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Implications of Sampling Methods on Geospatial Mapping of Methane Sources

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Implications of Sampling Methods on Geospatial Mapping of Methane Sources

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Thesis submitted to the Benjamin M. Statler College of Engineering and Mineral Resources

At West Virginia University

In partial fulfillment of the requirements for the degree of

Master of Science

In

Mechanical Engineering

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Abstract

Implications of Sampling Methods on Geospatial Mapping of Methane Sources

Dakota W. Oliver

Natural gas is deployed as an alternative fuel due to its cost and post-combustion emissions. However, methane, the main component of natural gas, is a greenhouse gas with a global warming potential (GWP) of at least 28 over 100 years. Currently, natural gas and petroleum systems are the highest emitters of methane to the atmosphere. Using conventional methods, the detection of natural gas leaks is time consuming. Currently, natural gas production sites deploy the Environmental Protection Agency's (EPA) Method 21 or optical gas imaging (OGI) for methane leak detection. Both methods require access to the natural gas site along with the time and workers necessary to conduct equipment leak checks. Industry and academia are seeking to develop and deploy mobile methane monitoring systems to geospatially identify methane emissions. There are a variety of sensor systems that can be combined to enable such monitoring but there may be implied limitations (implications) based on operating principle and sampling frequency. The goal of this research was to assess these implications and where applicable develop methods that could overcome limitations.

Using a vehicle mounted approach, two mobile methane detection systems were deployed in rural West Virginia (WV). Over the course of 90 days, a total of 43 trips were completed through Morgantown, WV and the surrounding area. During each trip, two systems were implemented simultaneously with different sampling frequencies and methane sampling methods. The slow system operated at 1 Hertz (Hz) with a closed-path methane analyzer, while the fast system operated at 10 Hz with an open-path methane analyzer. The effects of the sampling frequency and sampling method were observed for each system. The sampling frequency effects were examined with respect to geospatial limitations and wind speed limitations. The sampling method effects were compared between the systems using peak concentrations as the primary metric.

With the sample frequency effects, the closed-path methane analyzer required a signal reconstruction to report an accurate response in real time methane concentration. Methods of signal reconstruction, consisting of sequential inversion technique (SIT), inverse fast Fourier transform (IFFT), artificial neural network (ANN), and differential coefficients method (DCM), were investigated before the DCM and ANN were applied. A performance value was defined for improvement comparisons between the initial methane signal and the reconstructed signal. An application was created in MATLAB[®] to process the mobile methane detection data. After indicating the user defined parameters, the application created a MATLAB[®] workspace file and Google[®] Earth file consisting of a visual representation of the fast, slow, and reconstructed systems to elucidate the geospatial differences. The requirements for both the fast and slow systems were investigated with the intent of an operational mobile methane detection system. Suggested improvements and potential expansions of the mobile methane detection system were discussed.

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List of Acronyms

<u>Acronym</u>	<u>Word or Phrase</u>
ANN	Artificial Neural Network
ARPA-E	Advanced Research Projects Agency- Energy
App	Application
BTU	British Thermal Unit
CO ₂	Carbon Dioxide
DCM	Differential Coefficients Method
EDF	Environmental Defense Fund
EIA	Energy Information Agency
EPA	Environmental Protection Agency
°F	Fahrenheit
FFT	Fast Fourier Transform
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
GN	Gauss-Newton
GPS	Global Positioning System
GR	Geospatial Resolution
GWP	Global Warming Potential
H ₂ O	Dihydrogen Monoxide
Hz	Hertz
ICOS	Integrated Cavity Output Spectroscopy
IFFT	Inverse Fast Fourier Transform
IPCC	International Panel on Climate Change
IR	Infrared
kph	Kilometer Per Hour
LM	Levenberg-Marquardt
m	Meter
mm	Millimeter

mm ³	Cubic Millimeter
m/s	Meters Per Second
mbar	Millibar
MOS	Metal Oxide Sensor
mph	Miles Per Hour
NIST	National Institute of Standards and Technology
NOAA	National Oceanic & Atmospheric Administration
μ-m	Micro-Meter
μ-s	Micro-Second
OA-ICOS	Off-Axis Integrated Cavity Output Spectroscopy
OGI	Optical Gas Imaging
OTM 33a	Other Test Method 33a
PE	Peak Error
PIE	Plume Integration Error
ppbv	Parts Per Billion
ppmv	Parts Per Million
ppmv-m	Parts Per Million Meter
PV	Performance Value
r ²	Linear Correlation Coefficient
RSSI	Relative Signal Strength Indicator
SEE	Standard Estimate of the Error
SIT	Sequential Inversion Technique
slpm	Standard Liter Per Minute
UGGA	Ultra-Portable Greenhouse Gas Analyzer
US	United States
V	Voltage
$\frac{W}{m^2}$	Watt Per Meter Squared
WMS	Wavelength Modulation Spectroscopy
WV	West Virginia

1 Introduction

1.1 Background

The United States (US) produces the largest amount of natural gas in the world, with production of over 70 billion cubic feet a day [1]. In 2018, the US produced a total of 36 trillion cubic feet of natural gas [2]. According to the Energy Information Administration (EIA), the US has a surplus of natural gas for 90 years at the current consumption rate of 27.5 trillion cubic feet per year, indicating the potential long term reliance on natural gas [3].

To reduce emissions to the atmosphere, natural gas has been implemented as an alternative fuel.

Combustion of natural gas produces 27% and 46% lower carbon dioxide (CO₂), per British thermal unit (BTU), compared to petroleum and coal, respectively [4]. In 2015, both natural gas and coal created 1.5 billion metric tons of CO₂, while natural gas utilization was 81% higher than coal [5].

Natural gas's capability to serve as a lower emission fuel than petroleum or coal is dependent on losses along the supply chain of its main component, methane. Global warming potential (GWP) is the energy one ton of a gas absorbs in the atmosphere compared to the energy of one ton of CO₂ absorbs over a time span [6]. The International Panel on Climate Change's (IPCC) 2013 report defined methane's GWP as 28 over 100 years [7]. When breaking down the contributors to total methane emissions, the Environmental Protection Agency (EPA) reported that natural gas, petroleum, and coal systems were the largest sources of methane [8].

Models have compared the environmental impacts of natural gas leakage and production in the implementation of natural gas over other fuels [9, 10]. To reduce radiative forcing in the atmosphere, Alvarez et al. created a model to observe the leak ratio, or ratio of natural gas leakage to total production [9]. For immediate climate benefits, natural gas could potentially replace gasoline in light-duty cars, diesel fuel in heavy-duty vehicles, and coal in power plants, with leak ratios lower than 1.6%, 1% and

3.2% of production, respectively. Zhang et al. presented a model of replacing coal with natural gas power plants for electricity generation [10]. Assuming efficiencies of 60% for natural gas and 51% for coal power plants, a leak ratio above 2% would void the environmental benefit of using a natural gas power plant over a coal power plant. The models dictated that the benefits of natural gas as an alternative fuel decreased with high natural gas leaks.

Methane detection has been a priority of several US government agencies including: National Institute of Standards and Technology (NIST), National Oceanic and Atmospheric Administration (NOAA), and Advanced Research Projects Agency - Energy (ARPA-E), and non-governmental organizations such as the Environmental Defense Fund (EDF) [11–13]. NIST and NOAA partnered to develop a field spectrometer for permanent deployment at natural gas sites [11]. ARPA-E sponsored the Methane Observation Networks with Innovative Technologies to Obtain Reductions (MONITOR) program, where 12 organizations received funding to improve methane detection and quantification systems [12]. The EDF cooperated with Stanford University to host the Mobile Monitoring Challenge where researchers deployed their methane detection and quantification systems in a competition [13].

Researchers have implemented methane detection systems to quantify natural gas emissions [14–22]. Researchers have operated vehicles with methane analyzers for methane detection [14–18, 23], methane quantification [19–21, 24, 25], and methane quantification method comparisons [22]. Picarro Inc. and Los Gatos Research have created commercially available mobile methane detection services using their closed-path methane analyzers [26, 27]. Such systems commonly implement a methane analyzer with a pump and a sealed, or closed-path cell [14–17, 19–21, 24, 26, 27].

Phillips et al. and Jackson et al. performed methane detection using a closed-path Picarro G2301 methane analyzer sampling at 0.9 Hertz (Hz) in Boston, Massachusetts and Washington, D.C., respectively [14, 15]. Using a Picarro G112i analyzer, the isotopes of methane were identified [14]. Using both closed-path Picarro analyzers, the methane sources were predominantly associated with natural gas leaks, but required a handheld gas detector for source attribution [14].

Eapi et al. deployed a closed-path Picarro G2204 methane analyzer for methane detection in Tarrant, Wise, Denton, and Johnson counties in Texas [16]. They drove through plumes of methane multiple times for repeated measurements and the temporal variations were explained through atmospheric conditions only 23% of the time. Driving operation was attempted to remain at a constant 20 miles per hour (mph), or 32.19 kilometers per hour (kph), but was limited by roadway safety. The atmospheric conditions were determined regionally from the Dallas/Fort Worth Airport and were not determined locally [16]. Analysis of the sampling method of the closed-path Picarro, local atmospheric conditions, or vehicle speed were not conducted for explaining methane concentration differences.

Atherton et al. performed methane detection in the Montney Shale in British Columbia [17]. They deployed a Los Gatos Research UltraPortable Greenhouse Gas analyzer (UGGA) for methane detection. This was a closed-path analyzer sampling at 1 Hz. They found that 58% of methane leaks detected could likely be associated natural gas infrastructure. The probability of false identification of a methane plume was less than 0.01% but there was uncertainty in methane plume source association [17].

Von Fischer et al. and Weller et al. outfitted Google® Street View Cars with a methane analyzer for methane quantification and comparisons [22, 24]. Using controlled releases in Fort Collins, Colorado, a methane leak rate algorithm was created using the methane reported by a Picarro G2301 sampling at 2 Hz [24]. It was determined that wind speed did not play an effect in methane rate calculation but the methane analyzer underreported methane rates for high leak rates [24]. Comparing methane quantification to handheld methane detectors, the mobile methane system detected leaks the handheld methane analyzer was unable to determine [22]. This was assumed to be associated with the high precision of the methane analyzer. The mobile methane quantification overreported methane concentrations compared to surface flux measurements [22]. This may be associated with the implementation of methane plume size in the leak rate algorithm.

Rella et al. performed methane quantification in the Barnett Shale in Texas [19]. They collected flux methane measurements at 207 well pads using the mobile flux plane technique. Using a mast with 4-6

ports on a vehicle, each port collected 50 seconds of gas using a pump and delivered each sample individually to the methane analyzer. The methane analyzer deployed was a Picarro G2301 methane analyzer which was a closed-path analyzer sampling at 2 Hz [19]. To perform the mobile flux plane technique, time alignment of each sample from a port was required [19].

Tao et al. deployed a greenhouse gas detection system in both the United States and China [23]. For methane detection, they deployed a LI-COR LI-7700 that had an open-path cell and sampled at 10 Hz. The open-path methane analyzer was mounted to the top of their vehicle after modeling the wake zone of the vehicle [23]. Effects of the open-path sampling method were not compared to a closed-path analyzer.

In summary, natural gas has a prominent role in energy as an alternative fuel due to its availability and post-combustion emissions. However, methane is a prominent greenhouse gas that should be minimized, which requires continued advancements in detection methods. Of the mobile methane detection and quantification systems deployed in other research, analysis of the methane sampling methods was not conducted. The sampling methods of the closed-path methane analyzer were not compared to open-path methane analyzers prior to implementation in mobile methane systems. Therefore the goal of this researcher was to further examine any implications from choice of sampling method.

1.2 Objectives

The overall objective of this study was the evaluation of current, state-of-the-art methane analyzers and the implications of their deployment in mobile methane mapping. The application of two methane analyzers allowed for the comparison of their sampling methods when targeting the identification of methane concentrations just above ambient background. To achieve this objective, the research consisted of the following tasks:

- Conducted a literature review of currently available methane analyzers and identified their drawbacks for deployment in mobile methane detection systems.

- Developed a high and low frequency mobile methane detection system with each methane analyzer and other equipment necessary for geospatial mapping and identification (e.g. sonic anemometer and GPS).
- Compared the initial measurement results of each sampling methodology.
- Determined the sampling limitations of each system due to sampling frequency, the methane analyzer's operational principles, and vehicle speed.
- Examined methods of reconstruction that hinder the deployment of closed-path analyzers.
- Discussed the creation of a post-processing application for simplistic data presentation.
- Described the requirements and recommendations to perform mobile methane detection under transient driving operation.
- Examined potential applications for expanding the use of the mobile methane detection system(s) and other analyzers.

2. Review of Literature\Background

2.1 Methane Detection Methods

Currently there are many methane sensors and analyzers that use different fundamental techniques to accurately quantify the concentration of methane based on first principles and derivatives thereof. To review the potential methane analyzers, the requirements for a system were reviewed. The average atmospheric level of methane is 1.867 parts per million by volume (ppmv) [28]. Therefore, the methane analyzers must be capable of measuring low methane concentrations and include the resolution to detect subtle changes. In addition, if a device cannot operate in a moving vehicle, it is not an option for mobile methane detection applications.

To determine the best analyzer for mobile methane detection, various sensors and analyzers were reviewed and included: Flame Ionization Detector (FID), Fourier Transform Infrared Spectroscopy (FTIR), Optical Gas Imaging (OGI), Infrared (IR) sensors, Metal Oxide Sensor (MOS), catalytic bead sensors, and other spectroscopy techniques. The observed options varied in operating principles, precision, and mobility.

