Appendix: Supplementary Information

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

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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.

Identification of Department of Defense (DoD) sources which potentially contribute to ambient air toxic levels, mobile sources in particular, will permit DoD to devise strategies to control and minimize emissions of air toxic pollutants from its facilities and from its on-road and non-road sources. Accurate data on these emissions are also necessary for state base air permits. Vehicular emissions, including diesels, are addressed in the Clean Air Act's Final Mobile Source "Air Toxics" rule (amendment 202(l)) in which 21 compounds are identified as mobile source air toxics (MSATs) based on their potential health hazard (U.S. EPA, 2001).

Currently, the major DoD air emission database for toxic air compounds is the Air Program Information Management System (Baghoomian, 2003). The APIMS database is limited in scope since measurement methods for many of the MSATs have not been developed, especially for DoD vehicles that operate in transient modes. Modal emission measurements are needed to assess the impact of MSATs, if any, on ambient air toxic levels, and to determine what operational modes contribute significantly to these emissions.

The U.S. Army and Marines currently have over 100,000 tactical High Mobility Multi-purpose Wheeled Vehicles (HMMWVs) (GlobalSecurity, 2012a) as well as tracked vehicles including over 8,000 M1 Abrams tanks (GlobalSecurity, 2012b) and over 6,000 Bradley Infantry Fighting Vehicles (IFVs) (GlobalSecurity, 2012c) that account for approximately half of the DoD vehicle fleet. Some emissions data are available for the HMMWVs but none are known for the tracked vehicles. In particular, time-resolved aromatic concentrations from transient operating mode emission information for these vehicle types are not apparent in the available literature. These data are important to determining emission factors from fuel and vehicle types, characterizing operational modes that can reduce emissions, and minimizing soldier exposure.

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Various efforts have reported on emissions testing from HMMWVs. These have included projects with biofuel-powered HMMWVs for CO, total hydrocarbons (THC), NO_x, and PM (Holden *et al.*, 2006; Durbin *et al.*, 2007) and measurement of cumulative THC emissions on a General Motors 6.2L HMMWV running on the hot start transient portion of the heavy duty diesel engine Federal Test Protocol driving cycle (Yost *et al.*, 1996). These projects were typically limited to the more traditional criteria pollutants and did not measure gaseous air toxics nor did they provide transient emission responses to operating changes. Transient measurements of CO, CO_2, NO_x, and PM and filter-catch polycyclic aromatic hydrocarbons (PAHs) were measured from a 6.5 L indirect injection diesel HMMWV engine (Frame and Blanks, 2004). Their filter extraction method may not have accounted for those air toxics in the gas-phase that pass through the filter. Also, the study did not provide time-resolved data to follow transient responses.

Other larger tactical vehicles, such as the M1 Abrams and Bradley IFV, have no emissions data available; their emissions may be of more interest for the minimization of infrared signatures and acute exposure of soldiers than air quality issues. Two additional weapons platforms, an M1 Abrams tank and a Bradley IFV, were tested at the facility but not on the Roadway Simulator due to weight and track restrictions. The 62 metric ton M1 Abrams main battle tank is manufactured by General Dynamics Land Systems and powered by a Honeywell AGT 1118 kW (1500 hp) gas turbine. The Bradley is powered by a 447 kW (600 hp) Cummins VTA-903T water-cooled 4 cycle diesel engine. Both vehicles were fueled with JP-8, a standard military fuel.

Transient emissions of the M1 Abrams and the Bradley IFV were sampled during startup, stationary idle, increased idle, and shutdown without actual movement of the vehicles. The Bradley and Abrams' idle, cold start, and warm start emissions were sampled at a rate of 1 L/min by means of a 0.6 cm (¼-inch) diameter stainless probe inserted inside their exhaust line. In all studies, a slip stream of the sample exhaust was sampled through the pulsed valve of the REMPI-TOFMS system at a rate of 1 mL/min. Figure S1 shows the 30 s average, steady state idle emissions from the Abrams and Bradley, respectively, of twelve organic compounds analyzed by REMPI. REMPI was sequentially set to each compound's specific ionization wavelength throughout a 15 min period. Two types of idle measurements are reported for the Abrams (low and high idle) as well as the Bradley ("idle 0" and "idle 2" settings). The Bradley's concentrations are about 100-1000-fold higher than those of the Abrams. The Bradley's emissions are most abundant for the substituted naphthalenes and benzenes while the Abrams shows its highest concentrations in the lighter phenol, toluene, and benzene compounds. This may be due to a higher percentage of unburnt fuel in the Bradley exhaust versus the Abrams exhaust. The strong oscillations in exhaust concentrations of the Bradley under Idle 2 (but not under Idle 0) as shown in the inset of Figure S1 may be due to a non-optimized fuel injection.

