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GAP ANALYSIS FOR PARTICULATE MATTER EMISSION FACTORS FOR GAS-FIRED COMBUSTION SOURCES AND LARGE COMPRESSION-IGNITION ENGINES

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List of Acronyms

(4SLB)	4-stroke lean-burn
(API)	American Petroleum Institute
(AUPRF)	Alberta Upstream Petroleum Research Fund
(CDX)	Central Data Exchange
(CEPEI)	Canadian Energy Partnership for Environmental Innovation
(CI)	compression-ignition
(CPM)	Condensable Particulate Matter
(GE EER)	GE Energy and Environmental Research Corporation
(GRI)	Gas Research Institute
(MDL)	minimum detection limit
(mg)	milligrams
(NEI)	National Emissions Inventory
(NO _x)	oxides of nitrogen
(NYSERDA)	New York State Energy Research & Development Authority
(PM)	Particulate matter
(PQL)	practical quantitation limit
(PTAC)	Petroleum Technology Alliance Canada
(RICE)	reciprocating internal combustion engines
(SCR)	selective catalytic reduction
(SI)	Natural gas-fired spark-ignition
(SO _x)	oxides of sulfur
(US EPA)	United State Environmental Protection Agency

1.0 ABSTRACT

Particulate matter (PM) emission factors in US EPA's AP-42 publication for gas-fired combustion sources and large stationary diesel engines were evaluated against more recent data. For gas-fired turbines and external combustion sources, dilution sampling has yielded PM emission factors that are more than an order of magnitude lower than the AP-42 emission factors (determined using US EPA reference test methods). At these low levels, results of the US EPA reference methods are heavily influenced by artifacts in the acetone rinse and excessive conversion of SO₂ to sulfate in the impingers; US EPA is currently using the dilution sampling results to estimate emissions from these sources in its National Emissions Inventory. Emissions from spark-ignition gas-fired reciprocating engines are higher, and the EPA reference methods are not as influenced by the detection limit or sulfate issues; however, dilution sampling methods result in PM emission factors for that are lower by approximately a factor of two. For these sources, PM emissions are predominantly organic compounds and the difference between the methods can be attributed to differences in the extent to which they condense organic material. For large stationary diesel engines, emissions data can be highly variable as a function of changes in engine technology and fuel sulfur content and engine duty cycle, such that a single emission factor for a large and varied population of such engines is not recommended; however, for purposes of identifying emissions from specific engines, the use of manufacturer certification data (which are also obtained using dilution sampling methods) is recommended. Remaining data gaps are identified and a test plan for filling those gaps is identified.

2.0 EXECUTIVE SUMMARY

The Petroleum Technology Alliance Canada (PTAC) facilitates the Alberta Upstream Petroleum Research Fund (AUPRF) and requested a gap analysis of the filterable and condensable emission factors from the following stationary combustion sources:

- Natural gas-fired turbines
- External natural gas combustion
- External LPG combustion
- Natural gas-fired reciprocating engines
- Large stationary diesel and all stationary dual-fuel engines

For the turbines, extensive PM emissions data are summarized. Although recent compilations of data obtained using US EPA reference test methods support emission factors that are moderately lower than US EPA's AP-42 emission factors (i.e., by approximately a factor of two), data obtained using dilution sampling methods support emission factors that are lower by more than an order of magnitude. Most of the dilution sampling data are from an extensive research effort by the GE Energy and Environment Research Corporation (GE EER) that was sponsored by multiple industry associations and government agencies—i.e., the American Petroleum Institute (API), Gas Research Institute (GRI), California Energy Commission, New York State Energy Research and Development Authority (NYSERDA), and U.S. Department of Energy that included comparisons of dilution sampling methods to US EPA reference test methods. It is shown that key reasons for the different results of the two methods are (a) the fact that emissions are very low—below what US EPA has identified as a practical quantitation limit (PQL)—and that there are known artifacts (particularly associated with the acetone rinse); and (b) the fact that the impinger-based methods are shown to artificially convert much more of the SO₂ present into sulfate. GE EER's 6-hour runs and dilution sampler provided for larger sample sizes; data were provided to show that there was less error associated with excluding the acetone rinse than with including it; and sulfur mass balances for the GE EER method were consistent (and showed SO₂-to-sulfate conversion rates on the order of 1%, similar to what US EPA has identified for mobile sources), as opposed to conversion ratios near 100% for data obtained with the impinger-based methods. Formulas for adjusting emission factors for higher fuel sulfur content are provided.

For the boilers, data were not readily available for LPG-fired equipment; AP-42 factors are based on an assumption that emissions factors for these sources (i.e., kg emitted per GJ of gross heat input) are approximately equal to those for boilers fired with natural gas, but data supporting this assumption were not available. For natural gas-fired boilers, GE EER data again result in PM emission factors that are more than an order of magnitude below AP-42 emission factors. For both the turbines and boilers, US EPA is using the GE EER data (rather than AP-42 emission factors) in its own National Emissions Inventory.

For large diesel-fueled compression-ignition engines, emission technologies and fuels have changed over time and duty cycles can also significantly affect emissions; as a result, a single emission factor for the category is not recommended, and GE EER's work did not involve testing of engines of this size.

However, for purposes of reporting data for specific engines, emissions data for engines constructed within the last two decades are often available from engine manufacturers. Engine manufacturers' data are also based on dilution sampling methods, although these laboratory-based methods are different from the field sampling methodologies used by GE EER (and others). Essentially no data were available for dual-fueled CI engines.

For gas-fired spark-ignition engines, GE EER showed that essentially all of the particulate matter was organic material, with very little elemental carbon or sulfate. For a 4SLB engine, impinger-based methods gave results very similar to the AP-42 factor, but dilution sampling yielded results that were approximately half those of the impinger-based methods (and compared well with other published dilution sampling results). For a 4SRB engine equipped with a nonselective catalytic reduction (NSCR) catalyst, impinger-based sampling resulted in emissions that were approximately 20% of those in AP-42, and dilution sampling again yielded results that were approximately half those of the impinger-based methods. Tests on a 2SLB engine, GE EER's dilution sampling yielded results that were approximately half of the AP-42 factor.

Gaps in the available data exist for LPG-fueled external combustion sources and dual-fueled reciprocating engines. In addition, there are gaps for transient operating conditions (e.g., those that might be experienced by load-following gas pipeline compressors) and other unusual operating modes (e.g., operation of dry low-NO_x turbine combustors outside their low-NO_x operating modes, at cold temperatures). However, more importantly, since PM emissions are dynamic—i.e., changing due to repartitioning of gas-phase organics to particulate matter and vice versa—there is a need to better understand the meaning of the emission factors and how to use them. In all likelihood, proper interpretation will require more information than just PM mass; it will also require chemical speciation information, temperature information, and possibly information regarding the number of ultrafine particles and their size distribution.

3.0 BACKGROUND

Particulate matter (PM) in the air can have direct detrimental effects upon health and welfare (e.g., JAICC, 2005; US EPA, 2009) and is also believed to make an important contribution with respect to climate change (e.g., IPCC, 2007). As a result there is interest in quantifying PM emissions from sources, in part for purposes of assessing (a) the degree to which sources impact PM concentrations at nearby receptors, and (b) the relative impacts of various sources on regional PM concentrations, and Environment Canada requires that PM emissions be reported. PM emissions are also often used to estimate emissions of individual components of PM; for example, emissions of polycyclic aromatic hydrocarbons (PAHs) and other toxic particulates are often estimated by multiplying PM emissions by “speciation profiles” that identify the percentage of PM that is comprised of those particles.

The focus of this report is on the following five source categories specified by PTAC:

1. Natural gas-fired turbines
2. Natural gas-fired external combustion
3. LPG-fired external combustion
4. Large diesel and dual-fueled (gas/diesel) compression-ignition (CI) RICE
5. Natural gas-fired spark-ignition (SI) reciprocating internal combustion engines (RICE)

3.1 Emission Factors

While emissions from existing sources can be measured directly (“source tests” or “stack tests”), this can often be a relatively expensive proposition, and there is often a need to estimate emissions for new projects and equipment that have not yet been constructed. Therefore, for the source types addressed here, the quantity of PM emissions is typically estimated by multiplying the quantity of fuel consumed (or more specifically, the higher heating value associated with that fuel) by an emission factor—i.e., mass emitted per quantity of fuel consumed—which is in turn based on source test data. The most widely used emission factors are those in US EPA’s “AP-42” compilation (US EPA, 2013), and these are in turn incorporated into other emissions inventory resources in the US (e.g., Eastern Research Group, 2001a; US EPA, 2013b) and around the world (e.g., Environment Canada, 2012; Australian Government, 2013; European Environment Agency, 2009). However, the data used to generate AP-42 emission factors for these source categories date back to 2001 and earlier, and in some cases more recent information has indicated that these factors should be adjusted.

A key impetus for this report is an extensive research program conducted by GE Energy and Environmental Research Corporation (GE EER), that involved a series of studies sponsored jointly by the American Petroleum Institute (API), Gas Research Institute (GRI), California Energy Commission, New York State Energy Research and Development Authority (NYSERDA), and U.S. Department of Energy (England, 2004; England et al., 2005). These studies focused on three of the five source types identified by PTAC and involved a much more detailed evaluation of emissions and the methodologies used to quantify them than is typical of most commercial source tests (that are conducted on a routine basis for purposes of demonstrating compliance). For some source types, the results showed drastically different emission factors than what was identified in AP-42, and issues with traditional

source testing methods were also identified and addressed through the use of a different type of sampling methodology. Although these tests were conducted several years ago, the Canadian Energy Partnership for Environmental Innovation (CEPEI) sponsored a recent paper that drew awareness to these tests (Innovative Environmental Solutions, 2012).

