Particle Number and Size Distribution Emissions During Light-Duty Vehicle Cold Start Using the Total On-Board Tailpipe Emissions Measurement System

Paper No. 10-3038

Submission date: November 13, 2009
Number of Tables and Figures: 6
Total Word Count: 7476 (including 250 words for each Figure/Table)

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ABSTRACT

Vehicle emissions during cold start are known to be significantly higher than after optimal vehicle operating temperatures are reached. There is limited data however, on particle number and size distributions during cold start. Cold start tailpipe emissions from a 1999 Toyota Sienna minivan were quantified at ambient temperatures between 20˚C and 37˚C using a novel system (Total On-board Tailpipe Emissions Measurement System (TOTEMS); [see [1]]) assembled to quantify the full suite of exhaust emissions from light-duty vehicles. TOTEMS particle number distributions were measured from 5.6–562 nanometers using an Engine Exhaust Particle Sizer (EEPS) and total 3–3000 nanometer particle counts were measured using an Ultrafine Condensation Particle Counter (UCPC) with 1-second temporal resolution during cold start and on-road driving.

Second-by-second particle number distributions from 5 cold start emissions tests showed similar particle emissions patterns, allowing for 3 different cold start Phases to be identified based on particle number emissions behavior. Cold start duration ranged from 165 to 230 seconds and increased with decreasing ambient temperature. Different particle sizes during each Phase were emitted for different lengths of time, with the most abundant particles in the nanoparticle (diameter< 50 nm) range. The mean particle number distributions showed more than 99% of total particle number below 100 nanometers. Concentrations of ultrafine particles (<100 nanometers) during cold start were at least 10–100 times (EEPS), and as much as 1000 times (UCPC) above hot-stabilized idle emissions. Observations also suggest the presence of tiny particles below 6 nanometers during cold start.

INTRODUCTION

Recent evidence shows a strong relationship between fine particulate matter exposure and increased rates of lung diseases, cardiopulmonary diseases and mortality [2-5], as well as decreased lung development in children [6]. Vehicles are a major source of fine (particle diameter Dp< 2.5 micrometers), ultrafine (Dp< 100nm) and nanoparticles (Dp< 50nm). However, vehicle emissions tests, typically performed under idealized lab conditions, are not wholly representative of the variability and emissions levels associated with real-world vehicle operating conditions. This study is part of a larger project initiated to better understand emissions from vehicles under real-world, on-road driving conditions. The larger project (see [1] for more detailed description) is unique because total gas (28 species) and particulate (number distribution) tailpipe emissions are being collected for light-duty gasoline vehicles operating on a specified driving route in Vermont over four seasons of sampling. Here, 1-second data on particle size distributions from 5.6 to 562 nanometers and total particle number from 3-3000 nanometers collected from a single vehicle are examined to quantify particle number emissions behavior during cold start and warm-up route driving after engine off times greater than 12 hours. A 12-hour engine off time is sufficient to cool the engine and catalyst to ambient temperature [7, 8].

Cold start particle number emissions are significantly higher than emissions after a light-duty vehicle has warmed up to its normal operating temperature [9]. However, little real-world data exists on particle number distributions during cold start. Extensive studies have been conducted to quantify cold start gas-phase emissions [8, 10], but these studies are typically, though not always, limited to the criteria pollutants and lack high temporal resolution data for the full particle size distribution, often times focusing on only gases or particle mass. Furthermore, data on particle number most often lacks high temporal resolution for the entire distribution. When operating efficiently, the three-way catalytic converter has been found to remove 75% of hydrocarbon particle precursors under low speed and load operating conditions [9]. For the EPA FTP75 drive cycle, cold start produced more than 80% of the total hydrocarbon gaseous emissions [11], which suggests possible increases may be expected for cold start particle number emissions due to gas-to-particle nucleation upon exhaust cooling. Generally, peak particle emissions also tracked peak emissions of CO, NOx and hydrocarbons [9]. Understanding the magnitude of these cold start emissions is important because many trips – especially in urban areas – are short and never allow the vehicle to reach normal operating temperatures [10]. Furthermore, most trips begin in urban environments, resulting in significantly higher real-world emissions than predicted by existing models.

Previous studies have attempted to quantify the cold start size distribution and composition of particle number emissions from light-duty vehicles. Using a direct injection gasoline engine and Cambustion's differential mobility analyzer, particle number emissions were found to decrease over time during engine warm-up, often with particle size decreasing as well [12]. One study noted particles from gasoline engines are primarily in the 7 to 55 nm range during cold start [13]. It was found that only 29 percent of particles were in the solid phase: elemental carbon between 5 and 10 nm and carbonaceous particles in the 30 – 80 nm range [12], meaning substantial nucleation occurred. Now widely accepted, the low concentration of larger solid particles favors the formation of nuclei mode (diameter< 30 nm) particles [14] due to the small surface area available for gas-to-particle condensation. Also, many studies have focused more on diesel engines because they traditionally have had higher emissions rates, but diesel

vehicles have lower cold start emissions than gasoline vehicles [15, 16]. It is important to note that in all previous studies, the particle size range of the instruments used did not capture the whole particulate emissions size range, meaning a significant number of particles may not have been quantified.

