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Total Particle Number Emissions from Modern Diesel, Natural Gas, and Hybrid Heavy-Duty Vehicles During On-Road Operation

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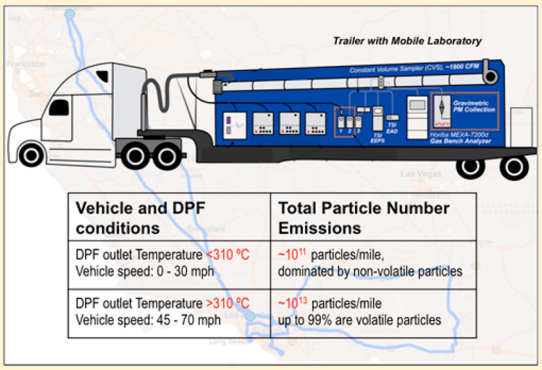
Supporting Information

ABSTRACT: Particle emissions from heavy-duty vehicles (HDVs) have significant environmental and public health impacts. This study measured total particle number emission factors (PNEFs) from six newly certified HDVs powered by diesel and compressed natural gas totaling over 6800 miles of on-road operation in California. Distance-, fuel- and work-based PNEFs were calculated for each vehicle. Distance-based PNEFs of vehicles equipped with original equipment manufacturer (OEM) diesel particulate filters (DPFs) in this study have decreased by 355−3200 times compared to a previous retrofit DPF dynamometer study. Fuel-based PNEFs were consistent with previous studies measuring plume exhaust in the ambient air. Meanwhile, on-road PNEF shows route and technology dependence. For vehicles with OEM DPFs and Selective Catalytic Reduction Systems, PNEFs under highway driving (i.e., 3.34×10^{12} to 2.29×10^{13} particles/mile) were larger than those measured on urban and drayage routes (i.e., 5.06×10^{11} to 1.31×10^{13} particles/mile). This is likely because a significant amount of nucleation mode volatile particles were formed when the DPF outlet temperature reached a critical value, usually over 310 °C, which was commonly achieved when vehicle speed sustained over 45 mph. A model year 2013 diesel HDV produced approximately 10 times higher PNEFs during DPF active regeneration events than nonactive regeneration.



1. INTRODUCTION

Exhaust from on-road heavy-duty vehicles (HDVs) has been identified as a major sources of air pollution.[1−4] Diesel HDVs emit substantial amounts of oxides of nitrogen (NOx) and particulate matter (PM). Recognizing the air quality and public health impacts of diesel HDVs emissions, the California Air Resources Board (CARB) and the U.S. Environmental Protection Agency (EPA) have adopted stringent certification standards for PM and NO_x. Beginning with model year (MY) 2007 and MY 2010 engines, the limits regulated by CARB are 0.01 g PM/bhp-hr and 0.2 g NOx/bhp-hr. CARB also adopted the Truck and Bus Regulation in 2008, which requires phase-out of older equipment and the adoption of MY 2010 or newer technology in several regions of the state by 2023.[5] Consequently, advanced aftertreatment technologies, such as diesel oxidation catalysts (DOC), diesel particle filters (DPF), and selective catalytic reduction (SCR) systems, have been widely used in on-road diesel HDVs.[6] These aftertreatment systems may reduce NOx and PM emissions by more than 90%, and under certain conditions by up to 99%.[3,7] The PM exhaust from DPF-equipped HDVs contains a large amount of nucleation mode particles (<30 nm) consisting of volatile material such as water, sulfate, and hydrocarbons, as well as the accumulation mode particles formed from combustion.[8]

Scientists and regulators have long known that PM is a mixture of different-sized particles. Within the PM category, ultrafine particles (UFPs) make up the smallest size fraction ($d \leq 100$ nm).[9−11] In the United States, PM is regulated on a mass basis as part of engine, vehicle, and ambient air quality standards. A small fraction of PM is attributed to UFPs, but when quantified on a number basis, UFPs may account for more than 90% of the total number of engine PM.[8] Both animal and human studies have provided evidence for respiratory and cardiovascular effects associated with exposure to UFPs.[12−14] Currently, there are no regulatory standards that directly control UFPs in the United States. U.S. EPA concluded that more research is needed to further investigate the role of UFPs

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Table 1. Heavy-Duty Test Engines, Emissions Information, And Manufacturer[a]

	vehicle 1	vehicle 2	vehicle 3	vehicle 4	vehicle 5	vehicle 6
manufacturer	OEM 1	OEM 1	OEM 1	OEM 2	OEM 3	OEM 3
model year	2007	2013	2013	2014	2013	2011
fuel type	diesel	diesel	CNG	diesel	diesel	hybrid diesel
displacement [L]	15.0	15.0	11.9	14.8	12.4	7.6
odometer [miles]	393 174	123 471	11 142	110 680	186 389	34 260
gross vehicle weight rating (GVWR) (lbs)	80 000	80 000	80 000	80 000	80 000	61 000
aftertreatment devices	DOC+DPF	DOC+DPF+SCR	TWC	DOC+DPF+SCR	DOC+DPF+SCR	DOC+DPF
PN measurement System	ejector dilutor	ejector dilutor	ejector dilutor	ejector dilutor/CVS	CVS	CVS
number of trips	19	21	11	14	8	15
total length of trips [minutes]	1508	2252	1057	1401	768	1275

[a]OEM = original equipment manufacturer.

