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Fuel Correlation to SimDis Method – Analysis and Reporting

Final Report

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FINAL REPORT

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CRC Project E-137

Prepared by:
Andrey Khlystov and S. Kent Hoekman

Desert Research Institute
Reno, NV 89512

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List of Acronyms and Abbreviations

ASTM	American Society for Testing and Materials
CRC	Coordinating Research Council
DBE	double bond equivalent
DHA	detailed hydrocarbon analysis
FID	flame ionization detector
GC	gas chromatography
GC-FID	gas chromatography – flame ionization detector
GC-MS	gas chromatography – mass spectrometry
GDI	gasoline direct injection
LDGV	light-duty gasoline vehicles
MS	mass spectrometry
MSS	micro-soot sensor
PADD	Petroleum Administration for Defense Districts
PEI	particulate evaluation index
PFI	port fuel injection
PIONAX	paraffins, isoparaffins, olefins, naphthenes, aromatics, oxygenates
PM	particulate matter
PME	Index of PM emissions
PMI	PM Index
RI	retention index
SIDI	spark ignition direct injection
SimDis	simulated distillation (ASTM D7096)
SSI	Separation Systems, Inc.
SWRI	SouthWest Research Institute
VUV	vacuum ultraviolet

1. Summary

This project analyzed particulate matter (PM) emission data collected during the CRC project RW-107 from four vehicles running Phase 1 of the LA-92 test protocol using 13 fuels characterized by a range of particulate matter indices (PMI). The vehicles included three with port fuel injection (PFI) engines and one with a spark ignition direct injection (SIDI) engine. Particulate matter (PM) emissions were measured with a filter-based gravimetric method and a micro-soot sensor (MSS). The fuels were analyzed using the simulated distillation method (SimDis) per ASTM D7096 (Simulated Distillation of Gasoline by GC) and detailed hydrocarbon analysis (DHA). Data from three DHA methods were used in the project: the modified ASTM D6730 methods using gas chromatography with flame ionization detection (GC-FID) (ASTM D6730 Detailed Hydrocarbon Analysis of Gasoline by GC-FID); gas-chromatography with mass spectrometry detection (GC-MS) (ASTM D6730 DHA of Gasoline by GC-MS); and the ASTM D8369 method using gas-chromatography with vacuum ultraviolet detection (GC-VUV) (ASTM D8369 DHA of Gasoline by GC-VUV). The SouthWest Research Institute (SWRI) performed analysis by GC-FID, GC-VUV, and SimDis. Separation Systems, Inc. (SSI) performed analysis by GC-FID and GC-MS.

The DHA data were used to calculate the PMI and the index of PM emissions (PME), as well as to estimate the fuel distillation profiles. A Python program developed within the CRC project AVFL-29-2 was used to calculate the PMIs to remove any uncertainties in compound naming, include the contribution of the generic (i.e. not explicitly named) compounds, and to avoid the observed numerous discrepancies among the previously reported PMIs for the test fuels. This also allowed a direct comparison of PMIs among the DHA methods. The data were analyzed using various statistical techniques to gain insight into the relative performance of the analytical methods; how PM emissions correlate with fuel composition and various indexes, such as PMI and PME; and how hypothetical distillation cuts could influence PM emissions.

The total weight contribution of paraffins, isoparaffins, olefins, napthenes, aromatics, and oxygenates (PIONAX) correlated well among the three DHA methods. However, there were consistent differences between the methods and laboratories that are more apparent in the derived PMI data than in the weight contribution data. The GC-VUV data produced the lowest PMI values, while the GC-MS indicated the highest, likely due to the method's compound identification power and large chromatographic range. The GC-MS data were used in correlations with PM emissions without any loss of generality due to the strong linear relationships between the different DHA datasets.

The DHA-derived distillation profiles agreed well with each other except for the very light and heavy ends due to differences in the chromatographic ranges between the methods. The SimDis profiles agreed well with the DHA-derived profiles for the heavier half of the fuel but deviated significantly for the lighter half for ethanol containing fuels.

The SIDI vehicle (a 2013 Tier 2 model) produced significantly higher PM emissions than the PFI vehicles (2019 Tier 3 models) – 23.2 mg/mi vs. 1.37 mg/mi, on average. Replicate measurements (the same vehicle and fuel combination) showed significant variations in PM emissions, with standard deviations of measured PM emissions for some vehicle / fuel combinations reaching

160%. The PM gravimetric and MSS data correlate well with each other though agreement is less for PM emissions below 3 mg/mi.

The average Pearson correlation coefficient between the PMI and PM emissions (based on filter measurements) was 0.86 vs. 0.81for the correlation between PME and PM across all tested vehicles (for MSS-measured emissions, the correlations were 0.89 vs. 0.85, respectively). The correlations for the SIDI vehicle (the highest emitter) were the same for both PMI and PME. The PMI provided higher correlations for all three PFI vehicles. It thus appears that at least for this dataset the simpler to calculate PMI is preferable to the more complicated PME.

A linear relationship was observed between the PMI and temperatures at which a certain fraction of fuel is evaporated, such as 95%, 97%, and 99%, for both the SimDis and DHA distillation profiles (Figure 1). However, the relationships between PMI and SimDis measurements differed from those observed in datasets collected in other projects.

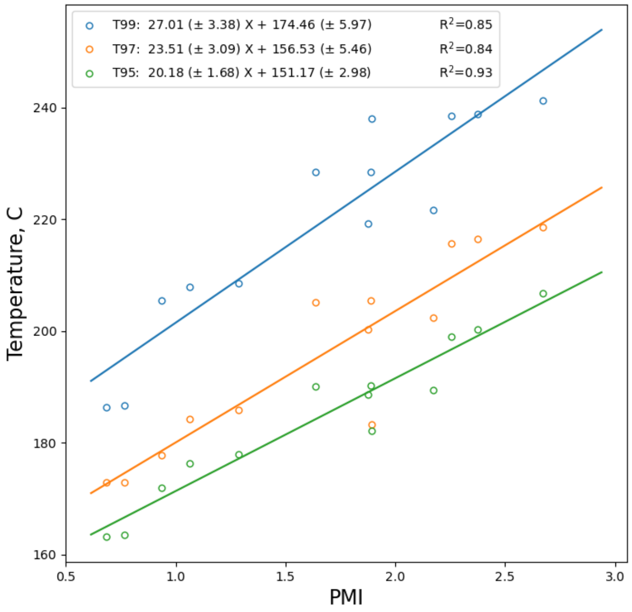

Figure 1. Temperatures of 95% (T95), 97% (T97), and 99% (T99) distillation cuts according to SimDis measurements vs. fuel PMI.

SimDis temperatures demonstrated weak correlations with measured LA-92 Phase 1 PM emissions, especially for the three PFI vehicles (Figure 2). Somewhat higher correlations were seen with the SIDI vehicle. Similar to the PMI regressions, fuels with distillation temperatures within a very narrow range produced variations in PM emissions that span about one half or more of the PM emission range of the total dataset. The linear regression gradients connecting cut temperatures to PM emissions showed variation not only between PFI and SIDI vehicles but also among different PFI vehicles themselves. Similarly, while certain individual compounds correlated strongly with PMI (reaching Pearson correlation coefficients of up to 0.8), neither specific compounds nor compound categories achieved correlation coefficients exceeding 0.3 when compared directly with measured PM emissions.

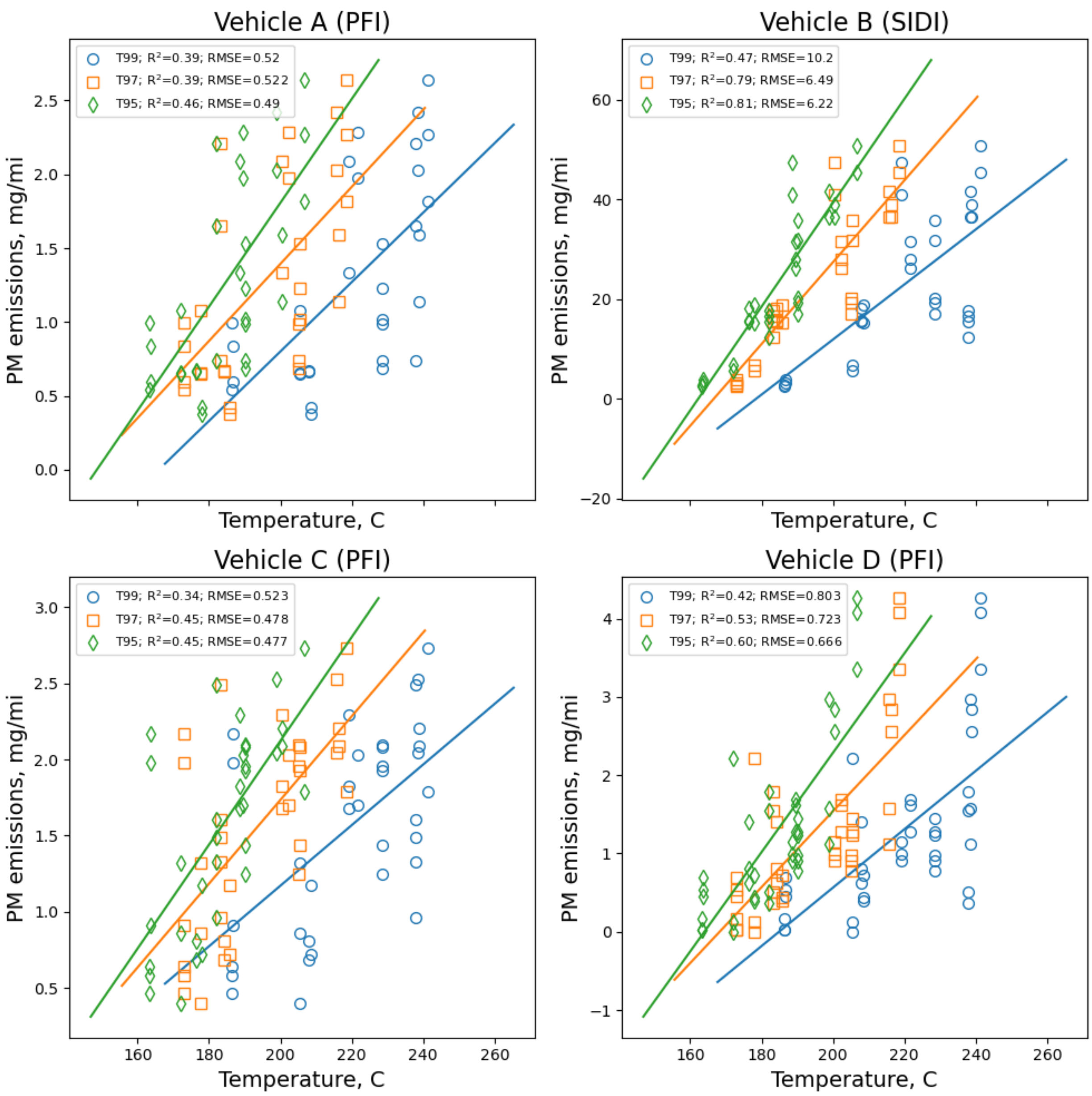

Figure 2. Measured LA-92 Phase 1 PM emissions vs. temperatures of 95% (T95), 97% (T97), and 99% (T99) distillation cuts according to SimDis measurements.

These results highlight the importance of experimental validation when examining connections between PM emissions and distillation cuts or other variables, particularly when these relationships are established using limited data samples. It is also essential to remember that distillation profiles generated using DHA and SimDis, as well as the hypothetical distillation cut temperature points (T95, T97, etc.) derived using these methods, are based on advanced chromatographic separation techniques that do not accurately represent real-world fuel distillation, where individual compounds do not distill one at a time.

