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Temperature and Driving Cycle Significantly Affect Carbonaceous Gas and Particle Matter Emissions from Diesel Trucks

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Abstract

The present study examines the effects of fuel [an ultralow sulfur diesel (ULSD) versus a 20% v/v soy-based biodiesel–80% v/v petroleum blend (B20)], temperature, load, vehicle, driving cycle, and active regeneration technology on gas- and particle-phase carbon emissions from light and medium heavy-duty diesel vehicles (L/MHDDV). The study is performed using chassis dynamometer facilities that support low-temperature operation (−6.7 °C versus 21.7 °C) and heavy loads up to 12 000 kg. Organic and elemental carbon (OC-EC) composition of aerosol particles is determined using a thermal-optical technique. Gas- and particle-phase semivolatile organic compound (SVOC) emissions collected using traditional filter and polyurethane foam sampling media are analyzed using advanced gas chromatography/mass spectrometry methods. Study-wide OC and EC emissions are 0.735 and 0.733 mg/km, on average. The emissions factors for diesel vehicles vary widely, and use of a catalyzed diesel particle filter (CDPF) device generally mutes the carbon particle emissions in the exhaust, which contains ~90% w/w gas-phase matter. Interestingly, replacing ULSD with B20 did not significantly influence SVOC emissions, for which sums range from 0.030 to 9.4 mg/km for the L/MHDDVs. However, both low temperature

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and vehicle cold-starts significantly increase SVOCs in the exhaust. Real-time particle measurements indicate vehicle regeneration technology did influence emissions, although regeneration effects went unresolved using bulk chemistry techniques. A multistudy comparison of the toxic particle-phase polycyclic aromatic hydrocarbons (PAHs; molecular weight (MW) 252 amu) in diesel exhaust indicates emission factors that span up to 8 orders of magnitude over the past several decades. This study observes conditions under which PAH compounds with MW 252 amu appear in diesel particles downstream of the CDPF and can even reach low-end concentrations reported earlier for much larger HDDVs with poorly controlled exhaust streams. This rare observation suggests that analysis of PAHs in particles emitted from modern L/MHDDVs may be more complex than recognized previously.

Graphical Abstract

Introduction

Of the approximately 150 billion liters of on-highway diesel fuel produced annually in the United States from 2014 to 2016, roughly 5 billion liters is biodiesel (www.eia.gov, last accessed August 2017). Biodiesel is produced in response to the renewable fuel standard (RFS) program authorized under the 2005 Energy Policy Act and later expanded under the 2007 Energy Independence and Security Act. Use of alternative fuels like biodiesel is expected to increase because of the perceived energy, economic, and environmental benefits, e.g., the RFS-specified biomass-based (B100) diesel fuel volume requirement is 7.6 billion liters for 2017. In practice, methyl-ester-based biodiesel (B100) is typically blended with petroleum diesel to produce B20 (20% v/v) because of the favorable performance characteristics of B20 and its compatibility with much of the transportation fleet and other specialized nonroad engines. Despite the potential benefits of biofuel use, there is public health concern about the possible direct and indirect environmental and air quality impacts. National biofuel policy includes an antibacksliding provision regarding the risk of negative or adverse air quality impacts due to RFS implementation. This provision also allows for mitigation.

Replacement of petroleum diesel with biodiesel in vehicles can reduce pollutant emissions, including particulate matter (PM), CO, elemental carbon (EC), polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and total hydrocarbons (THC). (1–3) However, reductions are not always realized and vary by pollutant. For example, compared with diesel, B30 use in Euro 3 commercial trucks operating under the extra urban driving cycle exhibited slightly increased CO and THC emissions.(4) Use of soy- and grease-based B20 fuels in military vehicles also showed frequently increasing albeit erratic CO and THC emissions trends dependent on driving cycle.(5) Increasing PM emissions

from burning biodiesel in vehicles are observed less frequently because oxygen-enriched biodiesel fuel removes elemental carbon (EC), the major PM mass component in diesel exhaust. In direct contrast, studies have also revealed that B20 use in trucks and buses increases the organic carbon (OC) concentration in PM.(6, 7) This OC in biodiesel PM is relatively soluble and thus poses an additional toxicological concern.(8) Although few studies investigate the health effects of biodiesel PM emitted from vehicles, there is evidence suggesting that biodiesel fuels can be more mutagenic(9) and cytotoxic than petroleum diesel (also see ref 8 and references therein) and also evidence showing reduced mutagenicity.(10)

Knowledge of compositional differences is indeed important for understanding the toxicological effects of aerosol particles from vehicles and is also required for proper accounting within the global emissions inventories that support dispersion, air quality, forecasting, and chemical mass balance models. Multiple factors influence aerosol composition, including vehicle design and age, engine technology and operating conditions, and biodiesel fuel type, among others. Yet relatively few, if any, studies examine and contrast aerosol emissions composition from modern heavy-duty vehicles burning bio- and petroleum diesels while also testing the many operating variables and technologies potentially influencing these emissions. To date, biodiesel studies that measure individual semivolatile organic compounds (SVOCs) in aerosol emissions focus exclusively on polycyclic aromatic hydrocarbons (PAHs) owing to their toxicity.(10–12) These studies omit analysis of additional hydrocarbon constituents, and except for Bagley et al.(10) also omit gaseous SVOC emissions contributions. More recent studies using diesel vehicles provide strong evidence that measuring gas-phase SVOCs is critical as these compounds undergo atmospheric photo-oxidation yielding secondary organic aerosols.(13, 14) While the newer studies offer relatively exhaustive volatility distributions and hydrocarbon speciation that change with fuel aromatic content, the potential effects on emissions due to changing fuel oxygen content have not been emphasized and thus are uncertain.

