



Real-Time Measurement of Trace Air Toxic Vehicular Emissions by REMPI-TOFMS during Dynamometer Driving Cycles

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ABSTRACT

Real time measurements of air toxic emissions were made from vehicles undergoing transient cycles on a dynamometer. Resonance-enhanced multi-photon ionization (REMPI) with time of flight mass spectrometry (TOFMS) was used to characterize rapid responses in trace aromatic emissions, including mobile source air toxics, to changes in driving cycles. Concurrent sampling of PM, CO, and CO₂, with vehicle parameters of horsepower, velocity, and total particle density allowed the air toxic emissions to be related to operating performance. Two models of the U.S. Army High Mobility Multi-purpose Wheeled Vehicle (HMMWV), a diesel (M1097) and a turbocharged diesel version (M1114), were tested. Emissions were measured while running on a dynamometer-based roadway simulator under the West Virginia and EPA Federal Highway Economy Test cycles and under steady state, constant velocity conditions. Emission factors were determined for criteria pollutants such as CO and CO₂, as well as for aromatic air toxics including benzene, toluene, ethylbenzene, and xylenes, as well as small polycyclic aromatic hydrocarbons such as naphthalene and methylnaphthalene. The combined dynamometer cycle and REMPI-TOFMS system relative accuracy (triplicate) varied from 15% to 79% for benzene, 31% to 109% for naphthalene, and 47% to 214% for 2-methylnaphthalene. CO and CO₂ emissions were found to poorly correlate with benzene, naphthalene, and 2-methylnaphthalene. The fast time response of REMPI-TOFMS documented the compound-specific trace concentrations during cold startups of the M1097, showing benzene at ~230 ppb but then rapidly (within 60 s) tailing off to a steady state level around 50 ppb. This work highlights the ability of REMPI-TOFMS to measure trace air toxics in real time, following rapid changes in emissions during roadway cycles that cannot be identified using typical long term (minutes) integrated sampling methods.

Keywords: REMPI-TOFMS; Mobile source air toxics; Trace aromatics; Transients; Polycyclic aromatic hydrocarbons; Particulate matter; Diesel; Dynamometer.

INTRODUCTION

Time-resolved measurements of aromatic air toxics during transient vehicle cycles are limited due to the logistical difficulty of taking the measurements and limitations on the instrumentation detection and response time. These measurements are important to assess emission factors for these air toxics and to understand how vehicle operation and engine type contribute to mobile source air toxics.

Transient emissions have been addressed in ambient air, near-roadway studies (Hagler *et al.*, 2009) but these efforts cannot isolate trace emissions to specific vehicle operating conditions. Likewise, time-averaged measurements of some

aromatic air toxics have been undertaken in tunnel studies on a mixed vehicle type, urban fleet (for example, Kristensson *et al.*, 2004), showing the influence of vehicle speed on emissions. Size distributions of particulate polycyclic aromatic hydrocarbons (PAHs) were measured in the exhaust from four heavy-duty diesel vehicles (HDDVs) operated under idle, creep, transient, and two high speed driving modes (Riddle *et al.*, 2007), indicating that the PAH composition emitted was a function of driving cycle and vehicle technology. These studies indicate significant variation in emissions of aromatic air toxics during vehicle operational cycles. These data, however, are extremely limited because the sensitivity, selectivity, and time resolution of measurement instruments are difficult to obtain. Measurements of trace air toxics typically involve complex instruments that are larger and heavier than typical rack mounted equipment and require high power consumption which are not amenable to on-board monitor systems. Recently, a portable system has been developed to sample

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a large variety of emissions (Wang *et al.*, 2012), but measurements of aromatics are limited to continuous total volatile organic compounds (VOCs) or batch sample collection with subsequent laboratory analysis.

To demonstrate a method of determining aromatic air toxic emission data from vehicle transients, a comprehensive series of measurements were made on dynamometer-mounted Department of Defense (DoD) vehicles. A mobile, laser-based instrument, combining resonance-enhanced multiphoton ionization (REMPI) with time of flight mass spectrometry (TOFMS), was used to characterize the emission responses to several roadway profiles. Parallel measurements with continuous emission monitors (CEMs) measured CO and CO₂. Vehicles were run through multiple trials on three programmed highway simulation routes on the U.S. Army's Roadway Simulator, a multi-axle dynamometer.

In this study, REMPI-TOFMS uses tunable, pulsed, ultraviolet (UV) laser light to ionize target analytes using a resonant two-photon ionization method. Following this soft ionization to preserve the parent structure, the ions are extracted into a compact TOFMS for mass separation. In combination with a pulsed valve inlet system, the method provides sufficient separation in wavelength to establish unique wavelengths for optimal ionization with no interferences from other (aromatic) analytes. Other advantages of REMPI-TOFMS are its measurement frequency (10 s⁻¹) and sensitivity (~low ppb range).

Previous applications of REMPI-TOFMS technology to measure aromatic air toxics from vehicle exhaust (Boesl, 1997; Püffel *et al.*, 1998; Püffel and Boesl, 1999; Boesl, 2000; Zhang *et al.*, 2001; Misawa *et al.*, 2008) are limited to proof of concept demonstrations. These studies were conducted using stationary vehicles with observed changes in emissions only related to changes in idling speed. Only recently has a REMPI-TOFMS system been used for measurement of aromatic air toxics on dynamometer driven vehicle (Adam *et al.*, 2011). Their use of a fixed wavelength (266 nm) for ionization purposes prevents the detailed emission characterization of e.g., benzene, xylenes, ethylbenzene, and phenol. Also, the use of this non-resonant ionization step resulted in a high detection limit of 670 ppb for benzene which is above observed benzene concentration in vehicle exhausts. Measurement of (diesel) exhaust by REMPI-TOFMS should include benzene as it is a Group 1 carcinogen to humans (WHO, 1987). Benzene is readily detected (low ppb detection limit) when a resonant wavelength is selected through use of a tunable laser system.

Other techniques for real time vehicle exhaust measurements of trace organics include single-photon ionization ion trap mass spectrometry (Butcher, 2000), laser desorption/laser ionization time-of-flight mass spectrometry for fine particle analysis of polycyclic aromatic hydrocarbons (Hankin and John, 1999), and proton transfer reaction mass spectrometry (Rogers *et al.*, 2006). Both single photon ionization and proton transfer reaction techniques cannot separate between contributions from individual isomers or other analytes with equal mass since their separation of analytes is only by mass. REMPI-TOFMS uses a combination of mass and wavelength for isomer selective detection,

thereby eliminating overlap.