on PM-mortality associations in its 2009 Integrated Science Assessment.[15] In recognition that UFPs may be associated with potential health impacts, U.S. EPA has encouraged conducting UFP measurements at near-road monitoring sites.[16]

Laboratory dynamometer emission tests[17−21] have evaluated the total particle number emissions (PN) from HDVs with and without aftertreatment devices. Previous on-road tests have measured the concentration of *solid* particles, which are defined as particles that remain in the aerosol phase after thermal treatment at around 300 °C with diameters between 23 nm to 2.5 μm, using the Particle Measurement Programme (PMP) method.[19,22] However, limited studies have examined *total* particle number emissions from HDVs driving on road, which are typically formed during dilution rather than combustion.[23−25] Therefore, the purpose of this study is to help improve the understanding of real-world total particle number emission patterns of various HDV technologies, which will also help to better understand the impacts of HDV on near-roadway UFP concentrations.[26−28]

In this paper, we present both total and solid particle number emissions measured during an on-road emissions study of six modern HDVs including engines fueled by diesel and natural gas. We recently reported that criteria emissions (i.e., CO, NO_x, PM, and total hydrocarbon) of several newly certified HDVs during on-road driving were influenced by route types; we also reported that the gravimetric PM emissions were at least two times below the mass-based certification standard.[29] Data reported in this paper further described particle number emission patterns of newly certified on-road HDVs. The effects of vehicle technology, emission control strategy, route classification, and other real-time parameters on particle number emissions are also presented.

2. MATERIALS AND METHODS

2.1. On-Road Emission Test. *2.1.1. Vehicles and Routes.* Six modern medium- or heavy- HDVs (vehicles, Table 1) were recruited in this study and each vehicle weight was 68 000 ± 1000 lbs. Vehicles were selected to represent four emission technology groups currently prevalent in California, including (1) one MY 2007 (Vehicle No. 1) diesel engine with no SCR and certified to a 2.3 g/bhp-hr NO_x family emission limit (FEL), (2) two MY 2013 (Nos. 2 and 5) and a MY 2014 (No. 4) diesel engines equipped with SCR, (3) one MY 2013 compressed natural gas (CNG) (No. 3) 12 L engine with a three-way catalyst (TWC) certified to the 0.2 g/bhp-hr NO_x standard, and (4) one hybrid diesel vehicle (No. 6) with a MY 2011 engine with no SCR and certified to a 0.47 g/bhp-hr NO_x FEL. All diesel vehicles were equipped with a DOC and a DPF. The numbering of vehicles follows the order of a previous paper from the same measurement project.[29]

Six route types (Supporting Information (SI) Figure S1) were included in this study to represent real-world driving conditions associated with freight operation in California:[29] (1) The Hill Climb Highway Route included driving through the pass on Hwy I-5 (i.e., the Grapevine) and Hwy I-15 (i.e., the Cajon Pass) to characterize emissions for freight moving into and out of the South Coast Air Basin; (2) Interstate Highway Route included driving at 60 mi/h or higher speeds on north−south corridors through the San Joaquin Valley on SR-99 and I-5, and on east−west corridors to the eastern California-Arizona border via SR-40 and I-10; (3) Regional Highway Route included driving at speeds commonly around 55 mi/h, but also had frequent slower, congested highway driving conditions; (4) Near-Dock Drayage Route was included to capture emissions associated with freight movement leaving the Ports of Long Beach and Los Angeles, which simulated the stop-and-go operations associated with cargo loading from ocean-going vessels followed by brief higher-speed driving onto local highways; (5) The Local Drayage Route simulated transport to regional rail yard in the City of Commerce near downtown Los Angeles, CA; and (6) Urban Arterial Route included stop-and-go driving with speeds frequently approaching 40 mile/h to simulate the "last-mile" delivery of goods to retail locations.

2.1.2. Instrumentation and Measurement Settings. In this study, all test vehicles pulled the West Virginia University's Transportation Emissions Measurement System (TEMS, SI Figure S2),[29] which was affixed to a flatbed trailer along with an on-board power generator. The TEMS housed a full scale constant volume sampling (CVS) and a suite of gaseous and particle emission measurement systems. Two dilution systems (SI Figure S2) were used for measuring total particle number concentrations in this study:

- A Dekati Ejector Dilutor (DI-1000, Dekati Ltd. Finland) was used to dilute raw exhaust at a fixed 8:1 dilution ratio at ambient air temperature. The diluted exhaust particle number concentrations were recorded by a water-based Condensation Particle Counter (CPC 3785, TSI Inc., St. Paul, MN) which detects particles between approximately 5 nm to 3 μm. The exhaust flow was measured using a high-speed exhaust flow meter (EFM-HS from Sensors Inc., Saline, MI).
- The CVS system was used for one standalone water-based CPC (CPC 3786 or 3788, TSI Inc., St. Paul., MN) which detects particles between approximately 2.5 nm to 3 μm. The CVS was operated at nominal 1800 cubic feet per minute (CFM), which resulted in an average dilution

