously regenerating traps (CRTTM), low sulfur (<30ppm) diesel fuel, and performing the comprehensive emissions tests. The emission test was

Table 1. Instrument information

Instrument	Model	Manufacturer	Address
Photoelectric Aerosol Sensor (PAS)	2000	EcoChem Analytics	22605 Valerio, West Hills, CA 91307, USA.
<p>Parameter Measured: PM-bound PAHs</p> <p>Principle of Operation: An exhaust gas sample containing PM is drawn through a quartz tube. An excimer lamp mounted around the quartz tube and operated at high frequency and high voltage directs 222 nm radiation at the gas sample to ionize PAH coated PM. After Photoionization, the positively charged particles are collected on a filter element mounted in a Faraday cage. The ion current from the charged particles monitored by an electrometer is proportional to the PAH mass collected by the filter.</p>			
Tempered Element Oscillation Microbalance	1105	Rupprecht & Patashnick Co., Inc.	25 Corporate Dr. Albany, New York, USA.
<p>Parameter Measured: PM mass/or concentration in real time; accumulated mass over driving cycles</p> <p>Principle of Operation: The TEOM detector is a tapered, hollow tube, fixed at the wide end, and holding a changeable filter at the narrow end. The gas sample containing PM is drawn through the filter element and tapered tube, exiting at the wide end. The tapered tube is maintained in continuous oscillation with the frequency of oscillation being accurately monitored. The square of the frequency of oscillation is proportional to the effective mass of the tapered element, filter, and collected PM. As PM mass on the filter increases, the change in frequency of oscillation is detected, from which the change in mass on the filter element can be calculated.</p>			
Diesel PM Analyzer	5100	Rupprecht & Patashnick Co., Inc.	25 Corporate Dr. Albany, New York, USA.
<p>Parameters Measured: Accumulated PM mass; organic carbon (OC) and elemental carbon (EC)</p> <p>Principle of Operation: The diesel PM analyzer collect PM on a filter element in a temperature-controlled cell generally for a full driving cycle. Collected PM on the filter element will be heated through a designed temperature heating program to burn off the organics as well as carbon element. Organic carbon (OC) and element carbon (EC) can thus be obtained from the CO₂ measurements at different temperatures.</p>			
Small-Scale Powder Disperser	3433	TSI Inc.	500 Cardigan Road, P. O. Box 64394, St. Paul, MN, USA.
<p>Principle of Operation: Designed to efficiently disperse small quantity (milligram) of dry powder using a venturi aspiration technique. The powder to be dispersed is brushed over the surface of the turntable and is removed from the turntable by means of a venturi aspiration and capillary delivery tube as the turntable rotates slowly. The gas stream passing through the venturi throat tends not only to break up the agglomerates but also acts as a sheath to reduce particle loss to the wall resulted in a diluted and deagglomerated aerosol stream.</p>			