2.1.1 Flame Ionization Detection (FID)

Created in 1957 by Ian McWilliam in Australia, the FID is a measurement device for determining the hydrocarbon concentration in a sample [29]. The sample gas encounters the flame and the combustion of the sample causes the mixture to emit ions based on the mole fraction of hydrocarbons in the sample. An ion detector converts the emitted ions into a recordable signal. A source of compressed FID fuel is required for operation.

The FID requires a special calibration for each species of hydrocarbons, along with its ratio of other elements such as oxygen [30]. Oxygen in the sample distorts the flame and creates errors in the measurement if the FID is not calibrated for the amount of oxygen present in the sample [30]. The FID

avoids errors with oxygen if the sample is separated, such as in gas chromatography which isolates the compounds in the sample.

Both Horiba Ltd. and Sensors Inc. produce commercially available emission measurement systems with FIDs for use in vehicle emissions testing. The Horiba OBS-ONE GS and the Sensors SEMTECH FID and Dual FID both only reach a precision as low as 10 ppmv of total hydrocarbons [31, 32]. With a precision of 10 ppmv, the commercially available FIDs were unable to accurately detect subtle changes near atmospheric, background levels of methane. In addition, the Horiba and SEMTECH do not easily measure only methane directly. The FID's use in a mobile methane detection system would require a greater resolution of pure methane, onboard FID fuel storage, and methods for speciation.

2.1.2 Infrared Spectroscopy (IR)

IR spectroscopy encompasses the electromagnetic spectrum from 0.78 to over 1000 micro-meter ($\mu\text{-m}$) wavelengths, as shown in Figure 1 [33]. The wide range of IR is broken into 3 parts; near-IR, mid-IR, and far-IR. Near-IR operates in the region from 0.78 to 2.5 $\mu\text{-m}$ and far-IR operates above 15 $\mu\text{-m}$ [34]. Mid-IR is the region between near-IR and far-IR. Some applications, such as the FTIR, operate in all IR ranges while commercially available OGI and IR products operate in the mid-IR range only [35, 36]. Despite all these analyzers using IR spectroscopy, each method was examined separately as some operating principles varied.

Figure 1: The Electromagnetic Spectrum [37].

2.1.2.1 Fourier Transform Infrared Spectrometer (FTIR)

The FTIR was created in the 1980s [33]. The development of these devices stemmed from the desire for a system that sampled at one second or less without separating the sample. The FTIR's principles are based on the absorption of infrared wavelengths in the sample. The molecules absorb certain IR wavelengths and begin rotating or vibrating due to an increase in the dipole moment of the compound. By performing a Fourier transform to the frequency domain with knowledge of the composition's coefficients, the composition of the sample is determined.

The FTIR spectrometer allows for a high reduction in reporting errors through few optical parts with a complex spectra [38]. The FTIR detects most non-diatomic gas species. However, due to a zero change of the dipole moment of diatomic molecules, they are incapable of measuring species such as oxygen and nitrogen [38]. The FTIR determines almost all compounds accurately, quickly, and without any additional processing steps so long as a general composition is known.

For applications outside the laboratory, the FTIR's main issue is maintaining an operating temperature while reporting at high precision. For the FTIR to function, the IR detector requires a cooling method, usually with liquid nitrogen [39]. Several studies implemented the use of the FTIR in mobile applications by keeping liquid nitrogen available in the vehicle [39, 40]. However, this requires additional safety considerations similar to the fuel requirements of the FID. The MKS MultiGas 2030-HS, a mobile liquid nitrogen cooled FTIR, has a sampling frequency of 5 Hz but has a lower detection limit of 1 ppmv of methane [41]. To overcome liquid cooling, FTIRs are available with Peltier, or electric cooling. For example, the ARCOptix Rocket is a Peltier cooled FTIR with a lower detection limit of 10 ppmv of methane [42]. Current commercial FTIRs' lower detection limits were not well suited for mobile methane systems.

2.1.2.2 Optical Gas Imaging (OGI)

Using the principles of IR absorption is OGI. With OGI, a camera detects IR at a specific wavelength for the desired molecules. For example, FLIR Systems' OGI cameras use 3.3 μ -m wavelength filters for hydrocarbon detection [35]. If the naturally emitted IR wavelength hits the molecule, the IR is absorbed by the molecule before it reaches the detector. Using the IR detector and visual lens, the camera creates an image for the viewer to see the location of the molecules. Because of its operation, OGI requires site access with proximity to the methane source. A commercially available camera detects a methane leak rate of about 20 grams per hour with a confidence of 90% from a distance of 3 meters (m) [43].

The operator must conduct their study during optimal weather conditions. The plume should be a different temperature and radiance than the background [35]. In addition, warmer days provide better detection of methane and the use of the sky as a backdrop provides optimal leak detection [44]. This is due to the temperature difference of the surface and sky and the sky providing constant radiance different from methane. The maximum allowable distance using a OGI is a function of the differences in temperature [45].

There is no commercially available OGI capable of an output other than a picture. The OGI produces an image during operation that cannot distinguish between hydrocarbons or excess heat. This requires an operator to interpret each picture. Rebellion Photonics' is currently developing a soda-can sized OGI capable of wirelessly uploading the video stream during operation [46]. The goCGI is under development as a wearable OGI with the goal of achieving flow rate calculations using complex algorithms without user interpretation.

The OGI's use in a mobile methane detection system is limited. Because a user interprets all the images captured, this introduces the possibility of human error in source determination. In addition, commercially available OGI are not capable of speciating multi-component mixtures or numerical representations of low concentrations. These factors reduced the OGI's applicability in mobile methane detection.

2.1.2.3 Infrared sensors

IR sensors operate using a similar principle as the OGI; however, OGI applies the IR detector to determine a picture while the sensor determines a volume concentration of the molecule. For IR sensors, an IR detector determines the quantity of the molecule based on the absorption of the IR wavelengths and is not affected by smoke [47]. However, the IR sensor cannot distinguish between molecules at some wavelengths. For example, water vapor absorbs a significant number of IR wavelengths from 2 to 8 $\mu\text{-m}$ [36]. This is an issue as methane has an absorption band in the 3.3 $\mu\text{-m}$ range. The interference of other molecules prevents the basic IR sensor from providing high accuracy measurements. Commercially available IR sensors such as, NET IRNET-P, Edinburgh Sensors Gascard NG, and Dynamet MSH-PS/HC/NC, operate in ranges of 0-5% concentration of methane in the sample [48–50]. All three sensors report accuracies at 50 parts per billion by volume (ppbv) but require 30 seconds to reach 90% of the target value. While their sampling frequency is 1 Hz, the time to reach 90% would induce significant temporal and spatial delays thus diminishing the IR sensor's applicability in a mobile methane detection system. In addition, their sensor response to other hydrocarbons limited their application to specific focus on methane.

2.1.3 Metal Oxide Sensor (MOS)

The MOS consists of a semiconductor heated between two wires. As the heated semiconductor contacts oxygen, it adsorbs and stores oxygen on the surface. Once the combustible, or reducing, gas encounters the semiconductor, the reducing gas removes the oxygen. The semiconductor resistance changes as a function of the oxygen levels on the semiconductor [51]. As such, a MOS cannot distinguish between gases that oxidize similarly [51].

Temperature, humidity, and oxygen dependence are the biggest factors in MOS operation. As the temperature increases, the amount of reducing gas detected varies [52]. In addition, water adsorbs to the semiconductor's surface and decreases the sensitivity of the MOS [52]. These two issues require external corrections based upon the temperature and humidity at the sensor. If the oxygen levels are too low, then

the metal oxide cannot adsorb oxygen and the MOS begins to fail [51], though this would not be a concern for atmospheric monitoring. The combination of temperature, humidity, and oxygen dependence significantly increases the error in measurements.

Commercially available MOS for methane do not reach precisions lower than 100 ppmv. Winsen MQ-4 is a commercially available MOS designed for methane detection, with a range of 300-10,000 ppmv [53]. The commercially available MOS operated at orders of magnitude larger than the range required for mobile methane detection.

2.1.4 Catalytic Bead Sensors

Catalytic bead sensors, or pellistors, operate similarly to a MOS. Instead of the semiconductor, a bead coated in a catalyst causes the reducing gas to oxidize before its combustible range [47]. The oxidation changes the resistance which is proportional to the amount of reducing gas.

The catalytic bead sensor cannot distinguish between gases with similar combustion properties [47]. The major downfall for catalytic bead sensors is the lower detection limit which is 1000 ppmv [47]. In addition, the catalytic bead sensors have a response time up to 10 seconds, which creates sampling inaccuracies [54]. The NET NP-17SHM is a methane catalytic bead sensor, capable of detection of 0-100% of methane concentration by volume with a response time of 20 seconds to reach 90% of the target value [55]. The NP-17SHM's error, 1% of methane concentration, indicates it is not capable of meaningful detection below 1% of methane concentration by volume. The detection and response time issues limited the implementation of catalytic bead sensors in a mobile methane detection system.

2.1.5 Other Spectroscopy Based Analyzers

Spectroscopy is the study of radiation and matter, and it encompasses all potential methods of detection using the light spectrum. Companies have developed their own forms of spectroscopy for detecting methane. Commercially available name brands include Picarro Inc, Los Gatos Research, and LI-COR Biosciences among others.

For methane detection, two potential methane analyzers are the Los Gatos Research Ultra-Portable Greenhouse Gas Analyzer (UGGA) and LI-COR LI-7700 (LI-7700). The UGGA operates inside a crushproof portable case designed for field conditions that uses closed-path operation. With portability, precision of 2 ppbv, and sampling frequency of 1 Hz, the UGGA is an option for mobile methane detection [56]. The LI-7700 operates with an open-path cell, allowing for instantaneous geospatial sampling for a given plane. The LI-7700 has a precision of 5 ppbv, and sampling frequency of 10-40 Hz [57]. Both analyzers are capable of mobility and meet the requirements for mobile methane detection.

2.1.6 Analyzers Selection

A review of the potential analyzers for methane detection is shown in Table 1. Only laser spectrometers could determine atmospheric differences of methane at low concentrations and are methane specific without additional processing of the methane sample. Laser spectrometers from Los Gatos Research and LI-COR Biosciences were selected for mobile methane detection because of their varying measurement methodologies, lower detection limits, and precision.

Table 1: A Review of Potential Methane Analyzers for Mobile Methane Detection.

Metric	FID	FTIR	IR	OGI	MOS	Catalytic Bead	Laser Spectrometers
Low Concentration	✗	✗	✗	✗	✗	✗	✓
Quantitative	✓	✓	✓	✗	✓	✓	✓
Methane Specific	✗	✓	✗	✗	✗	✗	✓

2.2 Spectroscopy

The use of the UGGA and the LI-7700 in mobile methane detection requires a basic understanding of the spectroscopy laws and the design of each analyzer. The Beer-Lambert law explains the basis for each analyzer's design and operation. The LI-7700 uses wavelength modulation spectroscopy (WMS) in an

open-path Herriott cell, while the UGGA uses closed-path, off-axis integrated cavity output spectroscopy (OA-ICOS) [57, 58].

2.2.1 Beer-Lambert Law

The Beer-Lambert law describes the relationship of species absorption by comparing the light intensity before and after passing through a sample. The idea of light dissipating began with works called ‘Traité d’optique’ by Bourguier and ‘Photometria’ by Lambert [59]. Beer’s contributions to the idea occurred almost 100 years later [59]. The Beer-Lambert law presented a combination of their works. The Beer-Lambert law is:

$$I = I_o e^{-\alpha} \quad (1)$$

where I is the received optical power, I_o is the initial optical power, and α is the absorbance [59]. In addition, absorbance is:

$$\alpha = -S(T)g(v - v_o)Nl \quad (2)$$

Where $S(T)$ is the absorption line strength as a function of temperature, $g(v-v_o)$ is a normalized line shape function for the line at v_o , N is the gas density and l is the path absorbance [60]. The expanded Beer-Lambert law is:

$$I = I_o e^{-S(T)g(v-v_o)Nl} \quad (3)$$

This law is the foundation for all spectroscopy techniques as it is modified when applied in various systems.

2.2.2 LI-COR LI-7700

The LI-7700 implements WMS across an open-path Herriott cell. WMS benefits from the abilities of tunable lasers for laser modulation. The setup is shown in Figure 2 and features a tunable near-IR laser, 2 detectors, a Herriott cell, and reference sample. The near-IR laser requires no cooling system as it does not reach high temperatures like other IR lasers.

Figure 2: WMS System in the LI-7700 [57].

2.2.2.1 Wavelength Modulation Spectroscopy (WMS)

WMS is a specific version of frequency modulation where the modulation frequency is much less than the frequency's half width [61]. Modulation of the light's wavelength occurs to measure the molecular absorption in the cell. The laser followed the pattern as shown in Figure 3. The resulting waveform is proportional to the density of the volume of molecules in the cell as:

$$\rho = K_s \left(\sum_{i=1}^M \hat{a}[i] a_{ref}[i] - K_z \right) \quad (4)$$

where K_s is the span gas value, M is the number of samples, i is the waveband from one to M , $\hat{a}[i]$ is the measured waveform, $a_{ref}[i]$ is the reference waveform, and K_z is the zero value [61]. Due to the calculation of density in WMS, methane, in units of $\mu\text{-mol/mol}$ or ppm, requires a temperature and pressure correction.

Figure 3: Modulation of the Laser Wavelength Occurring in the LI-7700 [57].

