

An Analysis of Methods for Measuring Particulate Matter Mass Emissions

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ABSTRACT

Studies have shown that there are a significant number of chemical species present in engine exhaust particulate matter emissions. Additionally, the majority of current world-wide regulatory methods for measuring engine particulate emissions are gravimetrically based. As modern engines considerably reduce particulate mass emissions, these methods become less stable and begin to display higher levels of measurement uncertainty.

In this study, a characterization of mass emissions from three heavy-duty diesel engines, with a range of particulate emission levels, was made in order to gain a better understanding of the variability and uncertainty associated with common mass measurement methods, as well as how well these methods compare with each other. Two gravimetric mass measurement methods and a reconstructed mass method were analyzed as part of the present study. The results have shown that each of the mass measurement methods analyzed compare well at higher emission levels, but show significant disparity at the ultra-low emission levels commonly seen from modern diesel engines. Additionally, at ultra-low emissions, the uncertainty in the measurement becomes large, thus reducing confidence in the accuracy of the measurement. Based upon these findings, it would be difficult to justify a comparison between any two gravimetric measurement methods and it may be more appropriate to perform a reconstruction of the particulate mass due to a lower susceptibility to measurement error.

INTRODUCTION

Increasingly stringent diesel engine emissions regulations continue to push particulate matter (PM) mass levels in engine exhaust to ever lower values through the implementation of aftertreatment devices such as diesel particulate filters (DPFs). Because of this, it is necessary to fully understand the effects that these low emission levels may have upon the accuracy of PM

mass measurements obtained from diesel engine exhaust. Further, it is necessary to develop an understanding of the composition of PM mass at ultra-low levels and how this may affect PM mass measurement methods.

Particulate matter is commonly known to consist of a wide variety of chemical compounds. These compounds can include elemental and organic carbons (EC and OC), trace metals, and inorganic ions. The organic portion of the PM is comprised of a large number of organic species and often these species are accounted for by applying a correction to the OC mass measurement as will be discussed later. The particulate organics are typically considered to be derived from diesel fuel and lubrication oil [1]. Additionally, many of these species may be produced by thermal alteration which can occur at high temperatures such as those typically found in diesel engine combustion processes or during filter regeneration [2, 3, 4, 5].

Typical PM mass speciation reveals a roughly even distribution between the organic and inorganic constituents at high to moderate PM mass levels [1, 6]. However, it is unclear if this correlation will hold true once total PM mass levels fall to values that are often found when DPFs are used for particulate species removal. Due to the volatile nature of the organic species found in diesel engine emissions, it is likely that these species will dominate the total PM mass measurement at ultra-low emission levels. This introduces the possibility for large measurement uncertainty due to the instability of organic species emissions. Further, at ultra-low emission levels, mass measurements become sensitive to temperature, humidity, and filter conditioning. This introduces an additional source of measurement uncertainty and a greater possibility for biased mass measurement data.

In the present study, three independent PM mass measurement methods were compared under a variety of emission levels. Using this data, it was possible to analyze the dependence of mass measurement

methods upon the amount of PM mass emitted. Further, it was possible to determine the variation between the measurement methods at each emission level in an effort to understand the necessary considerations when measuring PM mass emissions at ultra-low levels.

EXPERIMENTAL SECTION

TEST CONFIGURATIONS - In order to obtain a variety of PM mass emission levels, three test engines were utilized. Additionally, a selection of aftertreatment devices were used in order to achieve ultra-low emission levels that are in accordance with stringent regulations.

Engine 1 was designated as a high emission engine and was operated during testing with no exhaust aftertreatment devices. The engine was a heavy-duty (500 hp) diesel engine designed for both on-road and off-road applications. The engine was equipped with an exhaust gas recirculation (EGR) system which is typically used to modify the in-cylinder flame temperature and O₂ dilution ratio such that nitrogen oxide (NO_x) emission levels are in compliance with regulatory limits.