Figure 2a. CMAQ Project Driving Cycles

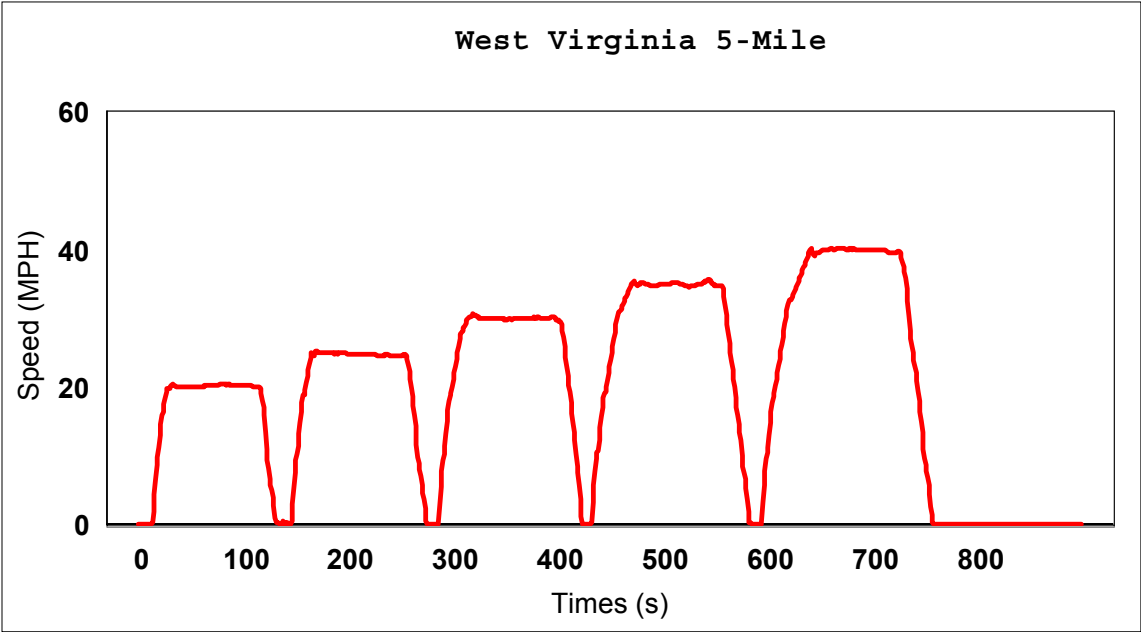
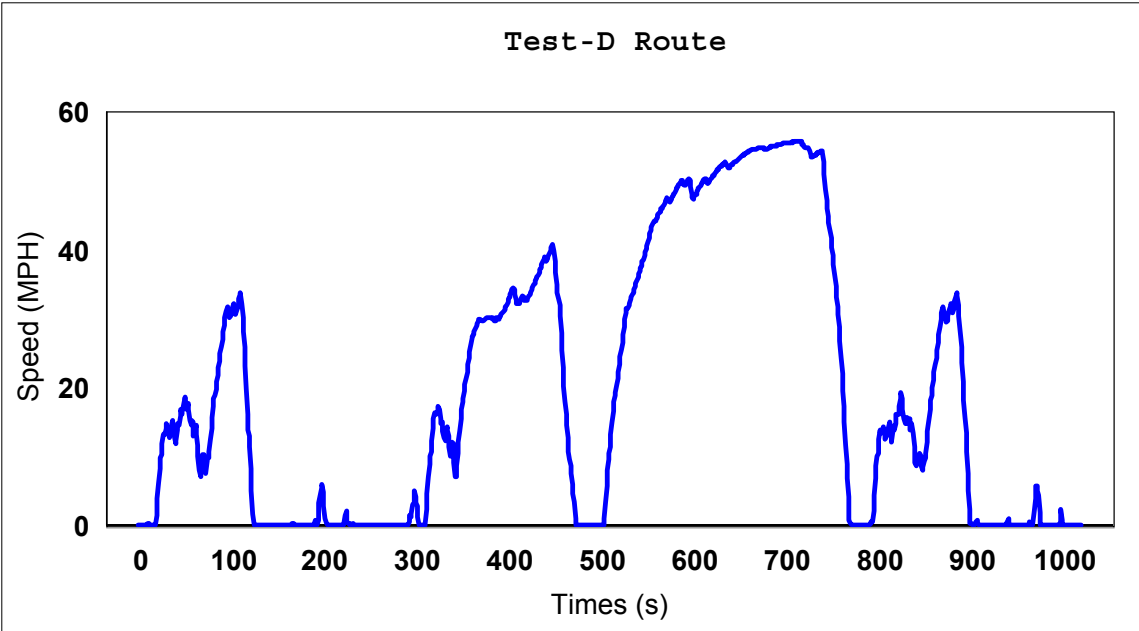
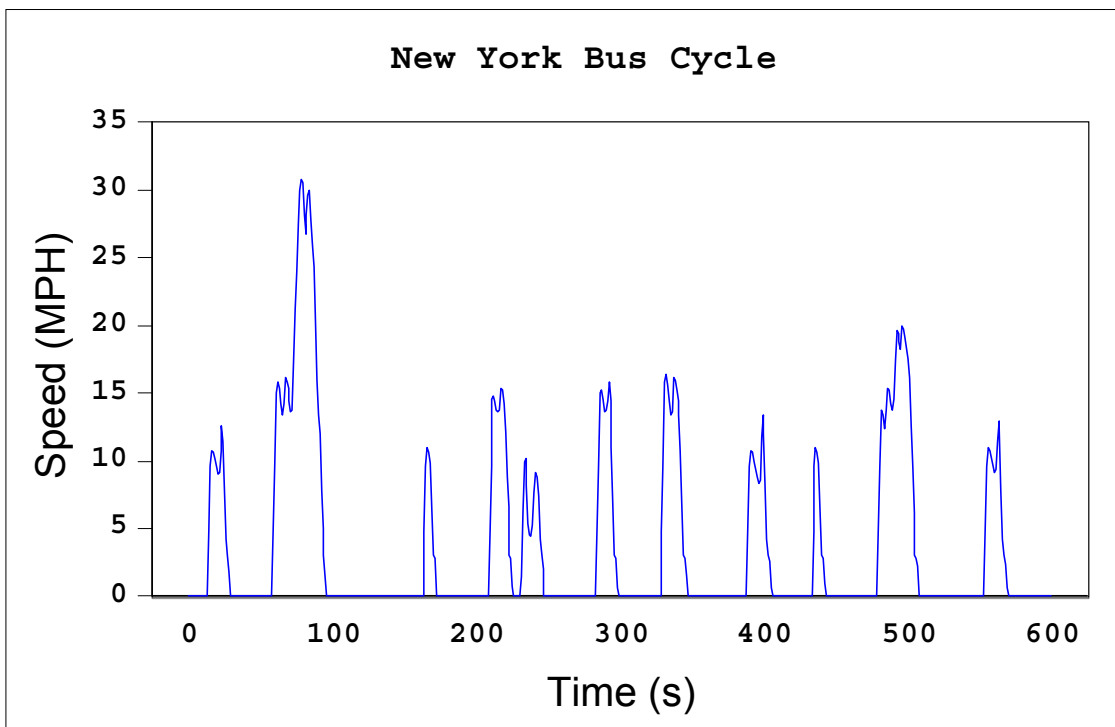
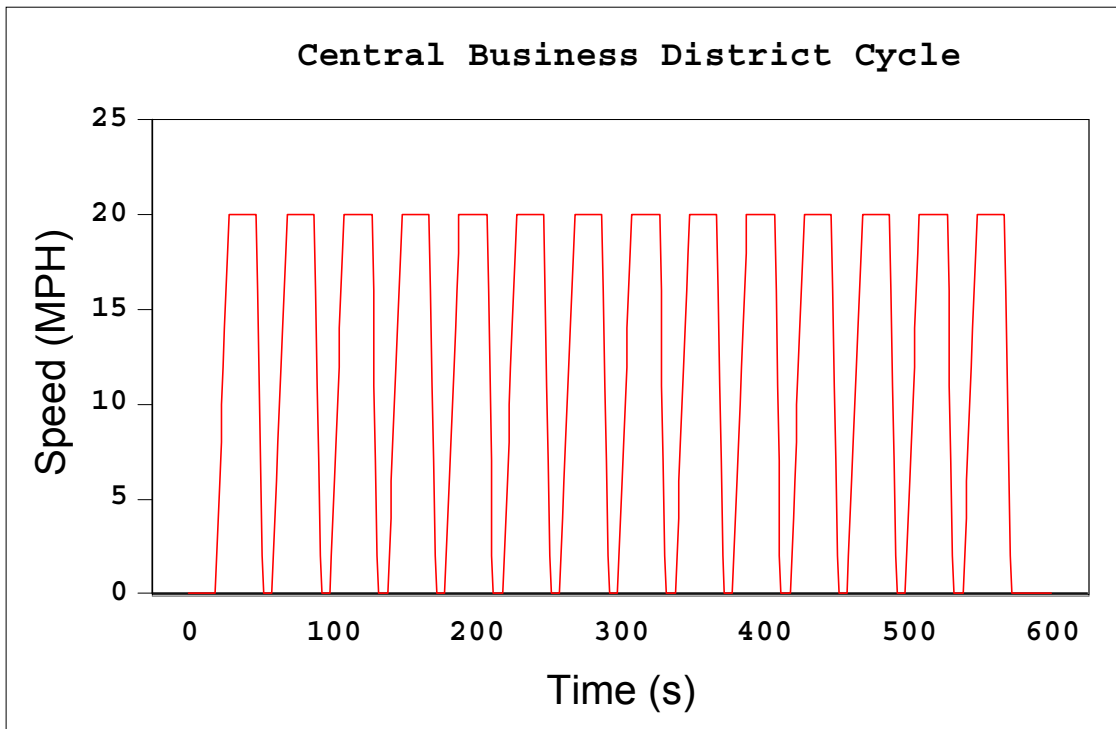


Figure 2b. CRT Project Driving Cycles



performed at Emission Research and Measurement Division of Environment Canada in Ottawa, Canada.