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Table 2. Average Speed, Total Distance, And Distance-, Fuel- And Work-Based PNEFs by Vehicle and Technology Group[a]

	unit	route type	MY 2007 diesel (DOC+DPF)	MY 2011 hybrid diesel (DOC+DPF)	MY 2013—2014 diesel (DOC+DPF+SCR)			MY 2013 CNG (TWC)
vehicle number			Vehicle 1	[b] Vehicle 6	Vehicle 2	Vehicle 4	[b] Vehicle 5	[c] Vehicle 3
average speed	[mph]		42	22.9	30.9	27.7	24.5	28.1
particle number emission factor	[particles/ mile]	hill climb	5.10×10^{12}	5.61×10^{11}	1.81×10^{13}	2.19×10^{13}	2.29×10^{13}	8.65×10^{12}
		interstate	1.24×10^{12}	2.94×10^{11}	3.34×10^{12}	2.16×10^{13}	4.59×10^{12}	9.01×10^{12}
		local	N/A	3.80×10^{11}	3.40×10^{12}	1.06×10^{12}	5.74×10^{12}	1.26×10^{13}
		near dock	4.23×10^{12}	3.85×10^{11}	3.05×10^{12}	7.39×10^{11}	5.06×10^{11}	2.58×10^{13}
		regional	2.41×10^{12}	1.58×10^{12}	4.79×10^{12}	4.01×10^{12}	6.16×10^{12}	7.52×10^{12}
		urban	N/A	6.84×10^{11}	N/A	3.89×10^{12}	1.31×10^{13}	N/A
	[particles/ kg diesel equivalent]	hill climb	5.52×10^{13}	1.67×10^{12}	1.78×10^{14}	1.09×10^{14}	1.69×10^{13}	3.24×10^{14}
		interstate	1.65×10^{13}	2.83×10^{12}	1.06×10^{14}	1.14×10^{15}	8.90×10^{12}	3.38×10^{14}
		local	N/A	1.31×10^{12}	1.64×10^{14}	1.38×10^{13}	1.32×10^{15}	2.35×10^{14}
		near dock	1.23×10^{14}	2.54×10^{13}	6.31×10^{12}	5.90×10^{11}	6.80×10^{11}	5.54×10^{14}
		regional	6.15×10^{13}	3.50×10^{13}	5.71×10^{13}	1.21×10^{13}	3.80×10^{13}	1.59×10^{14}
		urban	N/A	8.99×10^{11}	N/A	4.77×10^{13}	2.07×10^{13}	N/A
	[particles/ bhp-hr]	hill climb	1.19×10^{12}	1.89×10^{11}	4.25×10^{12}	4.54×10^{12}	6.96×10^{12}	1.94×10^{12}
		interstate	6.80×10^{11}	9.99×10^{10}	1.03×10^{12}	2.44×10^{13}	5.75×10^{12}	3.18×10^{12}
		local	N/A	2.73×10^{11}	8.49×10^{11}	2.59×10^{11}	1.16×10^{12}	3.53×10^{12}
		near dock	1.29×10^{12}	1.21×10^{11}	7.49×10^{11}	1.72×10^{11}	9.64×10^{10}	8.01×10^{12}
		regional	8.26×10^{11}	1.07×10^{13}	1.09×10^{12}	1.45×10^{12}	7.01×10^{12}	2.61×10^{12}
		urban	N/A	1.78×10^{11}	N/A	7.90×10^{11}	3.01×10^{12}	N/A

[a]Due to the number of repeat trips of the various route types, standard deviations (SD) of route-specific PNEFs were only calculated for intestate highway and regional highway, and are reported in SI Table S1 [b]These data were generated by the CPC in the CVS Dilutor, while the others were from the CPC in ejector dilutor. [c]The unit of fuel-based PNEF in the CNG-fuel vehicle is (particles/kg diesel equivalent).