3.2 Average” versus “Maximum” Emission Factors

US EPA’s AP-42 factors are specifically identified as being “average” emission factors (i.e., best estimates), not upper bounds. In the United States, sources are often required to identify a “maximum” emissions limit that they can never exceed, and conduct periodic testing to show this; US EPA cautions that

“Use of [AP-42] factors as source-specific permit limits and/or as emission regulation compliance determinations is not recommended by EPA. Because emission factors essentially represent an average of a range of emission rates, approximately half of the subject sources will have emission rates greater than the emission factor and the other half will have emission rates less than the factor. As such, a permit limit using an AP-42 emission factor would result in half of the sources being in noncompliance.”¹ (US EPA, 1995, p. 2)

Various methods have been employed to arrive at a “maximum allowable” or “conservative upper bound” on emission factors. For example, Innovative Environmental Solutions (2012) based their recommendations on the highest test result obtained by GE EER. While simple, the primary drawback of this approach is that when it is based on a relatively small number of tests, the number is likely to go up as more tests are conducted. Alternatively, statistical approaches based on assumed distributions can be considered; e.g., GE EER identified the % uncertainty, the 95% confidence level using the single-tailed Student t distribution, and 95th percentile emission factors; these were typically 2-3 times higher than the average emission factor (England, 2004). Statistical methods have the advantage that in theory, if many more tests were conducted on many different sources within this category, they might not change. That being said, statistical methods are typically based on an assumption of random variability, whereas there are several systemic sources of variability in emissions testing.

In short, “maximum allowable” or “upper bound” emission factors need to incorporate a margin of conservatism, but since emission factors are almost always based on test data that are only available for a relatively small number of sources and operating conditions, that margin needs to account for sources and operating conditions that were not tested—i.e., information that is not available—and is therefore somewhat subjective. For these reasons—as well as the fact that Canada often does not require sources to test for compliance against an emissions limit, the way the US does—we have focused this report solely on the development of average emission factors, which are also more appropriate for emissions reporting (to the extent that the purpose of the reporting is to have a “best

¹ This being said, some emissions limits in the U.S. are based on AP-42 factors, especially when (a) there are little or no other data available and/or (b) it is believed that the factors are conservative as a result of technology advances since the time the AP-42 factors were developed.

estimate” of emissions, rather than to bias them high based on a conservative upper-bound emission factor).

3.3 Particle Size and Number

Health impacts can depend upon particle size, and therefore with respect to mass emissions there has been interest in classifying PM based on its size—in particular, “PM-10” for particles smaller than 10 micrometers (μm) in equivalent aerodynamic diameter (sometimes also referred to as “respirable” PM) and “PM-2.5” for particles smaller than 2.5 μm (“fine” PM).

There has been considerable interest in “ultrafine” PM (particles smaller than 0.1 μm = 100 nanometers), which is not practical to measure gravimetrically but which is better characterized in terms of the number of particles and size distribution of the particles. There has been some discussion as to whether the number and size distribution of ultrafine particles is more relevant to public health than PM mass, and models for PM nucleation and growth are also more focused on ultrafine particles and size distributions than the particle mass. However, inventorying size distributions (rather than mass) presents its own challenges, is not required in Canada or the US, and is beyond the scope of this report.

3.4 Filterable and Condensable Particulate Matter

For the source types considered here, the most commonly used method for determining PM emissions is US EPA Method 5. Figure 3-1 shows key portions of the Method 5 sampling train; while there are other US EPA Reference Test Methods for measuring PM, they are all configured in a very similar fashion. Stack gases flow upwards on the left side of the diagram; a sampling pump (located to the right of the diagram, not shown) pulls stack gas through the nozzle and probe, and PM is captured on the filter (in addition to being deposited on the inside of the nozzle and probe upstream of the filter). The weight of material captured on the filter is determined by difference (weighing the filter before and after sampling) and the weight of material deposited upstream of the filter is recovered by brushing the surfaces, rinsing with acetone, and evaporating the acetone. For both the filter catch and the acetone rinse, weighings are repeated. The sum of the two weights is the total PM “catch” and is referred to as “filterable PM” (FPM); this is what is currently required for emissions reporting by Environment Canada (2012). The weight gain in the impingers downstream of the filter is used to determine the moisture content of the stack gas.

For decades there has also been recognition of the fact that stack gases are relatively hot, and that therefore some material which exists as a gas in the stack may quickly condense into PM once it is emitted into the air. This is referred to as “condensable” PM (CPM); while US EPA’s Reference Test Method for CPM (Method 202) has changed over time (and has involved different configurations downstream of the filter than what is picture in Figure 3-1), it has always involved the recovery and drying of material collected in the impingers. CPM can contain a variety of compounds, but two of the most prevalent constituents are often organic compounds and sulfates (SO_4^{2-}). The US EPA requires sources to report both FPM and CPM, and there has been some indication that Environment Canada may require reporting of both FPM and CPM in the future.

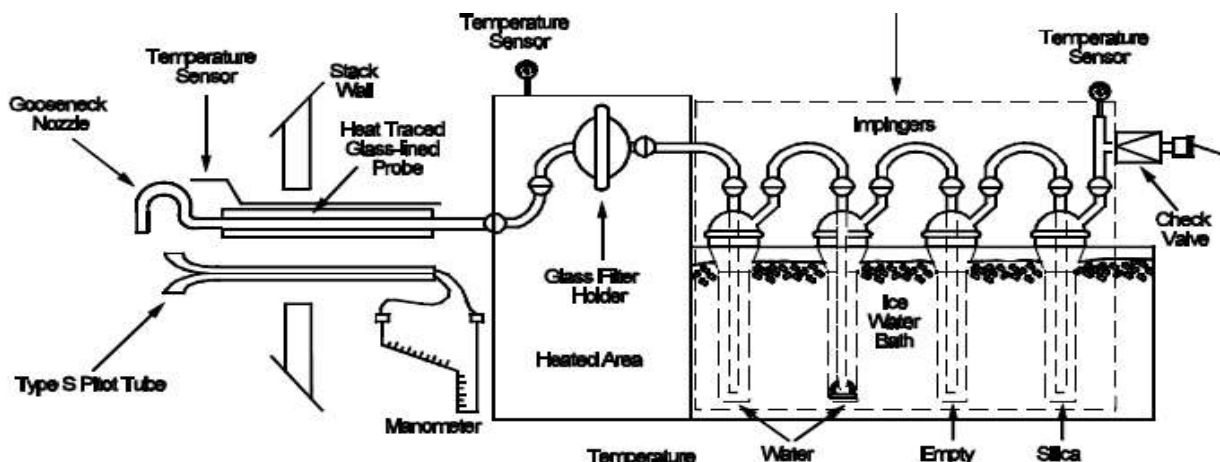


Figure 3-1. US EPA Method 5 Sampling Train for Filterable PM.

This framework has at least two shortcomings. The first is that the process of condensation in iced impingers is very dissimilar from the process of condensation resulting from dilution with ambient air, and therefore the mass of material condensing in the sampling train does not necessarily approximate the mass of material that would condense upon dilution in the ambient air. For example, Wien et al. (2004) showed that a sulfur mass balance (through monitoring fuel sulfur content, gaseous SO₂, and sulfate) did not close for impinger-based methods (i.e., impingers would artificially convert SO₂ to sulfate), whereas use of a dilution sampler (see Figure 3-2) resulted in much less sulfate and closed the mass balance. It has been suggested that sampling methodologies that incorporate dilution air systems (and no impingers) are a preferred means of addressing this problem, both for stationary sources (England et al., 2007a, 2007b; Lee, 2010) and mobile sources (Maricq and Maldonado, 2010). Hildemann et al. (1989) developed one of the earliest seminal portable dilution samplers; GE EER (England, 2004) built off of this work to produce a more portable sampler. An ISO standard (25597) has also been developed for dilution sampling.

The second shortcoming of the framework is that it has been shown that as stack gas is emitted and diluted, after the initial increase in PM mass due to CPM condensation, PM mass then decreases as the stack gas is diluted, as a result of semivolatile organics in the PM repartitioning into the gaseous phase. (This dynamic nature of PM is probably also the reason why details of dilution sampler design have also been shown to affect results, and why filter media used for collecting PM samples can be affected by positive or negative bias—i.e., due to adsorption/desorption from the media.) While most dilution samplers (including GE EER's) incorporate dilution on the order of 20:1 to 50:1, Lipsky and Robinson (2006) showed that increasing dilution from 20:1 to 350:1 decreased PM_{2.5} emissions from a diesel engine (operating at low load) by 50%. Robinson et al. (2010) have predicted that even 100:1 dilution samplers may overestimate the mass of the organic portion of PM (relative to its eventual concentration in the atmosphere) from by a factor of 2-3 or more for relatively high-emitting sources, but that for low-emitting sources, the same sampler could underestimate the mass by a factor of 2-3.

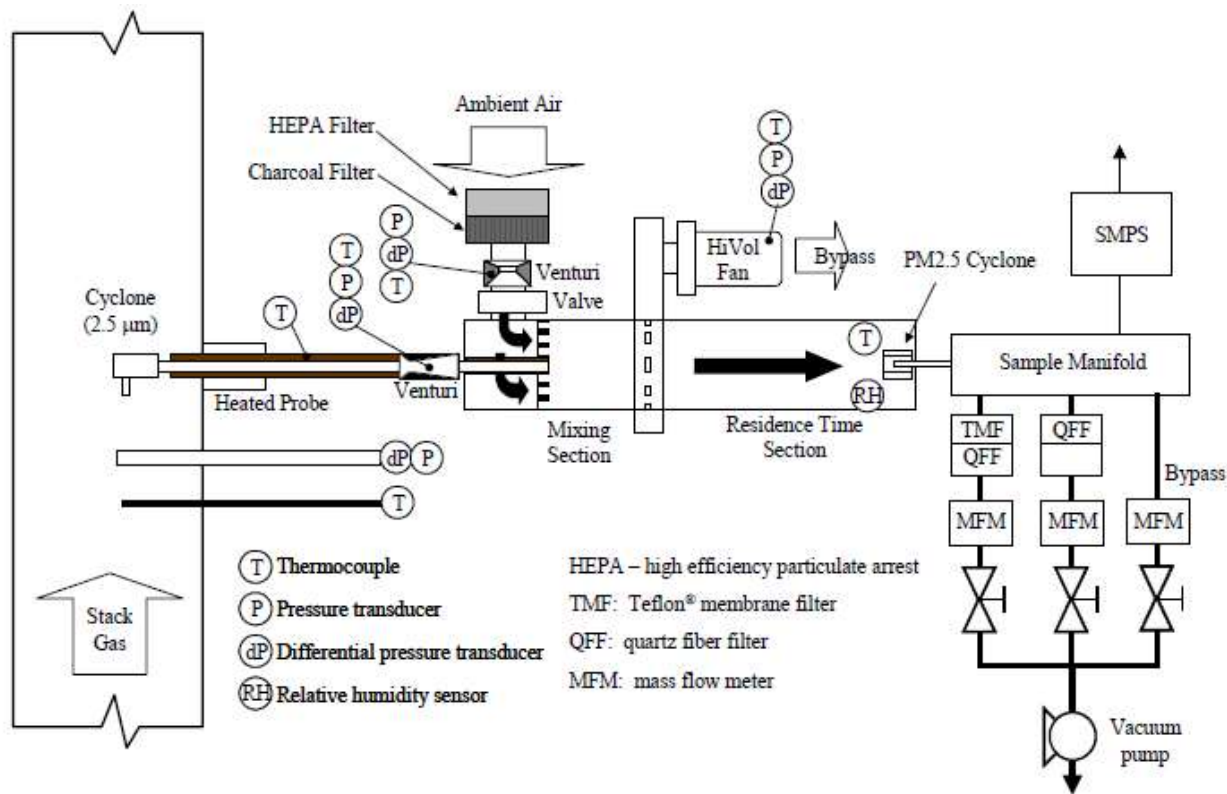


Figure 3-2. GE EER's Dilution Sampling System (England, 2004).