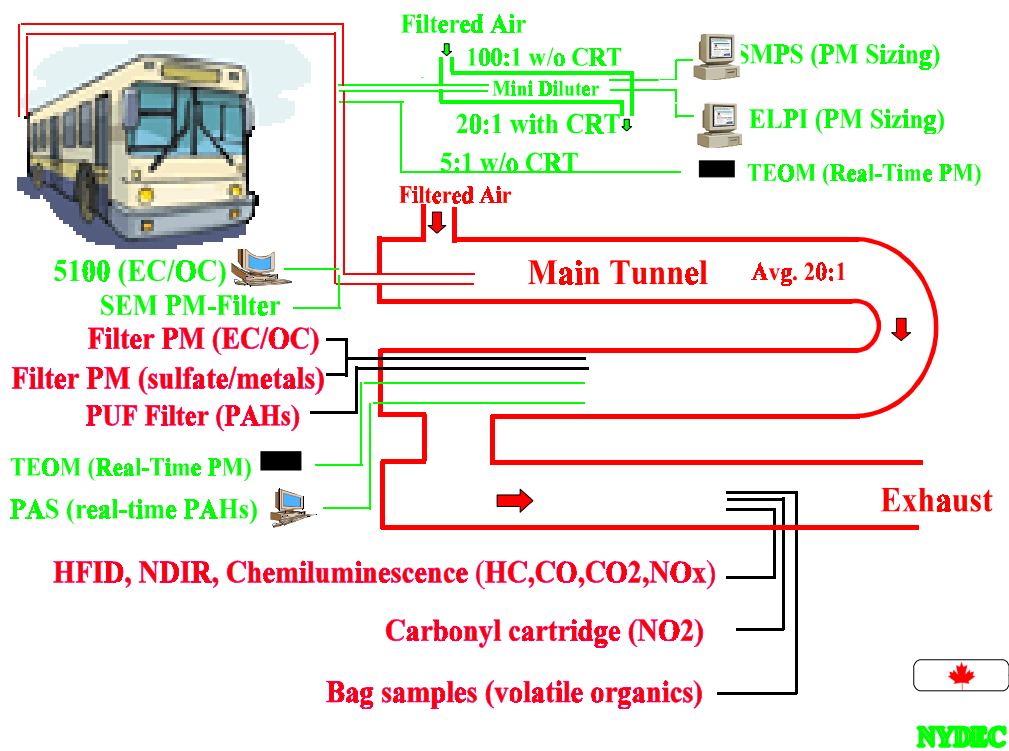
Primary goals of the project include verifying the emissions reduction benefits of the continuously regenerating trap technology and verifying the durability of the CRTs in actual use on buses operated in rigorous New York City duty services. An entire depot, approximately 130 buses, is being run on low sulfur diesel fuel. Fifty of these buses were retrofitted with CRTs. These buses operate over five different bus routes in normal revenue service in Manhattan and the Bronx. Twice during the project, a sample of four buses will be subjected to comprehensive emissions tests. Baseline testing completed to date included OEM buses (no CRT) with commercial fuel, OEM buses with low sulfur fuel, and CRT equipped buses with low sulfur fuel. The Central Business District (CBD) Cycle and New York Bus Cycle were used as the driving cycles for the emission test (Figure 2b). This testing will be repeated after the buses have completed nine months of revenue service to determine the durability of the CRT.

In addition to regulated emissions (HC, CO, NO_x and PM), VOC, carbonyls, PAHs and NPAHs were speciated and characterized, and the PM analyzed for SOF, sulfate and elemental carbon. Particle number and mobility diameter size distributions have also been characterized using a scanning mobility particle sizer, and particle number and aerodynamic size distributions using an electrical low pressure impactor. TEOM and PAS were also used for real-time PM and PM-bound PAH measurements. PM samples were also collected for morphologic study using scanning electron microscopy (SEM). A set-up schematic for the CRT bus testing is shown in Figure 3. Detailed results from the CRT project have been presented elsewhere.¹⁸

Performance with Standard Reference Materials - For the evaluation of PAS, analysis of PAHs in the standard reference material of diesel particulate matter from National Institute of Standards & Technology (NIST) was performed. It should be mentioned that NIST has recently updated

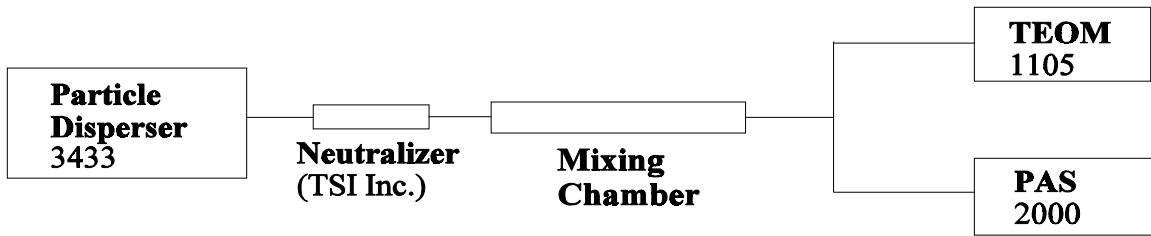
the certification for SRM 1650a and 17 PAHs (16 PAHs and one nitro-PAH) are currently certified with 25 additional noncertified PAHs and 3 noncertified nitro-PAHs (provided for information only). The experiment was designed to analyze a stream containing NIST SRM1650a aerosols generated by TSI's small-scale powder disperser. A TEOM was employed in the experiment to provide the PM mass concentrations of SRM 1650a in the aerosol stream. The diagram of the experiment arrangement is shown in Figure 4.

Figure 3. CRT Project Driving Cycles



Sampling Diagram of CRT Testing Program

Figure 4. Experimental Diagram for SRM 1650a Analysis



RESULTS AND DISCUSSION

Field-testing performance:

Composite PM-bound PAH emissions - Measurements of PM-bound PAH emissions from thirty-five HDD trucks tested in the CMAQ project were obtained using PAS with built-in calibration suggested by the manufacturer. As matrix-matched calibration was not available, the PAH emission data summarized in the table below should be considered preliminary.

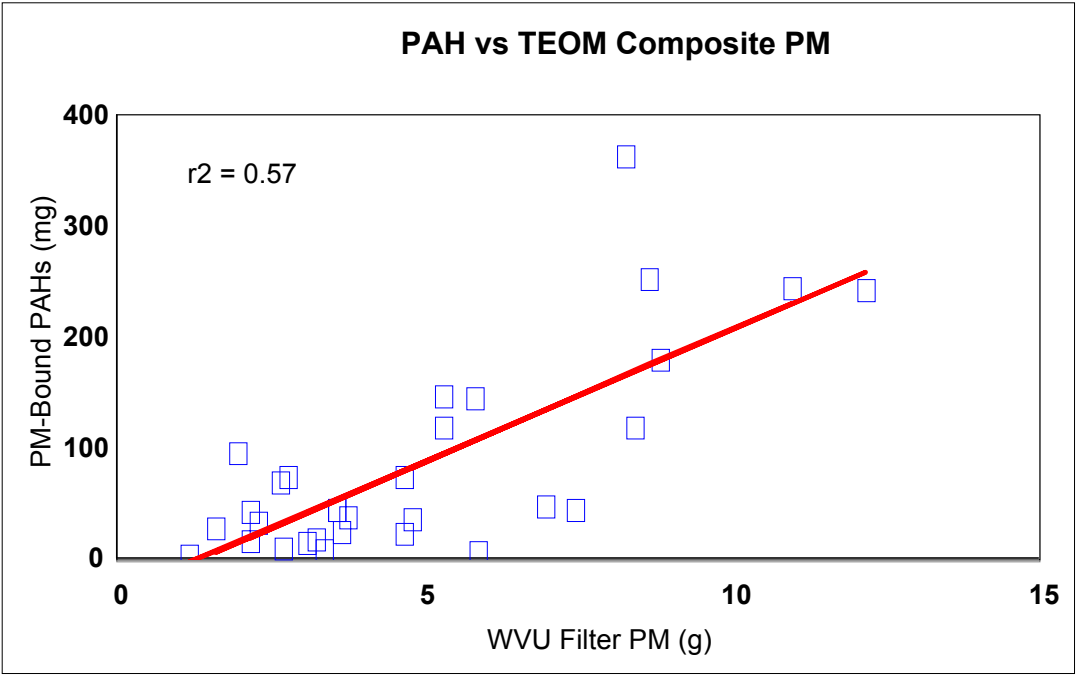
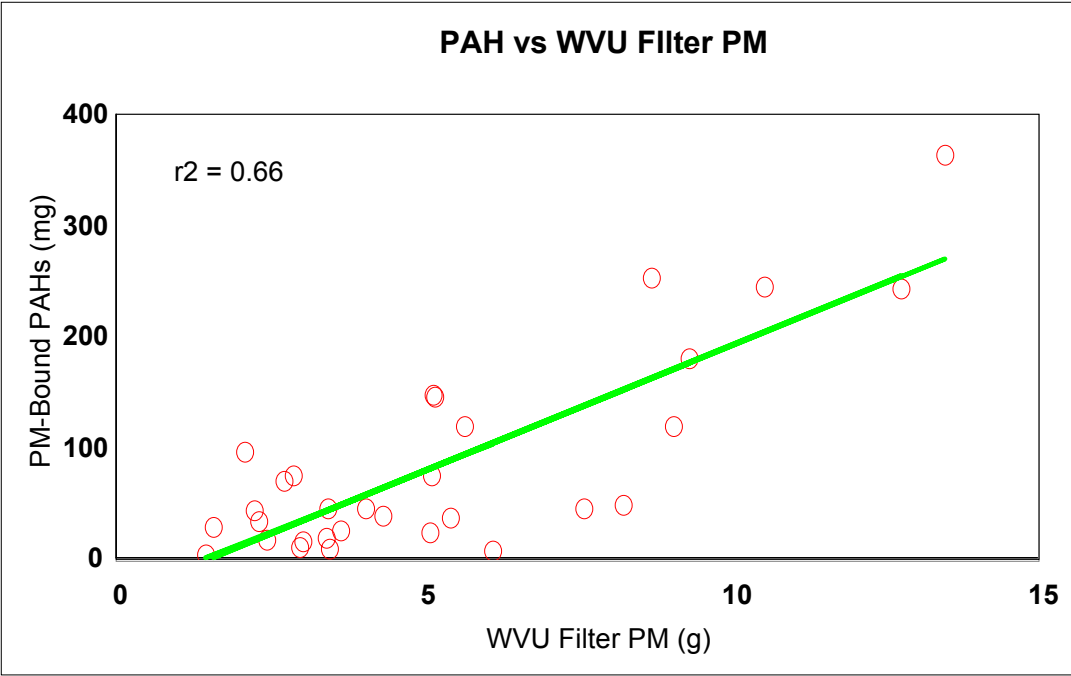
Table 2. HDD truck PM-bound PAH emissions measured by PAS