Decreases in ambient air temperature have been linked to increases in exhaust emissions that are an order of magnitude or more above hot-stabilized emissions [15, 17-19]. Ambient temperatures between -20˚C and +22˚C had a significant effect on criteria pollutants, including NOx, CO, HC, and particle mass [19], although the reported effects on particle mass are inconsistent [15, 19]. One group documented hydrocarbon emissions were 26 grams per start higher at -20˚C than at +23˚C [16] Another group reported hydrocarbon emissions were reduced by a factor of 4 during cold starts when ambient temperature rose from -2˚C to 32˚C [18].These changes in hydrocarbon emissions could have a similar effect on nuclei mode particles due to the relationship between hydrocarbon gas emissions and particle nucleation. Another group found similar results, with cold start emissions many times (and for some pollutants, order of magnitude) higher than hot operation, with this effect magnified as ambient temperature decreased [19]. Reported particle mass increased by a factor of 19 when cold start temperature was decreased from 22˚C to -7˚C [19]. A more recent study showed that particle mass was less influenced by ambient temperature than the gaseous criteria pollutants [15]. However, this result may have no relation to number emissions as particle number and mass seem to have little correlation [20]. Mass is often times reported because current regulations are mass-based (PM10 and PM2.5), but particle size and number have the greatest effect on human health. Therefore, this study focused on particle number from 3 to 3000 nanometers and quantified the distribution from 5.6 to 562 nanometers. Most particles measured in this study – nearly 100% – were below 300 nanometers in aerodynamic diameter.

METHODOLOGY

This section describes the vehicle and its operation during cold start tests, the Total On-Board Tailpipe Emissions Measurement System (TOTEMS) instrumentation and protocols relevant to this study and laboratory instrument validation test procedures. All data for this study was collected with a minimum temporal resolution of 1-second.

Test Vehicle and Emissions Data Collection

Individual emissions tests consisted of a single driver operating the vehicle under real-world driving conditions over a specified sequence of startup operations and a warm-up driving route in Burlington, Vermont. One driver was used throughout the testing to minimize inconsistencies resulting from driver behavior. Prior to starting the vehicle, a series of quality assurance/quality control (QA/QC) measurements and operations were performed in order to collect accurate instrument and vehicle baseline data for each run. These QA/QC procedures included 3-hour particle instrument warm-up, collection of instrument blank data, collection of exhaust pipe tunnel blank data and synchronization of all instrument computer clocks via GPS software.

A gasoline fueled 1999 Toyota Sienna minivan with a V-6, 194 horsepower, 3.0 liter engine and a 4-speed automatic transmission with LEV 1 emissions certification was used for all tests. At the time of testing, the minivan odometer ranged between 148,424 and 148,702 miles.

Although an older vehicle was tested here, a 2005 study reported an 8.9 year median age of passenger cars. This was up from a median of 6.5 years in 1990. Furthermore, between 1990 and 2005, the median age of vehicles trended steadily up year-to-year, representing a sustained interest in emissions from these older vehicles [21]. After completion of the blanks and determination that all instrumentation was functioning properly, the test vehicle's engine was started. The minivan then idled in Park for a period of time prior to shifting into Drive and traveling a 0.8 mile 'warm-up' route to a gas station. Three traffic signals and two stop signs were encountered along the this route. For this study, data are presented from engine start to engine stop at the gas station.

This activity was more than adequate for complete warm-up during the spring season data collection reported here. During future winter months testing, an additional 2.5 mile urban section with steep hills will be utilized to ensure complete engine warm-up prior to driving the full route.

Total On-Board Tailpipe Emissions Measurement System (TOTEMS)

As described in more detail elsewhere [1], a suite of 20 instruments and accompanying data acquisition were assembled to collect second-by-second vehicle operation and tailpipe emissions data as test vehicles operate in the real-world. This package, TOTEMS, collects emissions data on particle number, particle number distribution as well as 28 gas species. Here, only the instrumentation and methodology relevant to particle emissions and characterization of cold start vehicle behavior are described. An on-board battery system powered all instruments without drawing electrical power from the test vehicle. An automatic transfer switch was used to transfer on-board instrumentation from grid to battery power without shutting the instruments down, saving battery power while allowing adequate instrument warm-up.

Relative humidity and ambient temperature were monitored both in and outside the vehicle using identical HOBOware pro v2 sensors. An AutoEnginuity ST01 ScanTool collected 4 engine parameters; engine load, vehicle speed, mass air flow and engine RPM. Data acquisition cards were used to collect data for the following instruments via a Labview 7.0 interface: a type J thermocouple to monitor exhaust temperature at the end of the tailpipe, type T thermocouples to monitor temperature at the end of the heated line and the inlet of the emissions instruments, four differential pressure transducers to quantify exhaust flowrate and four parameters monitoring the exhaust dilution system for particle measurements. The dilution system for particle measurement included two separate components – the Matter Engineering MD19-2E Rotating Disk Mini-diluter and the TSI Air Supply Evaporation Tube (ASET 15-1) – designed to work together providing first stage (MD19-2E) and second stage (ASET 15-1) dilution in one self-contained device. A total dilution ratio of 1:120 (raw exhaust : HEPA filtered dilution air) was used throughout emissions testing.

Exhaust was transferred via a heated line from the tailpipe to the particle dilution system. Particle number emissions were quantified with two TSI, Inc. instruments: a Model 3090 Engine Exhaust Particle Sizer Spectrometer (EEPS) and a Model 3025A Ultrafine Condensation Particle Counter (UCPC). The EEPS counts (± 20% accuracy) and sizes (± 10% accuracy) particles across 32 different size ranges from 5.6 to 562 nanometers. The midpoint of each EEPS size range is the reported particle size based on aerodynamic diameter. The EEPS records particle number distribution data at a rate of 10 Hertz, but values were aggregated to a 1 Hertz rate. The 1 Hertz measurements are the discrete average of all measurements within a given second and

were recorded to the on-board emissions PC using TSI EEPS version 3.1.0 software. The UCPC counts particles from 3–3000 nanometers with a reported detection efficiency of 50% for 3 nanometer particles and 90% for particles greater than 5 nanometers. The total particle number concentration from the UCPC was recorded to the on-board emissions PC using Aerosol Instrument Manager Software (version 8.1.0).