Currently, essentially all of the available emissions data for the source types of interest were determined using impinger-based systems or dilution samplers, and those are the data presented in this report. “Correcting” data taken with either method to account for the type of extended dilution effects identified by Robinson et al. (2010) would be nontrivial and is outside the scope of this report.

3.5 Approach and Report Organization

The broad objective of this study is to provide a gap analysis of the filterable and condensable emission factors from the stationary combustion sources identified at the beginning of this section. With regard to the literature search, for several of the source types, the GE EER reports were the primary source of information aside from the AP-42 factors. Other countries’ emission factor compilations were searched, but these primarily referenced AP-42, had minor additions with relatively dated information, and/or did not have detailed support documentation. The approach to this report was to focus more on a relatively technical evaluation of good-quality available information (including information generic to all sources, such as that identified in Section 3.4 above) and less on comprehensively or exhaustively tracking down every published test result value. In the United States, source testing of stationary sources is relatively common, and US EPA has recently developed an Electronic Reporting Tool (ERT) for submitting data via a Central Data Exchange (CDX) so that the agency can then generate new factors for its WebFIRE database (ERG, 2013). However, at the time this study was conducted, no new data for the source types of interest could be accessed through that portal.

The lowest-emitting units—i.e., the turbines and external combustion sources—are discussed first, in Section 4. As will be described in more detail later, the nature of the emissions from these sources requires a relatively detailed examination of the emissions testing methods used to calculate the emission factors (in particular, the detection limits of those methods). Also, since the emission factors are primarily based on pipeline-quality natural gas or LPG with very low sulfur content, and upstream operations may involve the use of higher-sulfur fuel, we have included a discussion of the effect of fuel sulfur in this section.

Reciprocating engines are discussed in Section 5. Emissions from these sources are somewhat higher than for the sources in Section 4, and therefore data for these sources are less likely to be biased as a result of the detection limits of the methodology. That being said, emission factors for engines in particular can be subject to additional complexities associated with a wider range of applications and potential duty cycles as well as manufacturer emissions specifications for which compliance is determined using different methodologies. In addition, for diesel-fueled engines, there have been changes in engine technology (necessitated by emissions regulations specific to PM) and changes in fuel sulfur content over time. Data gaps for all of the source types and potential future test plans are identified in Section 6.

4.0 GAS-FIRED TURBINES AND EXTERNAL COMBUSTION SOURCES

Turbines and external combustion sources fired with natural gas or LPG have low PM emissions for several reasons, including:

- Fuel is either a gas or is very high volatility (either gaseous at the time that it reaches the combustion point or easily gasified), leading to good air/fuel mixing
- Low-molecular weight fuel (less tendency to condense)
- Low sulfur content (little or no sulfate formation)
- No reciprocating parts (no piston lubricating oil)

There have been far more evaluations of PM emissions from gas-fired turbines than from boilers, possibly due to the fact that within the last two decades, large-scale projects for utility-scale power generation are much more likely to involve turbines than boilers, and the large scale of these projects means that even very low emission factors (expressed in kg/GJ of heat input) can result in relatively large emission rates when expressed in kg/hr (and in the US, such large-scale projects are also generally subject to more public scrutiny and more likely to be subjected to requirements to conduct emissions testing). Therefore, this section is divided into two subsections: Section 4.1 addresses turbines (as well as several issues that are common to the testing of non-reciprocating gas-fired sources in general), and Section 4.2 addresses external combustion sources.

4.1 Turbines

4.1.1 Available Data

As mentioned above, several PM emissions datasets have been compiled for gas-fired turbines. In general, essentially all data sets indicate that essentially all of the PM is $PM_{2.5}$. For purposes of obtaining emission factors, the 2.8×10^{-3} kg/GJ factor (total PM – i.e., filterable PM plus CPM) in US EPA's AP-42 reference (US EPA, 2000a) is probably the most widely used, but it is also the oldest and most limited, given that the PM emission factors in it were based on five tests conducted in the mid-1990s on a single turbine equipped with water injection (Alpha-Gamma, 2000). Some of the more recent and extensive data compilations support somewhat lower emission factors, but they are still within roughly a factor of two or three and still indicate relatively consistent results. For example, Lusher (2010) found that the average of results of 42 PM tests on GE LM-6000 simple-cycle turbines equipped with SCR and CO oxidation catalysts (conducted between 2003 and 2009 at 7 different facilities) was 1.1×10^{-3} kg/GJ; variability was low (the range of results was between 0.4×10^{-3} kg/GJ and 2.2×10^{-3} kg/GJ) and results were consistent with emissions data from four other simple-cycle turbines without SCR and CO catalysts 1.5×10^{-3} kg/GJ to 1.9×10^{-3} kg/GJ). Lusher (2010) also noted that combined-cycle facilities had complied with slightly lower PM emissions limits (on a kg/GJ basis) than simple-cycle facilities. Corio (2012) identified that for aeroderivative turbines (such as the LM-6000), if 18 available datasets (comprising three tests each) were filtered such that only 2000 and later tests at full load showing no contamination in the CPM tests were considered, the filtered data (11 datasets) showed relatively low variability and averaged out to 1.9×10^{-3} kg/GJ.

While the abovementioned results indicate relatively low variability, Lanier and England (2004) summarized results in a California Energy Commission database and showed that for 92 tests on 36 different turbines (of various types and sizes), results varied across orders of magnitude, with filterable PM ranging from zero to approximately 7.5×10^{-3} kg/GJ and CPM ranging from zero to approximately 6×10^{-3} kg/GJ² (with both distributions being skewed closer to the zero side of the range). For this compilation, some of the variability may have resulted from the fact that the data do not appear to have been filtered, and may overstate variability as a result of some of the tests not reflecting improvements in testing practices that have been made over time.

More significantly, the extensive GE EER testing program mentioned previously showed good agreement for 13 tests at three different sites and resulted in average emission factor of 8.2×10^{-5} kg/GJ (England, 2004)—i.e., more than an order of magnitude lower than the factors identified by the other data sources—and these data are also supported by emission factors of 5.1×10^{-5} kg/GJ PM_{2.5} and 6.1×10^{-5} kg/GJ PM₁₀ developed by Denmark's National Environmental Research Institute (NERI), based on tests conducted on two turbines (Nielsen et al., 2007, 2010).

Lanier and England (2004) have provided an exhaustive discussion of all of the various possible sources of variability in turbine PM emissions measurement results, and this discussion will not be repeated in this report. However, the large discrepancy between the datasets is believed to be due to the fact that GE EER and NERI utilized dilution sampling, whereas the other studies used Method 5-based sampling methods. These methods were discussed briefly in Section 3.4 of this report, but to better understand the reasons for the large discrepancy requires a more detailed discussion of the methodologies. Sections 4.1.2 and 4.1.3 below identify common issues with filterable and condensable PM measurement using Method 5-based methods; Section 4.1.4 identifies details in the dilution sampling methodology.

4.1.2 Filterable PM Measurement Method Issues

A key problem with applying Method 5 to very low-emitting sources such as gas turbines—where the total particulate “catch” (i.e., mass collected on the filter and in the acetone rinses) is typically on the order of 1 milligram—has been that several techniques (not all of which are detailed in Method 5, or in stack test reports) need to be employed to avoid the formation of artifacts, and even if they are employed, the artifacts may not be entirely eliminated (Lanier and England, 2004). It is relevant to point out that the determination of PM weight for both the filter and the acetone rinse involves repeated weighings until results stabilize to within ± 0.5 milligrams (mg).

In 1993, PM artifact formation was evaluated by reviewing a total of 25 tests conducted on a gas-fired cogeneration turbine for varying durations (up to 24 hours) and evaluating the extent to which the quantity of particulate matter captured was proportional to the quantity of time sampled (as it should be, in the absence of artifacts) (Wilson and Frederick, 1993). No such correlation was seen for the

² Lanier and England (2004) expressed data in mg/dscm; these data have been converted to approximate kg/GJ here based on US EPA's default F-factor of 8710 (dscf @ 0% O₂)/MMBtu and an assumed stack oxygen content of 15% O₂, dry basis.

filterable PM. In addition, 22 of the 25 test reports identified the split between the amount of material collected on the filter and the amount collected in the acetone rinses of the nozzle, probe, and filter housing upstream of the filter; of these, 15 tests (including all but one of the tests that were run for less than 5 hours) showed that essentially all (95-100%) of the total filterable PM catch was in the rinses rather than on the filter itself (and the total catches in these rinses ranged from 0.3 to 8.78 mg). For this study, stainless steel probes were being used for PM measurement; in more recent years, it has generally been perceived that glass-lined probes might produce fewer artifacts, and therefore glass-lined probes are essentially universally specified for low-level particulate measurement.