2. Introduction and Background

2.1. Particulate Matter Emissions from Gasoline Vehicles

The continued drive to increase the performance and efficiency of light-duty gasoline vehicles (LDGV) and to reduce their emissions has led to development of modern fuel injection systems such as the gasoline direct injection (GDI) [also called spark ignition direct injection (SIDI)]. While GDI engines have higher efficiency and specific power output, they produce more particulate matter (PM) than traditional port fuel injection engines.[1] In GDI, liquid fuel is injected directly into the combustion chamber. This creates potential problems of incomplete droplet evaporation and wetting of the piston and combustion chamber walls with liquid fuel, which can lead to diffusion burning.

Different chemical constituents within gasoline have different propensities to form PM. In particular, aromatic species are more prone to form soot than are paraffinic species.[2] Aromatics are often thought of as the nucleus around which soot growth occurs. In addition, the boiling point (or vapor pressure) of a compound controls its evaporation processes. Heavier, less volatile fuel species are the last to vaporize, and hence are concentrated in the residual liquid droplets or films that undergo diffusion burning in the combustion chamber. The combination of low volatility and high aromatics (such as C_{10+} aromatic compounds) represents the worst situation with respect to PM formation.

2.2. Particulate Matter Index and Particulate Emissions

Several parameters have been developed that link gasoline's properties with its propensity to form PM,[3] including the Honda Particulate Matter Index (PMI)[4] and General Motors Particulate Evaluation Index (PEI).[5] The PMI is a very popular metric that generally provides good predictive accuracy, though with some exceptions.[6,7] The PMI is calculated using the following equation:[4]

$$PMI = \sum_{i=1}^{n} \frac{DBE_i + 1}{VP_i} W_i \tag{1}$$

In Equation 1, W_i is the weight percent of gasoline specie i, VP_i is its vapor pressure (in kPa) at a temperature of 443°K (170°C), and DBE_i refers to its "double bond equivalent". For hydrocarbons, DBE is equal to:

$$DBE = 1 + C - 0.5\,H \tag{2}$$

in which C and H refer to the number of carbon and hydrogen atoms in the specie, respectively. Straight chain paraffins have a DBE value of 0; cyclic paraffins and straight chain single olefinic compounds have DBE values of 1; aromatics have a DBE value of ≥4. Due to their large DBE, aromatics have a strong contribution to a fuel's PMI, especially the heavier compounds due to the inverse relationship of the PMI to the compound vapor pressure.

The Particulate Matter Emissions (PME) index was developed within the CRC Project RW-107-2[8] to further improve the predictive efficiency of the PMI for a broad range of gasolines including ethanol containing gasolines up to E20. It was designed to be directly proportional to PM emissions measured during Phase I of the LA-92 driving cycle. The PME was further revised within the CRC Project RW-107-3a that provided the following updated formula for its calculation:[9]

$$PME = \left(\frac{43.4}{LHV}\right)\left(N_{TECH}\sum_i \frac{W_i\, YSI_i}{VP_i^{\alpha=f(EtOH)}}\right)^{(1+\beta(99.9-FuelCoverage_{DHA}))} \qquad (3)$$

where LHV is the fuel lower heating value in MJ/kg of fuel, N_{TECH} is a constant (0.001025 for SIDI vehicles and 0.000558 for port fuel injection [PFI] vehicles), YSI_i, is compound i's yield sooting index, α is a function of ethanol content dependent on the engine type (SIDI or PFI), β is a constant (0.122), and $FuelCoverage_{DHA}$ is the percent of the total fuel weight identified by DHA.

2.3. Methods for PMI Determination

PMI and PME calculations require highly detailed information on the chemical composition of gasoline, since DBE, YSI, and VP values are needed for each of the hundreds of species present in the fuel. The original Honda study, as well as most of the follow-up studies on the PMI, performed the detailed hydrocarbon analysis (DHA) that uses high resolution gas chromatographic (GC) methods. Two existing ASTM methods used for this purpose are D6729 and D6730.[10,11] In all these cases, capillary GC columns are used to separate volatile fuel constituents, which are then detected and quantified using a flame ionization detector (FID). Of these three, ASTM D6729 and ASTM D6730 are the most widely used. They both utilize a 100-m capillary column of 0.25 mm inside diameter but differ in the use of a short pre-column (used in ASTM D6730) to improve the resolution of a few important pairs of species which otherwise co-elute and cannot be independently measured.

While the degree of species resolution and detection provided by ASTM D6729 and D6730 are sufficient for most purposes, they may not be adequate in certain situations, such as when determining PMI values of gasoline. A particular concern with use of these ASTM methods is their inability to identify and quantify low concentrations of the heaviest (least volatile) constituents in gasoline. These heavy constituents are rich in aromatics, and therefore have relatively high PMI values. Thus, the inability to measure these species, even though they may represent only a small fraction of the total fuel mass, could result in significant underestimation of a gasoline's PMI value.

To improve the resolution of heavy-end compounds, Separation Systems, Inc. (SSI), within a CRC-funded project AVFL-29, modified the standard ASTM D6730 method by including an additional temperature ramp for the GC column. Thus, instead of a final column temperature of 200 °C as specified in D6730, SSI's enhanced method includes an additional, rapid temperature ramp to 300 °C. This has the effect of eluting the highest boiling gasoline compounds as relatively sharp chromatographic peaks that can be integrated and quantified. Additionally, SSI significantly improved the identification of chromatographic peaks, both by use of mass spectrometry (MS) and additional authentic standard compounds. In this way, SSI developed an expanded (and more reliable) list of 822 gasoline constituents.[12]

Another GC-based method for DHA analysis is described in ASTM D8369. This method uses high resolution gas chromatography with Vacuum Ultraviolet Absorption Spectroscopy (GC-VUV) for the determination of individual compounds and compound classes by percent mass or percent volume with a final boiling point as defined by ASTM D86 up to 225 °C. The separation is accomplished using a 60 m, nonpolar phase capillary column and a moderately fast temperature ramp. The advantage of using VUV instead of the FID lies in its better specificity, as compound identification using the retention time can be supplemented with the compound VUV spectrum, such that some coelutions can be resolved by the detector using vacuum ultraviolet absorbance spectra and deconvolution. The specificity of VUV, however, is significantly lower than that of the MS techniques and thus could lead to less accurate determination of the PMI.

The main disadvantage of the DHA techniques lies in their complexity and long analysis times (a single chromatographic run on a 100 m column takes 3-4 hours to complete). To resolve this problem, simpler and faster (< 15 min) methods using simulated distillation techniques (such as based on ASTM D86 and D7096) were investigated as surrogates which could be highly correlated with PMI and potentially used for simpler prediction of PMI or tailpipe PM emissions. For example, a chromatography technique known as SimDis (ASTM D7096)[13] uses a non-polar, large-bore, thick film capillary column. The column temperature is raised at a linear rate such that hydrocarbons elute in their boiling point order and are measured by an FID. A linear relationship between the chromatographic retention time and hydrocarbon boiling point is determined using a known mixture of hydrocarbons and volume fractions are determined from chromatographic area slices using theoretical hydrocarbon volume response factors (oxygenated fuels require oxygenate response factors). In this way a boiling point distribution is obtained. To calculate a PMI from a boiling point distribution, it was proposed to use boiling point ranges that can be associated with certain classes of hydrocarbons, such as the aromatic class.[14]

As can be seen from the above description, different PMI determination methods in use today all have their advantages and disadvantages. The PMI formulation requires a highly detailed knowledge of the chemical composition of gasoline, as well as knowledge of vapor pressure of individual compounds. However, even with highly sophisticated chromatographic techniques it is not always possible to identify all compounds, nor is the vapor pressure data available for all compounds. This is especially true for the heavy end of a chromatographic run. All these factors could lead to discrepancies in PMI values obtained with the DHA methods. However, differences in the experimental approach are not the only source of uncertainty in reported PMI numbers. In our recent CRC-sponsored study,[15] it was found that DHA analysis results from different laboratories produced PMIs that differed significantly for the same fuel. Such differences need to be taken into account when comparing the relative performance of DHA and SimDis methods, as well as when investigating temporal or regional trends in reported PMI values.

3. Methods

3.1. Data harmonization

Prior to statistical analysis, the DHA data were checked to assure harmonization between the different analytical datasets. Inconsistencies were observed in the PMI values reported in CRC RW-107-3a,[9] which tested the same fuel set used in this project. The report contains multiple tables listing PMI values for each fuel; however, these values differ across tables despite ostensibly representing the same fuel measured by the same method. Furthermore, the reported PMIs do not match those in the original laboratory analysis reports for individual fuel samples (see Table A1 in the Appendix). Therefore, the Python program developed within the CRC-sponsored project AVFL-29-2[15] was used to estimate the PMI of the fuels. The program also includes the contribution of generic and unidentified compounds using their retention index. While GC retention time is determined for each chromatographic peak, the retention index (RI) is commonly used for peak identification purposes. As GC columns age and other chromatographic parameters vary, retention times of eluting peaks tend to "wander," making peak identification more difficult. In contrast, RI values remain more constant, which increases the reliability of peak identification. The program uses the Kovats RI values – either as reported directly from the laboratories or, when RI are not reported, as calculated by the program using the reported retention times. The formula for calculating Kovats RI values is shown below:

$$RI_i = 100\left(n + \frac{log(t_i) - \log(t_n)}{log(t_{n+1}) - \log(t_n)}\right) \tag{4}$$

where RI_i is the retention index of component i, n is the carbon number of n-paraffin, t_i is retention time of component i, t_n is the retention time of preceding n-paraffin, t_{n+1} is the retention time of the next n-paraffin.

Following the approach we adopted in Project AVFL-29-2, we used the RI of a compound to estimate its PMI factor, as well as its boiling point using regression formulas such as $log_{10}(PMI) = a + b * RI$. The regression is performed for each known compound within a PIONA class and then is used to estimate the parameters for generic compounds of that class. For unknown compounds, a regression is derived for all known compounds of all classes. Estimating the PMI contribution of generic and unidentified compounds helps to evaluate their contribution to the overall PMI and gain insight into any differences between different methods of PMI determination. The inclusion of generic and unidentified compound contribution resulted in a slightly higher (~3%) PMIs than those reported by the laboratories for the corresponding methods (Table A1).

3.2. Data Exploration and Statistical Analysis

All data processing, analysis, and plotting was done using Python (v.3.11.5) and its various numerical, statistical, and graphing libraries, such as the NumPy (v.1.24.3), Python for Data Analysis (Pandas, v.2.0.3), StatsModels (v.0.14.0), SciKitLearn (1.5.1), and MatPlotLib (v.3.7.2) libraries.

4. Results

4.1. The dataset

The dataset includes 13 fuels that were tested on four vehicles using the LA-92 Phase 1 protocol. The vehicle characteristics can be found in Table 2 of the final report for CRC project RW-107-3.[9] Three vehicles were PFI and one vehicle (B) was SIDI. PM emissions were measured using the gravimetric method and a number of tests were done with a Micro Soot Sensor (MSS) that provided measurements of elemental carbon. The number of experimental data points for which PM and MSS samples are available are given in Table 1 and Table 2, respectively. Most of the fuel-vehicle combinations were tested 2-3 times. More tests (4-5) were done with fuel A on vehicles B, C, and D. No MSS data were available for fuel C, nor is it available for fuels A and B on vehicles A and B and fuel B on vehicle D.