The second engine used for testing, Engine 2, was chosen to provide a moderate level of particulate emissions. This engine was operated under three conditions, with no aftertreatment, with a DPF, and with an SCR system. Like Engine 1, Engine 2 was a heavy-duty (435 hp) diesel engine but it was not equipped with an EGR system. The DPF used in conjunction with this engine consisted of a diesel oxidation catalyst (DOC) which is designed to convert NO to NO₂ to aid in the filter regeneration process. Additionally, the DPF contained a catalyzed soot filter (CSF) which filters diesel particulate emissions often with greater than 90% filtration efficiency [7, 8, 9]. Engine 2 was also tested with an SCR system which is commonly used as a method of controlling NO_x emission levels. SCR catalysts operate through the selective reactivity between NH₃ and NO_x to produce elemental N₂ and H₂O [10]. However, the effects of the SCR on PM mass emissions are typically not expected to be large [7, 8].

The third engine used in the present study was designated as the low emission source to meet stringent emission standards and again was a heavy-duty diesel engine (500 hp) equipped with EGR. Engine 3 was operated under two test configurations, both using a DPF similar to the one used for Engine 2, as a means of reducing PM mass emissions. For the first test condition, the engine and DPF were operated such that no filter regeneration would occur. This allowed the formation of a soot layer on the surface of the substrate which has been shown in the past to increase the filtration efficiency of the DPF while also producing a greater pressure drop [11]. Under the second test configuration, the engine and DPF were subjected to the filter regeneration process through the use of hydrocarbon dosing. Filter regeneration is the process by which the soot deposits on the surface of the DPF are removed by

combustion to reduce the pressure drop across the filter. This process is necessary to maintain optimal engine operating conditions.

TESTING PROCEDURE - Prior to testing, each engine was operated using a warming procedure which included two hours of operation at ISO mode 8 [12]. After the warming period, the engines were operated using the transient Federal Test Procedure (FTP) heavy-duty cycle which consists of a 20 minute cycle designed to simulate on-road engine operating conditions typically encountered by heavy-duty diesel engines [13].

The source sampling system used during testing consisted of a primary dilution tunnel, secondary micro-diluter, residence time chamber (RTC), and multiple sampling trains and is discussed at length in the literature [14]. Briefly, the full exhaust flow from the test engine was introduced into the primary dilution tunnel where it was allowed to mix with the pre-cleaned dilution air. From the primary dilution tunnel, a partial sample of the diluted exhaust flow was extracted to the secondary micro-diluter and RTC where the exhaust sample was given sufficient time for aging and uniform distribution to occur. From the residence time chamber an array of sampling trains extracted partial samples of exhaust flow for collection on the filtration media. The particulate matter samples were collected using polytetrafluoroethylene (PTFE) membrane and Teflon impregnated glass fiber (TIGF) filters. At least three samples were collected under each test configuration such that the sample variation could be calculated.

MASS MEASUREMENT METHODS - In order to provide a comparison between different methods for measuring PM mass, three common methods were chosen to be part of the present study. Additionally, to compare the composition of the PM mass at high and low emission levels, the filtration media was subjected to a detailed chemical speciation during which both inorganic and organic particulate emissions were quantified. Blank filters were collected during all stages of the process to allow for a comparison of corrected and non-corrected data. This permitted a determination of the impact that blank subtraction may have upon the total mass measurement results in terms of accuracy and precision.

The first method analyzed as part of the present study involved the collection of mass samples using TIGF filters. These filter sets were conditioned in a temperature and humidity controlled room prior to being weighed for total PM mass. All procedures used for determining the PM loading on the filters were in compliance with the regulations set forth in the Code of Federal Regulations [13] and are consistent with the U.S. Environmental Protection Agency's (EPA) 2004 heavy-duty diesel engine certification method.

The second method analyzed as part of the present study involved the use of PTFE membrane filters. These filter sets were conditioned and weighed in a temperature, humidity, draft, and electrostatic controlled

weighing room. Each filter set was handled using a robotic filter weighing apparatus and was weighed using a high precision electronic balance. The procedure used for this mass measurement method was in accordance with the regulations set forth for ultra-low emissions [15].

