Methane Emissions from Gathering and Boosting Compressor Stations in the U.S. Supporting Volume 2: Compressor Engine Exhaust Measurements

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Contents

S2-1 Me	asurement Protocol	3
S2-2 Me	thods	3
S2-2.1	Measurement Methods	3
S2-2.2	Data Processing and Reduction	3
S2-2.3	Comparison of FTIR Measurements to Gas Standards	11
S2-3 Tal	oular Results Data	15
S2-4 Co	mparison of Stack Flows to Manufacturer Ratings	15
S2-5 Co	mparison of Measured Combustion Slip to Common Emission Factors	17
S2-5.1	Emission Factor Comparison	17
S2-5.2	Emission Factors vs. Measured Emissions	20
List of	Figures	
S2-1	Field Example of In-stack Tracer Method	3
S2-2	Mass Flowmeter Data Reduction Flowchart	4
S2-3	FTIR Data Reduction Flowchart	5
S2-4	Test Result Data Plot Example	8
S2-5	Example Exhaust Stack Diagram	9
S2-6	Unit Level Result Summary Example Sheet	10
S2-7	Methane Calibration Standard Comparison	12
S2-8	Ethane Calibration Standard Comparison	12

S2-9	Carbon Monoxide Calibration Standard Comparison	13
S2-10	Carbon Dioxide Calibration Standard Comparison	13
S2-11	Nitrous Oxide Calibration Standard Comparison	14
S2-12	Study Measured Stack Flow vs Manufacturer Data	16
S2-13	Study Measured Stack Flow vs Manufacturer Data: Bland-Altman	16
S2-14	Indicated Load Percent: Sub-set of Tested Units	17
S2-15	Study Model: Fraction of Rated BSFC	18
S2-16	Study Model vs Method 19	18
S2-17	Study Measured Units: lb/MMBtu CDFs	19
S2-18	Mesured Emission Rates, Caterpillar Units: lb/MMBtu	19
S2-19	Study Measured Results: kg/h	20
S2-20	Study Emission factor lb/MMBtu	21
S2-21	AP42 Em. Factor, Calculated Results: kg/h	21
S2-22	GHGI Em. Factor, Calculated Results: kg/h	22
S2-23	Subpart C Em. Factor, Calculated Results: kg/h	22

List of Tables

Se i comparisons to Reference Gas Standards i i i i i i i i i i i i i i i i i i i	S2-1	Comparisons to Reference	Gas Standards	ls	11
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S2-1 Measurement Protocol

In-field measurement protocol for exhaust measurements is provided in "Appendix H Compressor Engine Exhaust Protocol.pdf"

S2-2 Methods

S2-2.1 Measurement Methods

The in-stack tracer method was used during the field campaign to measure unburned methane entrained in the exhaust of natural gas compressor engines ("combustion slip"). Combustion slip was estimated by injecting a tracer gas into the exhaust stream at a known flow-rate and measuring concentrations of both the tracer gas and methane at the exhaust stack exit. The total exhaust flow was estimated from the diluted tracer gas concentration measured at the exhaust stack exit. A detailed description of the method can be found in Appendix H to this report, and a manuscript in preparation [1].



Figure S2-1: Example in-stack tracer measurement setup. Tracer gas is injected into the exhaust stack upstream of the sample probe location. Well-mixed tracer and exhaust gases are collected at the sample probe and delivered through heated sample lines to an FTIR spectrometer in the van. The van also contains the tracer gas bottle and mass flow controller.