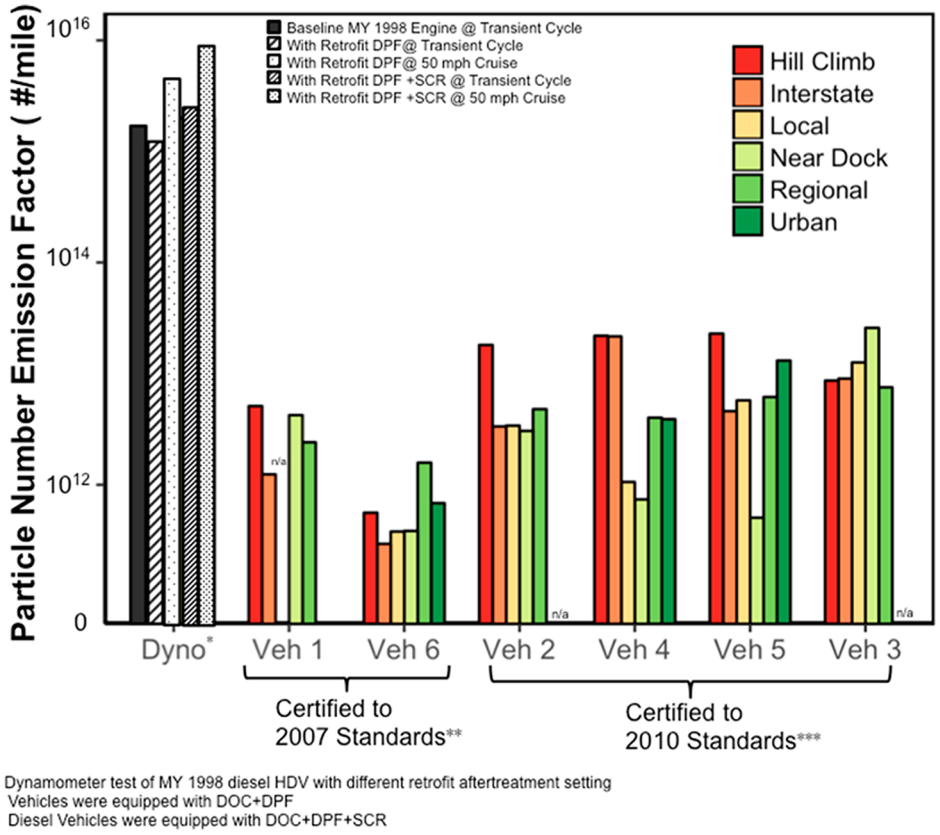

Figure 1. Route-specific PNEFs (in log scale) of MY 2007 standard diesel (Vehicle 1), MY 2011 hybrid diesel (Vehicle 6), MY 2013 diesel vehicles (Vehicles 2, 4, and 5), and MY 2013 CNG vehicle (Vehicle 3) compared to reference MY 1998 diesel vehicles in the transient and cruise at 50 mph cycles conducted by Herner et al.,.[18] Standard deviations are reported in SI Table S1.

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ratio of 22 for the entire study, with route-averages ranging from 16 to 42 times. The CVS operation temperature was 53.2 ± 16.3 °C in this study. No additional dilution was applied between the CVS and the CPC.

Particle number emission data from the CPC 3785 were available for four vehicles (i.e., Vehicle Nos. 1 through 4), while data from the CPC 3786/3788 were available for three vehicles (i.e., Nos. 4 through 6). Despite the differences in CPC cutoff size and sampling methodology, the two sampling systems reported study-average particle number emission factors (PNEFs) within 6% (i.e., $PNEF_{cvs}/PNEF_{eject}$ = 1.06, SI Figure S3). Thus, no corrections were made between the two sampling systems.

The volatility of particles was further investigated using a separate rotating disk thermal dilutor (model 379020A, TSI Inc., St. Paul, MN) coupled with a thermal conditioner (model 379030, TSI Inc., St. Paul, MN) located downstream of the CVS, and one CPC 3788 which detects particles between approximately 2.5 nm to 3 μm. The thermal dilutor temperature was set at up to 150 °C.

2.2. Data Processing and Analysis. Test-specific total particle number emissions (unit: particles/trip) were calculated based on measured particle number concentration (unit: particles/cm^3), exhaust flow rate (unit: L/s), and dilution ratio under standard conditions (273.15 K and 1 atm pressure). Distance-, fuel-, and work-based PNEFs were calculated by dividing particle number emissions with travel distance (unit: mile), cumulative fuel consumption (unit: kilogram), and cumulative work output (unit: bhp-hr), respectively. Distance-based real-time PNEFs were calculated based on real-time PN emission rates and real-time vehicle speed. The fuel rate of the CNG vehicle was converted to diesel equivalent (i.e., 1 kg CNG = 1.117 kg diesel).[30]

Several active regeneration events were observed during the on-road measurement based on the Boolean value from electronic control unit (ECU) broadcast and the exhaust temperature at DPF outlet. Since active regeneration events resulted in much greater amount of particles than the normal operation, such events identified by ECU was eliminated in the average PNEF analysis in Section 3.1. Data collected during regeneration were analyzed separately in Section 3.2 to investigate the impacts of DPF on particle number emissions after regeneration.

Previous studies have reported that particle renucleation can happen in the thermal dilution system.[31,32] We tried to eliminate this by maintaining higher dilution ratios and applying primary thermal dilution to the rotating disk dilutor, but renucleation still occurred occasionally. To remove renucleation data, one test of Vehicle 5 was used as the baseline during which both primary and secondary heating were turned off. During this test, the average $PNEF_{cvs}$ to $PNEF_{thermal}$ ratio was 0.6; therefore, any $PNEF_{cvs}/PNEF_{thermal}$ below 0.6 was regarded as particle renucleation and excluded from analysis.

3. RESULTS AND DISCUSSION

3.1. Average PNEFs for Different HDVs. *3.1.1. Route-Specific PNEFs.* PNEFs of six vehicles obtained based on 88 on-road tests are presented in Table 2 and Figure 1, separated by vehicle and route type. Distance-based PNEFs of diesel HDVs equipped with OEM DPFs and SCR systems (Vehicles 2, 4, and 5) were between 5.06×10^{11} and 2.29×10^{13} particles/mile depending on route classification; distance-based PNEFs of diesel HDVs equipped with OEM DPFs but no SCR systems (Vehicles 1 and 6) were between 2.94×10^{11} and 5.10×10^{12} particles/mile; and distance-based PNEFs of CNG HDV equipped with OEM TWC (Vehicle 3) were between 7.52×10^{12} and 2.58×10^{13} particles/mile. Figure 1 compares route-specific PNEFs of these newly certified vehicles with a previous study that tested a MY 1998 HDV on a chassis dynamometer.[18] Regardless of the difference due to on-road measurement and engine technologies, the newer OEMs had significantly lower PN emissions (i.e., approximately 355−3200 times lower) than the MY 1998 retrofit vehicles with and without aftertreatment. These measured reductions could be due to the lower engine-out PM and the use of ultralow sulfur diesel. Overall, Figure 1 demonstrates that total particle number emissions have substantially decreased, by over 2 orders of magnitude, as a cobenefit to mass reductions following the introduction of OEM DPFs.