Table 1. Number of experiments per vehicle and fuel, in which PM measurements are available

	A	B	C	D	E	F	G	H	I	J	K	L	M
Vehicle A	3	2	2	2	3	2	2	2	3	3	3	2	2
Vehicle B	4	2	3	2	2	3	2	2	3	2	2	2	2
Vehicle C	5	2	2	3	3	2	3	3	3	2	3	2	2
Vehicle D	4	3	3	3	3	3	3	3	3	3	3	2	3

Table 2. Number of experiments per vehicle and fuel, in which MSS measurements are available

	A	B	D	E	F	G	H	I	J	K	L	M
Vehicle A	0	0	2	3	2	2	2	3	3	2	2	2
Vehicle B	0	0	2	2	3	2	2	3	2	2	2	2
Vehicle C	5	2	3	3	2	3	3	3	2	3	2	2
Vehicle D	2	0	3	3	3	3	3	3	3	3	2	3

4.2. Fuel composition and PMI

The fuels that were used in vehicle emission testing were analyzed using two DHA methods (ASTM D6730 and D8369) and SimDis (ASTM D7096). DHA data were provided by SSI (using both FID and MS detectors), and by SWRI using FID and using VUV. The SimDis data were provided by SWRI. The fuel compositions per PIONAXU groups (n-paraffins, iso-paraffins, olefins, naphthenes, aromatics, oxygenates, and unknowns) reported by the four DHA methods are shown in Figure 3. No data for Fuels A and E were provided from SWRI. Likewise, there were no VUV data for Fuel F. In general, all methods agree reasonably well with each other, though there are differences (see Figure 4). The differences between the methods become more apparent in the reported total PMI (Figure 5), with SSI-MS and SSI-FID reporting the highest values and VUV the lowest. PMIs determined with all methods, however, correlate well with each other (Figure 6). Thus, in our analysis we will use PMIs (and PMEs) derived from the SSI GC-MS data, as all other methods would differ only by a linear relationship to that dataset.

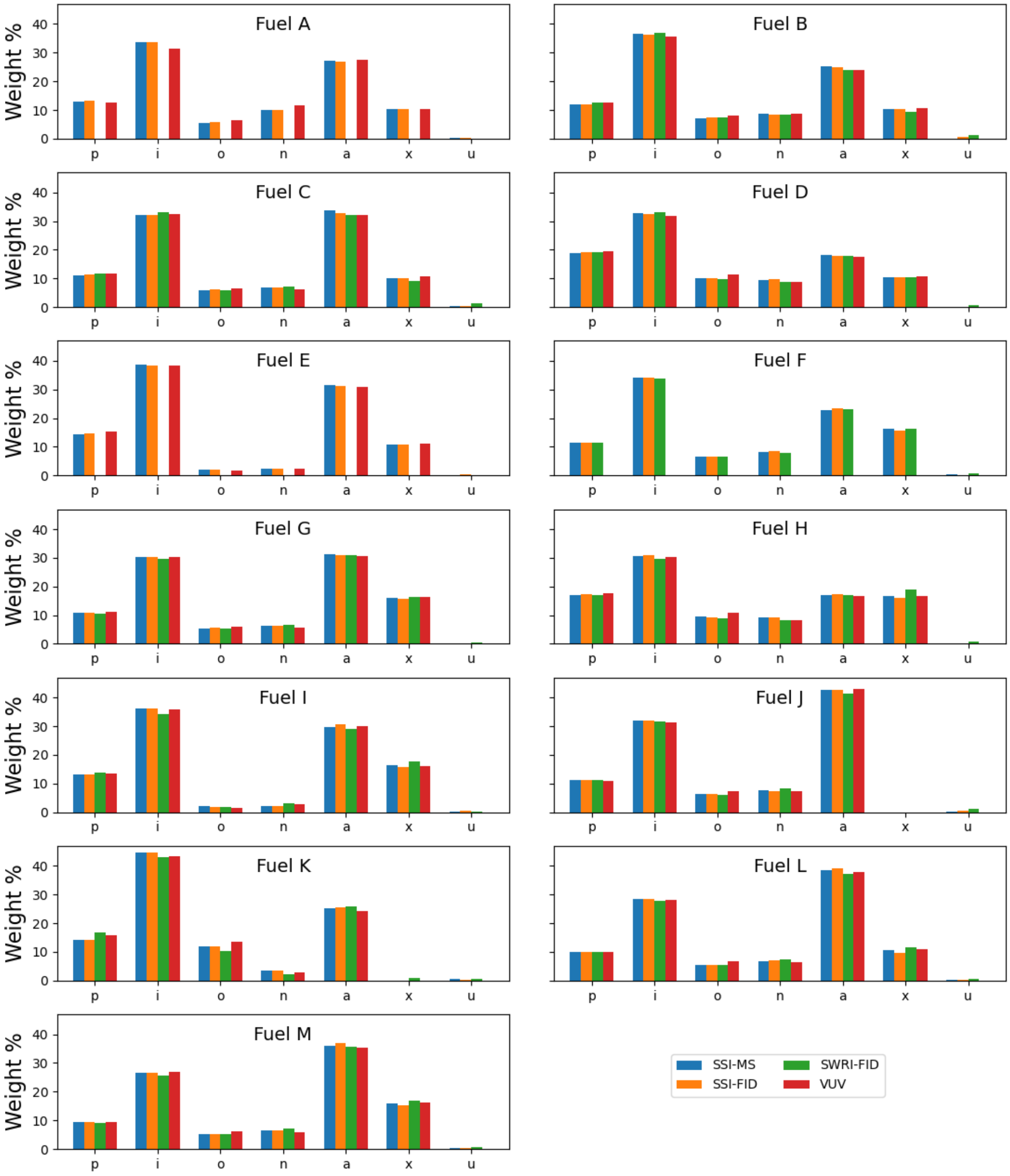

Figure 3. Composition of fuels per PIONAXU groups according to DHA analysis.

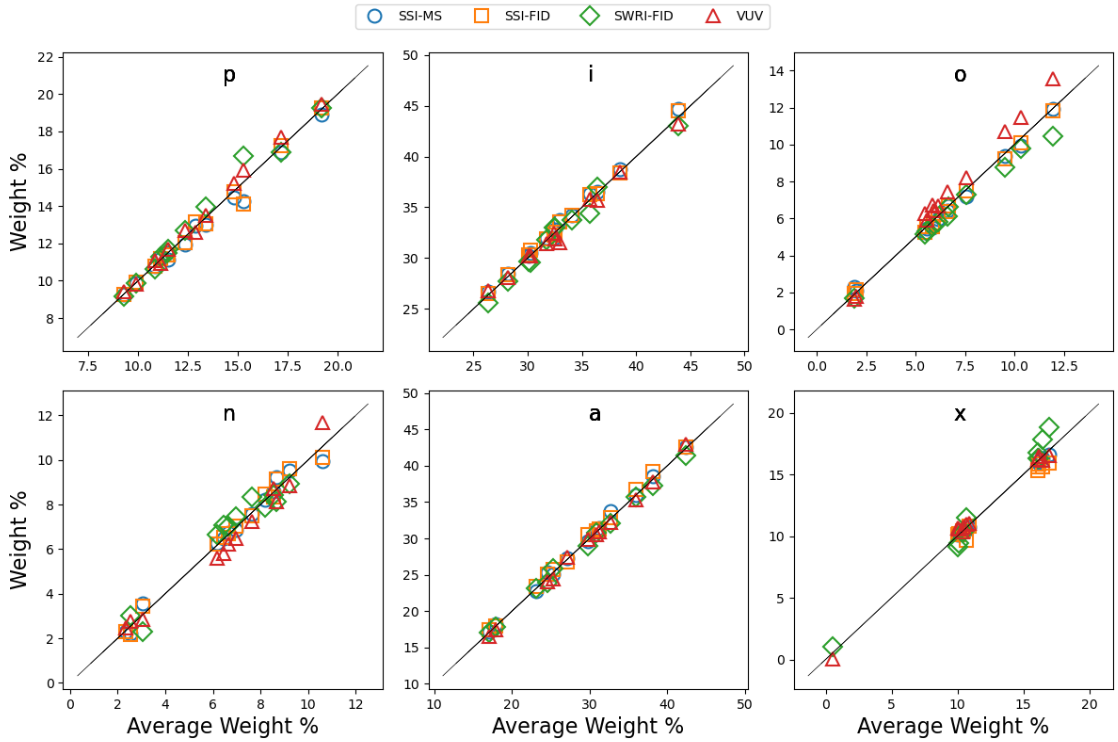

Figure 4. Per group comparison of the weight % reported by the four DHA analyses of the thirteen fuels. Solid line represents 1:1 line.

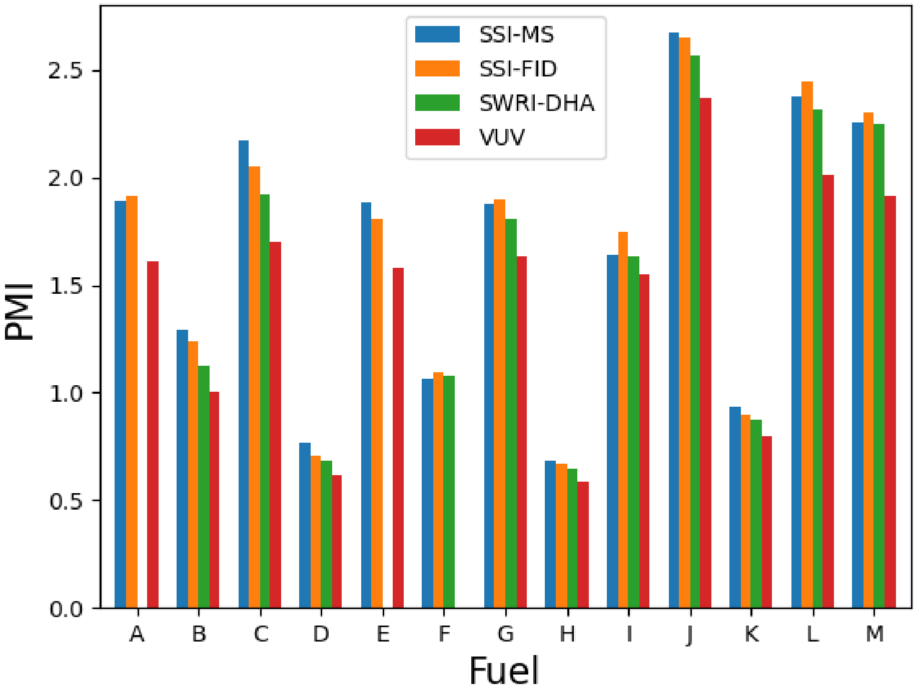

Figure 5. Total PMIs for the thirteen fuels reported by the four DHA analyses.