S2-2.2 Data Processing and Reduction

Time series data (samples) from the tracer gas mass flow meter and the FTIR were recorded at 10 second intervals. Most tests were ten minutes in length; however, test lengths varied from five to 70 minutes. Time series data from each test were reduced to mean values with an associated error. Typically, multiple tests were performed on each unit; mean values and associated errors from each test were combined to provide an overall combustion slip estimate and uncertainty for the unit. Tracer gas flow-rates from a single test were reduced from a time series to a mean value with error using the logic shown in Figure S2-2. Reducing methane and tracer gas concentration measurements from the FTIR required a more complicated approach to account for measurement interference from excessive water vapor present in exhaust streams (see Figure S2-3). FTIR measurements were reduced in a multi-step process. First, H₂O time series data were tested for outliers. Outliers were defined as data points 1.5 interquartile ranges (IQRs) below the first quartile, or 1.5 IQRs above the third quartile of the time series. If outliers were present, a frequency-weighted mean was



Figure S2-2: Tracer gas time series measurements were reduced to a mean value with an associated error using the logic shown.

used. A relative frequency histogram with \sqrt{n} evenly spaced bins was constructed from the time series data and the number of samples (n). The discrete probability in each bin was multiplied by the measured value at the bin center to form a weighted mean. The H₂O measurement error was computed in the same way as the tracer gas. The instrument error was applied to the mean (or weighted mean, as appropriate) and compared to the standard deviation. The greater of the standard deviation and the instrument error was considered the error for the test.

An example summary of stack testing time series data is shown in Figure S2-4. Summary plots from each test can be seen in Appendix A. Sub-plot titles show the:

species: mean \pm error units (relative error %)

for each time series. Dashed blue lines with weighting distributions are plotted for time series data where weighted means were used; solid blue lines without weighting distributions indicate the use of arithmetic means. Dash-dot orange lines indicate a ± 1 - σ error bound about the mean, while solid orange lines indicate instrument error bounds about the mean. Box and whisker diagrams summarizing time series data are also shown. Boxes represent the IQR and include the median value; whiskers represent values 1.5 IQRs below the first quartile, or 1.5 IQRs above the third quartile. Solid markers indicate arithmetic means, and unfilled markers represent outlier data points.

In addition to time series data summaries for each test, unit-level result summaries outlining each test on a unit can be seen in Appendix A. An example unit-level result summary is shown in Figure S2-6. Summaries include facility and unit information, a table with metadata and results from each test, tracer recovery ratio and tracer stratification checks (if applicable), a diagram of the unit configuration with tracer injection and sample probe locations shown, and total stack flows calculated for each test.

A data table summarizing the results of each test on a unit includes; information on tracer injection and sample probe configurations, tracer gas delivery flow-rates, measured tracer gas and methane concentrations, total stack flow, and combustion slip emission rates. Diagrams of typical exhaust stack configurations were created to help describe the tracer and sample probe locations.



Figure S2-3: FTIR time series measurement were reduced to mean values with an associated error using the logic shown.

Exhaust stacks were divided into numbered sections starting at the engine and ending at the exhaust stack exit.

Tracer Position is at "3W" in the example shown in Figure S2-6, where "3" indicates the third section of the exhaust, and "W" indicates that the tracer gas was injected through a fitting on the wall of the exhaust stack, without the use of a tracer probe.

Tracer Probe used in this test is therefore "none". In other cases, tracer probes were inserted into ports present on the exhaust stack. For example "2P" shown in Figure S2-5 indicates a tracer probe inserted into a port in section two of an exhaust stack. Tracer probes are classified as "Single" or "Multi" probes. Single-hole probes were simply open-ended stainless steel tubing extended into the exhaust flow. Multi-hole tracer probes were welded closed at the end and had multiple holes along their length that injected the tracer gas at several points across the stack diameter. In one test, an attempt was made to use a "shower" tracer injection probe. A hoop-shaped ring with holes along its perimeter was fed in from the exhaust stack exit in an attempt to perform a test on an engine without access for tracer injection. The test was unsuccessful and this method of tracer injection was not tried again. "MultiTee" indicates that a single multi-hole probe fed parallel sample trains connected by a tee fitting.

Drop Tube Used indicates whether drop-tubes (permanent sample lines installed on exhaust stacks for use with portable emission analyzers) were used for tracer injection. Sometimes droptubes offered an easy way to inject tracer gas, though oftentimes they were leaky, blocked, or full of (liquid) water.