Past work with REMPI-TOFMS has proven it to be a powerful characterization technique for combustion emissions including, for example, benzene, toluene, ethylbenzene, and xylene (the "BTEX" compounds) and polycyclic aromatic hydrocarbons (PAHs). Measurements of these compounds were made from various sources, all operating with transient modes, including a diesel generator (Oudejans *et al.*, 2004); an aircraft-assist turbine engine compressor (Gullett *et al.*, 2008a); a waste incinerator (Gullett *et al.*, 2008b); and an ambient air, near-highway sampling project (Hagler *et al.*, 2009). This present paper combines use of a vehicle dynamometer and REMPI-TOFMS to demonstrate the ability to characterize real time trace aromatic emissions from operational vehicles. The speed and sensitivity of the REMPI instrument, coupled with other real time combustion pollutant measurements (e.g., CO and CO₂) and in combination with a dynamometer, allows transient and steady state characterization of vehicle performance and engine emissions.

EXPERIMENTAL

Vehicles Tested

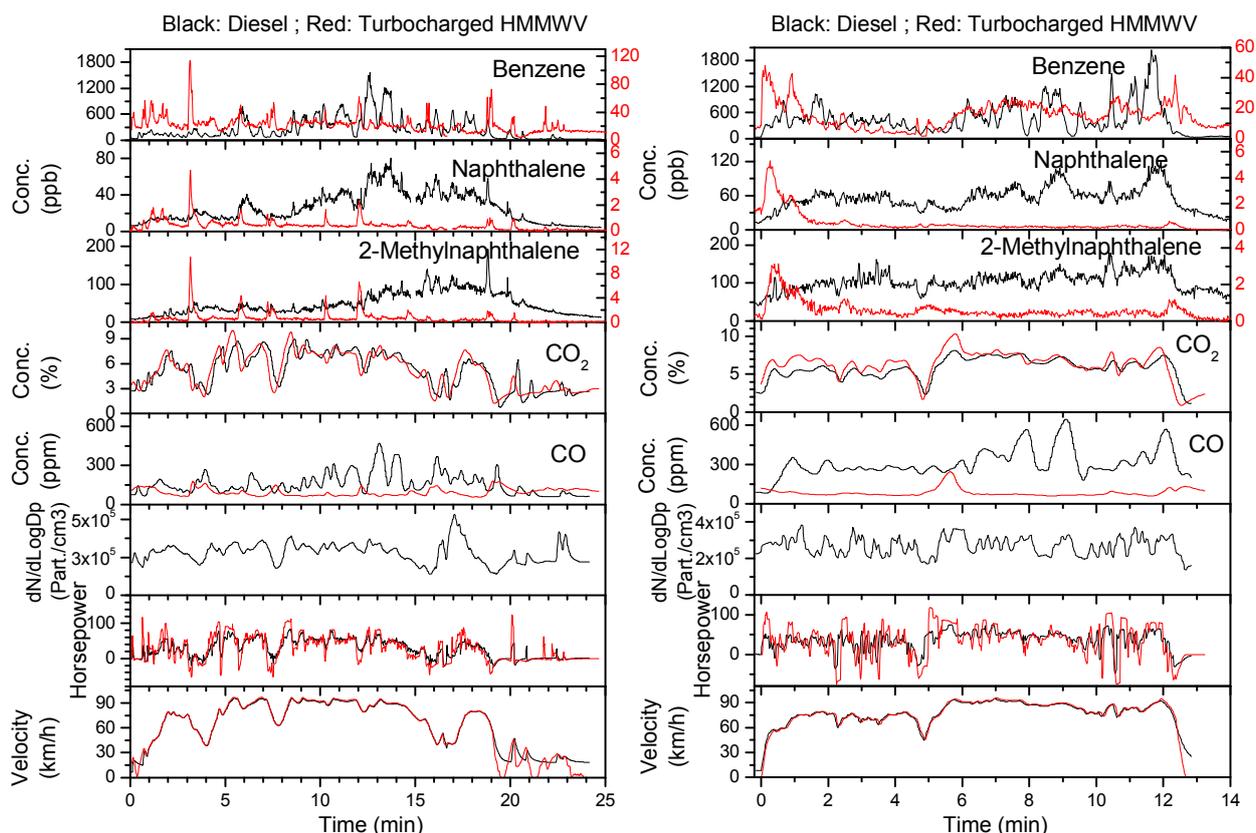
Criteria and organic pollutant emissions were characterized during transient operation of four U.S. Army weapon platforms (vehicles) at the U.S. Army Aberdeen Test Center, Roadway Simulator. The Roadway Simulator is the world's largest dynamometer, supporting vehicles ranging from 2,300 kg (5,000 lb), 2-axle light vehicles (up to 192 km/h or 120 mph) to 27,300 kg (60,000 lb), tandem-axle tractor trailers (Schultz *et al.*, 2005). Two versions of HMMWVs were tested for emissions on the Roadway Simulator. These included a heavy HMMWV (M1097 A1, hereafter referred to as "diesel") and a turbocharged diesel engine, up-armored HMMWV (M1114, hereafter referred to as "turbocharged") (see Table 1). The HMMWV is currently the main transport vehicle for the DoD. These 6.2 L, General Motors vehicles consume almost 15 million gallons of JP8 fuel each year, making it the top-consuming vehicle type (17%) in the DoD inventory (Kemme *et al.*, 2006). The 6.5 liter Turbo Diesel 142 kW (190 hp) up-armored M1114 version has a higher payload capacity and is equipped with a heavy armor protection package against improvised explosive devices (IEDs). Both of these vehicles were tested with two driving cycle protocols (described later) and stepped velocity/gradient cycles.