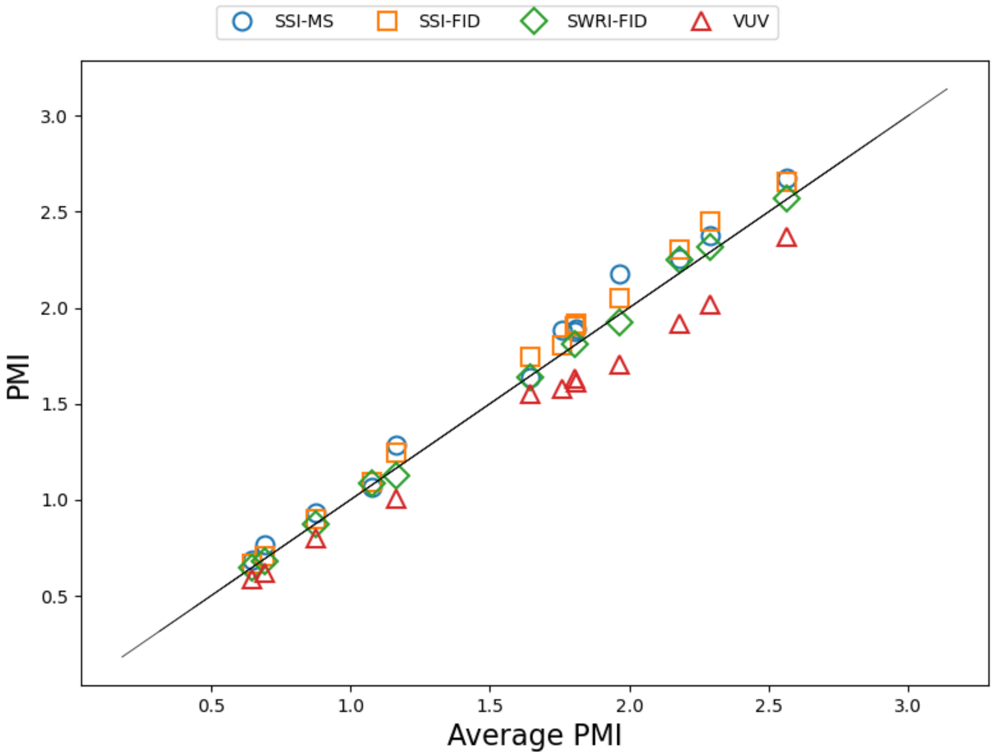

Figure 6. Comparison of PMIs reported by the four DHA analyses. Solid line represents 1:1 line.

4.3. Fuel distillation profiles

Distillation profiles measured with the SimDis (D7096) method as well as those derived from the DHA measurements are shown in Figure 7. The DHA-derived profiles agree well with each other except for the very light and heavy ends due to differences in the chromatographic ranges between the methods. The DHA-derived profiles agree well with the SimDis profiles for the heavier half of the fuel but deviate significantly for the more volatile half. This is similar to what has been observed for a large dataset investigated within the CRC project RW-121a / CM-138-22a.

The difference between the SimDis and the DHA-derived profiles appears to be linked to ethanol: the agreement between the methods for the two ethanol-free fuels (J and K) is better than for ethanol containing fuels. For example, the average temperature needed to evaporate 20%-30% of the fuel according to SimDis is approximately 12ºC lower for ethanol-free fuels, while it is 26ºC lower for fuels with approximately 10% ethanol (fuels A, B, C, D, E, L) and 38ºC lower for fuels with approximately 15% ethanol (fuels F, G, H, I, M). Even though the SimDis is chromatography based, its larger bore column could react differently to ethanol than the chromatographic columns used in the DHA methods. This discrepancy, however, is not expected to be of importance for the PMI or PME correlations, as these indexes are dominated by the heavier part of the fuel where the agreement between the methods is fairly good (1-2ºC on average).

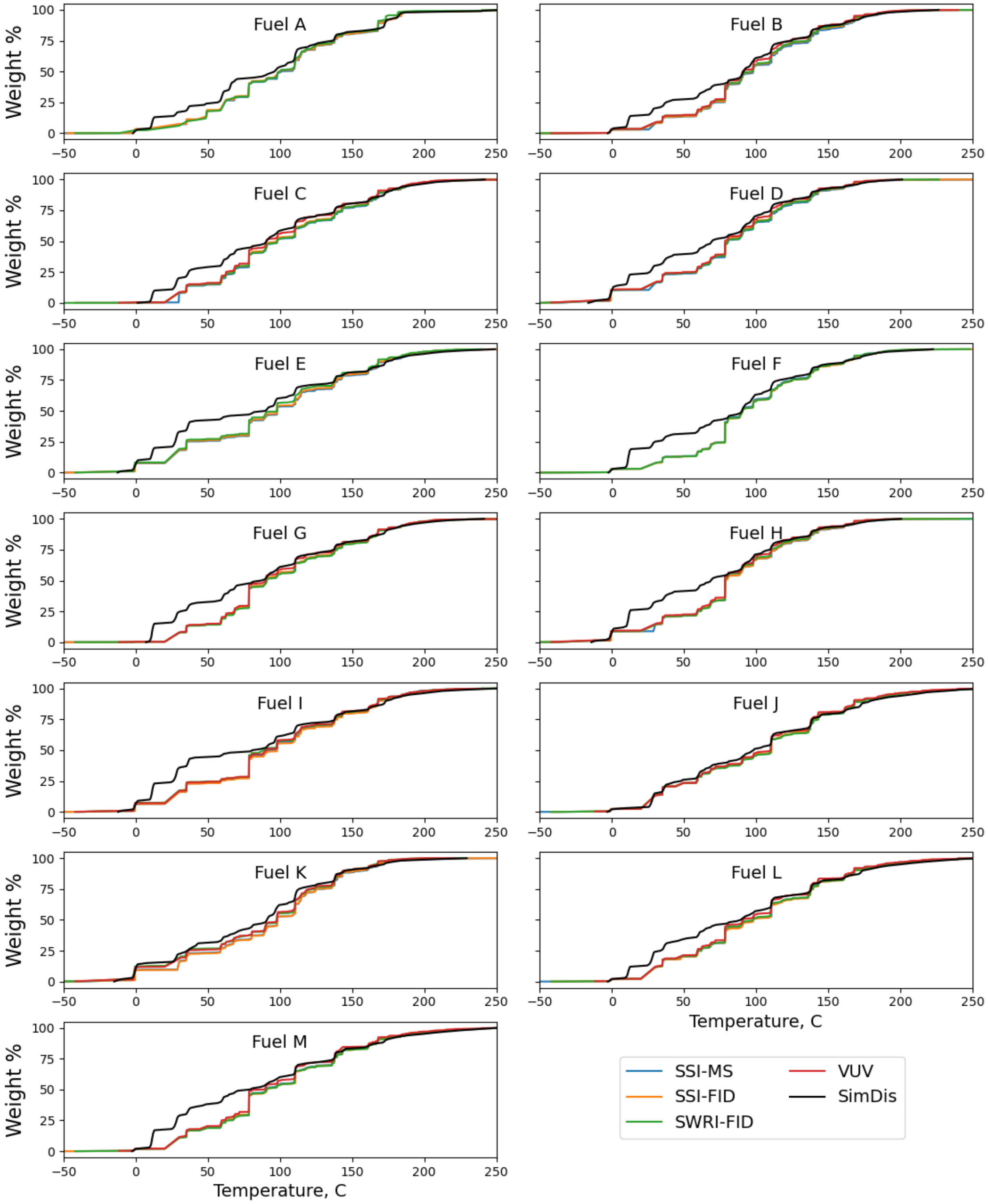

Figure 7. Distillation profiles measured with the SimDis method and derived from the DHA analysis.

4.4. Emissions vs. PMI and PME

Phase 1 vehicle emissions data per vehicle and fuel are given in Table 3. The highest emitter is the SIDI vehicle (B). It should be noted that there is a significant experiment-to-experiment variability in both PM and MSS emission measurements. The average relative standard deviation of the PM measurements is approximately 25%, while for the MSS measurements it is 19%. The maximum variability per individual vehicle-fuel pair experiments is 160% and 142% for the two methods, respectively. Though the variability tends to be higher at lower emission rates, it could be as high as 70% even at 1 mg/mi emission rates, such as for vehicle D with fuel A. The SIDI vehicle (B) with its higher emissions has the lowest relative variability in PM emissions per individual fuel of 10±3%.

Generally, the PM and MSS measurements correlate with each other very well (Figure 8). However, the agreement diminishes at PM emission rates below approximately 3 mg/mi, with less soot being reported per PM mass. This could have two reasons: (1) instrumental uncertainties and biases that are more pronounced at lower emission rates, and (2) a more pronounced contribution of non-soot particulates, such as condensable organics, at lower emission rates.

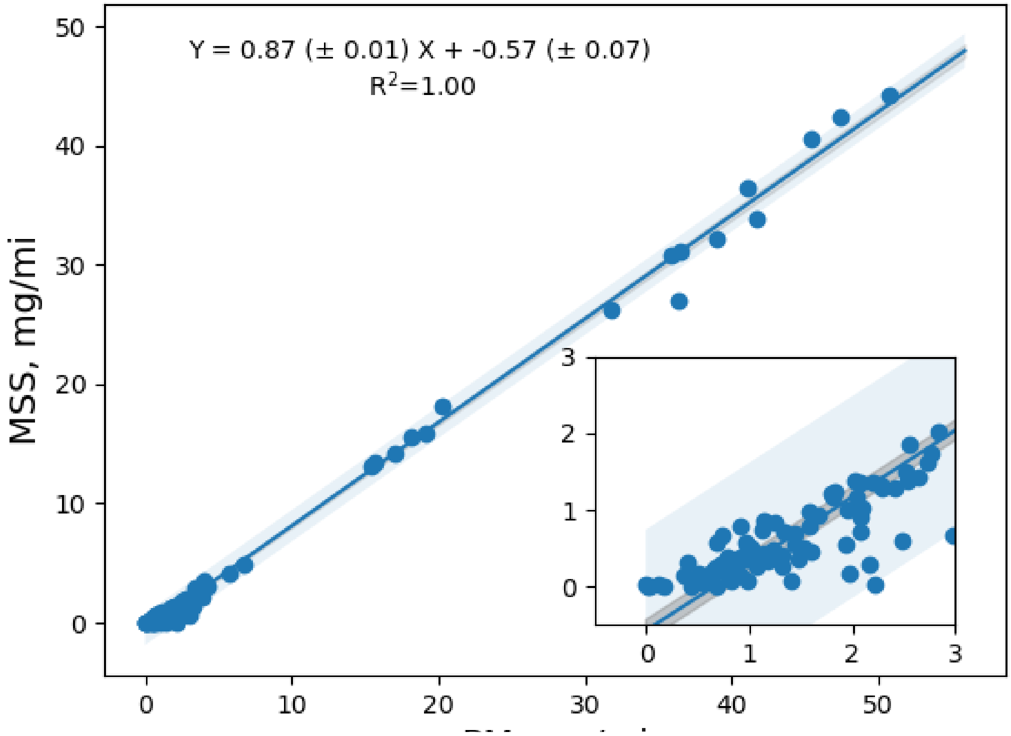

Figure 8. Soot emissions measured with MSS vs. PM emissions. The dark shaded region represents the 95% confidence bounds for the regression line, while the lighter shaded region shows the prediction bands.

Table 3. Phase 1 emissions per vehicle and fuel. "PM": PM emissions in mg/mi; "PM STD": standard deviation of PM emissions from several measurements; "MSS": soot emissions in mg/mi as measured with the MSS sensor; "MSS STD": standard deviation of soot emissions from several measurements. PMI and PME values are an average of data reported by the SSI and SWRI DHA without interpolation. Please refer to Table 1 and Table 2 for the number of experiments per vehicle/fuel combination.