That being said, the result was consistent with a subsequent evaluation of Method 5 by a US EPA contractor, who identified that acetone rinses (even with glass-lined probes) could be a key source of artifacts (Shigehara, 1996). Specifically, it was shown that acetone rinses of two blank sampling trains (that had not been used for sampling) were on the order of several milligrams up until the seventh probe rinse (i.e., one acetone rinse yielded 2.6-5.3 mg of PM for each of the first six washes and 1 mg on the seventh wash; another yielded 19 mg on the first wash, 1.0-1.3 mg for the next five washes and 0.5 mg on the seventh wash). While Method 5 does allow for blank catches to be subtracted from actual sample catches, (a) the variability in the catches from the acetone probe rinses alone shows that it would be very easy to calculate a small amount of catch (or negative catch) from a test, and (b) subtraction of blanks does not capture effects such as (a) “baking” the probe and filter with stack gases hotter than 500 °C, (b) contamination associated with transporting the sampling equipment back and forth between sampling locations and recovery areas, or (c) having to scrape the filter off of the filter holder after it has been “stuck” on in a stack environment for an extended period of time (and possibly scraping off a fraction of a milligram of filter holder in the process).

In 1997, US EPA identified that for sources with “low” particulate levels—i.e., catches of 50 mg or less—certain refinements to Method 5 were necessary to eliminate biases in the results (US EPA, 1997), and proposed “Method 5i”. This method was finalized in 1999 and included the following refinements:

- Modification of the filter recovery process, so that the filter does not need to be removed from its housing (i.e., the entire housing is weighed), to eliminate negative biases associated with sample loss during removal of the filter from the housing and positive biases associated with contamination of the sample (fugitive dust from the environment landing on the filter during recovery).
- Specification of low-residue, Pesticide grade acetone instead of reagent grade acetone (to eliminate biases associated with the acetone) and apparatus for ensuring that the probe is at a 90-degree angle to the direction of flow.
- Avoiding contamination by using a portable desiccator for use in transporting and holding the filters to and on the stack; using glass plugs on the filter assemblies to keep them “pure” prior to and after sampling; covering the desiccant with a 0.1 micron screen to eliminate potential external contamination of filter housing during transport; and handling the filter assemblies with powder free latex gloves.
- Requiring glass nozzles and probe liners, in lieu of the stainless steel ones allowed by Method 5.

- Requiring the use of paired (duplicate) sampling trains, and specifying that agreement between the results for the duplicate trains (relative standard deviation) needs to be within $\pm 10\%$ for concentrations of 10 mg/dscm and $\pm 25\%$ for concentrations of 1 mg/dscm (with no precision criteria for concentrations less than 1 mg/dscm).

Method 5i also identifies a minimum target mass for sampling as 10-20 mg, a practical quantitation limit (PQL) of 3 mg catch, and a minimum detection limit (MDL) of 1 mg. This means that if less than 3 mg is caught, there can be some assurance that PM is present, but quantifying it is not accurate, and if less than 1 mg is caught, there is not even sufficient evidence that any PM is actually present. In the Federal Register notice promulgating Method 5i, US EPA stated that

“We have promulgated Method 5i as a method because it provides significant improvement in precision and accuracy of low level particulate matter measurements relative to Method 5. Consequently, although Method 5i is not a required method, we expect that permitting officials will disapprove comprehensive performance test plans that recommend using Method 5 for low level particulate levels.” (US EPA, 1999, p. 52927).

That being said, it is worth mentioning that even today, when particulate levels are very low, Method 5 is still much more commonly used than Method 5i. The cost of duplicate sampling and the performance specification (which could potentially require a testing company to have to redo sampling if results do not meet the specification) are key disincentives towards the use of Method 5i. Some testing firms do implement some of the other practices identified in Method 5i, but in the data described in Section 4.1.1, the extent to which these procedures were utilized were not identified (and they are often not identified even in stack testing protocols or test reports).

Since not all of the procedures in Method 5i are used, the PQL and MDL for actual field tests are probably somewhat higher than what is identified for Method 5i. However, even if the quantitation limits were as low as those in Method 5i, most of the tests used to develop the emission factor in AP-42—and the other tests cited by Lanier and England (2004), Lusher (2010), Corio (2012), and Haywood et al. (2012)—probably do not meet the Method 5i PQL, and might not even meet the Method 5i MDL. Figure 4-1 shows how those test results compared to the PQL and MDL a typical sampling rate of 0.7 dscm per hour and an exhaust oxygen concentration of 15% by volume (dry basis); the PQL and MDL lines would be higher if sampling rate were lower or the %O₂ were lower. (Sampling time information was often not readily available, but the default sampling time used by source testers is one hour unless it is known that a longer sampling time is needed in order to assure that results are compliant with emissions limits, and in all likelihood none of the tests had durations of more than 6 hours.) Given that results are essentially right at the limits of detection (and below the limit of quantitation), and given that there are known artifacts, it is not unreasonable to discount these data heavily compared to data obtained from a more sensitive methodology.

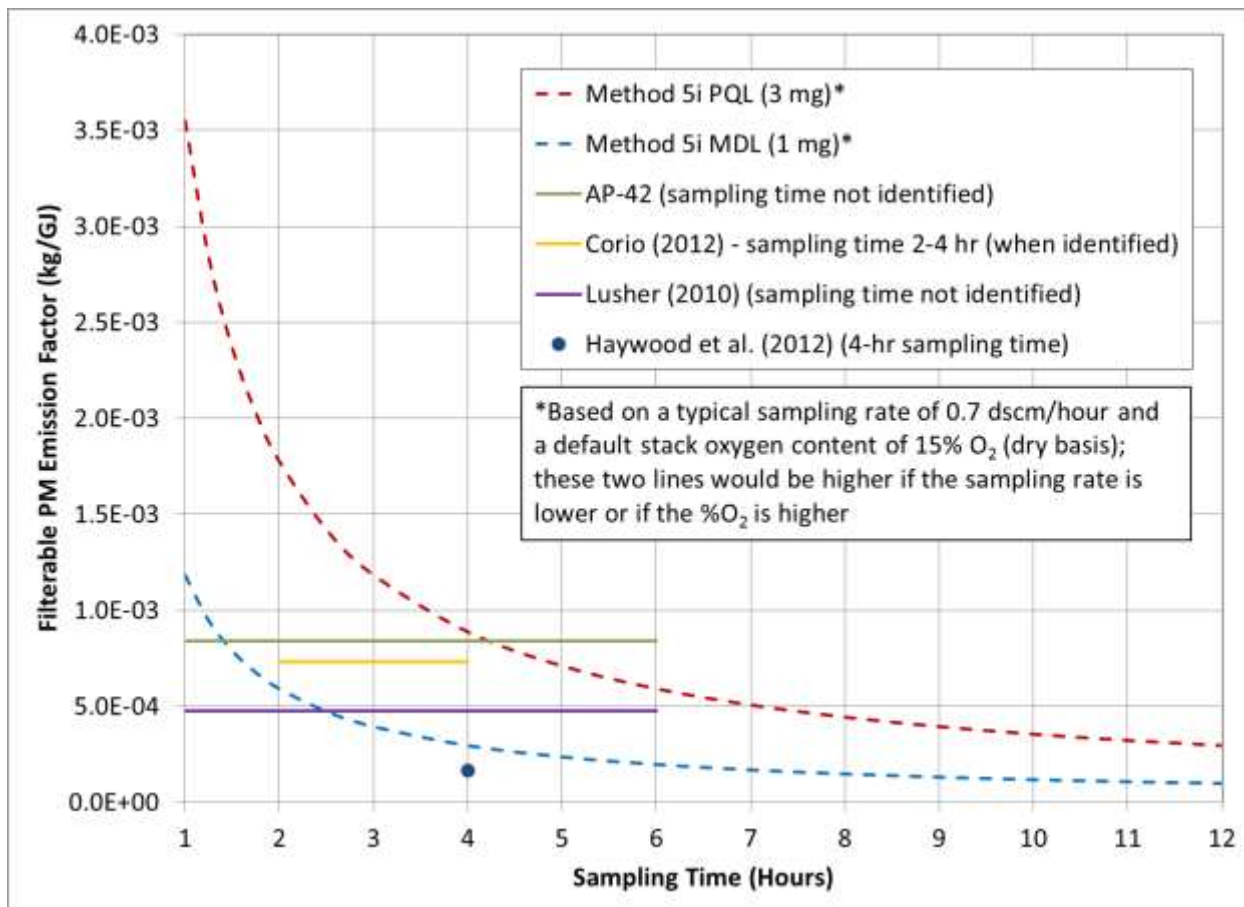


Figure 4-1. Filterable PM Emissions Data Compared to Method 5i PQL and MDL.

4.1.3 Condensable PM Measurement Method Issues

In 1971, US EPA proposed determining condensable PM by weighing the amount of particulate collected downstream of the filter in a Method 5 train, in the chilled water-filled impingers; however, in 1972 the agency removed that requirement, stating that

“...there is some question that all of the material collected in the impingers would truly form particulate in the atmosphere under normal dispersion conditions. For instance, gaseous sulfur dioxide may be oxidized to a particulate form—sulfur trioxide and sulfuric acid—in the sampling train. Much of the material found in the impingers is sulfuric acid and sulfates. There has been only limited sampling with the full EPA train such that the occasional anomalies cannot be explained fully at this time.” (Ruckelshaus, 1972)

From a purely methodological perspective, Hildemann et al. (1989) pointed out that the impinger-based method only incorporates the effects of cooling, not dilution in the ambient air, and this fact plus the use of ice-filled impingers could condense components that might not condense in the ambient air. US EPA

promulgated a “reference test method” for CPM (Method 202) in 1991; while some modifications were made to the back end of the Method 5 train, the methodology still effectively involved weighing the PM recovered in the iced impingers. To address concerns about the sulfur-related artifacts mentioned by US EPA in 1972, the method identified a one-hour nitrogen purge immediately after sampling, but stated that this was optional for low-sulfur sources. That being said, the method still created sulfate artifacts, overestimating CPM (e.g., EPRI, 1998; Corio and Sherwell, 2000; Wien et al, 2001b). In the agency’s 2008 rule implementing new ambient air standards for PM_{2.5}, EPA wrote that

“In this final NSR rule, EPA will not require that States address condensable PM in establishing enforceable emissions limits for either PM₁₀ or PM_{2.5} in NSR permits until the completion of a transition period...In response to significant comments on the variability of test methods available for measuring condensable emissions, we have adopted this transition period approach to allow us to assess the capabilities of the test methods and possibly revise them to improve performance.” (Johnson, 2008)

In 2010, US EPA updated Method 202, with key changes including the fact that (1) the impingers at the front of the train should be empty rather than filled with water (though the impingers are still placed in an ice bath and will still condense liquid out of the stack gas during the sampling run); (2) the nitrogen purge was mandatory for all sources; and (3) stack testers need to be able to recover a blank sampling train and collect no more than 2 mg of PM from the blank. This last requirement has been controversial, with some (but not all) stack testing firms identifying that they could not always meet the 2 mg criteria (and those claiming to be able to meet the requirement acknowledging that there are certain procedures which they use to be able to do so, that are not specified in the test method); in 2013, US EPA started an investigation of the reasonableness of the 2 mg criteria (and this evaluation is not yet complete), and to date has still not identified a MDL for this method, although the controversy regarding the ability to obtain less than 2 mg catch of a blank train suggest that the MDL is at least on this order of magnitude. Separately, there are still claims that the methodology creates PM artifacts.

