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Design and Use of a Full Flow Sampling System (FFS) for the Quantification of Methane Emissions

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Abstract:	The use of natural gas continues to grow with increased discovery and production of unconventional shale resources. At the same time, the natural gas industry faces continued scrutiny for methane emissions from across the supply chain, due to methane's relatively high global warming potential (25-84X that of carbon dioxide, according to the Energy Information Administration). Currently, a variety of techniques of varied uncertainties exists to measure or estimate methane emissions from components or facilities. Currently, only one commercial system is available for quantification of component level emissions and recent reports have highlighted its weaknesses. In order to improve accuracy and increase measurement flexibility, we have designed, developed, and implemented a novel full flow sampling system (FFS) for quantification of methane emissions and greenhouse gases based on transportation emissions measurement principles. The FFS is a modular system that consists of an explosive-proof blower(s), mass airflow sensor(s) (MAF), thermocouple, sample probe, constant volume sampling pump, laser based greenhouse gas sensor, data acquisition device, and analysis software. Dependent upon the blower and hose configuration employed, the current FFS is able to achieve a flow rate ranging from 40-1500 standard cubic feet per minute (SCFM). Utilization of laser-based sensors mitigates interference from higher hydrocarbons (C2+). Co-measurement of water vapor allows for humidity correction. The system is portable, with multiple configurations for a variety of applications ranging from being carried by a person to being mounted in a hand drawn cart, on-road vehicle bed, or from the bed of utility terrain vehicles (UTVs). The FFS is able to quantify methane emission rates with a relative uncertainty of ± 4.4%. The FFS has proven, real world operation for the quantification of methane emissions occurring in conventional and remote facilities.

Author Comments:	Thanks for the invitation to submit to your journal. We have highlighted the key sections of the protocol which should we would like to be included in the video, however, we are able to reduce the protocol lengths to include additional components. During the initial phone conversations we spoke of some in-field operation of the system, while we are not fixed to a deadline for publication I will note that we have a couple of sites where a portion could be filmed but this would have issues if it were pushed back until late winter.
Additional Information:	
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If this article needs to be "in-press" by a certain date to satisfy grant requirements, please indicate the date below and explain in your cover letter.	

TITLE:
Design and Use of a Full Flow Sampling System (FFS) for the Quantification of Methane Emissions

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SHORT ABSTRACT:
We have designed, developed, and implemented a novel full flow sampling system (FFS) for quantification of methane emissions and greenhouse gases from across the natural gas supply chain.

LONG ABSTRACT:
The use of natural gas continues to grow with increased discovery and production of unconventional shale resources. At the same time, the natural gas industry faces continued scrutiny for methane emissions from across the supply chain, due to methane's relatively high global warming potential (25-84X that of carbon dioxide, according to the Energy Information Administration). Currently, a variety of techniques of varied uncertainties exists to measure or estimate methane emissions from components or facilities. Currently, only one commercial system is available for quantification of component level emissions and recent reports have highlighted its weaknesses.

In order to improve accuracy and increase measurement flexibility, we have designed, developed, and implemented a novel full flow sampling system (FFS) for quantification of methane emissions and greenhouse gases based on transportation emissions measurement principles. The FFS is a modular system that consists of an explosive-proof blower(s), mass airflow sensor(s) (MAF), thermocouple, sample probe, constant volume sampling pump, laser based greenhouse gas sensor, data acquisition device, and analysis software. Dependent upon the blower and hose configuration employed, the current FFS is able to achieve a flow rate ranging from 40-1500 standard cubic feet per minute (SCFM). Utilization of laser-based sensors mitigates interference from higher hydrocarbons (C2+). Co-measurement of water vapor allows for humidity correction. The system is portable, with multiple configurations for a variety of applications ranging from being carried by a person to being mounted in a hand drawn cart, on-road vehicle bed, or from the bed of utility terrain vehicles (UTVs). The FFS is able to quantify methane emission rates with a relative uncertainty of ± 4.4%. The FFS has proven, real world operation for the quantification of methane emissions occurring in conventional and remote facilities.

INTRODUCTION:

Recent reports confirm the climate is changing because of human activities and further change is inevitable [1]. Climate change occurs from an increase in greenhouse gases (GHG) concentration of the atmosphere. Carbon dioxide (CO_2) and methane are the largest GHG contributors [2]. CO_2 and methane originate from both natural processes and human activities [3]. Present atmospheric levels of CO_2 and methane have respectively increased by 31% and 151% over the past two centuries, with the methane concentration increasing at a rate of 2% per year [4-6]. The climate repercussions of methane and CO_2 emissions depend upon the period considered as methane has a shorter atmospheric lifespan relative to CO_2 [7]. Methane's atmospheric lifespan is 12-17 years, after which oxidization to CO_2 occurs [8]. The impact of methane is 72 times greater than CO_2 in a 20-year period [9]. On a mass basis, methane is 23 times more effective at trapping heat in the atmosphere than CO_2 over a 100-year period [10]. Methane and CO_2 account for 10% and 82% of the total United States (U.S.) GHG emissions [11]. Global methane emissions from anthropogenic sources are approximately 60% and the remaining are from natural sources [8, 10].

In 2009, non-combusted methane emissions between production wells and local distribution network corresponded to 2.4% of gross U.S. natural gas production (1.9–3.1% at a 95% confidence level) [12]. Non-combusted methane emissions are not only harmful to the environment, but also represent a huge cost to natural gas companies [13]. Analysts estimate that the natural gas industry loses in excess of $2 billion dollars per year because of methane leaks and venting [14]. Non-combusted emissions are classified as fugitive or venting [15, 16]. Fugitive refers to the unintentional release of gas from processes or equipment, such as valves, flanges, or fittings to ambient air [17, 18]. Venting refers to the intentional release of gas from equipment or operation processes to ambient air, such as pneumatic actuators [19]. At onshore oil and natural gas facilities, fugitive emissions account for ~30% of the total methane emissions [20]. In 2011, the U.S. Environmental Protection Agency (EPA) estimates that more than 6 million metric tons of fugitive methane escaped from natural gas systems, which exceed the amount of GHG emissions (CO_2-equivalent over a 100-year period), emitted by all U.S. iron and steel, cement, and aluminum manufacturing facilities combined [21].

A critical gap exists in the determination of the climate impact of natural gas due to the lack of accurate and reliable estimates of associated emissions. However, there is a consensus that fugitive methane emissions occur at every stage of the natural gas life cycle and further research in accurately measuring and reporting these values is important [19]. Studies have reported fugitive emissions from specific sectors with results varying by up to twelve orders of magnitude [19, 22-28]. The lack of recognized industry standards and a shortage of consistent regulations in the field of leak detection and leak quantification enable the use of a variety of testing methods and equipment, with the accuracy of some measurement techniques as high as ± 50% [29-35]. Therefore, considerable uncertainty exists on the quantity of fugitive methane emitted over the natural gas life cycle [19, 28, 33, 36-39]. Figure 1 illustrates the amount of variability in published literature on measured and estimated methane emissions associated with the natural gas life cycle. Figure 1 shows the average published fugitive methane emissions emitted as a percent of total natural gas production. If an average value was not given the average of the published range was taken. The standard deviation between the 23 studies is 3.54, with the lowest and highest values differing by 96.5%.

[Place Figure 1 here]

Currently, the total amount of fugitive emissions is unclear due in part to measurement uncertainty and scaling techniques. Without accurate methane emission measurements, policymakers are unable to make informed choices on the matter. A review of current literature identified three primary methods for quantification of natural gas fugitive emissions: bagging, tracer gas, and a commercially available high flow sampler.

The bagging method involves placing an enclosure in the form of a "bag" or tent around a fugitive emission source [60]. There are two variations of the bagging method. In one, a known flow rate of clean gas (typically inert) passes through the enclosure to create a well-mixed environment for measurement. Once equilibrium is reached, a gas sample is collected from the bag and measured. The fugitive emission rate is determined from the measured flow rate of clean gas through the enclosure and the steady-state methane concentration within the enclosure [61]. Depending upon enclosure and leak size, the time required to reach the necessary steady state conditions for the leak rate measurement is between 15 to 20 minutes [61]. The bagging method can be applied on most accessible components. However, it may not be suitable for abnormally shaped components. This method type is capable of measuring leaks ranging in size from 0.28 cubic meters per minute (m^3/min) to as large as 6.8 m^3/min [60].The other bagging technique is known as calibrated bagging. Here, bags of known volume are sealed around a fugitive emission source. The fugitive emission rate is calculated based on the amount of time required for the expansion of the bag, and corrected to standard conditions.

Tracer gas methods quantify a fugitive emission rate based on the measured tracer gas concentration flowing through a fugitive source. Tracer gases commonly employed are helium, argon, nitrogen, sulfur hexafluoride, among others. The fugitive emission rate is determined from the ratio of a known release rate of tracer gas near the fugitive source, measurements of the downwind concentrations of tracer and fugitive source gas, and upwind baseline [24]. The fugitive emission rate is only valid assuming identical dispersion and complete mixing for the two

sources [62]. This implies that the tracer is released near the fugitive source at a similar rate and height, and the downwind measurement is from well-mixed plumes. This method is time consuming and does not provide for component level granularity [63].

A commercially available high volume sampling system consists of a portable battery operated instrument packaged inside a backpack to quantify fugitive emission rates [64]. The air surrounding the leak location is drawn into the sampler through a 1.5-inch inner diameter hose at a sufficiently high flow rate that it can be assumed that all of the leaking gas is being captured.

The sample flow rate is calculated with a venturi within the unit. For low concentrations of methane, 0.05–5% gas by volume, a catalyst methane sensor is used to measure concentration. This sensor is destructive to the methane and other hydrocarbons within the sample. For methane concentrations from 5-100% by volume, a thermal sensor is employed. The system uses a separate background sensor and probe which corrects the leak concentration relative to the background concentration. After the measurement is complete, the sample is exhausted back into the atmosphere away from the sampling area [64]. This method can be applied on most accessible components, with the limitation of measurable flowrates up to eight standard cubic feet per minute (SCFM). This system is capable of testing up to 30 samples per hour. Recently, this system has been shown to have varied accuracy and issues regarding the transition from the catalytic sensor to the thermal sensor [65]. Additionally, the system requires gas fractional analysis to correctly apply a response factor based on gas quality – it is not methane specific. The system has been widely used and may have attributed to discrepancies between top-down and bottom-up methods by under reporting methane emissions [65].

Due to limitations of these methods and systems, a new quantification system was developed. The FFS employs the same design concept as dilution systems used in automotive emissions certification [66-68]. The FFS consists of a hose that feeds an explosive-proof blower that exhausts the leak and dilution air sample through a mass airflow sensor (MAF) and sample probe. The sample probe is connected to a laser based methane analyzer through a sampling tube. The analyzers uses cavity enhanced absorption for measurement of CH_4, CO_2, and H_2O. The analyzer is capable of measuring CH_4 from 0-10% by volume, CO_2 from 0-20,000 ppm, and H_2O from 0-70,000 ppm. Repeatability/precision (1-sigma) for this configuration is <0.6 ppb of CH_4, <100 ppb CO_2, and <35 ppm for H_2O [69]. The sample is drawn from the stream at a constant volumetric rate. The system is instrumented with data logging equipment. Figure 2 illustrates the schematic of the FFS. Prior to operating the FFS, the grounding connection on the sampler hose is attached to a surface that allows the system to be grounded. This is a preventive action to dissipate any static charge on the end of the hose, which could result from airflow through the hose. Data acquisition occurs on either a smart phone, tablet, or laptop computer. Software was developed for data collection, processing, and reporting. Figure 3 provides a brief overview of the user interfaces for the following protocols.

[Place Figure 2 here]

[Place Figure 3 here]

PROTOCOL:

Note: The FFS has been engineered with safety in mind to eliminate or reduce the possibility of ignition of a methane or natural gas source. Natural gas is flammable in ambient conditions for volume concentrations from 5 to 15%. The system will be tested and demonstrated to meet intrinsic safety requirements. Modification or tampering with the system could cause serious injury.

1. Calibration of the MAF

Note: The MAF requires periodic calibration against a National Institute of Standards and Technology (NIST) traceable laminar flow element (LFE). Use the calibrations tools within the program to complete a MAF calibration against a known LFE. The program will collect all data necessary from the pressure transducers, humidity sensor, and MAF to create a new calibration. It is recommended that an 11-point calibration be completed. If a calibration is older than one month, a new calibration should be completed. Old calibrations can be viewed and used.

1.1. Choose a properly sized LFE to ensure that the flow range is larger than 25% of the lower flow range of the LFE.

1.2. Connect the MAF to a flow bench ensuring the inlet to the MAF is at least 10 diameters downstream of any restriction or expansion.

1.3. Connect a combined absolute/differential pressure meter to the differential pressure ports of the flow bench LFE.

1.3.1. Ensure the differential pressure transducer is within calibration. Connect the high side port of the sensor to the upstream LFE port. Connect the low side port of the sensor to the downstream port of the LFE.

1.3.2. Ensure that the absolute pressure transducer of the combined differential/absolute pressure meter is within calibration and connect via a ‘tee’ fitting to high side port of the differential pressure sensor.

1.4. Connect a K-type thermocouple to the data acquisition unit (DAQ).

1.5. Ensure that the dew point measurement device is within calibration and connected to the DAQ and the air stream.

1.6. Ensure that MAF and flow bench signals are acceptable (0-5 volts) and use the software calibrations screen to begin a MAF calibration.

1.7. Set the flow at 11 different flow rates across the expected range of the MAF and within the acceptable range of the LFE. Collect a minimum of 30 seconds of data at each flow condition at a minimum rate of 1 Hz by clicking the collect calibration data button.

Note: Ensure that the MAF calibration spans at least 25% of the minimum flow rate of the LFE

used for calibration. Do not exceed the maximum flow rate of the LFE, if larger flow rates are to be calibrated, use a larger LFE.

1.8. Run the calibration software by clicking Process Calibration Data button and select the curve fit that yields minimal total error without a single point error beyond ± 2%.

2. Calibration of the greenhouse gas analyzer

Note: The greenhouse gas analyzer should be calibrated internally on an annual basis by a third party. Users can use the calibrations tools within the software to complete an external calibration or verification. The calibration uses bottled gases of known concentration. The gas is mixed with nitrogen through a gas divider and exits to a flooded probe. The analyzer intakes the sample at the known flow rate and records the value. It is recommended that an 11-point calibration be completed over the range of interest. The program automatically adjusts for gas concentration and viscosity within the gas divider.

2.1. Prior to field-testing, perform an external verification or calibration if necessary (previous calibrations older than one month).

2.2. Power the GHG sensor on for 15 minutes prior to verification/calibration and connect the verification 'tee' fitting to the inlet port of the sensor.