2.2.2.2 Herriott Cell

A Herriott cell is two reflective lenses opposite each other, where one lens has a portion without reflection for the source light to exit through after a designed path length [62]. The path length increases by the reflection of the light by the lens. Named for Donald R. Herriott, the cell can be either an open-path, which is accessible from all sides, or closed-path, where the inlet/outlet ports are the only path into the cell. In the case of the LI-7700, the open-path cell consists of 30 m total path length with just 0.5 m of physical path [57].

2.2.2.3 Effects

The LI-7700 had a standard sampling rate up to 40 Hz, but it was sampled at 10 Hz during operation due to sampling frequency limitations of data acquisition modules [63]. At 10 Hz, the LI-7700 had a precision of 5 ppbv of methane. In addition, it had a measurement range of 0-40 ppmv for precise measurements [63]. The LI-7700 reported a linear error equal to 1% of the methane reading. Because of the LI-7700's high sampling frequency, open-path operation, and precision, the LI-7700 is the state-of-the-art ambient methane analyzer.

Because of the open-path operation, the implications of the LI-7700 consist of a having a relative signal strength indicator (RSSI) and measuring in parts per million-meter (ppmv-m). With the open-path cell, objects can interfere with the laser by obstructing its path. By quantifying the RSSI, the LI-7700 discloses the level of interference during operation. A minimum of 10% RSSI was required for accurate

measurements [64]. With the Herriott cell of 0.5 m, the LI-7700 records the total ppmv of methane across the cell in ppmv-m. The LI-7700 averages the methane reported across the cell, thus it cannot determine the distribution of methane concentrations across the cell path.

2.2.3 Los Gatos Research Ultra-Portable Greenhouse Analyzer (UGGA)

The UGGA uses Los Gatos Research's patented OA-ICOS technology to quantify methane, water (H₂O), and CO₂. The OA-ICOS was created based on cavity ringdown spectroscopy. Both methods consist of a closed sampling cell, a diode laser, a detector, and a sampling pump. However, OA-ICOS and cavity ringdown vary in their measurement principles.

2.2.3.1 Cavity Ringdown

The cavity ringdown technique was developed during the 1980s and used a laser and a closed cell with almost perfect reflectivity [65]. It was created to reduce the number of uncertainties in the cell due to small changes in wavelength absorption over small distances. The cavity ringdown technique determines the absorption of the species by quantifying the losses, or ringdown time, during each pass of the cell. The integration of the losses determines the quantity of each species in the cell. By pairing this with a pulsed laser, cavity ringdown is a cost effective and accurate measurement technique. Currently, Picarro Inc. produces commercially available analyzers using the cavity ringdown technique, sampling at a default frequency of 1/5 Hz, though higher frequencies are available [24, 66]. The sampling rate is limited in the design of cavity ringdown spectroscopy due to physical ringdown time [67]. To increase sampling rate, the OA-ICOS was created.

2.2.3.2 Off-Axis Integrated Cavity Output Spectroscopy

Using cavity ringdown as the foundation, integrated cavity output spectroscopy (ICOS) was created by Anthony O'Keefe, the founder of Los Gatos Research. ICOS is when the laser's wavelength enters the closed-path cavity and the wavelength output from the cavity determines the losses in the cell caused by

molecular absorption. The integration of the total signal transmitted and a previously defined baseline determine the absorption in the cell.

Normalization occurs to remove any broadening effects caused by the lasers. The signal of ICOS is:

$$I = I_o T^2 e^{-kl} [2 \log(R')]^{-1} \quad (5)$$

where I is the transmitted intensity, I_o is the incident light intensity, T is the mirror transmission, k is the intra-cavity absorption per unit length, l is the cavity sample length, and R' is the effective reflectivity [68]. Effective reflectivity is:

$$R' = R e^{-kl} \quad (6)$$

where R is the true mirror reflectivity [68]. The light in ICOS retraces the path throughout the cell without a delay in sampling. This allows for an increase in precision due to overlapping light passes. OA-ICOS uses a laser that is not aligned to the centerline axis. By changing the laser alignment, the light changes path shape and increases path length [69]. The system is shown in Figure 4.

Figure 4: OA-ICOS System in the UGGA [70].

2.2.3.3 Effects

Due to the closed-path operation of the UGGA's OA-ICOS method, the UGGA has some benefits over other spectroscopy methods. The ICOS method allows for precise measurements. Sampling at steady state for 100 seconds, the UGGA reports a precision of 2 ppbv [56]. The UGGA has a standard operational range of 0-500 ppmv of methane but has the capability to report as high as 10,000 ppmv of methane [56]. In addition, the UGGA used in this study had a maximum sampling frequency of 1 Hz. The Los Gatos Research Greenhouse Gas Analyzer and the Fast Methane Analyzer can report methane at up to 10 and 20 Hz, respectively [71, 72].

The closed-path cell of the UGGA is 343 cubic millimeters (mm^3). For the sample to reach the cell inside the portable case, the UGGA has an internal sampling line of 3.175 mm (millimeter) internal diameter and 1.12 m length. A positive displacement pump flows at a rate of 0.5 standard liter per minute (slpm) to create a vacuum in the closed cell. The vacuum pulls the sample through the cell, thus causing diffusion in the cell. The UGGA operates with a cell pressure near 140 Torr. The use of a pump creates a time delay as a function of the sample line length, both external and internal of the analyzer. The external line allowed for mounting the UGGA away from the sampling location (within a vehicle to avoid exposure to elements). Thus, the use of OA-ICOS in the closed cell creates signal processing issues when compared to the LI-7700. But because of its remote location and closed-path operation, it is not as sensitive to environmental weather conditions (i.e. rain drops, dust, or condensation on lenses).

2.3 Sampling Implications

The conversion of continuous operation into discrete signals creates signal processing issues. The signal processing effects of the equipment illustrates the sampling issues associated with the analyzers. The time delay and diffusion caused by the UGGA's operation impacts sampling and signal processing. Understanding basic signal terms and processes allows for the better understanding of analyzers.

2.3.1 Signals and Systems

In signal processing, there are signals and systems. Systems create discrete output signals from real world continuous inputs [73]. All sensors or analyzers are systems, and their outputs are signals that are available for interpretation.

2.3.1.1 Linear

For systems to be linear, their signals must be homogenous and additive. Homogenous is when a change in amplitude of the input signal caused a change of the amplitude of the output signal [73]. A signal is additive if the sum of two input signals produced the sum of their output signals [73]. All linear systems require both attributes, but a third property is necessary for some processing techniques, shift invariance. Shift invariance is time invariance, where a change in time does not change the output signal [73]. In the UGGA and LI-7700, shift invariance is the ability to record the same signal at different operational times. Both the UGGA and the LI-7700 are examples of linear systems.

2.3.1.2 Convolution

Convolution is a mathematical operator of discrete signals. The principle is the superposition of two signals to create a third signal. Convolution sum is:

$$y[i] = \sum_{j=1}^m h[j] * x[i - j] \quad (7)$$

where y is the output signal, x is the input signal, h is the impulse response, i is the current point, and m is the length of the impulse response. [74]. The impulse response is another signal, or a filter that creates the output signal. Any distortion or dilation is an impulse response and that convolutes with the input signal. For convolution to create the proper impulse response, the system must be linear and time invariant under all operating conditions. For the UGGA and LI-7700, any dilutions or other sampling effects were an impulse response that had been applied to the UGGA's or LI-7700's input signal.

Convolution has a few mathematical properties. They are commutative, associative, distributive, and transference. Commutative convolution is convolution regardless of the order of the signals. Associative

convolution is convolution regardless of their grouping if they remained in the same order. Distributive is best shown as the equation:

$$A(B + C) = AB + AC \quad (8)$$

where convolution distributes into a grouping. Transference is a linear shift to both the input and output signal, without changing the impulse response [75]. Transference is only a change in magnitude of a signal, while the signal retained its original shape. This is important to note as normalization of signals was a transference. With all the convolution and linear properties, all the impulse responses combine to create one impulse response.

All equipment used in the mobile methane systems were systems themselves. Their outputs to the computer were the signals for interpretation. The UGGA had an impulse response due to the diffusion in the closed cell. To overcome this, the impulse response required a correction for accurate measurement.

3. Experimental Setup

In order to formulate conclusions regarding limitations of methane analyzers in a mobile detection system, two experiments were designed. For mobile methane detection, both field and laboratory testing were performed to examine the various capabilities and/or limitations of each system.

3.1 Field Testing

Field testing required all the equipment to be deployed to a vehicle as a single unit. The equipment, data collection routes, and thresholds were determined prior to field testing. Field testing occurred in/near Morgantown, West Virginia (WV).

3.1.1 Vehicle Setup

The equipment was divided into two systems, fast and slow. The full breakdown of equipment is shown in Table 2. A few pieces of equipment were used in both systems. For mobile methane detection, each system (fast and slow) consisted of its own methane analyzer, sonic anemometer, and GPS. The sonic anemometer for each system quantified wind direction using vectors, where the sign indicated direction. This allowed for the determination of wind direction for potential source attribution. The GPS units quantified location for mapping of sources and vehicle speed for correcting wind speed. Each system was capable to quantify methane, determine potential source direction, and record geospatial information for mapping and user interpretation. All components were sampled at either 10 or 1 Hz, respectively.

Table 2: Equipment Used in Mobile Methane Detection.

Make	Model	Output (Units)	Frequency	Range	Error	System
LI-COR Biosciences	LI-7700 [63]	Methane (ppmv)	Max:40 Hz Used:10 Hz	0-40 ppmv	1%	Fast system
Gill Instruments	WindMaster [76]	Wind Speed (two horizontal components, one vertical component) (m/s)	Max:20 Hz Used:10 Hz	0-45 m/s	1.5%	
U-Blox	EVK-M8U [77]	Position (Latitude, Longitude), Speed (m/s)	Max:20 Hz Used:10 Hz	N/A	2.5 m; 0.5 m/s	
Los Gatos Research	Ultra-Portable Greenhouse Gas Analyzer [56]	Methane/CO ₂ /H ₂ O (ppmv)	Max: 1 Hz Used: 1 Hz	.01-500 ppmv (methane); 0-20,000 ppmv (CO ₂); 0-70,000 ppmv (H ₂ O)	1%	Slow system
Gill Instruments	WindSonic [78]	Wind Speed (two horizontal components) (m/s)	Max:4 Hz Used:1 Hz	0-60 m/s	2%	
GlobalSat	BU-353S4 [79]	Position (Latitude, Longitude), Speed (m/s)	Max:5 Hz Used:1 Hz	N/A	2.5 m; 0.1 m/s	
LI-COR Biosciences	LI-7500 [80]	CO ₂ /H ₂ O (ppmv)	Max:20 Hz Used:10 Hz	0-3,000 ppmv (CO ₂); 0-60 ppmv (H ₂ O)	1%	Both Systems
LI-COR Biosciences	LI-200 [81]	Solar Loading (Converts V to $\frac{W}{m^2}$ using ICP-CON PET-7019z [82])	Max:< 1 μ -s ICP-CON max:10 Hz ICP-CON used:1 Hz	0-3,000 $\frac{W}{m^2}$	1%	
Omega	iBTHX [83]	Temperature (°F), Pressure (mbar), Relative Humidity (%)	1/4 Hz	-40-185 °F; 10-1,100 mbar; 0-100 %	2.7 °F; 2 mbar; 4%	

Figures 5 and 6 show the full field testing setup mounted to a vehicle. All the equipment shown was mounted to the vehicle using a plate designed for accommodation of the LI-7700. The full equipment list included 2 methane analyzers, 2 sonic anemometers, 2 GPSs (not pictured), an open-path CO₂/H₂O analyzer, a pyranometer, a weather sensor, and a laptop (not pictured). The equipment mounted to the plate was designed to ensure methane detection without interfering with wind measurements. A rudimentary flat plate analysis was conducted by Ms. Rebekah Barrow (BSME, BSAE) to assess minimum clearance issues as related to vehicle wake. Lower mounted analyzers were mounted at the front of the plate while taller analyzers were mounted nearer the rear.

Figure 5: Testing Equipment Mounted to the Vehicle: (Left to Right) LI-COR LI-7700, LI-COR LI-7500, Gill WindMaster, Gill WindSonic.

For methane analyzers, both the LI-7700 and UGGA were presented earlier. The LI-7700 was calibrated by LI-COR Biosciences prior to its deployment. Due to the open-path operation of the LI-7700, it was required to be mounted to the plate on the outside of the vehicle. The LI-7700 was mounted in the front on the plate to reduce dispersion of the methane sample from other components. The UGGA was calibrated for methane prior to testing and is described in Appendix I. The UGGA was not calibrated for

CO₂ or water vapor prior to operation. The UGGA was mounted inside the vehicle and a 4.78 m line was attached outside the vehicle for sampling.

Figure 6: Small Testing Equipment Mounted to the Vehicle: (left to right) LI-COR LI-200, Los Gatos Research Ultra-Portable Greenhouse Gas Analyzer, Omega IBTHX.

Both the WindSonic 2D and the WindMaster 3D were manufactured by Gill Instruments. The WindSonic 2D only measured wind in the horizontal directions at 1 Hz, while the WindMaster 3D was capable of measuring at speeds of up to 20 Hz, though data collection occurred at 10 Hz. Their north direction was aligned with the front of the vehicle, denoted as vehicle north. In addition, the WindMaster's stand was used as a mount for the UGGA sampling line and the weather sensor, as shown in Figure 6. This allowed

for the shortest distance between the UGGA sampling line and the LI-7700 without an additional mount. The UGGA sampling inlet was therefore at the approximate height of the LI-7700 sampling plane. The two GPS units deployed were a U-Blox EVK-M8U and a GlobalSat BU-353S4. The EVK-M8U reported at a frequency of 10 Hz, while the BU-353S4 reported at 1 Hz. Both GPS units recorded speed in meters per second (m/s) and location in latitude and longitude coordinates. The fast system consisted of the LI-7700, the WindMaster, and the U-Blox, while the slow system consisted of the UGGA, the WindSonic, and the BU-353S4.