Although the sulfur content of natural gas is very low, the PM levels are also very low and therefore measurable sulfate effects can still sometimes be seen. For example, in the Wilson and Frederick (1993) study mentioned in the previous section, although the filterable PM catch did not increase with increasing sampling times, there was a relationship between the sampling time and the quantity of sulfate collected (approximately 0.6 lb/hr—plus or minus approximately 100%—which corresponded to approximately 6×10^{-4} kg/GJ³). That gas turbine was equipped with SCR, a CO oxidation catalyst, and steam injection (some of the material collected in the impingers was also attributed to minute amounts of minerals in the steam). Method 202 was not used to measure CPM (the back half of a standard Method 5 sampling train was used instead), and therefore artifact formation may have occurred; Wilson and Frederick dismissed all of the material in the impingers as “pseudo particulate” that would not have formed in the atmosphere. However, sulfites (SO₃²⁻) and sulfates (SO₄²⁻) cannot be categorically dismissed as artifacts.

³ This conversion was based on an assumed heat input rate of approximately 450 MMBtu/hr for the LM5000.

Using a variety of non-impinger based sampling techniques that take dilution into account, Stevens et al. (1976) determined that catalyst-equipped spark-ignition engines burning gasoline with a 0.03% (300 ppm) sulfur content converted about 12% of the fuel sulfur into particulate. Fritz and Starr (1998) saw generally higher PM concentrations from diesel engines when the fuel sulfur content was increased from 0.03% to 0.28%, and US EPA (2010) interpreted the data as corresponding to approximately 2.2% of the fuel sulfur being converted into particulate, but also assumed a conversion factor of 30% for “engines equipped with advanced oxidation catalyst technologies (e.g., catalyzed diesel particulate filters)”. The conversion of SO_2 to SO_4^{2-} involves the oxidation of sulfur from a +4 oxidation state to a +6 oxidation state, so it is not surprising that oxidation catalysts could increase the extent of sulfate formation; that being said, the conversion is also dependent on temperatures and residence times, and vendors of catalysts used for power generation equipment are aware of the potential for oxidation (and the associated potentially deleterious effect of ammonium bisulfate formation, which can foul equipment at sources with relatively high SO_2 emissions), and sometimes specify a maximum sulfur-to-sulfate conversion rate for their equipment. The presence of ammonia can also affect particulate formation: for example, Curtis (1988) found ammonium sulfite particulate in the sampling probe (upstream of the filter, so this would have been counted as filterable PM) and identified substantially reduced sample recoveries of SO_2 when SO_2 exhaust concentrations were 166-314 ppm and ammonia concentrations were 139-455 ppm (though recoveries were normal for ammonia concentrations (whereas recoveries were very good when ammonia concentrations were 69 ppm or less)).

In short, given the dissimilarity between the CPM sampling methodology and the fact that atmospheric processes incorporate dispersion and relatively slower cooling, while sulfates and sulfites cannot categorically be dismissed, the extent to which they are being emitted cannot easily be determined without the use of different sampling methodologies.

4.1.4 Dilution Sampling Measurements

The concept of dilution sampling—i.e., where exhaust gases are diluted with clean air (and cooled) prior to sampling has been around for many years, and US EPA requires that this type of methodology be used to by manufacturers to certify emissions from reciprocating engines. One key advantage of this type of approach over the impinger-based methods is that it explicitly includes the effects of both dilution and cooling, and does not involve the use of impingers or artificial concentration of constituents. However, for the most part, this type of sampling has been practiced more in research environments and engine testing laboratories than in field studies of in-use industrial equipment, in part due to the relative expense and size of the equipment (and the fact that most commercial stack testing contractors are unfamiliar with its use). In 2009-2010, when re-evaluating CPM methods, US EPA originally considered the idea of promulgating an official regulatory dilution sampling method (a conditional method CTM-039 exists), but ran out of funding to do so.

For very low-emitting gas turbines, the detection limit issues mentioned previously in this report were addressed in part by increasing the sampling size—i.e., having the sampling rate (1.2-1.5 scm/hr) be somewhat higher than what is typical for Method 5 and having each sampling run last for six hours (compared to typical Method 5 run durations of one or two hours)—and in part by eliminating the

acetone rinse of equipment upstream of the filter (and the associated artifacts identified in Section 4.1.2). The latter was justified primarily on the basis that for a sampling system much larger than GE EER's, Hildemann et al. (1989) had determined that PM losses upstream of the filter were very low for fine particulate (i.e., 7% for 1.3 μm particles and 15% for 2 μm particles) and that therefore the error associated with removing the rinse was less than the potential artifacts associated with including it (England et al., 2004). Hildemann et al.'s determination of losses was based on an unspecified concentration of artificially generated ammonium fluorescein particles, rather than actual exhaust from a source; however, when the GE EER system was used to measure emissions from higher-emitting sources (and the acetone rinses were not excluded), these results qualitatively supported Hildemann et al.'s conclusions (i.e., rinse catches were very low compared to filter catches) (England et al., 2007a).

All of the turbines tested by England (2004) were equipped with SCR and oxidation catalysts; it was identified that on average, 13% of the particulate mass was attributed to sulfate ion (SO_4^{2-}) and 6% was attributed to ammonium ion (NH_4^+), which is consistent with the formation of ammonium sulfate (because in $(\text{NH}_4)_2\text{SO}_4$, the mass of the sulfate would be approximately twice the total mass of the ammonium ions). By measuring fuel sulfur content, SO_2 , and sulfate with the dilution sampler, Wien et al. (2004) and England and McGrath (2004) showed that the proportion of sulfur that was emitted as sulfate particulate was typically in the 1-3% range—comparable to the 2.2% conversion estimated by US EPA (2010a) for diesel engines—with the remainder being SO_2 . The impinger-based method, on the other hand, converted essentially all of the sulfur to sulfate and double-counted the sulfur (i.e., the mass balance did not close).

England (2004) and England et al. (2007a) acknowledge that in general, different types of dilution samplers (and different operating parameters for those samplers) can yield different PM emissions—therefore begging the question of which samplers/operating conditions are the “right” ones for accurately quantifying CPM. However, for several key variables (such as dilution ratio), there appears to be a convergence (at least for natural gas-fired systems) showing that while a dilution ratio of 10:1 results in a different particle size distribution than a dilution ratio of 20:1 varying the dilution ratio from 20:1 up to 50:1 caused no change in the size distribution (England et al., 2007a). Also, additional tests of GE EER's method against other dilution samplers—applied to a higher-emitting source, a diesel engine—showed good agreement (Wien et al., 2004c).

4.1.5 Discussion and Recommended Emission Factors

In the preceding subsections, it has been demonstrated that (a) filterable PM emissions from turbines are below the practical quantitation limit for standard sampling technologies, (b) many of the published factors for CPM are grossly overestimated as a result of sulfate conversion in the sampling train, and (c) dilution sampler-based methodologies run for extended periods of time (6 hours) that do not recover probe rinses can more accurately determine both the PM and CPM emissions from these sources. Therefore, for sources firing pipeline natural gas (or similarly low-sulfur gas), and from a technical perspective, the 8.2×10^{-5} kg/GJ factor identified by England (2004) is the most appropriate factor. From a policy perspective, if consistency with US EPA is desirable, US EPA cites the GE EER work for its

own National Emissions Inventory, but uses a series of ratios to determine slightly different emission factors—i.e.,

$$\frac{2.1 \times 10^{-5} \text{ kg/GJ Filterable PM}_{2.5}}{5.9 \times 10^{-5} \text{ kg/GJ CPM}} \\ \frac{5.9 \times 10^{-5} \text{ kg/GJ CPM}}{8.0 \times 10^{-5} \text{ kg/GJ Total PM}_{2.5}}$$

The spreadsheet indicates that the filterable/CPM split was based on the original split between these two factors in AP-42 (which is not well-justified from a technical perspective, given the problems with that data that have been identified) and adds on an additional factor of 5.1×10^{-5} kg/GJ for estimating PM₁₀ (for reasons which are not entirely clear). NERI (Nielsen et al., 2010) also adds on a small additional factor to their PM_{2.5} factors when estimating PM₁₀ but does not identify how this factor was derived, and we believe that the “add-on” factors for PM₁₀ are likely to be small artifacts associated with test variability and/or the mixing of data sources.