The Bradley and Abrams cold starts had quite dissimilar peak benzene concentrations at 600 and 35 ppb, respectively (Figure S2). These peaks did not persist more than about 30 s and, like the M1097 and M1114, are derived from the unburnt fuel. The naphthalene and methylnaphthalene traces don't exhibit as sharp startup peaks, perhaps reflecting an origin from combustion byproducts rather than as unburnt fuel. The Bradley's methylnaphthalene concentrations were high, at almost 500 ppb even 6 min past the cold start. The naphthalene and methylnaphthalene emissions on the Abrams were very low, less than 2 ppb. The warm start on the Bradley showed similar pollutant-specific trends to its respective cold start. The Abrams appeared to have higher methylnaphthalene emissions on the warm start than during the cold start. This observation is biased since the response was observed in addition to residual methylnaphthalene (at much higher concentration) in the sampling line after the shutdown preceding the warm start.

The Abrams tank exhibits an interesting and repeatable emission profile during shutdowns. Figure S3 show that the Abrams undergoes a 3 min process to shut down in which the concentration of benzene undergoes a double peak followed in time by methylnaphthalene and, to a lesser extent, naphthalene.

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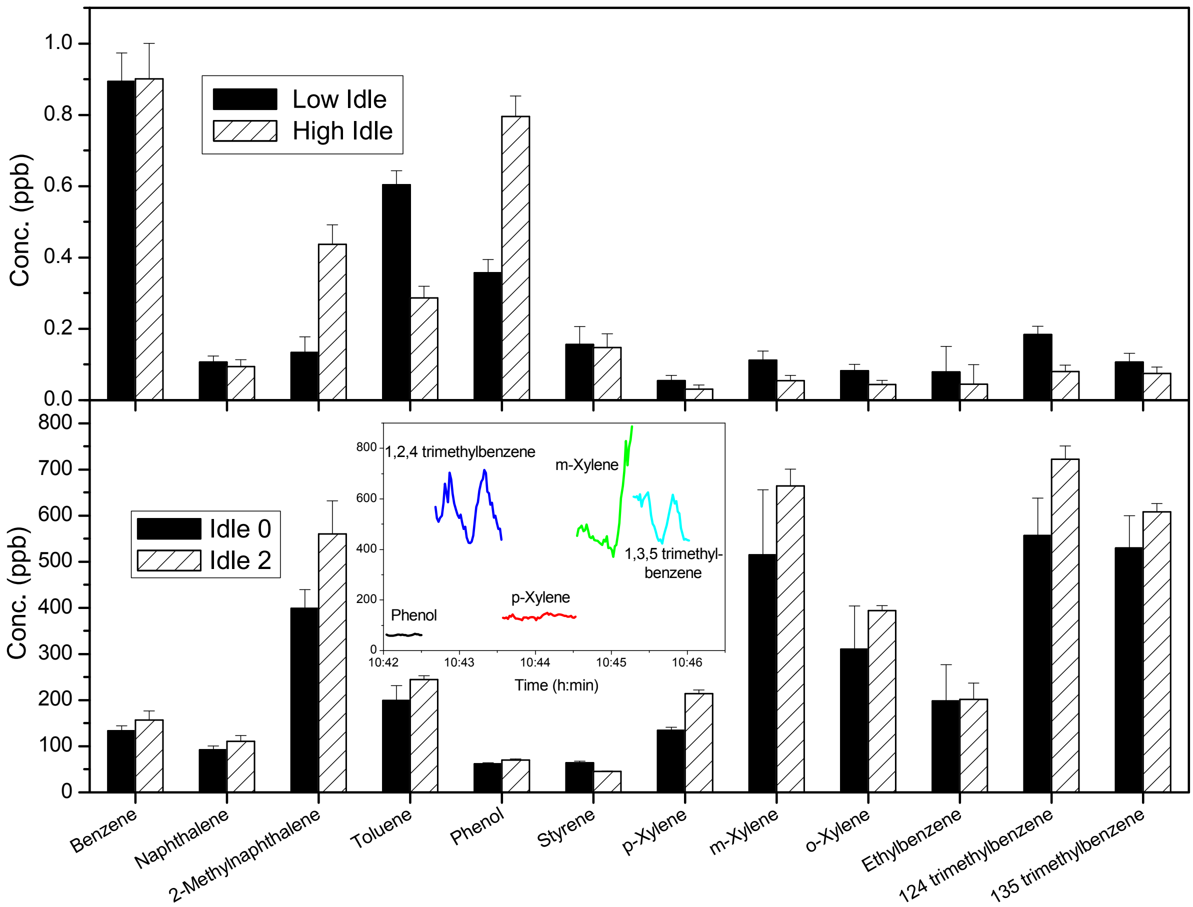