Sample Position indicates the location of the sample probe in the exhaust stack. For example, in Figure S2-5 "6P" and "6T" refer to sample locations in the sixth section of the exhaust stack, and "P" indicates a sample port was used and "T" indicates that the probe was inserted from the top of the stack. In most cases a multi-hole sample probe was used, but for smaller stacks a single probe was sometimes used.

Sample Probe Position describes the orientation of the sample probe in the exhaust stack as viewed from above. This orientation is relative to the clock-face shown in each exhaust configuration diagram.

Distance Estimate (ft) is a rough estimate of the distance along the exhaust stack centerline between the tracer injection point and the sample probe location. An example of the tracer injection or sample probe locations used in tests of one common stack configuration are shown in Figure S2-5.

Shown next in the unit-level result summary sheets are tracer recovery ratio and tracer stratification checks. In the example shown in Figure S2-6, two tracer recovery checks and two tracer stratification checks were performed. In the first tracer recovery ratio check, tests one and two were compared. In the second tracer recovery ratio check, tests three and four were compared. During these checks, tracer injection and sample probe locations and positions were kept the same while the tracer injection flow-rate was varied. The ratio of tracer gas measured to delivered (ppm/SLPM) was compared. In the first tracer stratification check, tests one and four were compared. In the second tracer stratification check, tests two and three were compared. In this check, the tracer gas flow-rate rate was kept the same, while the sample probe was rotated from the 6 o'clock to the 9 o'clock position. The measured tracer gas concentration (ppm) was compared for each injection point/sample location combination for a given tracer gas flow-rate. For both checks, "Pass" indicated that the errors in the check overlap and that check was successful. "Fail" indicated a failure in the check (the errors in one or more checks did not overlap), while "N/A" indicated that a check was not performed.

Finally the total stack flow predicted from each test is shown in the lower-right plot. The title indicates:

mean stack flow \pm error SLPM (relative error %)

similar to the subplot titles in Figure S2-4. The total stack flow from each test was reduced to a single value for each unit using a weighted mean according to Equation 1.

$$\bar{x}_w = \frac{\sum w_i x_i}{\sum w_i} \tag{1}$$

Similarly, the error associated with each test was reduced to a single value for each unit using a pooled, relative standard deviation according to Equation 2.

$$s_{r,p} = \sqrt{\frac{\sum (n_i - 1) s_{r,i}^2}{\sum n_i - 1}}$$
(2)

The complete summary data and test sheets for each unit and test data are in Appendix A, and are also shown in a supplementary file as described in S2-3.

Facility: 1488 Unit: 1 Test: 1



Figure S2-4: For each test on a given unit, summary plots were made for time series data used to calculate the in-stack tracer flow and combustion slip emission rates. The data include tracer gas injection flow-rate (CF_4 SLPM), and species of interest measured by the FTIR.



Figure S2-5: Example exhaust stack diagram showing tracer injection and sample probe locations. Inset shows the stack exit viewed from above, labeled according to the clock face. Inset figure for each exhaust stack diagram is used to describe the sample probe orientation.

Facility	1945
Unit	1
Make	Caterpillar
Model	G3606
Туре	4SLB
Rating (hp)	1775
Load	0.72