Additional equipment included a CO₂/H₂O analyzer, a pyranometer, a weather sensor, and a laptop. The CO₂/H₂O analyzer was a LI-COR LI-7500. It implemented the same WMS as the LI-7700 except the LI-7500 scanned wavelengths for CO₂ and H₂O. The LI-7500's results were part of another ongoing study, but it was still active during data collection. The pyranometer was a LI-COR LI-200, which determined the solar loading ($\frac{W}{m^2}$). The weather sensor was an Omega iBTHX which was used to record ambient pressure in millibar (mbar), temperature (°F), and relative humidity (%). Using the Omega and the LI-200, the weather conditions were defined as they played a role in methane transport. The atmospheric stability class was calculated using the LI-200 and Omega but these items were not used in this mobile methane detection research. However, they were installed to collect additional data that can be used in future research projects focused on quantification. A computer using an in-house developed data acquisition software, Scimitar, recorded all the data and displayed it for the user in real time. The fast system's sampling frequency was limited by Scimitar due to its maximum sampling frequency of 10 Hz. Once the equipment was mounted, it was wired accordingly for data acquisition.

For all the equipment to communicate to the computer in an orderly fashion, a mobile methane detection box was created. It was designed to receive all analog and digital inputs from the equipment and connected to the computer with a single USB and ethernet cable, as shown in Figure 7. Ports consisting of USB, ethernet, DB9, BNC connectors, and a terminal block were mounted to the sides of the box. Inside the box, separate cables were connected to the appropriate communication or power method. The

implementation of the mobile methane detection box was created to simplify the setup and data collection. Once the vehicle had the equipment mounted and connected, it was ready for data collection.

Figure 7: Design of the Mobile Methane Detection Box used for Data Collection.

3.1.2 Data Collection

Data collection began in January 2019 and continued into February 2019. Over the course of two months, the field testing equipment was applied to the vehicle totaling 8 days, 43 trip files, and over 15 hours of data. This yielded over 540,000 methane values at 10 Hz and 54,000 at 1 Hz. The number of days proved the systems robustness as it was exposed to various weather conditions during numerous tests. Because the UGGA was mounted inside the vehicle, it did not experience any sampling losses due to weather. However, the use of the LI-7700's analyzer was hindered based on weather conditions when condensation occurred on the Herriot cell lenses.

The system was operated primarily near the Morgantown, WV area. Most of the urban driving throughout Morgantown detected few sources of methane. Due to the abundance of natural gas wells in the area and

other methane sources (e.g. coal mines), rural driving outside city limits was shown to be an ideal region for mobile methane system evaluation. Figure 8 displays all routes taken during field data collection. Note, that in many cases routes were repeated when methane sources were identified as a method to compare and increase data samples collected under different conditions. The routes passed through Cassville, Core, and Pentress, WV and Mt. Morris and Point Marion, Pennsylvania.

Figure 8: All Field Data Routes Mapped in Google® Earth.

3.1.3 Background Threshold

Because methane disperses from high concentrations to low concentrations, small methane concentrations above background may indicate larger methane sources upwind. The dispersion of methane was a function of the wind in transport and the weather conditions. By pairing methane readings above background with the wind direction, methane detection may be able to lead to potential source attribution. For methane detection, a background threshold was required to determine if methane concentrations were elevated.

In Phillips et al., the mode of the data collected during transient operation was considered the background threshold [14]. In Eapi et al., the national average methane concentration of 1.867 ppmv was used as the background threshold [16, 28]. Atherton et al. defined the background threshold as the lowest methane concentration every 300 seconds [17]. In Fischer et al., a moving average of a two minute time period was used as the background threshold [24]. In addition, they noted that the use of a constant methane background threshold was not representative of real world operation in both time and space.

For initial results, the background threshold was set to be the lowest 5% of each trip data, identical to the methods performed by Brantley et al. [84]. The 5% background threshold was believed to contain the background concentration during data collection while allowing for varying background concentrations. The background threshold would only remove the lowest 5% of points, but concentrations less than 1% of the maximum background corrected concentration were considered background as well.

3.1.4 Detection Threshold

A detection threshold was required to determine if elevated methane concentrations, or peaks, were potential methane sources. Phillips et al. implemented 2.5 ppmv as the threshold for source attribution, which was the 90th percentile value of their total data set [14]. Eapi et al. used 3 ppmv as the detection threshold because it was at least 1 ppmv greater than their background [16]. Atherton et al. used the ratio of CO₂ to methane for three seconds to determine detection thresholds [17]. Fischer et al. used 110% of the background value as their detection threshold [24]. During research and evaluation, the initial detection threshold of 3 ppmv was selected. Note that the UGGA's background was zeroed to the LI-7700's background due to different calibrations.

3.2 Laboratory Testing

In the laboratory, the UGGA was exposed to a set volume flow rate of methane for a set duration. The full laboratory setup design, shown in Figure 9, included a three-way valve, relay, ICP-CON PET-7019Z, power supply, STEC SGD-710C gas divider, 101.3 ppmv methane bottle, and zero-air bottle. Appendix II

contains the calibration certificates, with uncertainties and errors, for the methane bottle, zero-air bottle, and the SGD-710C gas divider.

Using the methane bottle, the air bottle, and the gas divider, a controlled flow rate of methane with a known concentration was delivered to the UGGA. Prior to reaching the UGGA, a three-way valve and relay were connected to an ICP-CON PET-7019Z's digital output, which separated the flow into bursts of various lengths. After the three-way valve, a t-fitting was used as a flooded probe to provide the UGGA with a flow rate in excess of its sample flow rate. The sample flow rate of the UGGA was 0.5 slpm. The arrangement enabled background sampling when not exposed to a burst. Using Scimitar, the valve control and the response from the UGGA were recorded. The concentrations of methane delivered to the UGGA were spaced far enough apart that the UGGA had enough time to reach background prior to the sampling of the next burst.

Figure 9: Burst Testing Setup Flow Diagram.

The tests performed consisted of 101.3 and 50.65 ppmv methane concentrations. The 101.3 ppmv concentration was used as it was the concentration used in calibration of the UGGA. The 50.65 ppmv was used as it was above the range of the LI-7700. Despite the use of two separate concentrations of methane, the response curves had the same shape but varied in magnitude. These tests confirmed the UGGA's time invariant response.

4. Initial Field Testing Results

Using the initial field testing results, disparity between the LI-7700 and the UGGA became apparent. A mapping of the initial tests depicted the implications of the UGGA's closed-path operation. In order to statistically compare the analyzer responses, a performance value (PV) was later defined. Over the 15 hours of data collection, 12 hours consisted of data where the vehicle was in motion. Any values of vehicle speed that were lower than the GPS vehicle speed error were defined as stationary and the remaining points were defined as mobile.

4.1 Visual Interpretation

Using MATLAB® and Google® Earth, the trip files collected during field testing were mapped. The MATLAB® code, shown in Appendix III, created a Google® Earth file of the trip. The path taken was mapped with methane concentration extruded upwards to depict the concentration, with higher concentration having taller extrusions. In addition, the color scale ranged for each analyzer in each file with blue as the background methane concentration and red as the maximum methane concentration.

A trip section is mapped in Figures 10 and 11. Figure 10 displays the LI-7700's response to a suspected methane plume, and the Figure 11 displays the UGGA's response to the same plume of methane. Note, the Google® Earth mapping extrudes based on the ratio of methane concentration to the peak of methane in the analyzer's response. Here, Figure 11 has a higher extrusion of background methane because the UGGA underreports the methane peak of the LI-7700.

Despite both peaks being represented with red, the LI-7700's response was 8.69 ppmv above background and the UGGA's methane concentration was only 1.02 ppmv above background. The lower UGGA peak value and its shift in location highlighted the diffusion and delay associated with its closed-path operation. Figure 12 depicts both the mapped views of Figures 10 and 11 on a graph for a comparison of the responses in time.

Figure 10: LI-7700 Methane Concentration Displayed in Google® Earth.

Figure 11: UGGA Methane Concentration Displayed in Google® Earth.

Figure 12: Contiguous Methane Concentrations of LI-7700 and UGGA in Time During Initial Results.

This introduced a peak error and plume integration error. The peak error was the difference in peak methane concentrations. The plume integration error was the integrated amount of methane over the entire trip (i.e. the area under a methane versus distance or methane versus time curve). Both errors were significant in determining the analyzer's accuracy. To determine the response time of the UGGA, laboratory testing was required.

4.2 Numerical Results

Apparent from the visual interpretations of the LI-7700 and UGGA's responses during operation, the UGGA required a time delay correction prior to any statistical comparison due to its sampling method. Once the time shift was applied, a PV was established to compare the analyzer responses.

4.2.1 Sampling delay

Using the same external 4.78 m length and 3.175 mm internal diameter line from field testing, along with the internal 1.12 m length line and 3.175 mm internal diameter line inside the UGGA, the sampling delay of the line was calculated to be 5.6 seconds for a constant sample rate of 0.5 slpm. The calculation of the delay assumed no flow loss through the lines. However, the exact dimensions of all fittings and

connections were not easily quantified, so the time delay was measured experimentally to ensure accuracy.

The UGGA was exposed to a concentration of methane for a length of time using a valve. The UGGA was allowed to return to a background value between tests. With the knowledge of the valve opening time, the delay time of the UGGA was measured. Each methane concentration duration at its respective concentration was separated into individual files. Files for each of the 101.3 ppmv and 50.65 ppmv concentrations were processed using MATLAB®. The impulse responses for both concentrations are shown in Figures 13 and 14. Both concentrations of methane illustrated the same delay time of about 9 seconds that concurred with the delay shown in Figures 10, 11 and 12. The method assumed no loss of flow through the lines. In addition, the time calculated was the time to reach the cell and did not include the response time of the UGGA. Note that delay was limited to an integer value due to the sampling frequency of 1 Hz. The small stagger in the impulse responses was associated with the calibration of the UGGA.

Figure 13: Impulse Response of the UGGA with 101.3 ppmv Methane. Note: 1 indicates the valve is on and 0 indicates the valve is off.

Figure 14: Impulse Response of the UGGA with 50.65 ppmv Methane. Note: 1 indicates the valve is on and 0 indicates the valve is off.

4.2.2 Methane Distribution

Assuming the lowest 5% of methane was background for both the UGGA and LI-7700, any points above background indicated a potential methane plume. Figure 15 displays the frequency of methane concentration during all 12 hours of moving data on a log scale. The LI-7700 reported 89% of its methane concentrations below 3 ppmv at both 10 and 1 Hz. The UGGA reported 79% of its methane concentration below 3 ppmv.

Figure 15: The Distribution of Methane Concentration for all Moving Data. Note: The total number of samples was 444,991 for 10 Hz LI-7700 and 44,556 for 1 Hz LI-7700 and UGGA.

4.2.3 Define Initial Performance Value

The comparison between the LI-7700 and the UGGA required a PV to conduct statistical comparisons.

Prior to implementing the PV, normalization of the signals was performed. Using the normalized methane signals, a PV was defined and assigned for each initial trip file.

4.2.3.1 Normalization

Time alignment and normalization were required prior to the implementation of a PV. Laboratory flow testing of the UGGA quantified the sample delay time. Because each analyzer reported a different background due to their varying calibrations, the normalization corrected each analyzer to its own respective background. With the methane time aligned, a normalization was applied as shown:

$$UGGA_{norm}(t) = (UGGA(t) - UGGA_{Background}) / (\max(LI7700) - LI7700_{Background}) \quad (9)$$

$$LI7700_{norm}(t) = (LI7700(t) - LI7700_{Background}) / (\max(LI7700) - LI7700_{Background}) \quad (10)$$

where t is the time in the signal, $UGGA_{norm}(t)$ and $LI7700_{norm}(t)$ are the new normalized signals of the UGGA and LI-7700, $UGGA(t)$ and $LI7700(t)$ are the original signals of the UGGA and LI-7700, $UGGA_{Background}$ and $LI7700_{Background}$ are the background threshold value of the UGGA and LI-7700, and $\max(UGGA, LI7700)$ is the maximum methane concentration between either the UGGA's or LI-7700's signal. Figure 16 displays the normalized version of the methane plume in Figures 10, 11, and 12. This normalization corrected both signals by removing their respective background thresholds and dividing based on the maximum of the LI-7700's methane signal. All normalized points below 0.01 were considered background to remove methane concentrations near the background threshold.

Figure 16: A Normalized Response of the Same Methane Plume by the LI-7700 and the UGGA.
Note: The methane responses were time aligned prior to normalization.

4.2.3.2 PV Definition

In order to compare the differences between the UGGA's and LI-7700's normalized methane responses, a performance value (PV) was created for each trip file. The PV quantified the correlation between the UGGA and the LI-7700's signal. The implementation of the normalized methane responses bounded the PV between zero and one. A PV of one indicated that the UGGA perfectly matched the LI-7700's methane response. Four metrics were combined to create a single PV. The PV was defined as:

$$PV = W_{PE} * (1 - PE) + W_{R2} * r^2 + W_{SEE} * (1 - SEE) + W_{PIE} * (1 - PIE) + \quad (11)$$

Where PE is the peak error, r^2 is coefficient of determination, SEE is the standard estimate of the error, PIE is the plume integration error, and W is the weight of each component.