The present dynamometer study aims to clarify this uncertainty by examining the effects on gas and particle emissions following a switch from ultralow-sulfur diesel fuel (ULSD) to a soy-methyl-ester-based B20 fuel in three heavy-duty diesel vehicles (HDDV)(15) (see Title 40, CFR §86.082–2). Specifically, light and medium HDDV (L/MHDDV) vehicles are examined to provide emissions data in support of the EPA Motor Vehicle Emissions Simulation Model (MOVES), which currently lacks such information from this engine class. In 2007, new heavy-duty emission standards went into effect, with full implementation of catalyst-forcing NO_x emissions standards in 2010. This study was needed because previous studies focused on older emission certification levels for engines that were not equipped with catalytic NO_x controls (e.g., urea SCR or NO_x adsorption catalysts) or with catalyzed filters for PM emissions control. As of 2016, more than half of all heavy-duty truck vehicle miles traveled in the U.S. were for trucks equipped with catalytic exhaust emissions controls for both NO_x and PM control. Additionally, this study examines the effects of temperature, load, vehicle, driving cycle, and active regeneration technology on L/MHDDV emissions. Emissions are collected using a classical quartz filter-foam plug approach, which measured the SVOC mass as predominantly gas-phase. Use of the B20 decreases both OC and EC in PM on average but otherwise showed no significant effect on the SVOC emissions during

this study. Temperature and driving cycle are observed to influence the SVOC emissions significantly. Compared with earlier HDDV studies performed globally, lower SVOC emissions are observed for modern L/MHDDVs, although toxic PAHs with molecular weights greater than 252 amu are still observed. As indicated, semivolatile carbon is the present focus. CO₂, CO, THC, and CH₄ are also reported in the interest of exhibiting the total budget-relevant carbon mass in the diesel vehicle exhaust. A companion study(2) thoroughly interprets the impacts on THC gas emission levels due to the temperature, driving cycle, load, and fuel technology variables.

Experimental Methods

Vehicle testing and emissions characterization experiments were performed at the U.S. Environmental Protection Agency (EPA) Research Triangle Park, North Carolina. An exhaustive description of the L/MHDDVs, fuels, dynamometer test facilities, and testing and sampling methods was provided in George et al.(2) A brief description follows.

Vehicles and Fuels

The characteristics of the three diesel vehicles tested as part of this study are given in Table S1. All test vehicles—V1, V2, and V3—were 2011 model year and equipped with catalytic exhaust emission control technologies (selective catalytic reduction [SCR] or nitrogen adsorption catalyst [NAC] for NO_x control and CDPF/diesel oxidation catalyst [DOC]) that met 2010 EPA diesel emissions standards (www.epa.gov, accessed May 2017). In all cases, the NO_x catalysts were located upstream of the CDPF, necessitating active regeneration of the CDPF. The reasoning and future outlook underlying catalyst placement is provided in the Supporting Information. Vehicle odometer mileage varied from 4 333 km to 35 498 km. Ultralow sulfur diesel (ULSD) and a splash-blended 20% v/v soy-methy-ester-based biodiesel (B20) were obtained from Gage Products Co. (Ferndale, MI) and used for testing. Further details about test fuel blending, change-out procedures, and chemical and physical properties were provided in George et al.(2)

Dynamometer Testing

Two chassis dynamometers were used to conduct the semirandomized vehicle testing. Book et al.(16) provided exhaustive details of the testing facility and methods. Briefly, dynamometer 1 was an enclosed, climate-controlled (−30 to 45 °C) 48 in. roll MIM 4800 (Burke E. Porter Machinery Co., Grand Rapids, MI); dynamometer 2 was a 72 in. roll truck chassis dynamometer (Renk AG, Augsburg, Germany) that operated without low-temperature capability. The temperature at which light-duty vehicles must pass emissions certifications is −6.7 °C, and 21.7 °C is the ambient temperature of dynamometer 2. For this study, a total of 62 dynamometer tests over 16 conditions were performed. V1 was tested only on dynamometer 1 at −6.7 and 21.7 °C, in laden and unladen states, using both ULSD and B20 fuels. V2 was examined using the identical set of test conditions but only in the unladen state because the laden vehicle condition exceeded the weight limits of dynamometer 1. V3 also exceeded the weight limits of dynamometer 1; hence, V3 was tested on dynamometer 2 in the laden and unladen state but only at 21.7 °C. Each test condition was conducted at $N = 3$ following a vehicle preconditioning step. A single

dynamometer test comprised three driving cycles. Figure S1 shows the speed versus time trace, which identically mimics the lower-speed transient mode of the California Air Research Board (CARB) medium heavy duty urban dynamometer driving schedule (MHDULO).(17) This driving cycle was performed twice for each test, initially simulating a cold start (CS) and a later warm start (WS). Between the CS and WS cycles, the Federal Heavy-Duty Urban Dynamometer Driving Schedule (HD-UDDS) was performed (see CFR, Title 40, Part 86.1216–85). Two 20 min warm-soak periods followed the CS and HD-UDDS cycles. Notably, NAC and CDPF regenerations occurred separately only during the HD-UDDS cycle. The V1 NAC regenerated during every HD-UDDS cycle at 21.7 °C unless the CDPF was actively regenerating. Tests were repeated following CDPF regeneration to ensure triplicate measurements under “normal” operating conditions.