Anti-vibration platforms were constructed for both the EEPS and UCPC to minimize inaccuracy and instrument error due to noise resulting from vibration while driving. The instrument platform for the UCPC uses 6 natural rubber mounts, and because the UCPC is influenced little by vibrations, these mounts serve to help minimize instrument malfunctions that could result from being jostled. The EEPS is mounted on 10 silicone gel type mounts, which reduced electrometer noise caused by driving by 64%.

The TOTEMS emissions measurement setup pulls engine exhaust from the tailpipe adapter through the10-foot, 3/8-inch ID heated line set to 191°C at an exhaust sample flowrate of 13 liters/min (Lpm). The heated line (Atmoseal model IGH-120-S-6/X-G13) is lined with smooth, flexible stainless steel pipe to minimize particle losses. At the end of the heated line is a 4-way, stainless steel Swagelok fitting that splits the flow of undiluted exhaust to the emissions instruments: 12 Lpm to the FTIR for gas analysis and 1.0 Lpm to the dilution system for particle measurements. From the dilution system, particles are transported to the EEPS and UCPC via 42 inches of 1/4-inch ID conductive silicone tubing. The flow is split, first to the EEPS, then to the UCPC using 2 stainless steel Swagelok fittings. Data is collected on a Dell OptiPlex GX620 desktop "Emissions PC" outfitted with two National Instruments model 6024E data acquisition cards and 5 serial ports.

EEPS and UCPC particle number emissions data were plotted for analysis using MATLAB version R2008b . Instrument blanks were used in this program to calculate the lower detectable particle concentration limit for each EEPS size range. Because the EEPS operates on electrical principles, it is sensitive to noise. Therefore, emissions values less than three times the standard deviation of the instrument blank data were considered below detection and omitted from the analyses. Also, using the pre-run instrument blank for each run, the mean noise values for each of the 32 EEPS size ranges were calculated individually and subtracted from the EEPS concentrations. Noise quantification for the UCPC was unnecessary as it was not sensitive to noise .

Data Alignment for Instrument and Exhaust Flow Lags

All particulate number emissions data were aligned to the scantool data based on the "ignition on" point for reference. At this point, engine RPM changed from 0 (engine off) to the peak reading (ignition) in one recorded second of data. The EEPS and UCPC behaved similarly, where the concentrations jumped from background to maximum concentration in one recorded second. Therefore, the scantool and particle emissions data were time-aligned using the last point of 0 RPM and the last point for background particulates. No lag was assumed for exhaust temperature because it appeared to be sufficiently small (<0.5 seconds) to not affect data alignment.

Particle Number Instrument Comparison: Laboratory Tests

A comprehensive comparison between the EEPS and UCPC was conducted. From this comparison, it was determined that both particle instruments are necessary for both quality assurance and to fully understand the second-by-second tailpipe particle emissions data.

Laboratory tests were performed by generating constant concentrations (~3.5 x10^4 #/cm^3) and varied concentrations (5.4 x10^3 to 8.9 x10^4 #/cm^3) of 10–100 nanometer particles, ensuring no detection bias towards either particle instrument (The EEPS and UCPC have overlapping, but not identical, particle size measurement ranges). Two types of particles were generated: a sodium chloride solution with a concentration of 0.2 g/L in deionized water and a 10:1000 (v/v) emery oil : isopropyl alcohol solution. Both solutions were atomized using a TSI model 9302 atomizer and particle-free compressed air. From the atomizer, the NaCl aerosol passed through silica gel desiccant for drying. The desiccant was bypassed when using emery oil (drying not needed). Aerosol was transferred to the EEPS and UCPC through the dilution system (set to 80˚C) using the same setup described for emissions testing. A total of 28 tests using sodium chloride particles and 14 tests using oil particles were conducted. Particle type (emery oil versus sodium chloride) did not influence the total particle concentrations from either instrument.

No bias in aerosol flow to either instrument was seen for the setup described above. There was a detectable bias in total concentrations, however, because the EEPS has a much higher maximum concentration limit, which is dependent on the individual size ranges [10^7 #/cm^3 in size range 1 to 10^5 #/cm^3 in size range 32] and the UCPC frequently reached its maximum concentration [10^5 #/cm^3] during the cold start. The in-lab comparison confirmed that both instruments have response times to enable analysis of cold start data and that the EEPS instrument is capable of generating reproducible total particle concentrations.

The overall average percent difference between the EEPS and UCPC particle number concentrations was between 19% and 20%, with UCPC always higher. This was consistent regardless of particle composition and for both stable and varying particle concentrations. The instrument percent difference, which varied 5% to 25% during individual tests, results from the different measuring techniques of the two instruments and appears to be a consequence of the EEPS under-predicting concentration changes for the tested number concentrations

Constant and transient dilution factor tests were performed to compare the instruments. The potentiometer on the ASET, which controls stage-2 dilution, was always kept at 7.1. Constant concentration tests were performed step-wise by adjusting the MD19-2E potentiometer in increments of 10, beginning at 10% and ending at 100%. The potentiometer was kept at each increment for a minimum of 60 seconds. Transient tests were performed by rapidly changing the MD19-2E potentiometer to random values and was kept between 10 and 100%. FIGURE 1 shows typical results from both steady and transient concentrations.