Test	Tracer Position	Tracer Probe	Drop Tube Used	Sample Position	Sample Probe	Sample Probe Position	Distance Estimate (ft)	CF ₄ Delivered (SLPM)	CF_4 Measured (ppm)	CH_4 Measured (ppm)	Stack Flow (SLPM)	CH ₄ Rate (kg/h)
1	3W	None	No	6T	Multi	6clock	8	0.198±0.013	2.8±0.1	2166±100	71304±5055	6.1±0.5
2	3W	None	No	6T	Multi	6clock	8	0.405 ± 0.013	5.4±0.2	2187±97	74578±3220	6.4±0.4
3	300	None	No	61 6T	Multi	9clock	8	0.403 ± 0.011	5.4 ± 0.2	2193 ± 98	74026 ± 3039	6.4±0.4
4	300	None	INO	61	Multi	9сіоск	8	0.203±0.013	2.7±0.1	2102±97	74073±5104	0.3±0.5
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73459 + 4217 SLPM (6%)												
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Figure S2-6: For each unit tested, a unit level result summary shows facility and unit information, a table summarizing results of each test on the unit, a plot of tracer recovery ratio checks, a plot of tracer stratification checks, a diagram showing the approximate location of the tracer injection and stack sampling locations, and the in-stack tracer flow estimate for each test. Error bars for directly measured quantities indicate errors as described in Figures S2-2 and S2-3, or propagation of those errors through calculations using standard rules (e.g. quadrature). The weighted average, pooled error, and (relative error %) (from equations (1) and (2)) of total exhaust stack flow are shown above the lower right-hand sub-plot.

S2-2.3 Comparison of FTIR Measurements to Gas Standards

FTIR measurements were compared to reference standard gases throughout the field campaign, as shown in the following table and figures. Table S2-1 summarizes the results shown in Figures S2-7, S2-8, S2-9, S2-10, and S2-11 and includes the dates when FTIR measurements were compared to reference gas standards.

Species	Date	Calibration Standard	Measured Value	Unit	Measured Within Standard?	Errors Overlap?
C_2H_6	8/2/2017	$100{\pm}2$	$99{\pm}3$	ppm	True	True
CH_4	9/14/2017	$1946{\pm}39$	$1959{\pm}59$	ppm	True	True
CH_4	10/9/2017	$1946{\pm}39$	$1970{\pm}59$	ppm	True	True
CH_4	11/9/2017	$1946{\pm}39$	$1966{\pm}59$	ppm	True	True
CH_4	2/20/2018	$1946{\pm}39$	$1965{\pm}59$	ppm	True	True
CH_4	2/20/2018	$2986{\pm}60$	3023 ± 91	ppm	True	True
CO	7/11/2017	$98.1{\pm}0.5$	$95.9{\pm}2.9$	ppm	True	True
CO	7/12/2017	$98.1{\pm}0.5$	$97.8{\pm}2.9$	ppm	True	True
CO	7/13/2017	$98.1{\pm}0.5$	$94.6 {\pm} 2.8$	ppm	False	False
CO	2/20/2018	$245.6{\pm}5.0$	$245.5 {\pm} 7.4$	ppm	True	True
$\rm CO_2$	7/11/2017	$9.10 {\pm} 0.06$	$8.77 {\pm} 0.26$	%	True	True
$\rm CO_2$	7/12/2017	$9.10 {\pm} 0.06$	$8.79 {\pm} 0.26$	%	False	True
$\rm CO_2$	7/13/2017	$9.10 {\pm} 0.06$	$8.95{\pm}0.27$	%	True	True
$\rm CO_2$	8/1/2017	$19.00 {\pm} 0.15$	$18.76 {\pm} 0.56$	%	False	True
$\rm CO_2$	8/2/2017	$19.00 {\pm} 0.15$	$18.78 {\pm} 0.56$	%	False	True
$\rm CO_2$	8/3/2017	$19.00 {\pm} 0.15$	$18.56{\pm}0.56$	%	False	True
$\rm CO_2$	8/3/2017	$19.00 {\pm} 0.15$	$18.83 {\pm} 0.57$	%	False	True
$\rm CO_2$	2/20/2018	$10.01 {\pm} 0.20$	$9.98{\pm}0.30$	%	True	True
NO	7/11/2017	$93.0{\pm}0.5$	$89.3 {\pm} 2.7$	ppm	False	True
NO	7/12/2017	$93.0{\pm}0.5$	$91.8 {\pm} 2.8$	ppm	False	True
NO	7/13/2017	$93.0{\pm}0.5$	92.2 ± 2.8	ppm	False	True
NO	2/20/2018	$499.7{\pm}10.0$	$491.6{\pm}14.7$	ppm	True	True

Table S2-1: Summary table of all comparisons to reference gas standards.



