

Factors Influencing Mass Collected During 2007 Diesel PM Filter Sampling

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ABSTRACT

EPA's 2007 Diesel particulate matter (DPM) standard requires a large reduction in total mass emissions. In practice, this amounts to a fractional reduction in elemental carbon emissions. The reduction is balanced by a fractional increase in the semi-volatile component, which is difficult to sample and quantify accurately at low concentrations using filter-based methods. In this work, we show how five imprecisely defined filter-sampling parameters influence the mass collected on a filter. These parameters are: dilution air quality, dilution conditions (dilution ratio and dilution air temperature), particle size classification, filter media and artifacts, and face velocity. Each factor has the potential to change the mass collected by a minimum of 5% of the standard, suggesting there is room for improvement.

INTRODUCTION

Diesel exhaust contains a complex mixture of particles and gases. Gaseous emissions such as volatile hydrocarbons (HC), oxides of nitrogen (NO_x) and carbon dioxide (CO_2) are characterized by their concentration and composition. HC forms from incomplete combustion and range in volatilities. They may be found in the vapor [1-4] or in the particulate phase [2, 5-8].

Kittelson [9] identified exhaust Diesel aerosol size distributions as lognormal and trimodal, consisting of nuclei, accumulation, and coarse modes. Nuclei mode particles are typically <30 nm in diameter, primarily volatile, and consist of HC or sulfur compounds that nucleate or condense to the particle phase. When there is little carbonaceous surface area available to adsorb or condense vapors, nucleation is more likely [10, 11]. Typically, 0.1 to 10% of the particle mass is found in the

nuclei mode. Accumulation mode particles are typically in the range 30 to 500 nm and are composed primarily of carbon agglomerates with condensed and adsorbed HC vapors and sulfur compounds. Approximately 80 to 90% of the particle mass is contained in the accumulation mode. Coarse mode particles are typically reentrained agglomerates or crankcase fumes, are >1 μm , and contain 5 to 20% of the mass.

The physical and chemical characteristics of Diesel aerosol change with engine design, emission control devices, and fuel and lube oil composition. Thus, these modes are better defined by formation mechanisms than rigid size boundaries.

TRADITIONAL DPM MEASUREMENT – Diesel particulate matter is collected while the engine undergoes a simulated driving cycle known as the Federal Test Procedure (FTP). During the FTP, exhaust is routed into a constant volume sampling (CVS) tunnel where it is mixed with filtered ambient air. The exhaust plus dilution air flowrate is held constant by a changing dilution ratio. The dilute mixture passes through a pre-weighed filter¹ and the filter mass is determined by gravimetric analysis. This process defines Diesel particulate matter (DPM): the mass of 47°C Diesel exhaust collected on filter during a specified driving cycle.

EMISSION STANDARDS – Recent changes have been made to the heavy and light duty Diesel emission regulations for the US and European Union (EU). The

¹ Filters are abbreviated in the text as “ringless glass fiber” (common trade name: Pall TX40®), “PMP (polymethylpentene) ringed” (Pall Teflo®), and “PFA (perfluoroalkoxy) ringed” (Measurement Technology Laboratories)

new standards are well below previous levels. For example, there were 90% decreases (to 0.01 g/bhp-hr and 0.14 g/bhp-hr) in the US heavy-duty Diesel (HDD) particulate matter and HC standards, respectively. Emissions from engines equipped with emission control devices often fall well below the standard. Along with changes in emission standards, the procedures, methods, and instruments used to measure the emissions were changed. Certification facilities must follow rigorous sampling and measurement protocols to demonstrate compliance with these standards.

2007+ DPM MEASUREMENT – In 2007, EPA changed the DPM measurement methodology by better defining many aspects of the sampling process. Temperature requirements were added and tightened, dilution air filtering and sample flowrates were specified, and more equipment was standardized. A particle pre-classifier was added and crankcase emissions are now counted as DPM. Similar changes were made in the European Union. One objective of the EU Particulate Measurement Programme was to recommend changes to EU's DPM measurement procedure and EU's methods align with those of EPA [12].

The European Automobile Manufacturer's Association (ACEA) [13] estimated the repeatability and reproducibility of DPM measurements at 2007 levels would be worse than $\pm 20\%$ and $\pm 50\%$, respectively. Other authors have suggested that gravimetric analysis is not a sensitive nor adequate measure of 2007 emission levels [14-16] and have investigated sources of variability in the measurement [17, 18]. Conversely, EPA has achieved a repeatability of 5% and 10% at 100% and 40% of the standard, respectively [19].