Previously, we have reported that PM mass emissions measured from the MY 2013 CNG vehicle (Vehicle 3, approximately 0.002 g/bhp-hr) were about two times lower than the average of the three MY 2013−2014 diesel vehicles.[29] Vehicles fueled by CNG have low engine-out PM mass emissions by virtue of burning fuel composed of predominantly methane. Figure 1 indicated that the PN emissions from this CNG Vehicle were higher than all three diesel-fueled vehicles certified to the same emission standards in regional highway, local, and near-dock drayage routes. Similar results have been reported by bus emission studies,[33,34] although the CNG truck in this study was equipped with a large 11.9 L stoichiometric engine.

Figure 1 also shows that on-road PNEFs varied across route types. For all conventional diesel vehicles with or without SCR (Vehicle Nos. 1, 2, 4, and 5), the PNEFs during the Hill Climb Highway were the largest, compared to other route types of the same vehicle. The MY 2011 hybrid diesel vehicle (Vehicle 6) showed lower route-specific PNEFs than other vehicles, regardless of route type. Additional analysis of the hybridized drivetrain can further identify the mechanisms leading to the low PNEF for this vehicle. For the MY 2013 CNG vehicle (Vehicle 3), larger PNEF values occurred during near-dock drayage, local drayage, and urban routes where vehicle speeds were normally low (i.e., v_{mean} = 7, 14, and 16 mph, respectively). The PNEF route variations we observed also suggest that routine on-road testing for total PN concentration may be necessary to provide more precise ranges of emission as a function of route classification, vehicle technology, and the interaction of operating condition and technology.

The route-specific PNEFs of MY 2013−2014 diesel vehicles with SCR were higher than those of the MY 2007 diesel vehicle without SCR for three routes; and their route-specific PNEF ratio (i.e., average $PNEF_{MY\ 2013-2014}/PNEF_{MY2007}$ for each route type) was 4.17 ± 3.70. It is likely that the additional SCR aftertreatment module equipped on MY 2013−2014 vehicles further facilitated the sulfur oxidation of SO_2 into SO_3 and form nucleation-mode particles, and possibly contribute to total PNEF in the exhaust stream.[20,35] However, such an increase was not observed in near-dock drayage route, which may be due to lower exhaust temperatures during lower-load cycles.

With regard to fuel-based PN emissions, Preble and colleagues[25] reported that the on-road PNEF from HDVs equipped with SCR and DPF was 2.5×10^{15} particles/kg. Pirjola and colleagues[24] reported that the on-road PNEFs from

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CNG buses with TWC and diesel buses with SCR were 2.9 × 10^{13} and 7.01 × 10^{14} particles/kg, respectively. Both of these two studies directly measured the exhaust plume PN concentrations in the ambient air. The broad ranges of fleet-average emissions measured on the roadside were similar to those reported in our study, whereas this study measured real-time total PN emissions during a variety of on-road conditions, and highlighted the PN emissions during highway operations. Tracking new vehicles using controlled laboratory techniques as conducted in this study can be used to complement roadside plume sampling studies to determine and characterize trends in fleet-wide PN emissions.

It should be noted that the dilution ratio, dilution temperature and relative humidity could have effects on the nucleation mode particles.[36−38] The dilution systems used in this study, which have been widely used in the dynamometer tests, might result in less nucleation mode particle formation than ambient environment.[39] Nevertheless, our results were generally consistent with previous studies[23−25] measuring exhaust plume in the ambient air.

3.1.2. Total Particle Number versus Mass Emissions. Figure 2 shows the scatter plot of particle number and mass emission

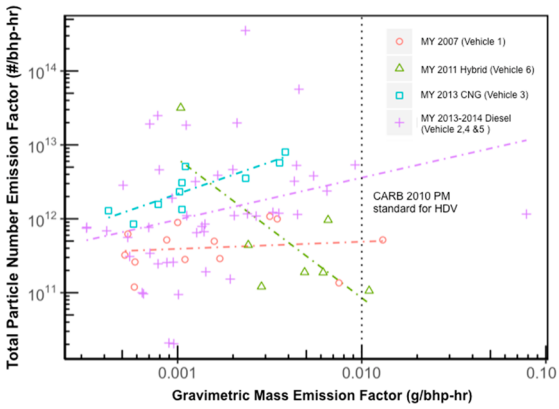

Figure 2. Brake-specific total particle number versus particle mass emission factors for each valid trip grouped by engine technology.

factors from four vehicle technology groups to illustrate trends related to PM mass and total number. Test-specific PM mass emission factors were measured gravimetrically from the same project and reported by Quiros et.al.[29] As seen in Figure 2, total PNEFs are highly variable within the range of PM mass emissions that fall below the certification standard. For instance, the MY 2011 hybrid diesel vehicle (Vehicle 6) with the lowest PNEF emitted relatively more PM mass; whereas the MY 2013 CNG vehicle (Vehicle 3) emitted the least PM mass, but more PN than other vehicles. The linear-regression curves show that there are no generalizable quantitative relationships between particle number and mass in these six newly certified HDVs. This is likely due to highly effective filtration efficiency of DPFs for controlling PM mass and removing solid PN, yet potentially promoting nucleation of semivolatile particles downstream. This will be discussed in the next few sections of this paper.