Vehicle	Fuel	PMI	PME	PM	PM STD	MSS	MSS STD
A	A	1.83	1.68	1.54	0.74		
	B	1.17	1.42	0.40	0.03		
	C	1.93	1.98	2.13	0.22		
	D	0.79	0.98	0.71	0.17	0.12	0.04
	E	1.75	1.85	1.26	0.26	0.50	0.01
	F	1.08	1.47	0.67	0.01	0.23	0.04
	G	1.82	1.99	1.71	0.53	0.81	0.12
	H	0.65	1.09	0.77	0.32	0.07	0.01
	I	1.66	1.97	0.81	0.16	0.59	0.07
	J	2.52	2.20	2.24	0.41	1.31	0.12
	K	0.87	1.18	0.79	0.25	0.24	0.05
	L	2.32	2.17	1.36	0.32	0.92	0.07
	M	2.20	2.22	2.22	0.28	1.34	0.06
B	A	1.83	1.31	15.55	2.33		
	B	1.17	1.00	16.98	2.48		
	C	1.93	1.50	28.52	2.73		
	D	0.79	0.64	3.54	0.44	1.80	0.51
	E	1.75	1.42	33.79	2.93	28.50	3.25
	F	1.08	1.03	16.44	1.53	14.05	1.29
	G	1.82	1.51	44.23	4.52	39.46	4.20
	H	0.65	0.71	2.65	0.17	1.62	0.17
	I	1.66	1.48	18.81	1.64	16.08	2.02
	J	2.52	1.62	48.11	3.77	42.38	2.64
	K	0.87	0.74	6.26	0.77	4.54	0.53
	L	2.32	1.71	37.72	1.67	31.67	0.69
	M	2.20	1.71	39.04	3.73	30.45	4.90
C	A	1.83	1.68	1.57	0.57	0.48	0.10
	B	1.17	1.42	0.95	0.32	0.32	0.04
	C	1.93	1.98	1.87	0.23		
	D	0.79	0.98	1.69	0.68	0.20	0.08
	E	1.75	1.85	1.82	0.34	0.65	0.09
	F	1.08	1.47	0.75	0.09	0.20	0.03
	G	1.82	1.99	1.94	0.32	1.16	0.19
	H	0.65	1.09	0.56	0.09	0.15	0.07
	I	1.66	1.97	1.77	0.45	0.96	0.11
	J	2.52	2.20	2.26	0.67	1.41	0.29
	K	0.87	1.18	0.86	0.46	0.30	0.02
	L	2.32	2.17	2.15	0.09	1.36	0.01
	M	2.20	2.22	2.29	0.34	1.27	0.14
D	A	1.83	1.68	1.05	0.72	0.16	0.01
	B	1.17	1.42	0.51	0.18		
	C	1.93	1.98	1.52	0.22		
	D	0.79	0.98	0.56	0.12	0.04	0.06
	E	1.75	1.85	1.32	0.12	0.44	0.09
	F	1.08	1.47	0.95	0.41	0.09	0.04
	G	1.82	1.99	1.01	0.12	0.40	0.03
	H	0.65	1.09	0.07	0.08	0.01	0.00
	I	1.66	1.97	0.89	0.10	0.51	0.24
	J	2.52	2.20	3.90	0.48	3.19	0.28
	K	0.87	1.18	0.78	1.25	0.03	0.00
	L	2.32	2.17	2.70	0.20	1.93	0.11
	M	2.20	2.22	1.89	0.97	0.73	0.06

The PMI values given in Table 3 were calculated as an average of the values provided by the SSI and SWRI analyses without using interpolation to estimate the contribution of compounds with unknown properties. It should be noted that the PMI values derived using the interpolated values correlate well with the values listed in Table 3 as shown in Figure 9. PMIs that include interpolated values are approximately 6% higher than those listed in Table 3. For further analysis, we will use the PMI with interpolated values. Given the strong correlation with the non-interpolated PMI, correlations of these indexes with the emissions will differ only by a small change in slope and some differences in R^2 values, but the conclusions will generally hold for both PMI sets.

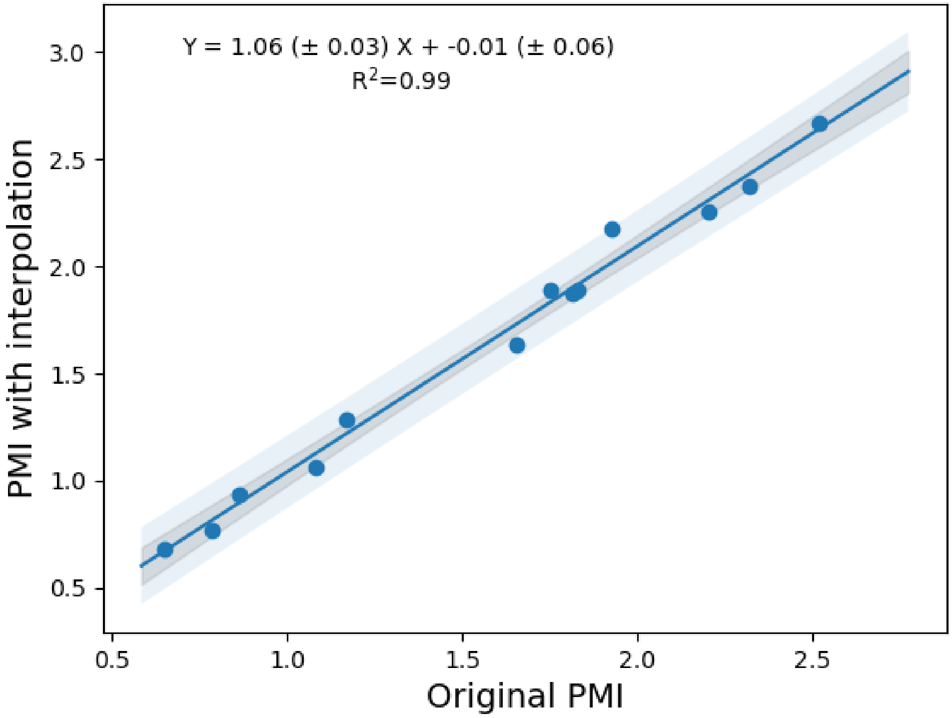

Figure 9. PMIs calculated using interpolated values for compounds with unknown properties vs. PMIs calculated as an average of values provided by the SSI and SWRI without using interpolation ("Original PMI"). The dark shaded region represents the confidence bounds for the regression line, while the lighter shaded region shows the prediction bands.

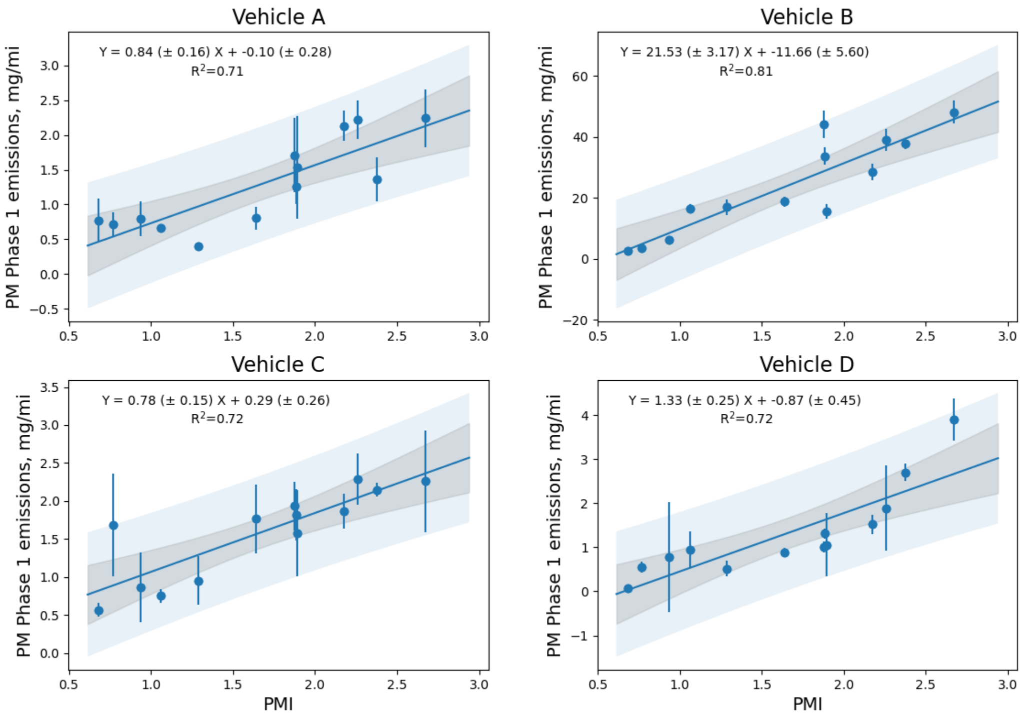

Figure 10. LA-92 Phase 1 PM emissions vs. fuel PMI for four vehicles tested.

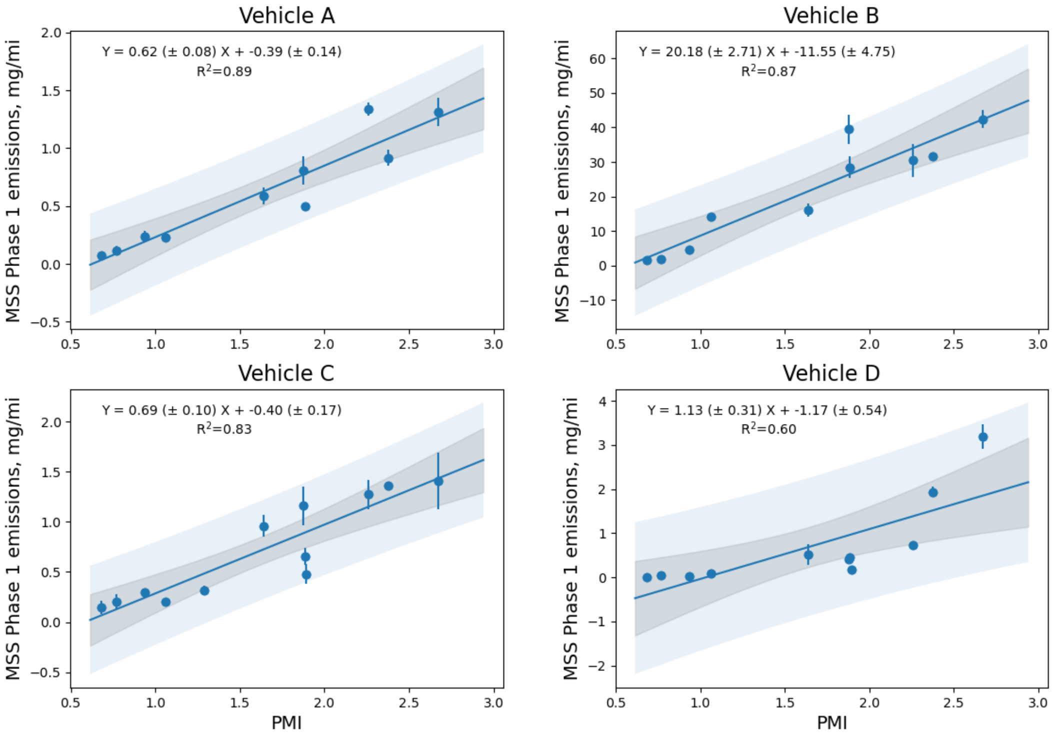

Figure 11. LA-92 Phase 1 soot emissions measured with MSS vs. fuel PMI for four vehicles tested.