OBJECTIVES & ORGANIZATION

The objective of this work is to evaluate the impact of low emission standards, laboratory test procedures, and filter requirements on DPM measurements and on the collection and measurement of suspended particulate matter (SPM). We begin by outlining two challenges surrounding the collection of rapidly varying low concentrations of semi-volatile aerosol with a filter. Next, we introduce instruments that are used to measure SPM because these measurements are frequently compared with filter measurements. Finally, we evaluate how five sampling factors affect the collection of DPM and in turn, estimate the extent to which each factor affects SPM. In order of appearance in the text, these factors are:

1. Dilution air quality
2. Dilution conditions (ratio and air temperature)
3. Particle pre-classifier
4. Filter media and artifacts
5. Face velocity.

For each case, we identify the issue with literature review and show the results from our models or experiments. We consider both filter types allowed for

US DPM measurements: PMP or PFA ringed and ringless glass fiber filters.

CHALLENGES AND ALTERNATIVE METHODS

INHERENT CHALLENGES OF FILTER-BASED DPM MEASUREMENTS

1. **Particles that are collected are not immediately "measured" and are retained until sampling is completed.** Particles held on the filter during sampling are subject to varying concentrations of HC vapors due to the transient driving cycle. The collected mass changes because of the evaporation and volatilization of semi-volatile particles [20-24] and the adsorption or desorption of vapors to or from collected soot particles [9, 25]. These effects are unavoidable, unpredictable, and result in the continuous addition and subtraction of material to and from the sampling filter.
2. **Particles and vapors are collected on an adsorbent surface.** It is usually and with a high degree of accuracy assumed that particles stick to filter media and vapor molecules do not. This assumption is not accurate at the one microgram-level. The affinity of gas molecules to a surface depends on the composition of the surface. Thus the extent of adsorption depends on the filter media [17, 26, 27]. When little mass is collected, the fraction of total mass that consists of adsorbed vapor is significant [17, 18, 27-29]. The amount of semi-volatile particulate collected depends on the filter face velocity [18, 30-33].

Performance of the Tapered-Element Oscillating Microbalance (TEOM, [34]) illustrates these points. The instrument is similar to conventional filter sampling in that mass is collected on a substrate, but unlike in traditional gravimetric analysis, the mass is measured instantaneously. As a result, the collection of DPM can be viewed and interpreted in real-time. Figure 1 shows a hand-drawn schematic representation of TEOM response during the FTP [35-37]. These data suggest that mass (whether it be SPM, water or hydrocarbon vapor) is continuously added and subtracted from a filter during the FTP cycle as a result of large and rapid changes in exhaust composition during the FTP. The response is also subject to pressure changes and engine vibration [35, 37]. The compositional changes cause the gas-particle-filter quasi-equilibrium value established by the last deposit to change, leading to the evaporation or adsorption of vapors. Previous work has shown the TEOM response can be improved by extended equilibration of the deposit [38]; this result is consistent with the general explanation. Further examples of artifacts associated with the TEOM and the Quartz Crystal Microbalance (QCM, [39]), an instrument that also collects mass on a surface, have been described elsewhere [40-42].



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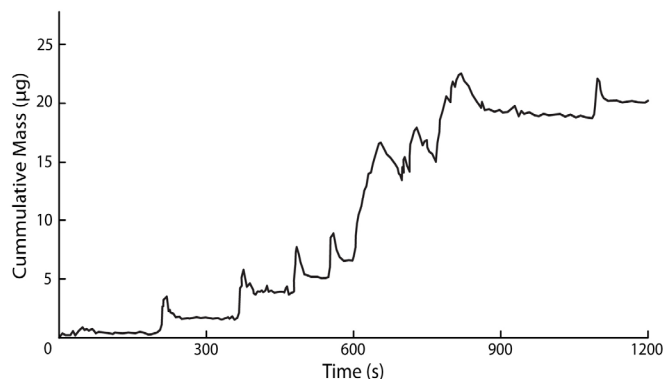


Figure 1. Schematic of TEOM response to DPM during the FTP.

ALTERNATIVE METHODS TO ESTIMATE THE MASS CONCENTRATION – Conclusions regarding filter measurements are inferred from comparisons with instruments designed to measure SPM. Burtscher [14] and Mohr et al. [15] reviewed many instruments and measurement principles and concluded that all provide quantitatively useful information, although not one method or instrument is without limitations. For instruments that measure particle size and estimate mass, limitations include uncertainties in particle diameter (aerodynamic, mobility, etc), density, volatility, and particle loss.

The following instruments can be used to directly measure or estimate SPM.