The sources evaluated by GE EER had fuel sulfur contents ranging from approximately 10-50 ppmw, not dissimilar from the natural gas sulfur contents identified in AP-42 (6-36 ppmw).⁴ However, for upstream operations with higher fuel sulfur contents, it makes sense to revise the GE EER factor upwards to account for the increased sulfate contribution. Assuming an approximate 2% conversion rate, the additional sulfate (kg/GJ) would be

$$\text{SO}_4^{2-} \text{ (kg/GJ)} = (0.02) \times \frac{\text{(ppmw S)}}{10^6 \times \text{Fuel Gross Heating Value (GJ/kg)}} \times \frac{96 \text{ kg SO}_4^{2-}}{32 \text{ kg S}} \quad (1)$$

That being said, it is less clear what other chemicals precipitate out with the sulfate ion. In the case of the GE EER studies, ammonia-based controls are being used, and data also indicate that ammonium sulfate is precipitating out; therefore, if it is assumed that (a) the ammonium would not have precipitated out without the sulfate being present and (b) that there are no waters of hydration (see, for example, Xu et al., 1998), then the additional particulate would be

$$\text{Addl. PM (kg/GJ)} = (0.02) \times \frac{\text{(ppmw S)}}{10^6 \times \text{Fuel Gross Heating Value (GJ/kg)}} \times \frac{132 \text{ kg (NH}_4)_2\text{SO}_4}{32 \text{ kg S}} \quad (2)$$

However, in the absence of ammonia, studies on marine diesel engines (burning fuels with sulfur content in excess of 10,000 ppmw S) have shown an average of 4.5 waters of hydration per sulfuric acid molecule (H₂SO₄ • 4.5H₂O) (Petzold et al., 2010), in which case the ratio on the far right of equation (2) would be replaced by (179 kg H₂SO₄ • 4.5H₂O)/(32 kg S); and US EPA assumes 7 waters of hydration per sulfuric acid molecule (H₂SO₄ • 7H₂O) (Samulski, 2007; US EPA, 2010), in which case the ratio on the far right of equation (2) would be replaced by (224 kg H₂SO₄ • 7H₂O)/(32 kg S). At this point in time, we have not found evidence supporting the 7-waters-of-hydration assumption, (whereas

⁴ The low end of this range is derived from the specification of 2,000 grains/MMscf from AP-42 Table 1.4-2, footnote d (and an approximate molecular weight of 17 for natural gas); the upper end of the range is from AP-42 Table 3.1-2a, footnote h, which identifies that 0.94S = 3.4 × 10⁻³ and therefore S = 0.0036% or 36 ppm.

there is data supporting the 4.5-waters-of-hydration assumption), and therefore the latter is likely to be more appropriate.

4.2 External Combustion Sources

4.2.1 Available Data

As mentioned previously, there have been fewer recent studies of particulate from gas-fired external combustion sources. Although AP-42 has separate sections for natural gas-fired external combustion and LPG-fired external combustion, AP-42 calculated PM emission factors for the latter by assuming that they were the same (on a kg/GJ basis) as those for natural gas-fired external combustion, which are identified as being 8.0×10^{-4} kg/GJ for filterable PM (based on 21 tests conducted on 7 boilers between 1992 and 1995) and 2.4×10^{-3} kg/GJ for CPM (based on 4 tests conducted on 4 boilers between 1992 and 1994). Assuming an excess oxygen concentration of 3% and a sample volume of 0.7 dscm, the filterable PM emission factor corresponds to a catch of approximately 2 mg for a 1-hour run (or 4 mg for a 2-hour run), which again puts it in the vicinity of the Method 5i PQL (and likely closer to the MDL of the actual method used). As discussed in Sections 4.1.3 and 4.1.4, the CPM factors (determined using impinger-based methodologies) are dominated by sulfate, and multiple studies have shown that the vast majority of the sulfate is an artifact.

England (2004) developed separate emission factors for (a) gas-fired boilers and steam generators (based on 10 tests at 3 sites) and (b) gas-fired process heaters (based on 11 tests at 3 sites); the factors are 1.5×10^{-4} kg/GJ and 3.8×10^{-5} kg/GJ, respectively. As was the case with the turbines in Section 4.1, both of these factors are more than an order of magnitude lower than the factors identified using impinger-based methods.

At two of the three sites tested, conversion rates of SO₂ to sulfate were 1-2%, similar to what was found for the turbines (Wien et al., 2004b, 2004d). For the third site (Wien et al., 2004a), the conversion rate was substantially lower, at 0.06% (it was identified that SO₂ may have been biased high by a factor of two; however, even if the conversion rate is doubled to 0.12%, it is an order of magnitude lower than the other sites). The reasons for this anomaly are not known.

4.2.2 Discussion and Recommended Emission Factors

For the same reasons discussed in Sections 4.2.2 through 4.2.5, the factors of England (2004) are again preferred from a technical perspective and are cited by US EPA for its own National Emissions Inventory (US EPA, 2012), although US EPA again derives (without detailed explanation) a somewhat different set of factors—i.e.,

$$\begin{aligned} &4.6 \times 10^{-5} \text{ kg/GJ Filterable PM}_{2.5} \\ &\underline{1.3 \times 10^{-4} \text{ kg/GJ CPM}} \\ &1.8 \times 10^{-4} \text{ kg/GJ Total PM}_{2.5} \end{aligned}$$

(the spreadsheet indicates that the filterable/CPM split was based on the original split between these two factors in AP-42) and applies these factors to boilers, steam generators, and process heaters fired

with natural gas, LPG, process gas, and refinery gas. US EPA also adds on an additional factor of 0.4×10^{-4} kg/GJ for estimating PM₁₀.

For higher-sulfur fuels, adjustments based on the formulas identified in Section 4.1.5 are recommended. (The 2% conversion rate has relatively broad support, and given that the external combustion site with the outlying conversion rate had issues with SO₂ quantitation, there may have been other factors at that site that affected the sulfate quantitation.)

5.0 RECIPROCATING ENGINES

Reciprocating engines—even those that are fired with just natural gas—have been shown to have significantly different PM emissions from gas-fired turbines and external combustion sources, which may in part be due to the fact that research has shown that emissions originating from the lubricating oil can make a significant contribution (Schauer et al., 1999; Sakurai et al., 2003). Therefore, some of the issues associated with emissions being near detection limits (identified in Section 4) are less significant for these sources. However, other issues are relevant to reciprocating engines, such as engines being required to meet increasingly more stringent PM limits over time and more varied applications and duty cycles (which can also significantly affect PM emissions).

This section is divided into three subsections. Section 5.1 addresses large stationary diesel-fueled compression-ignition (CI) engines (larger than approximately 450 kW output); Section 5.2 addresses CI engines that are dual-fueled (i.e., the vast majority of the heat input is from natural gas, with a small amount of distillate oil). Natural gas-fired SI engines, including the various types (4SRB, 4SLB, and 2SLB) are addressed in Section 5.3.

5.1 Large Stationary Diesel Engines

Of the sources covered by this report, diesel engines are unique with respect to the fact that (a) both the fuel and the emissions-relevant engine technology have changed significantly over time (and are continuing to change), and (b) many of the more recent emissions datasets are from testing laboratories, which were required to use methodologies substantially different from what is used for source testing.

5.1.1 Available Data

AP-42 states that “the primary domestic use of large stationary diesel engines (greater than [450 kW]) is in oil and gas exploration and production.” Although extensive literature is available regarding PM emissions from diesel engines, much of it involves either on-road diesel vehicles (which are smaller and subject to very different duty cycles and test procedures), marine vessels (which are extremely large engines using fuels that often contain in excess of 1% or 10,000 ppmw sulfur), or smaller engines more available to researchers. For the large diesel engine category, as of 1993, a test report for a single large-bore engine (Castaldini, 1984) was the sole source of the AP-42 emission factor for this source category and identified a filterable PM result of approximately 0.02 kg/GJ \approx 0.2 g/kWh PM_{10} (essentially all of which was $PM_{2.5}$) and a CPM result of 0.0033 kg/GJ = 0.033 g/kWh (Acurex and Pechan, 1993). These tests were conducted using US EPA Method 5, and as discussed in Sections 4.1.3 and 4.1.4 of this report, the CPM results were likely biased high. In 1996, AP-42 was updated and a “total PM” factor of 0.043 kg/GJ (or 0.45 g/kWh) was identified—the AP-42 documentation does not specify whether CPM was included in these measurements—but this was based on 19 test reports from 1987-1988, where most of the sources were standby generators located at commercial or institutional facilities located in Connecticut and none were in oil and gas exploration and production service (ERG, 2006; US EPA, 1996).

With regard to the issue of the engine application, it is known that emission factors are affected by the engine load. For example, emission factors at various constant loads are shown in Figure 5-1. Separately, Fritz and Starr (1998) showed that emissions during transient load operation in some types of mobile diesel engines (e.g., loaders, bulldozers, excavators, arc welders) could produce approximately twice the PM emissions that are produced during steadier-state operations (ISO C1 8-mode test procedure); US EPA (2010) generated “Transient Adjustment Factor” (TAF) multipliers to apply to emission factors generated for these sources, but did not apply these factors to nonroad engines used in oil and gas exploration and production activities. Data are not available to characterize the duty cycles (and prevalence of different duty cycles) for all large stationary diesel engines; however, it is not unreasonable to expect that most large stationary diesels will operate at relatively high and steady loads compared to mobile engines. (Also, multipliers on the order of a factor of two are not unacceptably large relative to the variability in emissions data that are used to create emission factors.)