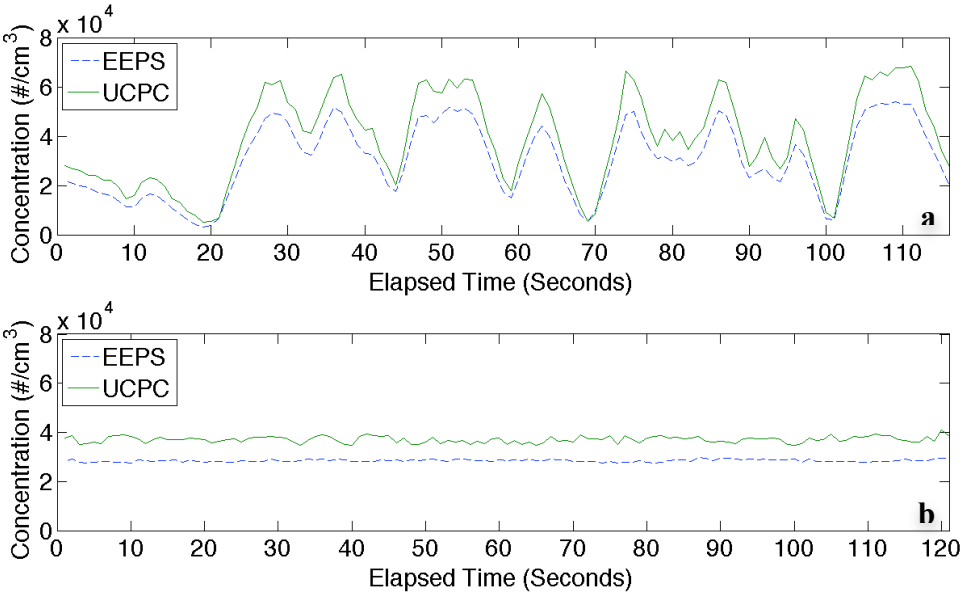

FIGURE 1 Tests to compare the EEPS and UCPC under a) transient concentrations and b) constant concentration of laboratory-generated sodium chloride particles.

The instrument response of both the EEPS and UCPC were very consistent. Comparing the EEPS to the UCPC, the two instruments track very well together with nearly identical response curves. From FIGURE 1, the EEPS seems to under-predict concentration changes when compared to the UCPC for these laboratory test conditions. However, neither instrument appears to show a hysteresis effect. Under low concentrations (<5,000 particles per cm^3), the EEPS was much more variable, and therefore less accurate, due to electrometer noise. Emissions concentrations below 5000 particles per cm^3 should therefore be interpreted with caution. The EEPS and UCPC had a consistent concentration difference, which is evident from the lines appearing to get closer under lower concentrations and farther apart under higher concentrations. The average percent difference between the two instruments remains near 19%.

The UCPC max concentration limit of 99,900 is a major drawback when looking at engine emissions. Even with a high dilution ratio (1:120), the UCPC reached its maximum limit during much of the cold start. Using a higher dilution ratio will cause lower concentrations to be undetected by the EEPS. For these reasons, TOTEMS employs both particle instruments.

Defining Cold Starts

Although previous studies used catalyst light-off [18] or engine coolant temperature [12] to characterize cold starts, this study used particle number emissions behavior because of patterns observed in the data. Total cold start duration was characterized by 3 separate Phases based on significant changes in particulate emissions behavior. FIGURE 2 shows these different Phases, and the end of each phase is labeled (note the flat tops to the UCPC curve in FIGURE 2 resulted when maximum concentration limits were reached).

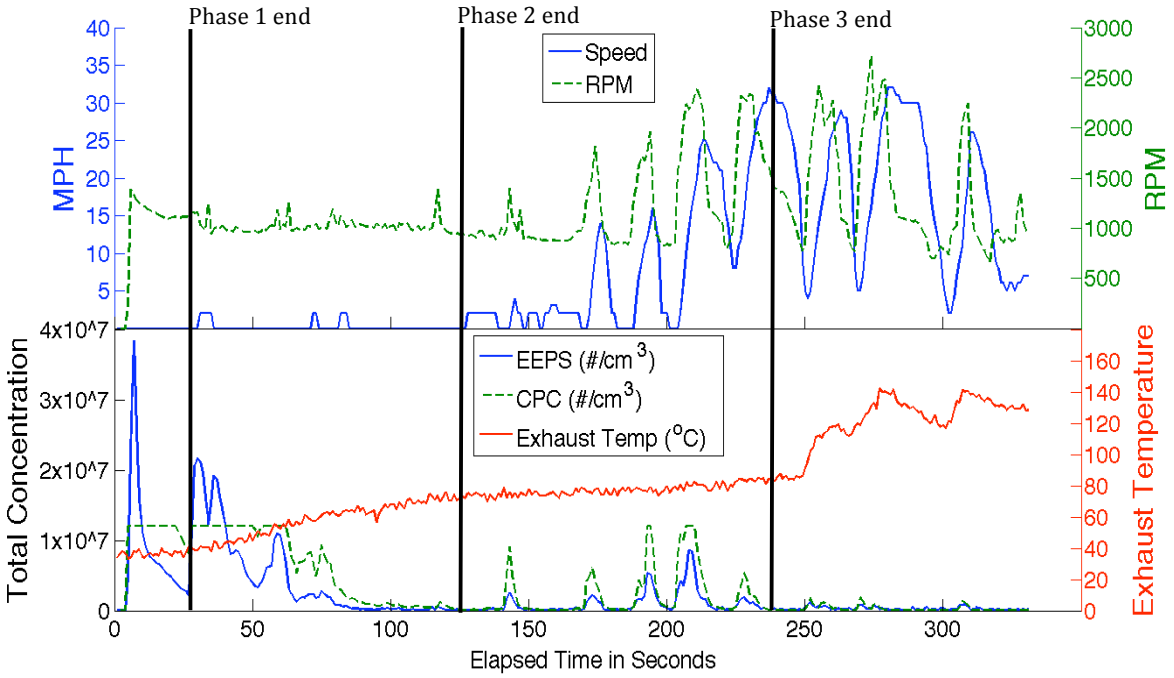

FIGURE 2 Total concentrations from the EEPS and UCPC during run 1, corrected for dilution (bottom panel). RPM, speed and exhaust temperature are included for reference. Three cold start phases are shown by vertical lines. Concentrations are in #/cm³ and exhaust temperature is °C.

