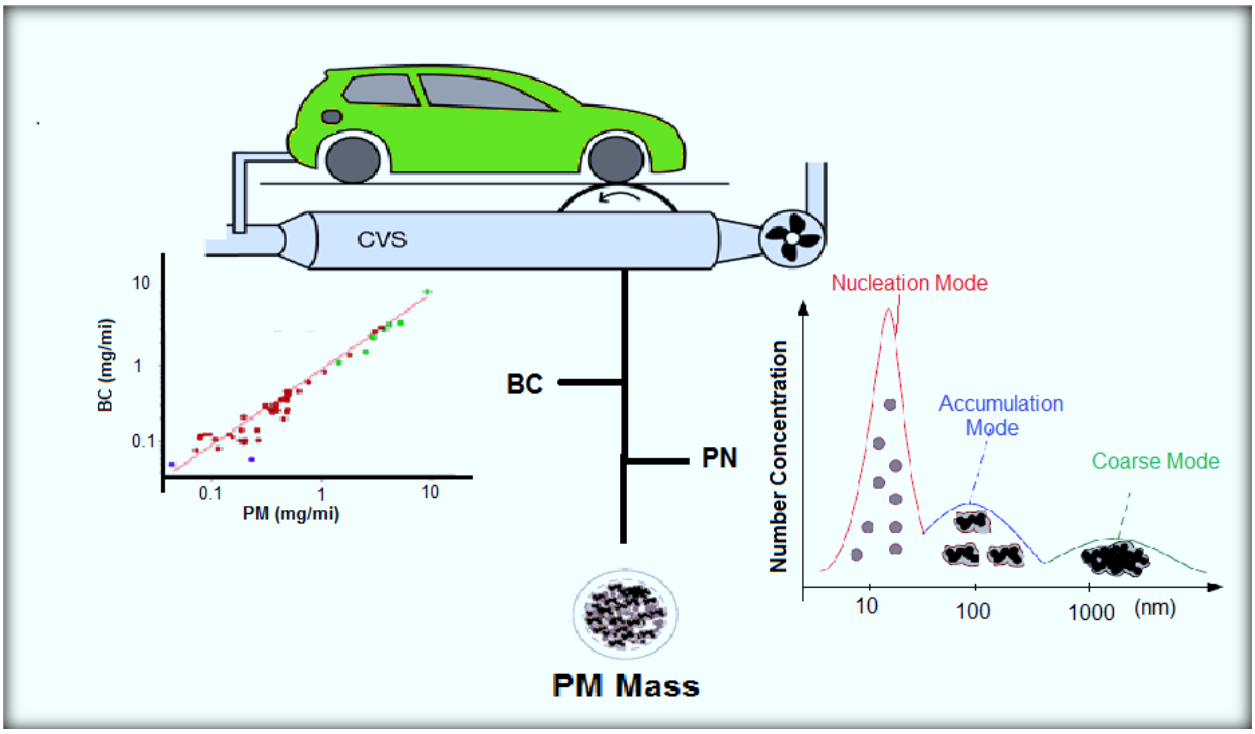
AN UPDATE ON THE MEASUREMENT OF PM EMISSIONS AT LEV III LEVELS



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EXECUTIVE SUMMARY

The California Air Resources Board (ARB) adopted more stringent particulate matter (PM) emission standards as part of the Advanced Clean Cars program and its Low Emission Vehicle (LEV) III regulations in 2012. During the proceedings, the Board directed staff to report back to address industry's concerns both on the feasibility of PM mass measurement at very low emissions levels and on the technicological feasibility for vehicles, especially those with technologies expected to be used to meet the national greenhouse gas standards, to meet the future standards. Since then, ARB staff, in collaboration with the United States Environmental Protection Agency (U.S. EPA), industry, and other stakeholders, has been working on the first of those two tasks and has completed extensive studies to verify the feasibility of measuring PM emissions at the levels required to comply with the LEV III 1 milligram per mile (mg/mi) standard. Several of these studies were focused on investigating concerns regarding the limitation of the gravimetric measurement method that has been historically used in vehicle testing to determine PM mass. In addition, ARB staff continues to explore and evaluate other metrics for measuring PM emissions. For the second task of confirming the feasibility of the standard for vehicles (and the appropriate implementation timing of the standard), testing will be carried out over the next year with a report back to the Board scheduled for late 2016.

Gravimetric Method is Suitable for Measuring PM Emissions below 1 mg/mi

Through this research, ARB staff has concluded that the gravimetric method specified for vehicle emission testing in 40 Code of Federal Regulations (CFR) Part 1065/1066 is indeed suitable for measuring PM mass emissions at the sub 1 mg/mi level. This conclusion is based on evaluations of the potential sources of measurement variability, determination of the PM measurement precision, and a comparison of collocated measurements of selected sampling options described in 40 CFR Part 1066.

Gravimetric Measurement Variability

The total variability in the gravimetric analysis can be estimated by combining the sources of variability related to filter sampling, handling, and weighing. These sources of variability are quantified by repeatedly measuring the "mass loading" on blank filters — filters exposed to various points of the sampling/measurement environment but not to the vehicle exhaust. The variability of reference blanks, which are only exposed to the weighing room environment, indicates microbalance stability and cleanliness in the clean room. Trip and field blanks are indicators of additional contamination introduced by sampling media preparation and handling outside of the clean room; whereas tunnel blanks, which are exposed to the entire sampling process including dilution air but still excluding vehicle exhaust, determine overall variability in sampling processes and the typical contribution from background dilution air.

In ARB studies, the average mass loadings of reference, trip, and field blanks are very close to zero, indicating that minimal contamination is introduced by ARB's filter

handling procedures. Typical levels of tunnel blanks in ARB's Haagen-Smit Laboratory (HSL) test cells average ~2.1 micrograms (µg, 1 µg = 0.001 mg). Relative to field blanks average, mass loading on tunnel blanks are slightly higher, representing the additional contribution from background dilution air and the sampling tunnel.

The variability of the gravimetric analysis is calculated from the standard deviations of reference blank measurements. The standard deviations of ARB's reference blanks are ~0.5 µg, indicating that the variability from the microbalance is very low. Trip and field blanks undergo more handling by testing personnel and exposure to the vehicle test cell and therefore, have an expected higher variability with one standard deviation of 2 µg at ARB. Tunnel blank results encompass additional variability due to dilution air background and potential sampling tunnel contamination, yet the standard deviation of tunnel blanks increases only slightly (by an additional 0.5 µg) to 2.5 µg. The average and variability of tunnel blank results show that the subtraction of up to 5 µg allowed by the official test procedures to account for background contamination is sufficient.

For frame of reference, if we take the worst case scenario of adding an additional one standard deviation of mass loading (2.5 ug) to each of the three phases of the FTP emission test and all in the direction of adding mass to the filter, the impact would be an uncertainty of less than 0.1 mg/mi, or 10% of the 1 mg/mi PM emission standard. Furthermore, if a single filter sampling method is used instead of the traditional 3-filter method, the contribution is reduced to approximately 5% of the 1 mg/mi standard.

Precision and Reproducibility of the Gravimetric Measurement

The precision of the gravimetric measurement was established by measuring PM mass with five collocated gravimetric samplers, and then comparing the relative deviations of the multiple measurements across a fleet of vehicles spanning a range of emissions at or below a 1 mg/mile level. Measurement precision is a quantification of the possible errors due solely to measurement, excluding any differences caused by variability of the vehicle emission levels. ARB's study determined that the precision is 11% (or 0.1 mg/mile) at sub 1 mg/mi levels.

To establish vehicle test reproducibility, ARB carried out an in-house correlation study with one vehicle and an average of nine repeat PM emission measurements per test cell in each of three different light-duty vehicle (LDV) test cells. The study showed that the three test cells utilized can reproducibly measure PM emissions at sub 1 mg/mile levels. The vehicle test-to-test variability was determined to be greater than the inter-laboratory (test cell-to-test cell) variability, suggesting that the instability of the emission source (vehicle) can be a critical factor in determining the total vehicle testing reproducibility.

Equivalency of CFR Sampling Options

ARB's study showed that the single filter, flow-weighted sampling method allowed in 40 CFR Part 1066 for FTP testing yields an emission rate equivalent to that of the conventional 3-filter sampling method, provided they are both corrected with the actual PM background (e.g., tunnel blank). The single filter method also has the advantage of reducing the material and labor costs needed. The test results show that these two sampling options are equivalent.

Evaluation of Alternative Methods

ARB staff has evaluated several approaches for measuring PM mass that incorporate alternative metrics for PM, including those based on solid particle number (SPN), integrated particle size distribution with effective density, and black carbon (BC) measurement. PM mass results determined by all three methods correlate well with gravimetric PM mass. However, the slopes of the correlations vary by test cycle and engine technology as does the variability in PM mass. The observed relationship between PM mass and real-time methods (particle number and BC) strongly suggests that regulating PM emissions through a mass standard will simultaneously reduce the emissions of solid particles and black carbon.

The SPN method is used as one of the metrics for LDV PM standards and emission measurement by the European Union. It is of special interest because it is the only method besides the gravimetric method that has been subjected to rigorous international round robin studies. Although previous studies have reported more repeatable emission measurements with the SPN method and there are potential cost savings with the method, one major drawback is that it only measures a portion of the constituents that make up the total PM emissions. Specifically, it does not measure the semi-volatile components nor particles smaller than 23 nm in diameter. Various studies have shown that the portion of PM attributed to semi-volatiles or to particles smaller than 23 nm can (and likely will continue to) vary substantially based on the engine fuel, engine technology, and exhaust aftertreatment applied. Given the uncertainty as to both the chemical nature of PM that future vehicles will emit and the possible effects in adverse public health from PM in these excluded portions, ARB will continue to utilize the gravimetric mass measurement method as the recognized method for official emission tests. However, staff will continue to monitor developments from the European Particle Measurement Programme (PMP) working group which is seeking improvements in the SPN instrument calibration and extension of the particle size measurement range to include smaller particles, possibly down to 10 nm in diameter. ARB will also continue to follow the improvements in other methods and instruments for measuring particle number and BC as well as any other promising emerging approaches.

I. BACKGROUND

ARB LEV III PM Emission Standards

The California Air Resources Board (ARB) adopted the Low Emission Vehicle (LEV) III PM emission standards as part of its Advanced Clean Cars (ACC) program in 2012. Full implementation of the 1 mg/mi PM emission standard is achieved by model year (MY) 2028. The standard is codified in title 13 section 1961.2, California Code of Regulations, "*Exhaust Emission Standards and Test Procedures - 2015 and Subsequent Model Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles*". The regulation lowers the Federal Test Procedure (FTP) PM emission standard for passenger cars, light-duty trucks, and medium-duty passenger vehicles in two phases. The first phase lowers the standard to 3 milligrams per mile (mg/mi) over a phase-in period starting with MY 2017 vehicles and reaching full implementation by MY 2021. The second phase further lowers the FTP PM emission standard to 1 mg/mi beginning with MY 2025, and reaches full implementation in MY 2028.

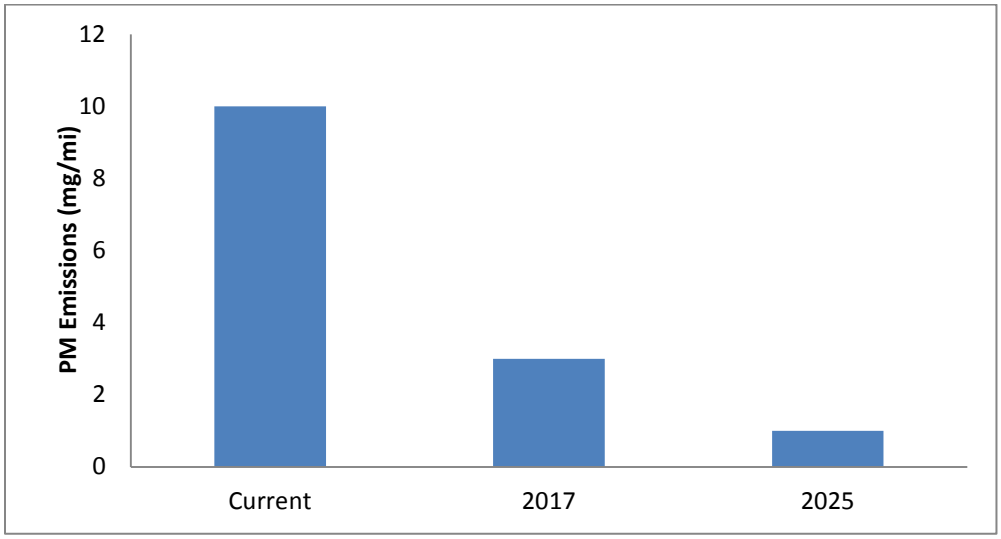


Figure I-1. LEV III FTP PM standards for passenger cars, light-duty trucks, and medium-duty passenger vehicles.

The U.S. Environmental Protection Agency (U.S.EPA) has also lowered the national PM emission standards as part of the Federal Tier 3 regulations. Identical to the LEV III program, the Federal Tier 3 program will limit FTP PM emissions to 3 mg/mi over a phase-in period beginning in MY 2017 and reaching full implementation by MY 2021. However, the EPA standards do not decrease to 1 mg/mi in later years like the LEV III standards. In October 2014, ARB adopted additional minor changes to the LEV III standards to more closely align with Federal Tier 3 standards without sacrificing any emission benefits or the more stringent 1 mg/mi standard.

While the vast majority of gasoline vehicles today easily meet the existing 10 mg/mi PM standard, the more stringent LEV III PM standards will prevent emission increases as vehicle manufacturers transition to low greenhouse gas (GHG) emitting technologies, some of which can increase PM emissions. The light duty vehicle fleet is currently dominated by port-fuel injection (PFI) gasoline vehicles, the majority of which emit PM at or below 1 mg/mi. In recent years, an increasing segment of the market share is comprised of gasoline direct injection (GDI) vehicles, a technology that reduces fuel consumption and therefore, GHG emissions, but sometimes increases PM emissions. Engine technology is rapidly evolving as manufacturers introduce new variations of GDI systems and components such as improved injectors, higher pressures, and different mounting locations to reduce any undesired increase in PM emissions. Some other GHG-reducing technologies such as non-stoichiometric gasoline operation have also been mentioned as concerns where PM emissions may increase. In some cases, vehicle manufacturers and suppliers are even investigating after-treatment devices such as gasoline particulate filters (GPFs), similar in concept to the diesel particulate filters (DPFs) already in use on light- and heavy-duty diesel vehicles.

Vehicle manufacturers have expressed concerns over the lower PM standards, particularly the future 1 mg/mi standard. The uncertainty of the traditional filter-based gravimetric method for measuring PM emissions at the 1 mg/mi level has been perceived to be relatively high, thereby making reliable measurement extremely challenging. In 2012, the Board directed staff to review and report back on the feasibility of reliable measurement at these low levels and to re-assess the technical feasibility (and appropriate implementation timing) of future vehicle technologies to meet these tighter PM standards.

The LEV III regulations also include a more stringent PM emission standard for the Supplemental Federal Test Procedure (SFTP), also known as the US06 cycle, which represents much more aggressive driving speeds and accelerations than the FTP test cycle. The magnitude of the US06 PM emission standard is significantly higher than that of the FTP standard and, therefore, PM measurement uncertainty has a much less significant impact on the test results. Accordingly, ARB staff focused its evaluation on the measurement feasibility at levels required to meet the future FTP standards.

ARB adopted the updated federal test procedures (40 CFR part 1066) as part of the LEV III update in October 2014. These new procedures include allowances for background correction, as well as provisions for new PM sampling options. Current PM sampling and measurement protocols along with the updated sampling options are discussed in further detail in Section II. Staff's findings on PM measurement feasibility and on the alternative PM measurement metrics are presented in Sections III and IV, respectively. Section V addresses stakeholders' concerns regarding the limitations of the gravimetric test method. Finally, Section VI summarizes findings and recommendations regarding the suitability of the gravimetric test method for the LEV III 1 mg/mile PM emission standard, benefits and limitations of new sampling approaches in LEV III and CFR test procedures, and an assessment of alternative PM measurement metrics.

Regarding the Board's request for staff to re-assess the technical feasibility of future vehicles meeting the 1 mg/mi PM standard and the appropriate implementation timing for that standard, staff has begun the analysis and will present its findings as part of the comprehensive midterm review of the national GHG standards and ARB ZEV regulation at a later date.

II. PM EMISSION TESTING

a. General Test Procedures

Light-duty vehicle (LDV) testing at ARB is conducted on a chassis dynamometer in a test cell equipped with a Constant Volume Sampling (CVS) system and the associated equipment for gaseous and PM mass emissions collection. Measurement of PM mass during testing is carried out using prescribed procedures defined in 40 CFR Part 1065 and 1066, which cover everything from vehicle/fuel preparation to vehicle test cycles, emissions sample collection, and the gravimetric determination of PM mass. Figure II-1 shows a picture of one of ARB's LDV emission test cells and Table II-1 summarizes the specifications of the three ARB LDV test cells used to carry out this evaluation. The typical CVS flowrate of the FTP test cycle at ARB is 350 standard cubic feet per minute (scfm).

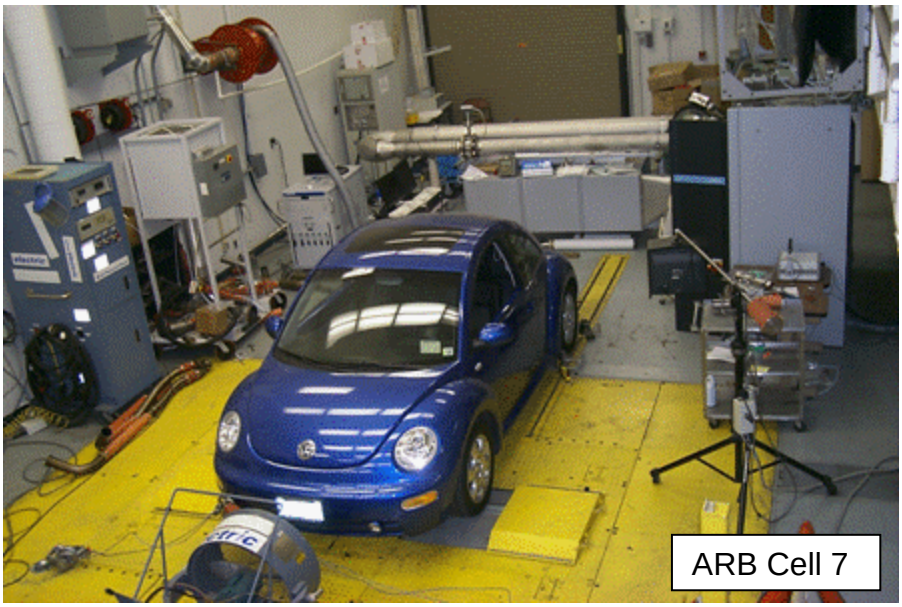


Figure II-1. A picture of an ARB test cell 7

LDV PM emissions are determined with gravimetric measurement by taking a sample of diluted vehicle exhaust from the CVS and collecting PM on a 47mm polytetrafluoroethylene (PTFE) filter. The sample is collected using a temperature-controlled (47 ± 5°C) PM filter sampling system at a nominal flow rate of 60 standard liters per minute (L/min, or 2.12 scfm). The typical filter face velocity for sample collection is near 100 cm/s. The filter sample is then subjected to the gravimetric analysis in an environmentally controlled clean room, maintained at a temperature of 22 ± 1°C and a dew point of 9.5 ± 1°C. The clean room cleanliness meets the International Organization for Standardization (ISO) standards for clean room environments (ISO 14644-1). Filters are equilibrated for a minimum of 30 minutes in the clean room prior to

carrying out the weighing on a microbalance (XP2U, Mettler Toledo, Columbus, OH). Currently, ARB's gravimetric analysis of filters is conducted using an automated weighing system controlled by an MTL robotic weighing system, shown in Figure II-2, with triplicate weighing and zero drift correction. The PM mass loading is the difference between the pre-test and post-test buoyancy corrected filter masses. The weighing procedure is detailed in SOP MV-AEROSOL-145 v5.2 (ECARS, 2011b) and the filter handling and preparation procedure is described in SOPs MV-AEROSOL-156 and 158 (ECARS, 2014a and 2014b).

	ARB HSL Test Cell		
	Cell A	**Cell B**	**Cell C**
Dynamometer	48" Burke Porter 2WD Electric Dyno	48" Clayton 2WD Electric Dyno	48" Horiba 2WD Electric Dyno
Constant Volume Sampler (CVS)	AVL CVS 150-900 SCFM	Horiba CVS 150-1,000 SCFM	Horiba CVS 150-814 SCFM
Gas Analyzers	Horiba MEXA-7200 LE	Pierburg AMA 4000	Horiba MEXA-7200 LE
PM Sampler	1. AVL SPC Sampler 2. Horiba Quad Sampler	AVL SPC sampler	Horiba HF-PM Sampler
Exhaust Transfer Tube	3-4" Stainless Steel Tube	3-4" Stainless Steel Tube	3-4" Stainless Steel Tube

Table II-1. Summary of testing equipment in ARB light-duty vehicle test cells

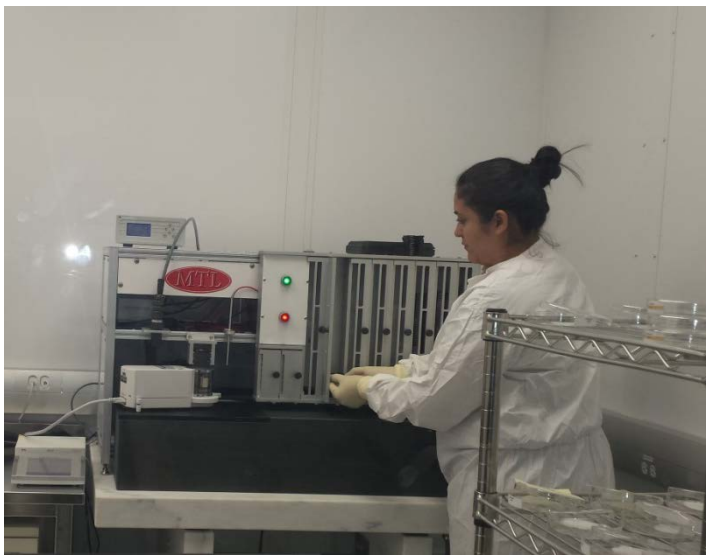


Figure II-2. An operator loads filters on ARB's automated filter weighing system.

Driving Cycles

LDV PM emission standards are tied to specific driving cycles on a chassis dynamometer. The driving cycle is intended to represent a specific duty or activity of a vehicle during its operation. The two most relevant drive cycles for LDV PM emission standards are the standard Federal Test Procedure (FTP) and the high speed, high acceleration portion of the Supplemental Federal Test Procedure (SFTP or US06).

Federal Test Procedure (FTP)

The FTP consists of two Urban Dynamometer Driving Schedules (UDDS) run in series (Figure II-3). Each UDDS is divided into two phases, with a start phase running for 505 seconds and a stabilized phase running for an additional 864 seconds. The first UDDS is considered a cold start test because the engine is started in a "cold" condition after an overnight engine off 'soak' period. The second UDDS is considered a hot start test because it begins with a "hot" engine from a car that has been sitting with the engine off for 10 minutes after the first UDDS ends. The stabilized phase in both UDDS cycles is assumed to have the same emissions; therefore, it is typically not run after the hot start. This "three-phase" driving schedule is commonly referred to as an FTP-75. The FTP-75 has a total distance travelled of 11.04 miles, an average speed of 21.2 miles per hour (mph), and a total duration of 1874 seconds. The emission result is a weighted average where the cold start and stabilized phase (the first UDDS cycle) is weighted at 43 percent and the hot start and stabilized phase (equivalent to the second UDDS) is weighted at 57 percent.