Emissions Sampling

A detailed schematic and description of the dilution and constant volume sampling system were provided elsewhere.(2, 18) Briefly, raw exhaust was directed to a dilution tunnel via an insulated transfer tube and then turbulently mixed with HEPA- and charcoal-filtered dilution air at a ~1:20 ratio (21 m³/min; 21 °C). The homogenized aerosol mixture was routed to a gas and particle sampling system comprising four multipoint isokinetic probe assemblies that permitted separate and proportional sampling of each driving cycle. The probe assemblies were enclosed in a steel box fabricated in-house and heated to 47 °C. Characterization of the gas- and particle-phase SVOCs in the exhaust was the focus of this study. The probe points dedicated to SVOC sampling contained a preconditioned (550 °C, 12 h) quartz filter (Q_f; Pall Corp., Ann Arbor, MI) and two polyurethane foam plugs (PUFs; Sigma-Aldrich; St. Louis, MO) positioned in series. Additionally, the method of Subramanian et al.(20) was used to estimate positive adsorption artifact on the Q_f. For this study, the WS and HD-UDDS cycles were combined to ensure sufficient mass was collected for further chemical analysis; henceforth, this composite is termed “WS-UDDS”. Q_f substrates sampled aerosol on a per test basis, whereas the PUFs collected organic gases cumulatively over multiple dynamometer tests ($N = 2$) running under the same set of conditions. All exhaust emissions sampling systems and operations complied with the CFR, Title 40, Part 1065. Details about CO₂, CO, and CH₄ monitoring were provided earlier.(2) While it is possible to conduct proportional transient upstream emissions sampling, adding such capability was well beyond the means and scope of this study.

Chemical Analysis

Sample handling and pretreatment and subsequent chemical analysis procedures were described earlier.(18, 19) Briefly, the Q_f samples were subject to thermal-optical analysis using a modified NIOSH 5040 Method for determination of OC and EC in the exhaust aerosol. This analysis was destructive and therefore limited to one 1.45 cm² filter punch per condition to conserve sample for further organic chemical analysis. Circular Q_f sections (~1 cm²) were also examined using thermal extraction gas chromatography–mass spectrometry (TE-GC/MS; TDS2, Gerstel, Inc., Germany and Agilent Technologies, Santa Clara, CA) to measure the SVOC composition of the organic aerosol. Exhaustive details of the TE-GC/MS system and its operation provided were provided by Herrington et al.(19) Two notable differences for the present study were that the TE oven was heated to 325 °C during PM

extraction, and the MS was operated in selected-ion monitoring (SIM) mode. The major nonpolar SVOC classes targeted in this investigation include polycyclic aromatic hydrocarbons (PAHs), saturated hydrocarbons (normal, branched and cyclic alkanes), and sterane and hopane molecules. SVOCs were quantified using an internal standard method. A list of the targeted SVOCs and deuterated standards is given in Table S2.

Gas-phase SVOCs were extracted from PUF by repeatedly compressing PUF in ~100 mL of a 5:3:2 v/v hexane, acetone, and dichloromethane solvent mixture. The extracts were reduced to ~250 μ L using N_2 concentration and injected (1 μ L) onto a GC-MS (7890/7000, Agilent Technologies). The MS was a triple quadrupole (qqq) operating in multiple reaction monitoring (MRM) mode.

Quality Control

Four-level, linear calibration curves over a 0.05–10 ng range were used for quantification of both the gas- and particle-phase SVOCs. For both chromatography approaches, routine accuracy checks were performed with a midlevel standard (1 μ L injection) and measured to be within 20% of known fixed concentrations for the vast majority of target SVOCs. Blank media standard spikes showed that 87% of the target SVOCs were recovered at 75–125%. Instrumental precision checks with compound standards performed over several months ($N = 16$) were well within 20%, exhibiting adequate method robustness and repeatability. Select PUF extracts and Q_f samples were also analyzed in triplicate to determine precision in the presence of sample matrix; SVOCs in Q_f and PUF were within 38%, on average. TE-GC/MS detection limits determined using EPA SW-846 ($N = 7$) were reported in Hays et al.(18) and ranged from approximately 10 to 400 pg on column. Method detection limits (MDLs) for the SVOCs measured using the qqq-MS in MRM mode were determined in an identical manner and ranged from 0.8 pg to 327 pg (see Table S2). Chromatographic retention time shifts were negligible ($<0.1\%$) throughout the analysis period. SVOC validation was determined using MS fragment and isotope ratios, assuming a $S/N \geq 3$, and a retention time proximity to midlevel check standards of ≤ 0.1 min. All SVOC concentrations were background-subtracted using a weekly CVS system blank. Background SVOC concentrations were converted to units of micrograms per cubic meter and considered constant over the weekly testing period. Background levels of individual SVOCs ranged from 21%–51% of the emissions on average and varied with the dynamometer facility, temperature, and driving cycle. Background of dynamometer 1 (~20%) was lower than that of dynamometer 2 (51%), and the -6.7°C tests and CS were substantially less influenced by background in general. Only background-subtracted concentration values greater than zero were considered valid. Fatty acid methyl esters (FAMES) were detected in the particle-phase samples but eliminated from further discussion due to a suspected sampling bias.