Test Protocols

Two standardized driving cycles and one velocity/gradient cycle were used to test both HMMWVs. The West Virginia highway driving cycle (WV) was developed originally from local delivery tractor-trailer activity logged by West Virginia University (Nine *et al.*, 2000) and described elsewhere (Clark *et al.*, 1999). The WV cycle represents the travel on four-lane highways of trucks to and from distribution depots located outside the city delivery areas (see bottom panel, Fig. 1, left panel). The EPA Highway Fuel Economy Test (HWFET) driving schedule (US

Table 1. HMMWV Vehicle Specifics.

| | HMMWV | |
|------------------------|-------------------------------|-------------------------------------|
| HMMWV classification | M1097 A1 | M1114 |
| Identification in text | diesel | turbocharged |
| Engine type | diesel engine, 6.2L | turbocharged diesel engine, 6.5L V8 |
| Manufacturer | General Motors | General Motors |
| Engine power | 112 kW (150 Hp) @ 3600 RPM | 142 kW (190 Hp) |
| Specifics | Heavy variant | Heavy armor |
| Torque | 340 Nm (250 ft/lb) @ 2000 RPM | 393 Nm (290 ft/lb) |
| Empty weight | 2,545 kg (5,600 lbs) | 4,450 kg (9,800 lbs) |
| Payload | 1,998 kg (4,400 lbs) | 1,045 kg (2,300 lbs) |

**Fig. 1.** Emission transients for the diesel and turbocharged HMMWVs. West Virginia cycle (left) and Highway HWFET cycle (right). Note second Y-axis on top three traces.

DOE/EPA, 2008) represents a mixture of rural and interstate highway driving with a warmed-up engine, typical of longer trips in free-flowing traffic (see bottom panel, Fig. 1, right panel). The M1097 HMMWV was run only once on both the WV and HWFET cycles (due to time constraints) while the M1114 had triplicate runs on both cycles. Both HMMWV types were run once on the stepped velocity and gradient cycle.

Sampling Approach

A 15.2 cm (6 in.) I.D. stainless steel sampling pipe was attached to the HMMWV tailpipes via a high temperature rubber adaptor to convey the emissions to the analyzers. The measured exhaust temperature was at or below about 273°C and the gas pipe was wrapped with heat trace to

maintain 200°C. No dilution air was added, and the flow rate was monitored with an annubar pitot tube. All gas samples were taken at a constant flow rate; isokineticity was not deemed necessary as the particles were assumed to be in the submicrometer size. Exhaust gases for the REMPI-TOFMS system, the particle measurement systems, and the continuous emissions monitors (CEMs) were pulled by individual sampling pumps through separate heated lines maintained at about 125–150°C.

The exhaust gas criteria pollutants were analyzed using a self-contained CEM bench that included two analyzers using EPA promulgated Method 10A (US EPA, 2000) for carbon monoxide [low CO: Rosemount NGA 2000, high CO: California Analytical Instrument and two analyzers using EPA Method 3A (US EPA, 2006), one for oxygen

(O₂: Rosemount NGA 2000) and one for carbon dioxide (CO₂: California Analytical Instrument)]. Each analyzer had a daily, 3-point calibration and a 3-point bias check before the start of the test, followed by a 3-point system calibration and bias check at the end of the test. Gas standards were introduced via the bias check port at the sample line inlets during pre-sampling CEM performance checks. The CEM is linked to a data acquisition system set for a sampling frequency of 10 s⁻¹.

Trace quantities of organic aromatic analytes were analyzed using REMPI-TOFMS which consists of the laser-induced photoionization of a target molecule using a two-step resonant process. A first ultraviolet (UV) wavelength photon is absorbed and the subsequent absorption of a second UV photon brings the internal energy of the molecule above its ionization energy to form a molecular ion. The UV wavelength dependence creates a spectral “fingerprint” of the target molecule. Ions are extracted into a TOFMS for mass discrimination. The combination of REMPI and TOFMS makes it possible to measure trace gas concentrations at high sensitivity, selectivity, and in real time. Additional details on REMPI/TOFMS principles are published in Oudejans *et al.* (2004) while other gas turbine engine emission results from this field-ready instrument can be found elsewhere (Gullett *et al.*, 2006, 2008a). The speed and sensitivity of the instrument allows emissions to be characterized as a function of operating conditions, such as startups, shutdowns, and load changes.

The REMPI-TOFMS instrument measured aromatic organic air pollutants in real-time, parallel to the standard CEMs. Benzene, toluene, ethylbenzene, xylenes, styrene, and gaseous PAHs, are among the non-exclusive list that were targeted for measurement. An approximately 1 L/min slipstream was pulled from the main sampling pipe through a 15 m long, 0.95 cm (3/8 in.) diameter Silico-Steel coated line at 150°C towards the REMPI-TOFMS inlet. A glass microfiber filter (Unique Heated Products, Inc.) mounted directly downstream from the main sampling pipe prevents particulate matter from contaminating the sampling line and REMPI-TOFMS valve. Two filter housings were operated in parallel in order to have the capability to replace a filter element on an hourly basis without interruption of the sampling flow. A modified pulsed inlet valve (General Valve Series 99) of the REMPI-TOFMS instrument pulls approximately 1 mL/min from the slipstream into the ionization chamber of the TOFMS.

The REMPI-TOFMS instrument was calibrated at the start and end of each test day using a TO-14 Aromatics Subset Mix (Supelco) calibration gas mixture which contains the BTEX target analytes at 100 ppb levels. The most favorable wavelength for unequivocal identification of each target analyte was determined prior to these tests. The laser wavelength can be readily switched across a wavelength sequence and a full sequence of 10 wavelengths takes about five minutes to complete with a 30 s sampling interval per analyte. Under transient conditions, with rapid and large concentration changes in the time span of seconds, this approach cannot be used. In such case, a fixed wavelength approach is used. Here, the most favorable

wavelength for benzene detection was chosen. At this specific wavelength (~259 nm), small PAHs such as naphthalene and methylnaphthalenes can also be detected in order to provide real time transient concentrations. In addition to the twice daily calibration with a TO-14 gas mixture, REMPI-TOFMS performance was monitored in real time with fully deuterated benzene (C₆D₆) added to the exhaust stream. C₆D₆ is readily detected by REMPI-TOFMS and is not an exhaust gas component. For small molecular mass aromatic compounds, a linear response has been established over several orders of magnitude of concentration (ppt to ppm range). REMPI-TOFMS performance has been verified against parallel, conventional EPA extractive sampling measurements. Good agreement has been observed between one-hour-averaged online REMPI-TOFMS results and standard methods for BTEX and PAHs in diesel engine pipe exhaust gas (Gullett *et al.*, 2006).

Real time particle size distributions were measured with a Dekati Ltd. electrical low pressure impactor (ELPI). The ELPI is a 12-stage impactor with a single pre-stage knockout, measuring particle size distributions ranging from 30 nm to 10 μm at a frequency of 1 Hz. The ELPI generates a particle size distribution by charging the particles based on geometrical diameter prior to them entering into a cascade impactor. The charged particles land on the impactor stages based upon their inertia and their charge is converted into a particle number and mass, given a known density. The sample was conveyed via a non-static, conductive tubing, diluted with two 10:1 Palas GmbH VKL venturi-based dilutors in series (for a 100:1 dilution), totaling 10 L/min at ambient temperature and pressure. Dilution ratios are verified by using measurements of pre- and post-diluted CO and CO₂. Daily QC checks on the ELPI are performed by zeroing the electrometer using a flush of HEPA purified air and by monitoring the current profiles of the ELPI while it samples room air and HEPA purified room air. Longitudinal and lateral vehicle velocities and forces as well as engine rotation and vehicle speed data were provided by the Roadway Simulator control system.