The peak error (PE) was the average of the percent error of the peak of each plume given by Equation 12:

$$PE = \frac{\sum_{i=1}^n \frac{|\max(U(S(i):E(i))) - \max(U_{UGGA}(S(i):E(i)))|}{\max(U(S(i):E(i)))}}{n} \quad (12)$$

where n is number of plumes, i is the i th plume, $U(S(i):E(i))$ is the LI-7700 concentration between the start and end of the plume, and $U_{UGGA}(S(i):E(i))$ is the concentration between the start and end of the plume. A plume was defined as contiguous elevated methane concentrations with five seconds of background between each plume. A peak was the maximum methane concentration in a given plume. By using the maximum value, PE compared the true maximums of each interval. Five seconds of background between each range allowed the LI-7700 to fluctuate without starting a new interval. Peaks that were not perfectly time aligned were credited despite inaccurate location. A PE of zero indicated perfect peak matching.

The coefficient of determination (r^2) served as a measure to quantify the variance between the two variables. In this application, r^2 quantified the variance between the LI-7700 and the UGGA's normalized methane responses. The r^2 was calculated by squaring the linear correlation coefficient. An r^2 of zero indicated that there was not a linear association between the methane responses and an r^2 of one indicated a perfect linear association between methane responses.

The standard error of the estimate (SEE) was the calculation of combined error from each point as given by Equation 13:

$$SEE = \sqrt{\frac{\sum_{t=1}^n (U(t) - U_{UGGA}(t))^2}{n}} \quad (13)$$

where n is the number of points in the data file, t is the current time step, $U(t)$ is the LI-7700's signal at the point t , and $U_{UGGA}(t)$ is the UGGA's signal at the point t . The SEE included an implementation of the squaring of the difference, or sum squared error, creating only non-negative numbers. This was useful for determining magnitude of error but not direction of error. Any exact responses from the LI-7700 and UGGA resulted in a SEE of zero.

The plume integration error (PIE) was percent error of integrated signals. The integration was the total amount of methane reported across the entire data file. PIE is given by Equation 14.

$$PIE = \left| \frac{\int U(t) - \int U_{UGGA}(t)}{\int U(t)} \right| \quad (14)$$

where $\int U(t)$ is the integrated LI-7700 signal, and $\int U_{UGGA}(t)$ is the integrated UGGA signal. The PIE term accounted for the total amount of methane in the data file but did not account for when the methane plume occurred in the data file.

The normalization of the methane signals for the use of PV required the implementation of varying weights between each PV component. To calculate the weights for each component, the variance of each component in the initial data was used to determine the weight for each component. Each component's weight was its variance divided by the sum of all the variances, which limited the PV calculation from zero to one. Variance in each PV component was selected to attribute a higher weight to components that had higher variance between each trip file.

4.2.3.3 Initial PV Statistics

Prior to comparisons, the LI-7700 was down sampled to 1 Hz using a forward average to match the UGGA. In addition, the four PV components were calculated for each trip file to determine the associated weights from the variances. Table 3 depicts a statistical breakdown of the 43 trip files including the average, variance, maximum, minimum, and each associated weight of each component of the PV. The SEE and PIE were shown to be 1% and 11% of the total variance, respectively. The lower variance led to lower weighting in the PV calculation. Using the calculated weights, the average, variance, maximum, and minimum of the PV was calculated and is shown in Table 3. Appendix IV contains all the PVs and their components along with the maximum methane concentration from each methane analyzer for each trip file. Table 3 shows that peak error was the largest source of variance between the data, which was of significant concern since methane peaks were one of the most common methods to detect a potential source of methane in other research programs [14, 16, 24].

Table 3: Statistical Breakdown of the PV and PV Components of the Initial Data.

	PE	r ²	SEE	PIE	PV
AVG	0.602	0.544	0.070	0.083	0.512
VAR	0.061	0.040	0.001	0.013	0.030
W	0.53	0.35	0.01	0.11	
MAX	0.953	0.981	0.136	0.500	0.939
MIN	0.071	0.274	0.017	0.003	0.217

For a further breakdown, Figure 17 depicts the contribution distribution of the PV components. The SEE and PIE were shown to contribute at least 0.9 during over 79% and 86% of the trip files, respectively. Equally weighted PV components would have skewed the PV to high values due to the distribution of SEE and PIE.

Figure 17: Distribution of each PV Component Contribution from the Initial Data Set. Note: The total number of each component value was 43.

4.2.4 Methane Detection using the Initial Threshold

To detect elevated levels of methane, the detection threshold of 3 ppmv was implemented with initial data after the UGGA's background was zeroed to the LI-7700's background. These plumes were defined as contiguous methane concentrations above the background threshold and were separated by five seconds

of background concentration between plumes. During data collection, a plume of methane was detected 363 times. Of the 363 sections, the LI-7700 at 10 Hz recorded above the 3 ppmv detection threshold in 112 plumes. Compared to the LI-7700 at 10 Hz, the UGGA reported zero false positive plumes. A false positive plume was denoted as a plume where the UGGA detected a peak and the LI-7700 did not detect a peak above the detection threshold. The UGGA reported 45 false negative plumes. A false negative plume was denoted as a plume where the UGGA did not report a methane peak but the LI-7700 reported a peak methane concentration above the detection threshold.

When down sampled to 1 Hz, the LI-7700 reported above the threshold 97 times. Compared to the LI-7700 at 1 Hz, the UGGA reported 0 false positives and 30 false negatives. The detection threshold failures did not account for the error associated between the peak concentrations. It was theorized that the false negatives reported by the UGGA were associated with small width, low methane concentrations whereby the smearing effect associated with its sampling method, averaged values below the peak threshold. A sensitivity analysis of the threshold quantity was required to determine if the 3 ppmv detection threshold reduced uncertainty in methane detection.

4.3 Sampling Issues

Using the initial data, it was shown that time alignment alone did not correct the UGGA to match the LI-7700. The PVs indicated issues with the UGGA in detecting peak methane concentrations, total methane concentrations, and signal matching. As shown, the UGGA's sampling method created a smearing effect in the methane signal, associated with diffusion in the cell.

The UGGA's advantages for its closed cell operation were diminished with a misrepresented signal. An accurate UGGA signal with time correction did not experience the weather, mounting, and range concerns of the LI-7700. To determine the sampling implications of using each system, the limitations due to sampling frequency, the methane analyzer's operational principles, and vehicle speed were further examined.

5. Sampling Limitations

A closer investigation into sampling limitations was conducted. This included geospatial, wind, and peak limitations associated with the sampling methods and frequencies of the methane detection systems. The collective limitations were observed to determine if any corrections were required for either methane detection systems.

5.1 Geospatial Limitations

Geospatial limitations were a concern when combining discrete sampling methods with moving vehicle speeds. The distance between sampling locations of the analyzer as a function of vehicle speed was defined as geospatial resolution (GR). The GR contained the methane sample, but its location occurred within the current and previous sample. With differing sampling frequencies, the LI-7700 and the UGGA experienced different GR in m, which was defined by Equation 15:

$$GR = \frac{VS_{avg}}{\omega} \quad (15)$$

where VS_{avg} is the average vehicle speed in kilometers per hour (kph), and ω is the sampling frequency in Hz. Figure 18 displays the GR of the LI-7700 and UGGA as a function of vehicle speed. Time alignment did not affect the GR, but time alignment did affect the error or uncertainty in geospatial location. Geospatial location error (GLE) was the distance between the sample being encountered and the analyzer's recorded response. GLE, as a function of GR, is:

$$GLE = GR * (t_{delay} + t_{response}) \quad (16)$$

where t_{delay} is the delay time and $t_{response}$ is the response time of the analyzer. Because of its closed-path operation, the UGGA's GLE experienced a sampling and response delay. The LI-7700 did not experience the delay time due to its open-path sampling method. With time alignment, the GLE of the UGGA was reduced to the response time within the cell.

Figure 18: Geospatial Resolution of the LI-7700 at 10 Hz and the Time Aligned UGGA at 1 Hz.

Implementation of closed-path methane analyzers in mobile methane detection applications required a time delay correction to reduce GLE to only be a function of response time. A speed limit proposed as a function of sampling frequency prevented excessive GR values to time corrected analyzers. A constant speed limit of 36 kph at 1 Hz resulted in a GR of 10 m. To achieve a GR of 10 m, the speed limit, in kph, as a function of sampling frequency, in Hz, is:

$$SL_{10} = 36 * \omega \quad (17)$$

Other researchers have implemented closed-path analyzers during driving operations with time corrections. Von Fischer et al. limited their vehicle speed to 70 kph with a methane analyzer sampling at 2 Hz [24]. Their vehicle speed limit produced a GR of 9.83 m after they applied a response time correction. Phillips et al. did not impose a speed limit to their Picarro G2112-i, but did correct for the response time of the methane analyzer [14]. The newest version of the Picarro G2112-i has a standard sampling rate of ½ Hz [85]. A vehicle speed limit of 18 kph would be required to maintain a GR of 10 m. Eapi et al. imposed a speed limit of 20 mph, or 32.19 kph, while implementing a Picarro G2204 with a sampling frequency of 1/3 Hz [16]. The GR of using the Picarro G2204 at 32.19 kph was 26.82 m.

The geospatial limitations associated with sampling methods and frequencies was shown to impact the sampling distance between points. To reduce the GR distance to 10 m, a speed limit as a function of sampling frequency should be employed.

5.2 Wind Speed Limitations

While the goal of this research was to assess system implications for methane mapping, others seek to include source attribution as a capability. Methane plumes were created from atmospheric diffusion and downwind advection. If a wind direction can be accurately determined, attribution may be possible. However, the effects of driving the vehicle may reduce this capability since atmospheric wind speed may be small compared to that induced by vehicle operation. In addition, there was error associated with the measurements of wind speed and vehicle speed (GPS speed error).

5.2.1 Deriving Wind Speed Limitations

The sonic anemometers reported wind speed vectors that used the sign of each component to indicate direction and the value to indicate magnitude. The wind speed error was based on the wind components reported by the anemometer. The wind speed error is:

$$WS_{\sigma} = \sigma_{WS} * \sqrt{U^2 + V^2 + W^2} \quad (18)$$

where σ_{WS} is the error of the anemometer, U is the wind speed component from the north and south direction V is the east and west wind component, and W is the vertical wind component, if available. Recall, the north direction was aligned to the front of the vehicle. Because the error was based on the reported wind speed, high vehicle speeds increased the wind speed error.

As vehicle speeds increased, the W approached zero. If the WindMaster was outside the wake zone, then the WindMaster reported an angle of attack of near zero relative to the center of the anemometer. The angle of attack was the angle between of the vertical wind component and the vehicle north wind component. There are naturally small vertical wind components created from turbulent eddies within the

boundary layer. By including a 3D anemometer, one can compare these eddies to the upward wind component to ensure that the sampling components are placed outside of the vehicle wake zone.

To calculate the wind direction, the U component must be corrected for vehicle speed. The corrected wind speed is:

$$U_{corr} = U - Vs \quad (19)$$

where Vs is the vehicle speed as reported by the GPS units. Due to the sonic anemometer and GPS containing errors in reporting, the corrected vehicle north wind speed with error is:

$$U_{corr,\sigma} = (U - Vs) \pm \sqrt{WS_{\sigma}^2 + \sigma_{GPS}^2} \quad (20)$$

where σ_{GPS} is the error of the GPS's vehicle speed calculation. The corrected north wind speed component contained a range of potential values due to the uncertainty associated with error propagation. The points in time where wind direction cannot be determined are based on the limiting equations:

$$|(U - Vs)| \leq \sqrt{WS_{\sigma}^2 + \sigma_{GPS}^2} \quad (21)$$

$$|V| \leq \sigma_{WS} * \sqrt{U^2 + V^2} \quad (22)$$

The limiting equation did not describe the magnitude of the wind direction range, but only determined wind with a directional range that contained two quadrants. Figure 19 displays a compass rose with each quadrant occurring every 90° and the sign that corresponds to each wind direction. For example, if the sonic anemometer reports a wind from the south-east and Equation 21 holds, then the wind could originate from either the south-east or north-east. Note that if the wind speed error was larger than the east and west wind direction, then the east and west direction cannot be determined. To determine cases where wind direction cannot be estimated, each component in both systems was further analyzed.

Figure 19: Compass Rose for Wind Direction with Wind Components Corresponding to Direction [78].

5.2.2 Fast System

The fast system consisted of the WindMaster and the U-Blox EVK-M8U. Both recording at 10 Hz, the WindMaster and U-Blox EVK-M8U were paired with the LI-7700 for methane detection. The WindMaster had an error of 1.5% between 0-30 m/s of wind [76]. The EVK-M8U had a constant speed error of 0.5 m/s [77]. With $\sigma_{WS} = 0.015$ and at moving speeds, the limiting equation is:

$$|(U - Vs)| \leq \sqrt{(0.015 * \sqrt{U^2 + V^2})^2 + 0.5^2} \quad (23)$$

Moving speeds were defined as all values above the GPS vehicle speed error. Equation 21 held true for 20.5% of moving operation and Equation 22 held true for 16.4% of moving operation. When both rules were applied, the general wind direction quadrant could not be determined in 33.9% of the moving data for the fast system.

5.2.3 Slow System

The slow system consisted of the WindSonic and the BU-353S4. Both recording at 1 Hz, the WindSonic and BU-353S4 were paired with the UGGA for methane detection. The WindSonic had an error of 2% [78]. The BU-353S4 had a constant speed error of 0.1 m/s [79]. In this case, $\sigma_{WS} = 0.02$ and $\sigma_{GPS} = 0.1$. With $\sigma_{WS} = 0.02$ and at moving speeds, the limiting equation is:

$$|(U - Vs)| \leq \sqrt{(0.02 * \sqrt{U^2 + V^2})^2 + 0.1^2} \quad (24)$$

Equation 21 held true for 19.7% of moving operation and Equation 22 held true for 3.5% of operation.