Statistics

SAS 9.4 (SAS Institute Inc., 2012; SAS/STAT 9.3 User's Guide, Cary, NC) was used for the statistical analysis. Linear mixed models of emission rate concentrations were fitted separately for each compound class to assess relationships with the covariates of driving cycle, temperature, fuel, vehicle, and vehicle weight. These models of emission rate concentrations used ln-transformed measurements restricted to concentration measurements

above the detection limit. The models accounted for the repeated measure structure of testing each vehicle in both driving cycles (CS and WS-UDDS). These class-specific models were also fitted for the CS cycle alone, omitting the covariate of driving cycle and the repeated measures structure. Similar class-specific models were fitted for the WS-UDDS cycle, also omitting the covariate for driving cycle and the repeated measures structure, and including the covariate “regen” which occurred only in the WS-UDDS cycle. The p -values for the tests of model fixed effects are given with the significance level set at $\alpha = 0.05$.

Results

Carbon-Based Pollutant Emissions

Anthropogenic greenhouse gas emissions are critical to measure and track owing to their influence on climate and the ecological systems on which all living organisms depend. Particle- and gas-phase SVOCs are the main focus presently. However, important study objectives also include (i) visualizing these organic species in the context of the total carbon species emissions in the exhaust and (ii) reporting a diesel vehicle emissions budget of relevance to the global carbon cycle. Hence, Figure 1 shows the driving cycle-composited, study-wide ($N = 16$) mean emissions of CO_2 , CO, CH_4 , total hydrocarbons [THCs {including CH_4 }], SVOCs ($Q_f + \text{PUF}$), and filter-based OC and EC. (These data are also available in Table S3.) The SVOCs explain 4% w/w of the nonmethane THC (NMHC) on average. Using the VOC data in George et al.(2) and SVOC data in Table S3, ~36% w/w NMHC is estimated to be nonspeciated. Put another way, assuming that the PUF is reflective of NMHCs that are not VOCs, which would break through the PUF, we estimate that ~10% w/w of the mass collected on PUF was speciated.

Figure 1 exhibits a classic combustion emissions trend that shows concentrations generally decreasing with the increasing refractory nature of the carbon species. CO_2 emissions ($658.3 \pm 120.2 \text{ g/km}$) outweigh the other combustion-generated gas- and particle-phase carbon species in the diesel exhaust by several orders of magnitude. On average, ~90% of the fuel carbon burned is converted to CO_2 during testing; less than 1% w/w of the fuel C is emitted as CO. Interestingly, there is a basic anticorrelation between CO_2 and the further reduced C species (i.e., THCs, EC, CO, and CH_4) shown in Figure 1; however, only the CO– CO_2 anticorrelation (-0.5) is significant ($p < 0.05$). In contrast, pairs of the more reduced carbon emissions species tend to correlate positively ($R > 0.5$, $p < 0.05$). Correlation-based trends in the SVOC and OC emissions data are uncertain when explored with these greenhouse gases. Perhaps constraining the “SVOC” class to GC-MS-identified compounds measured with the Q_f -PUF array produces underestimates that confound comparisons. Regardless, the emissions of OC and EC and SVOC species and the effects of temperature, driving cycle, and fuels are covered in further detail next.

OC-EC and Thermal-Optical Analysis

Table 1 provides mean (± 1 standard deviation) OC-EC emission factors (EFs) in milligrams per kilometer units that are specific to the Q_f samples. Test-integrated EFs for OC and EC are given in Table S3. For the present study, ambient temperature and driving cycle produce the most significant effect on the organic compound emissions (George et al.(2)). OC and

EC decrease with fuel oxygen content by 38% and 54% on average; however, fuel (ULSD versus B20) and test weight variables show no significant effect ($\alpha = 0.05$) when comparing mean OC and EC EFs. Hence, OC-EC EFs in Table 1 are composites presented on a vehicle, cycle, and ambient temperature basis. Additional rationale for using this compositing approach is provided when presenting the SVOC results. OC emissions for individual tests vary greater than 2 orders of magnitude (0.0017–0.82 mg/km) and are generally 5-fold higher during the cold start, at the lower test cell temperature, and for the larger vehicle (V3). EC emissions for each test, however, vary over an order of magnitude (0.008–0.18 mg/km), trend similarly to OC in general, but seem less influenced by ambient temperature and driving phase. Only V1 emits EC at -6.7°C , and its composite EC emissions are as high as 2.01 ± 0.42 mg/km on average. We note that the OC values are subject to positive adsorption artifact, which is estimated at roughly 89% w/w on average. The implications of this are discussed further below.

SVOC Emissions

The vast majority of SVOC emissions mass is collected as gas-phase, as higher volatility compounds are emitted in greater quantities. Test composites of individual SVOCs in Figure S2 quantile plots exhibit evidence of this gas-phase emissions dominance. On average, less than 10% w/w of the SVOCs are collected on the Q_f , and much of this mass is ascribed to the gas phase (89% w/w on average). Sampling conditions were fixed, and test variables are expected to influence the SVOC gas–particle partitioning only slightly. Hence, the Q_f and PUF are combined as we further investigate the effects of dynamometer testing on the SVOC emissions trends from the heavy-duty diesel trucks.