- Scanning Mobility Particle Sizer (SMPS, [43])
- Engine Exhaust Particle Sizer (EEPS, [44])
- DMS500 [45]
- Electrical Low Pressure Impactor (ELPI, [46, 47])
- Dekati Mass Monitor (DMM, [48])

All but the SMPS are capable of measuring transient emissions and all but the SMPS measure or estimate mass in near real-time. Sensitivities vary with dilution, averaging time, particle size and other factors, but all can generally measure dilute concentrations of $\sim 1 \mu\text{g}/\text{m}^3$ or less.

REVIEW, MODELS AND EXPERIMENTS

DILUTION AIR QUALITY – Engine exhaust must be diluted with air that is free of particles and vapors to eliminate the possibility of background contaminants influencing the measurement. Dilution air quality for measurements using partial flow, micro dilution systems was addressed by Swanson et al. [49]. Full-flow dilution tunnels require 100 to 1000 times more flow than partial flow systems so the methods of air cleaning are different. For 2007 DPM measurements, HEPA filtered air is required for secondary dilution and 98% filtering is required for primary dilution and there is no HC or relative humidity standard. The elimination of these vapors from CVS dilution air is desired but expensive and equipment-intensive. CVS dilution air cleaning was

addressed by the Dilution Air Refinement (DAR) system [50] and the Dilution Air Purification System [51]. An activated carbon filter is an alternative to more complex systems. Such filters are less expensive and can reduce, but not eliminate, gaseous dilution air contaminants. Activated carbon filters show time dependant performance [52], requiring that samples of the dilution air before and after sampling are needed to quantify contaminant breakthrough. 2007 DPM regulations allow a “tunnel blank” or filter measurement of the background contamination to be subtracted from the emissions collected during the FTP.

Background particle concentration

We developed a model to predict the mass of ambient PM that penetrates primary and secondary dilution air filters to estimate the influence of the background particle concentration and tunnel blank corrections. We evaluated hypothetical HEPA (99.97%) and 98% filters where the minimum filtration efficiency occurred at 300 nm. Following Hinds [53], curves were generated to predict the particle penetration through a dilution air filter as a function of particle diameter (Figure 2). A challenge PM_{10} mass concentration of $50 \mu\text{g}/\text{m}^3$ with a size distribution calculated using the “urban average” parameters from Friedlander [54] is used.

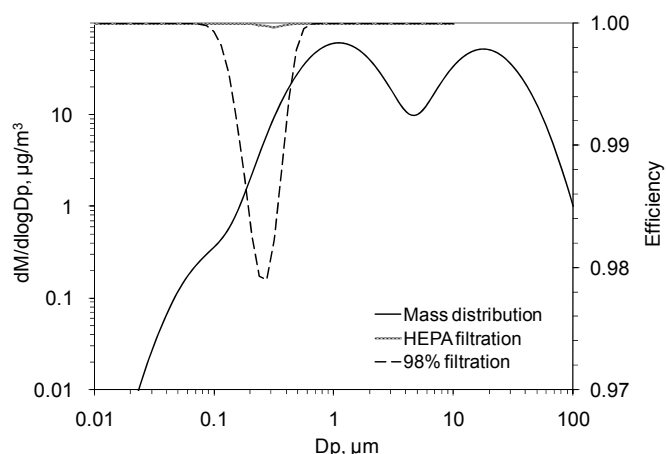


Figure 2. Filtration efficiency curves used to estimate background particle concentration. The mass concentration of particles $<10 \mu\text{m}$ is $50 \mu\text{g}/\text{m}^3$.

The background particle mass collected on a filter is estimated by calculating the penetrating particle mass that would be contained in 1.35 m^3 , the volume of dilution air that is sampled during the FTP. The results show that for HEPA and 98% efficient filters, the mass of ambient background PM does not exceed $0.1 \mu\text{g}$. For an ambient mass concentration 5 times higher ($250 \mu\text{g}/\text{m}^3$), the correction is 0.5 and $0.3 \mu\text{g}$ for the 98% and HEPA filters, respectively. This analysis suggests that for typical cases the mass collected on tunnel blank filters (if any) must be adsorbed vapor. It is unknown if background vapor contamination predictably adds to the dilute exhaust filter mass.