Lastly, the third mass measurement method analyzed as part of the present study involved the calculation of the total PM mass based upon a reconstruction of the masses of each of the major PM constituents. As previously mentioned, the primary constituents of PM mass included EC, organics, trace metals, and inorganic ions [1]. More detailed procedures for quantifying the individual components of PM mass for the reconstructed measurement are found in the following section.

CHEMICAL SPECIATION - Speciation of the particulate matter samples was performed by the Wisconsin State Laboratory of Hygiene. Each sample was analyzed for elemental and organic carbons, trace metallic compounds, inorganic ions, and particulate organic species. Elemental and organic carbons were each analyzed using a thermal optical method as described in the literature [16]. Briefly, each sample was heated under a helium atmosphere to evolve the OC which could then be oxidized to form CO₂, reduced to methane, and read by flame ionization detection. Next, the samples were cooled and again heated under a helium and oxygen atmosphere to remove all carbon that may be on the filter. To determine the final EC measurement, a correction was applied to account for any pyrolysis carbon that may have been formed during the analysis procedure. Two additional corrections were applied to the OC measurement to account for non-absorbed gaseous OC and for the oxygen, hydrogen, and nitrogen components [17, 18]. This corrected measurement was then reported as the particulate organic mass (OM) for each sample.

Additional filters were used for the collection of inorganic ions and trace metallic species. One such filter set was extracted in water before being analyzed for inorganic ions by ion chromatography [19]. Additionally, another set of filters were extracted in an aggressive acidic solution and analyzed for trace metallic species using high resolution inductively coupled plasma mass spectroscopy which allowed for the quantification of 37 unique metallic species [19].

RESULTS AND DISCUSSION

TOTAL PARTICULATE MASS MEASUREMENTS - Through an analysis of the mass measurements obtained for each measurement method under each of the testing configurations, it was possible to perform a variety of comparisons to determine measurement variation for a range of emission levels. From Figure 1, it is evident that at high emission levels such as those seen for the baseline emissions from Engines 1 and 2, as well as Engine 2 with the SCR aftertreatment device, the three mass measurement methods display comparable mass emission levels. Additionally, at low

emission levels which included each of the test configurations involving a DPF, the measurement methods do not compare well and have large levels of uncertainty associated with their measurement. Each of these measurements was corrected for background contamination by blank subtraction. Blanks were collected during each stage of the sample collection and analysis procedure to ensure that all possible sources of contamination were accounted for. At these ultra-low emission levels, it is apparent that there is no consistent pattern between the measurement methods. This reinforced the suggestion that mass measurements at these levels are sensitive to temperature, humidity, and conditioning as well as the methods under which the samples were collected. Based upon this data, it would be difficult to make comparisons between any two methods and ensure that the methods are completely compatible.

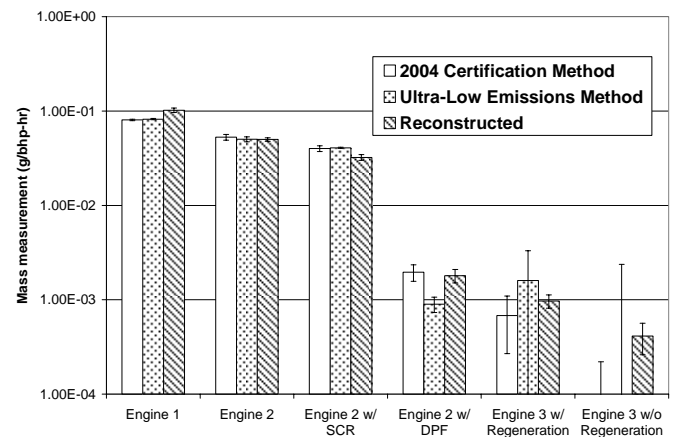


Figure 1 - Mass measurement method comparison at each mass emission level. Measurements are corrected for background contamination by blank subtraction.