Figure S2-7: Methane concentrations measured with the FTIR were compared to two different calibration gas standards, one at 1946 ppm, and one at 2986 ppm. No methane measurements made on operating units exceeded these values. Measured central values were all within gas standard uncertainty.



Figure S2-8: Ethane concentration measured with the FTIR was compared to a certified calibration gas standard at 100 ppm. The measured ethane concentration central value fell within the gas standard uncertainty.



Figure S2-9: Carbon Monoxide concentrations measured with the FTIR were compared to two different certified calibration gas standards, one at 98.1 ppm, and one at 245.6 ppm. Central values for all but one measurement were within gas standard uncertainties. The reason for this is unclear; however, the value is very nearly in the range of the FTIR measurement error.



Figure S2-10: Carbon Dioxide concentrations measured with the FTIR were compared to three different certified calibration gas standards, one at 9.1%, one at 10.0% ppm, and one at 19.0%. Most measured central values were within, or nearly within, calibration standard uncertainty. All measurement errors overlapped with calibration gas uncertainties.



Figure S2-11: Nitrous Oxide concentrations measured with the FTIR were compared to two different certified calibration gas standards, one at 93.0 ppm, and one at 499.7 ppm. All measurement errors overlapped with calibration gas uncertainties.

S2-3 Tabular Results Data

Tabular results data summarized in Appendix A of this report and in "CombustionSlip.csv"

S2-4 Comparison of Stack Flows to Manufacturer Ratings

In addition to comparisons with concurrent EPA Method 2 stack flow measurements described in the manuscript results, in-stack tracer flow estimates were also compared to stack flow estimates from manufacturer data sheets and software programs for a sub-set of tested units. The in-stack tracer method was compared to manufacturer stack flow estimates for 42 units; 15 four-stroke, rich-burn (4SRB), and 27 four-stroke, lean-burn (4SLB). All 15 4SRB units were manufactured by Waukesha (9 L5794, and 6 L7042), and all 27 4SLB units were manufactured by Caterpillar (19 G3606, and 8 G3516B). These 42 units were equipped with digital control panels showing operational data used for comparison to manufacturer stack flow estimates. Data were recorded during measurements throughout the field campaign.

For 4SRB engines, operational and environmental parameters were input into the Waukesha EngCalc3.6 site rating program to get a best-estimate of predicted stack flow for the actual operating conditions during testing. Input data included facility fuel composition, facility elevation, operating rpm and load noted during the field campaign. The "Exhaust Volume Flow (ACFM)" output by the program was normalized to the same standard conditions used for the in-stack tracer measurement.

For 4SLB engines, values were calculated based on manufacturer data sheets that provided total stack flow at operating conditions for 75% and 100% load. These manufacturer data were also set to the standard conditions used for the in-stack tracer method for comparison. Loads observed on digital readouts during testing were interpolated or extrapolated linearly for loads other than the manufacturer provided operating points. For G3606 units the rated stack flow was provided at 75% and 100% load at 1000 rpm. All units included in the comparison were operating between 82% and 98% load and 990—1000 rpm. For G3516B units the rated stack flow was provided at 75% and 100% load at 1400 rpm. Two G3516B units were operating at 1200 rpm, one at 61% load, and one at 74% load; the values estimated from data sheets for these units are therefore likely biased high. All other G3516B units were operating between 74% and 92% load and between 1310—1350 rpm.

In-stack tracer estimates trend with manufacturer-specified exhaust stack flow-rates as shown by parity charts in Figure S2-12. When the same data are compared by Bland-Altman difference plots (Figure S2-13), results show that in-stack tracer measurements may be biased low. However, 95% confidence intervals around the bias include zero which indicates that the bias is not significant.