2.3. Select an EPA Protocol or NIST traceable gas to verify and use ultra-high purity nitrogen (UHPN) as the balance gas.

2.4. Connect the verification gas (methane) to the component port of a calibrated gas divider using approved regulators (CGA 580 for UPHN, CGA 350 for methane). Connect the outlet of the gas divider to the 'tee' of step 2.2.

2.5. Set the component gas, outlet pressure to approximately 23 pounds per square inch – gauge (PSIG) by adjusting the regulator knob. Set the balance gas, outlet pressure to approximately 19 PSIG. Set the flow rate of the gas divider to at least two times the internal flow rate of the sample pump with the gas divider, flow control knob (Current sample pump operates at two standard liters per minute (SLPM) so the outlet of the gas divider should be set at 4 SLPM).

Note: Adequately flood the sample probe with the gas mixture to ensure a proper verification. Use secondary rotameter if available to ensure a net positive flow out of the flood probe 'tee' of step 2.3.

2.6. Click start calibration and enter the bottle concentration of the component gas (in ppm). Use the gas divider to select component gas ranges from zero to 100% (11 total points). Collect data for a minimum of 30 seconds at each setting of the gas divider to complete the linearization.

2.7. Select whether a new external calibration is applied.

Note: If the verification passes within the uncertainty of the gas bottle concentration (typically 1-2%) then a new external calibration does not need to be created.

2.8. Repeat the prior steps for single or multiple point verifications/calibrations of methane, carbon dioxide, or water vapor.

3. Full system recovery test.

Note: A full system recovery test is completed to ensure that the FFS recovers and accurately reports a known volume of calibration gas.

3.1. Power on the FFS and ensure the GHG sensor has been on for at least 15 minutes. Select a recovery gas to test – methane.

3.2. Connect the gas bottle to an appropriate regulator and set the outlet pressure to approximately 20 PSIG.

3.3. Connect a supply line to the gas bottle regulator and the inlet to a calibrated mass flow controller (MFC). Connect the outlet of the MFC to the inlet of the sampling hose. Select the gas recovery verification tab in the DAQ software and connect the serial connection of the MFC to the DAQ.

3.4. Click start the gas recovery test and record the background data for at least 30 seconds, the known flow rate of gas can be entered at this time.

3.5. Set the flow rate of recovery gas to an average leak size based on expected or previous values (20 SLPM or 30 SLPM). Begin flowing the recovery gas and let the system stabilize for 30 seconds.

3.6. After stabilization, click record, and allow the program to record the leak verification data for 30 seconds.

Note: Upon completion of sampling the software will create a report showing the error of the between the known gas flow rate and the recovered gas flow rate. An error of ±4.4% is acceptable (relative measurement uncertainty of the system), but the targeted recovery error is ±2%.

3.7. Repeat the gas recovery test at least three times and ensure that all errors are within the acceptable range.

3.8. Examine the system for any faults if the error is beyond ±4.4%. Double-check all connections, flow rates, remedy errors, and repeat steps 3.2 to 3.6.

Note: Faults may include that the supply line may not have been inserted into the FFS sampling hose or connections were loose on sample fittings. A new MAF calibration or sensor verification may be necessary if not previously completed (within a month).

4. Leak detection audit.

Note: Perform a site inventory to identify each potential source of fugitive emissions. The inventory will include the number of sources (valves, flanges, pumps/compressors, vents, etc.) broken down by source group (compressor building, storage farm, vehicle fueling rack, etc.) The leak detection audit can occur in parallel or series with the leak quantification. A handheld methane detector or optical gas-imaging camera can be used to examine components for leaks. When leaks are identified record a description, concentration, and take an image. Mark the leak for later quantification or quantify the leak at this time.

4.1. Create a new inventory file in the program. Enter details on the site for inventory and reporting purposes (name, type of site, etc.). Date, time stamp, and GPS location are automatically populated.

4.2. Zero the handheld methane detector on ambient air prior to use. Utilize a handheld methane detector with sampling probe to check all potential interfaces that are accessible for the presence of fugitive emissions. Position the probe sample inlet orthogonal to the surface to minimize dilution.

Note: The sensitivity of the handheld unit is 5 ppm above background when zeroed on ambient air.

4.2.1. Document any inaccessible sources or aggregated sources.

Note: Inaccessible sources could include vent pipes that are beyond a safely accessible height as determined by the site operator. Aggregated sources may include multiple pneumatic valves attached to a manifold or enclosed by a service box. If the source or multiple sources can be examined as a whole using an enclosure, aggregate the sources.

4.2.2 Aggregate multiple sources using an enclosure with at least one entrance and one exit. Document all sources within the perimeter of the enclosure. Label the source as an aggregate sample and proceed using quantification of section 5.

Note: Use of a leak detector solution is allowed to classify sources a “non-leaking”. Holding the bottle upright, apply enough leak detector solution to cover the interface. Allow 5-10 seconds for bubbles to form.

4.3. Place the probe inlet of the detection instrument at the surface of the component interface. Move the probe along the interface periphery while observing the instrument readout, taking care to consider the delayed response time of the instrument.

4.4. Slowly sample the interface where leakage is indicated until the maximum meter reading is obtained.

4.5. Leave the probe inlet at this maximum reading location for approximately two times the

instrument response time (20 seconds). If the maximum observed meter reading is greater than 500 parts per million (ppm), record, and report the result. Click take leak image for reporting purposes.

4.6. Alternatively, use an infrared imaging device to scan slowly the components to examine for leaks. This method is approved as an alternative work practice to detect leaks from equipment under EPA Method 21 – optical gas imaging.

4.6.1. Turn on the camera and allow for stabilization.

4.6.2. Remove the lens cover and use the camera screen to scan slowly the components for leaks.

Note: Optical gas imagining cameras are typically expensive but do reduce the time required to scan components for leaks. Use of high sensitivity modes may be required for small leaks.

4.6.3. If a leak is detected with the camera, either record video or an image for reporting purposes. Mark the leak locations for subsequent quantification with the FFS.

5. Leak rate quantification.

Note: Leak rate quantification may be complete at the same time as leak detection or after an inventory of leaks has been completed. Quantification occurs under the new leak button after entering site and leak data. The user must select whether to use a local or global background. In either case, the system will control the proper solenoid valves and record a timed sample. Once a background has been taken, the leak should be quantified three times or from three directions to ensure proper leak capture. The system will analyze the three measurements and report the variance. Users may save the leak data (separate and average), repeat the capture, or classify the source as variable.

5.1. Measure and record methane background concentrations periodically throughout the site visit and with every leak quantification.

Note: It is of high importance to take separate backgrounds for leaks that are within a similar region and under conditions when the dilatation air may contain a slipstream of nearby leaks. Combined leak analysis of systems is discussed below – 5.15.

5.2. Quantify any identified leaks. Prior to approaching the leak with the sample hose ensure that the grounding strap is in contact with the ground and clip the clip the sampler ground clamp to the item in question. Using the FFS, position the sampling hose at multiple points around the area of the leak source to obtain three consecutive leak rate quantifications for that source that included the continuously recorded sample flow and sample concentration.

5.3. Adjust the full flow rate to increase volumetric flow by opening or closing the iris duct on the intake of the blower. Adjust the duct valve to ensure that the maximum methane concentration is within 10% of the highest calibrated value or that minimum methane

concentration is at least 2 ppm higher than the background concentration.

5.4. In the program, press the quantify leak button. An option to use a global or local background will prompt the user.

5.5. When in doubt of contamination from other leaks, always take a local background. With the hose in the leak quantification position, click take local background. Once completed the program will prompt the user to quantify the leak.

Note: The program automatically switch the sampling location of the outlet of the FFS to a port just behind the inlet to the sampling hose for a local background. The sampling hose must be in the same measurement position as is used for the sample quantification.

5.6. Repeat the record leak prompt three times, especially in the cases of high ambient wind conditions or in complex geometries.

5.6.1. If the variance of the additional quantifications is above 10%, investigate to determine if the variance is the result of instrument malfunction or variability in leak rate.

5.6.2. If the source of variability in leak rate is due to instrument malfunction, remedy the source of malfunction and re-quantified. Otherwise, classify the leak as “variable” and record the suspected cause.

5.7. In the case of multiple sources in close proximity or a single source enclosed by a covering, treat the source(s) in question as a single source for leak quantification using an enclosure. Use the Enclosure tab to perform this type of quantification.

5.7.1. Fabricate an enclosure entirely of plastic sheeting or incorporated either flexible, non-permeable material, or rely on a permanent enclosure such as a compressor housing.

Note: The enclosure allows the quantification device to capture any natural gas that is leaking from components within its boundaries and allows for dilution of the captured natural gas via purposely-placed holes in the enclosure or from existing vent locations on permanent enclosures.

5.7.2. Allow any natural gas being diluted to be drawn from the enclosure and to achieve a steady reading from the GHG sensor. The duration of quantification sampling performed using an enclosure is dependent upon the size of the enclosure.

5.7.3. Situate the points at which the quantification sample drawn from the enclosure such that the dilution air flows across the potential leak source(s) to reduce the duration of sampling allowing for steady concentration readings

5.8. If a bag sample is required, place an evacuated sample bag of the bagging box to the outlet of the GHG sensor. Use the software to record bag sample, identification number and on-screen timer to ensure a full bag sample for off-site analysis has been taken.

REPRESENTATIVE RESULTS:
Multiple FFS were developed and used to quantify a variety of methane emission sources. Two major studies included the Environmental Defense Fund's Heavy-Duty Natural Gas Vehicles Pump to Wheels (PTW) study and the Barnett Coordinated Campaign (BCC). The PTW study focused on quantification of methane emissions from heavy-duty natural gas vehicle fuel systems, engine crankcases, compressed natural gas tanks, liquefied natural gas tanks, fuel station equipment, nozzles, and other leaks.

Multiple FFS systems were used during the BCC, which brought together leading experts from academic and research facilities from around the country to collect methane emissions data across the natural gas supply chain (production, gathering and processing, transmission and storage and local distribution) through a combination of aircraft, vehicle, and ground-based measurements. We conducted direct source quantification of methane emissions at natural gas compressor stations and storage facilities using the developed methodology and FFS system. A portion of the results from the Barnett Shale study relating to measurements obtained through the employment of the FFS has been presented and published at peer reviewed conferences and scientific journals [70-72].

For both the PTW and BCC, we employed methane leak detection equipment to survey site components including valves, tubing/piping, and other components that carried or held natural gas. A leak was detected with a hand held methane detector. This hand held detector aided in the identification of the leak location by identifying an increased methane concentration above background. Once a leak location was detected that surpassed the concentration threshold, researchers used the FFS to quantify the leak rate. The FFS leak sample was collected through a hose attached to the inlet side of a blower. The sample passed through a certified explosion proof blower where it was exhausted through a piping system that contained a MAF and methane sensor. The FFS system was able to sample at flow rates from 40-1500 SCFM dependent upon the system configuration. Using the measured sample flow rate and methane concentration, the leak rate in SCFM or g/hr was calculated.

Calibration Data
For calibration, a constant flow was established through the system. The pressure drop across the LFE was obtained through the measurement of the differential pressure between the high-pressure port and the low-pressure port on the LFE. The absolute pressure was recorded from the high-pressure port of the differential measurement line. Calibration pressures were measured and recorded with a combined differential/absolute pressure meter. The handheld unit used two modules, one for absolute pressure, and one for differential pressure. The absolute pressure module was a capable of measuring 0-30 PSI absolute with an uncertainty of 0.025%. The differential pressure module was a capable of measuring from 0-10 inches of water with an uncertainty of 0.06%. The temperature of the gas sample was measured prior to the LFE using a K-Type thermocouple with an uncertainty of ±1.1 °C or 0.4%. The voltage output from the MAF was recorded via an analog data acquisition card. The flow rate was varied with a variable restrictor valve on the inlet of the blower. Calibrations were performed on the MAF for various flow rates, ranging up to 1500 SCFM.

As a constant flow rate of air passed through both the LFE and MAF, the pressure differential,

sample temperature, absolute pressure, and MAF voltage were recorded simultaneously. The pressure differential across the LFE, sample temperature, and absolute pressure were used to calculate the actual volumetric flow rate through the LFE using coefficients provided by the manufacturer. The actual volumetric flow rate was converted to standard volumetric flow. The standard volumetric flow rate through the LFE was related to the voltage obtained from the MAF, as shown in Figure 4.

[Place Figure 4 here]

A least-squares regression was performed on the data set to determine the best-fit coefficients of the equation and to calculate the equation's regression statistics, R^2, to examine correlation between the data sets. Once the equation was developed, to relate the MAF voltage to the flow rate through the LFE, a comparison was made between the actual flow rate and the measured flow rate of the MAF. This is shown in Figure 5.

[Place Figure 5 here]

The calibration of the methane sensor with a 24,730-ppm methane gas cylinder is shown in Figure 6. The average deviation from the actual methane concentration after the external correction was applied was 0.7%. The largest deviation from the actual methane concentration after the external correction was applied was 1.9%.

[Place Figure 6 here]

After the calibration curves had been obtained and applied, verification of the entire system was performed by completing a gas recovery test. In which a known mass of methane was injected into the system using a methane calibrated MFC and a comparison made between the mass indicated by the system to the true mass injected. This procedure was based on the common practice of propane injections required by the Code of Federal Regulations for ensuring the capture and measurement ability of full flow dilution tunnels where a known volume of hydrocarbon emission are injected into the measurement system using an independently calibrated device and the recovery ability of the system is verified. The controlling MFC was calibrated on methane. The MFC was set at two flow rates of 20 and 30 SLPM of 99.9% pure methane. The results are presented in Table 1 for a system flow rate of 140 SCFM. It was shown that in both cases the FFS system measured values were within the expected 4.4%. The average error in the two measurements was +2.2%.

[Place Table 1 here]

In Field Data Collection

Continuous Leak Source

Figure 6 illustrates an example of a continuous leak sources. Figure 7 can be divided into 4 separate regions, a-d. These include the following portions: background, approaching leak source, leak capture, and retreating from the leak source. Leak quantification occurs during section c. Upon review, the second repeated measurement of the same leak occurs after section d. Figure 8 shows the leak as viewed from infrared camera – the left shows the methane plume

dispersing naturally – the right shows that the FFS collects all of the leak plus additional dilution air.

[Place Figure 7 here]
[Place Figure 8 here]

Intermittent Leak Source
The total mass associated with a certain event was obtained from the concentration-time profile through the application of numerical integration. In order to circumvent some of the inefficiencies associated with the trapezoidal rule, an adaptive composite Simpson's rule was employed. This adaptive quadrature type method allows for automatic step size adjustments in regions of sharp variations [73].