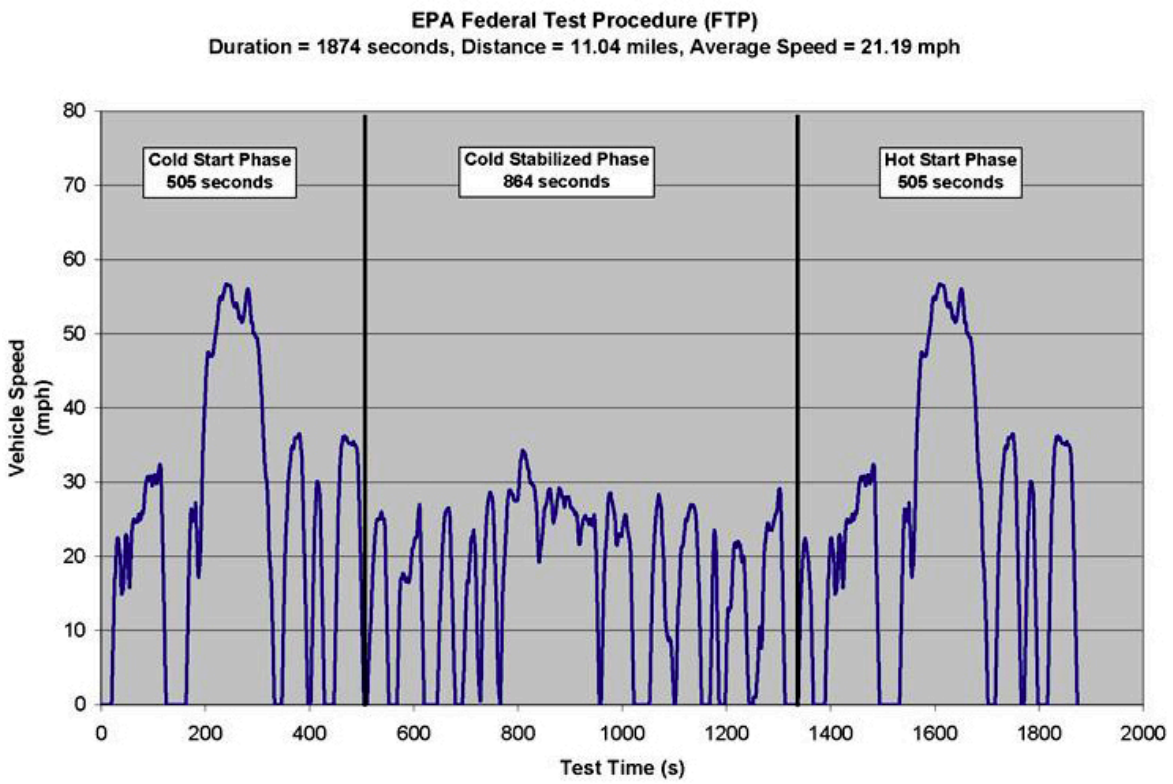


Figure II-3. The FTP cycle speed trace
Source: http://www.epa.gov/otaq/standards/light-duty/ftp.htm

Supplemental Federal Test Procedure (SFTP or US06)

The US06 was developed to reflect aggressive, high speed, and high acceleration driving behavior. The US06 driving cycle is shown in Figure II-4. It is a hot start test typically run with two replicate US06 cycles. The first US06 cycle is a prep cycle, run without emission measurement, to ensure the car is warmed up; the second US06 immediately follows the first, without an engine off or restart, and emissions are measured on the second cycle. The US06 cycle represents an 8.01 mile route with an average speed of 48.4 mph, maximum speed 80.3 mph, maximum acceleration rate of 8.46 mph/sec, and duration of 596 seconds. The higher acceleration rates and speeds of the US06 cycle lead to higher engine loads, which typically generate higher PM emission rates.

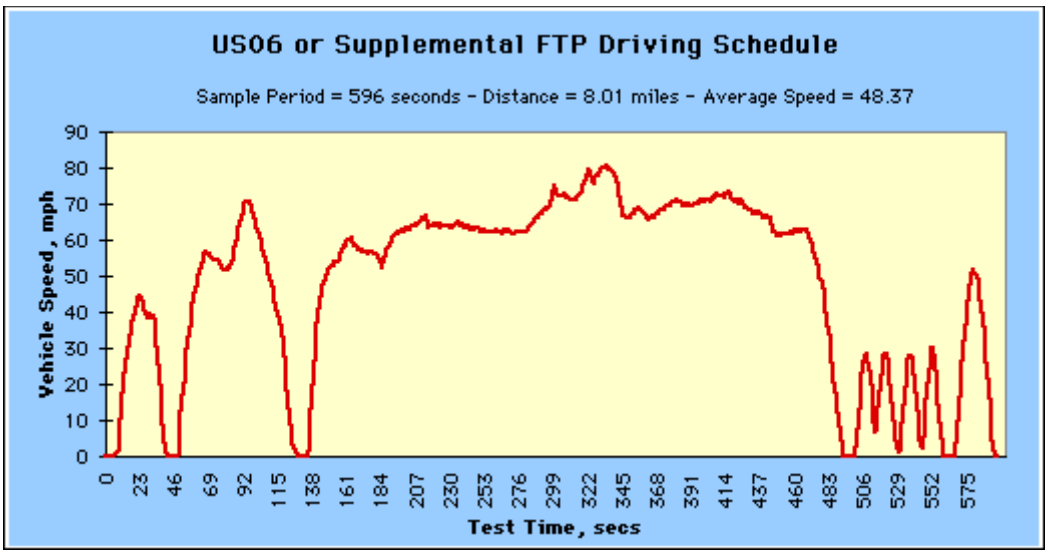


Figure II-4. The US06 cycle trace of the SFTP
Source:http://www.epa.gov/nvfel/methods/us06dds.gif

Test Fuel

The Phase 3 gasoline certification specifications were adopted as part of the LEV III regulations and specify a number of components in the test fuel. It has been shown that the sulfur, olefinic, and total aromatic hydrocarbon content in the fuel could affect PM emissions (Khalek et al., 2010 and Aikawa et al., 2010). Phase 3 certification fuel replaced MTBE with ethanol (E10) as the oxygenate, and set specifications for other parameters to better reflect the current composition of transportation gasoline sold commercially in California. These specifications are detailed in Part II, Section A.100.3.1.2 of the "California 2015 and Subsequent Model Criteria Pollutant Exhaust Emission Standards and Test Procedures and 2017 and Subsequent Model Greenhouse Gas Exhaust Emission Standards and Test Procedures for Passenger Cars, Light- Duty Trucks, and Medium-Duty Vehicles."

b. New Protocols for Light-Duty Vehicle Emissions Testing in 40 CFR Part 1066 PM Test Procedures

40 CFR Part 1066 provides two new features for PM emission testing that include 1) five different PM sampling options with their calculations, and 2) an allowance for background correction. These elements are described in the following paragraphs.

PM Sampling Options

The U.S. EPA has led an effort to improve and standardize the test methods prescribed in the CFR for vehicle testing. This effort resulted in the creation of Part 1066 which

ARB has adopted along with 40 CFR Part 1065 for its vehicle compliance testing programs. One of the updates to 40 CFR part 1066.815 (Exhaust emission test procedure for FTP testing) includes four additional PM sampling options, listed in Table II-2 as options 2 through 5. These sampling options were intended primarily to increase the amount of PM sampled and minimize uncertainties by reducing the number of filters used. However, some options require extending emission test time to encompass two full UDDS cycles, while others may result in laboratories needing two samplers. Option 1 is the original FTP test procedure and is used as a benchmark, whereas sampling option 4 has been evaluated extensively as part of ARB's efforts to determine the feasibility of PM measurement at levels below 1 mg/mi. The results of ARB's comparison are presented in Section III.

Option	Description	No. of Filters	Filter Face Velocity Weighting Target
1	1 filter/phase of three-phase FTP	3	1.0/1.0/1.0
2	1 filter/UDDS of four-phase FTP	2	1.0/1.0/1.0/1.0
3	1 filter/phase 1&2 + 1 filter/phase 2&3	2	1.0/1.0/1.0
4	1 filter/three-phase FTP	1	0.43/1.0/0.57
5	1 filter/four-phase FTP	1	0.75/0.75/1.0/1.0

Table II-2. Summary of five PM sampling options described in 40 CFR Part 1066. The maximum nominal filter face velocity is 100 cm/sec for all sampling options.

PM Background Correction

The subtraction of background PM mass allows corrections for a measurable bias. 40 CFR Part 1066 allows background correction of up to 5 μg, or 5% of the net PM mass. The major sources of bias include dilution air contamination, as well as sampling train and filter media adsorption/desorption effects. Not only do the contamination sources contribute to undesirable background interference, but they could also increase measurement variability. However, PM background interference and vehicular PM emissions cannot be quantified simultaneously. The interference caused by deposit of exhaust emission constituents onto the wall of the sampling train, and re-evaporation and re-entrainment of those deposits back to the sample stream is dynamic, and depends on the chemical nature of these constituents, as well as the temperature gradient between the exhaust stream, dilution tunnel, and dilution air. Furthermore, these interferences can undergo chemical reactions with the exhaust, the nature of which also varies in transient test cycles.

In addition to the interferences and uncertainties in the CVS tunnel, filter sampling media can also contribute to measurement uncertainties. Different filter materials have unique characteristics for adsorption and desorption of gaseous organics. The use of PTFE filters has resulted in the least degree of interference from gaseous organic compounds (Chase et al., 2004 and Khalek 2005), whereas, earlier studies show TX40 and quartz fiber filters have a propensity to adsorb organic hydrocarbons and tend to show much higher background levels and measurement uncertainty. Good filter handling practices can also minimize the PM mass measurement variability.

III. PM MASS MEASUREMENT FINDINGS

a. PM Emissions below 1 mg/mi levels from Pre-LEV III LDVs

Prior to the 2012 LEV III rulemaking, ARB began monitoring PM emissions from LDVs and assessing the capabilities of the gravimetric measurement method. The results were discussed in the LEV III PM Technical Support Document, Appendix P. In this effort, 19 LDVs, comprised of nine GDI and 10 PFI vehicles were tested using the FTP cycle and California Phase 3 commercial summer fuel containing 6% ethanol by volume. For the nine GDI test vehicles (Figure III-1), PM mass emissions were the highest in phase 1 (cold start), with an average of 14 mg/mi; after engine warm up, PM emissions were significantly reduced with an average of 1.1 mg/mi for phase 2 (stabilized phase) and 1.5 mg/mi for phase 3 (hot start). The FTP weighted average PM mass emissions for the nine GDIs was 3.87 mg/mi. Detailed GDI vehicle information and corresponding PM emission rates are listed in Appendix Table A-1.

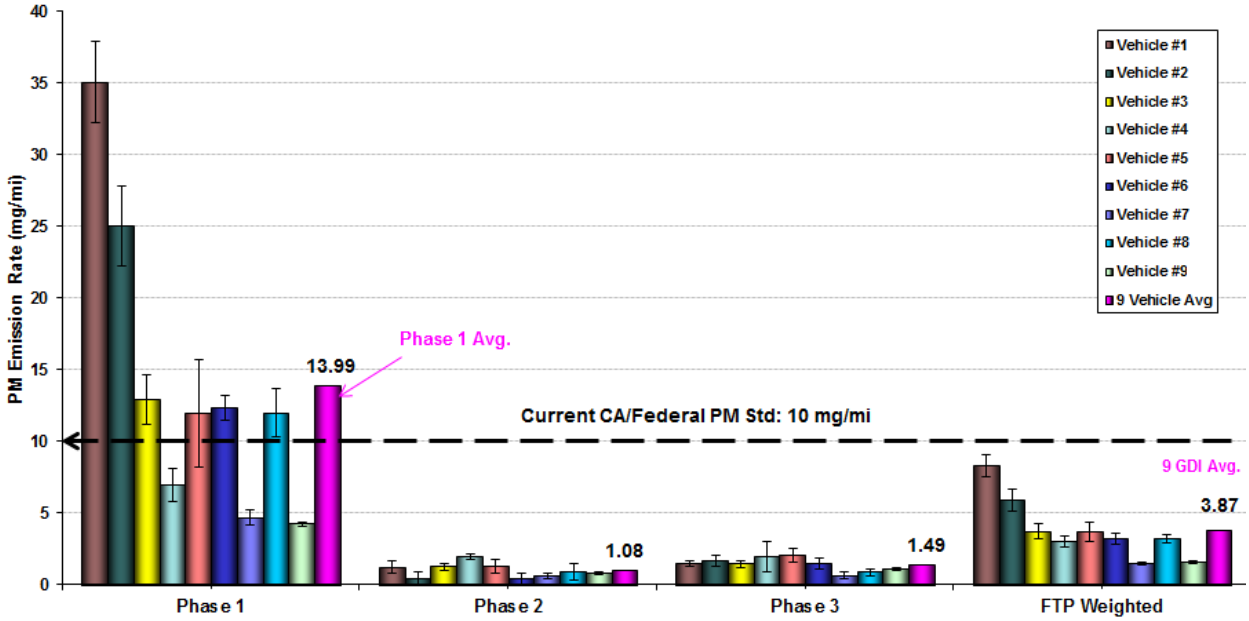
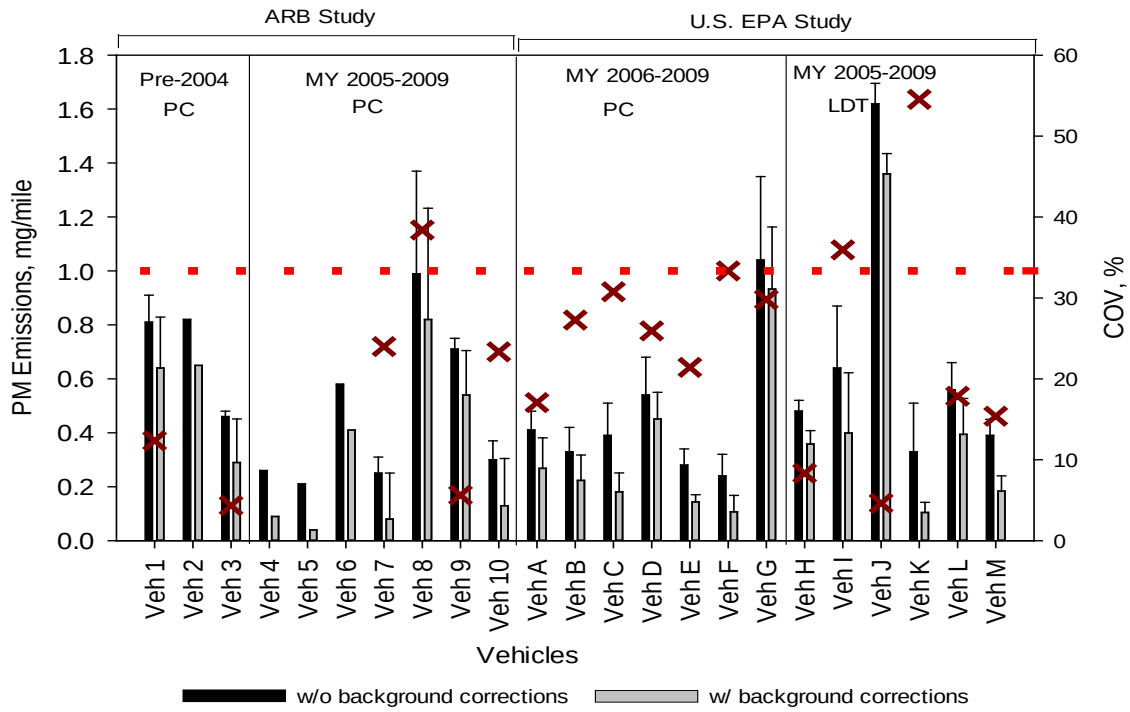


Figure III-1. PM mass emission rates on FTP cycle for 9 GDI vehicles using California E6 summer fuel (LEV III PM Technical Support Document, 2012)

The FTP weighted average PM emissions for the ten PFI vehicles (listed in Appendix Table A-2) was 0.5 mg/mi, with a range of 0.16 mg/mi to 0.99 mg/mi. The results are shown in Figure III-2, along with the US EPA's test results from a set of 13 vehicles, Vehicles A to M (detailed in Appendix Table A-2). These PM emissions were measured in three test cells at the HSL and one test cell at US EPA's National Vehicle and Fuel Emissions Laboratory (NVFEL). The coefficient of variance (CoV, the ratio of the

standard deviation divided to the mean of results from repeating tests, also known as relative standard deviation) from vehicles where there was three or four repeat tests varied from 5 to 56% and was found to be independent of the PM emission rates.



- X is the coefficient of variance of the testing results.
- No error bar indicates only one test was performed.
- Error bars show one standard deviation

Figure III-2. PM emission rates of LDVs tested at ARB's HSL cell A and US EPA's NVFEL cell (Hu et al., 2014)

Repeat gravimetric measurements of FTP phase 2 and phase 3 PM emission rates for GDI vehicles and FTP weighted PM emission rates for PFI vehicles demonstrated that the gravimetric PM mass measurement method was capable of measuring PM mass emission rates at ~1 mg/mi or lower.

In addition to the work at the U.S. EPA and ARB, other laboratories have also measured low level PM emissions. Chase et al. (2000) reported that PM emissions from 11 LDVs had a mean FTP-weighted emission rate of 0.60 ± 0.17 mg/mi for six low mileage vehicles and 0.67 ± 0.19 mg/mi for five high mileage vehicles. Maricq et al. (2011) also reported measurements of LDV PM emissions at LEV III levels.

A statistical analysis was conducted to verify the ability of a test cell to distinguish vehicles with various PM emission levels. The PM emissions from vehicles with more than three repeat tests and ranging from 0.2 to 0.99 mg/mi (Vehicles 1, 7-10) were pooled to calculate test-to-test variability (s_r^2), vehicle-to-vehicle variability (s_L^2), and total

variability (s_R^2) by the equations listed in "*Statistical Analyses _Repeatability and Reproducibility"* in the Appendix. Using this statistical analysis, vehicle-to-vehicle and test-to-test variability were compared to verify vehicles emitting at different PM levels could be distinguished in the test cell. The calculated results are shown in Table III-1. The vehicle-to-vehicle variability was found to be at least two times the test-to-test variability. When one outlying emission value from Vehicle 8 is excluded, the vehicle-to-vehicle variability becomes even more dominant while the CoV for test-to-test repeatability decreases from 30% to 16%. The vehicle-to-vehicle variability accounts for more than 90% (excluding the outlier) or 70% (all data) of the total emission variability. These results suggest that the test cell itself can distinguish different levels of vehicular PM emission below 1 mg/mi.

		Variability			Coefficient of Variance		
	Emissions mg/mile	Test-to-Test s_r^2	Vehicle-to-Vehicle s_L^2	Total Variability s_R^2	CoV_r	CoV_L	CoV_R
PM	**0.65±0.34**	**0.04**	**0.09**	**0.13**	**0.30**	**0.46**	**0.55**
PM[a]	**0.60±0.26**	**0.01**	**0.08**	**0.09**	**0.16**	**0.47**	**0.49**

a. One suspicious "outlier" value of 1.53 mg/mi was excluded from Veh 8 to evaluate the influence of this high value on the variability.

Table III-1. Repeatability and reproducibility of five vehicles (Vehicle 1, 7-10) tested at ARB HSL test cell A (Hu et al, 2014)

Although the ability to measure PM mass repeatedly below 1 mg/mi has been demonstrated, there are still some concerns regarding the measurement uncertainty related to vehicle emission testing. To better understand the sources of measurement uncertainty, ARB has conducted numerous tests to identify these sources, quantify variability, and further confirm the feasibility of the gravimetric method for vehicle emission certification testing.

b. Sources of Measurement Variability

To fully characterize the uncertainty of vehicle PM emission measurements, it is essential to understand how the test is conducted and where the measurement variability is influenced. Vehicle dynamometer testing contains three major potential sources of variability, shown in Figure III-3:

(a) Emission source: the vehicle itself and a driver
Repeatability of PM emissions can be influenced by the variation of the engine combustion process, and slight test-to-test variations in engine speed and load operation that occur as the driver follows within a transient driving trace.

(b) Sampling train: heated transfer tube, dilution tunnel, dilution air, PM sampling system, and sample collection media
The dilution air background and adsorption/desorption characteristics of semi-volatile organic compounds in the sampling train can contribute the total measurement variability. In addition, the PTFE filter's property of adsorption/desorption of organic hydrocarbons during sample collection can also contribute to variability.

(c) Gravimetric analysis to determine the PM mass
The stability of the microbalance and environmental conditions in the clean room can also contribute to measurement variability.

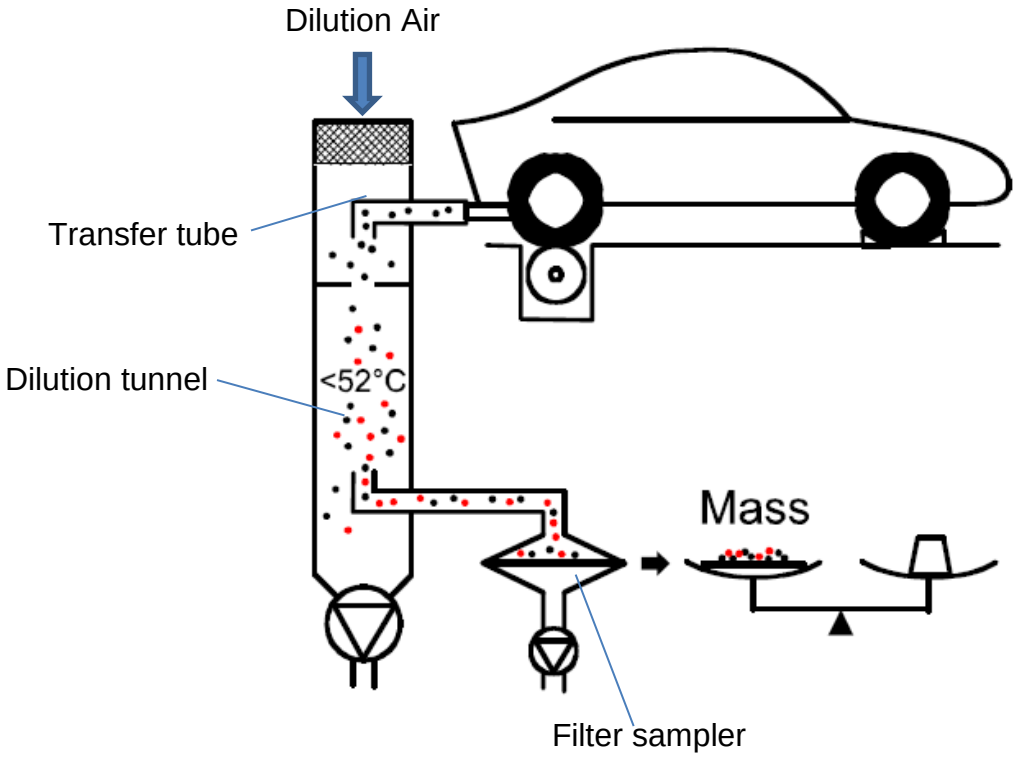


Figure III-3. Schematic illustration of the gravimetric method for determining PM mass emissions in vehicle exhaust. (Modified from Mayer, 2006)

Blank sample measurements as indicators of sources of variability

ARB routinely measures background/blank samples to identify possible areas of contamination as the filter is transported through each step of vehicle testing. The results are used to quantify the variability from gravimetric analysis (reference and replicate analysis), the filter handling process (trip and field blanks), and the sampling train (tunnel blanks) to estimate potential background contributions to total vehicle emission measurement variability. The various blank samples are diagrammed in Figure III-4 to illustrate their relative contributions (not to scale) to variability.

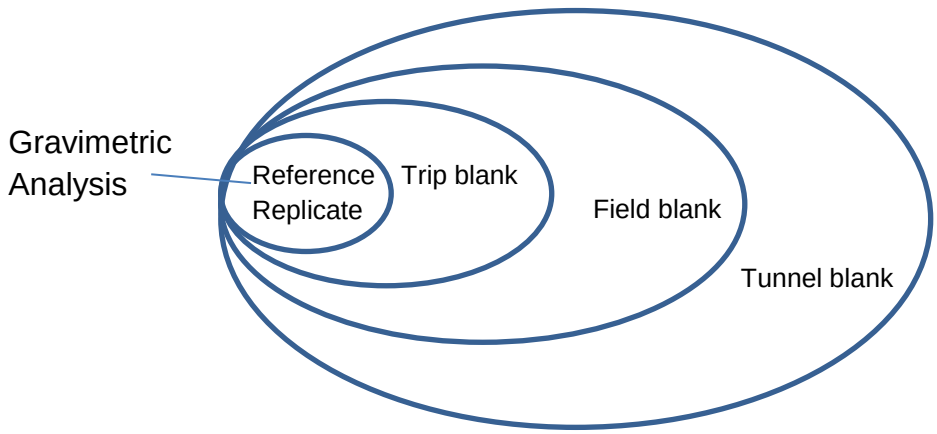


Figure III-4. Schematic of sources of total variability determined from filter blanks. The relative contribution is not to scale. (modified from Watson et al. 2013 CRC Workshop)

Variability from Gravimetric Analysis: Reference Filter and Replicate Analysis

The vehicle PM emissions are collected onto a PTFE filter and the filter weight determination can be influenced by environmental conditions. Therefore, it is important to evaluate the measurement variability of reference, replicate filters, and NIST traceable metal weights for quality assurance (QA).

The NIST Traceable Metal Weight

The filter weighing is conducted using an MTL robotic filter weighing system with triplicate weighing and zero drift correction The NIST traceable metal weight is used to validate the microbalance calibration. Figure III-5 shows the metal weight measurements from April to September, 2014. The NIST metal weight ranged within 0.7 µg in six months, indicating excellent microbalance stability.