Cold start emissions were defined to begin when the particle number concentration increased to 3 times greater than the tunnel blank background of 500 to 800 particles/cm^3 [EEPS] and 70 to 100 particles/cm^3 [UCPC] (FIGURE 2 at 4-seconds). Note that reported particle number concentrations were not corrected for losses in the transfer lines. Phase 1 of the cold starts occurred when the car was in park and the engine running; it is characterized by the highest total particle number emissions of each run. Phase 1 began at engine-on and depended on when the driver put the car in gear. Although not ideal for analysis, this is consistent with the variability associated with real-world driving.

Phase 2 of the cold start was characterized by vehicle operation – starting when the automatic transmission was shifted to "Drive" (FIGURE 2 at 27-seconds). The end of Phase 2 was defined by emissions behavior – when Phase 2 idle particle concentrations dropped to levels comparable to "hot-stabilized" idle concentrations. The vehicle was moving during Phase 2, but predominately at idle-creep (<5 miles per hour) in a parking lot setting.

Phase 3 was characterized by a particle emissions pattern showing elevated emissions during acceleration events (FIGURE 2 127-237 seconds). The end of Phase 3 occurred when particle concentrations satisfied three criteria: (1) total particle number concentrations were comparable to hot-stabilized idle (equivalent to ~2 times above EEPS instrument blank [or 1400 #/cm^3] and ~250 times above UCPC instrument blank [or 100 #/cm^3], prior to accounting for dilution), where hot-stabilized idle concentrations were determined from traffic signal idling data collected later in the full driving route; (2) the smallest particles (5.6 to ~10 nm) in the measured EEPS distribution are no longer detectable; and (3) there were no longer significant increases in total number concentration as a result of RPM increases. Therefore, Phase 1 was driver behavior dependent, while Phases 2 and 3 were characterized by particle number emissions patterns.

EXPERIMENTAL RESULTS

Cold Start Emissions Analysis

The broader measuring range of the UCPC at both the large and small particle diameter ends (3 – 3000 nm [UCPC] vs. 6 – 560 nm [EEPS]) seems to indicate there are large numbers of particles formed during cold start that are outside the EEPS's measurement range during cold start. This observation is drawn from the significant differences in particle number concentrations (at least a factor of 3) that are seen only during the cold start (FIGURE 2) but were not present while driving after the catalyst is hot or in the lab under controlled particle generation. The difference can most likely be attributed to the nucleation of small particles below the EEPS lower diameter limit of 5.6 nm, during engine start. Significant particle numbers larger than 562 nanometers (EEPS maximum size) are unlikely in vehicle exhaust.

Cold Start Total Particle Number Emissions Data

Cold start data were collected on five separate days with the ambient temperature range from 20˚C to 37˚C for all starts. TABLE 1 summarizes the cold start data.

TABLE 1 Summary of Cold Start Emissions Data*

Run No.	Cold Start Duration (seconds)	EEPS Total Cold Start (#/cm^3)	CPC Total Cold Start (#/cm^3)	Ave T (˚C)	Ave RH (%)
1	230	7.11E+08	1.09E+09 **	20	28
2	165	3.50E+08	6.68E+08 **	37	23
3	191	7.23E+08	Instrument Malfunction	25	42
4	201	5.13E+08	8.35E+08 **	33	39
5	199	4.97E+08	7.96E+08 **	32	37

**** EEPS and UCPC data are the sum of particle number concentrations for the full cold start duration (Phases 1-3 inclusive).***

***** Indicates the instrument reached its maximum concentration limit (9.99x10^4) during the cold start period, meaning data is biased low.***

The actual total concentration difference between the EEPS and UCPC was even greater than documented in TABLE 1 because the UCPC reached its upper measurement range (9.99x10^4) for extended periods during the cold start, whereas the EEPS never reached its maximum limits (Refer to FIGURE 2). Cold start duration presented in TABLE 1 was determined from engine-on to the end of Phase 3.

Cold Start Phases: Duration and Particle Modes

FIGURE 3 shows the contour plot of EEPS number distributions over the full duration of one cold start with corresponding vehicle speed, RPM and exhaust temperature. Data is presented as dN/dlogDp, which denotes the particle number concentration normalized to the individual diameter range on a given EEPS channel (or size bin), (i.e. channel 1 is from 5.6 to 6.4 nm but channel 32 is from 487 to 562 nm) Cold start Phase 3 clearly shows particle concentrations

spiking with increased RPM – which, in this case, indicates acceleration – for all particle sizes below 154 nm. This effect diminished as exhaust temperature gradually increased (see FIGURE 2, 140 to 237 seconds, for example).

Phase 1 lasted for 15 to 35 seconds and the highest measured concentrations were for particles between 8 and 60 nanometers (nm). Particles larger than 20 nm diameter had extremely high concentrations for only about 5 seconds after engine start before dropping significantly; this behavior can most likely be attributed to enrichment at engine start [9]. Even though the larger (>20 nm) particle concentrations dropped quickly in phase 1, their concentrations remained as much as 100 times higher than hot-stabilized idle for the duration of Phase 1.