The need for numerical integration of the collected data was applicable for intermittent events, such as Figure 9 illustrates an example of an intermittent source of methane emissions. This example was for a vehicle-refueling event. Background is shown from 150-240 seconds and from 425 seconds until the end. This particular event was for the refueling of a single liquefied natural gas (LNG) tank. The leak rate was integrated to determine the total mass emitted (9.5 grams).

[Place Figure 9 here]

Aggregated Source
Due to multiple sources being in tight proximity and enclosed by a covering, the compressor unit was aggregated and treated as a single source for leak quantification. Figure 10 shows an example of measuring the methane emissions from an aggregated source. These data were collected from a time-fill CNG compressor housing. The compressor housing was measured continuously for approximately 119 minutes. The compressor unit encountered did display a small amount of variability. Variations in leak rate and methane concentration were due to pressure fluctuations and variable leaks from compressor seals. For aggregated sources, data were collected for extended periods and the average leak rate was calculated.

[Place Figure 10 here]

Figure 1 Fugitive Methane Emissions. Published averaged fugitive methane emissions emitted as a percent of total natural gas production [13, 27, 40-59].

Figure 2 FFS Schematic and Image. Left - FFS schematic and right - portable FFS during Compressed Natural Gas (CNG) station audit.

Figure 3 Detection and Quantification Program Overview. Brief overview of the steps and user prompts for calibrations, recovery tests, and leak quantification.

Figure 4 MAF Output Signal Calibration. Multipoint calibration of the MAF with a NIST traceable LFE (see Sections 1 to 1.7).

Figure 5 MAF Flow Rate Correlation. MAF measured flow rate plotted against the LFE actual volumetric flow rate (see Sections 1.8).

Figure 6 Methane Sensor Calibration/Verification. External verification of the methane sensor using a calibrated gas divided and NIST traceable bottled methane (see Section 2).

Figure 7 Conventional Continuous Leak. Continuous leak source time trace showing the various measurement sections (a: background, b: approaching the leak, c: average leak rate, d: retreating from leak) (see Sections 5 – 5.6).

Figure 8 Infrared Image of Leak. Left - leaking fitting and right - captured/quantified leak from the same fitting (see Section 4.6).

Figure 9 Intermittent Leak. Intermittent 'leak' source from a vehicle-refueling event (concentration [ppm], dilution flow rate [scfm], leak rate [g/hr]) (see Section 5).

Figure 10 Aggregate Example. Leak rate, flow, and concentration data from an aggregated time fill CNG compressor housing (compressors and fans off) (see Section 5.7).

Table 1 FFS Recovery Results. Methane recovery tests and two different simulated leak rates.

Table 2 Component Uncertainty. Independent component uncertainties used to quantify system uncertainty.

DISCUSSION:

In order to improve accuracy and overcome current industry limitations, we created the Full Flow Sampling System (FFS) for methane quantification. Researchers used the system in a variety of forms in numerous locations across North America. Use of spectroscopy eliminates significant interference from C2+ compounds and the non-destructive sampling nature allows for bag sampling of the leak for alternative analysis offsite. When combined with alternative wind blocks the system has successfully and accurately quantified methane emissions from the following items: CNG fuel systems, LNG fuel systems, internal combustion engine crankcases, piping, tubing, connectors, flanges, compressor vents, well head components, water/oil separator tanks, valve, pneumatic actuators driven by natural gas, well casings, and numerous other natural gas related components. System platforms included portable carts, on-road, and off-road vehicles. Power consumption does require the use of a generator or house power through standard 120 VAC connections. However, through this use of 'grid' power the system can sample at higher flow rates yet still be used in conjunction with extension cords and long sampling houses for portability around a given site of interest. Current battery powered systems have decreased performance as a function of battery state of charge which is eliminated using grid power.

Periodic calibrations protocols have been developed and integrated into the user-interface. Protocols 1-3 should be completed prior to any new site audit or at a minimum on a monthly basis. If users do not diligently follow the protocols, the system may under or over-report emissions rates, which could negatively affect GHG reporting. The primary goal of the protocols

is to ensure an accurate system to estimate total site emissions with component granularity. If statistical analysis are used to create new emissions factors, then each non-leaking component must also be recorded.

The leak detection process can be time consuming with the use of handheld units. The use of an optical gas-imaging camera can significantly reduce the time required for leak detect. The camera must be capable of measuring volatile organic compounds including methane. Currently available commercial units have sensitivities on detectable leak rates of approximately 0.8 grams per hour (g/h) and are dependent upon wind conditions. Imaging devices are also sensitive to temperature. Be sure to adjust temperature scales as necessary. Extremely cold vapors (cryogenic natural gas) or superheated vapors (steam in exhausts and others) can appear as excessive leaks. Subsequent quantification must follow to determine accurately the actual leak rate of any imaged leak. Use of infrared cameras can significantly reduce leak detection inventories, but are sensitive to wind conditions. Smaller leaks under high wind conditions could diffuse more rapidly and not be spotted. When in doubt, always double check with a hand held methane detector.

A user-friendly interface ensures easy and proper use of the FFS. Integrated user prompts assist the user along the Protocol and reduce post-processing efforts. For example, once a leak quantification is completed (Section 5), the average leak rate based on calculations using at least 30 seconds of continuous concentration and flow rate recordings will be reported. User prompts will automatically use global or local background concentrations. Simple on-screen selection will cause solenoids to operate and sample for the correct locations. Users should follow all on-screen prompts to ensure accurate quantification of the leak. The program will automatically correct for the following: global or local background; temperature; mass flow rate (assumed air with carbon dioxide and methane corrections); humidity (measured from the GHG sensor); temperature (thermocouple – redundant check for ambient conditions)

The relative uncertainty of measured methane emissions rates is ±4.4% except in circumstances where the leak is inconsequential as the concentration measured approached background concentration. An example of component uncertainties is provided in Table 2.

[Place Table 2 here]

Overall, the system and its methods have proven beneficial in efforts to quantify accurately the methane emissions from various sources. The system is scalable and user friendly. The developed system has an uncertainty of ±4.4% compared to current commercial systems with an uncertainty of ±10% [74]. With proper calibrations, this system can easily quantify leak rates up to 140 SCFM compared to current commercial systems that are capable of quantifying leaks up to 8 SCFM with full battery charges [64,74]. While the system requires connection to house power, this offers advantages of consistent sample rates and sample rates much higher than current systems. The minimum detection limit of the current system is 0.24 g/hr or 3.0×10^{-3} SCFM. The user interface reduces post-processing requirements and reduces reporting efforts. In addition, the laser-based sensors are non-destructive to the leak sample, which allows for direct measurement of the sample with multiple analyzers [65]. Laser based measurements also do not require separate sensors for ambient, small, and large leak concentrations or sensor transitions, which contribute

to additional sources of inaccuracy. Future studies focus on continued optimization of the FFS and its user interface. Additional research is being conducted which combines experimental research data and computation fluid dynamics to develop additional best practices to ensure consistent and optimal measurement techniques.

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DISCLOSURES:
The authors, along with Mr. Christopher Rowe and Mr. Zachary Luzader have filed invention disclosures and provisional patents with West Virginia University's Research Corporation and Office of Technology Transfer to protect the intellectual property associated with this system.

REFERENCES:
1. Intergovernmental Panel on Climate Change. 2006 IPCC Guidelines for National Greenhouse Gas Inventories (2006).
2. Hansen, J., *et al*. Climate impact of increasing atmospheric carbon dioxide. *Science.* **213** (4511), 957-966, doi: 10.1126/science.213.4511.957 (1981).
3. Ramanathan, V., Feng, Y. Air pollution, greenhouse gases and climate change: Global and regional perspectives. *Atmos. Environ.* **43** (1), 37-50 doi: 10.1016/j.atmosenv.2008.09.063 (2009).
4. Sims, R. Renewable energy: a response to climate change. *Sol. Ener.* **76** (1), 9-17 doi: 10.1016/S0038-092X(03)00101-4 (2004).
5. Rasmussen, R., Khalil, M. Atmospheric methane in the recent and ancient atmospheres: concentrations, trends, and interhemispheric gradient. *J. Geophys. Res.* **89** (D7), 11599-11605 doi: 10.1029/JD089iD07p11599 (1984).
6. Rasmussen, R., Khalil, M. Atmospheric methane (CH4): Trends and seasonal cycles. *J.Geophys.Res.* **86** (C10), 9826-9832 doi: 10.1029/JC086iC10p09826 (1981).
7. Etheridge, D., Steele, L., Francey, R., Langenfelds, R. Atmospheric methane between 1000 AD and present: Evidence of anthropogenic emissions and climatic variability. *J. Geophys. Res.* **103** (D13), 15979-15993 doi: 10.1029/98JD00923 (1998).
8. Mosier, A. Soil processes and global change. *Biol. Fert. Soils.* **27** (3), 221-229 doi: 10.1007/s003740050424 (1998).
9. Shine, K.P., Fuglestvedt, J.S., Hailemariam, K., Stuber, N. Alternatives to the global warming potential for comparing climate impacts of emissions of greenhouse gases. *Clim. Chang.* **68** (3), 281-302 doi: 10.1007/s10584-005-1146-9 (2005).
10. Kruger, D., Franklin, P. The Methane to Markets Partnership: Opportunities for coal mine methane utilization. *11th U.S./North American Mine Ventilation Symposium.* 3-8 doi: 10.1201/9781439833391.ch1 (2006).
11. U.S. Environmental Protection Agency. Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2013. *EPA 430-R-15-004 (*2015).
12. Alvarez, R.A., Pacala, S.W., Winebrake, J.J., Chameides, W.L., Hamburg, S.P. Greater focus

needed on methane leakage from natural gas infrastructure. *Proc. Natl. Acad. Sci.* **109** (17), 6435-6440 doi: 10.1073/pnas.1202407109 (2012).
13. Pétron, G., *et al*. A new look at methane and nonmethane hydrocarbon emissions from oil and natural gas operations in the Colorado Denver-Julesburg Basin. *J. Geophys. Res.* **119** (11), 6836-6852 doi: 10.1002/2013JD021272 (2014).
14. Natural Resources Defense Council. Leaking Profits: the U.S. Oil and Gas Industry can Reduce Pollution, Conserve Resources, and Make Money by Preventing Methane Waste. (2012). http://www.nrdc.org/energy/files/Leaking-Profits-Report.pdf
15. Marano, J.J., Ciferno, J.P. Life-cycle greenhouse-gas emissions inventory for Fischer-Tropsch fuels. *Report Prepared for the US Department of Energy, Energy and Environmental Solution, LLC, Gaithersburg, MD, USA (*2001).
16. Venkatesh, A., Jaramillo, P., Griffin, W.M., Matthews, H.S. Uncertainty in life cycle greenhouse gas emissions from United States natural gas end-uses and its effects on policy. *Environ. Sci. Technol.* **45** (19), 8182-8189 doi: 10.1021/es200930h (2011).
17. Hostage, B., Perry, G. Federal notification requirements for releases of oil and hazardous substances. *International. Oil. Spill. Conference. Proceedings (*1), 631-634 doi: 10.7901/2169-3358-1993-1-631 (1993).
18. Fujita, E.M., Campbell, D.E. Review of Current Air Monitoring Capabilities near Refineries in the San Francisco Bay Area, *Desert Research Institute* (2013).
19. Bradbury, J., Obeiter, M., Draucker, L., Wang, W., Stevens, A. Clearing the air: Reducing upstream greenhouse gas emissions from US natural gas systems. *Washington, DC: World Resources Institute (*2013).
20. ICF International. Economic Analysis of Methane Emission Reduction Opportunities in the U.S. Onshore Oil and Natural Gas Industries (2014). https://www.edf.org/sites/default/files/methane_cost_curve_report.pdf
21. U.S. Environmental Protection Agency. Inventory of US Greenhouse Gas Emissions and Sinks: 1990-2012 (2014).
22. Brandt, A.R., *et al*. Energy and environment. Methane leaks from North American natural gas systems. *Science.* **343** (6172), 733-735, doi:10.1126/science.1247045 (2014).
23. Allen, D.T., *et al*. Measurements of methane emissions at natural gas production sites in the United States. *Proc. Natl. Acad. Sci.* **110** (44), 17768-17773, doi:10.1073/pnas.1304880110 (2013).
24. Shorter, J.H., *et al*. Collection of leakage statistics in the natural gas system by tracer methods. *Environ. Sci. Technol.* **31** (7), 2012-2019 doi: 10.1021/es9608095 (1997).
25. Alvarez, R.A., Pacala, S.W., Winebrake, J.J., Chameides, W.L., Hamburg, S.P. Greater focus needed on methane leakage from natural gas infrastructure. *Proc. Natl. Acad. Sci.* **109** (17), 6435-6440, doi:10.1073/pnas.1202407109 (2012).
26. Kirchgessner, D.A., Lott, R.A., Michael Cowgill, R., Harrison, M.R., Shires, T.M. Estimate of methane emissions from the U.S. natural gas industry. *Chemosphere.* **35**, 1365–1390 **DOI:** http://dx.doi.org/10.1016/S0045-6535(97)00236-1 (1997).
27. Howarth, R.W., Santoro, R., Ingraffea, A. Methane and the greenhouse-gas footprint of natural gas from shale formations. *Clim. Chang.* **106** (4), 679-690 doi:10.1007/s10584-011-0061-5 (2011).
28. Harrison, M.R., Shires, T.M., Wessels, J.K., Cowgill, R. Methane emissions from the natural gas industry. *US Environmental Protection Agency*, National Risk Management Research Laboratory (1996).