Cold start emissions were evaluated in this study using a regression model (Heeb *et al.*, 2001) which consists of a linear extrapolation to the ordinate of the idle state portion of the cumulative target compound (CO, CO₂, benzene, naphthalene, methylnaphthalenes, and others) evolution. The ordinate value is the target compound mass amount emitted from a single cold start event.

The repeatability of the Roadway Simulator facility operations and pollutant measurements was evaluated using the t-test statistical approach. Relative accuracy is used to compare differences in the means of the target measurements between two cycles. All cycles within one type of driving profile (HWFET or WV) are compared with respect to the first cycle. The relative accuracy (RA, %) is defined as follows:

$$RA = \frac{\left(\left| \bar{d} \right| + t_{0.975} \frac{S_d}{\sqrt{n}} \right)}{RM} \times 100 \quad (1)$$

where:

$|\bar{d}|$ = the mean of the absolute values of the differences between measurements taken at the same time during a complete cycle

$t_{0.975}$ = the t -value for the 95% confidence interval,

S_d = the standard deviation of the differences between measurements taken at the same time during a complete cycle

\overline{RM} = the mean of the reference cycle.

n = number of measurements taken with a rolling average of 10 s during a complete cycle

RESULTS AND DISCUSSION

REMPI-TOFMS and conventional CEMs were used to compare emissions from the diesel HMMWV with the turbocharged HMMWV. Concentration values of benzene, naphthalene, 2-methylnaphthalene, CO₂, and CO as well as the total particle density (N), applied power (HP) and velocity (v) are shown for both vehicles on the WV and HWFET protocols in Fig. 1.

The Roadway Simulator facility operations had excellent velocity repeatability between cycles for each driving cycle tested. The relative velocity accuracies for the HMMWV M1114 vehicle on the HWFET cycle was 0.04% and 0.44%, and 0.2% and 0.5% for the WV cycles. The relative accuracy for the criteria compounds measured using conventional CEMs varied from 2.4% to 8.1% for CO₂, and 7.4% to 31% for CO for both HWFET and WV triplicate cycles. The relative accuracy for the trace compound concentrations measured by the REMPI-TOFMS system varied from 15% to 79% for benzene, 31% to 109% for naphthalene, and 47 to 214% for 2-methylnaphthalene. The lower reproducibility of the emissions for naphthalene and 2-methylnaphthalene are due to the compounding effect of their relatively low concentration (sometimes just above the detection limit of the REMPI-TOFMS system) and the variance in the engine performance. It should be noted that the first two of the triplicate tests were run successively while the third test was performed later (4–5 h) on the same day with the lower reproducibility always between the non-successive runs.

WV Cycle

REMPI PAH measurements for the turbocharged HMMWV (red traces) on the WV cycle showed benzene peaks of about 120 ppb with a median value of 20 ppb (Fig. 1). Naphthalene and 2-methylnaphthalene peaks of 6 ppb and 12 ppb, respectively, were accompanied by median values of < 1 ppb. The average emission factors for benzene, naphthalene, and 2-methylnaphthalene for the WV cycle were 324.5 µg/km, 13.6 µg/km, and 28.8 µg/km, respectively (see Table 2). The presence of naphthalene is expected; its presence in diesel fuel emissions is due to both incomplete fuel combustion (24%) as well as pyrosynthetic processes (76%) from compounds such as methylnaphthalene or small unsaturated hydrocarbons (Rhead and Pemberton, 1996). Approximately 0.5% of the naphthalene in diesel fuel has been observed to have survived combustion (Badger and Novotny, 1963). Clearly, the emission factors for most of

the BTEX compounds and PAHs found in the exhaust system are dependent on multiple factors such as their initial concentration in the parent fuel, their survivability in the combustion chamber, combustion efficiency of the engine, potential reformation in the cooling zones, and load. CO and CO₂ were found to correlate poorly with benzene, naphthalene, and 2-methylnaphthalene emissions for the turbocharged engine (R^2 always less than 0.30), eliminating their use as a correlative indicator of air toxics levels.

The diesel engine had much higher emissions than the turbocharged engine, reflecting the adoption of a turbocharger in the latter (see Table 2). For example, the benzene peak value for the diesel engine was about 1600 ppb versus about 120 ppb for the turbo. CO emissions similarly were higher with the diesel. The two vehicles also had distinct, pollutant-specific responses to the WV cycle. For example, the 15–25 min trace of the diesel showed relatively high, sustained naphthalene and 2-methylnaphthalene emissions that were not evident during the same period with the turbo. The average emission factors for benzene, naphthalene, and 2-methylnaphthalene for the WV cycle reflect a 1–2 orders of magnitude higher emissions than the emissions from the turbo engine. Correlations between REMPI-TOFMS detected analytes and CO, CO₂ were found to be only marginally better for the diesel (R^2 up to 0.59) than the M1114.

HWFET Cycle

As with the WV cycle, tests of the diesel and turbo on the HWFET cycle showed the diesel to have significantly higher overall air toxic emissions. The emission factors, presented in Table 2, for both vehicles show a dependence with the driving cycle; however, the results are within the accuracy of the cycle reproducibility. Again, CO and CO₂ were found to correlate poorly with benzene, naphthalene, and 2-methylnaphthalene emissions for the turbo (R^2 always less than 0.34). Correlations were slightly better for the diesel (R^2 up to 0.48).

The first 1 min of the HWFET cycle startup with the turbocharged HMMWV from Fig. 1 is shown in Fig. 2. This illustrates the REMPI responsiveness as well as the relationship between aromatic emissions.

Velocity/Gradient Cycle

Steady state emissions from a prescribed protocol of velocity and gradient changes show distinctive trace emissions from the M1114 and M1097 (Fig. 3). With higher velocity, the M1097 produces higher CO and trace emissions, while gradient increases (at 80 km/h) appear to have no effect. The M1114 shows minimal effect of velocity and gradient increases. Trace organic emissions and CO tend to decrease with increased velocity but this is believed to be due to increased load and engine warm up. As already observed during the WV and HWFET cycles, observed concentrations with REMPI-TOFMS for trace analytes were found to be much lower in the M1114 exhaust when compared to the M1097 results. In fact, the highest emissions for the M1114 were temporary peaks after speed changes, especially from idle to 32 km/h.