For comparison purposes, the data presented in Figure 1 was also analyzed without correction for background contamination, as seen in Figure 2. The effect of blank subtraction appears to be minor at high to moderate emission levels. However, at low emission levels blank subtraction had a significant effect upon the total PM mass measured. This would suggest that the PM mass emissions from diesel engines equipped with a DPF are approaching the level of PM mass present in the dilution air or from other contamination sources. Additionally, the measurement uncertainty introduced by blank subtraction contributes a significant portion of the total measurement uncertainty.

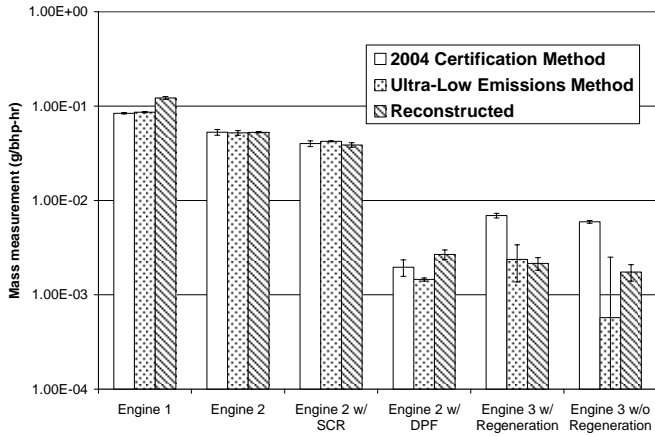


Figure 2 - Mass measurement method comparison with non-blank subtracted results.

For comparison, the ratio of each of the filter weighing methods to the reconstructed mass was calculated for each testing configuration. The reconstructed mass was chosen as the basis for comparison since it is less susceptible to bias from temperature, humidity, and conditioning effects and has been shown in the past to provide a good estimate of the total PM mass emissions [6, 20]. Consistent with previous discussion, Figures 3 and 4 show that each measurement method correlates well at high emission levels but deviates significantly at low PM mass emission levels. The ratios shown in Figure 3 for Engine 3 without regeneration go to zero due to the mass loading being lower than was quantifiable after correcting for background contamination.

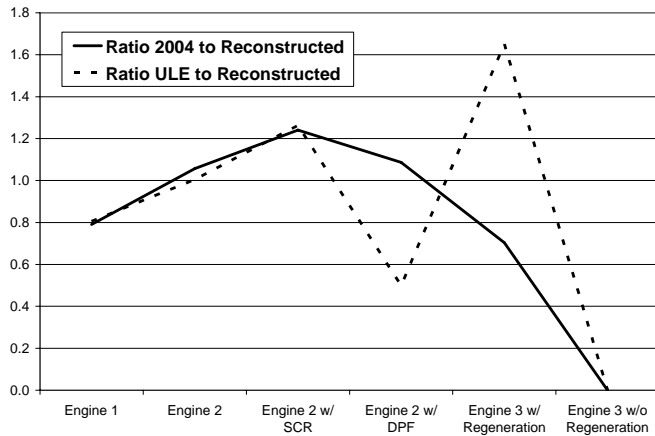


Figure 3 - Relative ratio of 2004 certification and ultra low emissions (ULE) method masses to reconstructed mass. Measurements are corrected by blank subtraction.