29. Mix, P.E. Introduction to nondestructive testing: a training guide. John Wiley & Sons (2005).
30. Murvay, P., Silea, I. A survey on gas leak detection and localization techniques. *J. Loss. Prev Process. Ind.* **25** (6), 966-973 doi: 10.1016/j.jlp.2012.05.010 (2012).
31. Chambers, A. Optical Measurement Technology for Fugitive Emissions from Upstream Oil and Gas Facilities (ARC Contract Report No. CEM e P004. 03). *CAPP, Calgary, AB (*2004).
32. Epperson, D., Barbour, W., Zarate, M., Beauregard, D. Preferred and Alternative Methods for Estimating Fugitive Emissions from Equipment Leaks (Technical Report for Point Sources Committee, Emission Inventory Improvement Program) (1996).
33. Shorter, J.H., *et al*. Results of tracer measurements of methane emissions from natural gas system facilities (1995).
34. Folga, S.M. Natural gas pipeline technology overview. *ANL/EVS/TM/08-5* (2007).
35. Bousquet, P., *et al*. Contribution of anthropogenic and natural sources to atmospheric methane variability. *Nature.* **443** (7110), 439-443 doi: 10.1038/nature05132 (2006).
36. Howarth, R.W., Santoro, R., Ingraffea, A. Methane and the greenhouse-gas footprint of natural gas from shale formations. *Clim. Chang.* **106** (4), 679-690 doi:10.1007/s10584-011-0061-5 (2011).
37. Kirchgessner, D.A., Lott, R.A., Michael Cowgill, R., Harrison, M.R. & Shires, T.M. Estimate of methane emissions from the U.S. natural gas industry. *Chemosphere.* **35**, 1365–1390 doi: http://dx.doi.org/10.1016/S0045-6535(97)00236-1 (1997).
38. Brandt, A., *et al*. Methane leaks from North American natural gas systems. *Science.* **343** (6172), 733-735 doi: 10.1126/science.1247045 (2014).
39. Wigley, T.M. Coal to gas: the influence of methane leakage. *Clim. Chang.* **108** (3), 601-608 doi: 10.1007/s10584-011-0217-3 (2011).
40. Weber, C.L., Clavin, C. Life cycle carbon footprint of shale gas: Review of evidence and implications. *Environ. Sci. Technol.* **46** (11), 5688-5695 doi: 10.1021/es300375n (2012).
41. Lelieveld, J., *et al*. Greenhouse gases: Low methane leakage from gas pipelines. *Nature.* **434** (7035), 841-842 doi: 10.1038/434841a (2005).
42. Percival, P. *Update on "lost and unaccounted for" natural gas in Texas. Basin Oil and Gas. 32* (2010).
43. Hayhoe, K., Kheshgi, H.S., Jain, A.K., Wuebbles, D.J. Substitution of natural gas for coal: climatic effects of utility sector emissions. *Clim. Chang.* 54 (1-2), 107-139 doi:10.1023/A:1015737505552 (2002).
44. Karion, A., *et al*. Methane emissions estimate from airborne measurements over a western United States natural gas field. *Geophys. Res. Lett.* **40** (16), 4393-4397 doi: 10.1002/grl.50811 (2013).
45. Peischl, J., *et al*. Quantifying sources of methane using light alkanes in the Los Angeles basin, California. *J. Geophys. Res.* **118** (10), 4974-4990 doi: 10.1002/jgrd.50413 (2013).
46. Mitchell, C., Sweet, J., Jackson, T. A study of leakage from the UK natural gas distribution system. *Energy Policy.* **18** (9), 809-818 doi: http://EconPapers.repec.org/RePEc:eee:enepol:v:18:y:1990:i:9:p:809-818 (1990).
47. Stephenson, T., Valle, J.E. & Riera-Palou, X. Modeling the relative GHG emissions of conventional and shale gas production. *Environ. Sci. Technol.* **45** (24), 10757-10764 doi: 10.1021/es2024115 (2011).
48. O'Sullivan, F., Paltsev, S. Shale gas production: potential versus actual greenhouse gas emissions. *Environ. Res. Let.* **7** (4), 044030 doi:10.1088/1748-9326/7/4/044030 (2012).
49. Cathles, L.M., Brown, L., Taam, M., Hunter, A. A commentary on "The greenhouse-gas

footprint of natural gas in shale formations" by RW Howarth, R. Santoro, and Anthony Ingraffea. *Clim.Chang.* **113** (2), 525-535 doi:10.1007/s10584-011-0333-0 (2012).
50. Burnham, A., Han, J., Clark, C.E., Wang, M., Dunn, J.B., Palou-Rivera, I. Life-cycle greenhouse gas emissions of shale gas, natural gas, coal, and petroleum. *Environ. Sci. Technol.* **46** (2), 619-627 doi: 10.1021/es201942m (2011).
51. Jiang, M., Griffin, W.M., Hendrickson, C., Jaramillo, P., VanBriesen, J., Venkatesh, A. Life cycle greenhouse gas emissions of Marcellus shale gas. *Environ. Res. Lett.* **6** (3), 034014 doi:10.1088/1748-9326/6/3/034014 (2011).
52. Hultman, N., Rebois, D., Scholten, M., Ramig, C. The greenhouse impact of unconventional gas for electricity generation. *Environ. Res. Lett.* **6** (4), 044008 doi:10.1088/1748-9326/6/4/049504 (2011).
53. Miller, S.M., *et al*. Anthropogenic emissions of methane in the United States. *Proc. Natl. Acad. Sci.* **110** (50), 20018-20022, doi:10.1073/pnas.1314392110 (2013).
54. Tollefson, J. Methane leaks erode green credentials of natural gas. *Nature.* **493** (7430), 12, doi:10.1038/493012a (2013).
55. Skone, T.J., Engineer, P.S. Role of alternative energy sources: Natural gas technology assessment. *NETL Office of Strategic Energy Analysis and Planning (*2012).
56. U.S. Environmental Protection Agency. Inventory of US Greenhouse Gas Emissions and Sinks: 1990-2009 (2011).
57. US EPA. Inventory of US Greenhouse Gas Emissions and Sinks: 1990-2010 (EPA 430-R-12-001) (2012).
58. U.S. Environmental Protection Agency. Inventory of US Greenhouse Gas Emissions and Sinks: 1990-2012 (2014).
59. Pétron, G., *et al*. Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study. *J. Geophys. Res.(1984–2012).* **117** (D4) doi:10.1029/2011JD016360 (2012).
60. U.S. Environmental Protection Agency Natural Gas STAR Program. Lessons Learned – Directed Inspection and Maintenance at Gate Stations and Surface Facilities (2003).
61. Picard, D., Stribrny, M. & Harrison, M. Handbook For Estimating Methane Emissions From Canadian Natural Gas Systems (1998).
62. Johnson, K., Huyler, M., Westberg, H., Lamb, B., Zimmerman, P. Measurement of methane emissions from ruminant livestock using a sulfur hexafluoride tracer technique. *Environ.Sci.Technol.* **282**, 359-362 (1994).
63. Shorter, J.H., *et al*. Results of tracer measurements of methane emissions from natural gas system facilities (1995).
64. Howard, H.M. *High flow rate sampler for measuring emissions at process components,* US Patent US5563335A *(*1996).
65. Howard, T., Ferrara, T.W., Townsend-Small, A. Sensor transition failure in the high flow sampler: Implications for methane emission inventories of natural gas infrastructure. *J.Air Waste Manage.Assoc.* **67**, 852-862 doi:10.1080/10962247.2015.1025925 (2015).
66. Wu, Y., Carder, D., Shade, B., Atkinson, R., Clark, N., Gautam, M. A CFR1065-Compliant Transportable/On-Road Low Emissions Measurement Laboratory with Dual Primary Full-Flow Dilution Tunnels, *ASME,* doi:10.1115/ICES2009-76090 (2009).
67. Clark, N.N., Gajendran, P., Kern, J.M. A predictive tool for emissions from heavy-duty diesel vehicles. *Environ. Sci. Technol.* **37** (1), 7-15 doi: 10.1021/es0113192 (2003).
68. Bata, R., *et al*. The first transportable heavy duty vehicle emissions testing laboratory. *SAE.* doi: 10.4271/912668 (1991).

69. http://www.lgrinc.com/documents/LGR_Ultraportable_GGA_Datasheet.pdf
70. Johnson, D., Covington, A., Clark, N. Environmental and Economic Assessment of Leak and Loss Audits at Natural Gas Compressor and Storage Facilities. *Energy Technology*. **2** (12), 1027-1032 doi: 10.1002/ente.201402086 (2014).
71. Johnson, D., Covington, A. Potential Reduction of Fugitive Methane Emissions at Compressor Stations and Storage Facilities Powered by Natural Gas Engines. *ASME*. doi:10.1115/IMECE2014-38582 (2014).
72. Johnson, D., Covington, A., Clark, N. Methane Emissions from Leak and Loss Audits of Natural Gas Compressor Stations and Storage Facilities," *Environ. Sci. Technol.* **49** (13), 8132-8138; doi:10.1021/es506163m (2015).
73. Davis, J. Methods of numerical integration. Courier Dover Publications (2007).
74. HI FLOW Sampler Operation and Maintenance, http://www.mybacharach.com/wp-content/uploads/2015/08/0055-9017-Rev-7.pdf (2015).

Figure

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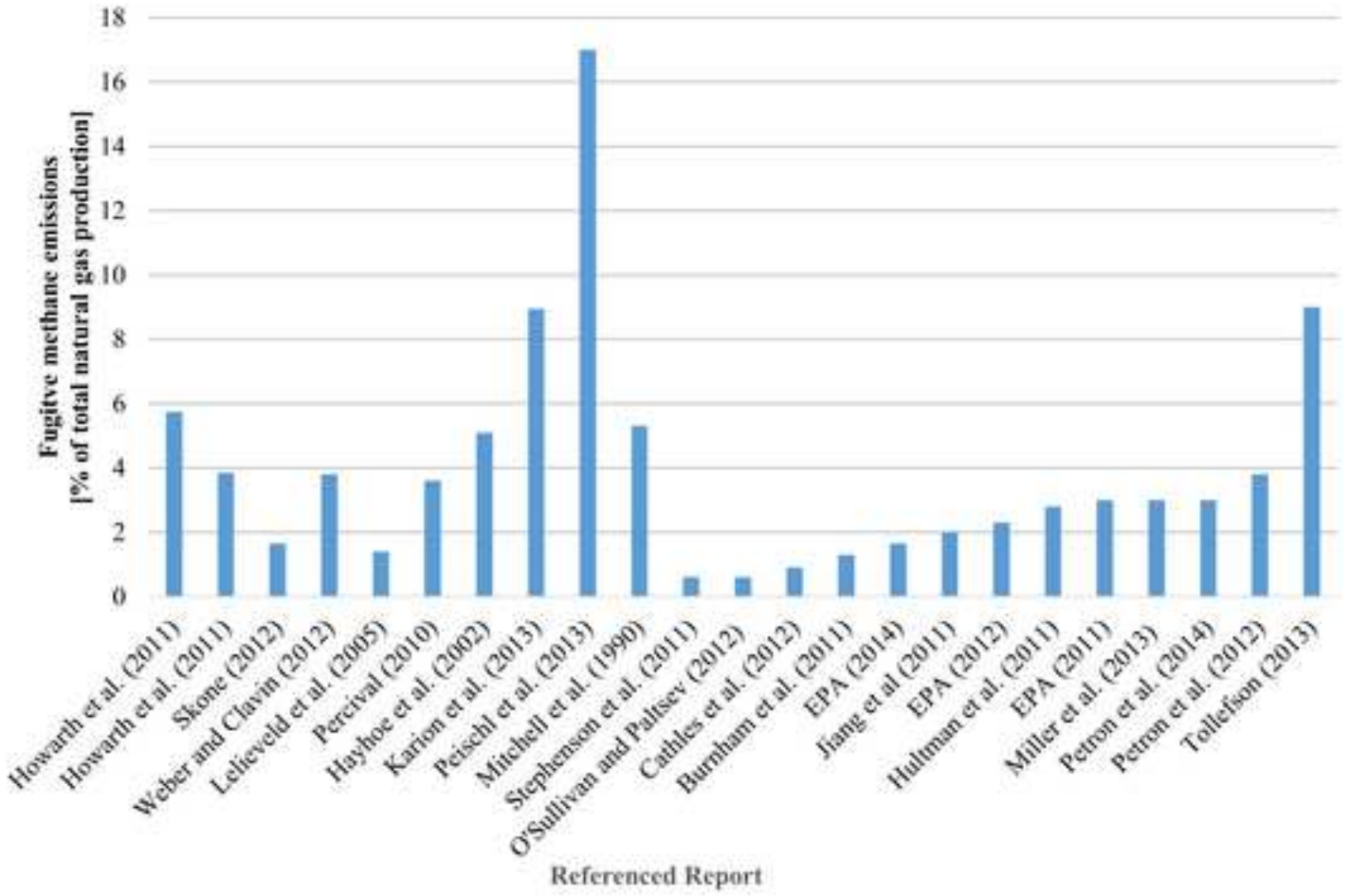

Figure 2

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Figure 3

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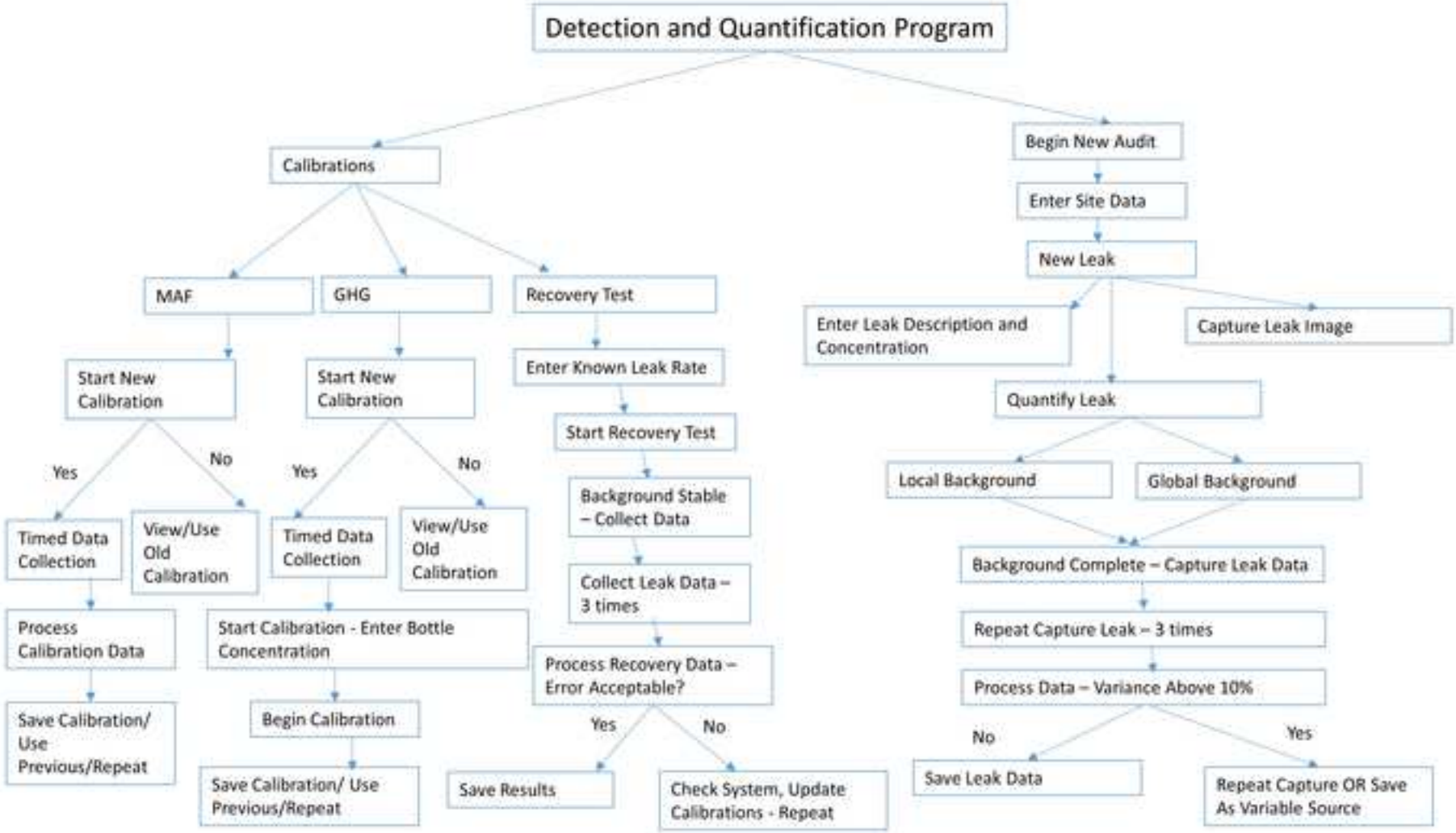