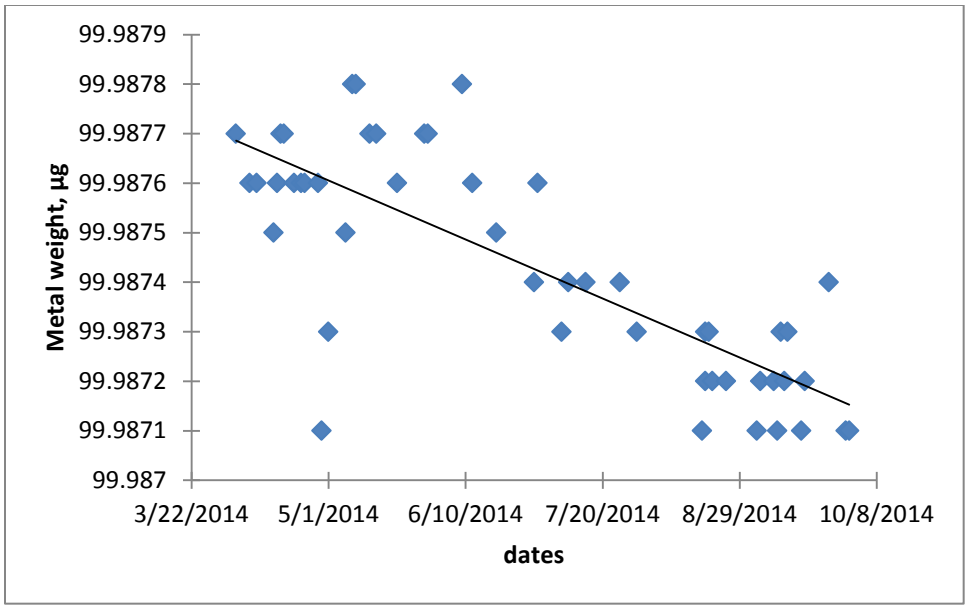


Figure III-5. NIST traceable metal weight measurements for a period of six months.

Reference Filter Blanks

Three reference filters, stored in the weighing room environment, are weighed at the beginning and the end of each sample (filter) weighing session. Typical weighing sessions last several hours, depending on the number of samples. Reference filters are used to check for particle contamination in the clean room environment and weighing system stability during a weighing session. The reference filters' mass difference (the change of buoyancy corrected net mass of reference filters during each weighing session) along with results from various types of blanks, are shown in Figure III-6. The mean difference for the reference filters was -0.4 µg with one standard deviation of 0.5 µg, determined by a total of 138 reference filter samples collected during the period of January to June, 2014.

Replicate samples

A replicate is a vehicle emission filter randomly selected for repeat weighing from each batch of ten samples. Replicate results were used to assess measurement repeatability for different filter PM mass loadings. The variability of repeat analysis is shown in Figure III-6 for over 100 samples collected from January through June 2014 at the ARB laboratory. The mean and standard deviation were 0.1 ± 0.5 µg. The results from replicate analyses demonstrated that the performance of the weighing system is stable.

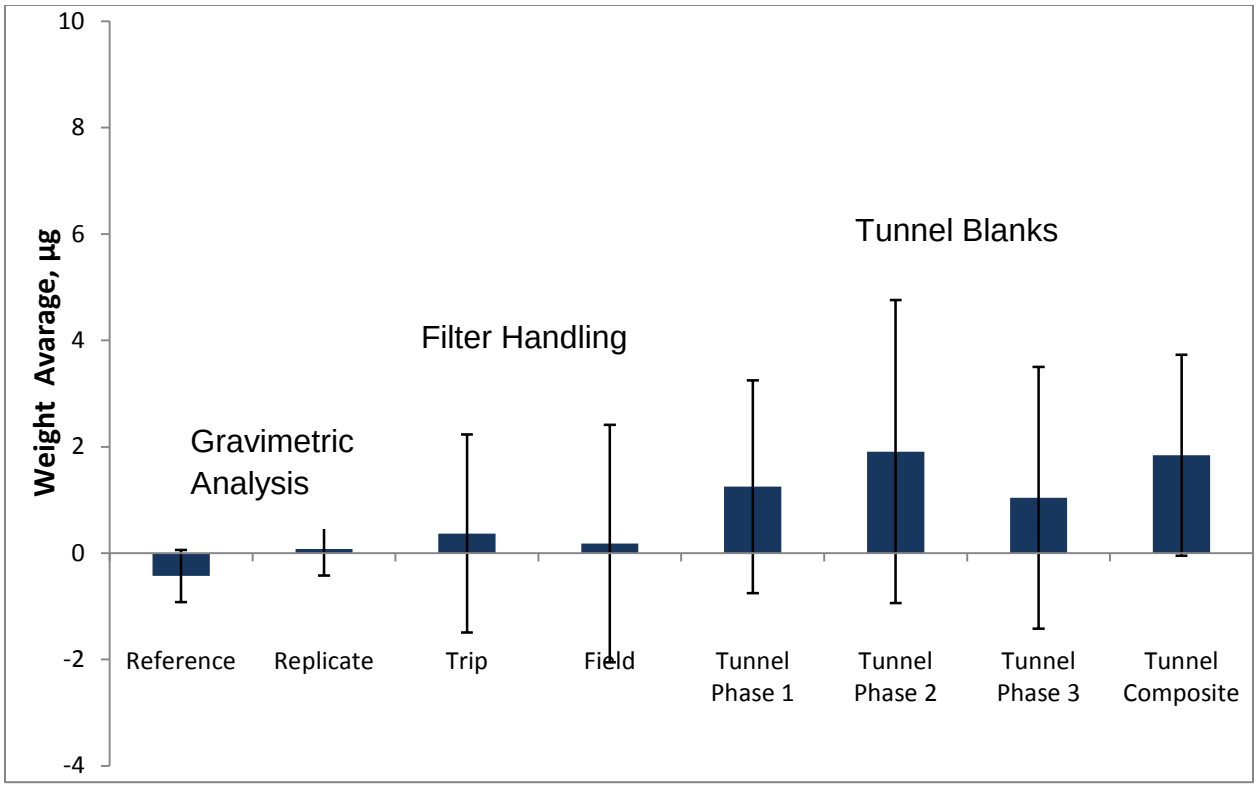
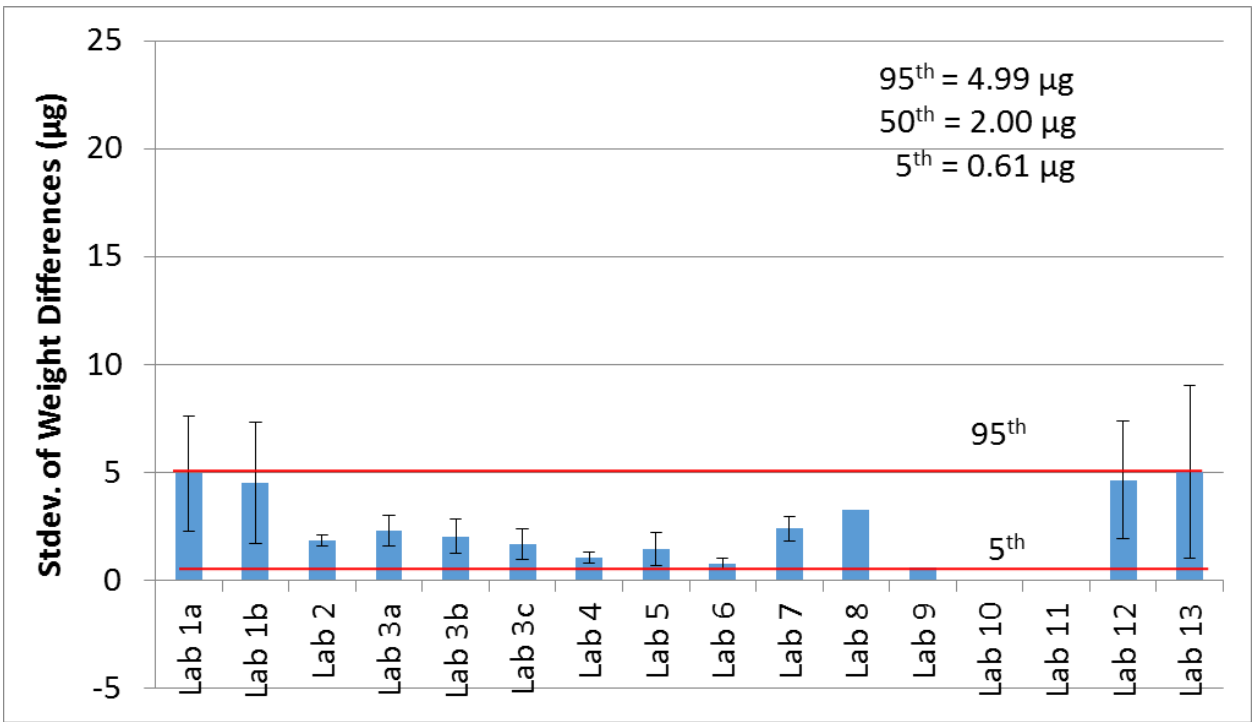


Figure III-6. Average and standard deviation of blank filters.

In summary, the QA system consisting of NIST traceable metal weights, replicate filters, and reference filters verified the stability of the robotic filter weighing system and cleanliness of the weighing room. The average and standard deviation results are relatively insignificant, compared to other blank measurements (discussed later).

Jung et al. (2015) compiled reference filter results from 13 laboratories using either manual or robotic weighing, as shown in Figure III-7. The robotic weighing system (labs 4, 6, and 9) exhibited the lowest average bias (mean of reference filters) and standard deviation of reference filters, and the results were very similar to ARB's. When including the results from manual weighing, the 50th percentile of the average variability for laboratories is 2 µg with the 5th and 95th percentile at 0.6 and 4.99 µg, respectively.



Error bars represents the one standard deviation of the average results for each short-term pair evaluated.

Figure III-7. Average reference filter weight differences for the pooled filters (outliers removed) (Jung et al., 2015)

Variability from Filter Handling: Trip and Field Blanks

Trip Blanks

A trip blank is a filter randomly selected among a set of pre-weighed filters, transported to the test cell where it is stored (but not used for sampling or exposed to the testing facility environment) during vehicle testing, and then returned to the weighing room. The designated trip blank is weighed in the same weighing session along with the PM samples. A total of 146 trip blanks were collected from four ARB test cells during 2013 and 2014, and the results are shown in Figure III-6. The average of the trip blanks is 0.4 µg, with a standard deviation of 1.9 µg. As expected, the trip blank has more variability than that of the reference filters. Trip blanks encompass additional sources of variability such as the assembly and disassembly of the filter cassettes used to house the sample filters.

Field Blanks

Compared to the trip blank, the field blank captures additional variability introduced by loading the filter onto the sample holder for the duration of vehicle testing, but without exposure to tunnel dilution air or vehicle exhaust. The average of the field blank results

is shown in Figure III-6. The average mass of 40 field blanks from two of ARB's test cells is 0.2 µg with a standard deviation of 2.2 µg. The lack of any increased mass loading over trip blank results indicates that the additional assembly and disassembly of the filter cassette onto the filter holder, and exposure to tunnel air (without flow) does not increase the mass loading or the measurement uncertainty.

The average mass loadings for trip and field blanks were close to zero, indicating that filter handing procedures do not result in significant filter contamination. However, an elevated standard deviation was observed for trip and field blanks when compared to that of the reference or replicate analysis.

Variability from the Dilution Sampling System: Tunnel Blanks

Vehicular tailpipe exhaust is drawn through a heated transfer tube to the CVS dilution tunnel, where the exhaust is diluted with filtered ambient air. ARB uses the tunnel blank to evaluate the contribution from sampling system to measurement variability with the transfer tube sealed.

Tunnel Blanks

At ARB's test cells, tunnel blanks are typically collected every week using the same PM sampling system used for vehicle testing, except that the vehicle exhaust inlet (or the transfer tube) to the CVS tunnel is sealed. The sampling duration and flow rate are the same as those in vehicle emission testing; however, the temperature profile in emission testing (e.g., due to variations in vehicle exhaust temperature and mass flow during an actual test) is not replicated. Tunnel blank results from three different programs at ARB are tabulated in the Table III-2.

Tunnel Blank	Average (µg)	Standard Deviation (µg)	Citation/program
Cell A (Phase 1, 2, 3)	2.5, 2.5, 1.8	2.7, 3.4, 3.1	Hu et al., 2014
Cell A (Phase 1, 2, 3, 1-filter-flow-weighted)	2.0, 2.1, 2.2 1.9	2.0, 1.9, 2.0 1.8	Sardar et al., (submitted)
Cell B (composite filter)	1.6	3.1	LDV surveillance test (UC cycle)

Table III-2. ARB's tunnel blank results from various vehicle test programs

Tunnel background levels were measured for tunnel blank tests from ARB's test cell A, prior to ARB's LEV III rulemakings in 2012 (Hu, et al., 2014). Additional tunnel blanks were collected from various ARB projects beginning in 2012. The utilization of only one brand of PTFE filter (Whatman) and the implementation of a robotic filter weighing system could help reduce the standard deviation of tunnel blank results (Sardar et al., submitted). ARB's test cell B, which primarily carries out the emission tests for in-use

surveillance testing programs, showed similar results as those collected in test cell A despite being exposed to significantly higher concentrations of PM mass.

Additional tunnel blank results, shown in Figure III-6, are from a total of 22 tunnel blank samples collected for test cell A from September, 2013 through February, 2014, including a full-flow 3-phase composite filter tunnel blank. The average and standard deviation for the three phases and composite are 1.3 ± 2.0 µg (phase 1), 1.9 ± 2.9 µg (phase 2), 1.0 ± 2.5 µg (phase 3), and 1.8 ± 1.9 (full flow composite).

The average tunnel blank mass loadings from ARB's test cells was ~2.1 µg. Some researchers suggest that the tunnel blank mass loading is from volatile or semi-volatile hydrocarbons from the contaminants or wall losses of PM in the CVS tunnel while others suggest it is from the dilution air. Nevertheless, official test procedures specified in 40 CFR Part 1066 allow for a background 'correction' (subtraction) of up to 5 µg which is sufficient to account for the observed tunnel blank background.

The average standard deviation of the tunnel blank results was approximately 2.5 µg, which was slightly larger than that of trip and field blanks at 2 µg. The unpredictable nature of contamination, either from the dilution air or tunnel wall, can increase measurement uncertainty. The maximum tunnel blank measurement variability - calculated by assuming that 2.5 µg is the PM mass loading for each FTP phase- is equivalent to a 0.1 mg/mi FTP weighted emissions rate (350 scfm CVS flow rate and 100 cm/s filter face velocity). This theoretical worst case variability is approximately 10% of the 1 mg/mi emission standard and becomes even less significant (~ 5%) when calculated using a single filter flow-weighted sampling option. Other investigators have assessed the impact of tunnel blank uncertainty based on a standard deviation of 5 µg (Bushkuhl et al., 2013), which is two times what has been observed at ARB. An elevation of the standard deviation from trip blanks to tunnel dilution air blanks was observed, attributed from the gaseous adsorption onto tunnel blank filters.

The results of a tunnel blank survey reported by Jung et al. (2015) are shown in Figure III-8. Each participating laboratory had different practices for its tunnel blank determination. The results show a large variation among laboratories. The average, 50th percentile, and standard deviation of all measurements (N=615) are 4.13, 2.8, and 3.62 µg, respectively. The 50th percentile of the variability (single standard deviation) for the pooled laboratories is 2.8µg. If this tunnel blank variability reflects the overall vehicle PM mass measurement uncertainty, improvements are needed for some laboratories to quantify very low PM mass emissions.

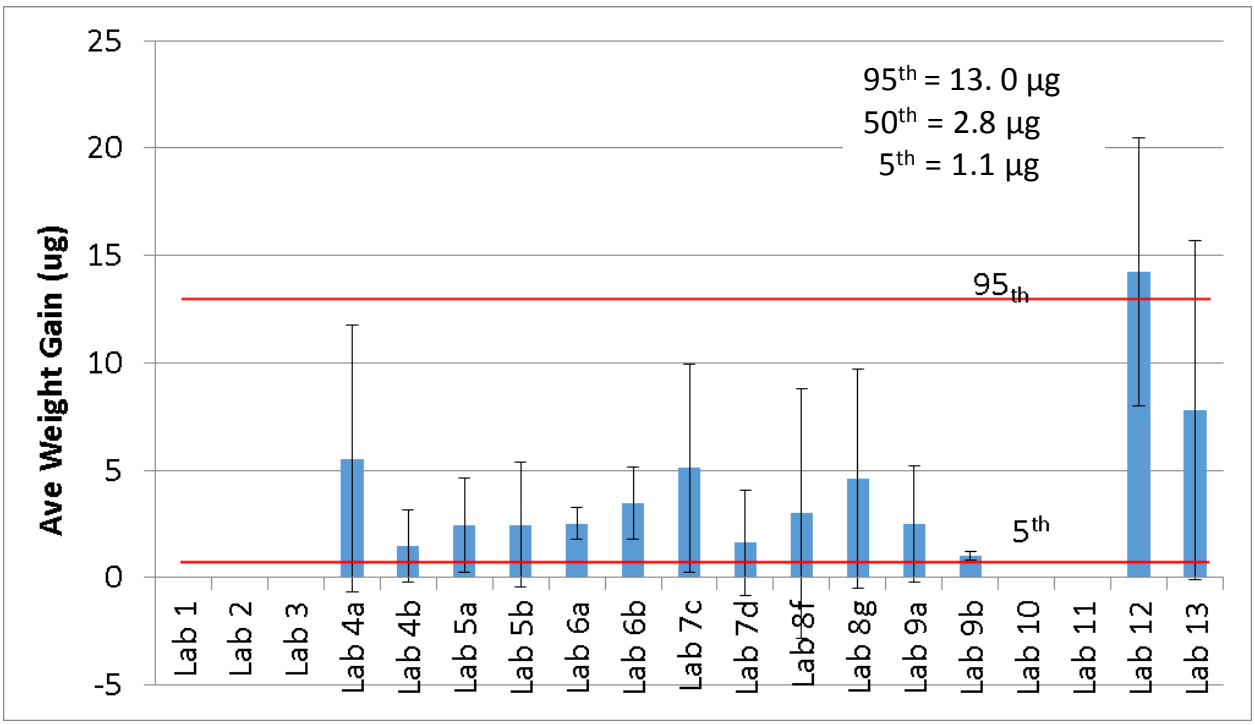


Figure III- 8. Tunnel blank results from various laboratories (Jung et al., 2015)

To better understand the chemical characteristics of tunnel blank PM, ARB analyzed PM samples for organic/elemental carbon. In addition to PM mass, collocated samples were collected onto quartz fiber filters over the California Unified Cycle (UC) as part of ARB's LDV in-use surveillance program Series-19 conducted in test cell B. Both tunnel blank tests (24 tests) and trip blanks (25 PTFE and 14 quartz fiber filters) were conducted during the period from April 2013 to July 2014.

Sampling with quartz fiber filters allows for carbon analysis, which can differentiate organic from elemental carbonaceous compounds. The quartz filter is pre-cleaned to remove any contaminants before measurements. After PM sampling, the filters are analyzed for organic carbon (OC) and elemental carbon (EC) using a Thermal/Optical carbon analyzer following the IMPROVE_A protocol. Detailed analytical procedures can be found in SOP MV-AEROSOL-139 v 1.1 (ECARS, 2011a).

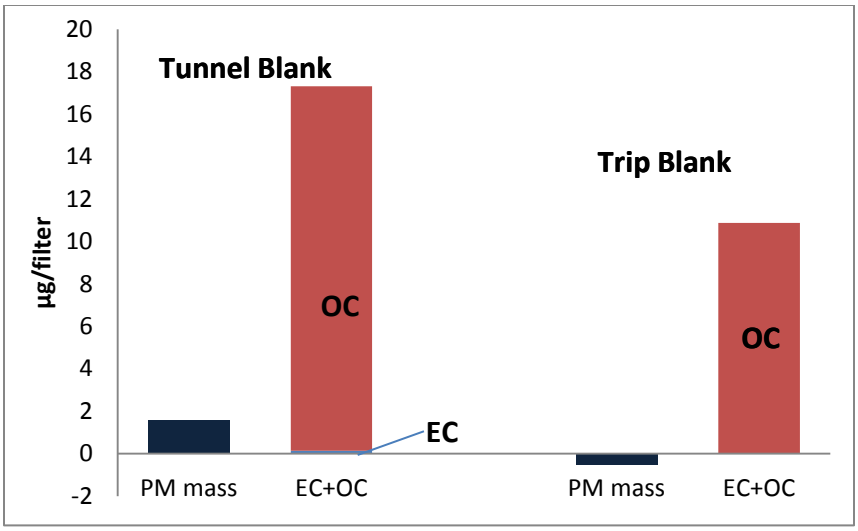


Figure III-9. Average tunnel and trip blank PM mass and carbon analysis results from ARB Test Cell B

As shown in Figure III-9, the average trip blank (25 samples) PM mass loading on the PTFE filter was -0.5 ± 1.4 µg. The quartz filters were pre-baked at 900°C to reduce background OC and EC. The quartz trip blank filters showed OC levels at 10.8 ± 4.1 µg and 17.2 ± 3.9 µg OC level for tunnel blanks. However, the EC for both trip and tunnel blanks were below the reporting limit (<2 µg). Although the high OC level in tunnel blank is found, the average tunnel blank mass of 1.6 µg suggests that the adsorption of OC from the dilution air onto PTFE filters is negligible.

The actual tunnel blank OC level should be much less when taking into account the trip blank results. It is well known that quartz materials tend to adsorb organic volatile and semi-volatile compounds to a greater extent than PTFE materials. This phenomenon, sometimes referred to as “artifact” has been extensively studied in ambient particulate matter sampling studies (Kirchstetter et al., 2001, and Turpin et al., 2000) as well as in studies that sampled a mixture of pentadecane/soot on a coated glass fiber (Högström et al., 2012). Although OC adsorption on filters is not completely understood, a variety of correction approaches have been investigated, such as secondary filters and denuders (Maricq et al., 2011, Mader et al., 2001, and Subramanian et al., 2004).

In an effort to reduce background contamination, ARB’s routine practice is to use charcoal filters followed by high-efficiency particulate air (HEPA) filters to remove PM and reduce organic carbon. The efficiency of contaminant reduction has been reflected in reduced tunnel blank levels.

c. Evaluation of PM Sampler Equivalency and Gravimetric Measurement Precision

Two PM samplers, a Horiba Quad PM sampler and a collocated AVL 472 SPC PM sampler, were used in a study to evaluate measurement precision and sampling unit equivalency. The Horiba Quad PM sampler was connected to the CVS dilution tunnel with a single inlet, which was subsequently divided into four air streams to feed into four identical PM filter units.

A total of twelve vehicles, including two GDI and 10 PFI vehicles, were tested over 86 tests (FTP and US06). Vehicle information is presented in Appendix Table A-3. Weighted PM emission rates over the FTP cycle were below 3 mg/mi and, predominantly, below 1 mg/mi.

The vehicles were tested using California Phase III certification gasoline fuel, with the exception of vehicles 6 and 7, which were tested using EPA Tier 2 Indolene fuel. Sample probes for PM measurement were located near the tunnel center line and 10 tunnel diameters downstream of the mixing point. The schematic of the sampling setup along with particle size and counting instruments is shown in Figure III-10.

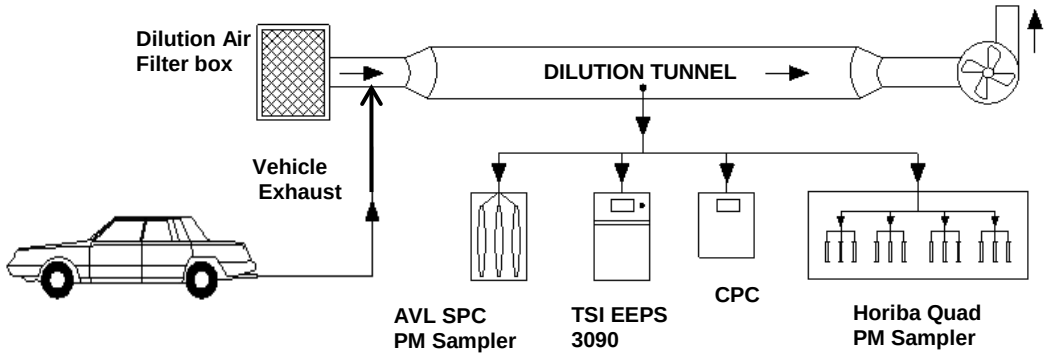


Figure III-10. A schematic of the ARB LDV emission laboratory setup including CVS dilution tunnel and simultaneous measurements utilizing two different PM samplers along with particle size distribution and counting equipment

At PM filter loadings from 0 to 400 µg, there was a very good linear correlation between the SPC and all four Horiba Quad units, as shown in Figure III-11 (a). Filter loadings of less than 100 µg are most relevant to the LEV III PM emission standards, as they correspond to emissions at or below 1 mg/mi. The correlation below 100 µg loading shows slightly greater scatter than the correlation for mass loadings from 0 to 400 µg, shown in Figure III-11 (b).