The slow system had fewer points that violated the limiting equation than the fast system due in part to the higher accuracy of the slower GPS unit. When both rules were applied, the general wind direction quadrant could not be determined in 22.6% of the moving data from the slow system.

5.2.4 Wind Limitations

The fast system and the slow system were observed collectively to determine rules for operation. Figure 20 displays the points that violated the limiting equation for both the fast and slow system. The wind direction was still able to be estimated for 66.1% and 77.4% of the data for the fast and slow systems, respectively. Prior to processing data, no rules for reducing errors can be inferred; however, because wind speed error increased as vehicle speed increased, the minimum required wind speed in the north direction increased as vehicle speed increased.

Figure 20: Wind Speeds that Violated the Limiting equation as a Function of Vehicle Speed and Total Error.

5.3 Peak Limitations

The peak error associated with the initial PV displayed the UGGA's success at reporting peak methane concentrations. Recall, peak error was the average of the relative errors between the maximum methane concentration reported by each analyzer for the plumes in a trip file. Figure 21 displays 100 seconds of the methane response above the background threshold of each analyzer for a plume in trip 554. Note that the peak UGGA methane response was only 11% of the LI-7700's peak methane response and the UGGA was not time aligned.

Figure 21: Trip 554, Differences in Peak Values of the LI-7700 and the UGGA.

Because of the differences in the peak values of the LI-7700 and the UGGA, a sensitivity analysis was performed on the detection threshold. There were 363 possible methane plumes identified. These plumes were defined as contiguous methane concentrations above the background threshold and were separated by 5 seconds of background concentration between plumes. Ranging from 2.5 ppmv to 3.5 ppmv, the detection threshold was varied to determine if both the LI-7700 and the UGGA indicated the same potential methane sources. Table 4 depicts the sensitivity analysis of the detection threshold using the LI-7700's data at both 10 and 1 Hz. Table 4 includes the total number of peaks detected by the LI-7700, the

false positives and false negatives reported by the UGGA, along with the false positive rate, false negative rate, and false reporting rate. The false positive rate is:

$$\frac{FP}{TN} \quad (25)$$

where FP is the number of false positive plumes reported by the UGGA and TN is total negative detection plumes by the LI-7700. The false negatives rate is:

$$\frac{FN}{TP} \quad (26)$$

where FN is the number of false negative plumes reported by the UGGA and TP is the number of total positive detection plumes by the LI-7700. The false reporting rate was:

$$\frac{FN + FP}{TN + TP} \quad (27)$$

TN and TP represent the total number of plumes.

For the initial 3 ppmv, the UGGA reported a false negative rate of 40.2% and 30.9% for 10 and 1 Hz LI-7700 peaks, respectively. Because the UGGA reported no false positives with any detection threshold, the best detection threshold was determined by minimizing the false negative rate. The best detection thresholds were 2.7 ppmv for 10 Hz and 2.6 ppmv for 1 Hz. The best false negative rates were 34.7% and 24.3% for the 10 and 1 Hz, respectively. The UGGA reported numerous false negatives that indicated the necessity for a correction to the UGGA to sharpen the diffuse signal.

The peak limitations highlighted the tendency of the UGGA to significantly underreport the peak methane concentration as compared to the LI-7700. The peak error only accounted for the maximum in the range, but Figure 21 depicted local peaks that the UGGA was unable to detect. A change in detection sensitivity can reduce the false negative rate but was not enough to warrant the implementation of the UGGA without an external correction since it would still under report possible methane sources by nearly 25%.

Table 4: Detection Threshold Sensitivity Analysis of the Initial Data.

Detection Threshold (ppmv)	2.5	2.6	2.7	2.8	2.9	3	3.1	3.2	3.3	3.4	3.5
LI-7700 Peaks Detected @ 10 Hz	150	136	124	121	115	112	108	104	103	100	97
False Positives by UGGA	0	0	0	0	0	0	0	0	0	0	0
False Positive Rate	0	0	0	0	0	0	0	0	0	0	0
False Negatives by UGGA	56	49	43	44	43	45	43	44	47	46	45
False Negative Rate	0.373	0.360	0.347	0.364	0.374	0.402	0.398	0.423	0.456	0.460	0.464
False Reporting Rate	0.154	0.135	0.118	0.121	0.118	0.124	0.118	0.121	0.129	0.127	0.124
Detection Threshold (ppmv)	2.5	2.6	2.7	2.8	2.9	3	3.1	3.2	3.3	3.4	3.5
LI-7700 Peaks Detected @ 1 Hz	125	115	109	102	100	97	91	88	85	82	81
False Positives by UGGA	0	0	0	0	0	0	0	0	0	0	0
False Positive Rate	0	0	0	0	0	0	0	0	0	0	0
False Negatives by UGGA	31	28	28	25	28	30	26	28	29	28	29
False Negative Rate	0.248	0.243	0.257	0.245	0.280	0.309	0.286	0.318	0.341	0.341	0.358
False Reporting Rate	0.085	0.077	0.077	0.069	0.077	0.083	0.072	0.077	0.080	0.077	0.080

5.4 Sampling Implications

The geospatial, wind speed, and peak limitations presented guidelines for mobile methane detection applications. The geospatial limitations indicated the necessity for time alignment and a vehicle speed limit based on sampling frequency. The wind speed limitations suggested rules of thumb in order to estimate wind direction of a plume while driving. The peak limitations illustrated the errors in the methane reported by the UGGA. The weather, mounting, and interference drawbacks associated with the open-path LI-7700 could be alleviated with an UGGA, if a method to correct the underreported methane response was applied. To overcome this limitation, signal reconstruction methods were examined to correct the UGGA's signal to recreate a sharpened response.

6. Data Processing of Methane Analyzers

During the detection threshold sensitivity analysis, the UGGA proved it was unable detect the same peaks as the LI-7700. A reconstruction technique with time delay correction was required to correct the UGGA methane response. There exist numerous reconstruction methods and the following were investigated: Sequential Inversion Technique (SIT), Inverse Fast Fourier Transform (IFFT), Artificial Neural Networks (ANN), and the Differential Coefficients Methods (DCM). The results of the UGGA's reconstruction were assessed by comparing relative improvements in the PV for various reconstruction methods and sampling frequencies.

6.1 Reconstruction Methods and Assessments

Signal reconstruction was divided into two major categories, forward or backward. Forward reconstruction used the input signal to determine the potential output signal. Ganesan and Clark performed a forward reconstruction with the input signal consisting of vehicle emissions and the output signal consisted of the analyzer output [86]. By comparing the forward reconstruction to the actual analyzer input, the analyzer's response was predicted. Backward reconstruction attempted to recreate the input signal using the analyzer's output signal. All the reconstruction methods observed were backwards reconstructions, as the UGGA's input signal was the desired result.

In order to recreate the UGGA's input signal, the LI-7700 was implemented as the best method of measuring instantaneous methane. Because of the weather, mounting, and interference effects with the LI-7700's open-path operation, a corrected UGGA would allow for the removal of the LI-7700 during operation. Prior to reconstruction, the methane signals were time aligned and normalized. Each methods' theory was investigated and applied to determine their potential success for UGGA reconstruction.

6.1.1 Sequential Inversion Technique (SIT)

6.1.1.1 Theory

The SIT was detailed in Madireddy and Clark [87]. There exist coefficients, C_j , where j ranged from one to the length of the signal. Beginning with an input, $U(t_i)$, and output signal, $Y(t_i)$, where t_i is the i th value in the signal's time, SIT follows the following pattern:

$$Y(1) = C_1 * U(1) \quad (28)$$

$$Y(2) = C_1 * U(2) + C_2 * U(1) \quad (29)$$

$$Y(3) = C_1 * U(3) + C_2 * U(2) + C_3 * U(1) \quad (30)$$

and so on. Expanding the SIT becomes:

$$Y(t_i) = C_1 * U(t_i) + C_2 * U(t_{i-1}) + C_3 * U(t_{i-2}) + \dots + C_k * U(t_{i-k+1}) \quad (31)$$

where i is the value in seconds ranging from one to the length of the signals and k is the i th term in the sequence of coefficients. For example, given $U = [3, 2, 0, 1]$ and $Y = [9, 0, 5, 12]$ results in $C = [3, -2, 3, 1]$. The SIT provides an exact solution for the given input and output signals under the correct conditions.

The SIT began to fail due to two reasons: roundoff error and varying lengths of the two signals. Each concurrent C_j uses the previous C_j s beginning at $t_i = 1$. Because C_1 uses in the determination of all other C_j s, it plays a major role in the error association of too large or small C_j s. If the initial C_1 is too high or too low, other C_j s increase error through values that are too high or low. Madireddy and Clark determined that signal reconstruction began to fail when C_1 fell below a threshold of 0.137 [87].

Because of the structure of the SIT, the length of the signals impact reconstruction. Madireddy and Clark proved that the reconstruction using SIT began to fail after about 100 seconds due to the compounding of errors [87]. When the coefficients and the signals are different lengths, the SIT requires a filtering or padding method.

6.1.1.2 Application

Using field data, an individual set of coefficients were created for each data file. With individual creation for each file, the SIT was capable of reconstruction with almost zero error. The coefficients perfectly recreated the file used to derive the coefficients. Down sampling the LI-7700 to 1 Hz and performing the SIT, Figure 22 depicts the reconstruction of trip 551. The PV of the SIT's reconstruction was one. The only errors associated with SIT were the rounding errors created due to calculation precision.

Figure 22: SIT Reconstruction of Trip 551:
PV=1, PE=0, $r^2=1$, SEE=0, PIE=0.

In order to remove the LI-7700 from operation, the SIT was applied to other files. Due to varying signal lengths, either the SIT coefficients or the UGGA signal were padded both before and after with zeros to ensure the same signal length. Figure 23 displays a section from the application of trip 551's SIT to trip 554. This resulted in a PV of 0.111, or a decrease of 73.4%. Due to the zero padding, the SIT reconstruction did not affect over half the trip points. Because of the transient nature of the mobile methane detection, the SIT was not implemented.

Figure 23: SIT Reconstruction of Trip 554 using Trip 551's SIT:
PV=0.111, PE=0.867, $r^2=0.018$, SEE=1, PIE=0.693.

6.1.2 Inverse Fast Fourier Transform (IFFT)

6.1.2.1 Theory

Recall that convolution is the compounding of two signals, the input signal and the impulse response, in the time domain. Convolution in the time domain is the same as multiplication of signals in the frequency domain. Multiplying signals in the frequency domain is simpler than performing convolution in the time domain.

A Fast Fourier Transform (FFT) or IFFT transform the signals from the time domain to the frequency domain or vice versa. The FFT of a signal is the real and the imaginary parts both using:

$$Re X[k] = \sum_{i=0}^{N-1} x[i] * \cos\left(\frac{2\pi ki}{N}\right) \quad (32)$$

$$Im X[k] = \sum_{i=0}^{N-1} x[i] * \sin\left(\frac{2\pi ki}{N}\right) \quad (33)$$

where $X[k]$ is the frequency domain signal with both real and imaginary parts, $x[i]$ is the time domain signal, N is the number of points in $x[i]$, and k is frequency ranging from one to $N/2$ [88]. To perform the IFFT in the frequency domain, the signal must be recreated from both the real and imaginary parts:

$$x[i] = \sum_{k=0}^{N/2} Re \bar{X}[k] * \cos\left(\frac{2\pi ki}{N}\right) + \sum_{k=0}^{N/2} Im \bar{X}[k] * \sin\left(\frac{2\pi ki}{N}\right) \quad (34)$$

where $\bar{X}[k]$ is the amplitude of the wave of the real or imaginary part [88]. As an example, FFT applied to the signal [3,2,0,1] resulted in the signal [1.5, 0.75+0.25i, 0, 0.75-0.25i] in the frequency domain. When the IFFT was applied to the new frequency domain signal, the original [3,2,0,1] was returned. The IFFT method contains two sections, solving for the impulse response and applying the impulse response.

The convolution in the time domain allows for the reconstruction of the output signal. Convolution in the time domain requires the impulse response. The flowchart in Figure 24 displays how to solve for the impulse response. Starting with both an input and output signal, FFT transforms the signals to the frequency domain. The division of the frequency domain input and output signals results in the impulse response in the frequency domain. Performing IFFT on the impulse response in the frequency domain creates the time domain impulse response.

Figure 24: Determination of the Impulse Function from Two Signals.

Figure 25 displays the method to determine the original input using the newly found impulse response. After converting both the output signal and impulse response to the frequency domain, division occurs between the signals. This division solves for the input in the frequency domain. The use of an IFFT results in the original input signal.

Figure 25: Application of Impulse Response Signal to Create an Input Signal.

6.1.2.2 Application

Using the field data accumulated, an impulse response was created for each data file. With individual creation for each file, the IFFT showed it was capable by reconstructing with almost zero error. Down sampling the LI-7700 and performing the IFFT, Figure 26 depicts the reconstruction of trip 551 which resulted in a PV of one.

**Figure 26: IFFT Reconstruction of Trip 551:
PV=1, PE=0, $r^2=1$, SEE=0, PIE=0**

To eliminate the need for continuous open-path measurements, the IFFT was applied to other files. The IFFT was applied on other files after the signal length was changed to match the impulse response. Figure 27 displays a section of the application of trip 551's IFFT to trip 554. With a PV of 0.258, the PV decreased by 38.1% from reconstruction compared to the original. Due to the zero padding, the IFFT reconstruction did not accurately represent over half the points. To implement the IFFT, each plume of the UGGA would require an impulse response to be created prior to implementation without the LI-7700. The IFFT could be applied to mobile methane systems when both the UGGA and LI-7700 were in operation. To implement the UGGA without the LI-7700, the IFFT was not applicable.