Figure S2-12: Total stack flows predicted by the in-stack tracer method vs manufacturer specifications for (a) four-stroke, rich-burn units, and (b) four-stroke, lean-burn units. The line of equality (y=x) is shown for reference. Ordinary least-squares regressions (not shown) were also performed for (a) y=1.19x-8986, $R^2=0.95$, and (b) y=0.89x+8918, $R^2=0.95$.



Figure S2-13: Bland-Altman difference plots for (a) four-stroke, rich-burn and (b) four-stroke, lean-burn units. Both (a) and (b) show a negative bias for the in-stack tracer method; however, the bias 95% confidence interval includes zero, which indicates that the bias is not significant.

S2-5 Comparison of Measured Combustion Slip to Common Emission Factors

S2-5.1 Emission Factor Comparison

Two motivations for using the in-stack tracer method in this study were to eliminate the need for direct measurement of both fuel flow, and stack flow during on-site measurements. However, since fuel flow was not measured directly, an estimate of fuel consumption was needed to enable comparison with the other factors. For the study, only 4SLB and 4SRB type units were measured. Many of these units were equipped with digital readouts that provided various operating parameters which were logged by CSU personnel during testing. Of the 116 units (70 4SLB in total, 46 4SRB) included in the final emissions distributions, load percent was available for 75 units (56 4SLB, 19 4SRB). For units where an indicated load was not available, the average of all other units of a specific type (4SRB or 4SLB) was assumed. The distribution of operating loads during testing for each type of unit is shown in Figure S2-14.



Figure S2-14: Indicated engine load percent as noted during testing for units equipped with digital readouts. Mean loads and 95% confidence intervals were calculated using bootstrap techniques for the two types of engines tested during the field campaign. The mean load observed in the field for (a) 4SRB engines was 82 (-5/+5) %, and (b) 4SLB engines was 86 (-3/+3) %.

Brake-specific fuel consumption (BSFC) data at rated (100%) load were obtained from manufacturer datasheets for 107 out of 116 units. For remaining units, the average rated BSFC of all other units of a similar type (4SRB or 4SLB) was assumed. To estimate fuel consumption during testing, a relationship between indicated load and (BSFC) was needed. Datasheets for several engines (both 4SLB and 4SRB) indicated that, on average, rated BSFC increases by 5% at 75% load, and 15% at 50% load. For all tested units, fuel input was calculated based on percent load, rated BSFC, and the curve labeled "Study Model" in Figure S2-15.

The in-stack tracer emission factors calculated in this way were compared to estimates made using EPA Method 19[2] for units were gas property data needed to calculate F-factors were available. In-stack measurements of CH_4 and CO_2 along with site specific fuel gas composition data were used to calculate emission rates according to EQ 19-7 of Method 19. Ordinary least-squares



Figure S2-15: Fraction of rated brake-specific fuel consumption (BSFC) vs fraction of rated horsepower for four compressor driver engine models commonly used in the gathering and boosting sector. The composite "Study Model" curve was used to predict BSFC for tested units to enable a comparison to other emission factors.

regression shows good agreement $(1.00x+2.2e-3, R^2=0.96)$ between the study tracer method and the Method 19 estimated combustion slip emission rates, as shown in Figure S2-16.



Figure S2-16: Emission rates predicted by the in-stack tracer method vs EPA Method 19 estimates made from the same test data, and on-site fuel gas composition. Comparison by ordinary least-squares regression shows reasonable agreement between these two methods. Marker shapes and colors correspond to those shown in Figure S2-17.

There appears to be a significant difference in combustion slip among two engine types that are both classified as 4SLB. Similar results were found in a previous analysis of 4SLB engine test data at gathering and boosting stations in the Fayetteville Shale[3]. The average study-measured emission factor for 4SLB engines is lower than AP-42, but combustion slip emissions from Caterpillar 3500 and 3600 series engines were 59% lower and 13% higher than AP-42, respectively. This indicates a need to consider the engine model when applying the AP-42 4SLB emission factor. The characteristics of these engine families that give rise to this difference may warrant a further stratification of the 4SLB emission factor category when such data are available.