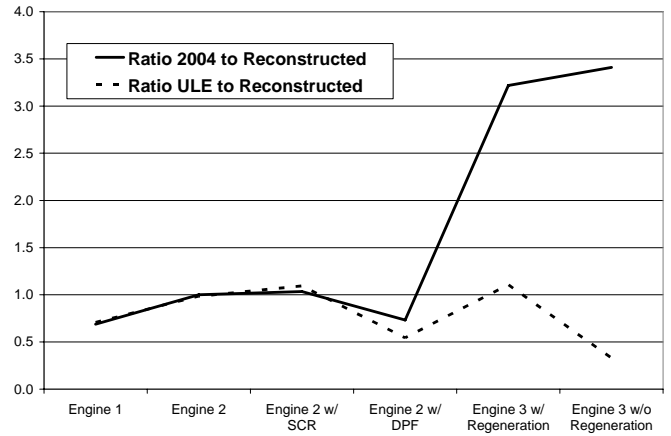


Figure 4 - Relative ratio of 2004 and ULE method masses to reconstructed mass. Not corrected by blank subtraction.

PRIMARY PARTICULATE SPECIES - The speciation of the primary particulate constituents included elemental carbon, organic species, trace metallic compounds, and inorganic ions that were chosen because they are typically considered to be the largest contributing species to the total particulate mass [1, 2, 21].

At high emission levels, the partitioning of the primary PM constituents is in agreement with what is typically found for diesel engine emissions [1, 6]. As can be seen in Figure 5, the elemental carbon and organic mass portions comprise the majority of the total PM mass with the remaining percentage being contributed by the trace metallic compounds and inorganic ions. For the mass measurement from Engine 2 equipped with the SCR system, it was found that the organic mass emissions contributed a much smaller portion of the total PM mass than they did for the baseline emissions from Engine 2. This was most likely due to the gas phase oxidation of the organic species prior to particle formation [22]. For each of these test configurations, the mass measurement methods compared well. This would suggest that the mass measurements under these conditions are relatively stable and different measurement methods can be expected to compare well when the total particulate mass is greater than 0.03 g/bhp-hr which is true whether or not the measurement was corrected for background contamination.

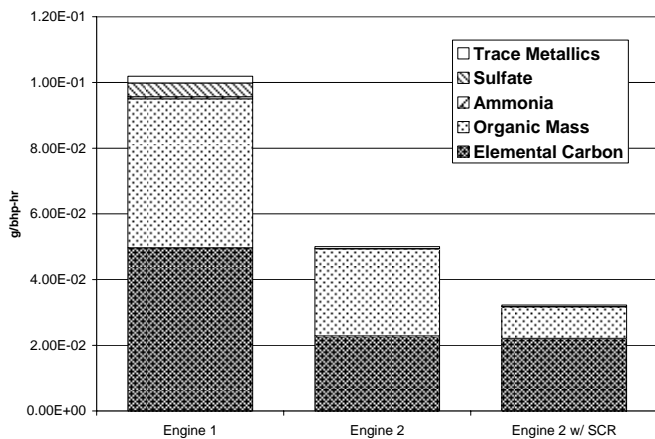


Figure 5 - Primary PM constituents breakdown for high to moderate mass emission sources.

Alternatively, at low total PM mass emission levels, the partitioning of primary PM mass constituents does not appear to follow any set pattern, as is evident from Figure 6. For Engine 2 equipped with a DPF, the particulate organic mass contributed greater than 93% of the total PM mass measurement. Correspondingly, the measurement methods did not compare as well as they did for higher total emission levels when a smaller portion of the mass was organic. This is potentially due to the volatile nature of organic species emissions which causes them to be sensitive to the conditions under which the samples were collected. For example, fluctuations in exhaust gas temperature due to transient engine operation can significantly influence the mass of the organic species measured within the engine out emissions.

Engine 3 was tested with a DPF for the reduction of PM mass emissions. Testing was conducted both with and without induced filter regeneration. When testing with regeneration, it was observed that the portions of the total mass contributed by the inorganic elements increased. This was most likely due to the reduced particulate filtration efficiency which would occur after removal of the cake layer [11]. Additionally, these increases may also be attributed to the high temperature oxidation of sulfur compounds due to the DOC [23, 24].

Although the organic portion of the total mass was not as large as it was for Engine 2 with the DPF, it is expected that the measurement discrepancies were due to the large measurement uncertainty found at ultra-low emission levels. Additionally, the regeneration process introduces a significant amount of variability into the mass measurements due to the temperature dependence of particulate emissions and the rapid temperature changes which are characteristic of the regeneration process.