Background vapor adsorption to filters

We designed an engine test to evaluate the influence of dilution air purity on filter artifacts to further elucidate the appropriateness of correcting for background contamination. A 2005 John Deere 4045 engine equipped with an oxidation catalyst and particulate filter and fueled with 15 ppm sulfur ECD1 fuel was used to generate Diesel aerosol with a concentration less than the 2007 standard. The engine speed was 1400 rpm and the load was 23%. The exhaust was diluted with two different air qualities using a Sierra Instruments BG1. One test air was compressed and filtered ambient air and the other was compressed ambient air cleaned with a pressure swing adsorber (PSA) that is referred to as high purity (HP) air. PSA reduces contaminant concentrations to <1 ppb HC, <1 ppb NO_x and <1 part/cm³ [49]. The temperature of the dilution air was 25°C. The dilution ratios (DR), defined as the sum of the volume of exhaust and dilution air divided by the volume of exhaust, were 5, 9.5, and ∞. After dilution, the dilute mixture was filtered so that it contained <0.01 part/cm³ so that the sample filter would only collect vapor. The mixture of exhaust and dilution air vapors was sampled using ringless glass fiber filters at a face velocity of 80 cm/s for 20 min. One condition was randomly selected to repeat (9.5, ambient air).

Figure 3 shows the average mass gained as a function of 1/DR. Each data point represents the average and standard deviation of five measurements. There were 26% and 215% increases in (vapor) mass for dilution ratios of 5 and 9.5, respectively, when ambient dilution air is used. If background vapor contaminants contributed to the filter mass in proportion with the volume of dilution air sampled, the filter mass gained with ambient dilution air (amb.) would follow the relationship:

$$M_{\text{amb., expected}} = (M_{\text{amb., DR} = \infty} - M_{\text{HP, DR} = \infty}) * \left(1 - \frac{1}{\text{DR}}\right) + M_{\text{HP}}$$

where M refers to the mass gained given the dilution ratio and air quality in the subscript. The actual curve does not follow the expected curve, possibly because the exhaust vapors are competing with the dilution air vapors for adsorption sites on the filter. In either case, there is ~5 - 15 µg of vapor adsorption.

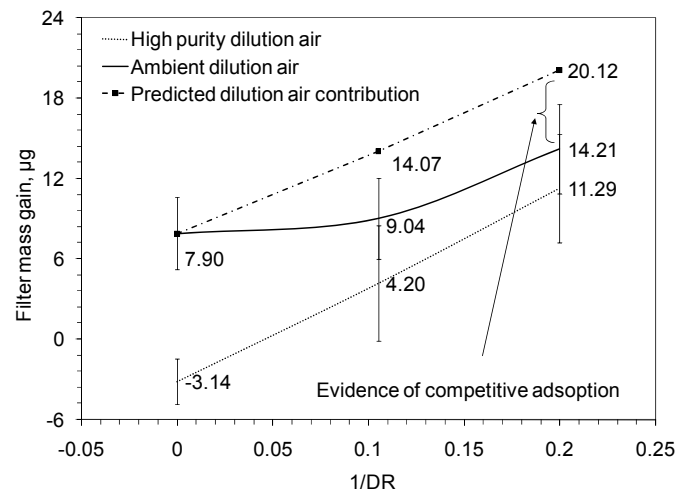


Figure 3. Average mass gained on ringless glass fiber filters at 1400 rpm, 23% load for two dilution air qualities with standard deviation error bars.

These results suggest that vapor collection cannot always be quantitatively predicted and that subtracting the background level is not valid in all situations. Other authors have expressed similar concerns. Andersson et al. [29] suggested that allowing a background subtraction is not appropriate. The Association of Emissions Control by Catalyst reported that in one test background corrections reduced all filter masses to 0 [55]. Khalek [56] and May et al. [57] found that tunnel blanks and engine emissions were indistinguishable when testing 2007 Diesel engines using 2007 testing methodology. In Khalek [56], EEPS - based tunnel blanks measured 10x less mass than filters blanks, which is consistent with our hypothesis that blanks collect mostly vapor.

DILUTION AIR CONDITIONS – The temperature of the dilution air and dilution ratio influence particle formation and growth by controlling the saturation ratio (S) of adsorbable and condensable vapors. Neither EPA or EU regulations specify a DR but require that the exhaust be diluted (air temperature >15°C) to reduce the temperature to <191°C in the primary tunnel and to further reduce the temperature to 47 ± 5°C in the secondary tunnel. The reduction in temperature is due to dilution and heat transfer from the dilution tunnel.

To explain the relationship between DR and particle mass, we calculate the variation of the saturation ratio of two alkane vapors, heptadecane (C₁₇H₃₆) and heptacosane (C₂₇H₅₆), as a function of DR and dilution air temperature. These molecules represent average Diesel and lube-oil molecules. The Clausius-Clapeyron relationship is used to calculate the variation of saturation vapor pressure with temperature. We assume the enthalpy of vaporization is independent of temperature [58] and enthalpies were obtained from Chickos and Acree [59]. Vapor concentrations were taken from Schauer et al. [2] and divided by two to simulate the effect of an oxidation catalyst. The results from a heat transfer model [60] were combined with an energy balance to estimate heat transfer. The effects of