**Figure 27: IFFT Reconstruction of Trip 554 using Trip 551's IFFT:
PV=0.258, PE=0.739, $r^2=0$, SEE=0.064, PIE=0.001.**

6.1.3 Artificial Neural Network (ANN)

6.1.3.1 Theory

In summary, an ANN is a response network that determines an output with given inputs. It models the brain, which uses neurons to send signals and modify them until it reaches its goal. An ANN is a combination of neuron layers that consists of a set number of neurons [89]. The neurons are a transfer function with a coefficient, which change the input and passes the output to next neuron. Once it has gone through all neurons, then evaluation of the output occurs.

To achieve the coefficients, the ANN must be trained with an input and output combination. This allows for the neural network to train to the given output based on the input. Once the neural network receives the simulated output, then comparison of the simulated output and true output ensue. The training method changes the coefficients with respect to the simulated and true outputs. Training continues for a set number of steps or until the ANN reaches a solution. An evaluation function determines the success of the ANN's training.

6.1.3.2 Application

An ANN was created in MATLAB® to calculate a correction to the UGGA. The ANN was designable by the user, consisting of neurons, transfer functions, or training iterations as desired. An option was a function fitting ANN, which would not allow the user to define its function, but instead determine the transfer function through its error calculation. The function fitting ANN calculated the best transfer function and reported its results.

To train for reconstruction, the ANN was supplied with only points in time where the LI-7700's signal was above background. Once a result was found, the ANN was applied to the whole data set. Two function fitting networks ANNs were created with 10 nodes and trained for 10,000 iterations. Because the ANN was created using MATLAB®'s deep learning toolbox, the training of the ANN is terminated before 10,000 iterations if the training function does not improve the ANN. In addition, the Levenberg-Marquardt backpropagation (LM) was implemented as the training method. LM is a combination of Gauss-Newton method (GN) and gradient-based decent [90]. As the ANN was far away from the solution, LM performed similar to gradient based. As the ANN approached the solution, LM performed similar to GN. GN minimized the sum of squared error by assuming the space was a quadratic locally [90]. The use of LM as the training function required the implementation of sum squared error as the evaluation function.

Two ANNs were created using a single file as training and applied to other files to determine the applicability of each ANNs inputs. The first ANN performed reconstruction with only the UGGA's methane signal as input. Figure 28 depicts an example of the ANN performance on trip 551. The ANN produced a PV of 0.69 or increase of 25.7%.

**Figure 28: ANN Reconstruction of Trip 551:
PV=0.690, PE=0.394, $r^2=0.786$, SEE=0.029, PIE=0.238.**

Trip 551's ANN was applied to trip 554. A section of the results is shown in Figure 29. The application of the ANN to a different data set produced a PV of 0.315, or a decrease of 24.5%. The application of the ANN to a data set required more inputs for better success.

**Figure 29: ANN Reconstruction of Trip 554 using Trip 551's ANN:
PV=0.315, PE=0.781, $r^2=0.406$, SEE=0.032, PIE=0.575.**

The second ANN consisted of the UGGA's methane and the derivatives of the UGGA's methane. The ANN was provided with the first three derivatives of the UGGA's signal. The derivatives were calculated using a backwards approximation. The derivatives used were based on the differentials used in the DCM. Figure 30 depicts an example of the ANN with derivatives of trip 551. The ANN's performance PV was 0.917, or an increase of 67%.

Figure 30: ANN with Derivatives Reconstruction of Trip 551:
PV=0.917, PE=0.099, $r^2=0.969$, SEE=0.013, PIE=0.177.

A section of the application of trip 551's ANN to trip 554 is shown in Figure 31. The PV of the application of the ANN was 0.716, or an increase of 71.7%. The ANN with derivatives improved the PVs better than the first ANN. An ANN with derivatives was created and applied to all the data. The creation of an ANN would allow for the implementation of the UGGA without the LI-7700. The total results of the ANN were investigated to determine if it was applicable for mobile methane detection.

**Figure 31: ANN with Derivatives Reconstruction of Trip 554 using Trip 551's ANN:
PV=0.716, PE=0.309, $r^2=0.816$, SEE=0.019, PIE=0.505.**

6.1.4 Differential Coefficients Method (DCM)

6.1.4.1 Theory

The DCM was introduced by Ajtay and Welienman for the reconstruction of vehicle emissions [91]. The DCM was founded on dispersion associated with mixing and transport. It used the principle of differentials to recreate a signal. If $U(t)$ was the input signal and $Y(t)$ was the output, then differentials of $Y(t)$ were $Y'(t)$, $Y''(t)$ and so on. Assuming a linear combination of first two differentials and the output to create the input, DCM is:

$$U(t) = Y(t) + a_1 Y'(t) + a_2 Y''(t) \quad (35)$$

where t is the time step in the signal. Madireddy and Clark compared the results of using more than two differentials and determined that for vehicle emissions more than three differentials did not contribute significantly to a better solution [92]. DCM of multiple differentials is:

$$U(t) = \sum_{i=0}^n a_i Y^{[i]}(t) \quad (36)$$

Where n is the number of differentials desired, a_i are the coefficients and $Y^{[i]}(t)$ are the differentials of the output signal.

Madireddy and Clark's analysis of the DCM was performed by observing the differential effects and initial constants [92]. Madireddy and Clark did not implement a coefficient for the constant which reduced the effect of the initial output signal. In addition, Madireddy and Clark determined that the third derivative accounted for rounding errors and that the backwards derivative was the best for consistency.

6.1.4.2 Application

The DCM was examined since the UGGA experienced diffusion in the cell. In this application, a_0 was solvable and the DCM consisted of three backwards differential terms. The solving option for the various a_i was an average least squared error, through varying the a_i linearly. Average least squared error was the minimization of the average squared error differences. The training set for the DCM was reduced to methane concentrations above background of the LI-7700. After training, the coefficients were applied to the entire data file. The DCM applied to trip 551 is shown in Figure 32. The DCM created a PV of 0.670 for a 22% increase from the initial PV of trip 551.

Figure 32: DCM Reconstruction of Trip 551:
PV=0.670, PE=0.540, $r^2=0.879$, SEE=0.020, PIE=0.012.

Applying the DCM coefficients of trip 551 to trip 554 is shown in Figure 33. The PV was 0.511 which was a 22% increase from the original PV of trip 554. Since DCM had the ability to define a set of coefficients and apply them to any set, it allowed for its implementation to all sets without the LI-7700's signal. The DCM was investigated further for its application in methane reconstruction.

Figure 33: DCM Reconstruction of Trip 554 using Trip 551's DCM:
PV=0.511, PE=0.847, $r^2=0.897$, SEE=0.011, PIE=0.036.

6.2 Reconstruction Results

The PV of all mobile methane data sets was determined at various frequencies. Both DCM and ANN with derivatives were attempted. The results were compared at 1 Hz. An attempt to up sample and reconstruct the UGGA was detailed.

6.2.1 1 Hz Reconstruction

The LI-7700 was down sampled to 1 Hz which allowed for reconstruction of the UGGA's methane signal. To perform down sampling, forward averages of the LI-7700 were taken. Using the PV defined previously, the success of reconstruction was compared between the reconstructed and original signals.

6.2.1.1 DCM

6.2.1.1.1 Self-Training

Using the DCM, all 43 files were self-trained. Because the least squared error used in DCM was computed iteratively, the PV was limited by boundaries of the coefficients. The range was defined as -5 to

5 for a_0 and -15 to 15 for a_1 , a_2 , and a_3 with precision to two decimal places. During the calculation of 172 total coefficients, only one coefficient reached its boundary.

Using the coefficient search range of the DCM, Table 5 displays the average, standard deviation, maximum, and minimum of the PV and its components. It was observed that the average PV of the trip files was 0.644. Table 6 displays the breakdown of the improvement from implementing the DCM to the trip files. The average PV increased by 0.132, or a 25% percent increase compared to the initial PV. The PV was shown to vary across all files. All the PVs and their breakdowns for self-training are given in Appendix V.

Table 5: PV Breakdown of Self-Trained Trips.

	PE	r²	SEE	PIE	PV
AVG	0.453	0.696	0.069	0.079	0.644
VAR	0.093	0.067	0.005	0.019	0.043
MAX	0.945	0.996	0.327	0.599	0.978
MIN	0.000	0.024	0.010	0.000	0.312

Table 6: Improvement of the PV Breakdown of Self-Trained Trips Compared to the Initial PV Breakdown. Note: Highlighted Cells Indicated a Positive Improvement.

	PE	r²	SEE	PIE	PV
AVG	-0.149	0.152	-0.002	-0.004	0.133
VAR	0.190	0.271	0.057	0.132	0.160
MAX	0.272	0.680	0.220	0.376	0.564
MIN	-0.665	-0.495	-0.073	-0.488	-0.143

In observance of Tables 4 and 5, a distribution of the PV components is shown in Figure 34. Each component's zero to one performance impact was binned into 0.1 sections. Compared to the initial PV components, PE's largest bin increased from 0.1-0.2 to 0.9-1 and r^2 's largest bin increased from 0.3-0.4 to 0.8-0.9.

Figure 34: (Top) Distribution of the Initial PV Components. (Bottom) Distribution of the Self-Trained PV Components Note: The total count for each component was 43.

To illustrate the effects of the DCM on the UGGA, Figure 35 displays trip 545 that was self-trained. Trip 540's PV was 0.774, or a 13.8% increase from trip 545's initial PV. The DCM coefficients calculated were available for application to other files.

Figure 35: Trip 545, DCM Self-Trained Reconstructed UGGA:
PV=0.774, PE=0.371, $r^2=0.921$, SEE=0.021, PIE=0.013.

6.2.1.1.2 Applying DCM Coefficients

During DCM training, each trip generated a unique set of coefficients. To determine the suitability of each set of coefficients, all sets of coefficients were applied to the remaining 42 trip files that did not create them. Appendix VI displays the average PV and its components from each DCM coefficients to all 43 trip files. The best set of coefficients were created from trip 552 which improved the average PV to 0.692 for a 35% increase of the average initial PV. Five of the 43 trips improved the average PV by at least 30% and 25 trips improved the average PV by at least 20%.

Examples of the coefficient application is shown in Figures 36 and 37. Figure 36 displays trip 545 trained with the coefficients from trip 540. Trip 540's self-trained PV was 0.312. When applied to trip 545, the PV decreased by 0.262, or a 41.2 % decrease from trip 545's initial PV. Figure 37 displays trip 545

trained with the coefficients from trip 533 applied for DCM reconstruction. Trip 533's self-trained PV was 0.843. When applied to trip 545, the PV increased by 0.219 which is a 34.4% increase compared to trip 545's initial PV.

Figure 36: Trip 545, DCM Reconstructed UGGA with Trip 540:
PV=0.374, PE=0.544, $r^2=0.069$, SEE=0.103, PIE=0.099.

**Figure 37: Trip 545, DCM Reconstructed UGGA with Trip 533:
PV=0.855, PE=0.362, $r^2=0.846$, SEE=0.030, PIE=0.034.**

The best applied DCM coefficients were not associated with the best PVs from self-training. Figure 38 displays a weak correlation between the self-trained PV and the average PV of the 43 files of each self-trained coefficients. The PV increased from the implementation of DCM, but the best PV coefficients did not guarantee the best average PVs from reconstruction. To judge the success of the DCM coefficients, a peak sensitivity analysis was conducted.

Figure 38: The Average PV of the Trip Coefficients vs the Self-Trained PV.

6.2.1.1.3 Detection Threshold Sensitivity Analysis

To determine the peak finding ability of the DCM coefficients, the recreated plumes using the DCM coefficients were subjected to detection threshold sensitivity analysis. To convert the UGGA reconstructed normalized methane to a ppmv concentration, the inverse of the UGGA normalization was applied. The denormalized methane concentrations are shown in equations 37 and 38. The UGGA's background was the LI-7700's background due to the zeroing of backgrounds between analyzers.

$$UGGA(t) = UGGA_{norm}(t) * (\max(LI7700) - LI7700_{Background}) + UGGA_{Background} \quad (37)$$

$$LI7700(t) = LI7700_{norm}(t) * (\max(LI7700) - LI7700_{Background}) + LI7700_{Background} \quad (38)$$

Using all 43 trip file coefficients, all 363 plumes were reconstructed. The initial sensitivity values were observed for each file. Appendix VII contains each trip coefficient's false reporting, false positive, and false negative rates for 2.7 ppmv detection of the 10 Hz LI-7700 peaks, and 2.6 ppmv detection of the 1 Hz LI-7700 peaks. Of the 43 sets of coefficients, only one file did not improve the false negative rate; however, every set of coefficients created false positives. A detection sensitivity was conducted to investigate for improved detection thresholds.

Using the initial range of 2.5 to 3.5 ppmv, detection threshold sensitivity analysis was performed.

Appendix VII contains each DCM coefficient's best threshold and false reporting, false positive, and false negative rates at 10 and 1 Hz. Table 7 displays the best trip coefficients with their minimum false reporting rate at the minimum detection threshold. To determine the best threshold, the false reporting rate was minimized because reconstruction created false positives by the UGGA while lowering the false negative rate. For 10 Hz LI-7700 peaks, the detection threshold of 3.5 ppmv reduced the false reporting rate by 57.6% from the initial threshold of 2.7 ppmv. For 1 Hz LI-7700 peaks, the detection threshold of 3.4 ppmv reduced the false reporting rate by 75.3% from the initial threshold of 2.6 ppmv.