Figure 4

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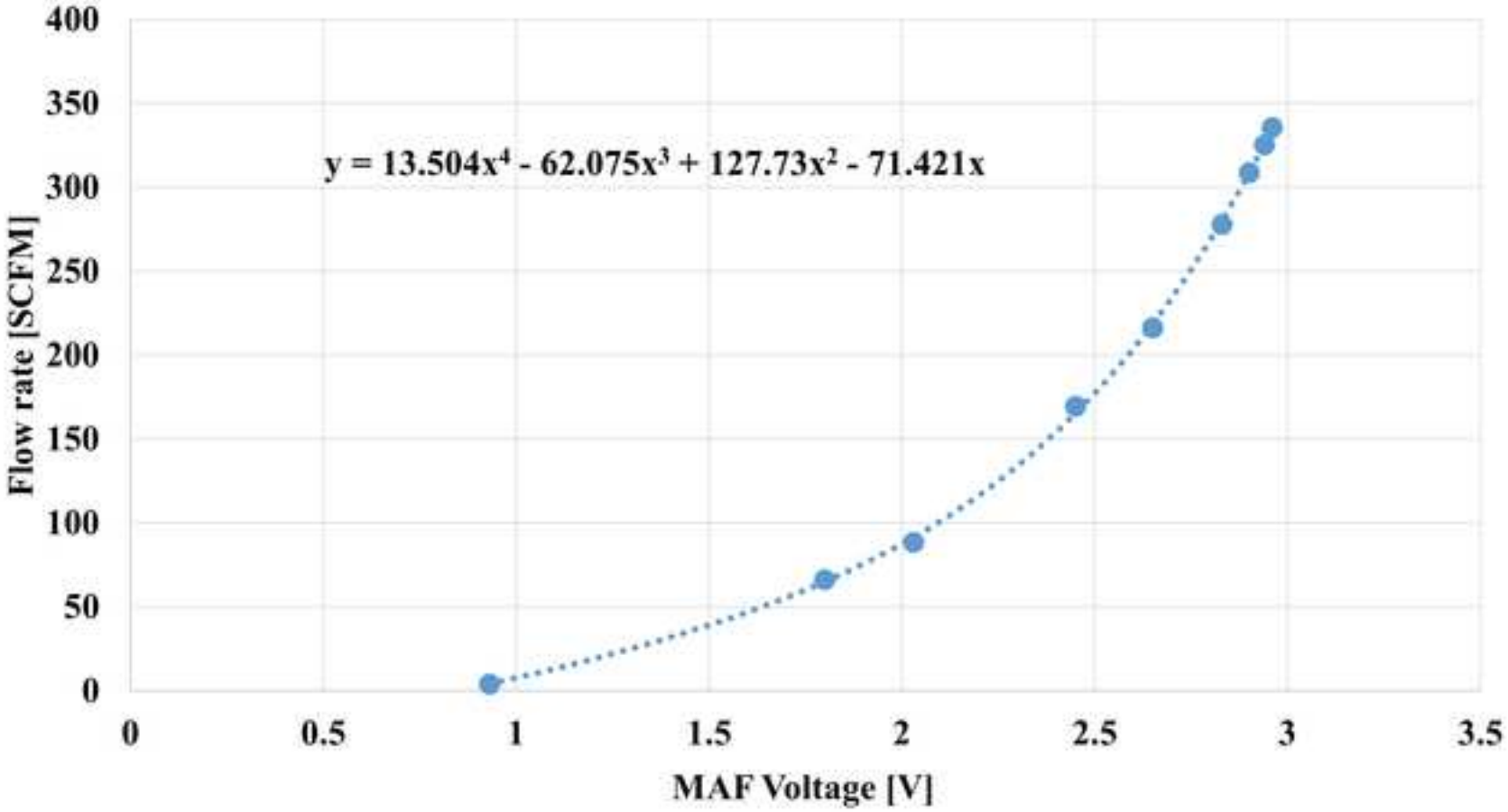

Figure 5

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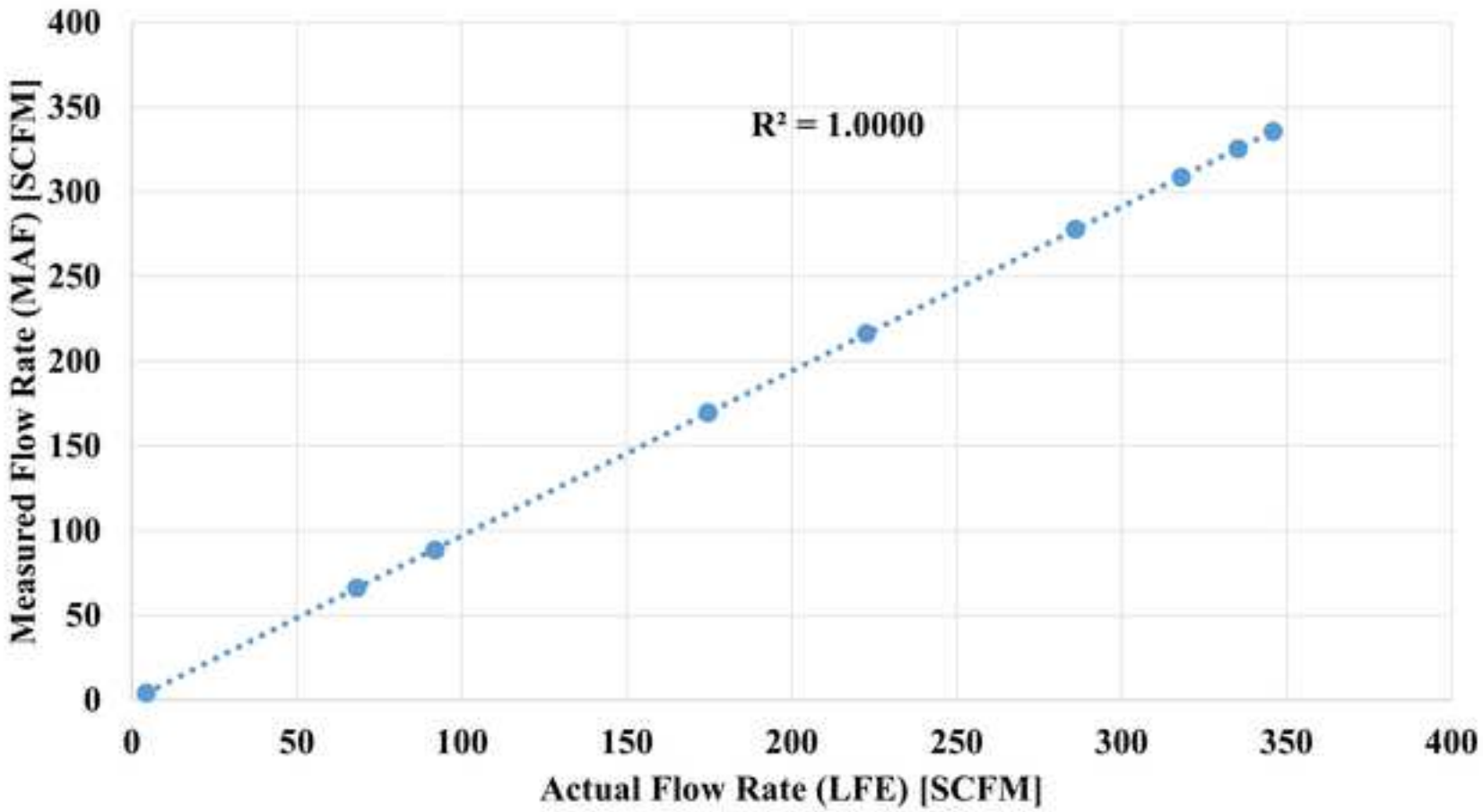

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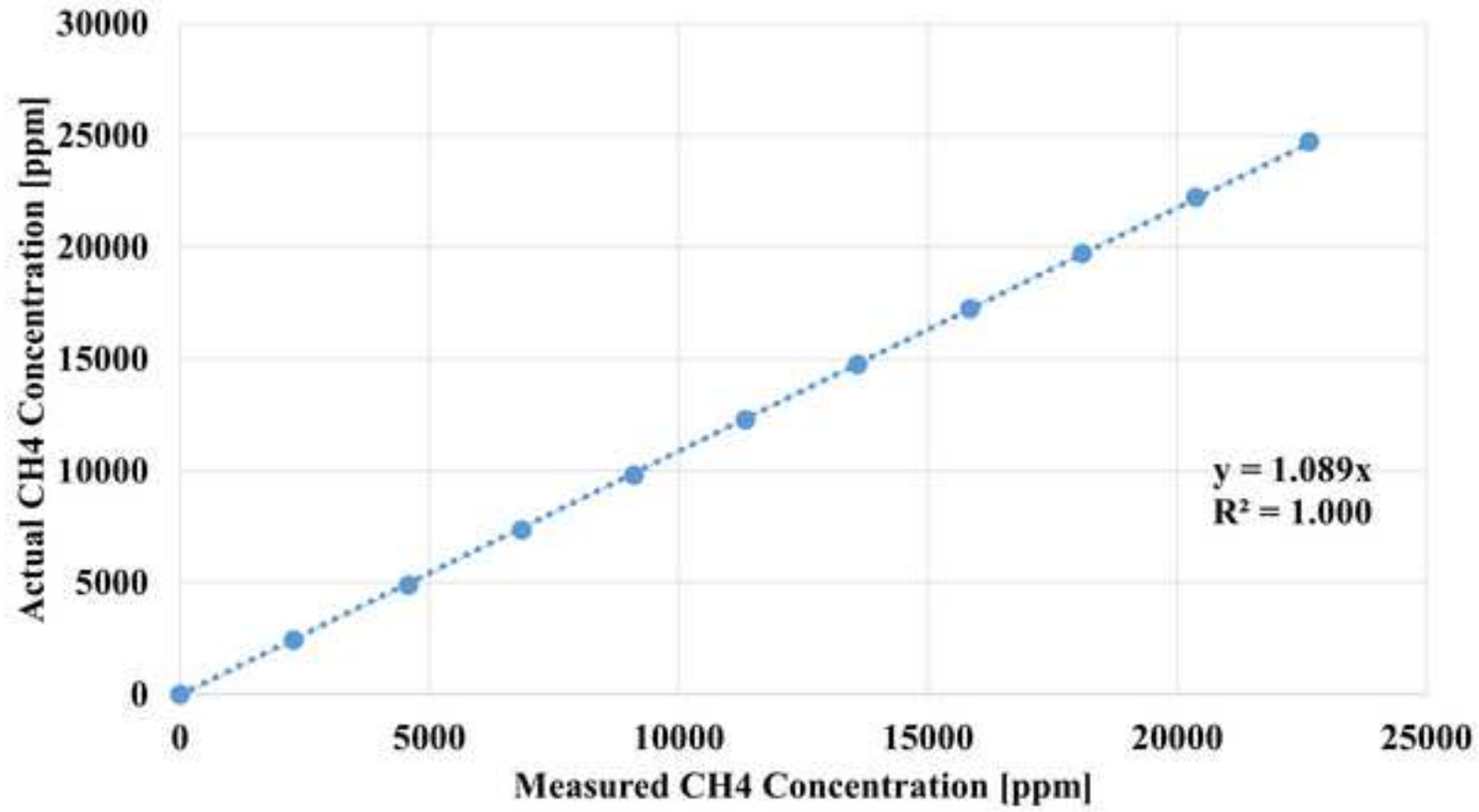

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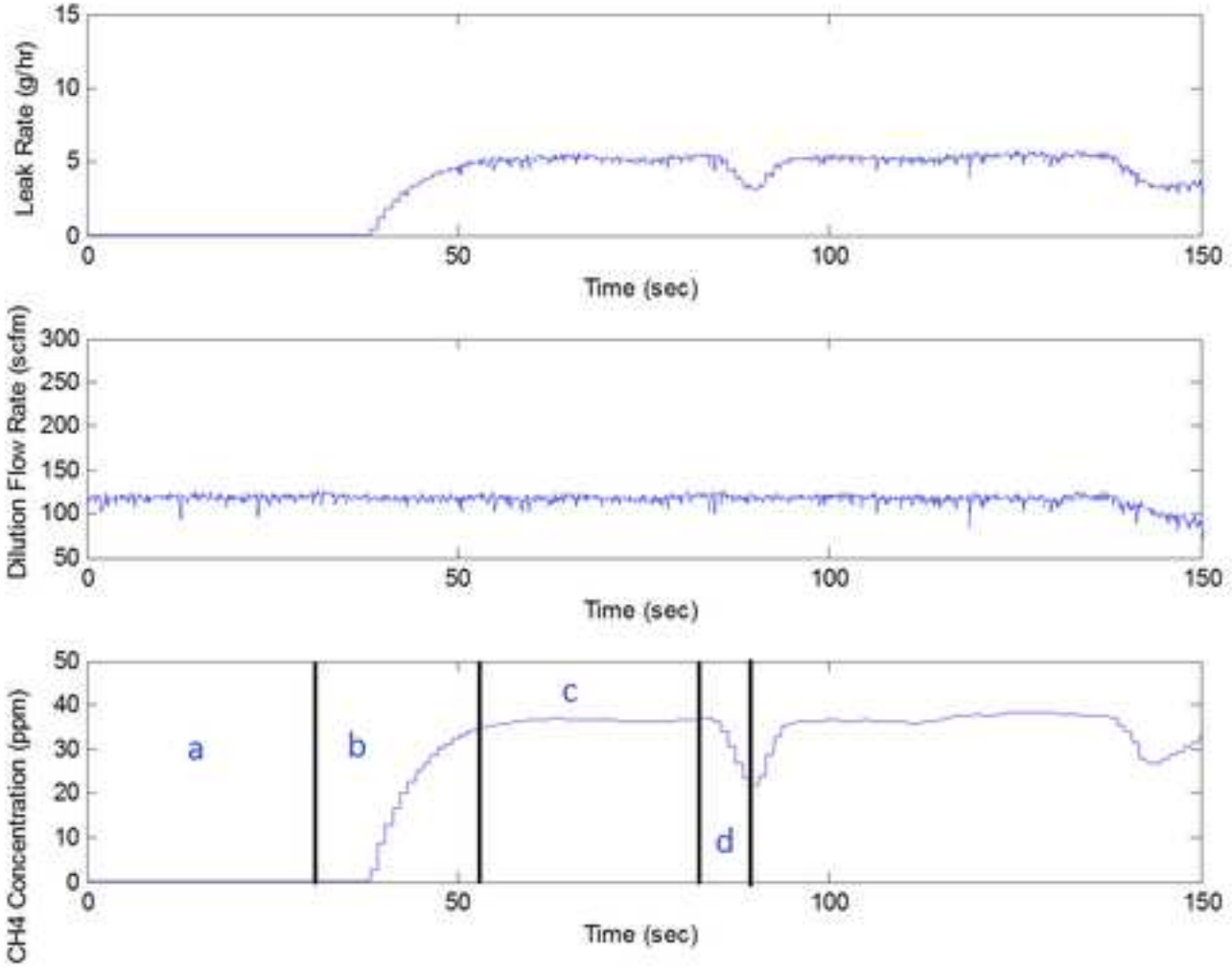