Individual SVOCs (C_{10} – C_{38} *n*-alkanes [$N = 29$], *b*-alkanes [$N = 8$], C_{10} – C_{24} PAH [$N = 25$], and steranes/hopanes [$N = 7$]) are summed by class for each test ($N = 16$) and then averaged study-wide (Table S3). Test-composite SVOC emissions vary from 0.03 to 9.4 mg/km (Figure 1). Over the whole 12.1 km driving trace, the average *n*-alkanes = 22 mg followed by the PAH = 3.0 mg, *b*-alkanes = 1.1 mg, and steranes and hopanes = 0.060 mg. In each SVOC class, test-based emissions totals vary over several orders of magnitude. Table S4 gives descriptive statistics for SVOC emissions divided by compound class, vehicle, driving cycle, temperature, fuel, and regeneration technology and its condition. The substantially greater SVOC emissions during the CS is the most recognizable data trend, and the mixed effect model results confirm its significance ($\alpha < 0.05$) for each compound class (Table 2). Significant temperature and vehicle effects are also observed in the models ($\alpha < 0.05$), but these are sporadic and isolated to the PAH and *n*-alkane classes. Only the *n*-alkanes emitted during the CS seem responsive to vehicle test weight adjustments. Importantly, the current study implies that fuel use (ULSD vs B20) and the active regeneration events occurring during the WS-UDDS impart no significant effect ($\alpha < 0.05$) on class-based SVOC emissions.

The three main effects of driving cycle, temperature, and vehicle and their influence on the class-based SVOC emissions from diesel trucks can be visualized in Figure 2. The figure supports the observations stated above and also resolves subtleties in the data. For example, the figure shows that lower test cell temperatures typically produce higher diesel truck

emissions. The influence of temperature on SVOC emissions is pronounced for V2, for which test reproducibility is greatest. The *b*-alkanes and steranes/hopanes are less sensitive to changing temperatures across vehicles and cycles with the exception of emissions from V2 during the WS-UDDS. V1 is the highest emitter on average except at $-6.7\text{ }^{\circ}\text{C}$ under WS-UDDS operating conditions. Generally, the WS-UDDS cycle produces a wider range of emissions about each test sum mean, although the PAH class responds less to temperature effects during the WS-UDDS operation. The rationale underlying several of the above observations will be discussed further.

In terms of the individual PAH emissions sums ($Q_{\text{F-PUF}}$; see Figure S3) for the L/MHDDV exhaust, naphthalene is emitted in the greatest quantity, up to $4500\text{ }\mu\text{g}/\text{km}$, followed by methyl- and dimethyl-naphthalene. Figure S4 offers a closer view of emissions factors for the individual heavier PAH (MW = 252) of interest due to their toxicity.

Benzo[*g,h,i*]perylene is emitted in the greatest quantity, $1.1 \pm 0.4\text{ }\mu\text{g}/\text{km}$ on average, followed by benzo[*b*]fluoranthene ($0.8 \pm 0.7\text{ }\mu\text{g}/\text{km}$) and benzo[*a*]anthracene ($0.7 \pm 0.4\text{ }\mu\text{g}/\text{km}$). Figure S4 shows the following additional trends: (i) Heavier PAH emissions are vehicle-dependent, varying from fully removed (V2) to present at levels $>1\text{ }\mu\text{g}/\text{km}$ (V3). (ii) Formation of PAHs with MW = 252 amu is most prominent for the CS at $21.7\text{ }^{\circ}\text{C}$. (iii) PAH emissions for V1 and V3 are associated with ULSD and B20, respectively.

Discussion

This study examines gas- and particle-phase carbonaceous emissions from late-model L/MHDDVs. A review of the published literature indicates (i) extensive historical interest in older-model, heavier freight vehicles and (ii) that newer L/MHDDVs have seldom been investigated until recently. Hence, testing and engine displacements, controls, age, and systems management differ substantially across the available studies, complicating direct comparisons among emissions data sets. However, assessments are provided with context to offer important perspective, improve our national and global carbon inventories, and further our understanding of changing diesel vehicle emissions trends. The vehicles in this study were all L/MHDDV models certified to fully phased-in 2010 U.S. Federal emissions standards. Previous studies of post-2010 heavy-duty diesel emissions were conducted using engines and exhaust emissions control systems more typical of heavy-duty Class 7 and Class 8 truck applications with NO_x catalysis occurring downstream of the CDPF in order to facilitate passive regeneration of the CDPF via oxidation of trapped particles with NO_2 . The exhaust emissions control systems of the vehicles in this study place the NO_x catalysts (SCR, NAC) upstream of the CDPF and thus do not have sufficient NO_2 entering the CDPF for passive regeneration of trapped particles to occur. Thus, the tested L/MHDDV systems rely entirely upon active regeneration via direct and/or indirect addition and combustion of fuel hydrocarbons in the exhaust to raise exhaust temperatures above the $600\text{--}650\text{ }^{\circ}\text{C}$ necessary for soot oxidation over the CDPF.