Phase 2 lasted 60 to 95 seconds with significant increases in number concentrations for particles 5.6 to 200 nm in diameter. The highest concentrations, however, occurred for 10 to 30 nm particles and were 2 orders of magnitude above hot-stabilized idle concentrations. Increases in RPM, which indicate vehicle acceleration, during Phase 2 resulted in significant particle concentration – and subsequently emission rate – increases with particle diameter centered around 10 nm.

Phase 3 had variable particle number emissions that depended on driver behavior in urban traffic and lasted for 90 to 140 seconds. During Phase 3, when at idle (~700 RPM), the concentrations remained comparable to hot-stabilized idle concentrations. When RPM increased, which again indicates acceleration, 6 to ~154 nm particle concentrations increased with the highest concentrations at 10 and 30 nm. This is largely because the catalyst is unable to efficiently remove particle precursor vapors during Phase 3 due to the catalyst being below it's optimal operating temperature and decreased residence time. The particle number increase for sizes between 6 and ~154 nm occurred even under engine loads of 30% to 40% and acceleration of 2 to 3 mph/sec. The emission of Phase 3 particles can likely be attributed to enrichment during acceleration (>30 nm) events [9], mechanical release of particles (>30 nm) and increased flowrates (<30 nm). As exhaust flowrate increases, the catalytic converter becomes more inefficient due to reaction kinetics and shorter residence time in the catalyst. Although acceleration rates during the warm-up driving were relatively low (2 to 3 mph/sec), even small increases in flowrate may be enough to cause significant increases in particulate number emissions if the catalytic converter is not operating at its optimal level. This may therefore indicate a gradual increase in the efficiency of the catalyst relative to its temperature until the optimal temperature is reached. The larger particles (>60 nm) observed throughout the cold start may, in part, be attributed to re-entrainment from the mechanical release of solid particles from the exhaust system caused by increased flowrates. At the end of Phase 3 (which is also the end of the cold start at 237 seconds on FIGURE 3), the smallest particles measured by the EEPS (5.6 to ~10 nm) are no longer detectable or have very low concentrations (see FIGURE 3, 237 to 330 seconds), indicating the catalyst is efficiently removing compounds that potentially nucleate to particles.

As expected, the highest particle number concentrations occurred for particles in the nanoparticle (Dp<50 nm) range, which accounted for over 97% of the particles over the entire cold start (Phases 1-3).

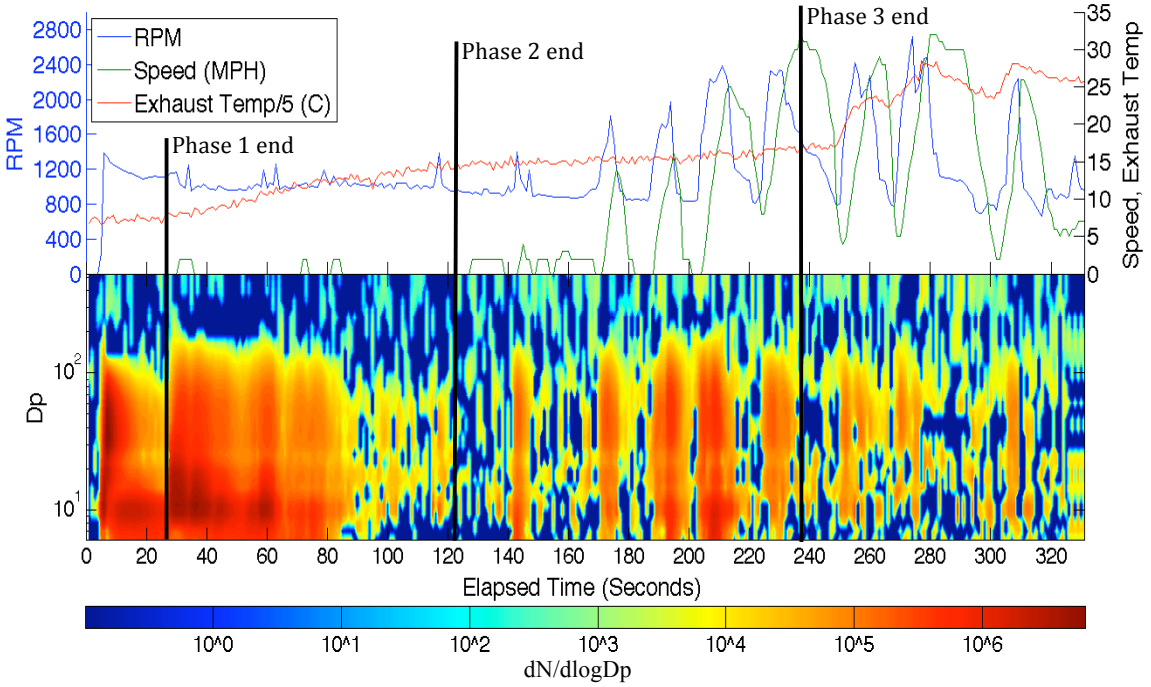

FIGURE 3 Contour plot of particle number distribution (bottom) over first 330 sec of Run 1 test period. Upper plot is time-aligned data on engine speed, vehicle speed and exhaust temperature. Exhaust temperature was divided by 5 to achieve same scale as vehicle speed. Engine on at 4 seconds, vehicle in gear at 27 seconds and moved only at idle-creep speed out of parking area. Vehicle accelerated onto Colchester Avenue at 141 seconds.