3.2. The Impact of Emission Control Devices on PNEF.

3.2.1. Exhaust Temperatures at DPF Outlet. Tailpipe exhaust temperature is typically affected by recent engine operation activity and other thermal influences. In the DPF, high temperature of exhaust gases can facilitate passive regeneration and nucleation, where accumulated soot is oxidized into mostly CO_2 and small-sized particles.[40,41]

Figure 3a, c, and e present the boxplots of real-time (i.e., second-by-second) distance-based PNEFs of three MY 2013−2014 diesel vehicles at different DPF aftertreatment temperature bins. The lower and upper hinges of the box are 25th and 75th percentile, respectively; lower whisker is the smallest observation ≥ (lower hinge -1.5 × IQR); upper whisker is the largest observation ≤ (upper hinge +1.5 × IQR); the black horizontal line is the median. Active regeneration events indicated by the ECU were removed from this plot to ensure that aftertreatment temperatures were achieved through combustion at the engine alone. Real-time PNEFs of the three MY 2013−2014 vehicles from all six route types were included in this analysis. The PNEFs increased sharply by 7.2−140 times when aftertreatment temperature reached a threshold temperature (i.e., 340 °C, 310 °C, and 330 °C for Vehicles 2, 4, and 5, respectively). It should be noted that Figure 3a and e were based on all test trips of Vehicles 2 and 5; while Figure 3c was based on 10 trips of Vehicle 4. We noticed substantially different DPF temperature patterns and PNEF levels in the other four Vehicle 4 test trips, and excluded them in Figure 3c. Those four tests and their PNEF patterns are discussed in detail in the SI (Figures S4, 5 and 6).

The precipitous emission rate increases that were dependent upon temperature thresholds between 310 and 340 °C could be attributed to nucleation mode volatile particle formation at high temperature. Figure 4 shows the relationship between mean nonvolatile PNEF (black, measured by a standalone CPC 3788 connected with a rotating disk dilutor) and volatile PNEF (gray, subtraction of total PNEF and nonvolatile PNEF) at every 5 °C exhaust temperature bins for Vehicles 2, 4, and 5. Particle renucleation periods were removed using the method described in Section 2.2. Nonvolatile particle loss could also occur in the thermodenuder;[41] however, this level of particle loss is not likely to affect the conclusion of Figure 4. The maximum nonvolatile PNEFs (unit: particles/mile) from this thermal-treated sampling system were 1.19 × 10^{13} at DPF outlet temperature 380 °C for Vehicle 2, 3.06 × 10^{13} at 330 °C for Vehicle 4, and 1.56 × 10^{13} at 255 °C for Vehicle 5. Figure 4 indicates that volatile particles were the dominant components of tailpipe particle number emissions from diesel vehicles with OEM DPF, and can be up to 99%, especially when the exhaust temperature reached 300 °C.

Our observed threshold temperature in Figure 3 (i.e., 310−340 °C) has been reported to be the temperature that sulfuric nucleation mode particles start formation.[18] Above these temperatures, volatile nucleation mode particles are formed by the sulfur oxidation of SO_2 into SO_3 and then SO_3 hydration to sulfate.[42−44] In addition to sulfur, hydrocarbons from the engine may also play a role in forming nucleation mode particles. Previous studies have reported that the condensation of semivolatile hydrocarbons during dilution would allow nuclei to grow.[45−48] Ion chromatography analyses of gravimetric PM filter samples collected during this study showed that a large percentage of PM emissions from the three MY 2013−2014 vehicles were organic compounds.[29] To conclude, after approaching and exceeding the defined exhaust temperature thresholds, both sulfate nucleation and semivolatile organic particle condensation are likely responsible for the observed PNEF increases.

High temperature in DPF has been previously reported to increase particle number emissions during dynamometer

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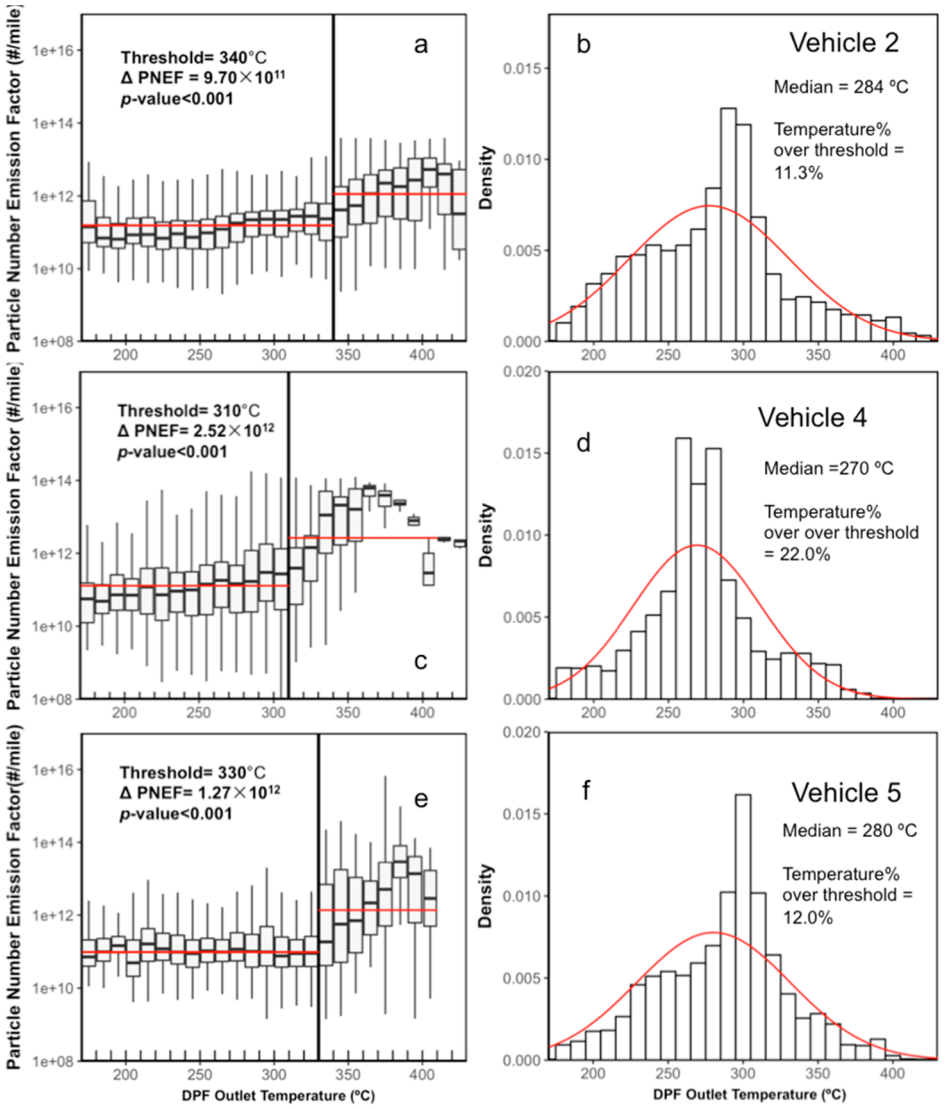