Table 2. Summary of Emission Factors for the HMMWV M1097 and M1114.

| M1097 HMMWV. CO, CO₂ (g/km), Others (µg/km) | | | | | | | | | |
|---------------------------------------------------------------|---------|---------|---------|---------|------------|------------|------------|-------|-------|
| | 32 km/h | 48 km/h | 64 km/h | 80 km/h | 80 km/h | | | HWFET | WV |
| | | | | | 1.0% grade | 1.5% grade | 2.5% grade | | |
| CO ₂ | 231 | 206 | 268 | 356 | 398 | 418 | 419 | 361 | 380 |
| CO | 0.38 | 0.75 | 1.07 | 0.84 | 1.64 | 1.74 | 1.73 | 1.23 | 0.74 |
| Benzene | 246 | 1163 | 3228 | 3248 | 5271 | 7732 | | 5096 | 3482 |
| Naphthalene | 64 | 244 | 673 | 727 | 1133 | 1197 | NA* | 1001 | 564 |
| 2-Methylnaphthalene** | 128 | 386 | 1573 | 1658 | 1726 | 1463 | | 2072 | 1184 |
| Styrene | 54 | 160 | 785 | 718 | 2165 | 1055 | 592 | | |
| Phenol | 60 | 116 | 421 | 428 | 1536 | 978 | 577 | | |
| 1,2,4-Trimethylbenzene | 64 | 145 | 627 | 526 | 587 | 400 | 231 | | |
| p-Xylene | 27 | 66 | 196 | 218 | 412 | 289 | 158 | | NA* |
| m-Xylene | 71 | 195 | 791 | 265 | 739 | 466 | 482 | | |
| 1,3,5-Trimethylbenzene | 61 | 145 | 540 | 641 | 749 | 428 | 367 | | |
| o-Xylene | 38 | 127 | 501 | 476 | 354 | 337 | | | |
| Toluene | 97 | 302 | 1132 | 1641 | 1376 | 1735 | | NA* | |
| Ethylbenzene | 24 | 70 | 329 | 526 | 70 | 221 | | | |
| M1114 HMMWV. CO, CO₂ (g/km), Others (µg/km) | | | | | | | | | |
| | 32 km/h | 48 km/h | 64 km/h | 80 km/h | 80 km/h | | | HWFET | WV |
| | | | | | 1.0% grade | 1.5% grade | 2.5% grade | | |
| CO ₂ | 383 | 354 | 350 | 421 | 522 | 581 | 647 | 493 | 435 |
| CO | 0.61 | 0.37 | 0.28 | 0.21 | 0.20 | 0.19 | 0.18 | 0.42 | 0.55 |
| Benzene | 177.3 | 110.5 | 116.1 | 28.8 | 129.1 | 161.3 | 225.5 | 275.1 | 324.5 |
| Naphthalene | 23.2 | 9.1 | 5.4 | 3.0 | 2.0 | 2.0 | 2.0 | 12.7 | 13.6 |
| 2-Methylnaphthalene** | 21.8 | 4.2 | 6.8 | 6.5 | 3.7 | 2.7 | 2.3 | 19.8 | 28.8 |
| Styrene | 3.5 | 2.6 | 0.9 | 1.4 | | | | | |
| Phenol | 7.7 | 6.4 | 6.8 | 9.8 | | | | | |
| 1,2,4-Trimethylbenzene | 3.9 | 2.6 | 1.8 | 2.7 | | | | | |
| p-Xylene | 5.4 | 3.3 | 1.7 | 1.1 | | | | | |
| m-Xylene | 19.4 | 15.7 | 6.3 | 2.6 | | | NA* | | |
| 1,3,5-Trimethylbenzene | 8.8 | 5.2 | 4.0 | 2.8 | | | | | |
| o-Xylene | 10.6 | 7.2 | 5.7 | 1.6 | | | | | |
| Toluene | 37.8 | 30.3 | 20.9 | 3.2 | | | | | |
| Ethylbenzene | 15.5 | 2.9 | 0.6 | 0.6 | | | | | |

*NA emission factors not available

** Emission factor for 2-methylnaphthalene may include up to 25% 1-methylnaphthalene

Startups

The fast time response of REMPI-TOFMS allows for documentation of trace emissions during startups. Fig. 4 shows pollutant-specific responses for the M1097 and M1114. The M1097 cold startup shows benzene at ~230 ppb which rapidly (within 60 s) tails off to a steady state level around 50 ppb. This highlights the responsiveness of the REMPI system as well as the characteristics of the cold start emissions. The other trace pollutants, naphthalene and 2-methylnaphthalene, show distinctive traces from that of the benzene, increasing over 60 to 120 s only to decline slightly to a steady state value. This distinctive behavior is not observed while following transients in the WV and HWFET profiles thereby excluding the possibility that the delays observed in the cold start traces are due to different elution times of the targeted pollutants through the sampling lines. A similar benzene spike is observed for the M1114, although its period is less than 15 s, suggesting that benzene peaks are indicative of fuel benzene vaporization during cold engine fuel starts. Calculation of the cold start

benzene emissions for the M1097 and M1114 HMMWVs indicate, respectively, that a 2.5 min and 5.5 min period of steady state emissions are equivalent to those of a single cold start. Similar time equivalents were found for naphthalene to be 0.9 min and 7.5 min for the M1097 and M1114 HMMWVs, respectively.

Number Size Distributions

Fig. 5 reports steady state number size distributions (NSDs) for the M1097 and M1114 HMMWVs through the stepped velocity and gradient cycles shown in the bottom panels of Fig. 3. The cold start and the lower velocities on the M1097 tended to result in high particle numbers for all six median particle diameters between 39 and 484 nm as compared to the higher velocities. The NSDs showed little shift in particle diameter for all velocities, with number maxima at a particle diameter around 100 nm, consistent with mass fractions from Chien *et al.* (2009) but distinct from others (Srivastava *et al.*, 2011) who showed maximum particle counts at diameters less than 70 nm over three diesel loads.