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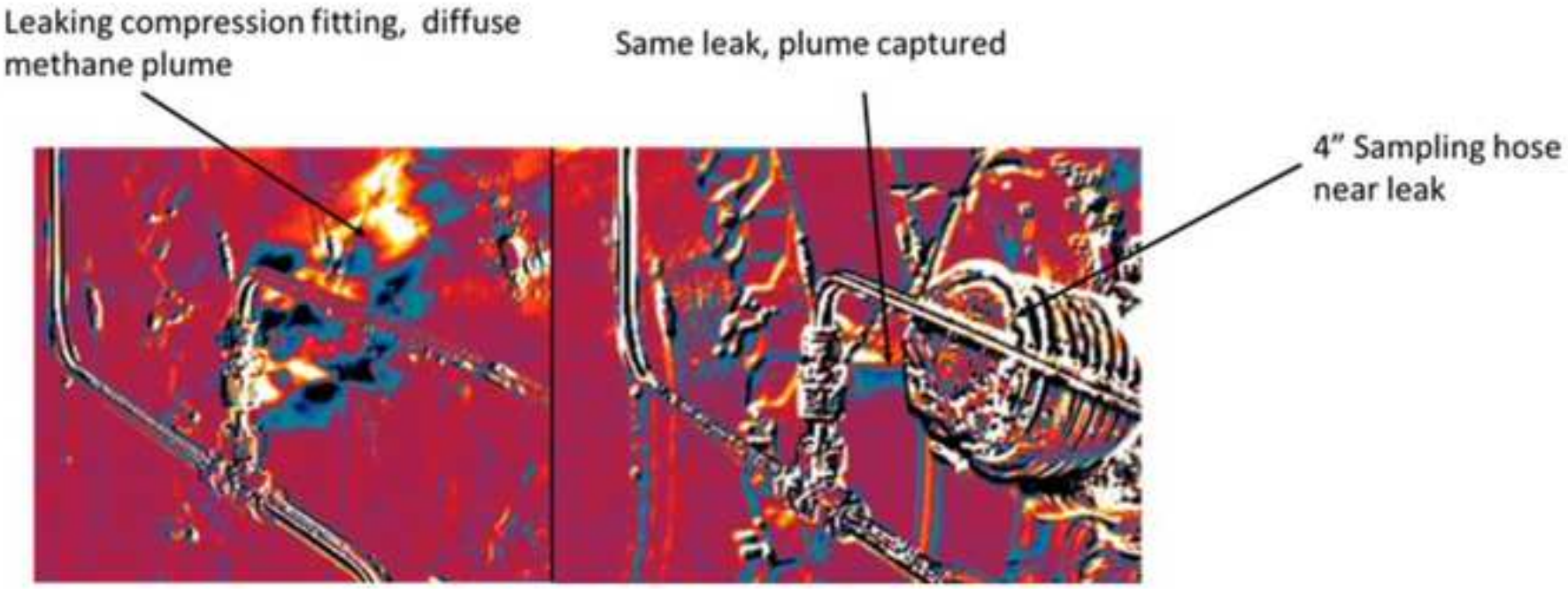

Figure 9

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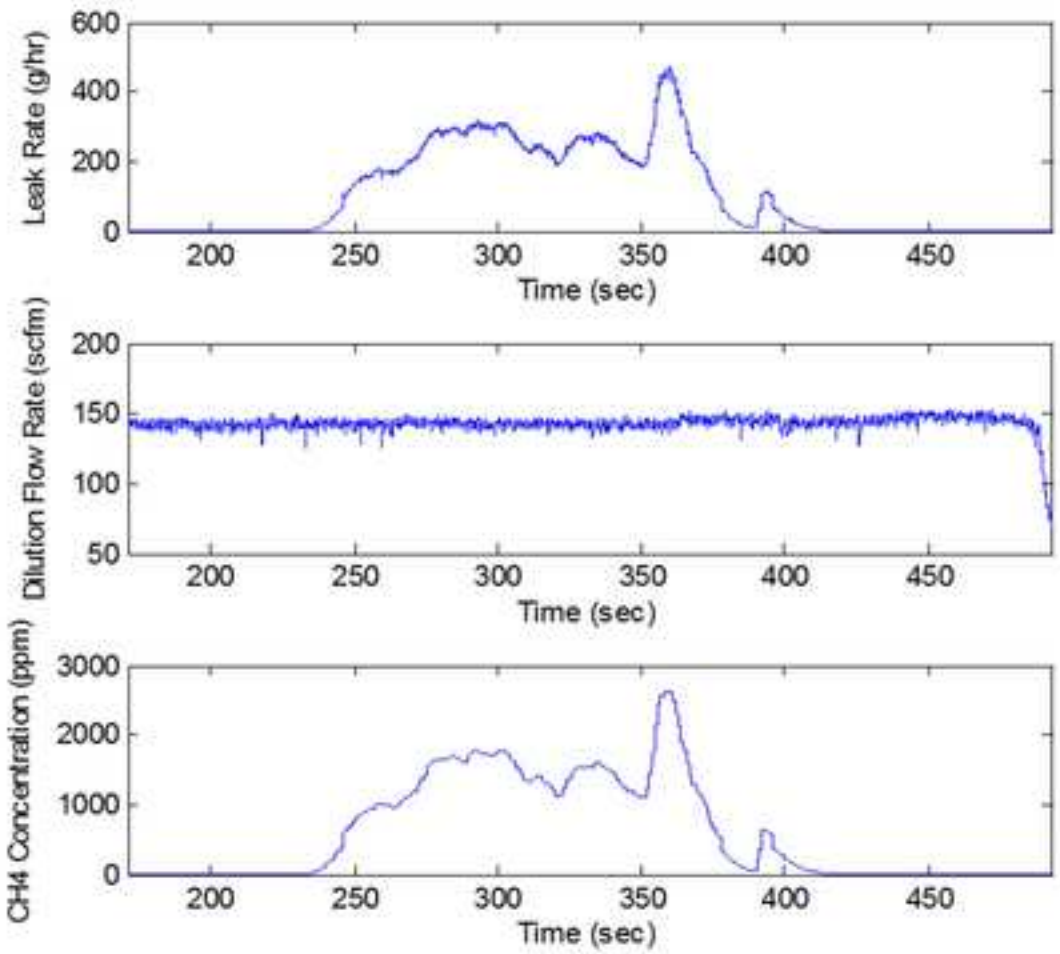

Figure 10

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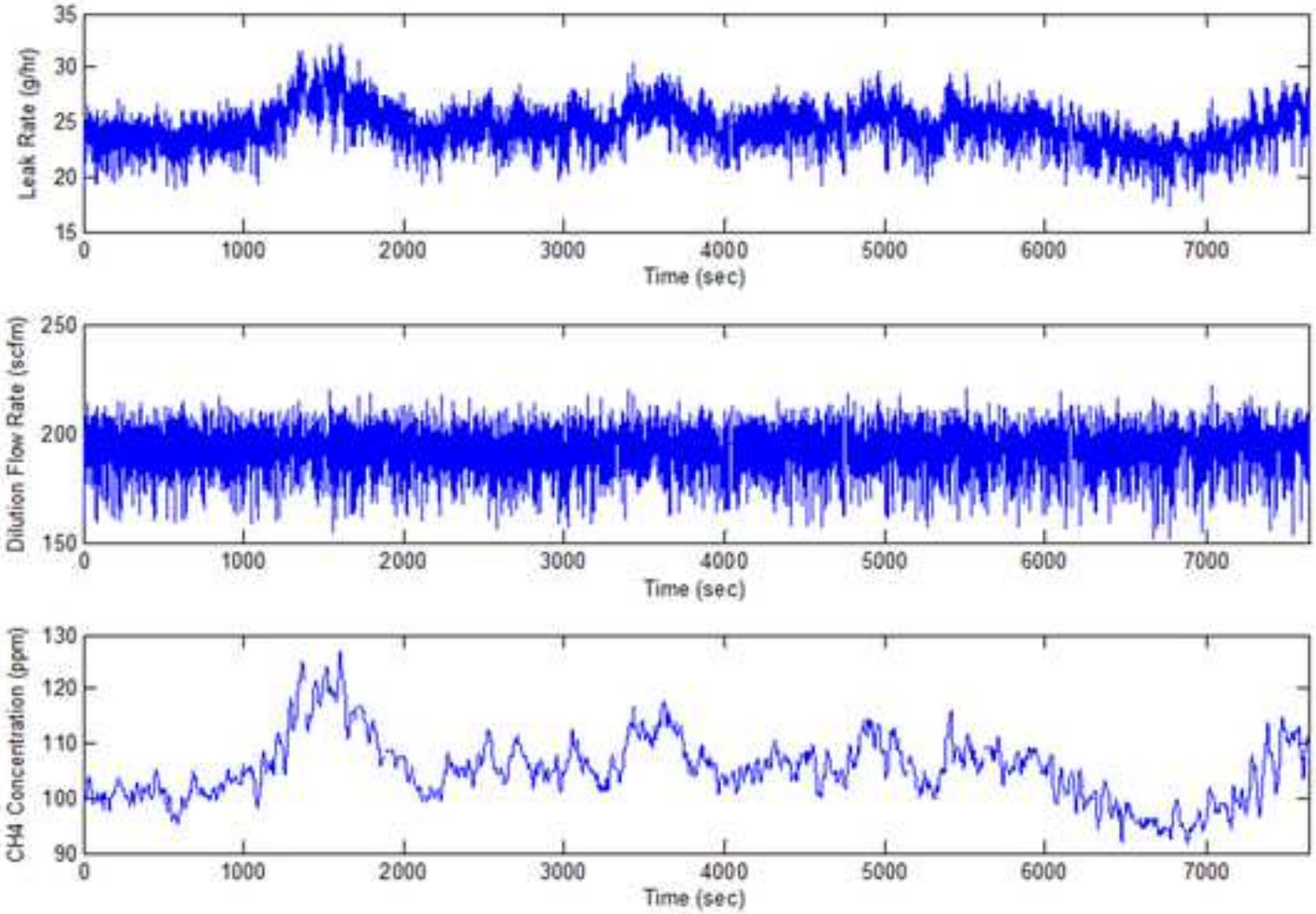

Table 1

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MFC Setpoint	FFS Recovery	Recovery Error
SLPM	SLPM	%
20	20.3	1.70%
30	30.8	2.7
Average		2.20%

Table 2

Source	Uncertainty (%)
Methane Sensor	1
Methane sensor calibration correlation	0.73
Methane gas bottle	1
Zero air gas bottle	0.1
LFE	0.7
MAF	4
Differential pressure module	0.025
Absolute pressure module	0.06
Thermocouple	0.4
MAF calibration correlation	0.09
Gas divider	0.5

Name of Reagent/ Equipment	Company	Catalog Number
Abaco DBX 97 mm	Abaco Performance, LLC	http://www.abacoperformance.com/products.htm
Ultraportable Greenhouse Gas Analyzer	Los Gatos Research	http://www.lgrinc.com/analyzers/ultraportable-greenhouse-gas-analyzer/
3AA20 Fume Exhauster	Daytona	http://www.sustainablesupply.com/Dayton-3AA20-Exhauster-Fume-Smoke-p/w267066.htm?gclid=CI2Dm9ffrcgCFUYTHwodyusFRg&CAWELAID=1307486526
Eagle II	RKI Instruments	http://www.rkiinstruments.com/pdf/eagle2brochure.pdf
MCR 50	Alicat Scientific	http://www.alicat.com/
Laminar Flow Element, Model Number: Z50MC2-6, Serial Number 707230-Y1	Meriam	http://www.meriam.com/product-category/laminar-flow-element/
K-Type thermocouple	Omega	http://www.omega.com/

PTE-1 Calibrator	Heise	http://www.heise.com/products/calibrators/
Model HQS-2	Dresser/Ashcroft	http://www.ashcroft.eu/download/data%20sheet/english/MODULE_E.pdf
Model HQS-1	Dresser/Ashcroft	http://www.ashcroft.eu/download/data%20sheet/english/MODULE_E.pdf
Gas Divider - SGD-710C	Horiba	http://www.horiba.com/us/en/
Methane (99.9%)	Mathenson TriGas	http://www.mathesongas.com/
Methane (+/-1%) 2.5%	Mathenson TriGas	http://www.mathesongas.com/
Methane (+/-1%) 2010 ppm	Mathenson TriGas	http://www.mathesongas.com/
Ultra High Purity Nitrogen (UPHN)	Mathenson TriGas	http://www.mathesongas.com/

10 Liter Tedlar Bag	Dupont	http://www.dupont.com/products-and-services/membranes-films/pvf-films/brands/tedlar-pvf-films/uses-and-applications/tedlar-gas-sample-bag-applications.html
PET-7018Z	ICP DAS USA	http://www.icpdas-usa.com/pet_7018z.html
Edgetech Dew Prime Hyrgrometer	Edgetech Instruments	http://www.edgetechinstruments.com/moisture-humidity
Stainless steel Swagelok fittings (1/4 inch)	Swagelok	https://www.swagelok.com/products/fittings.aspx
PTFE Tubing	McMaster-Carr	http://www.mcmaster.com/#standard-hollow-tubing-(made-with-teflon-ptfe)/=z8xrzl

FLIR GF 320	FLIR	http://www.flir.com/ogi/display/?id=55671
CGA 580 Regulator	Airgas	http://airgas.com/category/_/N-1z13vaq
CGA 350 Regulator	Airgas	http://airgas.com/category/_/N-1z13vaq
Leak detection solution (Snoop)	Swagelok	https://www.swagelok.com/search/find_products_home.aspx?show_results=Y&item=5e208092-ed6c-4251-9202-ed8a2aae5811

Comments/Description

mass air flow sensor

methane, co2, and water sensor

blower/dilutor

Handheld detector

calibrated on methane

calibrated on air

handheld unit for use with Dressor modules

absolute pressure module

differential pressure module

calibrated gas divider

pure methane for gas recovery test

high concentration

low concentration

99.9% nitrogent gas

used for bag samples for alternative gas sampling

DAQ unit

hygrometer for flowbench

tee and other fittings

tubing for sampling and calibration

infrared camera

UHPN regulator

Methane in nitrogen regulator

bubble solution for non-leak verification

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Author(s): Derek Johnson, April Covington, Nigel Clark

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CORRESPONDING AUTHOR:

Name: Derek Johnson

Department: Mechanical + Aerospace Engineering

Institution: West Virginia University

Article Title: Design and Use of A Full Flow Sampling System (FFS) for the Quantification of Methane Emissions

Signature: [signature] Date: 9/30/15

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Dear Dr. Johnson,

Your manuscript JoVE54179R1 "Design and Use of a Full Flow Sampling System (FFS) for the Quantification of Methane Emissions" has been peer-reviewed and the following comments need to be addressed.