Figure 3. Boxplots of real-time distance-based PNEFs of three MY 2013−2014 diesel vehicles at different DPF aftertreatment temperature bins: (a) Vehicle 2; (c) Vehicle 4; (e) Vehicle 5, and histograms of aftertreatment temperature distribution of the corresponding vehicles: (b) Vehicle 2; (d) Vehicle 4; (f) Vehicle 5 with normal fit. Red horizontal lines in a, c, and e show median PNEFs of the specific temperature range, and black vertical lines denote the threshold temperatures. The lower and upper hinges of the box are 25th and 75th percentile, respectively; lower whisker is the smallest observation ≥ (lower hinge -1.5 × IQR); upper whisker is the largest observation ≤ (upper hinge +1.5 × IQR); the black horizontal line is the median.

tests.[18,49] Previously, Kittelson and colleagues hypothesized that high temperature at a catalyzed DPF system would increase sulfate formation, although their study did not observe the phenomenon due to the use of a relatively new DPF.[41] Giechaskiel and colleagues[50] presented the relationship between temperature and SO_2 to SO_3 conversion and reported the peak conversion occurred at approximately 400 °C. Our study of MY 2013−2014 vehicles observed a similar trend that, for all three vehicles, their total PNEFs start decreasing at 380−400 °C (Figure 3). It should be noted that emission control strategies for other pollutants require elevated aftertreatment temperatures (e.g., SCR catalyst light-off for reducing NO_x emissions by reaction with ammonia).

3.2.2. Active Regeneration of DPF. Active regeneration periodically removes accumulated soot from DPFs in order to maintain a clean substrate, minimize backpressure, maintain continuous operation of DPFs, and has been reported to be associated with brief increased particle mass[51] and number[52] emissions. In this study, two active regeneration events on a MY 2013 diesel vehicle equipped with DPF and SCR (Vehicle 5) were captured by the ECU broadcast, and confirmed by DPF outlet temperature data. Event 1 lasted 3 min and event 2 lasted 16 min. Real-time PNEFs in these two DPF active regeneration events were compared to the real-time emissions during normal operation (Figure 5), which is defined as having a wheel speed within the incidental speed range when no active DPF regeneration was triggered. Using this method, the average-speed difference between event 1 ($\overline{v}_{active}$) and its corresponding normal condition ($\overline{v}_{normal}$) was ≤10%; while for event 2, the speed difference, though large (i.e., $\overline{v}_{active}$ = 6 mph, $\overline{v}_{normal}$ = 19 mph), was not a confounding factor because both the average speeds of event 2 and its corresponding normal operation periods were low. Corresponding normal operation periods were further divided into two conditions based on DPF aftertreatment temperature (T_{AT}): (1) no regeneration (T_{AT} < 250 °C),[53] and (2) passive regeneration (T_{AT} > 250 °C).