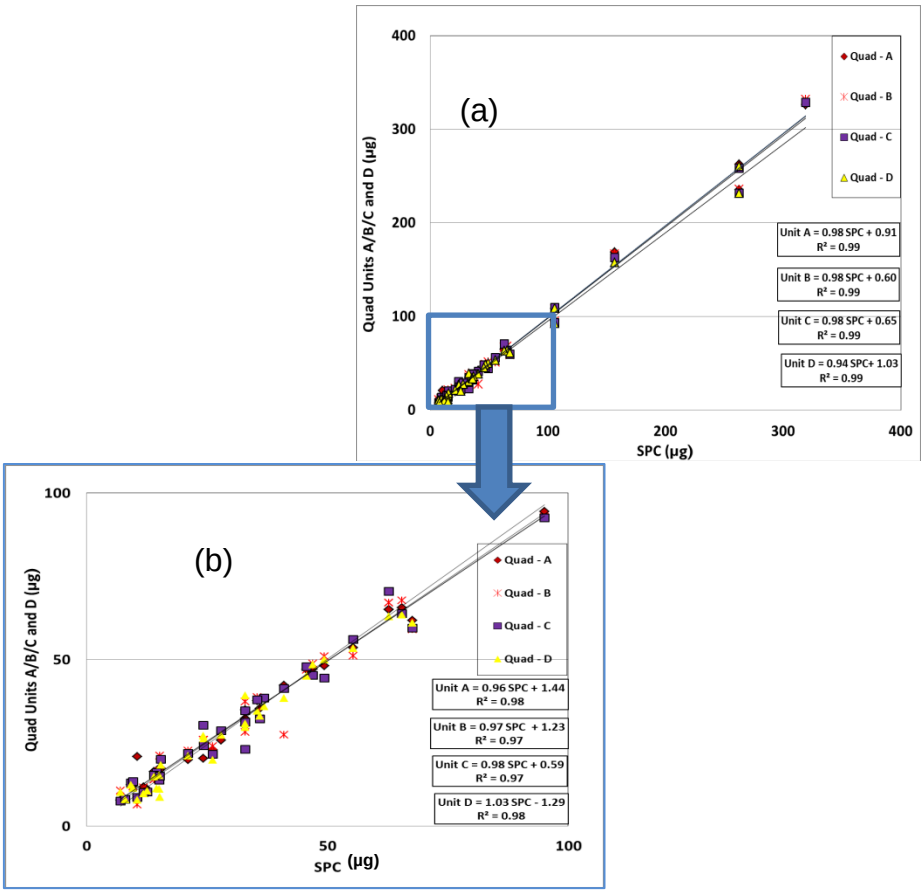


Figure III-11. PM filter loading correlation between SPC and Quad units for mass ranges (a) 0-400 µg and (b) 0-100 µg. (Sardar et al., submitted)

For filter loadings below 100 µg, the percent deviation of the five sampling units is illustrated in Figure III-12. The majority of the deviations is within ±20%, but is noticeably higher where the filter loading is below 20 µg (± 40%). The deviation is relatively stable for measured levels between 20 to 60 µg, and then generally decreases as the average loading increases.

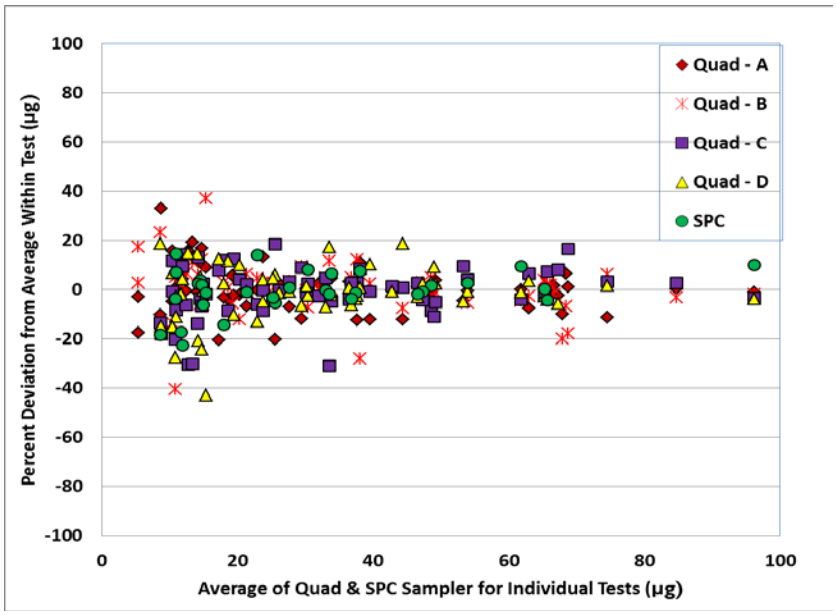


Figure III-12. Percent deviation from average loading for Quad and SPC samplers (Sardar, et al., submitted)

PM emissions varied substantially across vehicles and test cycles, so "precision" was calculated as percent variation applicable to emissions from 10 to 60 µg because of the relevancy to PM emissions at levels of sub 1 mg/mi. A two-way Analysis of Variance (ANOVA) was used for simultaneous evaluation of equivalency and measurement precision. Table III-4 shows the ANOVA results. The overall F test for the samplers is not statistically significant. The p-value (greater than 0.05) also indicated the equivalence (95% confidence interval) of the five sampler units.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows (Tests)	0.09	20	0.00	0.43	0.98	1.70
Columns (PM Monitors)	0.01	4	0.00	0.32	0.87	2.49
Error	0.88	80	0.01			
Total	0.99	104				

Table III-4. ANOVA table for PM loadings from 10 to 60 µg (Sardar, et al., submitted)

The mean square error (MSE) in Table III-4 (the intersection of the column "MS" and the row "Error") is equal to 0.011, an experimental estimate of the "error variance" to which individual observations are subjected. The root mean square error (RMSE)

characterizes the precision of measurement. The precision is determined to be 11.1%. This value is most appropriate around the 35 µg PM loading (mid-range of 10 to 60 µg loadings).

Measurement - Repeatability and Reproducibility

Repeatability and reproducibility analyses were performed to evaluate the intra-lab and inter-lab variability of the measurement systems in ARB's HSL test cells. The repeatability of a test cell is defined as the variability that results from repeat tests of the same vehicle in a short time period under the same sampling conditions (including the same operator and the same sampling system). Reproducibility is defined as the total variability that results when different laboratories measure the same vehicle. It is important to confirm that the results are reproducible between different test cells and different operators.

One vehicle (Veh 9, a 2009 Nissan Altima in Appendix A2) was repeatedly tested in three of ARB's test cells (A, B, and C) to determine repeatability and reproducibility. The vehicle was chosen because its PM emissions were in the range of interest - below 1 mg/mi. A summary of the PM emission statistics are presented in Table III-5. Of 28 tests in total, two results were above 1 mg/mi. Both of these measurements were obtained from Test Cell B, which had the highest average emission results.

	Cell A	***Cell B***	***Cell C***	***All Tests***
# of Tests	9	8	11	28
Mean	0.67	0.87	0.61	0.70
Standard Error	0.05	0.07	0.05	0.04
Median	0.69	0.86	0.58	0.71
Standard Deviation	0.16	0.19	0.16	0.20
Sample Variance	0.03	0.04	0.03	0.04
Range	0.58	0.62	0.51	0.80
Minimum	0.37	0.56	0.38	0.37
Maximum	0.95	1.17	0.89	1.17
Confidence Level (95%)	0.13	0.16	0.11	0.08

Table III-5. PM emission statistics of vehicle 9 tested in three test cells

The average PM emission rate and tunnel blank values from the three test cells are shown in the Figure III-13. A set of three tunnel blanks was collected from each test cell in the morning before each test. The tunnel blank mass was converted to an emission

rate using the actual FTP testing conditions (CVS flow = 350 scfm, PM sampler flow = 2 scfm, distance driven = 11.1 miles).

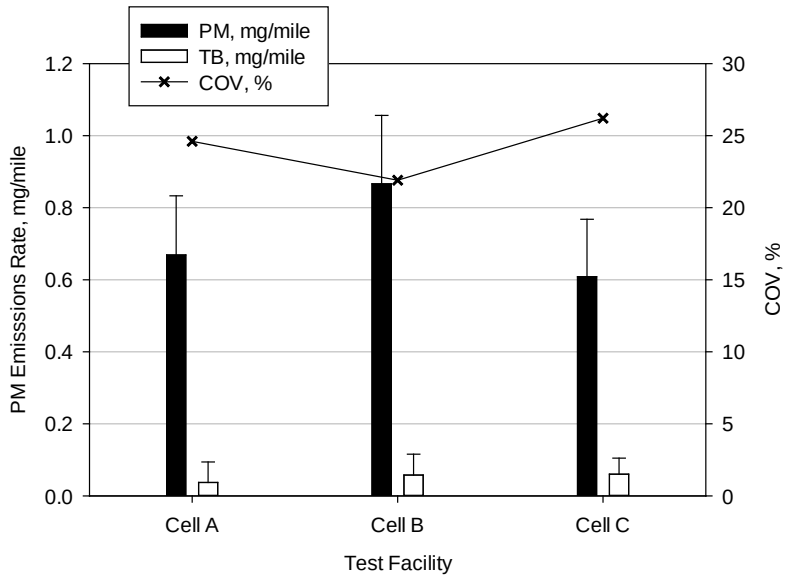


Figure III-13. PM emission levels (data not corrected for tunnel blank, TB) of vehicle 9. Error bar represents one standard deviation. (Hu et al., 2014)

The average and one standard deviation of FTP weighted PM emissions in cell A, B, and C were 0.67 ± 0.16, 0.87 ± 0.19, and 0.61 ± 0.16 mg/mi, respectively. Mean tunnel blank values were consistently an order of magnitude lower than test results among all three test cells, with values as follows: cell A (0.04 ± 0.06 mg/mi), cell B (0.06 ± 0.06 mg/mi), and cell C (0.06 ± 0.04 mg/mi). The variability of tunnel blanks was negligible relative to that of the overall PM measurement. The test results from all three test cells showed consistent test-to-test variability (CoV=22 to 26%). The range in measured PM emissions across all three test cells was not a statistically significant difference at the 95% confidence level (Hu et al., 2014).

The intra-lab (test-to-test) variability (s_r^2) , inter-lab (lab-to-lab) variability (s_L^2), and reproducibility (s_R^2) are calculated by following the statistical analyses equations listed in the Appendix. The results are shown in Table III-6.

		Variability			Coefficient of Variance		
	Emissions mg/mile	Intra-Laboratory s_r^2	Inter-Laboratory s_L^2	Total Variability s_R^2	CoV_r	CoV_L	CoV_R
PM	**0.70±0.21**	**0.03**	**0.01**	**0.04**	**0.24**	**0.17**	**0.30**

Table III-6. Repeatability and reproducibility of one vehicle (Nissan Altima) tested at three ARB HSL test cells (Hu et al., 2014)

For the vehicle tested in the three cells, the intra-lab variability (s_r^2) accounted for 75% and the inter-lab variability (s_L^2) accounted for the remaining 25% of total variability (s_R^2, reproducibility). The dominance of the intra-lab variability was also observed by Giechaskiel et al. (2008) when measuring particle number emissions of a light-duty diesel vehicle with diesel particulate filter. The intra-lab variability can be attributed to the emission source (such as vehicle stability and operator) and tunnel adsorption/desorption of semi-volatile organic compounds.

d. Equivalency of CFR PM Sampling Options

Equivalency of Single and Three-Filters Sampling Methods

As mentioned in Section II b, 40 CFR Part 1066.815 allows for five different sampling options. ARB has evaluated the equivalency between two of these options, the conventional 3 filter FTP and the single filter flow-weighted sampling methods.

The single filter approach is of interest due to its lower cost (reduced number of filters) and potential for reducing variability, given that much of the variability is associated with the very low mass loading of phases 2 and 3. For this sampling option (Table III-7, Option 4), PM is collected on a single filter over the cold-start UDDS cycle and the first 505 seconds of the hot-start UDDS. The sample flow rate is adjusted proportionally to the filter face velocity over the three intervals of the FTP based on weighting targets of 0.43 for phase 1, 1.0 for phase 2, and 0.57 for phase 3. Filters from the single filter flow-weighted and conventional 3-filter sampling methods were collected from ARB's test cell A using the two collocated samplers illustrated in Figure III-10. Detailed vehicle information is shown in Appendix Table A-3.

Shown in Table III-7 is a list of eight vehicles and their PM emission levels for evaluating different sampling methods. An average result from 25 tunnel blanks is also included. The CoV of the repeated tests is shown in Figure III-14. The CoV of vehicle emission

repeatability ranges from 1 - 55% and is somewhat inversely related to the emission rate, in that the high CoV is typically associated with a lower emission rate.

Vehicle Make/Model	Number of Tests	Average PM Emission* ± SD	
		3 Filter	Single Filter
Honda Civic	12	0.58±0.13	0.54±0.11
Chevy Malibu LT	16	0.35±0.11	0.34±0.10
Toyota Camry LE	11	0.48±0.13	0.43±0.19
Dodge Grand Caravan	12	0.13±0.06	0.11±0.06
Nissan Altima	7	0.90±0.23	0.91±0.20
Honda Accord	3	0.16±0.05	0.15±0.03
Buick Regal	3	3.44±0.08	3.40±0.05
Ford Explorer	3	4.03±0.44	3.81±0.36
Tunnel Blank	25	0.09±0.07	0.04±0.04

*Emission results were not background corrected.

Table III-7. A list of vehicles and their PM emission levels for evaluation of 3-filter and single-filter-flow-weighted sampling options

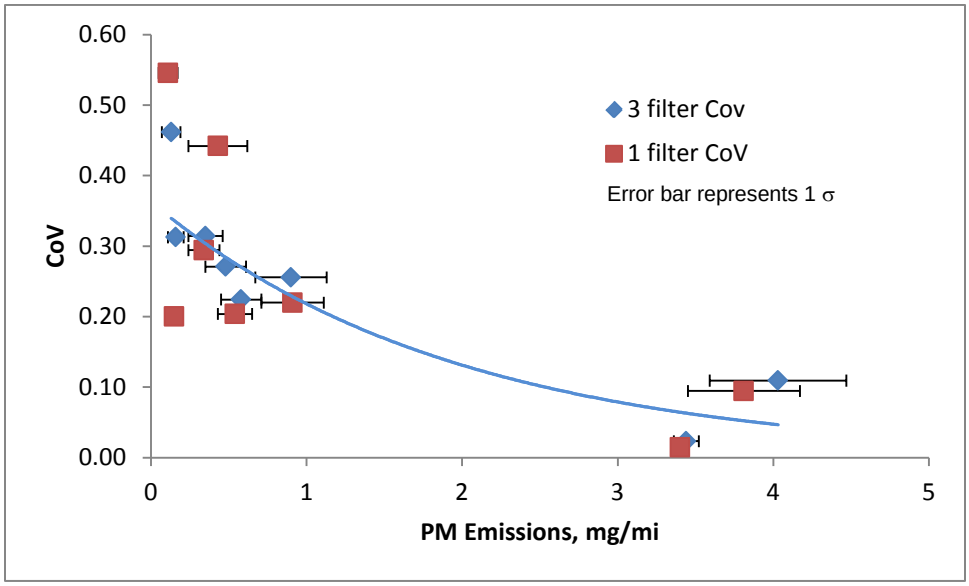


Figure III-14. CoV as a function of PM emission rates for the 3-filter and single filter sampling methods

As shown in Table III-7, the conventional 3-filter and single filter method had comparable variability despite the lower mass loading with the single filter method. The benefit of reduced measurement variability with weighing only one filter was offset by the increased variability at lower mass loading.

The differences in the average PM emissions between the two sampling methods were found to be less than 10%, with the exception of Dodge Grand Caravan which showed a deviation of 14%. With the exception of the Nissan Altima, the single filter method has slightly lower average emission levels compared to the 3-filter method. Bushkuhl et al. (2013) compared PM mass emissions between the single filter at a constant flow (not flow-weighted) and the 3-filter method. PM mass from the single filter method was systematically lower than the sum of the three individual filters used over a FTP cycle. These differences might be attributed to an increase in total organic compound adsorbed when using more filters.

The correlation between the single and 3-filter methods (without background correction) is depicted in Figure III-15 (a) for vehicular PM emissions below 3.5 mg/mi. The R^2 value of 0.99 indicates a very high degree of correlation between these two methods. Figure III-15 (b) depicts the correlation of vehicle PM emission levels in the sub 1 mg/mi range. The scatter increases slightly with an R^2 of 0.92.

To further investigate the anomaly of PM levels determined by the two methods, the sub 1 mg/mi PM mass data were corrected by subtracting the average tunnel blank PM mass for each filter. The average tunnel blank PM loadings for phases 1, 2, and 3, and for the single flow-weighted filter are found to be 2.0, 2.1, 2.2, and 1.9 µg, respectively. Figure III-15 (c) shows the correlation between the two methods after the background correction. The background correction improves the R^2 slightly to 0.94 and the slope noticeably to 0.98.

A statistical analysis (paired t-test) was also performed for the background (tunnel blank) corrected emission data. Results of the paired t-test at the 95% confidence level (α=0.05) indicated no statistically significant difference between these two methods.

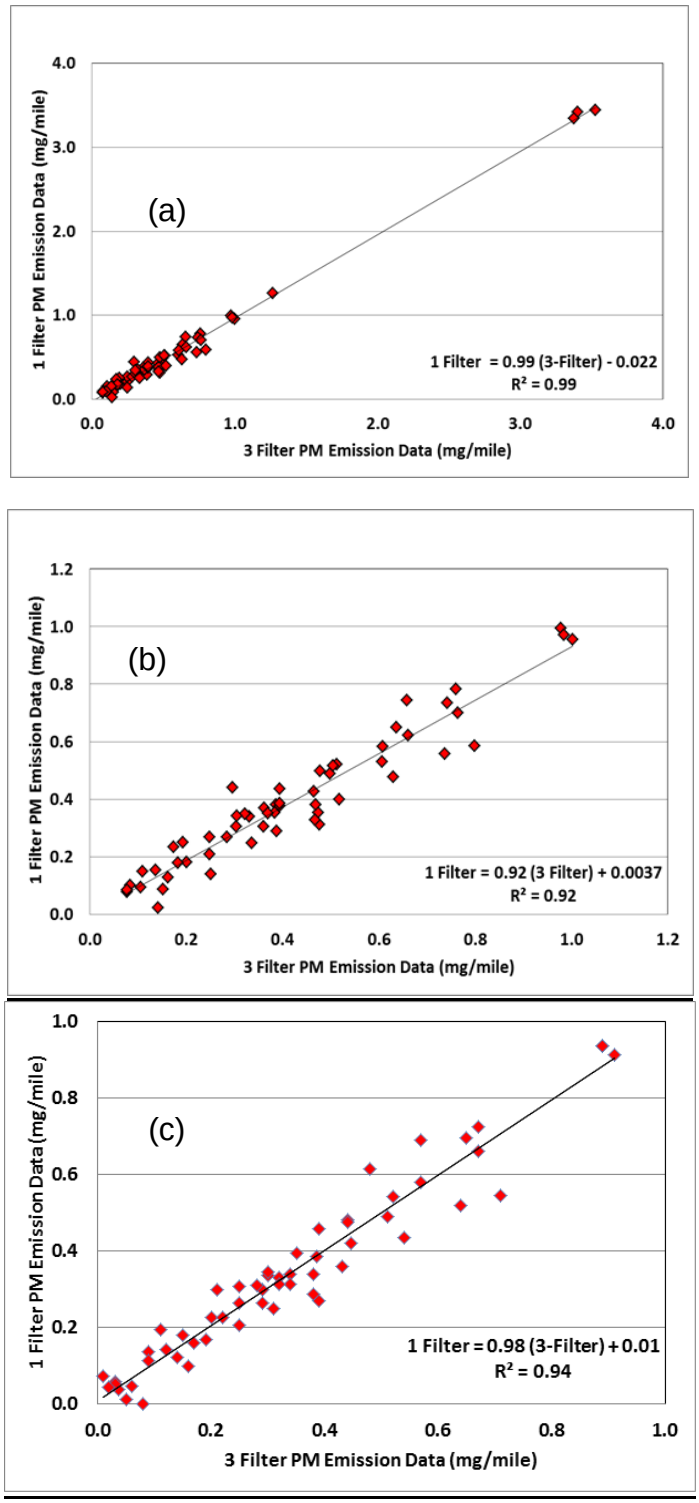


Figure III-15. Single and 3-filter method comparison: (a) For emission levels between 0 and 3.5 mg/mi; (b) For emission levels less than 1 mg/mi range without background correction, and (c) Emission levels less than 1 mg/mi with background corrections (Sardar et al., submitted)

Equivalency of Three- and Two-Filters Sampling Methods

ARB also evaluated a two-filter method, 40 CFR Part 1066.815 Option 2, by collecting PM on one filter over the cold-start UDDS and on a separate filter over the hot-start UDDS. However, only one vehicle (Nissan Altima) was tested for this sampling option. A total of 7 paired samples for the 2-filter and conventional 3-filter methods were collected. The results of these two methods for this vehicle are equivalent at an emission level of 1 mg/mi. The PM emission rates for 2-filter and 3-filter were 0.94 ± 0.15 and 0.96 ± 0.14 mg/mi, respectively.

Partial Flow Dilution (PFD) for PM Sampling

EPA's CFR Part 1065 Engine Test Procedures and Part 1066 Vehicle Test Procedures permit an option for diluting exhaust either through a full flow CVS or a partial flow dilution (PFD) sampling system prior to PM collection. PFD sampling dilutes only a fraction of raw exhaust, which reduces the flowrate of dilution air needed but requires a real-time exhaust flow signal to maintain the proportionality of dilution air.

A study by Khalek (2007) on diesel particulate measurement evaluated five different PFD units for heavy duty engine testing. All of the PFD units demonstrated good sample flow response times (on the order of 100 ms), and most had excellent correlation between the sample flow and the exhaust flow with R^2 exceeding 0.99 and a standard error <5%. Using a diesel particulate filter with continuous regenerative technology and a bypass, the PM mass emission measurements from four out of five PFD units showed that they performed well under steady-state engine operation. However, three of five PFD units reported higher PM mass emission levels under transient engine operation.

Though heavy duty PFDs have been evaluated for quite some time now, little has been done to evaluate the applicability of PFD's in LDV emissions. Two prototype PFD's have been evaluated for LDV application (Foote et al., 2013). Both prototype PFDs were able to meet the flow proportionality requirements for traditional powertrains, but not for hybrid electric vehicle (HEV) powertrains due to intermittent zero flow conditions. The weighted PM emissions of the two PFDs and the CVS full flow dilution correlate linearly when emissions were less than 3 mg/mi, yielding slopes of 1.03 and 0.74 with R^2 of 0.95 and 0.86, respectively. The scatter increased when emissions were less than 1 mg/mi, yielding R^2 of 0.58 and 0.38. Improvements to PFDs are still needed when measuring emissions less than 1 mg/mi.

A partial dilution system can potentially add flexibility to compliance testing. However, ARB currently has no such capability and will continue to evaluate the applicability of PFDs in emission testing.

IV. ALTERNATIVE METRICS FOR PARTICULATE MASS DETERMINATION

Vehicle PM emissions are a physically and chemically complex heterogeneous mixture comprised of solid, liquid, semi-volatile, and gaseous compounds that are a byproduct of incomplete combustion and have been recognized as a significant anthropogenic source of ambient PM.

The characterization of PM emissions can be complex and challenging. Over the past two decades, considerable progress has been made in both sampling and measurement methodologies for determining a variety of physical and chemical properties of PM, such as particle number, size distribution, and black carbon. Methods that can measure ambient and source samples, including aerosol gravimetric determination, are of great interest. Commonly used instruments for measuring particle number, size distribution, and black carbon of vehicle PM emissions are described in the Appendix along with their operating principles and capabilities.