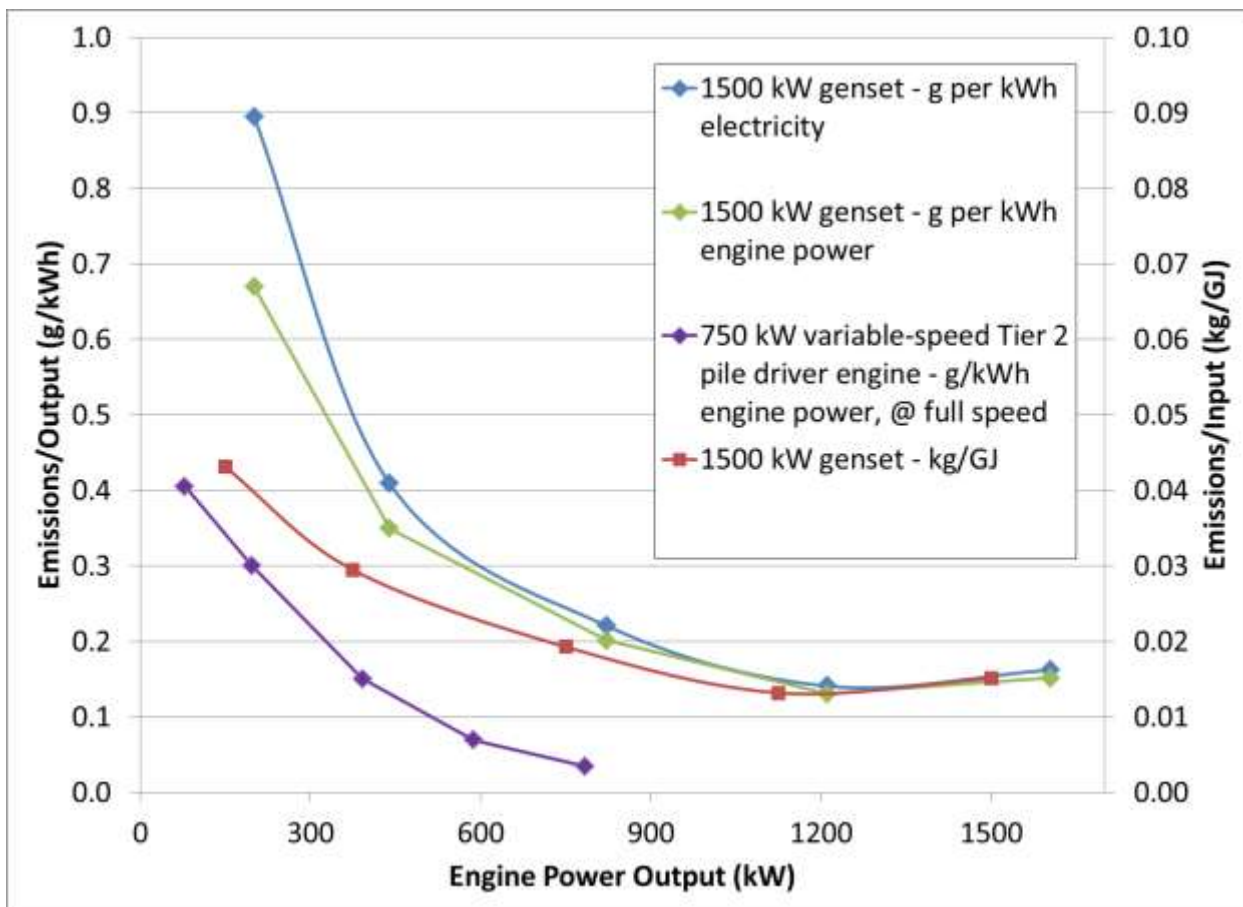


Figure 5-1. Variation in PM Emission Factor as a Function of Load for Two Diesel Engines (Manufacturer Data).

Relatively extensive emissions data are likely to be available for newer engines. Since the 1996 model year (MY), manufacturers of “nonroad” diesel engines sold in the United States—i.e., engines that are in or on equipment that is self-propelled or serve a dual purpose by both propelling and performing other functions (such as off-highway mobile cranes, bulldozers, etc.) or which are mobile and do not remain in one place for 12 consecutive months (e.g., portable pumps, generators, drills, hoists, etc.)—have been required to conduct emissions testing on their engines and certify that they meet increasingly stringent emissions standards (see Table 5-1). (The Tier 4 standards are based on different test cycles than the Tier 2 standards, and include a 20-minute transient test cycle for variable-speed engines.⁵) These nonroad standards became applicable to stationary diesel engines beginning in MY 2007.⁶ That being said, estimating actual emissions from specific engines based on the standards presents challenges, in part because (a) the “safety margin”—i.e., the extent to which the engines perform better than the applicable standard—is not known, and (b) the duty cycles used to certify engines to the standards in Table 5-1 may differ from the engines’ actual load cycles. For example, in Figure 5-1, the emission factor for the 750 kW Tier 2 engines is much lower than the 0.2 g/kWh value identified in Table 5-1 at high loads, but exceeds 0.2 g/kWh at low loads. Some engine certification data are available from US EPA’s website,⁷ and detailed load- and/or speed-specific data such as those shown in Figure 5-1 are also sometimes available from engine manufacturers.

Table 5-1. US EPA PM emission standards (grams per kWh of power output) for manufacturers of large nonroad diesel engines, and model years (MY) that the standards began applying.

	Engine rating	
	130-560 kW	> 560 kW
Tier 2 standard	0.20 g/kWh eff. MY 2002+	0.20 g/kWh eff. MY 2006+
Interim Tier 4 standard*	0.20 g/kWh eff. MY 2011+	0.10 g/kWh eff. MY 2011+
Tier 4 standard*	0.02 g/kWh eff. MY 2015+	0.03-0.04 g/kWh** eff. MY 2015+

*Test procedures for Tier 4 are different than for Tier 2.

**Lower limit applies to gensets, upper limit applies to other engines

Source: US Code of Regulations, Title 40, Parts 89 and 1039. (Note: manufacturers can meet requirements based on the average emissions of multiple engine families (family emissions limits or FELs; maximum emissions for any individual FEL are required to be no more than 0.54 g/kWh under Tier 2 and 0.04-0.20 g/kWh under the Interim Tier 4 and Tier 4 standards)

⁵ Specifically, transients are included for the Interim Tier 4 standard for engines < 560 kW and for the Tier 4 standard for both engine sizes shown in Table 4.

⁶ US Code of Federal Regulations, Title 40, Part 60, Subpart III.

⁷ <http://www.epa.gov/otaq/certdata.htm#largeng>

The test methods that engine manufacturers have been required to use incorporate dilution sampling (and therefore include PM and some degree of CPM), but details of the method are substantially different from those used by GE EER, and the equipment setup is also different (see Figure 5-2). Equipment upstream of the filter is not rinsed and recovered, even for relatively high-emitting sources. A full evaluation of the extent to which the results of manufacturer methods (which have also been modified over time) differ from GE EER’s methods has not been conducted.

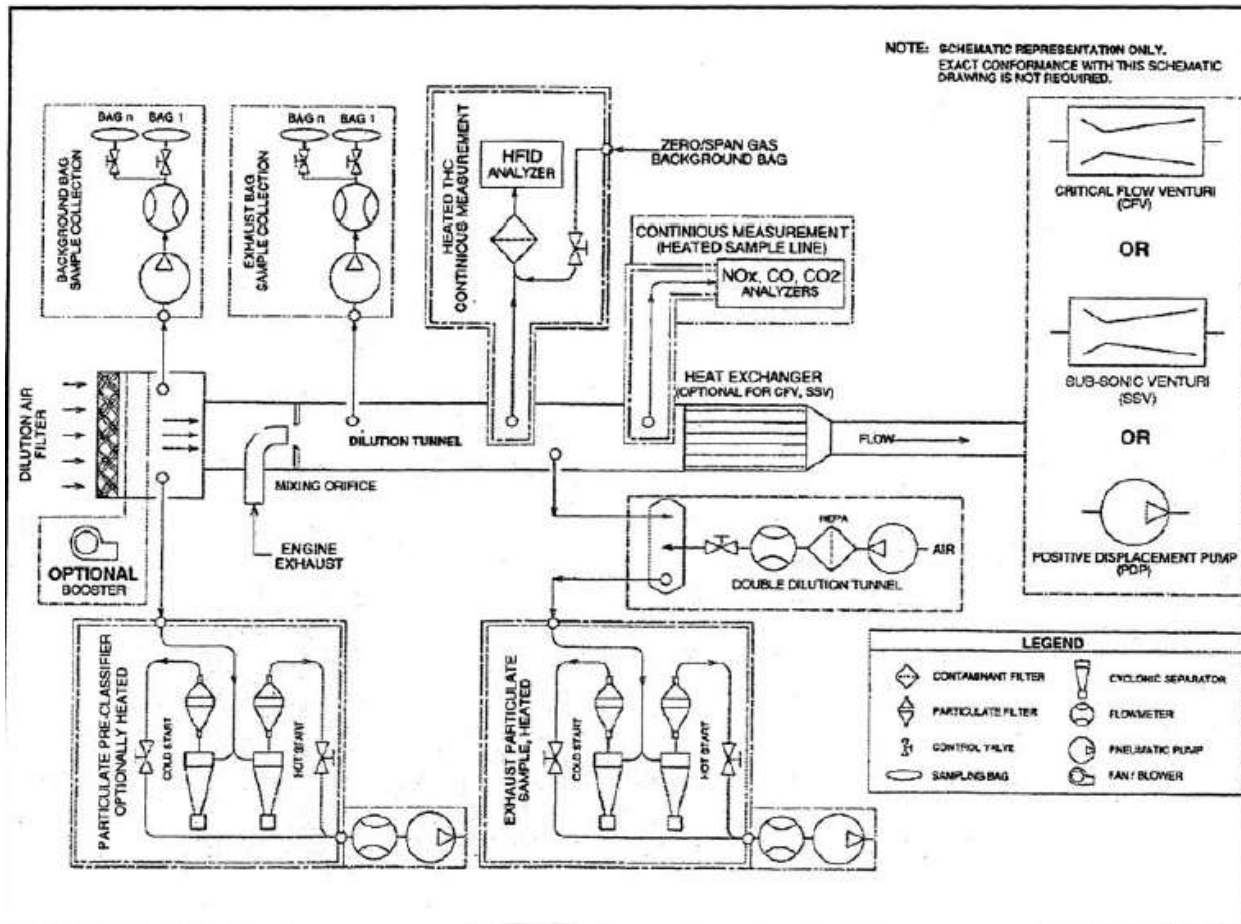


Figure 5-2. Schematic of Engine Manufacturer Test Apparatus for Engines (Source: 40 CFR 1065).

Another factor which needs to be considered when evaluating manufacturer emissions data is the changing sulfur content of the fuel. For example, Fritz and Starr (1988) measured PM emissions from a set of diesel engines running 0.03% sulfur fuel and 0.28% sulfur fuel, and on average, for each additional gram of sulfur combusted, PM emissions rose by approximately 0.16 grams, and as mentioned in Section 4.1.3 of this report, US EPA (2010) estimated that this corresponded to 2.2% of the fuel sulfur being converted into sulfate PM. Environment Canada (2012) estimates that although the average sulfur content of diesel fuels was approximately 0.12% (1200 ppm) in 1995-1997, concentrations dropped below 800 ppm in 1998, steadily decreased to 0.04-0.05% (400-500 ppm) by 2005, and dropped significantly after that, with non-road engines being required to use diesel with sulfur

content of no more than 0.0015% (15 ppm) effective in 2010. These statistics are dominated by transportation fuels; the average sulfur content used in stationary diesel engines in Canada—especially those used in upstream oil and gas operations—was not readily available. However, the formulas identified in Section 4.1.5 can be used to calculate corrections based on available fuel sulfur content information. US EPA (2010) estimates a substantially higher sulfate conversion ratio (30%) for engines with catalyzed diesel particulate filter technology; however, that same technology also substantially limits the allowable fuel sulfur level, so that no corrections should be needed.