When Engine 3 was tested without an induced filter regeneration, the filtration efficiency was found to increase significantly due to the formation of a thick cake layer. The absence of the regeneration caused the mass

emission of the inorganic compounds to decrease such that the organic species contributed approximately 50% of the total PM mass compared with 30% when filter regeneration did occur. Under these conditions, there was increased variability between the mass measurement methods as well as increased measurement uncertainty due to the ultra-low emission levels, which were approximately 0.0004 g/bhp-hr as determined by the reconstructed mass measurement. It is important to note that at such low emission levels, it became difficult to achieve a quantifiable measurement by filter weighing procedures. However, using the reconstructed mass measurement, it was possible to obtain a value for the total mass due to the ability of chemical speciation techniques to quantify the mass of individual compounds even at ultra-low emission levels.

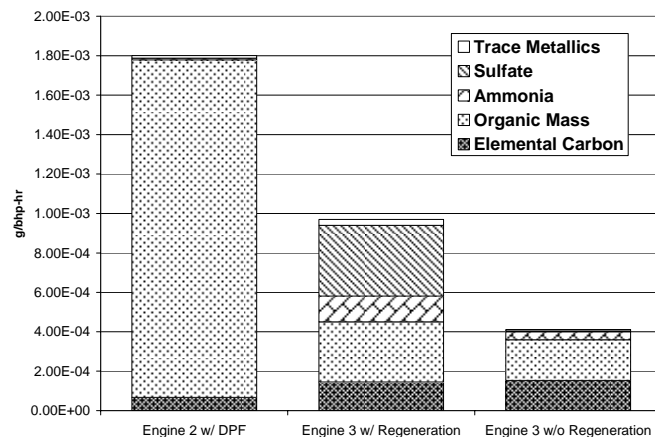


Figure 6 - Primary PM constituents breakdown for moderate to low mass emission sources.

CONCLUSION

The results from previous discussion indicate a variety of conclusions regarding the measurement of particulate matter mass in diesel engine emissions.

- Each of the mass measurement methods compared well at higher PM mass emission levels but showed significant discrepancies at ultra-low emission levels.
- The inorganic/organic partitioning of the total particulate mass is subject to variation depending upon the conditions under which the samples were collected.
- At ultra-low emission levels, the mass collected on each sample filter is approaching the measurement limits of the instrumentation, causing large uncertainty. Further, at such low levels, the effects of temperature, humidity, and other external variations have a greater influence upon the mass measurement.
- The correction for background contamination by blank substrate subtraction introduced another source of measurement uncertainty and variability.
- Gravimetric mass measurement methods have difficulty achieving consistent results for ultra-low

emission engines. It may be more appropriate to utilize alternative methods for determining PM mass emissions, such as the reconstructed mass.

ACKNOWLEDGMENTS

The authors acknowledge Dr. Barbara Zielinska of the Desert Research Institute and Prof. David Kittelson of the University of Minnesota for their valuable discussions. We also acknowledge Thaddeus Swor, Denise Ford, and Tom Wosikowski of Cummins Filtration and Emission Solutions for their help with sample collection and data analysis as well as Chris Worley of the University of Wisconsin-Madison, Jeff DeMinter, Steve Strebel, and Steve Geis of the Wisconsin State Laboratory of Hygiene for their help with the chemical analysis.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

CSF: Catalyzed soot filter

DOC: Diesel oxidation catalyst

DPF: Diesel particulate filter

EC: Elemental carbon

EGR: Exhaust gas recirculation

EPA: Environmental Protection Agency

GC/MS: Gas chromatography mass spectrometry

NO_x: Oxides of nitrogen

OC: Organic carbon

OM: Organic matter

PM: Particulate matter

PTFE: Polytetrafluoroethylene

RTC: Residence time chamber

ULE: Ultra low emissions method