Part of the complexity of measuring particle emissions relates to the transformations that take place as the particles are emitted from the tailpipe at a high temperature, and then measured after dilution and cooling in order to simulate its immediate formation in ambient air. Figure IV-1 provides a simplified overview of the particle transformation process, starting from a vehicle and ending at the measurement instruments, which are connected to the CVS dilution tunnel to determine PM mass and particle number (PN) emissions (Giechaskiel et al., 2014). The primary soot particles (typically small spherules) form in the combustion chamber. After exiting the tailpipe and the transfer tube and entering the CVS tunnel, soot particles agglomerate whereas semi-volatile organic compounds either nucleate (both heterogeneously and homogeneously) or condense onto soot particles. As they are transported through the dilution tunnel, there can be a tri-modal size distribution with nucleation, accumulation, and coarse modes, as shown in the upper left corner of Figure IV-1.

Typical PN and PM mass distributions for an uncontrolled diesel engine emission are shown in Figure IV-2 (Kittelson, 1998). Although the nucleation mode particle number concentration is high, the PM mass is much less compared to the accumulation mode.

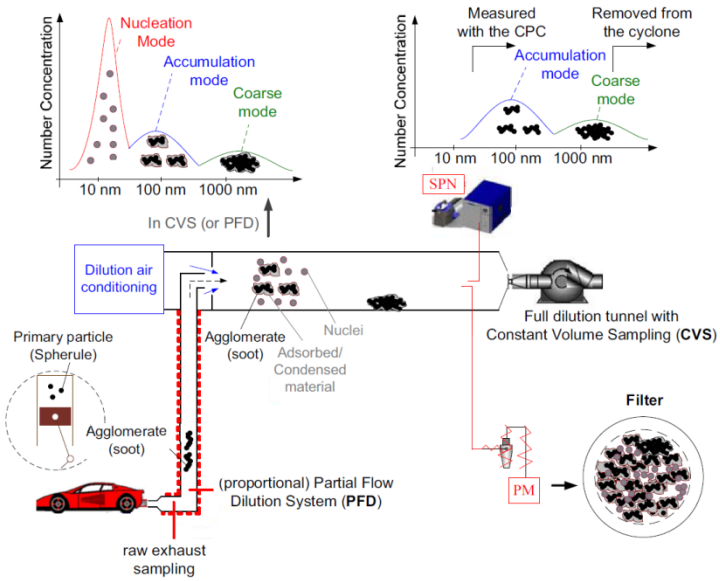


Figure IV-1. Typical sequence of particle transformation from the engine to the measurement location (modified from Giechaskiel et al., 2012)

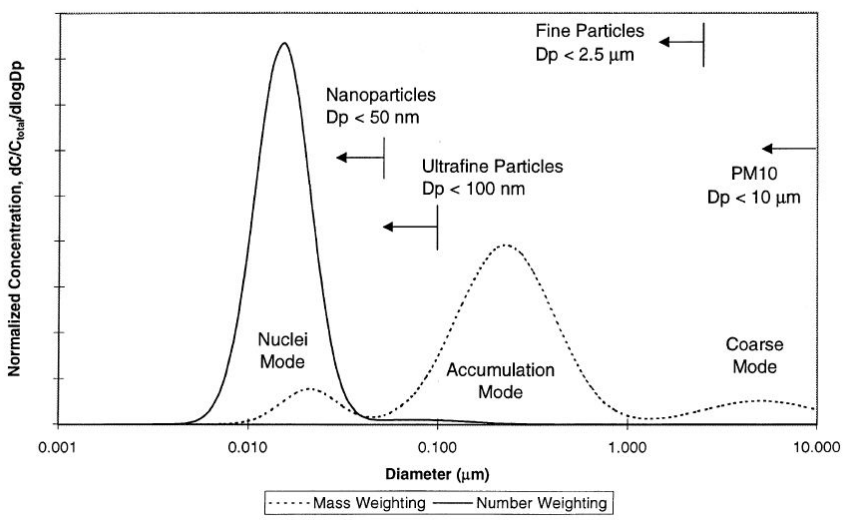


Figure IV-2. Typical engine exhaust size distribution for both PM mass and PN (Kittelson, 1998)

The relationship of total particle number and PM mass emissions for LDVs were examined with TSI Engine Exhaust Particle Sizer (EEPS) measurements between 5.6 and 560 nm and filter-based gravimetric mass measurements. Based on a dataset with more than 150 FTP tests from 34 LDVs, a correlation between total particle number and PM mass is presented in Figure IV-3. In this analysis, the particle number to mass ratio

for different vehicle technologies was found to be 2.8 x 10^{12} particles/mg (PFI vehicles), 1.6 x 10^{12} particles/mg (GDI vehicles), and 8.7 x 10^{11} particles/mg (Diesel Particulate Filter (DPF) equipped Light Duty Diesel (LDD) vehicles), respectively. The data demonstrate that, per unit mass, conventional PFI gasoline vehicles emit a greater number of particles than GDI vehicles.

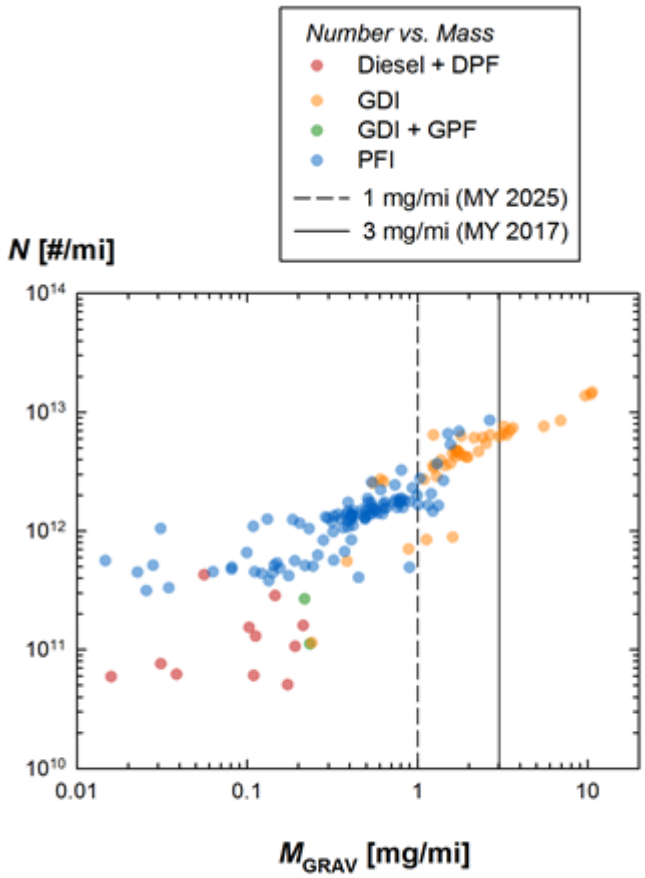


Figure IV-3. Scatter plots for total particle number versus gravimetric PM mass (Quiros et al., 2015b)

Figure IV-4 presents the average particle number emission rates calculated using the EEPS data. Data are presented for (a) vehicles meeting the 1 mg/mi standard and (b) vehicles meeting the 3 mg/mi standard. The majority of the particle number emissions for all classifications of LDVs were in the sub-100 nm range (usually referred to as ultrafine particles (UFP)). A smaller but still significant fraction of total particle number is within the sub-23 nm size fraction: 28% when numerically averaged over all tests plotted in Figure IV-3. As noted earlier, the sub-23 nm size particles are of interest

because the current EU particle number standards only count particles with a diameter greater than 23 nm. The EU method for measuring solid particle number (SPN) >23 nm was also evaluated using most of the same dataset, and is presented and discussed in the following section.

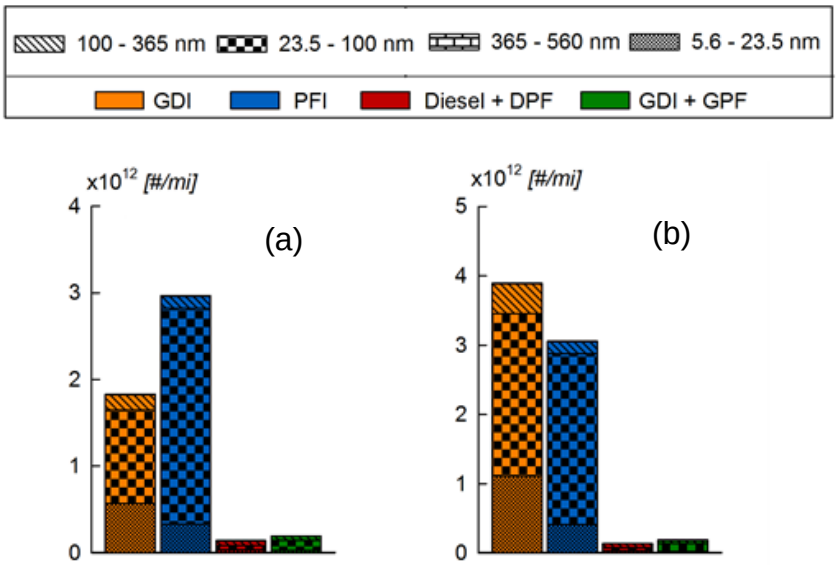


Figure IV-4. Total number emissions (a) for vehicles meeting the 1 mg/mi standard (n=115) and (b) for vehicles meeting the 3 mg/mi standard (n=152) (Quiros et al., 2015b)

a. PMP Method: Solid Particle Number Measurement

Based on the recommendation of the Particle Measurement Programme (PMP), the European Union introduced an SPN standard as a supplemental limit to PM mass in Euro 5/6 (United Nation's Economic commission for Europe (UN-ECE) regulation 83) for direct injection vehicles (GDI and diesel).

The Particle Measurement Programme was launched in 2001 under the auspices of the UN-ECE Group of Experts on Pollution and Energy (GRPE). The program was designed to deliver a regulatory procedure for Europe that would either replace or complement the existing method used for PM mass measurement for vehicle certification. Based on the inter-laboratory correlation results (Andersson et al., 2007), the program showed that the PM mass measurement was feasible and that a SPN-based limit was also able to distinguish between the emission regimes of various technologies. It provided the scientific basis for the Euro 5/6 limits for particle number and PM mass for EU type approval.

The SPN measurement requires a particle number measurement system, consisting of a Volatile Particle Remover (VPR) and a Particle Number Counter (PNC) that measures

particles with a diameter greater than 23 nm. The specifications of the SPN system are shown in Figure IV-5. When the exhaust enters the VPR, it is heated up to 300-400°C, the temperature at which most of the volatiles and semi-volatiles evaporate. The nucleation mode particles, when they are dominated by volatiles and semi-volatiles, are reduced significantly. Two other methods, based on the principles of adsorption on activated carbon or oxidation by catalytic stripper, can also be utilized to remove volatile components (Giechaskiel et al., 2014). From a practical standpoint, commercial SPN systems use the evaporation method. The particle number counter, such as CPC, measures particles with a counting efficiency of 50% and >90% at 23 and 41 nm, respectively. Unlike the gravimetric method validation with a known traceable metal weight, calibration of the PMP method is based on measurement comparisons to a reference instrument rather than measurement of a known calibration standard. GRPE is working on further refinements including the development of a calibration procedure based on an ISO test method (27891:2015) which uses an electrometer for instrument calibration. Figure IV-1 (upper right corner) illustrates the PMP method for particle number measurement. Compared to the total particle number results, the nucleation mode particles are almost completely excluded by this method.

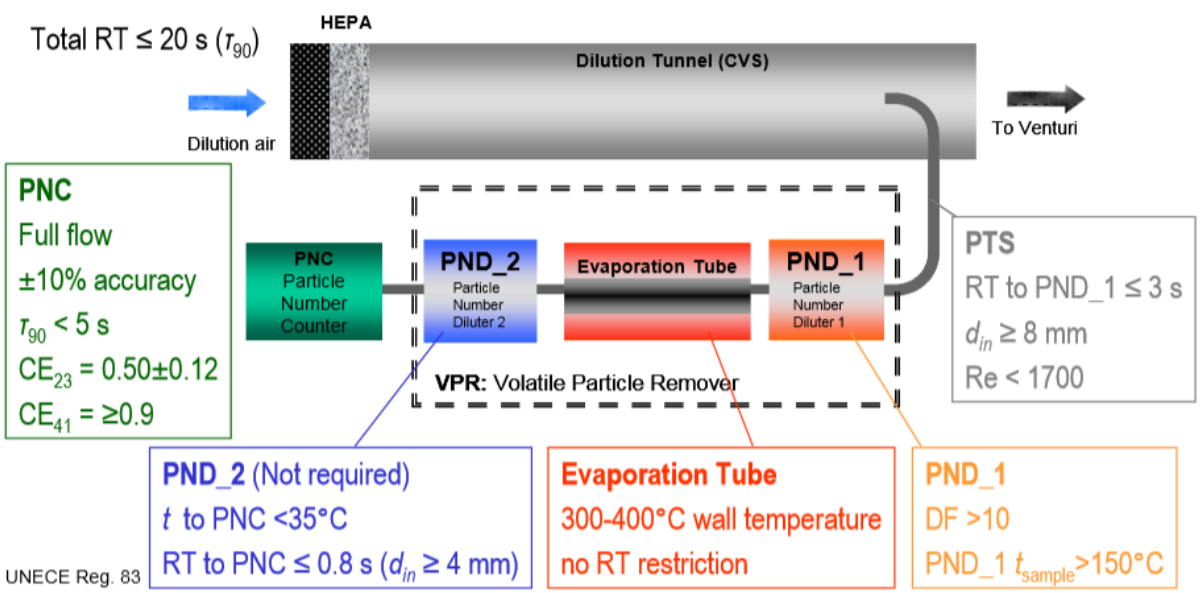


Figure IV-5. Description of solid particle sampling protocol (B. Giechaskiel, and G. Martini, 2013)

The key goal of the PMP is to achieve repeatable emission results, especially since the method would be used for certification testing. To improve measurement repeatability,

the PMP method requires removal of volatile/semi-volatile compounds, which can be heavily influenced by the sampling conditions.

Research conducted at the Joint Research Center (JRC in Ispra, Italy) has concluded that 20 to 40% of particles emitted from GDI vehicles are smaller than 23 nm (Giechaskiel and Martini, 2013). It has been shown that solid particles with smaller sizes can be also measured with good repeatability (Herner et al., 2007). In recognition of sub-23 nm solid particles in LDV exhaust, JRC is investigating the feasibility of lowering the 23 nm cutpoint (Giechaskiel and Martini, 2013). The performance of PNCs and VPRs for the standard PMP method was systematically evaluated for the purpose of extending measurements to sub-23nm solid particles. The investigation concluded that extending SPN measurement to ~10 nm may be possible, with a recommended addition of a catalytic stripper (CS). However, certain outstanding issues would need to be resolved.

The 23nm cutoff size in the PMP method causes the undercounting of a potentially large but variable fraction of the total particle number. An example for the solid and total particle number distribution for FTP phase 2 is shown in Figure IV-6. Herner et al. (2007) showed that under certain duty cycles, a DPF-equipped engine can emit solid particles and that approximately 25-75% of the solid particles are below 20 nm, and therefore, not counted by the PMP method. Khalek et al., (2010) studied particle emissions from a 2009 MY GDI vehicle using three different commercially available fuels for FTP and US06 driving cycles. The study showed that about 15 to 20% of the solid particles are smaller than 23 nm in diameter.

Another limitation of the PMP method is that it excludes volatile and semi-volatile compounds, which intends to improve measurement repeatability but disregards potentially harmful PM components. The volatile fraction can account for 10-30% of the PM mass and 70-90% of PN (Biswas et al., 2008). Semi-volatile particles include organic compounds (such as PAHs) and inorganic compounds (such as nitrates) that can impact human health (Kado et al., 2005).

At this time, ARB does not recommend the use of the PMP method for determination of PM mass based on the findings on the repeatability and correlation to the PM gravimetric method, as discussed below. However, ARB will continue monitoring the method’s development and improvement going forward.

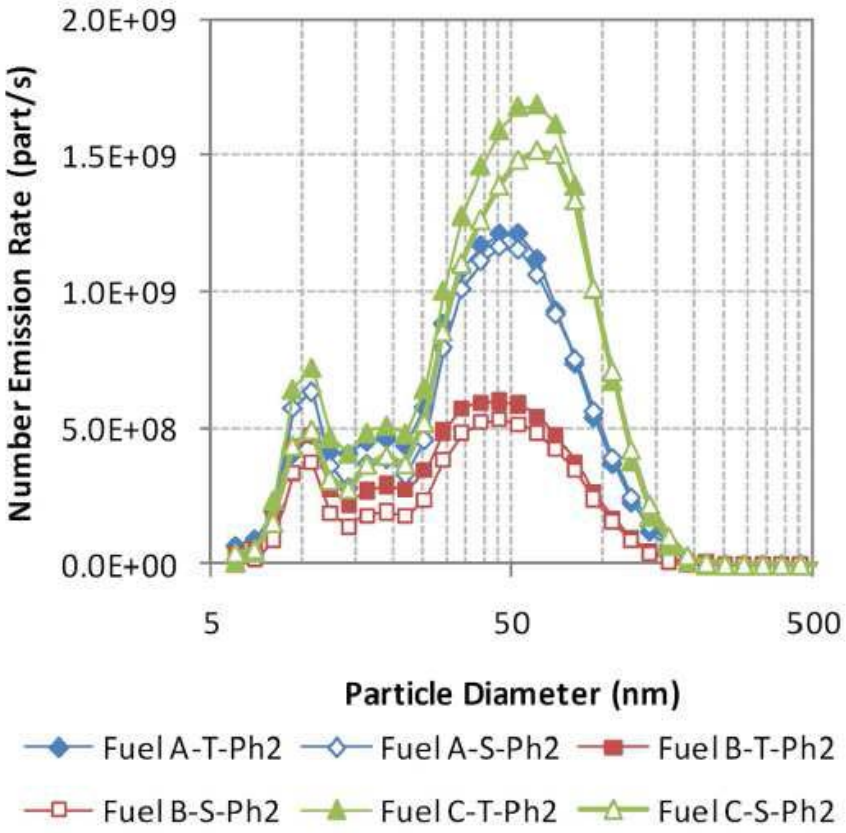


Figure IV-6. Total (T) and solid (S) particle number size distributions of FTP phase 2 testing for a MY 2009 GDI vehicle using three different fuels. (Khalek et al., 2010)

Relationship between SPN and PM Mass

In 2012, ARB evaluated PM mass and SPN emissions in several studies as part of the LEV III rulemaking effort. In the PM emission range of 1-100 mg/mile, the SPN-PM data correlated very well with a slope of ~ 2.2-2.5 x 10^{12} particles/mg. These results are summarized in Figure IV-9.

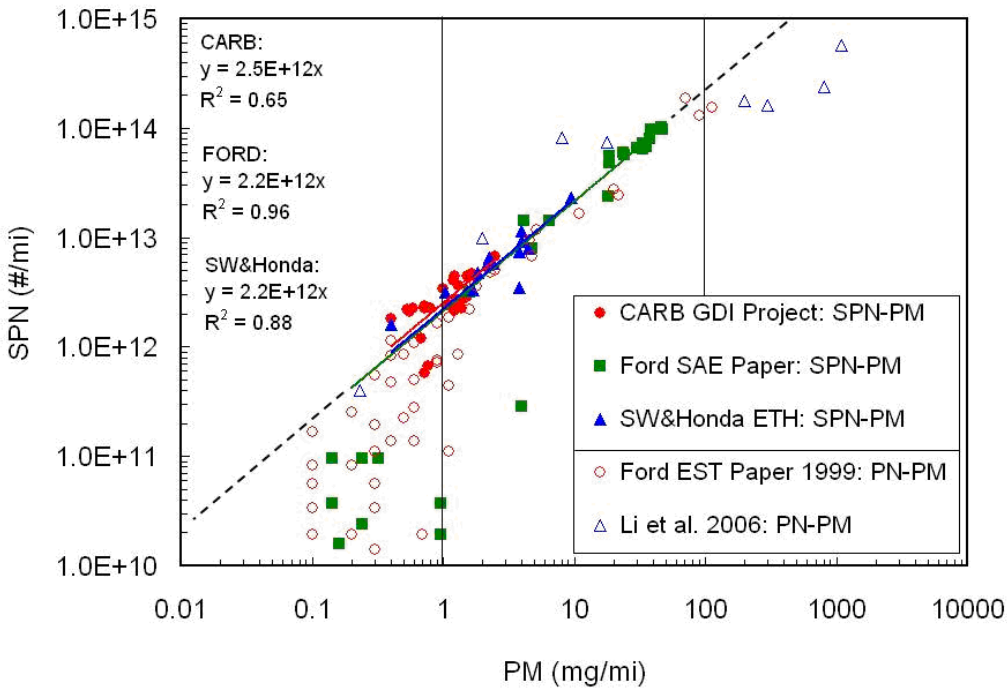
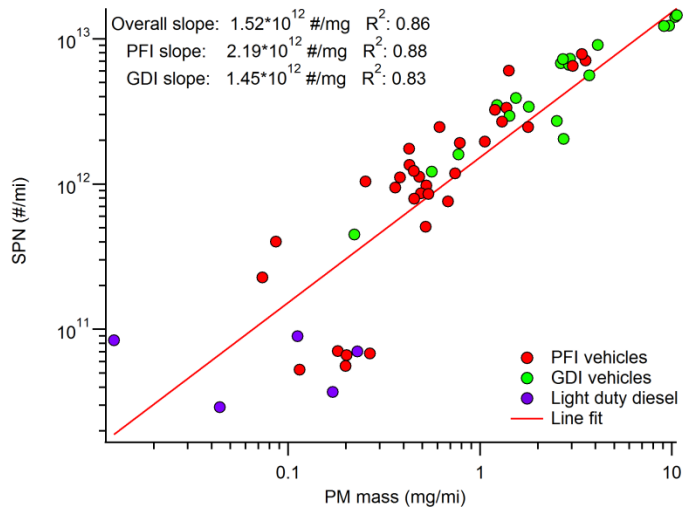


Figure IV-7. PM mass and SPN emissions for all available test results (LEV III, 2012)

As part of ARB's continued efforts to evaluate the SPN method, the correlation between PM mass and SPN were re-assessed with a more extensive dataset, collected from six emissions testing programs. A total of 45 vehicles were tested, including 22 PFI, 18 GDI, and five DPF- LDD vehicles. Vehicle information is presented in the Appendix Table A-4, and test results are summarized in Appendix Tables A-5 and A-6.

Figure IV-8 presents the relationship between SPN to PM mass for FTP and US06 driving cycles. For the FTP cycle, the general trend for PFI vehicles is similar to our earlier findings, as well as other previously reported correlations of $2x10^{12}$ particles/mg. However, the slope is lower for GDI vehicles due to the relatively low SPN to mass ratio for some vehicles. Over the US06 cycle, there is greater scatter than for FTP tests.

(a) FTP cycle



(b) US06 cycle

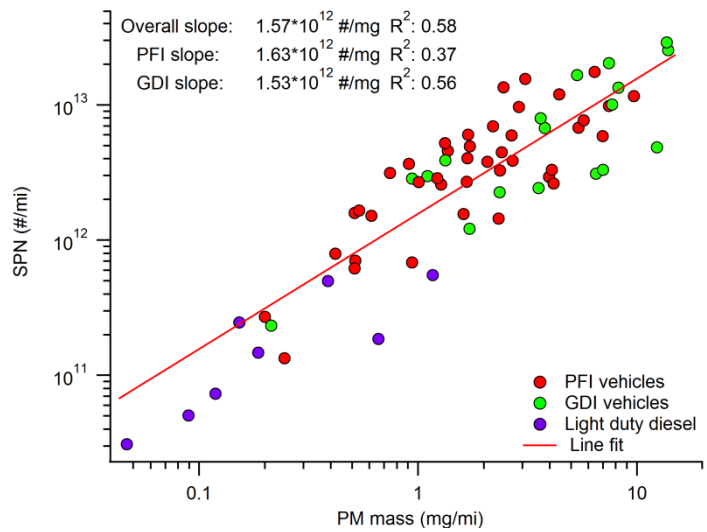


Figure IV-8. SPN (particles/mi) vs. gravimetric PM mass (mg/mi) for entire (a) FTP tests, and (b) US06. (Chang and Shields, submitted)

All of our results show a correlation between SPN and PM mass with slopes that are within the range that have been reported from various studies, from 1 to 4 x10^{12} particles/mg (Giechaskiel et al., 2012; Maricq et al., 2011). The variation in these results suggests that SPN and PM mass correlations may vary with different engine technologies, and could continue to evolve as engine and aftertreatment technologies advance. Since the slope is not a constant, it is difficult to employ SPN as a surrogate for PM mass determination.