Vehicle type	Test cycle	Observed range (mg/mile)	Mean (mg/mile)	Mass fraction (%)*
HDD Truck	WVU 5-mile	0.58-27.76	7.08	N/A
HDD Truck	TEST-D	0.87-65.72	14.42	0.07-5.46

* Percentage of PAHs mass over total PM mass obtained by filter method

CMAQ-HDD PM mass was determined by two techniques: gravimetric filter collection (performed by WVU) and TEOM (performed by AEL). Figure 5 shows the averaged composite PM-bound PAH mass emissions vs. composite PM mass emissions obtained by WVU filter method and TEOM for 31 of the 35 HDD diesel trucks tested in the CMAQ project with the TEST-D cycles. No strong correlation is visually apparent in the data, especially for PM emissions below 9.0 g. Note, however, that the five highest PM emission rate observations (TEST-D emissions greater than 9.0 g) are also associated with the 5 highest PAH emission rates. It should be pointed out that the PAH mass emission data in Fig. 5 are higher than reported in the literature for diesel vehicles.^{4,19} One magnitude higher PAH measured by PAS has also been reported for ambient air PM by others.²⁰

Figure 5. Relationship between PAS measured PAHs and PM mass measured by WVU filter method and TEOM with TEST-D cycles



Although a full comparison of CMAQ-HDD filter method PM mass (PM_{Filter}) vs. CMAQ-HDD TEOM PM mass (PM_{TEOM}) awaits presentation elsewhere, preliminary regression analysis indicates a strong linear relationship:

$$PM_{\text{TEOM}} \text{ (g/mile)} = 0.91 \times PM_{\text{Filter}} \text{ (g/mile)} + 0.10 \quad r^2 = 0.98$$

Correlation between TEOM and filter PM will not be further discussed. The ~ 10% underestimation of PM emission measured by TEOM may be due to physical measurement characteristics of the TEOM filter design. Preliminary results with a new TEOM filter design have shown a close to 1:1 correlation between TEOM PM mass and filter PM mass under laboratory conditions. Given the strong linear relationship between filter PM mass and TEOM PM mass, the close similarity of Figure 5 TEST-D graphs for PM-bound PAH mass vs. filter PM mass and PM-bound PAH vs. TEOM PM mass is expected.

PAH mass fractions for CMAQ vehicles ranged from about 0.07% to 5.46% (Table 2). Again, the PAH mass fraction values may be overestimated by PAS. Diesel exhaust PM generally contains more elemental carbon (EC, carbon chemically bound only to other carbon atoms) than organic carbon (OC, carbon in organic chemical molecules that includes other elements) although considerable variation exists among individual vehicles²¹. As mentioned in the experimental section, a diesel analyzer (R&P 5100) was employed in the CMAQ project for EC/OC measurements. Preliminary results have shown that OC fractions for the HDD diesel trucks range from 15% to 88% with an average of 48%. Given the large vehicle-to-vehicle variation in OC fractions observed for the vehicles tested in the CMAQ project, variation in the PAH mass fraction seen in Table 2 is not unexpected.

PM-bound PAH is likely influenced by several factors such as: survival of fuel PAH; creation of PAH from non-PAH fuel components; modification of fuel PAH; contribution from the lubrication oil; and entrainment from PAH deposited in the exhaust and sampling system.⁴ Attempts to develop a generalized relationship for PM-bound PAH vs. PM may be confounded by differences across vehicle, engine, and cycle types. Another complicating factor is the current

PAS particle size limitation. The PAS method is sensitive only to PAHs on PM smaller than $1\ \mu\text{m}$; consequently, any PAH bound to $\text{PM} > 1\ \mu\text{m}$ may not be detected by PAS.⁶ Thus, data in Figure 5 may be flawed by methodology inconsistencies relative to particle size.

Realtime PM-bound PAHs vs. cycle speed - Realtime PM-bound PAH emissions over the TEST-D Route cycle are shown in Figures 6 and 7 for two HDD trucks. The vehicle in Figure 6 is a 1994 box truck with a Mack/Renault MIDR engine while Figure 7 is from a 1989 Ford service truck with a Ford KFM07-8FPEZ engine. As the PAS data-output rate was 0.5 Hz and emission test cycle speeds are recorded as 1 Hz average values, the PAS data signal was interpolated using a cubic spline curve fit to obtain estimated 1 Hz PAH data. High PAH emission rates ($\mu\text{g/s}$) in Figures 6a and 7a appear to be generally related to periods of hard acceleration (high loads). This is expected as PAHs are generally produced by incomplete combustion. Note, however, that the 1989 Ford service truck in Figure 7 appears to emit PM-bound PAH in a manner more closely related to the vehicle speed than the Mack/Renault box truck in Figure 6. This difference is most evident in the TEST-D region from about 500 seconds to 800 seconds. Possible reasons for this observation and potential implications are unknown at this time and require further study.