Please keep JoVE's formatting requirements and the editorial comments from previous revisions in mind as you revise the manuscript to address peer review comments. Please maintain these overall manuscript changes, *e.g.*, if formatting or other changes were made, commercial language was removed, *etc.*

Please track the changes in your word processor (*e.g.*, Microsoft Word) or change the text color to identify all of the manuscript edits. When you have revised your submission, please also upload a separate document listing all of changes that address each of the editorial and peer review comments individually with the revised manuscript. Please provide either (1) a description of how the comment was addressed within the manuscript or (2) a rebuttal describing why the comment was not addressed if you feel it was incorrect or out of the scope of this work for publication in JoVE.

Your revision is due by Nov 13, 2015. Please note that due to the high volume of JoVE submissions, failure to meet this deadline will result in publication delays.

To submit a revision, go to the *JoVE* Submission Site and log in as an author. You will find your submission under the heading 'Submission Needing Revision'.

Sincerely,

Nam Nguyen, Ph.D.
Science Editor
JoVE
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Editorial comments:

The manuscript has been modified by the Science Editor to comply with the JoVE formatting standard. Please maintain the current formatting throughout the manuscript. The updated manuscript (54179_R1_100615.docx) is located in your Editorial Manager account. In the revised PDF submission, there is a hyperlink for downloading the .docx file. Please download the .docx file and use this updated version for any future revisions.

Changes made by the Science Editor:

1. There have been edits made to the manuscript.

Changes to be made by the Author(s):

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues. The JoVE editor will not copy-edit your manuscript and any errors in the submitted revision may be present in the published version.

The document has been modified based on the reviewer comments and a separate review for formatting and grammar has been completed.

2. Formatting:
-Please provide catalog numbers to items in the Materials/Equipment list.

Catalog numbers are not given for the components used in this protocol. Websites are given where all available equipment or calibration gases can be obtained along with specific model numbers for user reference.

-In step 2.4, is the reference to 2.3 correct? Or should this be 2.2?

Changed to 2.2.

-There are several instances where portions of steps are not in the imperative, and such information could be included as Notes. For example, step 2.7 (“If…to be created.”) and step 3.8 (“Faults..sample fittings.”).

Non-imperative steps modified as notes.

3. Please correct the grammar in the Introduction: “The values in Figure 1 the average published fugitive methane emissions…”

Grammar fixed.

4. The second sentence of 4.2.1 will be difficult to visualize. We recommend incorporating this into the associated Note. Alternatively, please provide direction on aggregating and sampling these sources.

The second sentence was included as a Note and a separate step 4.2.2 was included.

5. Additional detail is required
-1.6/1.7-What constitutes "acceptable" signals or ranges?

1.6 – The output voltage of the MAF should be between 0-5V. This range was included in the step.

1.7 – The following note was added.

Note: Ensure that the MAF calibration spans at least 25% of the minimum flow rate of the LFE used for calibration. Do not exceed the maximum previously calibrated flow rate of the LFE, if larger flow rates are to be calibrated, use a larger LFE.

-1.7-8, 2.6-What needs to be clicked on in the software to accomplish these actions?

Button reference added.

-4.2-Should the probe of the detector be positioned/held in a specific way?

Added: Position the probe sample inlet orthogonal to the surface to minimize dilution.

-4.2.1-What are examples of inaccessible sources?

Modified Note - Note: Inaccessible sources could include vent pipes that are beyond a safely accessible height as determined by the site operator. Aggregated sources may include multiple pneumatic valves attached to a manifold or enclosed by a service box. If the source or multiple sources can be examined as a whole using an enclosure, aggregate the sources.

6. Branding should be removed:
-4.1/5.4/5.5/5.8-Snooper program—unless this is open source, the software should appear in the materials table and not be referenced by name in the text.

It is based on open source code and written internally but references were removed.

-Results-Meriam.

Removed.

7. In the Results, please include a general label (e.g., Reference) on the X-axis in Figure 1.

Added.

8. In the Discussion, please elaborate on the advantages of this technique over others, and provide independent superscript references.

Last paragraph modified to highlight advantages, references included.

Overall, the system and its methods have proven beneficial in efforts to quantify accurately the methane emissions from various sources. The system is scalable and user friendly. The developed system has an uncertainty of +/-4.4% compared to current commercial systems with an uncertainty of +/-10% [72]. With proper calibrations, this system can easily quantify leak rates up to 140 SCFM compared to current commercial systems that are capable of quantifying leaks up to 8 SCFM with full battery charges [64,72]. While the system requires connection to house power, this offers advantages of consistent sample rates and sample rates much higher than current systems. The user interface reduces post-processing requirements and reduces reporting efforts. In addition, the laser-based sensors are non-destructive to the leak sample, which allows for direct measurement of the sample with multiple analyzers [65]. Laser based measurements also do not require separate sensors for ambient, small and large leak measurements or sensor transitions, which contribute to additional sources of inaccuracy. Future studies focus on continued optimization of the FFS and its user interface. Additional research is being conducted which combines experimental research data and computation fluid dynamics to develop additional best practices to ensure consistent and optimal measurement techniques.

Reviewers' comments:

Editor's Note: Please note that the reviewers raised some significant concerns regarding your method and your manuscript. Please thoroughly address each concern by revising the manuscript or addressing the comment in your rebuttal letter.

We thank the Editor and the reviewers for their feedback and the opportunity to address their comments to improve the overall quality of the paper. Please see the bolded responses in this rebuttal and the tracked changes to ensure that we have addressed all comments.

Editor's Note: We do not require in depth or novel results for publication in JoVE, only representative results that demonstrate the efficacy of the protocol. However, please ensure

that all claims made throughout the manuscript are supported by either results or references to published works.

We have added additional references to specific comparisons of similar approaches. Please let us know if there are other specific concerns regarding this comment.

Reviewer #1:

Manuscript Summary:

General comments: The authors rightly state that measurements of methane emissions are sorely needed from many different aspects of the natural gas supply chain, and the existing techniques for making these measurements all have drawbacks. However, I am not convinced that this proposed method will make the measurements easier. There are three main drawbacks to the method proposed in this paper, all of which are minimized in the paper and which make the instrument problematic: 1), the power needs are never described although I assume the system needs a substantial generator which makes it hardly "portable"; 2), these methods need to be intrinsically safe, meaning they will not explode in a high-methane environment like a natural gas compressor station, and I think many of these components are likely not intrinsically safe; and 3), there is no information about the sensor that measures methane such as the concentration range, accuracy, etc. Since the end of the paper specifies this is a Los Gatos instrument, these data should be included. I have not worked with this instrument previously but I suspect it is most accurate at lower (near atmospheric) concentrations. The range of measurements possible with this method is also not clear and this is a critical piece of information for potential users.

We appreciate the feedback from the reviewer and have made changes where possible but have also included objections against certain recommend changes. Please see the following rebuttal and tracked changes version.

We do not necessarily present out method has easier than the other methods/technologies. We develop this technology and protocols to mimic what is currently used in industry but to do so with higher accuracy and over a much larger range compared to currently available methods.

1.) **We have included the power requirements that do show we require a grid connection. However, the system is still portable in the sense that it is movable around an entire site. See the following.**

System platforms included portable carts, on-road, and off-road vehicles. Power consumption does require the use of generator power or house power through standard 120 VAC connections. However, through this use of 'grid' power the system can sample at much higher flow rates yet still be used in conjunction with extension cords and long sampling houses for portability around a

given site of interest. Current battery operating systems have decreased performance as a function of battery discharge, which is eliminated using grid power.

2.) **We agree that safety of the site and the user is of the highest importance. Currently the system has been designed to minimize or mitigate any explosive issues. Upon production of a marketable system, it would require the testing and demonstration of compliance when required. The system was developed with safety in mind and in conjunction with industry. The certification of intrinsic safety has not been completed at this time, even for the currently sale and use of the Los Gatos Research Ultra-Portable Greenhouse Gas Analyzer. See the added safety note.**

Note: The FFS has been engineered with safety in mind to eliminate or reduce the possibility of ignition of a methane or natural gas source. Natural gas is flammable in ambient conditions from volume concentrations from 5 to 15%. When marketed the system will be tested and demonstrated to meet intrinsic safety requirements. Modification or tampering with the system could cause serious injury.

3.) **We have provided information regarding the current use of the LGR. See below. Beyond the current configuration we have also examined this and other laser based sensors that operate well beyond 10% methane by volume to produce total system uncertainties at or below +/-10% of the HI FLOW system. If we targeted this level of uncertainty the measurable leak rate range, (which is already and order of magnitude higher than the HI FLOW) would be extended by another order of magnitude.**

Due to limitations of these methods and systems, a new quantification system was developed. The full flow sampling system (FFS) employs the same design concept as dilution systems used in automotive emissions certification 66-68. The FFS consists of a hose that feeds an explosive-proof blower that exhausts the leak and dilution air sample through a mass airflow sensor (MAF) and sample probe. The sample probe is connected to a laser based methane analyzer through a sampling tube. The analyzers uses cavity enhanced absorption for measurement of CH4, CO2, and H2O. The analyzer is capable of measuring CH4 from 0-10% by volume, CO2 from 0-20,000 ppm, and H2O from 0-70,000 ppm. Repeatability/precision (1-sigma) for this configuration is <0.6 ppb of CH4, <100 ppb CO2, and <35 ppm for H2O 69. The sample is drawn from the steam at a constant volumetric rate. The system is instrumented with data logging equipment. Figure 2 illustrates the schematic of the FFS. Prior to operating the FFS, the grounding connection on the sampler hose is attached to a surface that allows the system to be grounded. This is a preventive action to dissipate any static charge on the end of the hose, which could result from airflow through the hose. Data acquisition occurs on either a smart phone, tablet, or laptop computer. We developed software for data collection, processing, and reporting.

The paper was also somewhat confusing to review. Part of it reads like a normal journal article, but a large part of it is just a numbered list that is hard to follow. I also have

problems with the references cited. Some of the numbers cited in the text do not make sense for that particular paragraph, so either the references are misnumbered or they are inappropriate. I have noted some cases of this below.

We agree that there were some errors in numbering/missing references, which have been fixed in this edit. We have followed the formatting that is for use in this journal. For sections outside of the protocol, we present cited literature and detailed results as would be presented within a typical journal. The protocol sections do appear as numbered lists but are in line with the formatting of this journal. We will work with the editor to ensure the final paper meets the quality and formatting requirements.

Finally, I received a request to review another paper by the same authors from another journal that is extremely similar to this one, and neither paper cites the other. Publishing the same material in two different papers is not viewed favorably in my field.

We agree that we have multiple publications that reference the general full flow sampling system. In fact, it was one of these publications (Environmental Science and Technology) that aroused interest in developing an article for JoVE by a JoVE Editor. We were contacted by an editor to provide a paper that specifically focuses on additional details and operation of the system, which we have presented here. We have double-checked all language to ensure that there is no self-plagiarism. The new article has also been included as reference 72.

Specific comments:
Abstract: As stated above, it is critical to discuss the power needs, safety requirements, and the possible measurement range in the abstract (and addressed in the paper as well).

See above and below responses to this and other reviewer comments, which address these issues.

Line 68: Human activities can contribute biogenic greenhouse gas emissions too.

Edited as follows. CO_2 and methane originate from both natural processes and human activities [3].

Line 78: Cows are not a natural source of methane and these references are not appropriate for this statement.

Call out of specific examples was removed.

Line 83: Also not the correct reference.

We agree that during formatting this reference was entered incorrectly.

14. Natural Resources Defense Council. Leaking Profits: the U.S. Oil and Gas Industry can Reduce Pollution, Conserve Resources, and Make Money by Preventing Methane Waste. (2012). http://www.nrdc.org/energy/files/Leaking-Profits-Report.pdf

Line 89: Is reference 20 a peer-reviewed article? Not clear what this is.

This is not a peer reviewed article but a report by ICF to the EDF. A link to the full report has been included in the updated citation.

https://www.edf.org/sites/default/files/methane_cost_curve_report.pdf

Lines 95-96: Need to make reference to the lower CO2 emissions from burning natural gas versus oil or coal here.

We respectfully disagree on this need for additional reference. Based on 100% combustion efficiency and only examining the combustion process there will be lower CO2 emissions. However, this is an area of hot debate due to combustion efficiency, complete life-cycle analysis, equivalent CO2, thermal efficiency losses, etc.

Line 110: Some of the studies cited here are review papers or estimates only, and the references in the figure are not numbered according to the references cited section.

We agree and a note on measured and estimated values has been included. We chose to use the author name and data as when presented with just a reference number, the chart seemed confusing. We will work with the editor to see what method works best for publication.

Line 112: At this point it is still unclear whether measurement inaccuracies, problems with scaling up, or both are responsible for the uncertainty in fugitive methane emissions.

While we agree that there are multiple causes of possible error the statement is true that without accurate measurements, the uncertainty is only compounded but we did add a note for clarity.

Line 121 - 127: Here you kind of mix and match two different bagging references. The

"Calibrated Bagging" is a bag expansion method used specifically for vent measurements ("Vent- Bag") and typically takes 3 to 20 seconds to make a measurement; the 15 - 20 minutes in that paragraph is for flow through standard bagging.

We agree that the presentation was confusing between the methods and have reorganized as follows.