Hesterberg et al. (2011) have pointed out that for on-road diesel engines, the character of the PM emissions has changed significantly from the older, higher-emitting engines to that of the newer, very low-emitting engines, and that the latter are comprised of a much higher percentage of OC and sulfate than the former. This may also be the case for the stationary engines, which means that the extended dilution effects mentioned in Section 4.1.4 will have even more of a relative impact on the emissions from the newer engines than was the case for the older engines. However, the full extent of this has not been studied.

5.1.2 Discussion and Recommended Emission Factors

As identified above, there are a very large number of factors affecting the emission factors for individual large stationary diesel engines, which makes it very difficult to determine an “average” emission factor for the population of engines as a whole. The fact that the in-use engine fleet is becoming newer and newer over time (and therefore on average has lower- and lower-emitting technology) means that the average emission factor is also changing over time. US EPA (2010) and CARB (2010) have spent substantial resources developing emission inventory models for nonroad engines which attempt to take the effect of the calendar year and engine “turnover” into account (as well as other factors such as fuel sulfur content, transient operation, distribution of engine sizes, etc.), but questions about the model for turnover have been raised, and in the past it has been shown that these models have greatly overpredicted total emissions (indicating that the models are not very accurate). No similar models have been developed for stationary engines, and even if they were, it is not clear that regionally representative data for inputs (such as fuel sulfur content) would be readily available.

That having been said, it is still possible to identify emission factors (or resources for determining emission factors) for owners/operators of individual engines who need to report actual emissions for those specific engines. For newer engines, the best data are going to be the data from the manufacturers—ideally, load-specific data (and speed-specific data, for variable-speed engines) like those shown in Figure 5-1. If manufacturers are also able to provide information about the corresponding sulfur content of the fuel, and the fuel actually being used in the engine is substantially different, then the emission factor can be corrected based on the information provided in Table 5-2. For older engines, AP-42 data are probably the most appropriate

5.2 Dual-Fueled CI Engines

Insufficient data are available for dual-fueled CI engines. AP-42 does not list an emission factor. McTaggart-Cowan et al. (2007) used a dilution system to measure PM emissions from a dual-fuel

engine operating under various operating conditions and found emissions as low as 0.01 g/kWh and as high as 0.2 g/kWh; however, this was a relatively unusual setup, involving a 6-cylinder engine rated at 300 kW that had been modified to operate on only one cylinder, and as a result the “kWh” of power were not calculated from brake parameters but were “gross indicated” values calculated by integrating curves of in-cylinder pressure versus volume. Korakianitis et al. (2011) reviewed available research on emissions from dual-fueled engines and concluded that emissions are “very low and in some cases undetectable”. While some researchers have detected emissions on the order of 1-5 g/kWh, these have typically been on relatively high-emitting single-cylinder research engines and appear to have been conducted for purposes of comparing results for different oil/gas mixtures (typically involving much more oil than the pilot amount needed in commercially available dual-fuel engines) rather than obtaining an emission factor representative of current in-use dual-fuel engines (Carlucci et al., 2008; Mustafi et al., 2013; Papagiannakis et al., 2010a, 2010b).

5.3 Natural Gas-Fueled SI Engines

5.3.1 Available Data

Manufacturers of natural gas-fueled SI engines have been subject to increasingly stringent regulations, but not for PM, and it is not believed that the replacement of older engines with newer engines is likely to affect this source category as much as the diesel engine category. AP-42 lists separate filterable PM emissions for three different subcategories of gas-fueled SI engines; i.e.,

- 3.3×10^{-5} kg/GJ for 4-stroke lean-burn (4SLB) engines, based on two 1994 tests (a Cooper Bessemer LSV-16 engine rated at 4200 hp, running at 101% load; and a Cooper Bessemer LSV-16 engine rated at 4200 hp, running at 99% load);
- 4.1×10^{-3} kg/GJ for 4-stroke rich-burn (4SRB) engines (with no documentation of the number of tests conducted); and
- 1.7×10^{-2} kg/GJ for 2-stroke lean-burn (2SLB) engines, based on three 1994 tests (of a Cooper Bessemer GMVA-10 engine rated at 1350 hp, running at 73% load; a Clark BA-6 engine rated at 1140 hp, running at 87% load; and a Cooper Bessemer GMV10-TF engine rated at 1100 hp, running at 105% load).

AP-42 also lists a CPM emission factor of 4.3×10^{-3} kg/GJ for all three subcategories, but this (a) was derived from the two tests on the 4SLB engine and assumed to apply to the other two engine types, and (b) was evaluated using impinger-based methods and therefore likely biased very high as described in Sections 4.1.3 and 4.1.4.

GE EER evaluated these same engine types with both the dilution sampler described in Section 4.1.4 and (for the 4-stroke engines) impinger-based methods (England et al., 2005). For all three engines and both methods, PM was dominated by organic compounds. For the impinger-based method, GE EER's value for total PM and CPM for the 4SLB engine agreed very well with AP-42 factors, differing by less than 15%; results for the 4SRB engine were less consistent (with GE EER's results being approximately 20% of AP-42), but this difference may be partially explained by the fact that the engine

tested by GE EER was equipped with a 3-way catalyst. For both of the 4-stroke engines, results with the dilution sampler (2.2×10^{-3} kg/GJ for the 4SLB and 7.7×10^{-4} kg/GJ for the 4SRB with catalyst) were approximately half of the results with the impinger-based methods, and for the 2-stroke engine, results with the dilution sampler (8.6×10^{-3} kg/GJ) were approximately half of the AP-42 value. The 4SLB result for the dilution sampler was also comparable to a published factor of 0.0148 g/kWh ($\approx 1.5 \times 10^{-3}$ kg/GJ) for a 4SLB determined using a different type of dilution sampler (Quillen et al., 2008)

5.3.2 Discussion and Recommended Emission Factors

For this source type, differences in the available data could potentially be explained by two simple factors: (a) the 4SRB results being reduced approximately 80% by the 3-way catalyst, and (b) the dilution tunnel results being approximately half of the results determined using impinger-based methods. Based on simply the previously-identified biases associated with the impinger-based results, our recommendation would as follows:

- If factors for filterable PM only are needed, use the AP-42 factors for filterable PM;
- If factors for total PM are needed, use the GE EER results (and for uncatalyzed 4SRB, multiply the GE EER results for the catalyzed 4SRB by five).

6.0 DATA GAPS AND RECOMMENDED TEST PLAN

6.1 Data Gaps

For the source types evaluated, the most obvious data gaps are for LPG-fired external combustion and dual-fueled reciprocating engines. While the AP-42 assumption that PM emissions from LPG-fired external combustion may not be entirely unreasonable, it would be preferable to have data which support the assumption. For dual-fueled reciprocating engines, obtaining either field data or manufacturer data would be preferable to obtaining data from a research setting. For dilution tunnel sampling, data for older large diesel engines were also not available; however, to the extent that PM emissions from the older engines are more likely to be dominated by soot (elemental carbon) than modern engines, the difference between PM emissions determined using dilution sampling and impinger-based methods may not be that significant.

For internal combustion units (turbines and reciprocating engines), there are gaps associated with potential operating conditions. Specifically, with the exception of some of the diesel engine manufacturer data, essentially all of the available data have been at relatively normal, steady-state operating conditions. Some units, such as some load-following gas-fired engines and turbines used for natural gas pipeline compression, may be more likely to experience load swings on a routine basis, and while emissions from transient operation are expected to be higher, they have not been quantified for these sources. Separately, data gaps associated with operating modes that change for operation at low-temperatures—e.g., less than 0 °C or less than -20 °C (Witherspoon, 2008) may be relevant for some Canadian operations.

There are also gaps at a much broader level. Specifically, given that the mass of PM emissions is dynamic (initially increasing as gaseous organics form particulate downstream of the stack, then decreasing as they partition back to the gaseous phase), there is a need to understand the point in this process at which PM emissions should be inventoried. From a technical perspective, it probably does not make sense for the inventory to incorporate the effects of dilution and partitioning all the way to ambient air, since as Robinson et al. (2010) point out, this quantitation is dependent on factors such as the concentrations of semivolatile organics in the ambient air. Therefore, it would be more appropriate to incorporate most of that dilution and partitioning into a dispersion model, with inventory results as an input to that model. But there is still a need to identify a “reference point” at which the inventory should be based. If the reference point were to be zero dilution, then focus should be on inventorying FPM only (e.g., FPM measured by EPA reference methods, for sources that emit sufficiently high amounts to be quantifiable), and not CPM. However, for the case of the gas-fired reciprocating engines, FPM is orders of magnitude below CPM, and it is not clear that dispersion models are likely to be sophisticated enough to accurately capture both the initial (significant) condensation processes that cause PM mass to rise and the dilution and partitioning processes which cause it to fall. Alternatively, the reference point could be instead based on a fixed amount of dilution—and more specifically, a fixed type of dilution method, such as GE EER’s or the new ISO method. Either way, it needs to be recognized that since data are being collected using a variety of methods, there is a need to understand how they relate to data collected at the reference point. Given the different character of PM emitted from different sources, that relationship is likely to be dependent on more than just the quantity of PM determined; it

will likely depend on chemical speciation, and stack temperature as well, and may also depend on the number of ultrafine particles and their size distribution.

6.2 Test Plan

GE EER's evaluation of their dilution sampling method was so extensive that we do not believe that additional evaluation of that method is required. The test plan to obtain emissions data for the sources of operating conditions identified in Section 6.1 more sources or more operating conditions could be as simple as selecting sources and using GE EER's sampler and procedures. Alternatively, sampling could be conducted using US EPA's conditional dilution sampling method, DRI's dilution sampler, or the new ISO dilution sampling method.

But the fact that there are so many different PM dilution sampling methods leads to the broader question of how to bring the results obtained using different methods to a common basis, and how to identify what information needs to be inventoried in order to do so. There have been and continue to be several dilution sampling evaluations (usually on higher-emitting sources than the ones in this scope of work that were addressed by GE EER) and theoretical developments. Although a full review of these evaluations and developments was outside the scope of this project, it would make sense to do such a review before proceeding with the development of a test plan.

In addition, for impacts analyses, there is a need to develop a dispersion model that takes dilution and gas-particle partitioning into account. However, development of such a model is not a "test plan", nor is it within the scope of this project.

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