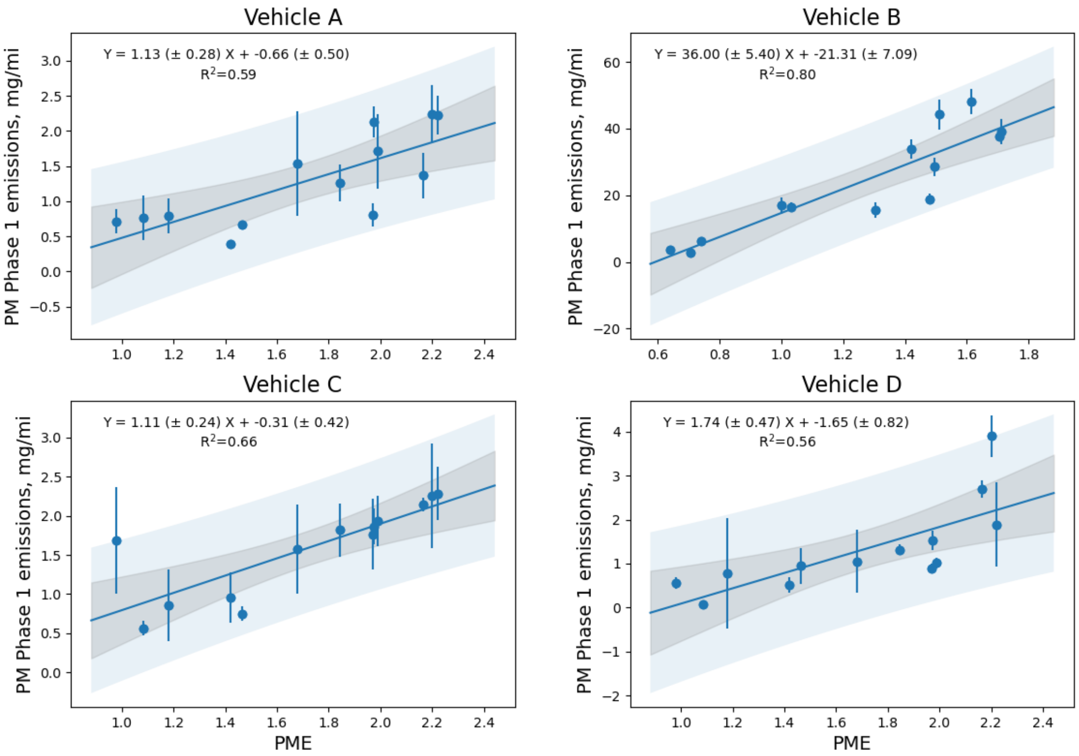

Figure 12. LA-92 Phase 1 PM emissions vs. fuel PME for four vehicles tested.

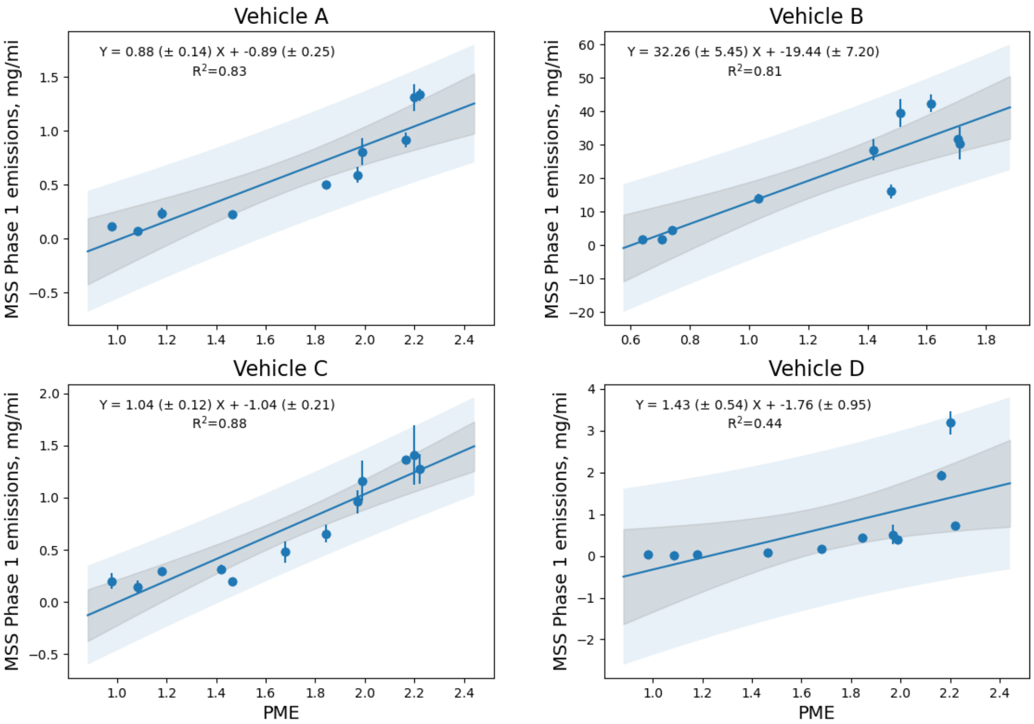

Figure 13. LA-92 Phase 1 soot emissions measured with MSS vs. fuel PME for four vehicles tested.

Correlations of LA-92 Phase 1 PM and soot (MSS) emissions with fuel PMI are shown in Figure 10 and Figure 11, respectively. Such correlations with PME are shown in Figure 12 and Figure 13, respectively. The emissions correlate generally well with both PMI and PME, though there is a significant uncertainty in the regression slopes for both indexes. What is surprising, however, is that PME produces poorer fits relative to PMI. This is evidenced by lower R^2 values of the fit and a non-linear relationship between PME and emissions for PFI vehicles which is most apparent in the MSS measurements. PME was developed as an improvement over PMI, specifically to remove any non-linearity in correlations of PM emissions with fuel properties, especially for ethanol containing fuels.[8] This could be a statistical aberration of this dataset due to its relatively small number of samples, but it does raise questions about the general accuracy of PME for predicting PM emissions.

4.5. “Distillation” cuts vs. PM indexes and emissions

A distillation cut (removing the higher boiling point part of a fuel) was suggested as a way to reduce PM emissions.[16] The reasoning comes from the propensity of the heavier compounds to form PM, as is apparent from the expressions for PMI or PME (Eq. 1 and 3). Indeed, there is a linear relationship between PMI and temperatures at which a certain fraction of fuel is evaporated, such as 95%, 97%, and 99% as determined using the SimDis method (Figure 14). A similar correlation is observed with distillation cuts estimated using the DHA measurements (Figure 15). It should be noted that the correlations between PMI and the distillation cut temperatures as shown in Figure 14 and Figure 15 are based on highly sophisticated chromatographic separations, which are not applicable to real-life distillation processes, where compounds do not distill as perfectly separated chromatographic peaks observed in the SimDis and DHA methods.

Correlations between the various distillation cuts and the measured LA-92 Phase 1 PM emissions are not as clear, however, as demonstrated in Figure 16. The linear fit parameters for the relationships between the distillation cut temperatures and the measured PM emissions are provided in Table 4. The highest correlations are observed for vehicle B with R^2 varying between 0.47 (for the 99% cut temperature) and 0.81 (for the 95% cut temperature). For vehicle A, R^2 varied from 0.39 to 0.46; for vehicle C from 0.34 to 0.45; and for vehicle D from 0.42 to 0.60. The lower R^2 values for the PFI vehicles could, at least partly, be explained by the higher variability of the measured PM emissions for these vehicles. However, the sensitivity of PM emissions to cut temperatures for the SIDI vehicle is also very uncertain. For example, for fuels with the T95 ranging from 188.6ºC to 190.2ºC (or T97 from 200ºC to 206ºC), PM emissions of the SIDI vehicle varied from 16.9 mg/mi to 47.5 mg/mi. This variability corresponds to more than 60% of the PM emission range measured for this vehicle, while the T95 temperatures varied by less than 2ºC. Further, the sensitivity of PM emissions to cut temperatures varies not only between the PFI and SIDI vehicles, but also among the PFI vehicles (Table 4). While the sensitivity, as expressed by the linear regression slope, of vehicles A and C is similar, it is about 2 times higher for vehicle D. These considerations together with the poor correlation between the actual PM emissions and SimDis distillation cuts emphasize the need for experimental verification of how real-life distillation cuts affect PM emissions from internal combustion engines.

Table 4. Linear fit parameters (Y = a X + b) for the relationship between PM emissions and distillation cut temperatures shown in Figure 16.

Vehicle	Cut	a	a err	b	b err	R^2
A	**T95**	0.035	0.007	-5.22	1.31	0.46
	T97	0.026	0.006	-3.83	1.20	0.39
	T99	0.024	0.005	-3.90	1.20	0.39
B	**T95**	1.041	0.095	-168.8	17.5	0.81
	T97	0.820	0.079	-136.5	15.4	0.79
	T99	0.552	0.108	-98.4	23.9	0.47
C	**T95**	0.034	0.007	-4.69	1.21	0.45
	T97	0.027	0.005	-3.76	1.03	0.45
	T99	0.020	0.005	-2.80	1.07	0.34
D	**T95**	0.063	0.009	-10.40	1.57	0.60
	T97	0.049	0.008	-8.16	1.47	0.53
	T99	0.037	0.007	-6.89	1.59	0.42

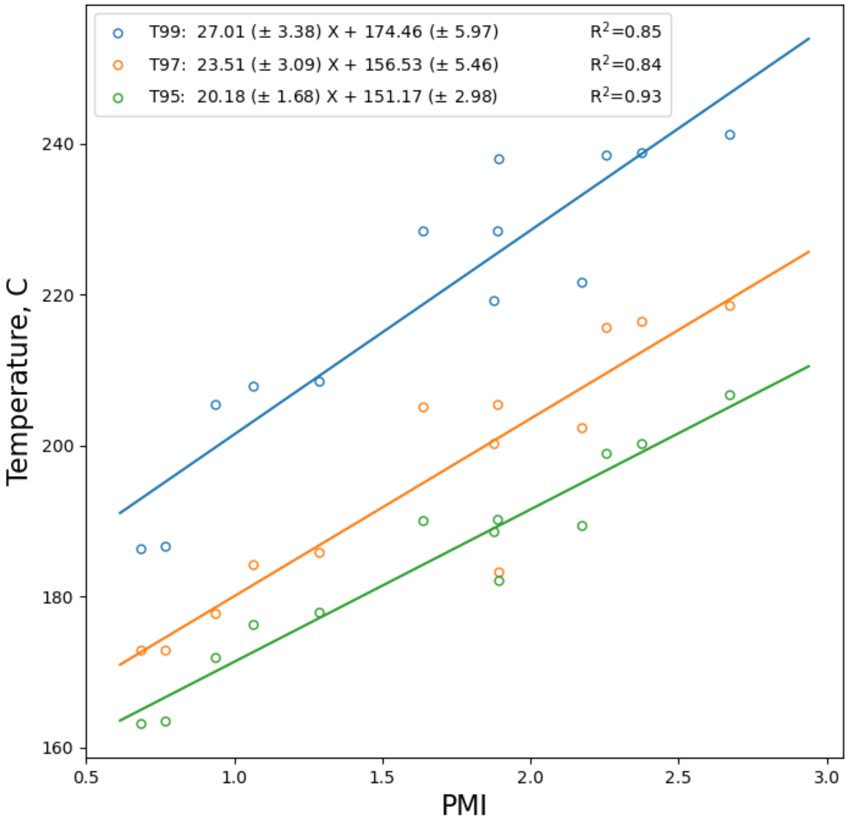

Figure 14. Temperatures of 95% (T95), 97% (T97), and 99% (T99) distillation cuts according to SimDis measurements vs. fuel PMI.