Realtime PM-bound PAHs vs. PM mass emissions - As mentioned in the experimental section earlier, PM mass was monitored in realtime using a TEOM instrument. Comparisons of realtime PM-bound PAH (estimated 1 Hz mass emissions from the 0.5 Hz PAS signal) vs. realtime TEOM PM mass emissions from the Mack/Renault box truck and Ford service truck are given in Figures 6b and 7b. As with PAH vs. cycle speed, realtime PM-bound PAH mass and realtime TEOM mass appear to be in closer agreement for the 1989 Ford service truck in Figure 7 which has a relatively higher PAH mass fraction than the 1994 Mack/Renault box truck in Figure 6. For most of the vehicles with relatively good PAS and TEOM relationships, further analysis has found that PAH mass fractions for these vehicles were relatively high.

Figure 6. Real-time PAH mass emission vs vehicle speed and PM mass emission measured by TEOM for a 1994 box truck with PAH mass fraction of 0.51%

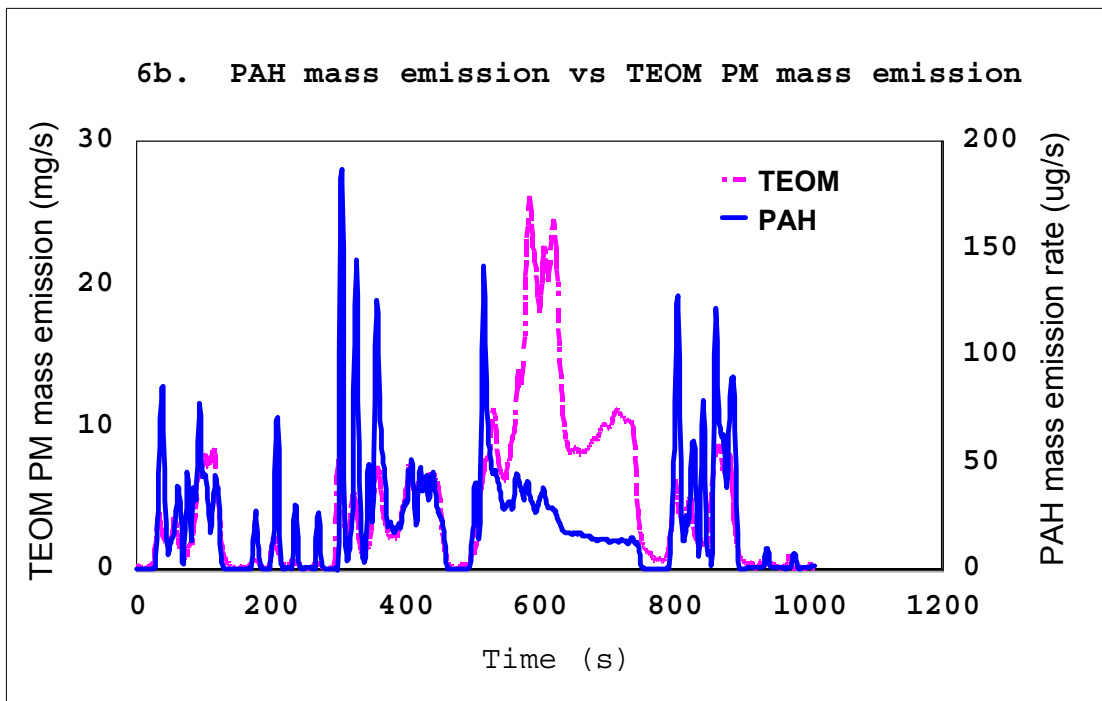
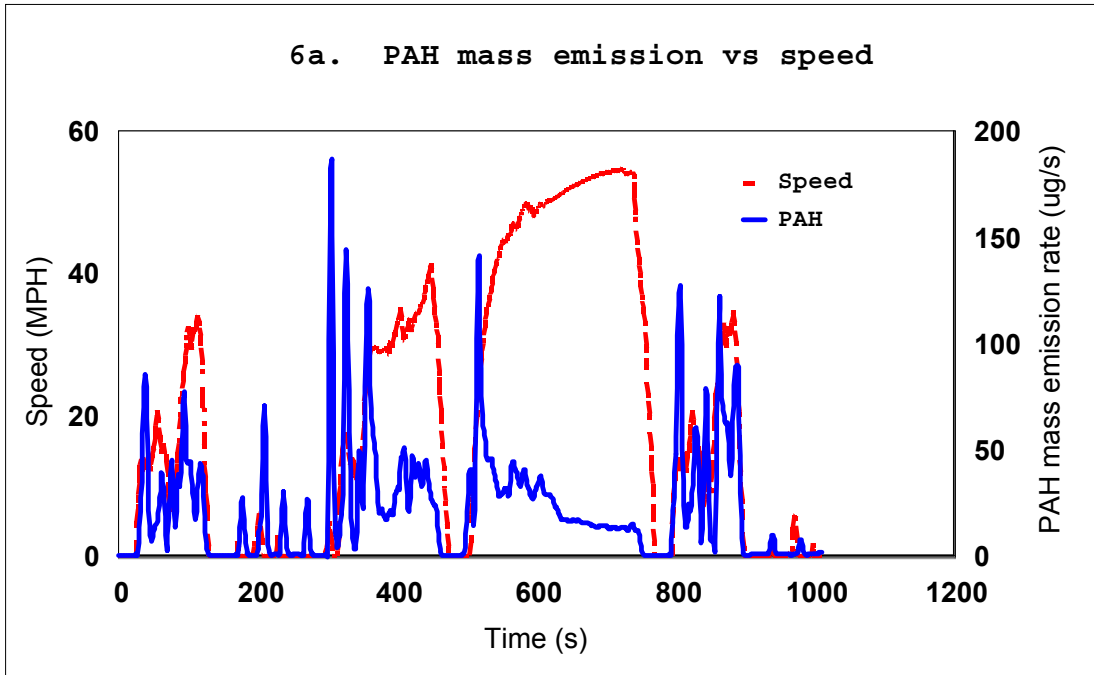
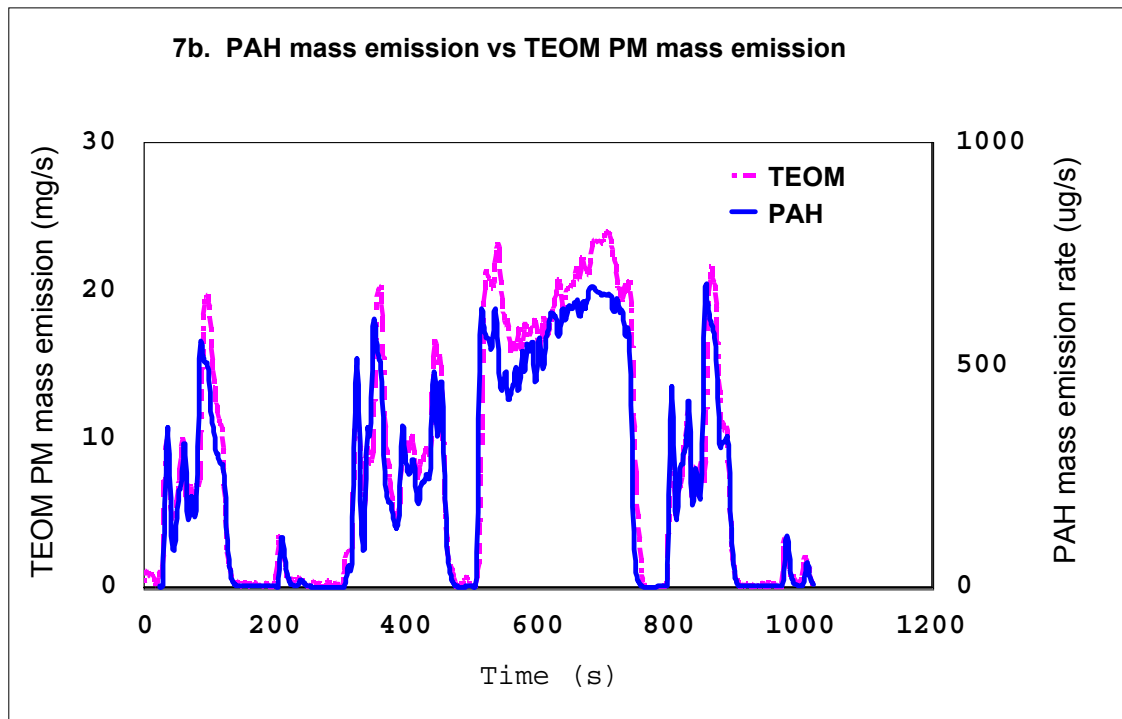
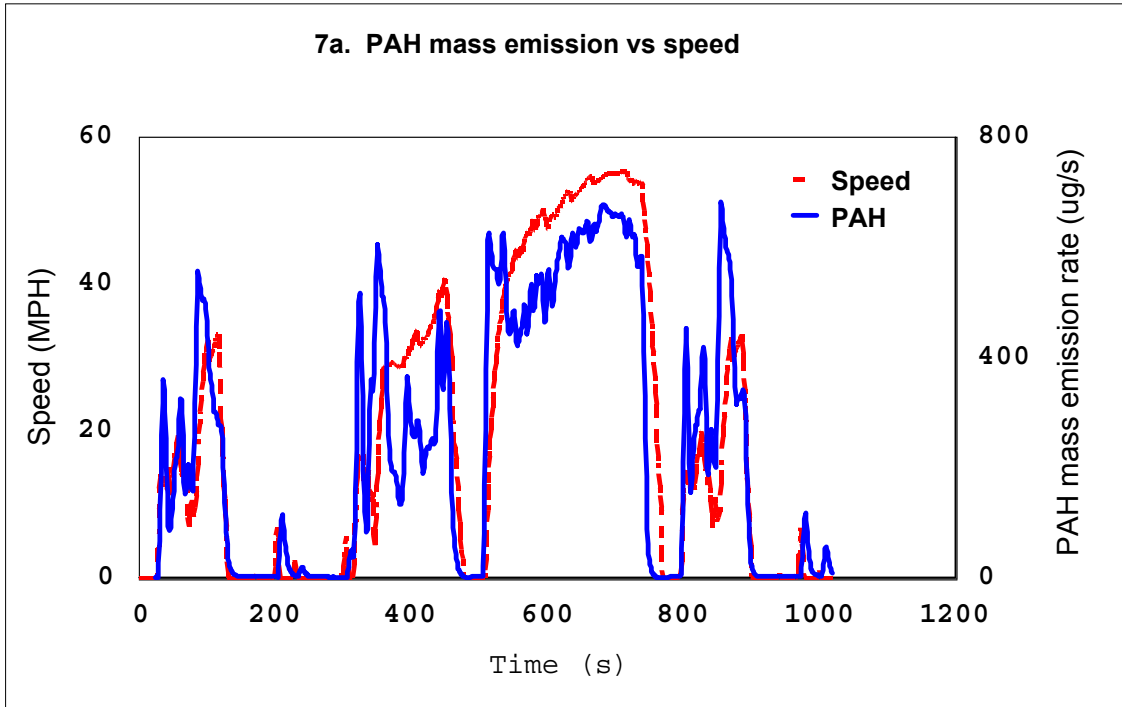