CO and Greenhouse Gas Emissions

The transportation sector accounts for roughly 14% of the global greenhouse gas emissions inventory, of which CO_2 is the major w/w fraction (2010 data; available in ref 21 and

references therein). In the United States, transportation sources contribute 26% of the total greenhouse gas emissions with CO₂ accounting for 81% of the inventory in 2014;(21) annual diesel engine contributions to CO₂ in the U.S. are estimated as $95 \pm 5 \times 10^6$ (tC).(22) The CO₂ emission factor of 658.3 ± 120.2 g/km (Table S3) reported here is similar to an estimate (733.9 g CO₂/km) determined using the fuel economy diesel factor (2690 g CO₂/L; 40 C.F.R. 600.113) and the mean fuel economy observed here (3.8 km/L). The L/MHDDVs examined emit up to a factor of 4 less CO₂ than transit and school buses and refuse trucks. (23) The buses and refuse trucks are older and heavier and were examined using a mixture of on-road and chassis dynamometer tests that apply multiple driving cycles. CO₂ emissions appear negligibly influenced by after treatment devices, although use of the DPF slightly elevated the CO₂ levels, presumably due to the fuel injection processes used during active regeneration. The L/MHDDVs also emit proportionally less CO (CO/CO+CO₂) compared with these earlier models, possibly due to the increased efficiency of DOCs, CDPFs, and in some cases the ammonia oxidation catalysts (AMOX) used with SCR systems, all of which contain platinum group metals (PGM) and other catalysts capable of oxidizing CO to CO₂ under net-oxidizing conditions in the exhaust. Relatively slight albeit consistent CO emissions decreases are detected over the 1990–2010 period for on-road diesel vehicles in urban domains.(24) A conversion of their fuel-based emission factor to one that considers distance using our fuel economy data shows 2.2 g CO/km for 2010, which is nearly an order of magnitude greater than what is measured for the L/MHDDVs presently. A slightly lower CO emission factor, 1.8 g/km, is reported during a real-time, plume capture study that examined greater than 500 diesel trucks in a California highway tunnel over a brief 2010 sampling period.(25) L/MHDDV CO emissions are also substantially lower than those compiled using earlier (pre-2000) truck (>3859 kg) chassis dynamometer studies.(26)

Compared with CO₂, the transportation sector contributes substantially less CH₄ mass to the greenhouse gas inventory. CH₄ in HDDV exhaust is present at trace levels and presumably emitted as a byproduct of incomplete combustion. When CH₄ is observed in the L/MHDDV exhaust ($n = 49$ of 474 trials), it is typically associated with the UDDS cycle and within the range of values reported earlier for the older transit buses (0.006–0.02 g/km).(23) In contrast, CH₄ is not detected during testing of 2010 emissions-compliant HDDVs with higher displacements (8.3 and 12.8 L) using a variety of driving cycles including the UDDS. (27) CH₄ oxidation is expected to be sensitive to exhaust and catalyst temperatures, yet these results suggest that vehicle engine technology may also govern CH₄ emissions. Generally, CH₄ emissions from diesel trucks are less widely measured, often undetected during measurement attempts, and thus more uncertain.

Q_f-Based Carbon

The reduction of the once predominant EC fraction in diesel PM due to the introduction of CDPFs is a striking global emissions trend that needs to be accounted for in emissions inventories. The negligible difference in EC following the switch from the ULSD to the more oxygenated B20 (see Figure S5) indicates that the PM removal by CDPF dwarfs the soot or EC removal effect widely expected with B20. Thus, results show that the benefit of PM-EC reduction is realized through the CDPF but not the fuel technology. May et al.(13) compile multiple diesel emissions studies and demonstrate a reduction by 2 orders of

magnitude in EC emissions for DPF-equipped versus nonequipped vehicles. This study(13) also tests five diesel vehicles with an engine displacement range of 6–15 L using ULSD fuels with varying aromatic content, multiple cycles including the UDDS, and CVS dilution system. Using the emissions data in ref 13 and the fuel density and fuel economy data given above, mean EC estimates of 0.22 mg/km or lower (DPF) versus 45 mg/km (non-DPF) are obtained. Results given here for V2 and V3 agree well with these literature-observed EC averages for DPF-controlled emissions. The extended fuel-rich conditions required to regenerate the NAC are likely the root cause of the relatively high EC emissions seen for V1. An unusual increase in accumulation mode particles observed for V1 is also possible evidence of less than 100% soot-trapping efficiency within the CDPF.(16) Regardless, this condition lowers the OC:EC ratio to values typically observed in non-DPF diesel emissions, suggesting that even newer HDDVs running B20 can exhibit EC-enriched PM emissions. The OC range in diesel PM emissions estimated as described directly above is 0.5–2.2 mg/km, similar to the mean OC values in Table 1. Higher OC emissions for low-temperature (–6.7 °C) and CS phase are likely due to the positive linear relationship between the temperature and oxidation efficiency for OC emissions over the exhaust catalysts. All vehicles have identical engine displacement, so the high OC emissions from the heaviest (V3) are expected. The relatively low OC values observed, especially for WS-UDDS, are quite likely impacted by gas-phase filter adsorption artifact imparted during sampling as explained earlier.(13) The overwhelming lack of evidence for B20 increasing OC in the diesel exhaust (see Figure S5) implies that this may be masked by the efficiency for oxidizing OC within the PGM catalysts used by the emissions control systems.