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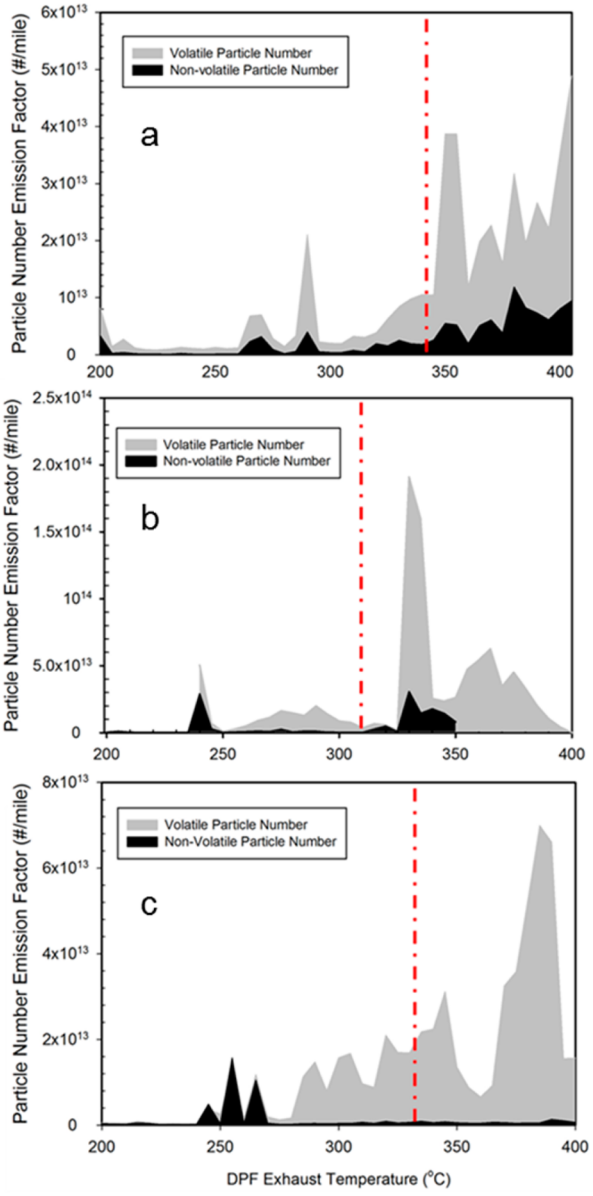
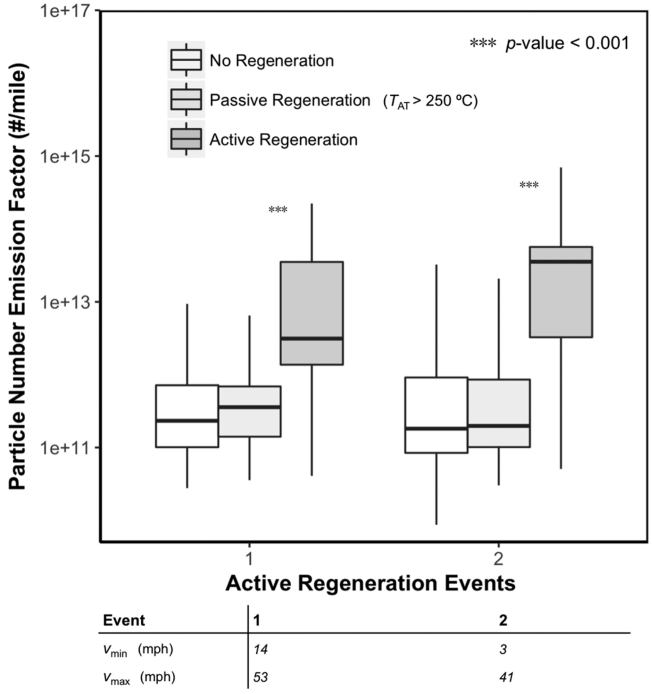


Figure 4. Non-volatile PNEF (black) and volatile PNEF (gray) distributions of three MY 2013−2014 vehicles when DPF exhaust temperature over 200 °C (a, Vehicle 2; b, Vehicle 4; c, Vehicle 5). Red lines denote the threshold temperature. A CPC 3788 linked with a rotating disk dilutor was used for solid particle number collection. For Vehicle 4, nonvolatile PNEFs above 350 °C were not shown because zero values were recorded. Periods with particle renucleation events were not included.

Figure 5 shows that the median PNEFs during active regeneration (i.e., 2.97×10^{12} and 3.54×10^{13} particles/mile for events 1 and 2, respectively) were 13 and 195 times higher than without regeneration, 8 and 179 times higher than passive regeneration, respectively (Mann−Whitney−Wilcoxon test p-values both < 0.001). These trends suggest that active regeneration could substantially increase total PNEFs, especially if a vehicle operates predominately at low speeds and relatively low particle number emission levels (event 2). The PNEF during active regeneration event 1 was lower than during event 2 (Mann−Whitney−Wilcoxon test p-values < 0.001). This indicates that at a higher vehicle speed where total PNEF is likely dominated by volatile particles, there would be



Event	1	2
v_{min} (mph)	14	3
v_{max} (mph)	53	41

Figure 5. Boxplots of real-time PNEFs of Vehicle 5 during two active regeneration events, compared with their corresponding passive regeneration and no regeneration status at the same vehicle speed range and route classification. T_{AT} is DPF aftertreatment temperature. The lower and upper hinges of the box are 25th and 75th percentile, respectively; lower whisker is the smallest observation ≥ (lower hinge −1.5 × IQR); upper whisker is the largest observation ≤ (upper hinge +1.5 × IQR); the black horizontal line is the median.

less dramatic increases in total PNEF during a brief active regeneration.

It is important to note that these emissions were measured from in-use rental trucks that have exceeded their degreening period by a few thousand miles, but do not represent the vast majority of trucks operating on highways that travel significantly beyond their regulatory useful life of 435 000 miles for heavy-HD on-road diesel engines. After several hundred thousand miles, emission control system deterioration may occur, which could change the frequency, magnitude, and other characteristics of PM emissions during DPF regeneration events. As of May 2015, there were an estimated 8% of diesel HDVs operating within California that ARB staff concluded had appreciably damaged DPFs.[7,25] The total and solid particle number emissions from these vehicles with damaged aftertreatment systems, and their relationships to PM mass emissions, to our knowledge, has yet to be rigorously quantified.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b06464.

Table for the standard deviations of particle number emission factors by vehicle and technology group; figures for testing route, instrumentation of the transportation emission measurement system, PNEF correlation between CPC_CVS and CPC_Ejector, trip-specific average PNEFs and DPF temperature differences in Vehicle 4, the impact of DPF temperatures (intake and

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outlet) on PNEF, and PNEF distributions of additional tests in Vehicle 4 (PDF)

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Notes

The authors declare no competing financial interest.

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