Figure 7. Real-time PAH mass emission vs vehicle speed and PM mass emission measured by TEOM for a 1989 service truck with PAH mass fraction of 2.97%



Comparison with off-line chemical analysis - Comprehensive chemical analysis, including chemical analysis for PAHs, has been performed in the CRT™ bus demonstration project. A new engine bus was tested with low (300 ppm) sulfur fuel with OEM muffler, ultra low (30 ppm) sulfur fuel with OEM muffler, and ultra low (30 ppm) sulfur fuel with a retrofitted continuous regenerating trap (CRT™). The testing for this project was done at Environmental Canada where detailed PAH analysis from filter samples was performed in parallel with real-time PAS measurement. This provided an opportunity to compare results for PM-bound PAHs measured by PAS with those obtained by chemical analysis. However, it should be pointed out that PAH chemical analysis obtained by Environmental Canada is the total PAH emission which includes gaseous and PM-bound PAHs. Therefore, we should expect higher chemical analysis PAH emission values compared to PAH emissions obtained with PAS for buses tested in the CRT project. The results from the two Detroit Diesel Series 50 buses and two 6V92 two-stroke engine buses tested with and without CRTs are summarized in Table 3.

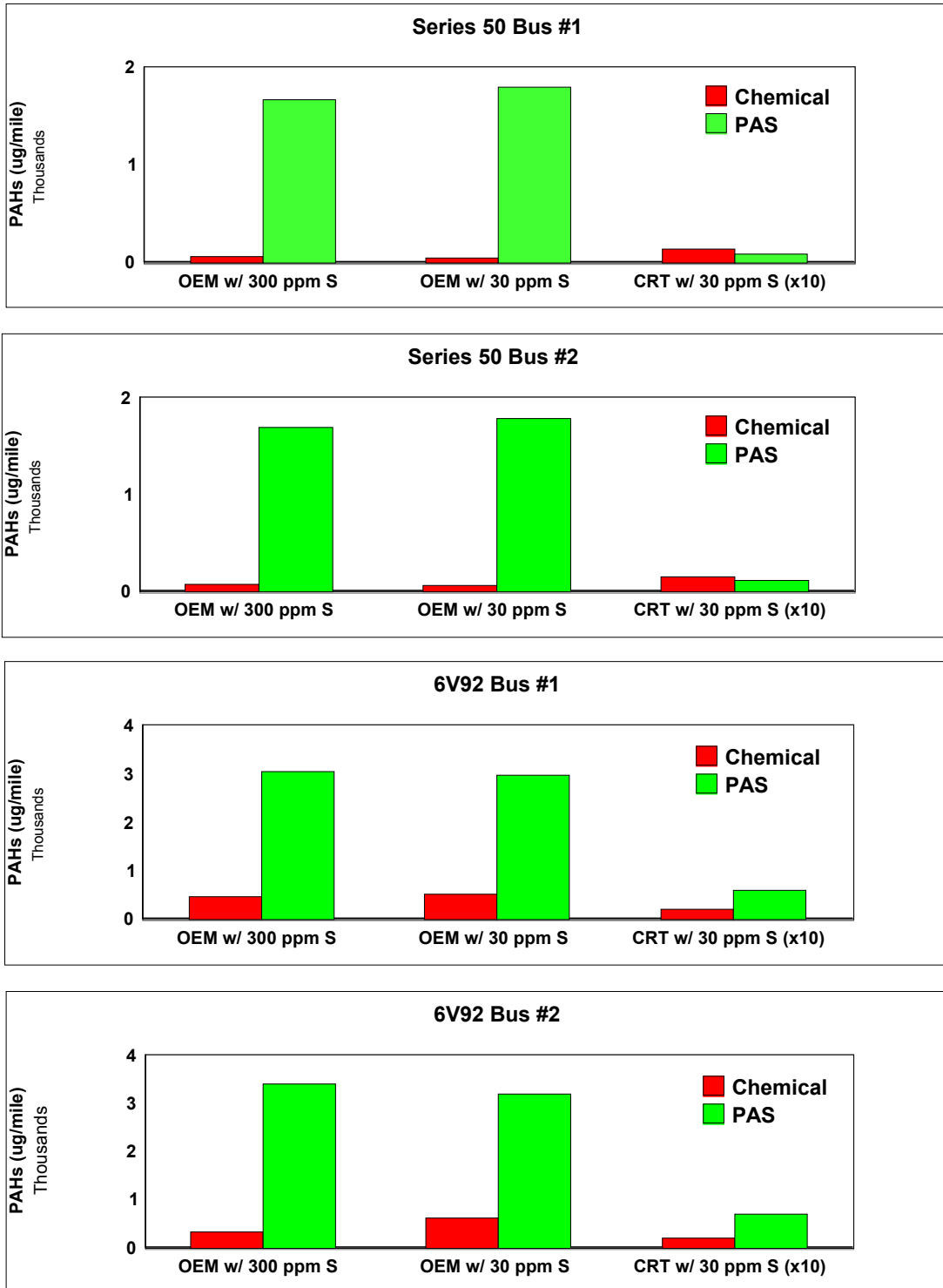
Table 3. Diesel Bus PM-bound PAH Emissions with and without CRT*

Bus Type	Series 50						6V92					
Bus ID	Bus #1			Bus #2			Bus #1			Bus #2		
PAHs (ug/mi)	Chem.	PAS	Ratio	Chem.	PAS	Ratio	Chem.	PAS	Ratio	Chem.	PAS	Ratio
OEM with 300 ppm S	62	1663	27	66	1695	26	463	3053	6.6	340	3399	10
OEM with 30 ppm S	49	1796	37	63	1780	28	521	2968	5.7	615	3190	5.2
CRT with 30 ppm S	14	8	0.6	15	11	0.7	20	60	3	21	70	3.3
% Reduction w/ CRT	71.4	99.6		76.2	99.4		96.2	98.0		96.6	97.8	

* Results are obtained with CBD driving cycles

Comparisons of PAH emissions from the CRT buses by PAS and chemical analysis are depicted in Figure 8. It is very clear and interesting to see from Figure 8 that PAHs emissions measured

Figure 8. Comparison of PAH measurement by PAS and chemical analysis



by PAS are systematically higher than those obtained with chemical analysis for buses with OEM mufflers (no CRT). Furthermore, Detroit Diesel Series 50 and 6V92 buses exhibit different ratios for the PAH measured by PAS over PAHs by chemical analysis. Although it is possible that some PAH species detected by PAS may not be identified and quantified by the chemical analysis because the chemical analysis identifies only 27 PAHs, it is more reasonable to believe that PAS has overestimated PAH emissions as discussed in the CMAQ PAH emission section earlier.

It is also interesting to notice that PM-bound PAH emissions measured by PAS and chemical analyses are more comparable for buses retrofitted with CRTs (Figure 8). In other words, PAS may have significantly overestimated PM-bound emissions when PAH emission is high without CRT. This is not in agreement with the relatively good correlation between PAS and chemical analysis previously reported.^{5,16,22} However, it should be pointed out that it may not be appropriate to compare PAHs measured by these two techniques. The PAS measures PAHs on PM dynamically in an aerosol stream while the chemical technique measures both gaseous and PM-bound PAHs collected on filter materials. Further, although a laboratory study¹² has found that the responses from various PAH species are additive, PAS can be best described as a semi-quantitative tool for PAH estimation because of its potential limitation regarding instrument calibrations; response variability vs. PAH composition; and a 1 micron PM size selection²³ — PAH on PM particles larger than 1 micron may not be measured although preliminary data suggest that more than 99% of diesel PM are < 1 micron¹⁸.

PAS calibration is difficult and uncertain because different PAH species exhibit somewhat different ionization potentials, and the PAH composition of the target PM may not be known. A source specific calibration — using matrix matched PM with known PAH mass adsorbed on the PM surface and PAH composition representative of the emission source — would seem desirable but not readily available practically. On the other hand, there are three potential problems inherent with PM filter samples in the chemical analysis technique: 1). PAH trapped on the filter may be volatilized by the continued passage of samples over the filter surface (“blow-off”); 2). Vapor phase PAH may adsorb onto particles already trapped on the filter; and 3). PAH trapped