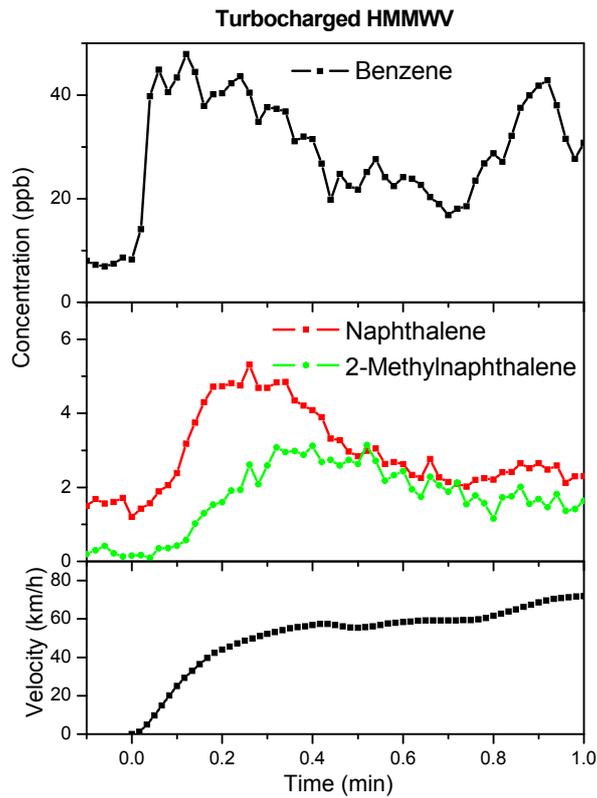


Fig. 2. Response of REMPI for benzene, naphthalene, and 2-methylnaphthalene concentrations during a 1-min velocity increase (turbocharged HMMWV), HWFET cycle.

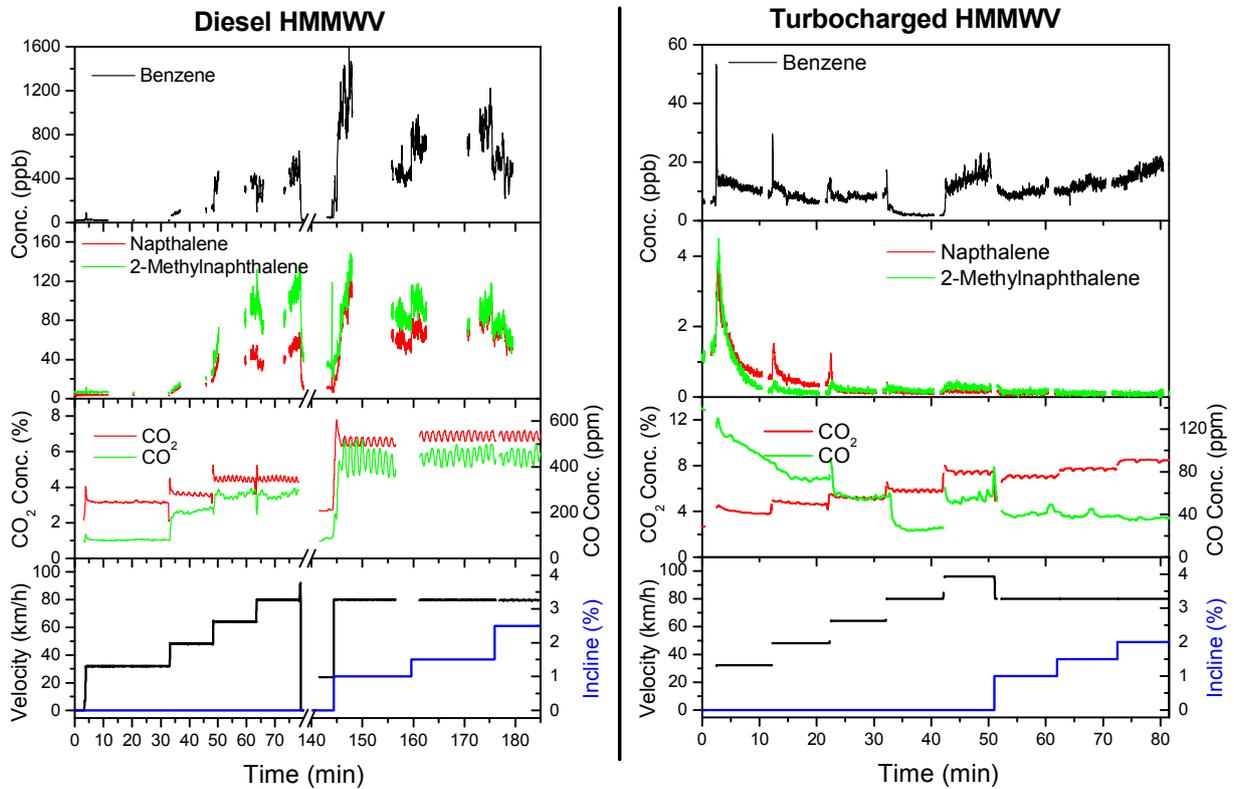


Fig. 3. Steady state benzene, naphthalene, 2-methylnaphthalene, CO, and CO₂ emissions from the diesel and turbocharged HMMWVs during a velocity and gradient stepped cycle. Breaks in the REMPI trace are due to periods where data was recorded for other aromatic pollutants thereby excluding measurement of benzene concentrations.