Emissions Repeatability of PM Mass, SPN, and Black Carbon

Any repeat tests that were part of the correlation study were used to compare the emissions repeatability of PM mass, SPN, and black carbon (BC). Black carbon is quantified with an AVL Micro Soot Sensor (MSS) utilizing photoacoustic spectroscopy. Table IV-1 summarizes these results for FTP and US06 tests. For PFI vehicles tested on FTP cycles, emission variability of PM mass is 20.9%, compared to 27.7% and 23.3% respectively for SPN and BC. For GDI vehicles, the emissions variability is 5.7%, 13.3%, and 9.2% respectively for PM mass, SPN, and BC.

When comparing different driving cycles for the same engine technology, emissions variability for US06 is higher than that of FTP for both mass and SPN measurements. This higher variability may result from a combination of vehicle and driver in an aggressive, high-acceleration US06 cycle. For the US06, the emission variability of PM mass is higher than that of SPN, the opposite of FTP results.

FTP	Mass		SPN		BC	
	Pooled Avg (mg/mi)	Pooled SD (mg/mi)	Pooled Avg (#/mi)	Pooled SD (#/mi)	Pooled Avg (mg/mi)	Pooled SD (mg/mi)
PFI	0.64	0.13	2.56E+12	7.03E+11	0.60	0.13
GDI	5.67	0.32	9.37E+12	1.25E+12	3.07	0.28
LD Diesel (DPF)	0.11	0.11	5.98E+10	1.77E+10	0.05	0.006

US06	Mass		SPN		BC	
	Pooled Avg (mg/mi)	Pooled SD (mg/mi)	Pooled Avg (#/mi)	Pooled SD (#/mi)	Pooled Avg (mg/mi)	Pooled SD (mg/mi)
PFI	1.84	1.30	4.49E+12	1.27E+12	0.87	0.98
GDI	6.82	3.52	1.02E+13	4.06E+12	4.98	2.90
LD Diesel (DPF)	0.23	0.22	1.76E+11	1.54E+11	0.08	0.05

Table IV-1. Summary of repeatability for gravimetric PM mass and SPN (Chang and Shields, 2015, submitted)

b. Estimation of Particulate Mass Using Particle Size Distribution and Particulate Effective Density

Various instruments available today can measure particle size distribution in real-time and thus can be used to characterize PM emissions. When measuring real-time electrical mobility diameter, and applying a relevant effective density function, an estimate of the suspended PM mass can be determined. Using this approach to characterize PM mass, real-time PM emission events can be monitored. This method is attractive because the detection limit is potentially lower and there is no uncertainty associated with collecting and weighing filters as in the gravimetric method. This method has been called Integrated Particle Size Distribution (IPSD) because the size distribution is integrated over a relevant size range.

The IPSD approach has previously been demonstrated to reduce overall emission measurement variability and showed a good one-to-one relationship with gravimetric measurements of emissions from heavy-duty diesel trucks (Liu et al., 2009, Maricq et al., 2004 and Quiros et al., 2014). However, because no such evaluations had been conducted on LDVs, ARB sought to evaluate the IPSD method as a possible alternative to the gravimetric PM method. This evaluation consisted of determining the effective density of PM from LDVs meeting the LEV III standards and evaluating the IPSD method during steady-state and transient operating conditions, such as during the FTP and US06 cycles.

Using the combination of Differential Mobility Analyzer (DMA) and a Centrifugal Particle Mass Analyzer (CPMA), ARB found the emissions from GDI vehicles were nearly identical to those reported by Maricq and Xu (2004). For the first time, ARB reported the effective density functions for conventional PFI gasoline engines, and PM emissions of a light-duty diesel (LDD) vehicle downstream of a DPF (Quiros, et al. 2015a). The determination of effective density of PM emitted from vehicles meeting the LEV III PM standards were similar to those in previous studies over the past decade. Figure IV-9 shows the effective density functions determined during ARB's evaluation for use during the evaluation of the IPSD method to estimate PM mass.

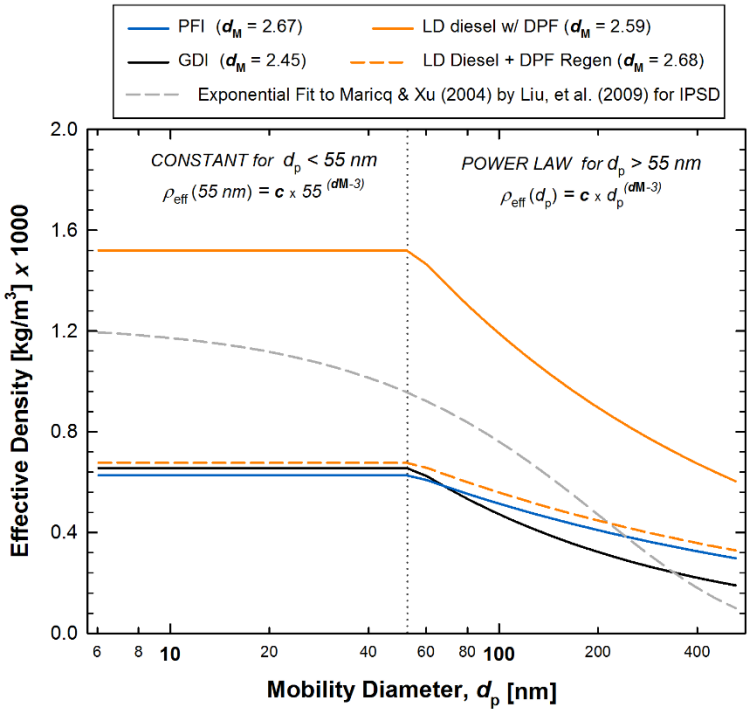


Figure IV-9. Particle effective density functions applied to the FTP and US06 test cycles. (Quiros et al., 2015b)

A comprehensive dataset including 168 FTP and 87 US06 tests, from 34 different vehicles that included PFI, GDI, and DPF-LDD technologies, was used to calculate the IPSD mass using the TSI EEPS (electrical mobility diameter between 5.6 and 560 nm), over transient cycles. Results showed that the estimated IPSD mass was persistently lower than filter-based gravimetric mass by 56-84%. These relationships are broken down by FTP and US06 tests, and by vehicle technology in Figure IV-10.

There are two possible reasons why IPSD could underestimate PM mass. The first is the accuracy of fast-sizing spectrometers such as the TSI EEPS, especially for particles larger than 100 nm, which in vehicle exhaust are externally mixed with particulate of various morphologies and chemical compositions. Because the unipolar charging state of soot is highly variable, defining a single calibration to invert particle charge into size distribution may fundamentally limit their use for measuring vehicle exhaust over transient cycles. The ratio between the response of a reference size distribution method, the Scanning Mobility Particle Sizer (SMPS), and the EEPS was shown to diverge greatly with increasing particle size beyond 100 nm. The calibration of the EEPS response is under current exploration by multiple academic groups and instrument manufacturers to further improve its accuracy and application for characterizing vehicle exhaust.

The second possible reason that IPSD underestimates PM mass is that the EEPS has an upper measurement size of 560 nm in electric mobility, whereas sampling filters

typically collect particles in aerodynamic diameters up to 2.5 µm. During steady-state vehicle operating conditions, Quiros, et al. (2015a) showed that by combining an SMPS and an aerodynamic size distribution instrument, a near one-to-one relationship between IPSD and gravimetric PM mass was achieved. However, this relationship was not observed when applied to transient emissions sources and measuring size distribution using a TSI EEPS.

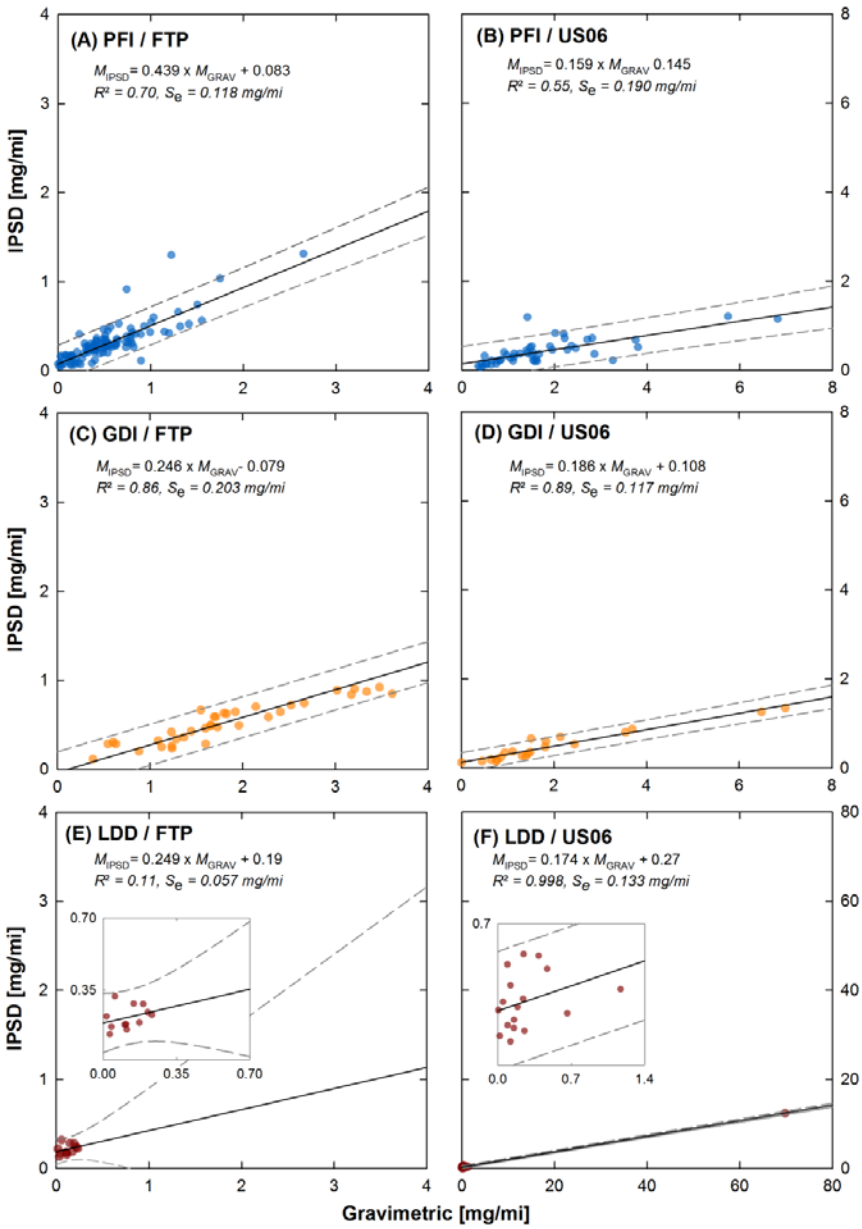


Figure IV-10. Correlations of M_{IPSD} versus M_{GRAV} for vehicle tests over the FTP (A, C, E), and US06 (B, D, F) test cycles. Dashed lines indicate the 95% prediction intervals; annotations include equations for the best fit lines (least squares), and fit parameters including R^2 and standard error of the estimate (S_e). (Quiros et al., 2015b)

Li, et al., (2014) confirmed ARB findings that the IPSD method consistently underestimates PM mass by a large proportion (by 37%) when only using an EEPS despite using a different density function for various vehicle technologies including gasoline and different PFI, GDI, and DPF-LDD.

Therefore, the IPSD method in its current form is not a suitable alternative for measuring PM at sub 1 mg/mi emission levels. Nevertheless, the relationship between IPSD and gravimetric mass provided further support to demonstrate that measurement uncertainty of the gravimetric and IPSD methods is small, and that test-to-test variability largely originates from differences in PM emissions from the vehicles. Figure IV-11 shows test-to-test variability between gravimetric and IPSD methods for multiple repeat tests using three vehicles with distinct emission levels. A positive correlation was observed for vehicle emissions above the gravimetric background levels, while a negative correlation was observed for PM emissions close to the gravimetric tunnel background.

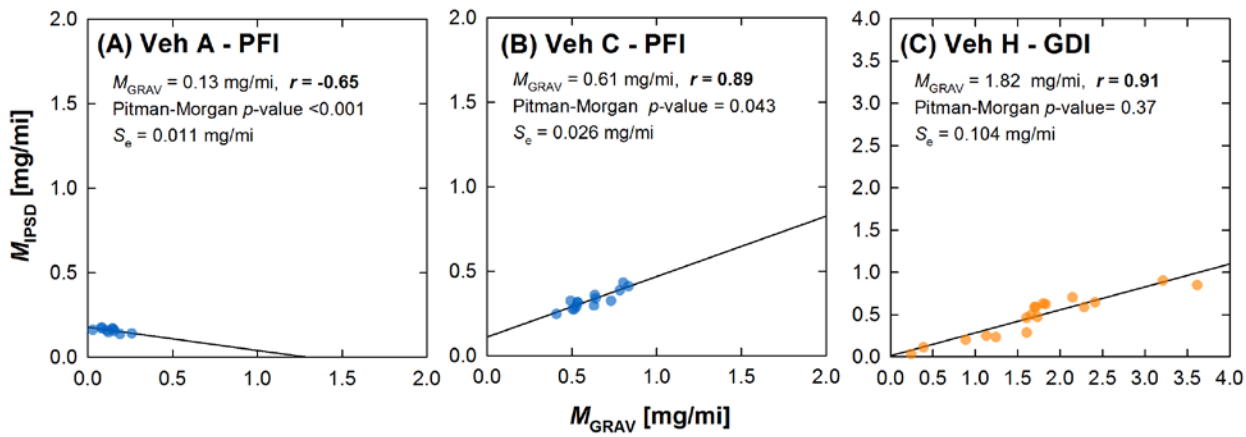


Figure IV-11. Evaluation of test-to-test variability shown for two PFI vehicles (A, B) and one GDI vehicle (C)

c. Black Carbon Measurement

Relationship between EC, BC and PM mass

ARB utilizes two methods to measure black carbon routinely: thermal/optical carbon analysis and photoacoustic spectroscopy. Thermal/optical carbon analysis is a well-established method and widely used in ambient air quality measurement for the determination of elemental carbon (EC), which is used as a surrogate for BC (Chow et al., 2007; National Institute for Occupational Safety and Health [NIOSH], 2003). The thermal/optical carbon analysis performed by ARB staff typically follows the IMPROVE_A Protocol to determine the OC and EC in PM. The analysis procedures can be found in ARB SOP MV-AEROSOL-139 v 1.1. However, EC measurements

based on thermal properties is not necessarily equivalent to BC. The measured EC may not have a one-to-one linear relationship to light absorption. ARB staff has observed an overall ratio of approximately 70% EC in the PM mass, although this ratio varied from vehicle to vehicle as shown in Figure IV-12.

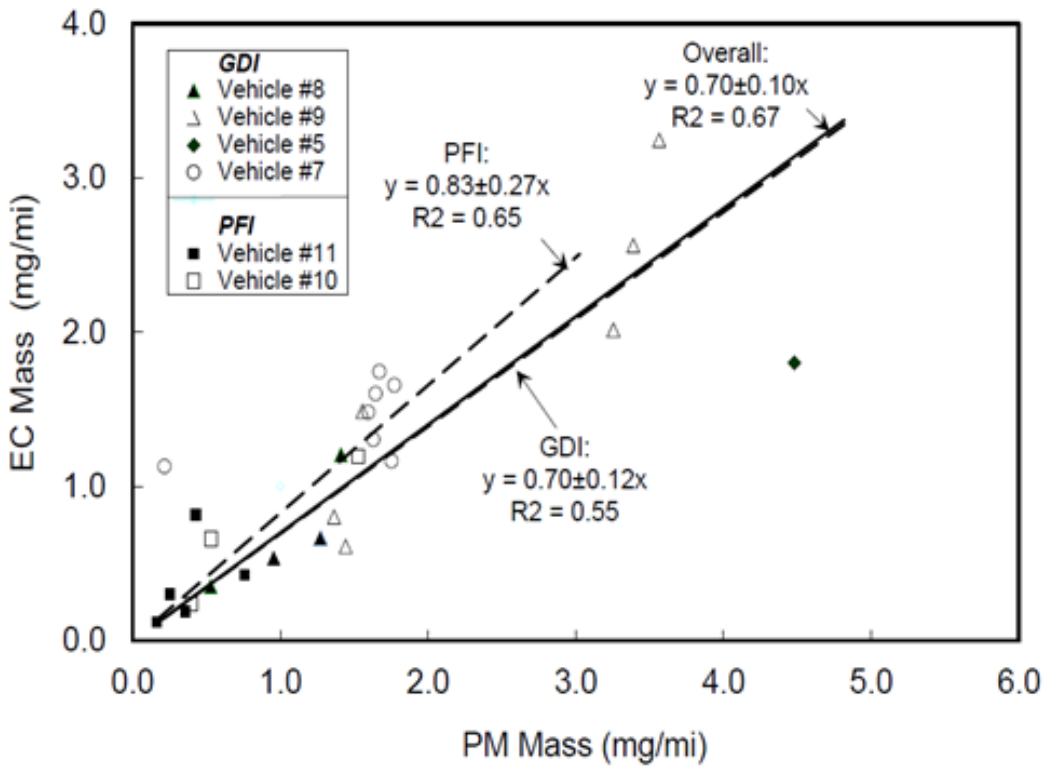
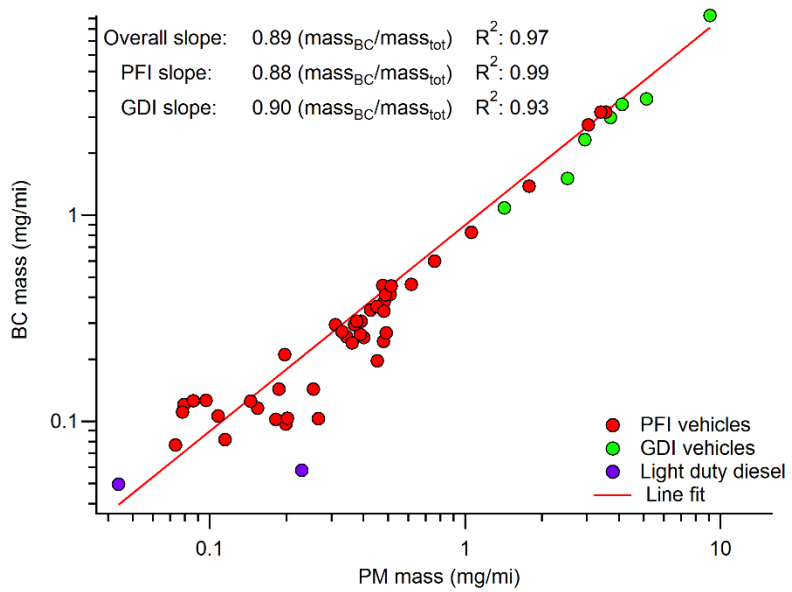


Figure IV-12. EC and PM correlation for four GDI and two PFI vehicles undergoing FTP test (LEV III, 2012)

Another instrument utilized in the ARB laboratory is the Micro Soot sensor (AVL 483, MSS) which employs photoacoustic spectroscopy to determine the BC concentration in exhaust. The BC data collected after the 2012 LEV III rulemaking showed an excellent correlation to PM gravimetric mass for all types of vehicles, with an average slope of 0.9 for the FTP tests as shown in Figure IV-13 (a). The BC to PM mass ratio is close to the 0.94 value reported by Bushkuhl et al. (2013). The BC to PM mass also correlates well for US06 tests, shown in Figure IV-13 (b), except at a lower BC/PM mass ratio. It should be noted that the emission levels below 1 mg/mi were primarily from PFI vehicles.

The variability of EC and BC to PM ratio suggests that the relationship between these two metrics may depend on the LDV fleet in the test program, and could continue to change as vehicle technology evolves.

(a)



(b)

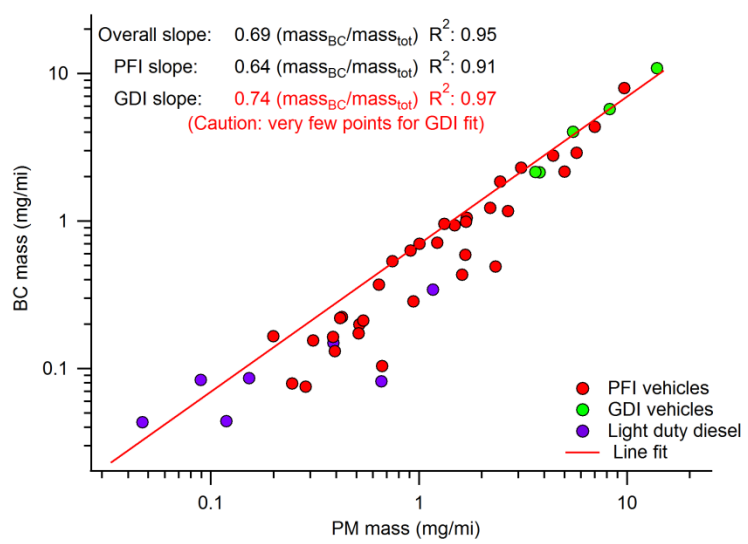


Figure IV-13. Correlation of BC (measured by MSS) and PM mass for vehicles undergoing (a) FTP and (b) US06 test

Combination Methods: Apportionment of PM mass with BC measurement

Bushkuhl et al. (2013) have reported that an integrated filter-based measurement combined with a real-time instrument shows an improvement in the measurement repeatability of PM mass. This combination method utilizes a composite PM mass collected using a full, unapportioned, flow rate during the entire FTP cycle, and the PM mass is then apportioned to each phase according to the response of a real-time instrument (Photoacoustic soot sensor) to calculate the FTP-weighted PM mass emissions. ARB has examined the combination method because of the excellent correlation reported between PM mass and BC results. Two real-time instruments were deployed for the study, an AVL MSS and an Aethalometer (Magee Scientific, AE51). The MSS detects concentrations of suspended black carbon using photoacoustic spectroscopy, while the AE51 quantifies the BC deposit on a filter by determining temporal changes in light attenuation.

An earlier study at ARB showed that increasing the PM mass loading reduces the variability of the filter-based PM emissions measurement. The combination method could improve the measurement variability by (1) maximizing the filter mass loading and (2) reducing the uncertainty of filter weighing and handling from 3 filters to 1 filter. However, the method is based on an assumption that the real-time instrument's response to PM mass is a constant, regardless of the emission composition, the engine technology, or the driving cycle.

Figure IV-14 compares PM mass emission rates obtained by the gravimetric and the combination methods (Kamboures et al., submitted). Both the MSS and AE51 measure soot and ash, but neither is sensitive to semi-volatile hydrocarbons or sulfate components. Semi-volatile and sulfate species can become part of the particles either by adsorption onto existing particles or by nucleation. In both of these cases the BC measurement will underestimate the total PM mass contribution whether it is determined by MSS or AE51.

The combination method showed improved repeatability, regardless of the BC measurement method or the vehicles tested. The standard deviations of the conventional 3-filter sampling method, the combination method with MSS, and with the AE51 are 0.11, 0.08, and 0.07 mg/mi, respectively. When all data are considered, the correlation between the methods is good ($R \approx 0.9$), but the correlation coefficients differed substantially for vehicles. For example, the vehicle-specific correlation between the combined method with MSS and PM mass ranged from -0.16 for the Caravan to 0.99 for the Malibu. The poor correlation between the methods in the Caravan tests was likely due to the low mass loadings in these tests. The Caravan's PM emission rates were typically < 0.2 mg/mi. There was a negligible difference between the combined and gravimetric method, with the exception of the 2009 Toyota Camry LE. The difference was attributed to high OC emissions and/or lower levels of BC. BC is not sensitive to organic hydrocarbons, which can result in mis-apportionment of PM mass amongst the three FTP phases.

The average PM mass emission rate of the four vehicles tested in this study was 0.38 mg/mi, which is less than half of the LEVIII 1 mg/mi emission standard. The good repeatability of the gravimetric measurements (σ=0.11 mg/mi) supports the conclusion that the existing gravimetric method is suitable for quantifying vehicular PM emissions below 1 mg/mi.