Figure S1. Steady state organic emissions at analyte-specific wavelengths, M1 Abrams, low and high idle conditions (top), and Bradley IFV, "idle 0" and "idle 2" trials (bottom). Inset: real-time variance of organics at low idle.

Figure S2. Cold and warm start emissions of benzene, naphthalene, and 2-methylnaphthalene for the Bradley IFV (top) and M1 Abrams (bottom).

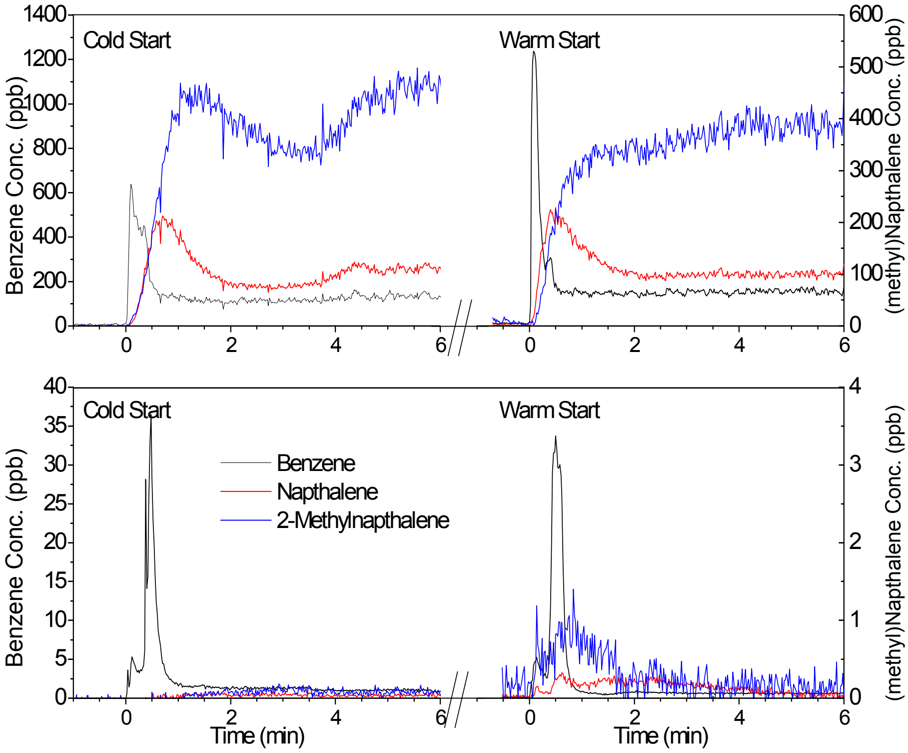

Figure S3. Benzene, naphthalene, and 2-methylnaphthalene emissions during a shutdown of the M1 Abrams. Two tests are shown to illustrate repeatability.