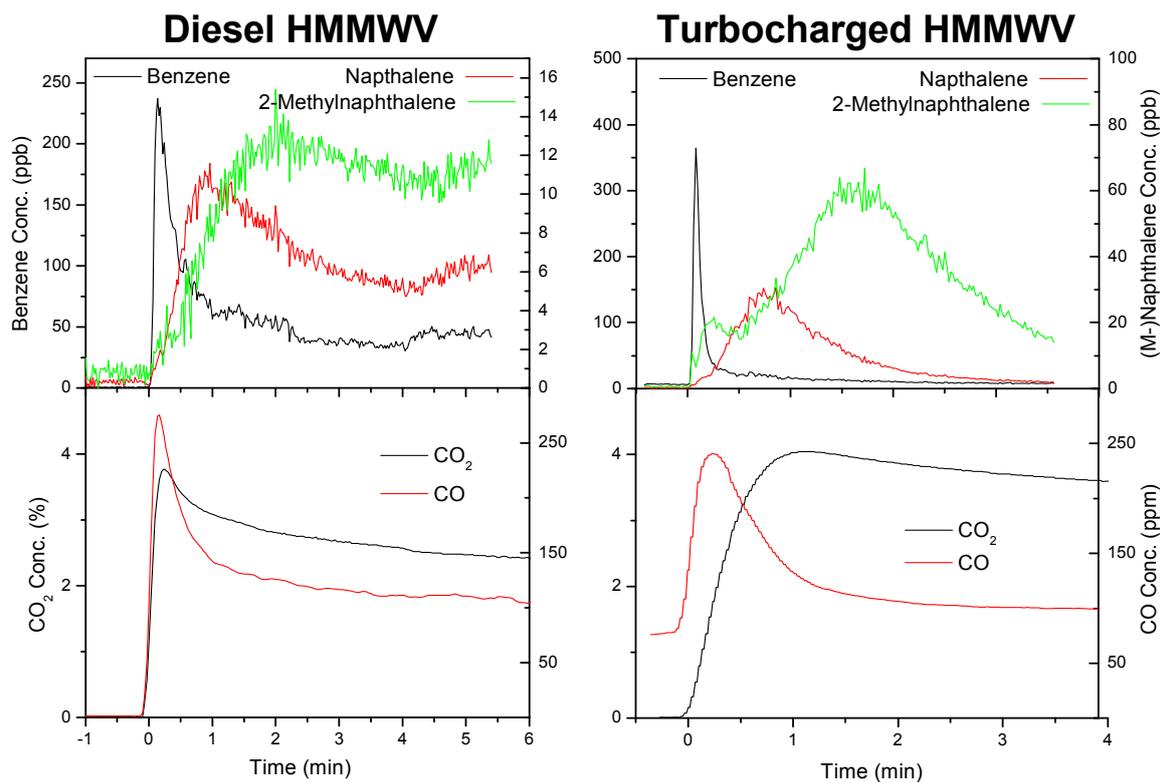


Fig. 4. Cold start emissions of benzene, naphthalene, 2-methylnaphthalene, CO, and CO₂ and PM size distribution for the diesel (left) and turbocharged (right) HMMWVs.

Time-resolved (calculated every 15 s) NSDs for the M1097 showed no size shifts from 0 to 90 s, although the maximum particle diameter decreased 50% (not shown). The M1114 showed somewhat lower particle counts than the M1097 but had about the same maximum particle diameter. Its response to velocity and gradient changes were quite different than the M1097, with higher particle emissions with velocity increases and a distribution shift to higher particle diameters at higher roadway gradients. This is seen more easily in Fig. 6 which shows number concentrations versus speed and gradient changes, as well as CO, CO₂, and organics.

Both vehicles' PM size distributions are in the range of ultra-fine inhalable particles peaking at around 100 nm diameter typical of diesel emissions found in other studies. Although particle number density is not regulated in the U.S. and is proposed in Europe, its significance is very important because of the pulmonary response to respiratory infections as well as adverse cardiovascular events (Helfenstein *et al.*, 2008). The particle number densities per km found in both vehicles are in the order of 10^{14} . These are 100–1000 times higher than the proposed European particle number emission standard for diesels of 5×10^{11} per km (Good, 2009).

Emission Correlations

Correlations between organic compounds, vehicle parameters [engine revolutions per minute (RPM), power (hp)], criteria pollutants (CO, CO₂), O₂, and NSDs by stage were analyzed across the various operating cycles to provide insights into pollutant mechanisms, surrogates for emission

predictions, and operational modes to minimize pollutant generation. This method was used (Schultz *et al.*, 1999) to gain insights into combustion mechanisms of pollutant formation. Highlights of these correlations are discussed below.

The M1097's concentrations of toluene, benzene, naphthalene, and 2-methylnaphthalene were the most closely correlated of the 12 organics with RPM, hp, CO, CO₂, and O₂. Across the range of steady state test conditions, these four compounds had an average R² of 0.82. The M1114, however, was poorly correlated for these four compounds with R² = 0.40. The o-, m-, p-xylenes for the M1114, however, had an average correlation of R² = 0.82. Benzene provides an illustrative example: the average correlation for benzene with vehicle parameters and criteria pollutants for the M1097 is 0.82. For the M1114, these R² values are 0.04 and 0.23 for two days of testing.

For the M1097, the 12 organics had an average intracorrelation of R² = 0.60. This was highest for naphthalene at R² = 0.89 and lowest for ethylbenzene, with R² = 0.22. The M1114's organic intracorrelation was lower than the M1097's at R² = 0.57; the lowest was for benzene at R² = 0.04 (ethylbenzene was 0.58) and the highest at R² = 0.85 for o- and m-xylene.

For the M1097 and M1114, the NSDs by stage had an average intracorrelation R² of 0.84 and 0.88, respectively, for stages 3 (0.1193 μm) and larger. This suggests that particle NSDs were similarly altered (if at all) by changes in velocity, cycle type, and incline gradient. The fine particle stages on the M1097, but not on the M1114, were highly