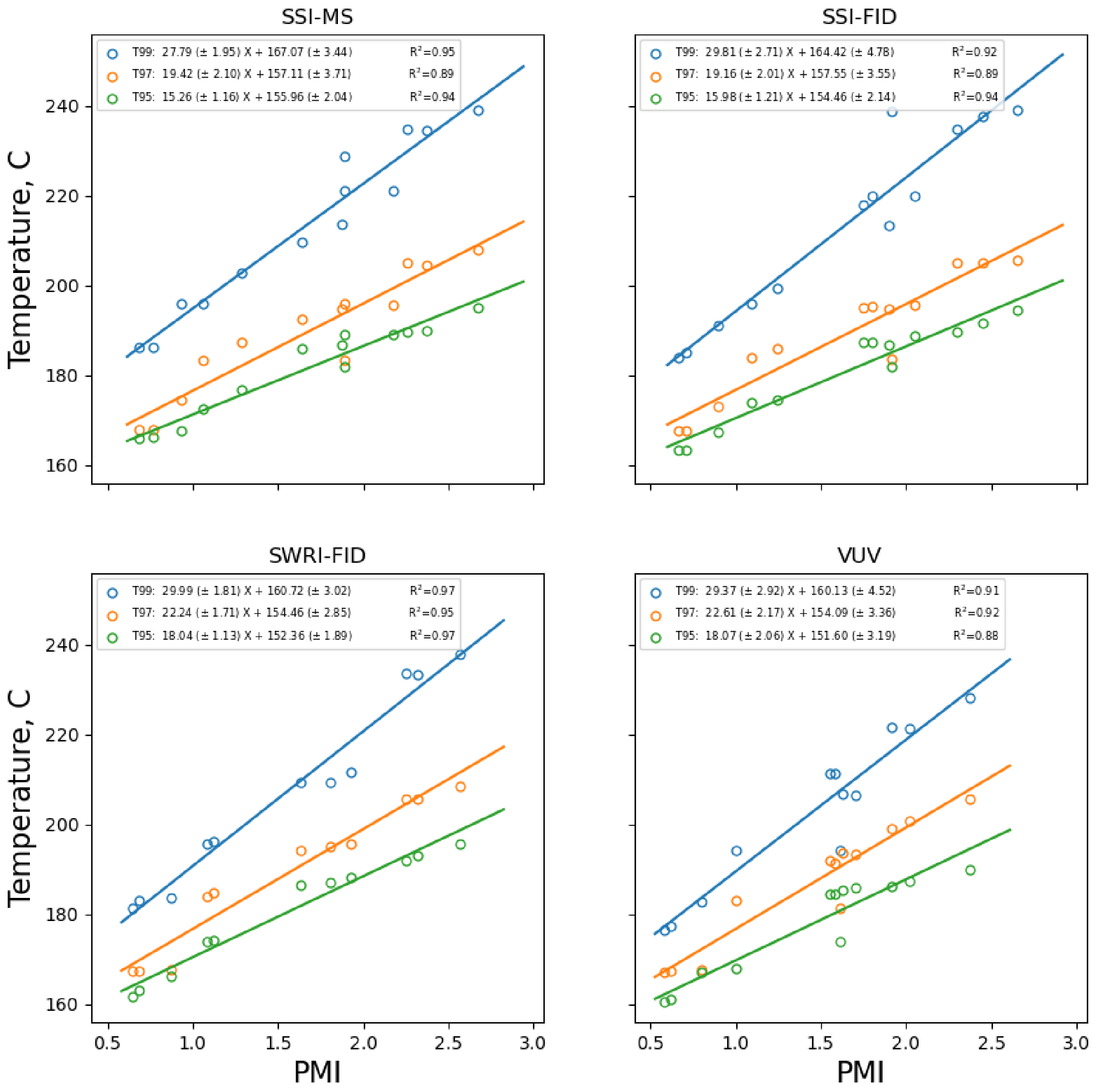

Figure 15. Temperatures of 95% (T95), 97% (T97), and 99% (T99) distillation cuts according to DHA measurements vs. fuel PMI.

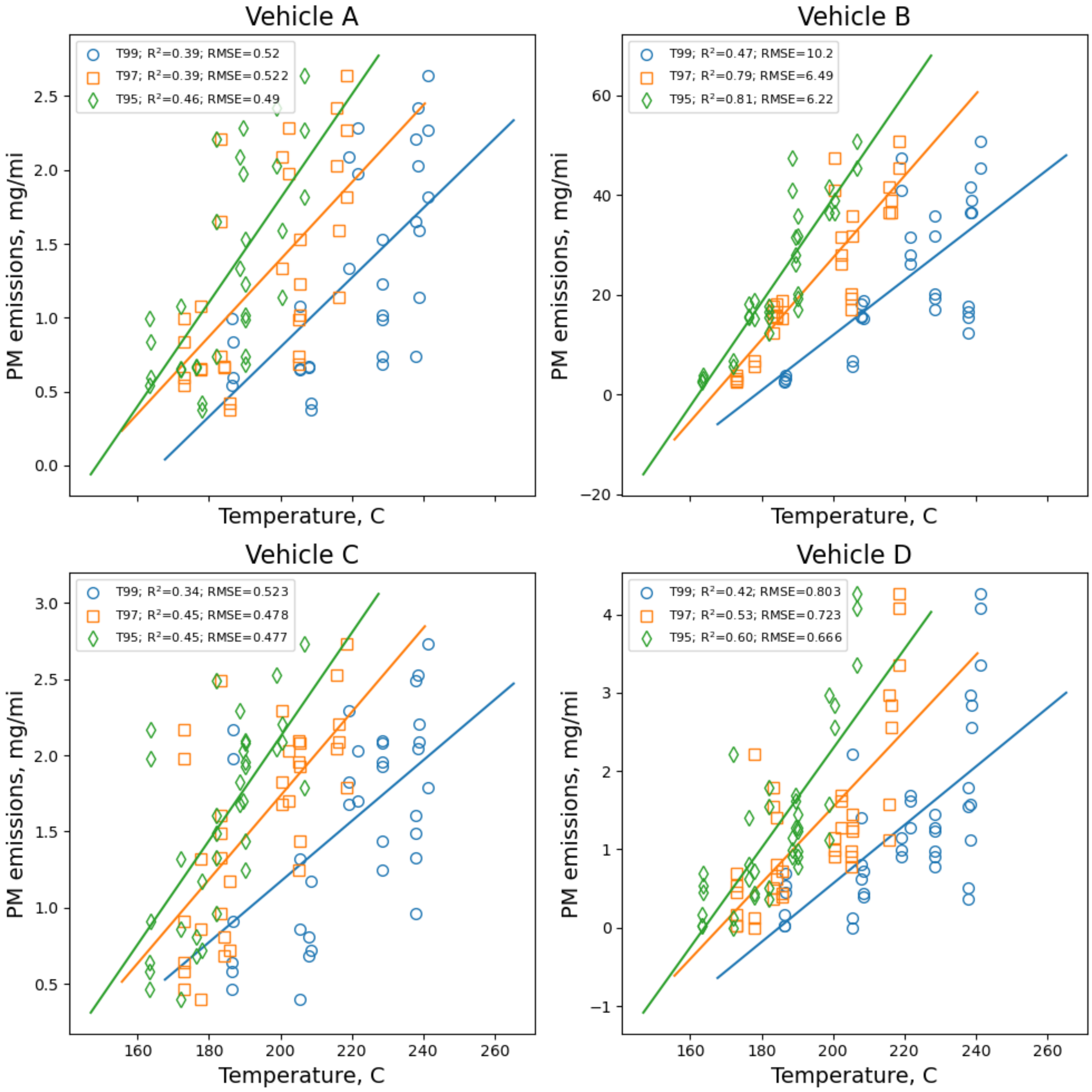

Figure 16. Measured PM emissions vs. temperatures of 95% (T95), 97% (T97), and 99% (T99) distillation cuts according to SimDis measurements.

4.6. Estimation of PMI from SimDis data

We investigated whether SimDis can be used to predict PM emissions or PMI. Table 5 lists Pearson correlation coefficients between the measured PM emissions for the four vehicles and several distillation cut temperatures sorted according to the average correlation coefficient across all vehicles. Correlations with soot emissions, PMI, and PME are also provided. The highest correlation is observed with the soot emissions (also see Figure 8). The second highest predictor is PMI, while PME has a lower correlation value. Among distillation cuts, 95% and 96% temperatures according to the SimDis measurements provide the highest correlation with the PM emissions.

A high correlation coefficient between some distillation cut temperature and PM emissions or PMI, however, does not guarantee that such parameters can accurately predict emissions or PMI of a given fuel. Figure 17 shows relationships between fuel PMI and the T95 and T97 temperatures as determined by the SimDis method for the dataset used in this project, as well as the summer and winter datasets of the CRC project RW-121a. There is a considerable spread of data around the regression lines. For example, for the RW-121a summer dataset, PMI of fuels with T95 of approximately 190ºC vary from approximately 1.25 to 2. PMI of summer fuels with T97 of about 210ºC vary from approximately 1.25 to 2.15. These ranges correspond to approximately half of the PMI range for the whole dataset that includes 169 fuels. This implies that the predictive value of such regressions is limited at best.

Table 5. Pearson correlation coefficients between PM emissions and soot emissions (MSS), PMI, PME, and temperatures to achieve various distillation cuts according to SimDis measurements listed as the corresponding distillation cut percentages. The data were sorted in descending order according to the average of correlations for the four tested vehicles.

	Vehicle				
	A	**B**	**C**	**D**	**Mean**
MSS	0.94	1.00	0.87	0.96	0.94
PMI	0.84	0.90	0.85	0.85	0.86
95	0.75	0.92	0.81	0.86	0.83
96	0.72	0.91	0.84	0.84	0.83
94	0.74	0.90	0.80	0.84	0.82
97	0.71	0.91	0.83	0.81	0.81
72	0.76	0.87	0.80	0.81	0.81
98	0.69	0.91	0.81	0.83	0.81
PME	0.77	0.90	0.81	0.75	0.81
71	0.72	0.83	0.71	0.89	0.79
73	0.72	0.84	0.82	0.72	0.77
74	0.73	0.85	0.84	0.66	0.77
3	0.83	0.82	0.69	0.66	0.75
85	0.75	0.79	0.79	0.67	0.75
93	0.66	0.87	0.72	0.74	0.75

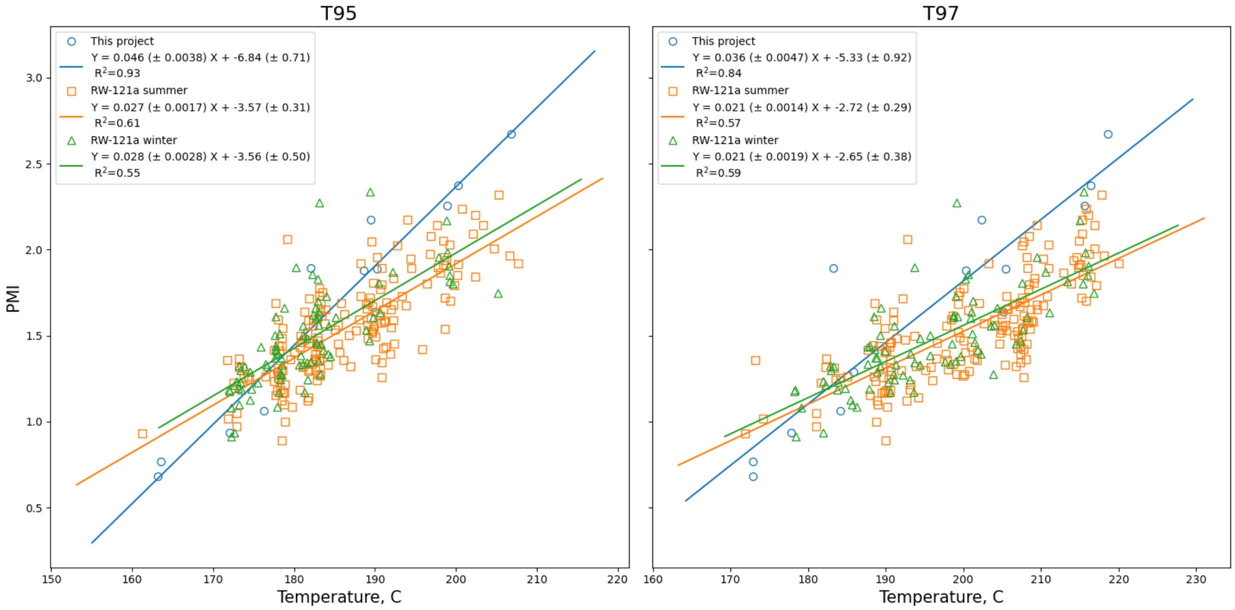

Figure 17. Fuel PMI vs. T95 temperature (left panel) and T97 temperature (right panel) as determined by SimDis for the dataset used in this project and summer and winter datasets from the CRC project 121a. Values in the brackets within regression equations show 95% confidence intervals.