Temperature and Driving Cycle Affect SVOC Emissions

Lower combustion efficiency is expected at low engine temperatures. This lower combustion efficiency and a cool DOC likely explain the general increase in the gaseous SVOC emissions at –6.7 °C and during the CS (Figure 2). Sterane emissions are less influenced by test cell temperature in either driving phase because they are emitted from volatilized engine oil which requires higher engine temperatures.(28) The relative stability and lower boiling points of the *b*-alkanes may clarify why these are less affected by cell temperature than the linear chain *n*-alkanes. Unburned fuel is the likely source of both *b*- and *n*-alkanes, whereas PAHs are byproducts of incomplete combustion. The limited PAH response to test cell temperature during WS-UDDS reflects the relatively constant engine operating temperature and thus combustion conditions for this phase. Catalytic exhaust emissions controls have dramatically reduced total PAH emissions from HDDVs over the past decade or so (ref 29 and references therein). For example, a larger (engine displacement = 11 L), 1998 HDDV tested without emissions control shows a mean PAH = 8.5 mg/km for the UDDS driving profile, an order of magnitude greater than our PAH results. However, the identical HDDV tested with multiple DPF-DOC-SCR retro-fit technologies and configurations shows a maximum PAH = 0.5 mg/km for the UDDS that is well within the range of the current study. Similarly, 90% w/w of these postcontrol PAH emissions are detected as gas-phase. Quantification of this intermediate volatility or SVOC mass is essential as recent evidence suggests that it undergoes photochemical oxidation in the atmosphere yielding secondary organic aerosol.(30)

Active versus Passive CDPF Regeneration and Heavier PAH Emissions Comparisons

Individual particle-phase PAHs in diesel PM emissions also merit further attention owing to their known toxicity.⁽³¹⁾ This is accomplished by focusing on PAH with molecular weights (MW) greater than 252 amu because these are detected mainly in the particle phase and tend to exhibit higher toxicity equivalence.⁽³²⁾ Figure 3 provides study-averaged emission factors for PAH (MW = 252) across multiple diesel truck emissions studies conducted over the past two decades. The comparison raises several interesting points. First, the on-road study performed in China by Cao et al. using L/MHDDVs with oxidation catalysts as after-treatment but without DPF indicates high PAH emissions that diverge strongly from dynamometer emissions projections.⁽³³⁾ It should be noted that the lowest-emitting L/MHDDVs in the Cao et al.⁽³³⁾ study were certified to China 4 emissions levels, which are considerably less stringent than U.S. 2007 or 2010 U.S. heavy-duty diesel NO_x and PM emissions standards. Next, Pakbin et al.⁽³⁴⁾ show that use of a DPF in the after-treatment scheme removes virtually all of these PAH, and Hu et al.⁽²⁹⁾ basically agree, showing only ultratrace quantities (<3 ng/km) of a few PAHs with MW = 252 amu. Paradoxically, the present study finds that these heavier PAHs can be emitted from modern L/MHDDVs using CDPFs and also shows that PAH concentrations in these emissions are within range of but typically below those reported for older HDDVs operating without controls. However, we note that these older HDDVs emit relatively more PAH-adsorbing EC in PM possibly producing lower concentrations for PAH with five or more rings depending on the extraction methods applied.⁽³⁵⁾ Finally, Laroo et al.⁽³⁶⁾ indicate much lower emissions of PAH, including PAH with MW = 252 amu, than the present study. Considering the similarities between the engine used in the Laroo et al. study and those used in the present study, the differences in emissions may be due to differences in exhaust emissions control system architecture. The system architecture in Laroo et al.⁽³⁶⁾ placed the SCR/AMOX catalysts downstream of the CDPF and relied primarily on passive CDPF regeneration. Khalek et al.⁽³⁷⁾ compared emissions from Class 8 truck engines compliant with 2007 U.S. heavy-duty emissions standards that relied primarily on active CDPF regeneration to comparable engines compliant with 2010 heavy-duty emissions standards using primarily passive CDPF regeneration. PAH emissions for the engines relying on active regeneration were more than an order of magnitude higher than those of engines relying on passive regeneration. The emissions control system architecture and PAH emissions results for the 2010-compliant systems in Khalek et al.⁽³⁷⁾ were also comparable to the systems and PAH emissions results from Laroo et al.⁽³⁶⁾ The results of the Khalek and Laroo studies and this present study indicate that emissions control system architecture plays a significant role in resultant PAH emissions and that 2010-compliant heavy-duty emissions control systems that rely primarily on passive CDPF regeneration have potential for significant PAH emissions reductions relative to systems that rely primarily on active CDPF regeneration. Finally, the relationship among fuel, vehicle, and PAH formation warrants further study to explain why PAH emissions for V1 and V3 are associated with ULSD and B20, respectively.

Conclusions

Knowledge of changing HDDV emissions trends has implications for public health, air quality, and for designing future engine, vehicle, and control technologies. Past emissions