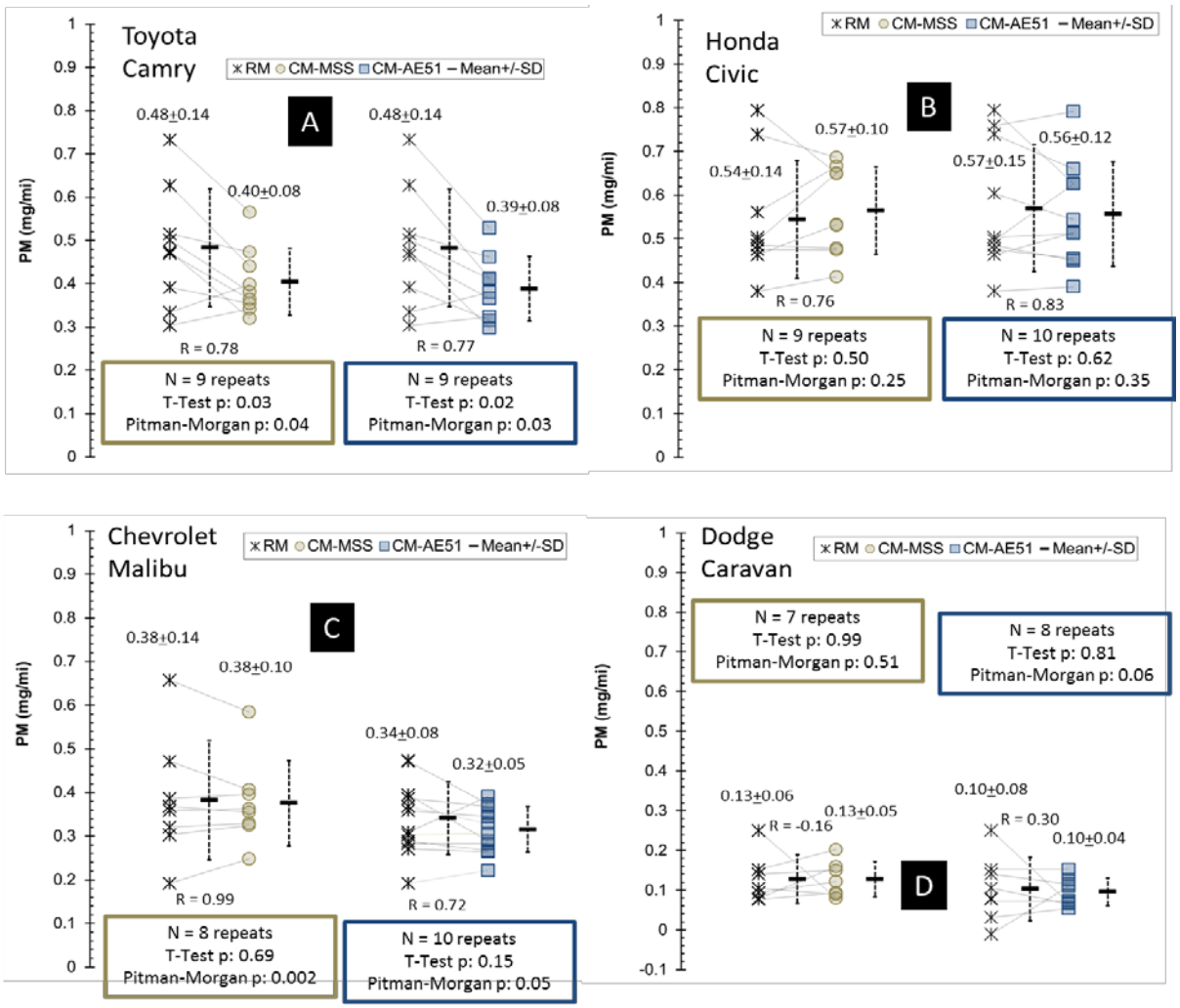


Figure IV-14. PM emission results for the three-filter reference and combination methods (Kamboures et al., submitted)

V. Concerns Regarding PM Mass Emission Measurement at Low Levels

Staff has met collectively and individually with vehicle manufacturers and other stakeholders several times over the last few years to discuss issues and test program findings related to PM measurement. Over the course of those discussions, several concerns and issues have been raised.

1. Sources of PM measurement variability make the gravimetric method infeasible.

   The major source of background measurement variability results from the potential contamination of dilution air, dilution tunnel, and PM sampling equipment. Therefore, it is important to understand how to prevent, detect, and clean the tunnel and PM sampling equipment if it becomes highly contaminated.

   Based on ARB's extensive dataset of tunnel blank results, the average background level is ~2 μg with a standard deviation of ~2.5 μg. These tunnel blanks were collected according the FTP test procedure with only dilution air drawn through the CVS system. To put this in perspective, these background results are equivalent to an emission rate of 0.08 ± 0.1 mg/mi relative to the 1 mg/mi standard. Furthermore, contamination from the background can be corrected for as permitted by the CFR on actual emission tests. Frequent checks of the tunnel blanks and the additional use of real-time PM instruments for background determination can help to identify contamination issues. When contamination is detected in the CVS system, running a known clean vehicle with high temperature exhaust may help to 'clean/condition' the tunnel. However, ARB's testing experience suggests that high tunnel contamination is rare.

2. Sampling artifacts and their impact on the variability of PM mass determination creates large uncertainties.

   Sampling artifacts refer to contamination from resuspension of PM from the wall of the sampling train (including CVS) from prior emissions testing, as well as some exhaust constituents that interact with the sampling train and sampling filters. These sampling artifacts can be either positive or negative in nature and, therefore result in measurement variability. Unfortunately, the sampling artifacts cannot be measured simultaneously with the emission test as the process is dynamic. However, 40 CFR Part 1066 allows an adequate background correction to reduce the impact of contamination on emission results.

3. Based on data from several round robin studies, inter-laboratory ('lab-to-lab') measurement variability for PM mass determination is too high to ensure robust results for a vehicle meeting the 1 mg/mi emission standard.

   ARB's own study conducted across three of its test cells did not find a high variability as suggested by the older round robin studies that relied on older test methods and generally were focused on pollutants other than PM. On the contrary, the coefficient

of variance of repeat tests demonstrated that PM emissions at the 1 mg/mi level can be repeatedly measured. Industry has generally acknowledged that they are still in the process of upgrading their facilities for the new test procedures and methods required for 40 CFR part 1066 compliance and has suggested delaying any new, PM-focused round robin studies until such upgrades are complete.

4. Limited data suggests that barometric pressure and possibly ambient humidity may affect tunnel blank results.

   Industry recently provided a limited data set showing some variation in tunnel blank background during periods of time where barometric pressure and/or relative humidity were varied. The data is inconclusive as to whether there is a correlation between these ambient parameters and the tunnel blank background. The distribution of the presented tunnel blank levels appears to be within a typical range of tunnel blanks. Therefore, ARB does not expect environmental conditions to have a significant impact on the tunnel blank background.

5. The multiple PM mass sampling options allowed for official testing by the CFR can lead to higher variability in results.

   ARB is continuing to evaluate all five sampling options and their results. To date, ARB has evaluated the two most likely options (the conventional 3-filter method and the newer single-filter, flow-weighted method) and found them to be equivalent. ARB has partially evaluated a third option utilizing two filters and preliminary data suggests it is likely equivalent. ARB discontinued further evaluation at this time because this method is less likely to be used as it requires additional vehicle test time and does not reduce the number of filters (and their associated analysis time) as much as other methods.

6. The cost of gravimetric measurement is high.

   There is an expense associated with any measurement including PM mass determination. Historically, minimal PM testing has been done for certification or compliance on gasoline vehicles and, as a result, vehicle manufacturers are facing an additional test burden to include PM emission measurement for the majority of testing in the future. However, this was taken into account when the standards were adopted both by phasing in the standard over several model years and by requiring test data to be submitted each year for no more than 25 percent of a vehicle manufacturer's models. Additionally, ARB's evaluation finding the single-filter flow-weighted sampling method as equivalent to the traditional 3-filter method is an example of how the new test alternatives provide options to manufacturers to reduce filter and analysis time and costs significantly. To further reduce costs, manufacturers are expected to continue employing real-time PM instruments that correlate well with PM mass measurements for much of their development and calibration testing needs.

7. ARB's findings are from laboratory testing that reflects more of a research environment than a production environment like the vehicle manufacturers' labs.

   Vehicle manufacturers have often argued that ARB's laboratory is not representative of the types and volume of tests that they are required to run in their own laboratory facilities. Accordingly, they have suggested that ARB's PM measurement findings are better than other laboratories and not reflective of what one of their laboratories can realistically achieve. This argument, however, is inconsistent with ARB's experience and knowledge of manufacturer testing facilities.

   Just like manufacturer facilities, ARB runs multiple vehicles per day per test cell and tests vehicles over different cycles with associated varying emission levels in each cell. Furthermore, ARB and vehicle manufacturers alike recognize the need for good laboratory practices and engineering judgment in scheduling and the assignment of test vehicles to test cells. For example, even though ARB's experience is that sampling tunnels in the test cell are not contaminated easily, prudent steps are still taken to use dedicated test cells for vehicles with similar emission levels and testing purposes. ARB often will rely on a specific test cell or two for test programs testing the lowest emitting vehicles and include emission measurement equipment with the lowest ranges for increased sensitivity to the expected low pollutant levels. Likewise, ARB programs that target much older and higher emitting vehicles often are directed to different test cells where instrumentation is set-up to account for the higher expected emission levels. Manufatures have dedicated test cells for specific purposes such as those used for research, development and calibration, or official certification-grade tests. Therefore, when predominantly testing relative new vehicles, they may have the luxury of not having to test as wide a range of vehicle emissions as ARB. ARB expects such practices to continue both at ARB and at vehicle manufacturers' facilities. Past experience suggests such practices will lead to PM measurement results comparable to ARB's laboratory.

VI. CONCLUSIONS

This report reflects ARB's efforts to date on the first of two tasks the Board had requested of staff with respect to the future 1 mg/mi PM standard adopted in 2012 for 2025 model year implementation. The first task was to validate the feasibility of robustly measuring PM emissions at these low levels given concerns by industry and others about the reliability of such measurements. In conducting this assessment, staff focused on confirming the feasibility of gravimetric measurement for determining PM emissions at 1 mg/mi. Additionally, during the course of this evaluation, significant knowledge was gathered on the development and evaluation of promising alternative approaches to measure or characterize PM emissions. For the second task, confirming the technical feasibility (and reasonable implementation date) of future vehicles to meet the 1 mg/mi standard, work has begun at ARB and will continue throughout next year before reporting back to the Board.

In assessing measurement feasibility, ARB conducted several studies to verify the applicability of PM mass measurements and to address industry and stakeholder concerns regarding the perceived high variability of the gravimetric measurement method at sub 1 mg/mi levels. These studies focused on the variability and precision of gravimetric measurements, and provided an evaluation of CFR permitted sampling options that had opportunities for measurement cost reduction and precision improvement. In addition to the traditional gravimetric measurement method, three non-gravimetric approaches were evaluated for their ability to determine PM mass emissions: the PMP method; the IPSD approach; and a method that combines a gravimetric approach (single full flow composite filter) with real-time BC measurement.

Based on the key findings summarized below, staff has concluded that gravimetric measurement is a suitable test method for reliably determining vehicle PM emissions relative to the 1 mg/mile standard. Staff has also found that the allowable option of using a single flow-weighted filter is equivalent to the traditional 3-filter method and likely offers measurement analysis time and cost reductions. Regarding the non-gravimetric approaches that were investigated, staff has found that, as of today, none of the methods are sufficiently developed or studied to be considered as an equivalent substitute measurement for PM mass. However, some of these alternative methods continue to show promise especially in quantifying characteristics of PM other than the total mass (e.g., particle number, particle size distribution). Accordingly, while official emission testing will continue to be carried out with the gravimetric method at ARB's laboratory, staff will also continue to monitor advances in alternative approaches to stay current with further developments in PM measurement.

Sources of Gravimetric Measurement Variability

Following 40 CFR Part 1065 or 1066 specifications, a dynamometer test cell (with CVS dilution) in conjunction with gravimetric analysis conducted on a microbalance (with 0.1 µg resolution) in a temperature- and humidity-controlled clean room environment can repeatedly measure vehicle PM emission at levels below 1 mg/mi.

With good laboratory practices, measurement variability can be minimized. The standard deviation calculated from measuring various types of blank samples shows that the variability from the gravimetric analysis of reference blank and replicates is ~0.5 µg, and increases with filter handling of trip and field blanks to ~2 µg. The magnitude of averaged trip and field blanks is very close to zero µg, indicating that there is no significant contamination from filter handling procedures.

Typical mass loadings of tunnel blanks in ARB's HSL test cells average ~2.1µg. Although the actual contamination and the resulting measurement uncertainty for each emission test cannot be determined simultaneously, the tunnel blank is a good indicator for potential interference. The increased mass loadings of the tunnel blanks, as compared to those of trip and field blanks, indicates the contamination of organic hydrocarbons comes from tunnel dilution air and from the CVS tunnel walls. The mass loadings of the weekly tunnel blanks evaluated over a period of five years in HSL test cells were consistent and stable. The impact of the tunnel contamination is likely to be very low. The 40 CFR Part 1066 background correction allowance of up to 5 µg is more than sufficient, based on ARB testing, to adequately account for background contamination in a PM emission test.

The slightly higher observed variability (one standard deviation, 2.5 µg) in tunnel blanks relative to blanks capturing filter handling effects (2.0 µg), may also result from the potential uncontrolled adsorption/desorption of organic hydrocarbons on filters. However, the total measurement uncertainty (estimated from tunnel blanks, σ = 0.1 mg/mi assuming 2.5 µg for each phase) is a small fraction, ~ 10 %, when compared to the emission standard at 1 mg/mi.

Evaluation of Gravimetric Measurement Precision

The precision of the gravimetric method was determined by collecting PM emissions from various LDVs with collocated samplers. The precision averaged 11% for filters with a mass loading ranging from 10 to 60 µg, which is the typical range for emissions at or below a 1 mg/mi emission level.

Most importantly, PM emissions can be measured reproducibly. In some cases, test-to-test variability from the vehicle is greater than the inter-laboratory variability. Data obtained from one selected vehicle tested across three ARB test cells showed that the vehicle test-to-test variability accounted for three-quarters of the total vehicle test reproducibility. The repeatability of vehicle emissions is likely to contribute the largest component of total variability in quantifying vehicle PM emissions, compared to the variability of the gravimetric method.

Equivalency of CFR PM Sampling Options

The single filter flow-weighted sampling method allowed in 40 CFR part 1066 yields an equivalent emission rate (if the background is corrected with tunnel blanks) to that of the conventional 3-filter sampling method for FTP test cycles and has the advantage of reducing resources (analysis time, handling, and materials) needed for one filter instead of three filters per test.

Alternative Metrics for Particulate Mass determination

ARB utilizes several instruments to measure PM properties other than mass, including particle size and number distributions, and black carbon. Particle number and black carbon have been implicated in adverse impacts on public health and environment. Three methods of particular interest are PMP solid particle number, IPSD, and a combination method of gravimetric mass and BC measurement.

The PM mass emissions estimated by each of the three alternative methods showed a good correlation with the gravimetric method. Generally, a reduction in the PM mass also coincided with a reduction in the alternative metrics, including total particle number, solid particle number, and black carbon. However, the correlation of the alternate methods to the gravimetric mass varied considerably among test cycles and engine technologies, and is likely to continue to change as newer engine technologies are introduced. Further, the overall variability observed in repeated measurements for each of the alternative methods was similar to the gravimetric method. Given staff's findings that the variability of the vehicle itself is substantially larger than the variability of the gravimetric method, a similar level of overall variability for these alternative methods suggests that any difference in measurement variability of the alternative methods is minor and relatively insignificant compared to vehicle variability.

Overall, staff's analysis suggests that real-time instrumentation can provide semi-quantitative data during engine development and calibration efforts. As noted above, a good correlation was observed between alternative methods such as the PMP and the gravimetric method in that reductions in one generally resulted in reductions in the other even though the exact relationship between the two varied for different test cycles and technologies. Directionally, increased stringency in standards based on either method should achieve additional (but not necessarily equivalent) reductions in both mass and sold particle number. And, although previous studies reported the PMP method can be more repeatable and cost-effective, staff's testing found PMP measurement repeatability and overall test-to-test repeatability to be similar to the gravimetric method. Additionally, all of the alternative methods investigated have some specific limitations (e.g., for PMP, exclusion of particles less than 23 nm and semi-volatiles) that increase the risk that the method will not adequately capture a portion of the PM that could turn out to be critical to improve air quality or mitigate adverse health impacts. Accordingly, ARB will continue to utilize the gravimetric mass measurement method as the recognized method for official emission tests. ARB staff will, however, continue to monitor the ongoing development of alternative methods such as the PMP SPN method

as the European Commission - Joint Research Centre (JRC) study looks to make further refinements such as inclusion of particles as small as 10 nm in diameter.

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VIII. APPENDIX

Vehicle No.	MY Type	Fuel Injector Type		Total PM Mass Emissions (mg/mi)			
				Phase 1	Phase 2	Phase 3	FTP weighted
1	2009 GMC Acadia	GDI - Wall-guided	Emissions	**35.13**	**1.29**	**1.53**	**8.38**
			STDEV	2.84	0.43	0.21	0.75
			CoV(%)	8.1	33.7	13.6	8.9
2	2008 Lexus IS350	GDI - Wall-guided	Emissions	**25.12**	**0.55**	**1.75**	**5.97**
			STDEV	2.76	0.48	0.38	0.78
			CoV(%)	11.0	87.6	21.7	13.1
3	2009 Mazda Speed3	GDI - Wall-guided	Emissions	**12.98**	**1.34**	**1.54**	**3.80**
			STDEV	1.74	0.26	0.23	0.52
			CoV(%)	13.4	19.1	14.7	13.7
4	2008 VW GLI	GDI - Wall-guided	Emissions	**7.05**	**2.04**	**2.01**	**3.07**
			STDEV	0.87	0.37	0.39	0.37
			CoV(%)	12.4	18.0	19.2	12.2
5	2007 VW Passat	GDI - Wall-guided	Emissions	**12.04**	**1.37**	**2.12**	**3.79**
			STDEV	1.15	0.23	1.07	0.40
			CoV(%)	9.53	16.57	50.21	10.61
6	2009 Porsche Carrera	GDI - Wall-guided	Emissions	**12.46**	**0.53**	**1.57**	**3.29**
			STDEV	3.73	0.47	0.45	0.69
			CoV(%)	29.9	88.1	28.4	21.1
7	2009 BMW 335i	GDI - Spray-guided	Emissions	**4.77**	**0.70**	**0.71**	**1.55**
			STDEV	0.54	0.22	0.26	0.10
			CoV(%)	11.4	31.6	35.7	6.4
8	2009 BMW 750i	GDI - Spray-guided	Emissions	**12.06**	**1.00**	**0.94**	**3.28**
			STDEV	1.67	0.55	0.24	0.26
			CoV(%)	13.8	55.1	25.5	7.8
9	2010 VW Jetta	GDI - Wall-guided	Emissions	**4.33**	**0.90**	**1.20**	**1.69**
			STDEV	0.16	0.10	0.11	0.10
			CoV(%)	3.7	10.8	9.2	5.7
		9 GDI Vehicle Avg.	Emissions	**13.99**	**1.08**	**1.49**	**3.87**
			STDEV	10.05	0.49	0.47	2.13
			CoV(%)	71.8	45.0	31.3	55.0

Table A-1. FTP PM mass emissions rates from GDI vehicles

Vehicles Tested at CARB HSL Test Cell A

Vehicle	Make/ Model	Model Year	Vehicle Category [a]	Odometer (miles)	Emission Category
Veh 1	Saturn SL2	2002	PC	43k	LEV I
Veh 2	Nissan Maxima	2000	PC	115k	LEV I
Veh 3	Lexus	2002	PC	66k	LEV I
Veh 4	Honda Accord	2005	PC	19k	LEV II
Veh 5	Toyota Camry	2006	PC	42k	LEV II
Veh 6	Saturn VUE	2006	PC	32k	LEV II
Veh 7	Ford Focus	2007	PC	15k	LEV II
Veh 8	Hummer	2009	LDT3?	21k	LEV II
Veh 9[b]	Nissan Altima	2011	PC	29k	LEV II
Veh 10	Spectra	2007	PC	34k	LEV II

Vehicles Tested at US EPA NVFEL Test Cell

Vehicle	Make /Model	Model Year	Vehicle Category	Odometer (miles)	Emission Category
Veh A	Honda Civic	2009	PC	121K	Tier 2/Bin 5
Veh B	Toyota Corolla	2009	PC	121K	Tier 2/Bin 5
Veh C	Honda Accord	2007	PC	124K	Tier 2/Bin 5
Veh D	Dodge Caliber	2007	PC	115K	Tier 2/Bin 5
Veh E	Chevrolet Impala	2006	PC	114K	Tier 2/Bin 5
Veh F	Ford Taurus	2008	PC	115K	Tier 2/Bin 5
Veh G	Honda Accord 2	2007	PC	37K	Tier 2/Bin 5
Veh H	Toyota Tundra	2005	LDT2	121K	Tier 2/Bin 5
Veh I	Chrysler Caravan	2007	LDT2	117K	Tier 2/Bin 5
Veh J	Jeep Liberty	2009	LDT2	122K	Tier 2/Bin 5
Veh K	Ford Explorer	2009	LDT3	122K	Tier 2/Bin 4
Veh L	Ford F150	2005	LDT4	112K	Tier 2/Bin 8
Veh M	Chevrolet Silverado	2006	LDT4	111K	Tier 2/Bin 8 SULEV1(CA)

a. PC: Passenger car; LDT: light-duty truck

b. Veh 9 was also tested at CARB HSL Test Cell B and C. \

Table A-2. Summary of vehicles tested at CARB HSL Test Cell A and US EPA NVFEL Test Cell

Veh No.	Make/ Model	Model Year	Vehicle Category	Tech	Odometer ($x10^3$ miles)	Emission Category
1	Honda Civic	2012	PC	PFI	32	PZEV
2	Chevy Malibu LT	2012	PC	PFI	26.5	PZEV
3	Toyota Camry LE	2009	PC	PFI	67	SULEV
4	Dodge Grand Caravan	2013	LDT	PFI	40	SULEV
5	Nissan Altima	2011	PC	PFI	30	PZEV
6	Buick Regal	2011	PC	PFI	11.5	ULEV
7	Ford Explorer	2012	LDT	PFI	21	ULEV
8	Honda Accord	2012	PC	PFI	32	PZEV
9	Chevy Silverado	2007	LDT	PFI	158	ULEV
10	Ford Fusion	2013	PC	GDI	9	SULEV
11	Nissan Juke	2011	PC	GDI	51	ULEV
12	Smart Fortwo	2008	PC	PFI	77	ULEV

Table A-3. Test vehicles information for ARB Test Cell A sampler precision study

Model Year	Manuf. Code	Model	Fuel Inj.	Mileage	Emission Standard	Engine Displ.	Cyl.	Trans. Type	Turbo
1990	BUIC	Le Sabre	PFI	121504	TIER0	3.8	6	A4	
2000	HOND	ACCORD	PFI	108113	SULEV	2.3	4	A4	
2001	CHEV	CAVALIER	PFI	101511	LEV	2.2	4	A4	
2003	FORD	F150	PFI	104560	LEV	5.4	8	A4	
2007	CHEV	Silverado	PFI	0	ULEV		8	A4	
2007	HOND	CIVIC HYBIRD	PFI	105671	L2SUL	1.3	4	A4	
2008	CHEV	Uplander LS	PFI	90369	L2LEV	3.9	6	A4	
2008	DAG	PASSION CABRIOLET	PFI	76636	ULEV		3	S5	
2009	CHEV	IMPALA LS	PFI	93461	L2ULV	3.5	6	A4	
2009	TOTA	CAMRY	PFI	64033	LEV	2.4	4	A5	
2010	JEEP	LIBERTY	PFI	33137	L2ULV	3.7	6	A4	
2011	BUIC	REGAL CXS	PFI	11754	ULEV	2	4	A6	x
2011	CHRG	GRAND CARAVAN	PFI	8772	ULEV	3.6	6	A6	
2011	NISS	ALTIMA	PFI	30666	PZEV		4	CV	
2012	CHEV	MALIBU	PFI	26576	PZEV	2.4	4	A6	
2012	HOND	CIVIC	PFI	31742	PZEV	1.8	4	A4	
2012	TOTA	CAMRY	PFI	30776	PZEV	2.5	4	A6	
2012	TOTA	COROLLA	PFI	23060	ULEV		4	A4	
2012	TOTA	COROLLA	PFI	30655	ULEV	1.8	4	A4	
2013	CHEV	TAHOE	PFI	24057	ULEV	5.3	8	A6	
2013	DODG	DART	PFI	14088	LEV	1.4	4	A6	x
2013	DODG	GRAND CARAVAN	PFI	40323	ULEV	3.6	6	A6	
2013	KIA	FORTE	PFI	26580	L2SUL	2.4	4	A5	
2008	MINI	MINI COOPER S	GDI	50237	ULEV	1.6	4	M6	x
2010	VOLK	JETTA	GDI	11302	PZEV	2	4	A6	
2011	NISS	JUKE	GDI	51341	ULEV	1.6	4	A5	x
2012	BUIC	LACROSSE	GDI	13386	L2SUL	2.4	4	A4	
2012	CHEV	EQUINOX	GDI	25226	PZEV	2.4	4	A6	
2012	FORD	FOCUS	GDI	36714	SULEV	2	4	A6	
2012	MINI	COOPER S	GDI	12943	L2LEV	1.6	4	M6	x
2013	CAD	ATS	GDI	23441	ULEV	2	4	A5	x
2013	CHEV	IMPALA LTZ	GDI	28084	L2SUL	3.6	6	A4	
2013	FORD	FUSION	GDI	13417	PZEV	1.6	4	A4	x
2013	FORD	FUSION	GDI	8951	PZEV	1.6	4	A6	x
2013	HYND	ACCENT	GDI	18284	ULEV	1.6	4	A4	
2013	HYND	VELOSTER	GDI	11486	ULEVB	1.6	4	M6	x
2013	MAZD	3	GDI	21779	L2ULV	2	4	A4	
2013	NISS	JUKE	GDI	19919	L2ULV	1.6	4	CV	
2013	VOLK	JETTA GLI	GDI	13783	SULEV	2	4	A4	x
2013	VOLK	JETTA HYBRID	GDI	8883	PZEV	1.4	4	A4	x
2014	DAG	MERCEDES E350	GDI	11294	L2SUL	3.5	6	L7	
2014	KIA	OPTIMA GDI	GDI	4464	PZEV	2.4	4	A6	
2002	DODG	RAM 2500	LDD/DPF	228390	TIER1	5.9	6	A4	x
2011	DCAG	E350	LDD/DPF	24412	ULEV	3	6	OT	x
2012	VOLK	PASSAT	LDD/DPF	15427	ULEV	2	4	A6	x
2013	VOLK	JETTA	LDD/DPF	4844	TIER2	2	4	A6	x
2014	CHRG	RAM 2500	LDD/DPF	13540	L2ULV	6.7	8	A5	x