Further, caution is warranted when deriving correlations using limited datasets. The T95 temperatures (as well as other "cut" temperatures) of this project's dataset correlate better with PMI than what is observed with the significantly larger RW-121a datasets (R^2 of 0.93 vs. 0.61 and 0.55). The regression slopes between this and RW-121a are also significantly different, with the current dataset tending to have a stronger dependence of PMI on the "cut" temperature (the higher the temperature, the higher the PMI). The large variation of PMI values within a narrow distillation temperature range is also very clear for the RW-121a datasets. For example, PMI values of fuels in a 2°C distillation temperature range (approximately 4% of the total temperature range) span approximately half of the total dataset PMI range. This makes any predictions of individual fuel PMI from a distillation cut temperature highly uncertain.

Given the positive correlation of PMI with PM emissions, it is thus possible that whatever correlations exist between the SimDis distillation cuts and PM emissions in this project would not hold for a different fuel set, such as the RW-121a datasets. Indeed, even within the same dataset, random samples taken from it can produce very different results. For example, we have attempted multi-parameter correlations that use several distillation point temperatures to predict the PMI. Using the summer dataset from the CRC project RW-121a that has 169 samples, we drew random samples containing 20% of the total number, i.e., about 34 samples. R^2 values obtained for multi-parameter fits for each of such subsets varied by 0.147 to 0.407 depending on the subset of distillation points chosen for the fits. Even if we employ a single parameter linear fit using a distillation point that provides the highest correlation with PM, the 95% point (Table 5), the spread of the points around the 1:1 line is significant. When the fit equation obtained for the summer dataset is applied to the winter dataset, the fit becomes even less good (Figure 18). Thus, caution should be exercised when using SimDis to predict PMI or PM emissions.

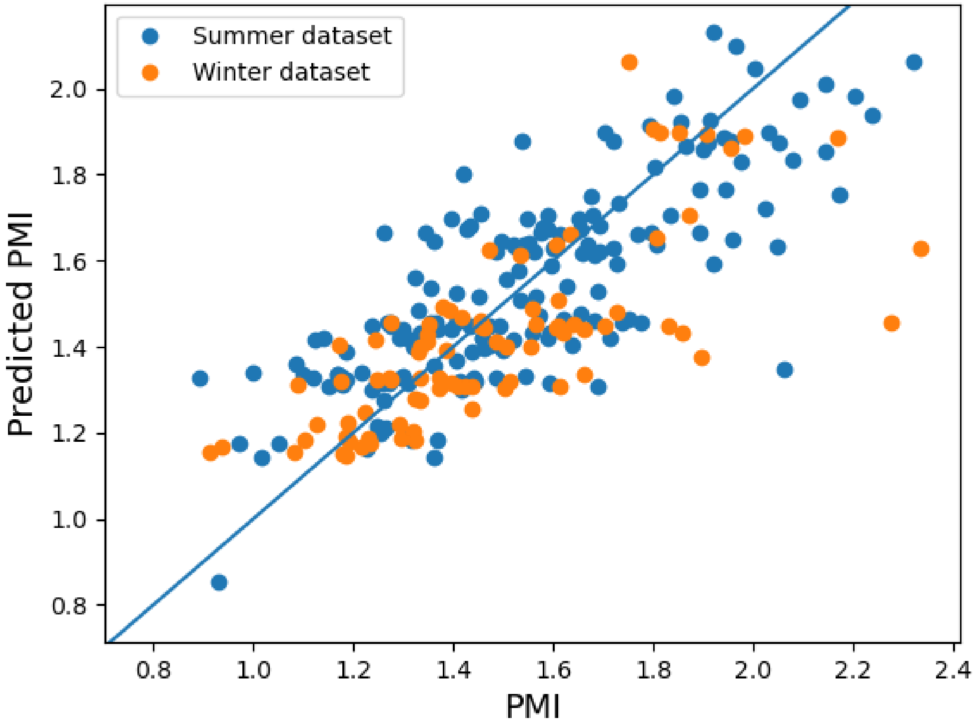

Figure 18. PMI predicted using SimDis T95 (temperature required to evaporate 95% of a fuel) for the summer dataset of the CRC Project RW-121a vs. PMI determined from DHA measurements. The solid line represents 1:1 relationship.

We have also considered using simplified DHA data for predicting PMI, such as using an individual compound's concentration for such predictions. Correlation coefficients of individual compounds with the overall fuel PMI are listed in Table 6 for the fuel dataset of this project and for the datasets of winter and summer fuel surveys analyzed within the CRC project RW-121a. To minimize the effects of artificially high correlation coefficients for compounds with only a few observations, only compounds that were found in the majority of samples in each dataset were considered. For the dataset of this project (E-137) only compounds found in at least 10 out of 13 fuels were considered, for the CRC RW-121a summer dataset 100 out of 169, and for the RW-121a winter dataset 70 out of 85. 1-methylnaphthalene was the best PMI predictor across all three datasets, with 2-methylnaphthalene, naphthalene, 1,2,4,5-tetramethylbenzene, and 1,3-dimethylnaphthalene also having correlation coefficients above 0.7. These compounds could potentially be used for estimation of PMI without resorting to a full DHA analysis.

We have also considered correlations of the broader compound classes grouped by the PIONAX classification and carbon number (Table 7). Aromatic compounds with 11 carbons have the strongest correlation with the measured emissions and PMI. However, while they show a very strong correlation with PMI (0.96), their correlation with PM emissions is very weak (0.30). Thus, while these compound classes could be used for estimating PMI, they may not be very accurate in predicting real life emissions. It should be also stressed that correlations derived for a limited dataset do not necessarily hold for other datasets, as was discussed above.

Table 6. Top 10 compounds with highest Pearson correlation coefficients with fuel PMI across three datasets (this project [E-137] and summer and winter datasets from CRC project RW-121a).

	E-137	RW-121a Summer	RW-121a Winter	Mean
1-methylnaphthalene	0.82	0.86	0.74	0.81
2-methylnaphthalene	0.87	0.83	0.70	0.80
naphthalene	0.85	0.74	0.66	0.75
1,2,4,5-tetramethylbenzene	0.77	0.80	0.68	0.75
1,3-dimethylnaphthalene	0.71	0.70	0.68	0.70
1,7-dimethylnaphthalene	0.71	0.72	0.65	0.70
1,2,3-trimethylbenzene	0.55	0.48	0.41	0.48
1,2,4-trimethylbenzene	0.65	0.44	0.32	0.47
1,3,5-trimethylbenzene	0.57	0.41	0.25	0.41
propylbenzene	0.57	0.38	0.26	0.40

Table 7. Pearson correlation coefficients of the top 10 compound classes with PM and MSS emissions and the PMI, sorted according to their correlation with the PM emissions. The compound classes are indicated by the letter corresponding to their PIONAX class followed by the carbon number.

	PM	MSS	PMI
A11	0.30	0.32	0.96
A12	0.27	0.27	0.93
A9	0.25	0.27	0.81
A10	0.24	0.23	0.84
P11	0.22	0.24	0.73
A13	0.22	0.22	0.88
I5	0.21	0.26	0.71
I6	0.20	0.20	0.57
A7	0.18	0.19	0.62
P5	0.17	0.18	0.62

5. Conclusions

This project investigated correlations between PM emissions measured under the Phase 1 of the LA-92 protocol and fuel properties, such as chemical composition and distillation profile. The performance of various particle emission indexes, such as PMI and PME, in predicting PM emissions from internal combustion engines was evaluated. The relative performance of the ASTM D6730 DHA of Gasoline by GC-FID, ASTM D6730 DHA of Gasoline by GC-MS, ASTM D8369 DHA of Gasoline by GC-VUV, and ASTM D7096 SimDis of Gasoline by GC methods when analyzing the same fuels was assessed. Potential effects of distillation cuts on PM emissions were also investigated.

Fuel composition measured with different DHA methods correlated well between individual methods, though consistent differences were observed. The D6730, especially with MS detection, appears to be preferable for DHA analysis given its larger chromatographic range and better compound identification.

The DHA-derived distillation profiles agreed well with each other except for the very light and heavy ends due to differences in the chromatographic ranges between the methods. The SimDis profiles agreed well with the DHA-derived profiles for the heavier half of the fuel but deviated significantly for the lighter half for ethanol containing fuels.

The PM emissions varied among the tested vehicles, with the SIDI vehicle emitting significantly more PM relative to the PFI vehicles (23.2 mg/mi vs. 1.37 mg/mi, on average). A significant variation in PM emissions (25% on average and up to 160%) was observed in replicate measurements. The high variability in PM emissions observed for a single fuel, especially for PFI vehicles, delineates the limits of predictive accuracy of PM emission indexes, such as PMI and PME.

For the dataset investigated in this project, the PMI demonstrated a better performance in predicting PM emissions than the PME. The PM vs. PMI relationship has higher R^2 values and was more linear than that between PM and PME. This raises questions about the general accuracy of PME for predicting PM emissions.

A linear relationship was observed between the PMI and temperatures of hypothetical distillation cuts. However, there is a considerable spread in PMI values even within a narrow distillation temperature range. For example, fuels with 95% cut temperatures within 2°C of each other (approximately 4% of the whole dataset range) have PMI values that vary within a range of approximately 0.75, which is half of the PMI range of the total dataset. Further, correlations between PMI and SimDis data were found to be dataset-specific.

SimDis temperatures correlated poorly with the actual PM emissions, especially for the PFI vehicles. The linear regression slopes between the cut temperatures and PM emissions varied both between PFI and SIDI vehicles and among PFI vehicles. Likewise, some individual compounds were found to correlate with PMI with Pearson correlation coefficient as high as 0.8.

None of the compounds or compound classes, however, produced correlation coefficients above 0.3 when correlated with the measured PM emissions.

These findings emphasize the need for experimental verification of the relationship between PM emissions and distillation cuts or any other parameters, especially if such relationships are derived using small datasets. It should also be kept in mind that the DHA- and SimDis-derived distillation profiles are based on sophisticated chromatographic separation, which is not representative of real-world fuel distillation.

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Appendix