research focuses more on older HDDVs with greater engine displacements, marking the need for studies exploring L/MHDDV exhaust. This study examined the total carbon emissions mass showing that CO₂ emissions far outweigh the emissions of other carbon species and may have increased slightly owing to fuel injection-based CDPF regeneration strategies and the use of DOCs which convert CO to CO₂. CH₄ emissions have remained consistent over decades but are generally uncertain because of low levels in the HDDV exhaust. Fuel effects on the OC-EC and SVOC emissions are clearly muted following CDPF after-treatment. We present a case that shows low OC:EC proportions are possible in PM from modern L/MHDDVs using NACs. CDPF use clearly captures much of the solid carbonaceous PM mass, leaving the vast bulk of the hydrocarbon emissions as VOCs(2) and gaseous SVOC mass. Quantification of this mass is essential as these gases may undergo photochemical oxidation in the atmosphere yielding secondary organic aerosol. Specific organic markers for following the extent of this process are unavailable currently, but further quantitative evaluation of the individual gas-phase compounds and SVOC classes as accomplished here may contribute to developing novel and scientifically sound regulatory strategies for controlling smog. As expected, SVOC emissions increase with CS and oftentimes with cooler temperatures. These results suggest a need for dispersion and air quality models that consider regional emissions strategies by temperature zones. Assessing heavier, particle-phase PAH compounds 252 amu in diesel particles following after treatment with CDPFs is more complex than previously realized. This study clarifies that if these PAH emissions are present in the L/MHDDV exhaust, they can reach the low end of the concentration range reported earlier for much larger HDDVs known for their poorly controlled emissions. This may be due in part to the use of active CDPF regeneration. Comparisons of the results from this study to other studies indicate that systems relying primarily on passive CDPF regeneration may have potential for significant PAH emissions reductions relative to systems that rely primarily on active CDPF regeneration.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Carbon-based pollutant emission factors for diesel vehicles (V1, V2, and V3) averaged over all test conditions. SVOCs characterize test sums of GC-MS identified species in the Q_f and PUF sampling arrays. OC and EC values were determined using Q_f only. Outliers (red circle), means (bold line), and median are shown. Box ends define the 25th and 75th percentiles; whiskers define the 10th and 90th percentiles. Note that the “SVOC” class sums include only GC-MS-identified compounds measured with Q_f -PUF array, underestimating the total SVOC emission contribution. Additionally, THC includes CH_4 and may include a fraction of the OC and SVOCs.

Figure 2. Means and ranges of SVOC class-based emissions sums by driving cycle, vehicle, and temperature. Lower (−6.7 °C) and higher (21.7 °C) temperature tests are indicated by triangle symbol direction. Lower seasonal temperatures equate to higher emissions. Ranges are indicated using error bars. To assist in across-vehicle comparisons, the gray reference lines are set to 538 µg/km, which is the mean SVOC class-based emissions sum.

Figure 3.

Multistudy comparison of particle-phase PAH emission factors from diesel trucks. Averages are used or calculated, and vehicles are sorted by size (engine displacement) if possible. Additionally, if required, emission factors using fuel weight were converted using the fuel density and economy described in the main text. The Supporting Information contains further details about each study, compound abbreviations, and references.

Table 1.

Particle-Phase OC-EC Emissions Factors (mg/km) Calculated from Thermal Optical Measurements^a

vehicle	temp (°C)	phase	N (OC/EC)	OC (mg/km)	EC (mg/km)	OC range (mg/km)	EC range (mg/km)
V1	21.7	CS	4/4	1.5 ± 0.28	1.48 ± 0.98	1.04–1.69	0.6–2.55
		WS-UDDS	4/4	0.32 ± 0.17	1.94 ± 2.14	0.17–0.55	0.78–5.14
	–6.7	CS	4/4	1.79 ± 0.62	2.01 ± 0.42	1.09–2.59	1.5–2.4
		WS-UDDS	3/4	0.09 ± 0.05	0.51 ± 0.11	0.05–0.15	0.41–0.61
V2	21.7	CS	2/1	0.32 ± 0.16	0.11	0.21–0.43	–
		WS-UDDS	1/1	0.29	0.02	–	–
	–6.7	CS	2/0	1.96 ± 0.02		1.94–1.97	–
		WS-UDDS	2/0	0.19 ± 0.06		0.15–0.23	–
V3	21.7	CS	4/2	8.13 ± 10.1	0.39 ± 0.08	1.13–23.1	0.33–0.44
	21.7	WS-UDDS	3/2	1.77 ± 0.53	0.30 ± 0.15	1.38–2.37	0.19–0.41

^aResults are reported as means and one standard deviation where applicable. OC values are substantially impacted by positive adsorption artifact (89% w/w). Values given in this table are specific to the Qf.

Table 2.

Mixed Effects Model Results by Compound Class and Driving Cycle

effect					
compound class	temp.	fuel	vehicle	cycle	vehicle test weight regeneration
Full Models (Includes Both CS and WS-UDDS)					
PAHs	0.2825	0.7628	0.0282	< 0.0001	0.9918
<i>n</i> -alkanes	0.0097	0.5395	0.0288	< 0.0001	0.3825
<i>b</i> -alkanes	0.1292	0.9869	0.7253	< 0.0001	0.8513
steranes/hopanes	0.0604	0.6222	0.0530	< 0.0001	0.3182
CS Only Models					
PAHs	0.0217	0.8691	0.1514	–	0.8157
<i>n</i> -alkanes	0.0088	0.7751	0.0002	–	0.0148
<i>b</i> -alkanes	0.2655	0.3117	0.7962	–	0.4582
steranes/hopanes	0.6749	0.2943	0.5781	–	0.3112
WS-UDDS Only Models					
PAHs	0.6946	0.7569	0.9378	–	0.7454
<i>n</i> -alkanes	0.0012	0.1461	0.0223	–	0.4505
<i>b</i> -alkanes	0.0889	0.1095	0.5209	–	0.4672
steranes/hopanes	0.1667	0.3463	0.4387	–	0.9085