Table A-4. Vehicles tested, including mileage, fuel injection type, emission standard certified under, engine displacement and cylinder number, transmission type, and presence of turbocharger. (Chang and Shields, 2015, submitted)

Model Year	Manuf. Code	Model	Tests (#)	Avg mass (mg/mi)	mass SD (mg/mi)	Avg SPN (mg/mi)	SD SPN (mg/mi)	Avg BC (mg/mi)	BC SD (mg/mi)
1990	BUIC	Le Sabre	1	0.36		9.45E+11		0.24	
2000	HOND	ACCORD	1	0.52		5.07E+11			
2001	CHEV	CAVALIER	1	0.09		4.02E+11		0.13	
2003	FORD	F150	1	0.68		7.58E+11			
2007	CHEV	Silverado							
2007	HOND	CIVIC HYBIRD	1	1.78		2.47E+12		1.38	
2008	CHEV	Uplander LS	1	1.30		2.69E+12			
2008	DAG	PASSION CABRIOLET	3	0.56	0.20	1.33E+12	5.1E+11		
2009	CHEV	IMPALA LS	1	1.06		1.95E+12		0.83	
2009	TOTA	CAMRY	15	0.48	0.13	1.25E+12	1.78E+11	0.28	0.09
2010	JEEP	LIBERTY	5	0.54	0.10	2.45E+12	7.38E+11	0.54	0.24
2011	BUIC	REGAL CXS	6	3.33	0.26	8.3E+12	1.39E+12	3.36	0.49
2011	CHRG	GRAND CARAVAN	7	0.19	0.05	6.63E+10	1.09E+10	0.10	0.01
2011	NISS	ALTIMA	9	1.38	0.21	2.66E+12	1.33E+12	1.01	0.31
2012	CHEV	MALIBU	12	0.35	0.10	1E+12	8.43E+10	0.31	0.08
2012	HOND	CIVIC	17	0.67	0.39	1.41E+12	1.63E+11	0.45	0.14
2012	TOTA	CAMRY	1	0.54		8.53E+11			
2012	TOTA	COROLLA							
2012	TOTA	COROLLA	1	0.07		2.27E+11		0.08	
2013	CHEV	TAHOE	1	1.20		3.24E+12			
2013	DODG	DART	3	1.41		5.74E+12	4.07E+11	1.85	1.01
2013	DODG	GRAND CARAVAN	10	0.14	0.06			0.12	0.01
2013	KIA	FORTE	1	0.45		7.93E+11		0.20	
2008	MINI	MINI COOPER S	3	2.83	0.16	6.89E+12	3.61E+11	2.33	
2010	VOLK	JETTA	1	1.68					
2011	NISS	JUKE	3	10.23	0.49	1.37E+13	1.16E+12		
2012	BUIC	LACROSSE	1	2.70		7.22E+12			
2012	CHEV	EQUINOX	1			1.05E+13		3.77	
2012	FORD	FOCUS	1	0.77		1.6E+12			
2012	MINI	COOPER S							
2013	CAD	ATS	1	2.51		2.72E+12		1.51	
2013	CHEV	IMPALA LTZ	1	1.42		2.95E+12		1.08	
2013	FORD	FUSION	1	1.54		3.91E+12			
2013	FORD	FUSION	2	1.23		3.61E+12			
2013	HYND	ACCENT	1	9.10		1.23E+13		9.32	
2013	HYND	VELOSTER	3	3.91	0.29	7.57E+12	1.79E+12	3.31	0.28
2013	MAZD	3	1			4.52E+12		2.17	
2013	NISS	JUKE	1	5.13				3.67	
2013	VOLK	JETTA GLI	1	1.79		3.41E+12			
2013	VOLK	JETTA HYBRID	1	0.22		4.49E+11			
2014	DAG	MERCEDES E350	1	0.56		1.21E+12			
2014	KIA	OPTIMA GDI	1	2.72		2.05E+12			
2002	DODG	RAM 2500							
2011	DCAG	E350	2	0.06		8.68E+10			
2012	VOLK	PASSAT	2	0.14		4.98E+10		0.05	
2013	VOLK	JETTA	2	0.17		4.27E+10		0.05	
2014	CHRG	RAM 2500	1					1.33	

Table A-5: Average emissions and standard deviations FTP test cycles. (Chang and Shields, in preparation)

Model Year	Manuf. Code	Model	Tests (#)	Avg mass (mg/mi)	mass SD (mg/mi)	Avg SPN (mg/mi)	SD SPN (mg/mi)	Avg BC (mg/mi)	BC SD (mg/mi)
1990	BUIC	Le Sabre	1	2.42		4.46E+12			
2000	HOND	ACCORD	1	4.17		2.62E+12			
2001	CHEV	CAVALIER							
2003	FORD	F150							
2007	CHEV	Silverado	1			2.68E+12			
2007	HOND	CIVIC HYBIRD	1	5.00				2.16	
2008	CHEV	Uplander LS	1	7.45		9.85E+12			
2008	DAG	PASSION CABRIOLET	3	2.96	1.03	3.66E+12	2.98E+11		
2009	CHEV	IMPALA LS	1	6.98		5.87E+12		4.34	
2009	TOTA	CAMRY	8	2.29	1.59	3.72E+12	1.42E+12	0.80	0.16
2010	JEEP	LIBERTY	1	6.40		1.75E+13			
2011	BUIC	REGAL CXS							
2011	CHRG	GRAND CARAVAN	5	0.29	0.29	1.2E+11	4.23E+10	0.08	0.01
2011	NISS	ALTIMA	4	1.76	0.31	4.82E+12	3E+12	0.95	0.27
2012	CHEV	MALIBU	6	1.51	0.70	4.82E+12	1.19E+12	0.82	0.29
2012	HOND	CIVIC	12	0.75	0.61	1.06E+12	4.63E+11	0.25	0.12
2012	TOTA	CAMRY	1	0.20		2.7E+11		0.17	
2012	TOTA	COROLLA	1	0.51		1.59E+12			
2012	TOTA	COROLLA							
2013	CHEV	TAHOE	2	4.30		8.68E+12		2.90	
2013	DODG	DART	4	4.91	3.29	1.32E+13	1.81E+12	3.72	2.85
2013	DODG	GRAND CARAVAN							
2013	KIA	FORTE	1	0.61		1.51E+12			
2008	MINI	MINI COOPER S	3	5.60	3.26	7.34E+12	8.61E+11	2.14	0.00
2010	VOLK	JETTA							
2011	NISS	JUKE	4	7.35	3.67	3.43E+12	1.02E+12		
2012	BUIC	LACROSSE							
2012	CHEV	EQUINOX							
2012	FORD	FOCUS							
2012	MINI	COOPER S	1	7.71		1E+13			
2013	CAD	ATS							
2013	CHEV	IMPALA LTZ	1	2.36		2.26E+12			
2013	FORD	FUSION	1	1.33		3.89E+12			
2013	FORD	FUSION	3	1.02	0.12	3.02E+12	1.94E+11		
2013	HYND	ACCENT							
2013	HYND	VELOSTER	6	9.02	3.87	2.1E+13	6.34E+12	6.87	3.55
2013	MAZD	3	1	1.72		1.21E+12			
2013	NISS	JUKE							
2013	VOLK	JETTA GLI	1			3.57E+12			
2013	VOLK	JETTA HYBRID							
2014	DAG	MERCEDES E350	1	0.21		2.33E+11			
2014	KIA	OPTIMA GDI							
2002	DODG	RAM 2500	1			3.21E+14			
2011	DCAG	E350	3	0.33	0.28	1.93E+11	4.94E+10	0.08	0.00
2012	VOLK	PASSAT	3	0.25	0.19	1.22E+13	2.07E+13	2.02	3.34
2013	VOLK	JETTA	3	0.43	0.64	2.11E+11	2.96E+11	0.16	0.16
2014	CHRG	RAM 2500	1			5.45E+12			

Table A-6: Average emissions and standard deviations US06 test cycles. (Chang and Shields, submitted)

Statistical Analyses _Repeatability and Reproducibility

The intra-lab variability (s_r^2) and inter-lab variability (s_L^2) can be calculated by the following equations:

$$s_r^2 = \frac{\sum_{i=1}^{p}\sum_{j=1}^{n_i}\left(x_{ij} - \overline{x_i}\right)^2}{N - p} \qquad (1)$$

$$s_L^2 = \frac{\frac{\sum_{i=1}^{p} n_i\,(\overline{x_i} - \bar{x})^2}{p-1} - s_r^2}{\frac{(N^2 - \sum_{i=1}^{p} n_i^2)}{N(p-1)}} \qquad (2)$$

Where, *p* is the total number of test cells, *N* is the total number of measurements, *j* is the j-th test from the test cell *i* (e.g., cell A, B, and C), *x* is the emission measurement, $\overline{x_i}$ is the estimated mean value of PM emissions from i-th test cell, and $\bar{x}$ is the estimated mean value of all of the PM emission measurements.

$$N = \sum_{i=1}^{p} n_i \qquad (3)$$

$$\overline{x_i} = \frac{1}{n_i}\sum_{j=1}^{n_i} x_{ij} \qquad (4)$$

$$\bar{x} = \frac{1}{p}\sum_{l=1}^{p} \overline{x_i} \qquad (5)$$

The sum of intra-lab and inter-lab variability equals total variability s_R^2 (reproducibility):

$$s_R^2 = s_r^2 + s_L^2 \qquad (6)$$

The coefficient of variances (CoV) within labs, between labs (or vehicles), and reproducibility are defined, respectively as Equations 7-9:

$$CoV_r = \frac{S_r}{\bar{x}} \qquad (7)$$

$$CoV_L = \frac{S_L}{\bar{x}} \qquad (8)$$

$$CoV_R = \frac{S_R}{\bar{x}} \qquad (9)$$

It should be noted that when *p* =1, equation (1) is the conventional definition of the variance of the testing results. Equation (8) is the coefficient of variance (CoV) of repeat tests.

Particle Number and Size Distribution Measurement

The pertinent functions and features of commonly used instruments to measure particle size and number are tableted in Table A-7.

Instrument	Principle	Data Output	Size range (nm)	Advantages
DMM	Uni-polar Charging Aerodynamic classifying Counting	Mass Size Number	6-1200	Cover major size range for PM in emissions Fast response, 1s Estimate of effective density Good agreement with PM mass
EEPS	Uni-polar Charging Electrical mobility classifying Counting	Size Number	5.6-560	Fast response, 1s Fine size resolutions (22 sizes) Can measure transient phase
SMPS	Bi-polar Charging Electrical mobility classifying Counting	Size Number	3-1000	Accurate size High size resolution Can measure very high concentration
CPC	Frequency of Light scattering being interrupted by particles passing through	Number	3-2500 (depends on model)	Fast measurement, 1s Calibration ISO standard available Can measure very low concentration

Table A-7. Commonly used instruments for measuring particle number and size distribution of vehicle exhaust

Dekati Mass Monitor (DMM)

PM mass can be estimated at a one second resolution by the Dekati Mass Monitor (DMM) which combines electrical mobility and aerodynamic particle size measurements (Mamakos et al., 2006). Particles are charged in a corona discharge environment, separated by mobility, and passing through a mobility classifier enter a six-stage cascade impactor. The resulting electrical currents estimate particle numbers, then yield PM mass when the particle numbers are combined with the effective particle density profile calculated from the aerodynamic and mobility size reported by instrumentation . The Phase 1 of CRC project E-66 (Khalek, 2005) reported that the DMM-230 correlated very well ($R^2 > 0.95$) with the gravimetric measurement method for an engine equipped with a Continuously Regeneration Trap- Diesel Particle Filter (CRT-DPF). Another study (Mamakos, et al., 2006) showed, for the Euro 2 and 3 vehicles, that the two measurements also correlated well, yet DMM results are significantly higher than the gravimetric PM mass. It is expected that the DMM can yield semi-quantitative trends in particle mass emissions.

Engine Exhaust Particle Sizer Spectrometer (EEPS)

EEPS is mostly used to measure fast response particle size and number data. The EEPS is a mobility-base particle sizing instrument. An aerosol stream entering the instrument is subjected to two unipolar diffusion chargers to put a predictable net positive charge on the particles. The charged particles are separated and detected by size in an electrical field to determine particle numbers and sizes simultaneously.

Scanning Mobility Particle Sizer (SMPS)

SMPS measures particle counts for each size in a scanning cycle which is as short as 2 minutes. It is usually used for measurements at steady-state engine operation. It consists of a Krypton 85 bipolar ion charger/neutralizer to charge particles, a classifier to select mobility size, and a particle counter.

Condensation Particle Counter (CPC)

Most CPC determines particle number concentration by condensing butyl alcohol on the particles via supersaturation process to grow them to an optically detectable size, approximately 2 µm. Adjusting the supersaturation ratio will change the effectiveness of growing smaller particles therefore can accordingly change the 50% courting efficiency of the lowest particle size. CPC developed over the past decade can effectively grow particle either through diffusional process, with deionized water, or a combination of both. The CPC in the European legislation must be full-flow (the total inlet flow must pass the counting optics), and have a 50% counting efficiency at 23 nm (Giechaskiel, et al., 2009) with butyl alcohol.

Black Carbon Measurement

The commonly used instruments for BC measurement and their operation principle and capacity are listed in Table A-8.

Principle	Method/ instrument	Property measured	Real-time	Size range (nm)	Advantages
Thermal/ Optical	IMPROVE or NIOSH	EC and OC mass	No	All	Used in ambient monitoring Long-standing database in emissions inventories.
Attenuation	Aethalometer	BC mass	Yes	All	Fast response Easy to use
Absorption/ Sound wave detection	Photoacoustic	BC mass	Yes	>10	No sampling medium interference Fast response
Absorption/ Incandescence	Laser-induced incandescence	BC mass Primary soot size	Yes	70-500	Fast response Sensitivity

Table A-8. Commonly used instruments/methods for measuring BC or EC

Thermal/optical carbon analysis

It is a well-established method and widely used in the measurements of ambient air quality or exposure to mining working environment for the determination of EC as a BC surrogate (Chow et al., 2007; National Institute for Occupational Safety and Health [NIOSH], 2003). The analysis consists of two steps: first, the sample is heated to ~ 600°C in an inert atmosphere to volatilize organic compounds, which is subsequently oxidized (to CO2) then converted to methane for flame ionization detection (FID). Carbon measured in the step is designated as OC. In the second step, oxygen is introduced to the remaining sample and heated to higher temperature (up to 900°C). The measured carbon in this step is designated as EC. OC, if thermally decomposed during the process, may char and be quantified as EC. The charring is then operationally corrected, depending upon the thermal/optical protocol.

One important advantage of using thermal/optical carbon analysis is the availability of widely accepted calibration methods (Chow et al., 2007; NIOSH, 2003). Four calibration standards used in this procedure include potassium hydrogen phthalate (KHP), sucrose, CO_2, and methane.

Light attenuation (Aethalometer)

Light attenuation instruments quantify the reduction in light intensity due to the presence of BC collected on a sampling medium (Hansen et al., 1984; Kirchstetter and Novakov, 2007). The attenuation mass coefficients used by these instruments are wavelength dependent and can vary substantially between BC-containing particles from different sources. Many studies have found a strong correlation between the BC by aethalometer and EC by thermal/optical methods; however, the real-time aethalometer can measure lower by 20-50% (Giechaskiel et al., 2014; Moosmüller et al., 2001; Allen et al., 1999; Hitzenberger et al., 1999; Babich et al., 2000). Filter-based absorption can be strongly influenced by the structural arrangement of filter fibers and PM deposit pattern on the filter (Arnott et al., 2005; Cappa et al., 2008), and may require algorithms for correction.

Photoacoustic methods

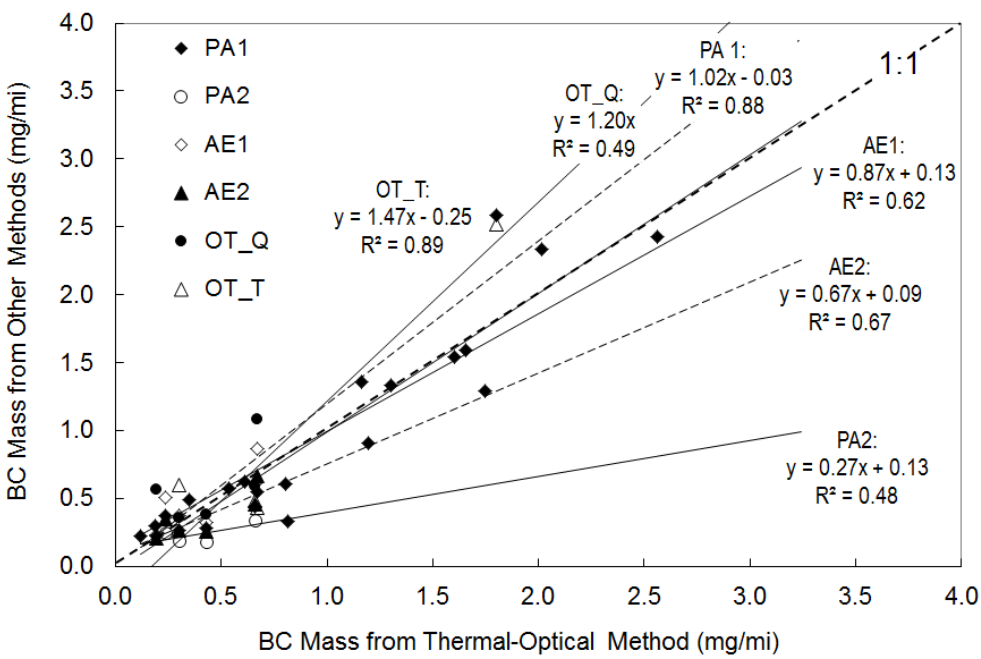
The photoacoustic method measures the intensity of a sound wave generated by expansion and contraction of neighboring gas molecules when BC is heated by a laser beam and emits black body radiation (Truex and Anderson, 1979). An advantage of this method is that it measures realtime BC suspended in the gas phase without interference from sampling media. However, a factory-assigned conversion factor (from measured signal to BC mass) may not be appropriate to quantify BC due to the interference from various amounts of organic compounds and other gaseous species (e.g. NO_2) in the vehicle exhaust PM that can absorb light and contribute to the signal. The photoacoustic response can also be influence by the thickness of the condensed material on BC (Slowik et al., 2007; Cross et al., 2010).

Laser-induced incandescence (LII)

Particles are heated with a short laser pulse to just below the carbon sublimation temperature and the subsequent incandescence decay is measured by a photomultiplier. The incandescence intensity and decay rate are analyzed to derive the number and average size of primary particles and, thereby, soot volume. Data from a study showed that these instruments are capable of measuring BC without being affected by the presence of OC coatings (Slowik et al., 2007), which may impact measurements made using photoacoustic or light attenuation methods. The LII method requires calibration to measure PM mass, commonly by comparison to extinction measurement of flames.

BC and EC measurement in ARB

EC is the only mass-based carbon measurement method and is often used as a reference method when comparing BC results measured with different principles. ARB conducted a correlation study to investigate the relationship between EC and six different BC measurements, and results are shown in Figure A-1 (LEV III, 2012; Kamboures et al, 2013). Overall, good correlations are observed between some of BC measurements and EC, yet the slopes varied depending on the range of emissions and instrumentation used.



Instrument	Analyte	Operating Principle	λ	Time Resolution	Intake Flow Rate	ID
ECOC/IMPROVE_A	EC	Thermal/Optical	633 nm	Time Integrated	60 L/min	EC
Light Attenuation Based Instrument	BC	Light Attenuation	880 nm	Time Integrated	60 L/min	OT
Photoacoustic Instrument	BC	Photoacoustic	808 nm	1 sec	1.9 L/min	PA1
Photoacoustic Instrument	BC	Photoacoustic	781 nm	1 sec	1.0 L/min	PA2
Light Attenuation Based Instrument	BC	Light Attenuation	880 nm	5 sec	2.0 L/min	AE1
Light Attenuation Based Instrument	BC	Light Attenuation	880 nm	1 sec	0.10 L/min	AE2

Figure A-1**.** Same test BC and EC data from LDV Undergoing FTP testing and the instruments used for the measurements are listed in the table below the figure. (LEV III, 2012)

The ARB also participated in a series of studies to evaluate the LII (Huai et al., 2006). These studies compared LII measured BC to same-test PM mass and EC diesel exhaust. Overall, LII BC was well correlated with both PM and EC, yet returned BC values that were higher than total PM. The erroneously higher values of BC, determined by LII, were determined to have been due to inadequate calibration.

IX. ACRONYMS AND ABBREVIATIONS

ACC	Advanced Clean Cars
ARB or CARB	California Air Resources Board
AE	Aethalometer
BC	Black Carbon
CFR	Code of Federal Regulations
CNG	Compressed Natural Gas
CoV	Coefficient of Variation
CPC	Condensation Particle Counter
CPMA	Centrifugal Particle Mass Analyzer
CRC	Coordinating Research Council
CS	Catalytic Stripper
CVS	Constant Volume Sampling
DF	Dilution Factor
DMA	Differential Mobility analyzer
DMM	Dekati Mass Monitor
DPF	Diesel Particulate Filter
E10	Gasoline with 10% Ethanol
E85	Gasoline with 85% Ethanol
EBC	Equivalent Black Carbon
EC	Elemental Carbon
EEPS	Engine Exhaust Particle Sizer
FFV	Filter Face Velocity
FTP	Federal Test Procedure
GDI	Gasoline Direct Injection Technology
HC	Hydrocarbons
HD	Heavy-Duty
HEPA	High Efficiency Particulate Air
HSL	Haagen-Smit Laboratory
IPSD	Integrated Particle Size Distribution
ISO	International Organization of Standardization
JRC	Joint Research Center of the European Commission
LDD	Light-Duty Diesel
LDT	Light-Duty Trucks
LDV	Light-Duty Vehicles
LEV	Low Emission Vehicle
LII	Laser Induced Incandescence
MY	Model Year
MSS	Micro Soot Sensor
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
NVFEL	National Vehicle and Fuel Emissions Laboratory
OC	Organic Carbon
PA	Photoacoustic
PAH	Polycyclic Aromatic Hydrocarbons

PC	Passenger Cars
PFD	Partial Flow Dilution
PFI	Port Fuel Injection
PFSS	Partial Flow Sampling System
PM	Particulate Matter
PMP	Particulate Measurement Programme
PN	Particle Number
PNC	Particle Number Counter
PSD	Particle Size Distribution
PTFE	Polytetrafluoroethylene
QC	Quality Control
SCFM	Standard Cubic Feet per Minute
SFTP or US06	Supplemental Federal Test Procedure
SMPS	Scanning Mobility Particle Sizer
SOP	Standard Operating Procedures
SPN	Solid Particle Number
TD	Thermal Denuder
UC	California Unified Cycle
UDDS	Urban Dynamometer Driving Schedules
UFP	Ultrafine Particles
UN-ECE	United Nation's Economic Commission for Europe
UN-ECE-GRPE	United Nation's Economic Commission for Europe - Group of Experts on Pollution and Energy
U.S. EPA	United States Environmental Protection Agency
VPR	Volatile Particle Remover