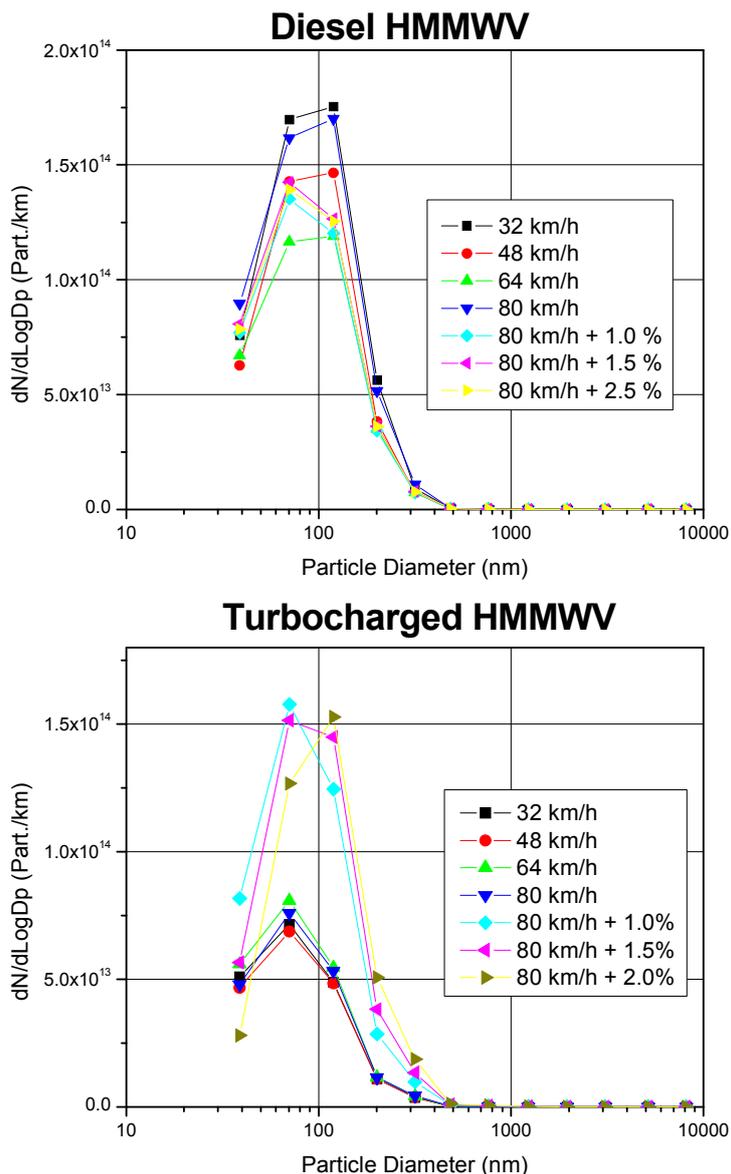


Fig. 5. Steady state PM size distribution for the diesel HMMWV (top) and turbocharged diesel HMMWV (bottom) during a stepped velocity and gradient cycle.

correlated with the other stages.

From this limited dataset, it appears that good correlations between pollutants and operating conditions do not always exist. If they did, correlations would significantly aid vehicle emission characterizations by allowing one to predict levels of unmeasured pollutants from more easily measured pollutants. However, these correlations must be established beforehand on a source- and pollutant-specific basis.

CONCLUSIONS

The utility and precision of the REMPI-TOFMS method was demonstrated for determination of real-time, mobile source air toxics from a diesel and turbocharged diesel vehicle running on varied highway cycles. Significant differences in air toxic emissions between the vehicles were easily distinguished using REMPI-TOFMS. Cold-start

emissions of air toxics show vehicle- and pollutant-specific temporal values with, for example, prompt (< 10 s) spikes in benzene and lagging (> 90 s) peaks in 2-methylnaphthalene. Particle NSDs showed a maximum particle diameter at around 100 nm, a diameter within the inhalable range. Correlations between criteria pollutants, vehicle performance measures, and air toxic emissions were vehicle- and pollutant-specific.

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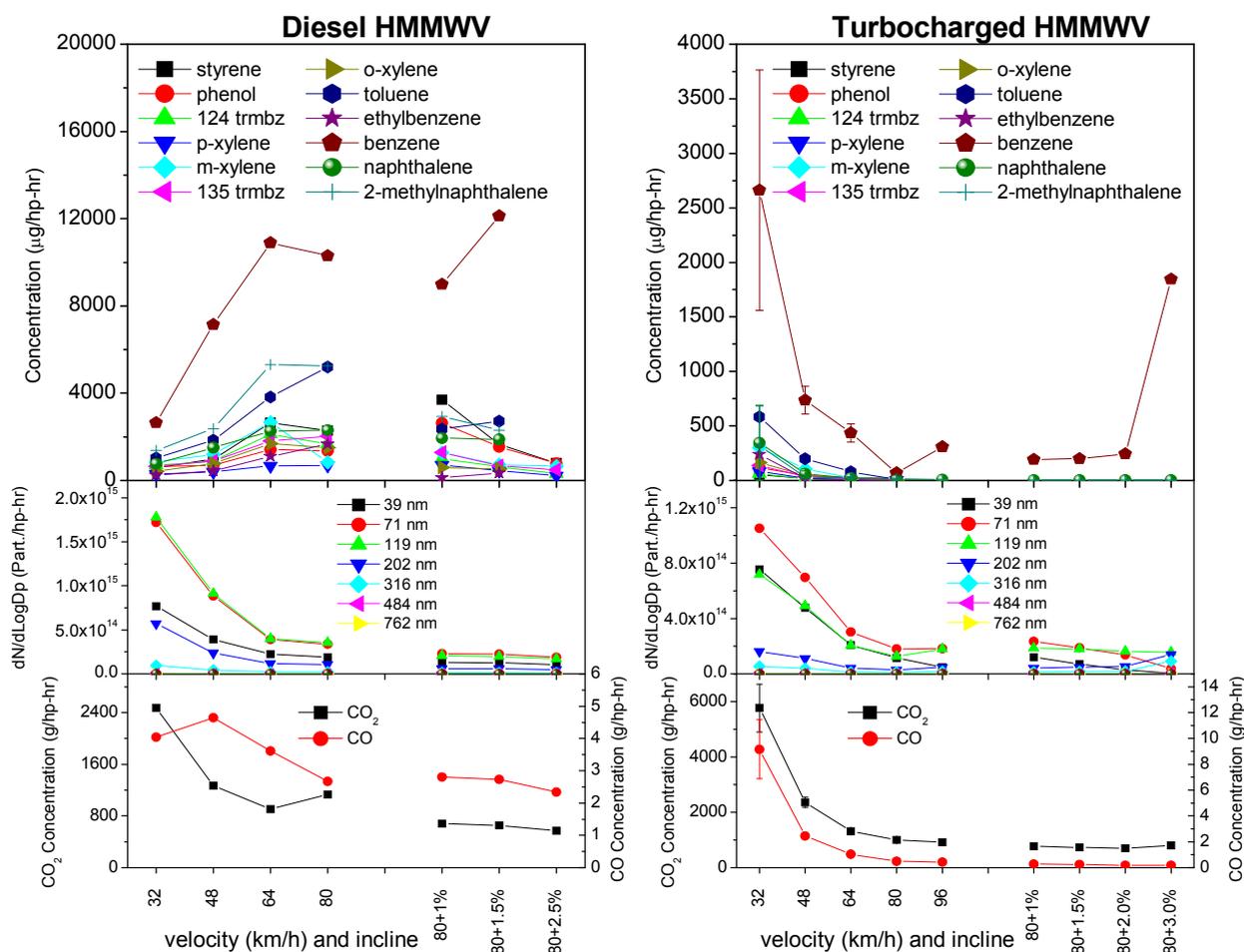


Fig. 6. Steady state REMPI concentrations (top), ELPI particle number distributions (middle), and CEM CO and CO₂ (bottom) data for the diesel HMMWV (left) and turbocharged diesel HMMWV (right).

APPENDICES

Information on measurement of trace organic emissions from DoD HMMWVs, a Bradley Infantry Fighting Vehicle, and an Abrams M1 battle tank during startups, shutdowns, and idling is reported.

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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