Mean Particle Size Distribution

EEPS data for each phase of the cold start over the 5 runs were averaged to evaluate changes in particle distribution over time after engine ignition. The particle number distributions changed consistently between phases of the cold start (FIGURE 4), but the particle diameter of the distribution "modes" was consistent run-to-run. The "modes" are the particle diameters of the distribution's peaks. Modes are typically assigned as sequential numbers based on particle diameter (x-axis), not the concentration (y-axis). In Figure 4, mode 1 (10 nm) had the highest concentration, mode 2 (18 nm) had the lowest concentration, and mode 3 (50 nm) was intermediate in concentration.

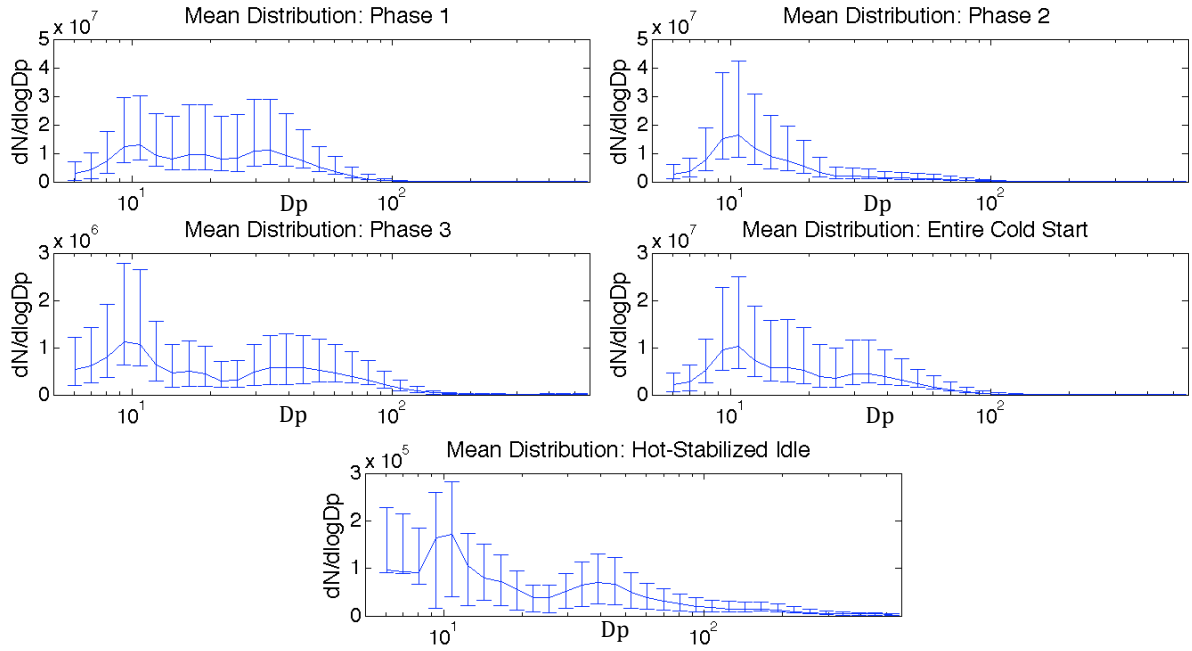

FIGURE 4 Cold Start Mean Particle Number Distributions. Note the different y-scales. The solid line represents mean EEPS concentrations over 5 cold start runs and the error bars represent the overall range from 5 runs. The distribution under hot-stabilized idle operation is included for reference (note it has much lower concentrations and a chiefly bimodal distribution).

Mode 1 (10 nm) was present in all three phases of the cold start, but mode 2 (18nm) and mode 3 (50 nm) were distinct only for Phases 1 and 3. Phase 1 had the highest variability in particle number for all particle diameters. During hot-stabilized idle operation (FIGURE 4, bottom), the greatest variability and highest emissions were for sizes between 8.65 and 11.55 nm, corresponding to Mode 1 of the cold start distributions. Like Phase 2, hot-stabilized idle operation lacked a distinct mode 2 (18nm)..

Magnitude and Duration of Different Particle Sizes During Cold Start

Concentrations from the EEPS were aggregated to 10 bins based on similar trends during cold start. EEPS sizing ranges are equally spaced on a log-scale, so the smallest ranges – and therefore the best resolution – are in the smallest particle sizes. TABLE 2 shows the different aggregate bin size ranges, the average particle concentration (magnitude) from all combined runs and the temporal duration over which that particle size was detectable for each phase of the cold start. Concentrations from hot-stabilized idle operation are also provided for comparison. The duration of particles for each size range, except for particles from 5.6 to 7.5 nm, began at the beginning of each Phase and lasted, on average, the length of time provided in TABLE 2. Particle sizes from 5.6 to 7.5 nm demonstrated slightly different behavior from all other sizes and therefore comprised the first aggregated bin. Particle number did not increase significantly after engine start for 3 to 5 seconds, then increased to the levels reported in TABLE 2. The particle number concentrations in bin 1 also changed very little through Phases 1 and 2, whereas sizes greater than 7.5 nm showed a clear end to Phase 1. Particle sizes between 7.5 and 100 nm showed very similar patterns in time series concentration, so these sizes were aggregated to 8

bins based on the duration the particles were detectable. For example, in TABLE 2, bin 7.5 to 10 nm and bin 10 to 13.3 nm had nearly identical mean duration over each cold start Phase. During the aggregation process, particle sizes from the EEPS 32 size ranges demonstrating these similarities were combined. Larger particle size concentrations (i.e., diameters 100 to 562 nm), even when aggregated, were always at least 2 times (only representing ~1% of total number emissions) lower than other aggregated particle concentrations, so a more disaggregate approach was deemed unnecessary for this 10th bin.

TABLE 2 Mean particle number magnitude (#/cm^3) and duration (seconds) for the three cold start phases and hot-stabilized idle for aggregated particle size ranges.