Figure S2-17: Combustion slip emission rates measured in this study using the in-stack tracer method for (a) four-stroke, rich-burn and (b) four-stroke, lean-burn engines. Mean combustion slip measured as found was (a) 0.10 (-0.03/+0.06) lb/MMBtu for 4SRB engines and (b) 1.15 (-0.13/+0.13) lb/MMBtu for 4SLB engines. Means and 95% confidence intervals about means for study data were obtained using bootstrap averaging.



Figure S2-18: Combustion slip emission rates measured in this study using the in-stack tracer method for two 4SLB engine models. Combustion slip from engines in the (a) Caterpillar G3500 series were 0.52 (-0.12/+0.20) lb/MMBtu on average, or 59% lower than the AP-42 4SLB emission factor. Combustion slip from Caterpillar G3600 series engines was 1.41 (-0.09/+0.09) lb/MMBtu on average, or 13% higher than the AP-42 4SLB emission factor. Means and 95% confidence intervals about means for study data were obtained using bootstrap averaging.



S2-5.2 Emission Factors vs. Measured Emissions

Figure S2-19: Combustion slip emission rates measured in this study using the in-stack tracer method for (a) four-stroke, rich-burn and (b) four-stroke, lean-burn engines. Mean combustion slip, as measured, was (a) 0.40 (-0.16/+0.27) kg/h/unit for 4SRB engines and (b) 5.77 (-0.75/+0.73) kg/h/unit for 4SLB engines. Means and 95% confidence intervals about means for study data were obtained using bootstrap averaging.



Figure S2-20: Combustion slip emission rates calculated from Study Emission Factors developed from units measured in this study with the in-stack tracer method for (a) four-stroke, rich-burn and (b) four-stroke, lean-burn engines. Mean combustion slip for the population of measured units was (a) $0.40 \ (-0.03/+0.02)$ kg/h/unit for 4SRB engines and (b) $5.62 \ (-0.47/+0.55)$ kg/h/unit for 4SLB engines. Means and 95% confidence intervals about means for study data were obtained using bootstrap averaging.



Figure S2-21: Combustion slip emission rates calculated from AP-42 emission factors applied to units measured in this study for (a) four-stroke, rich-burn and (b) four-stroke, lean-burn engines. Mean combustion slip for the population of measured units was (a) 0.94 (-0.07/+0.06) kg/h/unit for 4SRB engines and (b) 6.13 (-0.50/+0.60) kg/h/unit for 4SLB engines. Means and 95% confidence intervals about means for study data were obtained using bootstrap averaging.



Figure S2-22: Combustion slip emission rates calculated from the GHGI engine combustion slip emission factor, applied to both types of units measured in this study for (a) four-stroke, rich-burn and (b) four-stroke, lean-burn engines. The same emission factor (0.24 scf/hp-hr) was applied to both types of unit. Mean combustion slip for the population of measured units was (a) 5.09 (-0.37/+0.32) kg/h/unit for 4SRB engines and (b) 7.20 (-0.65/+0.77) kg/h/unit for 4SLB engines. Means and 95% confidence intervals about means for study data were obtained using bootstrap averaging.



Figure S2-23: Combustion slip emission rates calculated from the Subpart C combustion slip emission factor, applied to both types of units measured in this study for (a) four-stroke, rich-burn and (b) four-stroke, lean-burn engines. The same emission factor was applied to both types of unit. Mean combustion slip for the population of measured units was (a) 0.01 (-0.00/+0.00) kg/h/unit for 4SRB engines and (b) 0.01 (-0.00/+0.00) kg/h/unit for 4SLB engines. Means and 95% confidence intervals about means for study data were obtained using bootstrap averaging.

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