The bagging method involves placing an enclosure in the form of a "bag" or tent around a fugitive emission source [60]. There are two variations of the bagging method. In one, a known flow rate of clean gas (typically inert) passes through the enclosure to create a well-mixed environment for measurement. Once equilibrium is reached, a gas sample is collected from the bag and measured. The fugitive emission rate is determined from the measured flow rate of clean gas through the enclosure and the steady-state methane concentration within the enclosure [61]. Depending upon enclosure and leak size, the time required to reach the necessary steady state conditions for the leak rate measurement is between 15 to 20 minutes [61]. The bagging method can be applied on most accessible components. However, it may not be suitable for abnormally shaped components. This method type is capable of measuring leaks ranging in size from 0.28 cubic meters per minute (m^3/min) to as large as 6.8 m^3/min [60].The other bagging technique is known as Calibrated bagging. Here, the bags sealed around a fugitive emission source are of a known volume. The fugitive emission rate is calculated based on the amount of time required for the expansion of the bag, and corrected to standard conditions.

Lines 133-134: Not consistent with using the written name of a compound, the chemical formula, or other ("R12").

Edited to remove inconsistency.

Tracer gases commonly employed are helium, argon, nitrogen, sulfur hexafluoride, among others.

Lines 147-159: This section describing the Hi-Flow system doesn't describe the background probe which is an important part of how the instrument works.

Sentence added for clarity.

The system uses a separate background sensor and probe which corrects the leak concentration relative to the background concentration.

Line 165: only states they used a laser based methane analyzer but don't give specs - min and max concentrations measurable?

The paragraph was rewritten to include additional specifics. See below.

Due to limitations of these methods and systems, a new quantification system was

developed. The full flow sampling system (FFS) employs the same design concept as dilution systems used in automotive emissions certification [66-68]. The FFS consists of a hose that feeds an explosive-proof blower that exhausts the leak and dilution air sample through a mass airflow sensor (MAF) and sample probe. The sample probe is connected to a laser based methane analyzer through a sampling tube. The analyzers uses cavity enhanced absorption for measurement of CH_4, CO_2, and H_2O. The analyzer is capable of measuring CH_4 from 0-10% by volume, CO_2 from 0-20,000 ppm, and H_2O from 0-70,000 ppm. Repeatability/precision (1-sigma) for this configuration is <0.6 ppb of CH_4, <100 ppb CO2, and <35 ppm for H_2O [69]. The sample is drawn from the steam at a constant volumetric rate. The system is instrumented with data logging equipment. Figure 2 illustrates the schematic of the FFS. Prior to operating the FFS, the grounding connection on the sampler hose is attached to a surface that allows the system to be grounded. This is a preventive action to dissipate any static charge on the end of the hose, which could result from airflow through the hose. Data acquisition occurs on either a smart phone, tablet, or laptop computer. We developed software for data collection, processing, and reporting.

Line 215: Again you need more description of the greenhouse gas analyzer and its measurement range, accuracy, and precision. Why can't you be specific in the paper about which analyzer you are using?

See above for species, ranges, etc. Per JoVE requirements, name brands/logos/companies cannot be mentioned within the paper itself. However, we have added the above details.

Line 371 - this is in the section that reads like an instruction manual but it says to take a local background and says to click on that button but it doesn't say how it does it - i.e, where the back ground probe is located, does it switch to that probe, and are there different delay times. Background concentration measurements will be very important here because the method uses flow rates from 40 to 1500 scfm, which means you're drawing in far more background air to dilute the leak with than with the High Flow. It is important to have the background measured while the system is capturing the leak.

An additional note has been included for the discussion of local background. The system offers local and global backgrounds. See below.

Note: The program automatically switch the sampling location of the outlet of the FFS to a port just behind the inlet to the sampling hose for a local background. The sampling hose must be in the same measurement position as is used for the sample quantification.

Line 433 - sounds like the only part of the system that's explosion proof or intrinsically safe.

This could cause a fatal safety hazard if you suck a large leak in and exhaust it around the equipment.

We agree that the measurement of natural gas or methane leaks does pose a safety risk. The system has been designed to eliminate or minimize these risks. When marketed the system will undergo the necessary testing and demonstration to be approved as Class 1 Division 1 acceptable. A special note was added to the beginning of the protocol.

Note: The FFS has been engineered with safety in mind to eliminate or reduce the possibility of ignition of a methane or natural gas source. Natural gas is flammable in ambient conditions from volume concentrations from 5 to 15%. When marketed the system will be tested and demonstrated to meet intrinsic safety requirements. Modification or tampering with the system could cause serious injury.

Line 486 - they used 20 and 30 slpm injections of 99.9% methane and got agreement to within 2.2%. That's good, but they don't tell us what their sample flow rate was during that checkout - 40 scfm, 1500, or something in between? It would be good to check it out at several sample flows.

We agree that it should be checked out and different sample flow rates, especially those that are of interest to a particular measurement campaign. However, due to length restrictions we have provided a two-point verification at a single flow rate of 140 SCFM. This reference value has been included.

The results are presented in Table 1 for a system flow rate of 140 SCFM.

Major Concerns:
N/a

Minor Concerns:
N/A

Additional Comments to Authors:
N/A

Reviewer #2:
Manuscript Summary:
This paper presents a sampling approach for quantifying methane leaks from upstream components of the natural gas system. There currently is no standardized approach for these measurements, so the description of the Full Flow Sampling system (FFS) is timely and

of interest to groups seeking to improve estimates of methane leakage rate. The FFS has been adapted from dilution systems used in automotive emissions certification, and employs a blower that pulls sample in via hose, then exhausts the sample air and dilution air through a mass flow sensor and sample probe, which is connected to a laser based methane analyzer. Instructions for calibrating the mass flow sensor and methane analyzer are given, as well as steps to quantify the leak. A "Snooper" software program was developed to handle the data and calculate leak rate. Overall uncertainty of methane emissions rate was demonstrated to be +/- 4.4%.

We appreciate the feedback from the reviewer and have worked to address their concerns within the scope of this article.

Major Concerns:

-The text does not include a description of the methane analyzer. I see in the equipment list that it was a Los Gatos Research ultraportable greenhouse gas analyzer, but a description of it and how it works should be in the text. Why was the LGR chosen over any other methane analyzer?

The LGR was chose during this initial phase because of its co-measurement of CO2, H2O, and CH4. It is also readily available in a rugged case for use in the field. The following paragraph was rewritten to include additional details but following the instruction not to include any commercial names.

Due to limitations of these methods and systems, a new quantification system was developed. The full flow sampling system (FFS) employs the same design concept as dilution systems used in automotive emissions certification [66-68]. The FFS consists of a hose that feeds an explosive-proof blower that exhausts the leak and dilution air sample through a mass airflow sensor (MAF) and sample probe. The sample probe is connected to a laser based methane analyzer through a sampling tube. The analyzers uses cavity enhanced absorption for measurement of CH_4, CO_2, and H_2O. The analyzer is capable of measuring CH_4 from 0-10% by volume, CO_2 from 0-20,000 ppm, and H_2O from 0-70,000 ppm. Repeatability/precision (1-sigma) for this configuration is <0.6 ppb of CH_4, <100 ppb CO_2, and <35 ppm for H_2O [69]. The sample is drawn from the steam at a constant volumetric rate. The system is instrumented with data logging equipment. Figure 2 illustrates the schematic of the FFS. Prior to operating the FFS, the grounding connection on the sampler hose is attached to a surface that allows the system to be grounded. This is a preventive action to dissipate any static charge on the end of the hose, which could result from airflow through the hose. Data acquisition occurs on either a smart phone, tablet, or laptop computer. We developed software for data collection, processing, and reporting.

-The authors presented current sampling methodologies with advantages/disadvantages of each in the introduction. In the discussion section, the authors should revisit this topic and

present ways in which the FFS is superior or inferior to the other methodologies. For example, given that it uses an LGR analyzer it will be quite a bit more expensive than a Bacharach HI Flow sampler will but perhaps it has better sensitivity. This would be a very important part of the paper because if it cannot be demonstrated that the FFS is an improvement as a sampling approach then it does not have merit.

We have added some additional detail on why the system is superior to currently available systems. Please see the edited last paragraph of the discussion section.

Overall, the system and its methods have proven beneficial in efforts to quantify accurately the methane emissions from various sources. The system is scalable and user friendly. The developed system has an uncertainty of +/-4.4% compared to current commercial systems with an uncertainty of +/-10% [74]. With proper calibrations, this system can easily quantify leak rates up to 140 SCFM compared to current commercial systems that are capable of quantifying leaks up to 8 SCFM with full battery charges [64,74]. While the system requires connection to house power, this offers advantages of consistent sample rates and sample rates much higher than current systems. The user interface reduces post-processing requirements and reduces reporting efforts. In addition, the laser-based sensors are non-destructive to the leak sample, which allows for direct measurement of the sample with multiple analyzers [65]. Laser based measurements also do not require separate sensors for ambient, small and large leak measurements or sensor transitions, which contribute to additional sources of inaccuracy. Future studies focus on continued optimization of the FFS and its user interface. Additional research is being conducted which combines experimental research data and computation fluid dynamics to develop additional best practices to ensure consistent and optimal measurement techniques.

-I have concerns about the screening for leaks with the handheld unit (step 4.2 under "Leak detection audit"). The sensitivity of this unit looks something like +/- 25 ppm. Potential leak points are excluded from quantification with the FFS if they are below detection with the Eagle II unit. What is the sensitivity of the FFS in g/hr? Uncertainty is given (+/- 4.4%) but how does that translate to sensitivity? One would have to report minimum detection based on the +/- 25 ppm sensitivity of the Eagle II if leaks that are too small to be picked up by the Eagle II are not quantified with the FFS.

Many sources in literature use 500 ppm as the leak quantification threshold. The sensitivity of the Eagle II is 5 ppm above local background (zeroed at the site). We have added a note on this. In addition, we have reported on the minimum detection limit of the current system in the last paragraph.

Note: The sensitivity of the handheld unit is 5 ppm above background when zeroed on ambient air.

The minimum detection limit of the current system is 0.24 g/hr or 3.0×10^{-3} SCFM.

-A better description of the Snooper software would be beneficial. Perhaps a flowchart of prompts/data input steps could be included as a figure.

-The use of the infrared camera seems arbitrary. Is it recommended for use for this system or not? These cameras are very expensive.

We agree the cameras are expensive. The system is focused on use of the handheld methane detector but the note and alternative method were included for those that may have access to this method.

Note: Optical gas imagining cameras are typically expensive but do reduce the time required to scan components for leaks. Use of high sensitivity modes may be required for small leaks.

-The authors presented results for three different types of leaks. Were these controlled releases? It does not seem as though they were, but the paper should demonstrate the accuracy of the FFS by measuring controlled leaks with known methane emission rate, and also compare its readings to those obtained via another approach such as a HiFlow sampler.

These were not controlled releases and the actual sources are provided. Pursuant to the standards of this journal, representative results are to be presented and we have provided those in this article. We have though, presented results of a gas recovery test at two known methane leak rates. These results are presented in the paragraph starting at line 510. The goal of the paper is to highlight the system and the protocols for use of the system. While we provide our advantages compared to currently available systems we did not complete a direct comparison to the currently available products. A direct comparison is beyond the scope of this article but would be an interesting research project.

-Unless more discussion is included, I do not yet see how this system is a clear improvement over "bagging" or HiFlow samplers. It seems like it would be more time consuming and expensive. The limitation of bagging not being suitable for abnormally shaped components can be solved with different sized bags and creative sealing. The limitations of the HiFlow sampler having problems switching from catalytic to thermal sensor can be overcome by more frequent calibration checks.

We have highlighted the advantages of the system in the final paragraph, which we present here again for ease of reference. Based on review of recent publications there is still debate over whether more frequent calibration checks overcome the current

limitations of the HI Flow sampling system. Our focus are on other advantages such as improved accuracy (even compared to a properly operating HI FLOW +/-10% compared to our +/-4.4. Our system also has a wider leak capture range. See below.

Overall, the system and its methods have proven beneficial in efforts to quantify accurately the methane emissions from various sources. The system is scalable and user friendly. The developed system has an uncertainty of +/-4.4% compared to current commercial systems with an uncertainty of +/-10% [74]. With proper calibrations, this system can easily quantify leak rates up to 140 SCFM compared to current commercial systems that are capable of quantifying leaks up to 8 SCFM with full battery charges [64,74]. While the system requires connection to house power, this offers advantages of consistent sample rates and sample rates much higher than current systems. The minimum detection limit of the current system is 0.24 g/hr or $3.0x10^{-3}$ SCFM. The user interface reduces post-processing requirements and reduces reporting efforts. In addition, the laser-based sensors are non-destructive to the leak sample, which allows for direct measurement of the sample with multiple analyzers [65]. Laser based measurements also do not require separate sensors for ambient, small and large leak measurements or sensor transitions, which contribute to additional sources of inaccuracy. Future studies focus on continued optimization of the FFS and its user interface. Additional research is being conducted which combines experimental research data and computation fluid dynamics to develop additional best practices to ensure consistent and optimal measurement techniques.

Minor Concerns:

-The "Snooper" program is referenced in 4.1 of section 4 (Leak detection audit) but it had not been previously described or defined.

Reference to "Snooper" has been removed.

-In lines 285-286, 4.4% is suggested as an acceptable error but no justification for the selection of this number is given.

The 4.4% is suggested as acceptable as this is the relative measurement of uncertainty of the entire system. The note was modified per below. 4.4% was calculated based on propagation of uncertainty of individual components, which are presented in Table 2.

Note: Upon completion of sampling the software will create a report showing the error of the between the known gas flow rate and the recovered gas flow rate. An error of ±4.4% is acceptable (relative measurement uncertainty of the system), but the targeted recovery error is ±2%.

-The sentence in lines 98-99 does not make sense and should be reworded. Its meaning is unclear.

Both sentences were modified for clarity. See below.

However, there is a consensus that fugitive methane emissions occur at every stage of the natural gas life cycle and further research in accurately measuring and reporting these values is important [19]. Studies have reported fugitive emissions from specific sectors with results varying by up to twelve orders of magnitude [19, 22-28].

Additional Comments to Authors:
N/A

Reviewer #3:
Manuscript Summary:
The section describing the protocol would benefit from a few introductory paragraphs describing the steps in the over-all protocol and their rationale, before providing a detailed description of each step.

This is our first time using this Journals formatting. We have included some statements within the protocols as notes for the readers. We have, based on this request, added a few introductory sentences to each protocol section. We will work with the editor in the final process to see if these statements should remain or be placed in the discussion section. We appreciate this feedback.

Major Concerns:
None

Minor Concerns:
None

Additional Comments to Authors:
N/A