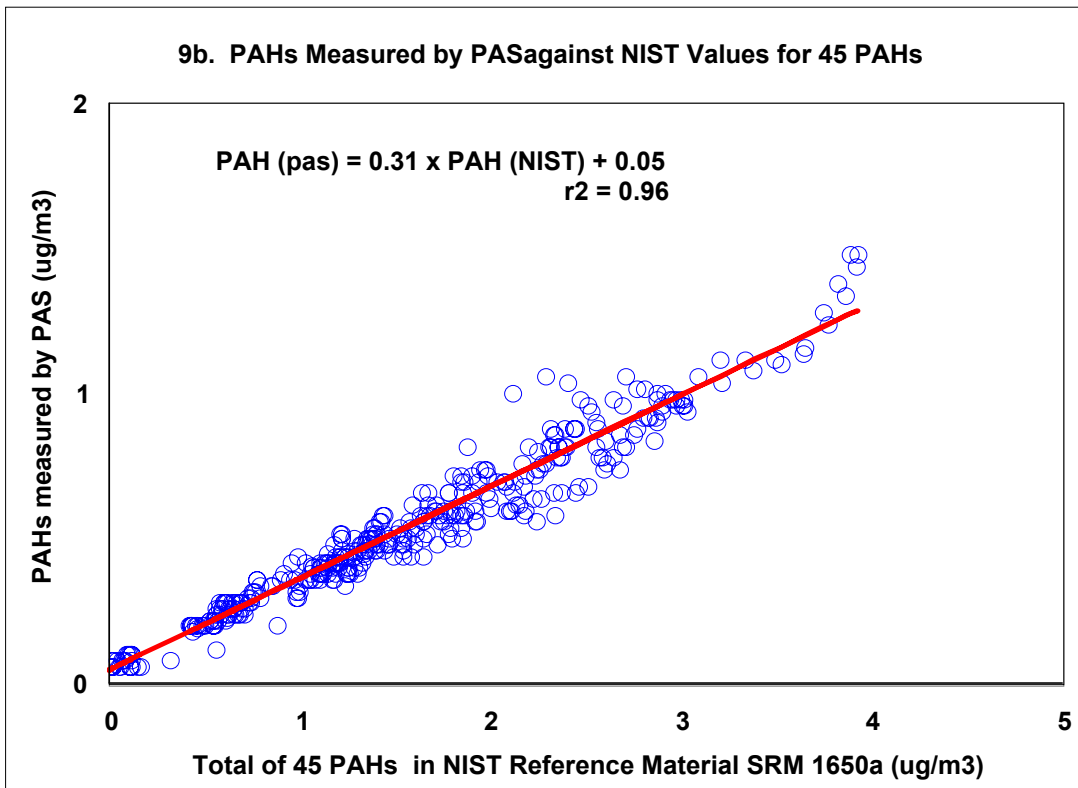
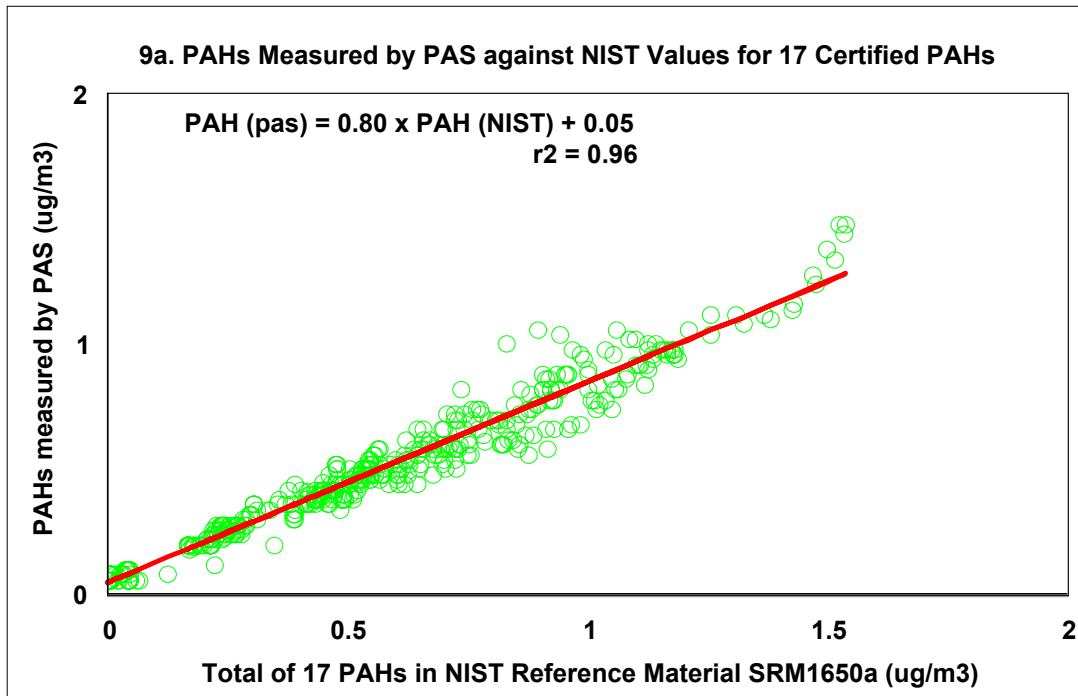
on the filter medium may undergo continuing chemical reactions on the filter surface (degradation/artefact formation).⁴ Therefore, the lack of specific correlation between PAS and filter analysis rests on both techniques to degrees which may not be able to be analyzed in the current study.

The reason for the more comparable PAH emission results between PAS and chemical analysis with CRT is not known. Preliminary data indicates significant difference in soluble organic fraction (SOF) for PM with and without CRT retrofitted. For buses without CRTs, SOF of 23% and 26% were observed with the two series 50 buses while 15% and 17% were obtained with the two 6v92 buses. Higher SOF percentages (> 40%) have been observed for buses retrofitted with CRTs but this may suffer substantial uncertainties due to the very small quantities of PM mass collected (more than 90% reduction of PM has been experienced with CRTs). Furthermore, scanning electron microscopy (SEM) analysis of PM collected on filter samples revealed significant physical difference between PM in the bus exhaust with and without CRT. PM with a CRT has been shown to be larger and more spherical relative to shapeless PM generated without CRT¹⁸. However, PM size distribution by electric low pressure impactor (ELPI) has not shown significant reduction of only ultra fine PM with CRTs but an overall reduction of PM across the PM diameter spectrum from 30 nm to 6 μm .¹⁸

Performance with National Institute of Standards & Technology (NIST) standard reference material (SRM) - Performance of PAS with NIST SRM diesel particulate 1650a was carried out using the experimental set-up shown in Fig. 4. Generally, an aerosol stream containing NIST SRM 1650a was generated with TSI's small-scale powder disperser. The aerosol stream was neutralized and then mixed well in a mixing chamber after the disperser. PM mass concentration in the aerosol stream was monitored by using TEOM. PAS was used to monitor the PM-bound PAH concentrations.

Correlations of PM-bound PAH concentration measured by PAS and the calculated PAH concentrations are shown in Figure 9a for the total of 17 certified PAHs and Figure 9b for the sum of 45 certified and uncertified PAHs. The calculated PAH concentrations in Figure 9 were

Figure 9. Performance of PAS on NIST SRM 1650a



obtained based on the PM mass concentrations measured by TEOM and the PAH concentration information provided by NIST in the certification. The results from Fig. 9 are very encouraging, showing that the universal calibration curve suggested by the manufacturer is actually a reasonable estimation.

Incomplete deagglomeration of NIST SRM PM which resulted in the existence of undetectable PAHs embedded inside the PM may attribute to the underestimation of PAS in this study.

However, matrix effect cannot be ignored either because the aerosol stream containing NIST SRM 1650a generated by the disperser in the laboratory is not the same as fresh diesel exhaust. Thus, development of matrix-matched calibration for PAS is still preferred for specific application(s).

CONCLUSION

The capability of PAS as a PM-bound PAH monitoring device for heavy duty diesel vehicles (trucks and buses) transit testing was evaluated with different driving cycles. Preliminary data have shown that high PAH emissions appear to be generally related to hard accelerations possibly due to incomplete combustion. Correlation between total PAHs measured by PAS and total PM mass is not strong reflecting the variation of PAH mass fractions between individual vehicles. Relatively better correlation between PAS and real-time PM mass emission has been observed, especially for vehicles with relatively high PAH mass fractions. Comparison study between PAS and conventional chemical analysis of PAHs generated different results on limited diesel buses tested. It seems that PAS grossly overestimated PAH emissions for buses with OEM mufflers when PAH emissions are relatively high. Considering the difficulties and uncertainties involved in the chemical analysis of PAHs, the agreement between the PAHs measured by chemical analysis and PAS for buses with CRTs is encouraging. Finally, the analysis of NIST standard reference material SRM 1650a by PAS has shown encouraging agreement with the total certified and non-certified PAHs using the universal calibration suggested by the manufacturer. In conclusion, PAS may be used as a rapid and economic tool for

near-real-time semi-quantitative estimation of automotive PAH emissions. This is a feature that couldn't be achieved by the conventional chemical analysis and may be very important for research and study on engine and after-treatment device development. Although preliminary results are encouraging, more research on PAS, especially PAS calibration is needed.

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