Particle Size Range	Phase 1			Phase 2			Phase 3			Hot-Stabilized Idle
	Magnitude	Duration	StDev of Duration	Magnitude	Duration	StDev of Duration	Magnitude	Duration	StDev of Duration	Magnitude
5.6 – 7.5	4.52E+05	24	6.56	3.83E+05	43	28.02	6.78E+04	91	36.06	7.20E+03
7.5 – 10	1.23E+06	27	4.73	1.43E+06	42	27.54	1.14E+05	91	37.15	1.31E+04
10 – 13.3	1.38E+06	27	4.73	1.76E+06	42	27.54	1.01E+05	93	27.41	1.72E+04
13.3 – 17.8	1.10E+06	20	5.13	1.01E+06	42	27.54	5.56E+04	97	31.33	1.30E+04
17.8 – 23.7	1.09E+06	20	5.13	5.48E+05	27	26.10	4.26E+04	97	31.33	6.93E+03
23.7 – 31.6	1.19E+06	15	2.65	2.50E+05	25	28.02	4.66E+04	92	24.01	9.31E+03
31.6 – 48.7	1.74E+06	16	2.73	2.85E+05	25	28.02	1.05E+05	97	15.28	2.69E+04
48.7 – 75	6.62E+05	12	2.31	1.87E+05	27	26.10	8.30E+04	100	36.06	1.84E+04
75 – 100	7.79E+04	6	1.73	5.91E+04	20	10.41	3.04E+04	60	52.92	6.38E+03
100 – 562.3	2.05E+04	2	1.15	3.49E+04	7	2.52	1.93E+04	40	57.74	7.75E+03

Phase 3 was different than the first two Phases due to the differing behavior during on-road driving (variable RPM, vehicle speed and exhaust flowrate). Particle number increased for most particle sizes up to 154 nm (as shown in FIGURE 3) when RPM and flowrate increased, so the average durations of most aggregate size bins were quite similar in Phase 3. Also, Phase 3 concentrations were 1.6 to 17 times lower (depending on particle size) than Phases 1 and 2. This was a direct result of having generally low emissions during many episodes of idle operation from on-road travel under urban driving conditions. As was also indicated by [12], mean particle size decreased through each Phase, which is shown in TABLE 2 by smaller particles having longer durations. Lastly, the variability in cold start duration, and subsequently total cold start number emissions, is evident in the standard deviation. The standard deviation was typically larger for the smaller particles, indicating greater variability from day to day in the time period over which the smallest particles were emitted.

Effect of Ambient Temperature

Although all data collected to date were for relatively warm days, with ambient temperatures between 20 and 37˚C (refer to TABLE 1 for ambient conditions), a trend was observed between ambient temperature and total cold start duration. The maximum particle number concentrations emitted, as measured by the EEPS (the UCPC always reached its maximum concentration limit), were not influenced by the ambient temperature over the range of ambient temperatures sampled, but the sum of particles emitted throughout the entire duration of the cold start clearly indicated that, because of increased cold start duration, cooler days resulted in greater total cold start particle number emissions. The EEPS total particle number was 2 times higher for a 20˚C day versus a 37˚C day. However, despite a shorter duration, the 25˚C day cold start emissions were slightly higher than the 20˚C day by 2%. This is the only inconsistent day from the general trend.

The UCPC was tentatively quantified, but because it reached its maximum limit during much of the cold start, its concentrations are biased low. The UCPC recorded the 20˚C day as 1.6 times higher than the 37˚C day. The observed effect of ambient temperature on cold start emissions is consistent with previous work [9, 12, 19], including studies that only quantified gaseous emissions such as HC and CO [17, 18], which are precursors to particulate emissions [9].

CONCLUSIONS

Although this dataset was small, based on only one vehicle, and measurements were performed with ambient temperature above 20˚C, the value of second-by-second particle number distributions, which is rarely available in previous studies, is documented. High temporal resolution of the EEPS instrument allowed identification and quantification of shifting distributions between phases of the cold start. This means a slower Scanning Mobility Particle Sizer instrument is inadequate for fully understanding particle behavior during the entire cold start. Also, all cold starts were performed with ambient temperatures above 20˚C. Although there was clearly a relationship between cold start duration and magnitude and ambient temperature, more data needs to be collected in fall and winter months to determine how great of an influence ambient temperature has on particle number distributions.

It's extremely important to understand the distribution, as well as the magnitude and duration of cold starts. Most exhaust particles (~99%) are less than 100 nm in diameter. For the minivan tests, 3 modes were present at 10 nm, 18 nm and 50 nm with the highest concentrations and longest duration occurring at 10 nanometers. Cold start duration was greatly influenced by ambient temperature ranging from 165 to 230 seconds, where concentrations measured by the EEPS were at least 10 times and most 100 times greater than hot-idle concentrations. If the UCPC is considered, cold start particle number concentrations were at times at least 3 orders of magnitude greater than hot-stabilized idle concentrations. This has implications for better understanding the health affects associated with particle number emissions from vehicles.

Instrument capabilities currently have serious limitations when quantifying vehicle particle number emissions. From this study, it is seen that the full particle number distribution cannot be collected from light-duty vehicles with the necessary particle size resolution using any single commercially available instrument. The increased difference between the EEPS and UCPC occurring during the cold start indicated significant numbers of particles outside the EEPS measuring range. Therefore, comprehensive, multi-instrument studies must be conducted representative of vehicle types, fuels, maintenance levels, emissions control devices, vehicle age, and varying weather conditions to better understand cold start emissions.

ACKNOWLEDGMENTS

This project was funded by the US DOT through the UTC research program at the University of Vermont Transportation Research Center under Signature Project 2.

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