The bounds were adjusted to 2.5 to 5.5 ppmv to determine if a better local minimum was available. The larger sensitivity analysis bound results are included in Appendix VII and the best are shown in Table 7. The best false reporting rates were 0.039 and 0.019 for 10 and 1 Hz, respectively. The 5.2 ppmv detection threshold for 10 Hz resulted in a decrease of the false reporting rate by 67%. Because other mobile methane systems determine enhanced concentrations of methane near 2-3 ppmv, a detection threshold outside the initial 2.5 ppmv to 3.5 ppmv was not recommended.

Table 7: Peak Sensitivity Analysis of the Self-Trained Coefficients Applied to all Trip Files.

Sensitivity Range	LI-7700 Frequency	Minimum False Reporting Rate	Minimum Detection Threshold	Minimum Trip Coefficients
2.5-3.5 ppmv	10	0.050	3.5	575
	1	0.019	3.4	550
2.5-5.5 ppmv	10	0.039	5.2	542
	1	0.019	3.4	550

Figure 39 displays a weak correlation between the self-trained PV and the false reporting rate of the trip coefficients. The DCM coefficients improved the peak sensitivity but were not predictable based on their PV.

Figure 39: False Reporting Rate of 10 Hz LI-7700 vs the Self-Trained PV of each Trip File's Coefficients.

6.2.1.2 ANN with Derivatives

6.2.1.2.1 ANN Determination

An ANN was created from the function fitting network defined previously. For the data input, all the normalized trip data were split into training data and validation data sets using the holdout cross-validation method. The holdout method performed a simple split of the data into training and validation sets using a splitting ratio. The conventional splitting ratio used in the holdout method was 2/3 training data [93, 94]. Dobbin and Simon tested various holdout method ratios and determined that 2/3 training data resulted in near optimal mean squared error of their data set [93]. To achieve a holdout ratio near 2/3 training data, the data was split to ensure that the ANN was trained with almost 70% of the total methane plumes.

Using the training data, the ANN was trained using LM and 10,000 iterations. Figure 40 displays a section of the training data reconstructed using the ANN. The PV of the reconstruction of the training data was 0.899. For comparison, the average initial PV of the trip files used for the training data was 0.512.

The PV increased from the ANN by 75.6%. Appendix VIII contains details regarding the ANN including the structure, transfer functions, and weighting applied.

Figure 40: Reconstruction of the Training Data using ANN:
PV=0.899, PE=0.143, $r^2=0.954$, SEE=0.022, PIE=0.083.

6.2.1.2.2 Applying ANN

Once the ANN was trained, the ANN was validated using the validation data set. Figure 41 displays a section of the validation data reconstructed using the ANN. The PV of reconstruction of the validation set was 0.86. For comparison, the average initial PV of the trip files used for the training data was 0.511. The validation data PV increased by 68.3%. To determine the success in peak finding, a detection threshold sensitivity was conducted.

Figure 41: Reconstruction of the Validation Data using ANN:
PV=0.86, PE=0.140, $r^2=0.820$, SEE=0.047, PIE=0.025.

6.2.1.2.3 Detection threshold Sensitivity Analysis

To determine the peak finding ability of the ANN, the recreated plumes using ANN were subjected to detection threshold sensitivity analysis. To convert the UGGA reconstructed normalized methane to a ppmv concentration, the inverse of the UGGA normalization was applied.

The initial sensitivity values of 2.7 ppmv and 2.6 ppmv were observed for 10 and 1 Hz LI-7700 peaks. The ANN created the false negative rates of 0.169 and 0.059 which was a reduction by 51.3% and 75.72%. The ANN created false positives that increased the false reporting rate by 0.006 and 0.011. A detection sensitivity was conducted to investigate for improved detection thresholds.

Using the initial range of 2.5 to 3.5 ppmv, detection threshold sensitivity analysis was performed using the reconstructed methane created by the ANN. Table 8 displays the best detection threshold for 10 and 1 Hz. The false reporting rates of 0.061 and 0.017 resulted in a decrease of 48.3% and 77.9% from the initial detection thresholds of 2.7 and 2.6 ppmv for 10 and 1 Hz, respectively.

Table 8: Peak Sensitivity Analysis of the ANN of the Training and Validation Data.

Sensitivity Range	LI-7700 Frequency	Minimum False Reporting Rate	False Positive Rate	False Negative Rate	Minimum Detection threshold
2.5-3.5 ppmv	10	0.061	0.004	0.216	3.5
	1	0.017	0.007	0.047	3.3

To confirm the successful training of the ANN, both the training and validation data were subjected to detection threshold sensitivity analysis. In order to draw comparisons, the peaks of the validation set of the UGGA prior to reconstruction were observed. Table 9 displays the peak sensitivity of the training data for both the UGGA and reconstructed UGGA using the ANN. With the expanded search range, the false reporting rate decreased by 53.4% and 78.6% for 10 and 1 Hz, respectively. Table 10 displays the peak sensitivity of the validation data for both the UGGA and reconstructed UGGA. With the search range of 2.5 to 3.5 ppmv, the false reporting rate decreased by 38.5% and 71.4% for 10 and 1 Hz, respectively. For 1 Hz of the validation data, the ANN only created two errors out of 111 plumes.

Table 9: Peak Sensitivity Analysis of the Training Data Before and After Reconstruction using the ANN.

Sensitivity Range	LI-7700 Frequency	UGGA				UGGA Reconstructed			
		Minimum False Reporting Rate	Minimum Detection Threshold	False Positive Rate	False Negative Rate	Minimum False Reporting Rate	Minimum Detection Threshold	False Positive Rate	False Negative Rate
2.5-3.5 ppmv	10	0.107	2.8	0	0.355	0.052	3.5	0.005	0.203
	1	0.056	2.8	0	0.222	0.012	3.3	0.010	0.019
2.5-5.5 ppmv	10	0.103	4.7	0	0.317	0.048	3.7	0.000	0.214
	1	0.056	2.8	0	0.222	0.012	3.3	0.010	0.019

Table 10: Peak Sensitivity Analysis of the Validation Data Before and After Reconstruction using the ANN.

Sensitivity Range	LI-7700 Frequency	UGGA				UGGA Reconstructed			
		Minimum False Reporting Rate	Minimum Detection Threshold	False Positive Rate	False Negative Rate	Minimum False Reporting Rate	Minimum Detection Threshold	False Positive Rate	False Negative Rate
2.5-3.5 ppmv	10	0.117	3.1	0	0.317	0.072	2.9	0	0.186
	1	0.063	3.4	0	0.226	0.018	3.4	0	0.065

6.2.2 2 Hz Reconstruction

6.2.2.1 Initial 2 Hz Data

As discussed earlier, faster sampling rates are available for closed-path analyzers. The goal was to include a 5 Hz version of the UGGA (methane and ethane) in these analyses, but the analyzer was not available due to construction delays of the analyzer. However, the up sampling of the current UGGA was conducted to understand any implications. Linear interpolation was required to create the 2 Hz signal and its derivatives for the UGGA. The LI-7700 was down sampled to 2 Hz using a forward average. Table 11 presents the PV and its components of the initial data at 2 Hz.

Table 11: PV Breakdown of Initial Data at 2 Hz.

	PE	r²	SEE	PIE	PV
AVG	0.692	0.215	0.085	0.101	0.346
VAR	0.053	0.058	0.002	0.018	0.027
MAX	0.979	0.949	0.216	0.531	0.774
MIN	0.100	0.000	0.019	0.005	0.079

6.2.2.2 Self-Training DCM

Using the 43 trips, 2 Hz reconstruction was attempted using the DCM. The coefficients were limited to the same search space as 1 Hz, despite the increased computational time with a longer signal. Table 12 shows the average, variance, maximum and minimum of the 43 trips with each trips PV and components presented in Appendix IX. The average PV was 0.037 higher than the initial data at 2 Hz. Table 13 displays the improvement of the PV at 2 Hz compared to the initial PVs at 1 Hz.

Table 12: PV Breakdown of Self-Trained DCM at 2 Hz.

	PE	r²	SEE	PIE	PV
AVG	0.602	0.221	0.098	0.220	0.383
VAR	0.068	0.069	0.003	0.073	0.028
MAX	0.957	0.939	0.263	0.955	0.790
MIN	0.019	0.000	0.020	0.000	0.114

Table 13: Relative Changes of the PV Breakdown of Self-Trained Trips DCM at 2 Hz Compared to the 2 Hz Initial PV Breakdown.

	PE	r^2	SEE	PIE	PV
AVG	-0.082	0.007	0.013	0.121	0.033
VAR	0.014	0.013	0.001	0.057	0.001
MAX	-0.023	-0.009	0.047	0.424	0.015
MIN	-0.081	0.000	0.001	-0.005	0.035

A section of trip 545 at 2 Hz is shown in Figure 42 with a PV of 0.473. The DCM provided only a 10.7% improvement at 2 Hz and thus was not investigated further. It was noticed that 2 Hz reconstruction was not properly time aligned. Because time alignment was only available at 1 Hz, 2 Hz reconstruction experienced errors in PV calculation.

**Figure 42: Trip 545, LI-7700 vs Reconstructed UGGA Self-Trained DCM at 2 Hz:
PV=0.473, PE=0.477, r^2 =0.222, SEE=0.062, PIE=0.015.**

6.2.2.3 ANN with Derivatives

Using all the collected trip data at 2 Hz, the data was split into training and validation data. A different ANN was trained and validated for 2 Hz using the same setup parameters. Figure 43 displays a section of

the training data at 2 Hz. The 2 Hz PV for the initial data was 0.354 and the PV of the 2 Hz training data was 0.699. The improvement was an increase of 97.5%.

**Figure 43: Reconstruction of a Section of Training Data using ANN at 2 Hz:
PV=0.699, PE=0.362, $r^2=0.759$, SEE=0.048, PIE=0.219.**

Figure 44 displays a section of the validation data at 2 Hz. The 2 Hz PV for the initial data was 0.335 and the PV of the 2 Hz validation data was 0.663. The improvement was an increase of 97.9%. The ANN at 2 Hz displayed the time alignment issue and up sampling issues as the DCM; however, the improvement of the training and validation data using the ANN led to the implementation of the detection threshold sensitivity analysis at 2 Hz.

**Figure 44: Reconstruction of the Validation Data using ANN at 2 Hz:
PV=0.663, PE=0.326, $r^2=0.565$, SEE=0.059, PIE=0.105.**

To determine the optimal detection threshold, detection threshold sensitivity analysis was conducted. Tables 14, 15, and 16 display the results of detection threshold sensitivity analysis for the entire data, testing data, and validation for the UGGA and reconstructed UGGA. The 2 Hz ANN created more false positives and negatives during reconstruction which increased the false positive, false negative, and false reporting rate from reconstruction.

Table 14: Peak Sensitivity Analysis of all the Data Before and After Reconstruction at 2 Hz using the ANN.

Sensitivity Range	LI-7700 Frequency	UGGA				UGGA Reconstructed			
		Minimum False Reporting Rate	Minimum Detection Threshold	False Positive Rate	False Negative Rate	Minimum False Reporting Rate	Minimum Detection Threshold	False Positive Rate	False Negative Rate
2.5-3.5 ppmv	10	0.118	2.7	0	0.347	0.242	3.5	0.124	0.567
	2	0.069	2.8	0	0.245	0.215	3.5	0.128	0.519
2.5-5.5 ppmv	10	0.113	4.7	0	0.500	0.157	5.2	0.014	0.663
	2	0.058	5.3	0	0.368	0.113	5.5	0.026	0.589

Table 15: Peak Sensitivity Analysis of the Training Data Before and After Reconstruction at 2 Hz using the ANN.

Sensitivity Range	LI-7700 Frequency	UGGA				UGGA Reconstructed			
		Minimum False Reporting Rate	Minimum Detection Threshold	False Positive Rate	False Negative Rate	Minimum False Reporting Rate	Minimum Detection Threshold	False Positive Rate	False Negative Rate
2.5-3.5 ppmv	10	0.107	2.8	0	0.355	0.274	3.5	0.155	0.661
	2	0.056	2.8	0	0.222	0.246	3.5	0.153	0.620
2.5-5.5 ppmv	10	0.103	4.7	0	0.531	0.155	5.2	0.010	0.787
	2	0.056	2.8	0	0.222	0.103	5.5	0.009	0.706

Table 16: Peak Sensitivity Analysis of the Validation Data Before and After Reconstruction at 2 Hz using the ANN.

Sensitivity Range	LI-7700 Frequency	UGGA				UGGA Reconstructed			
		Minimum False Reporting Rate	Minimum Detection Threshold	False Positive Rate	False Negative Rate	Minimum False Reporting Rate	Minimum Detection Threshold	False Positive Rate	False Negative Rate
2.5-3.5 ppmv	10	0.117	3.1	0	0.317	0.153	3.3	0.042	0.359
	2	0.063	3.4	0	0.226	0.135	3.4	0.063	0.323

6.3 Signal Reconstruction Conclusions

The reconstruction methods of SIT, IFFT, ANN, and DCM were examined to create a sharp UGGA methane response to match the LI-7700 and therefore reduce false negatives (i.e. missed plumes). The SIT and IFFT were determined to be unusable in mobile methane systems without continued operation of the LI-7700. Both the DCM and ANN were investigated further at 1 and 2 Hz.

At 1 Hz, the DCM was applied using the average least squared error to determine the DCM coefficients. Using the 43 trip files, each file was trained for a unique set of coefficients. The average PV improvement of the trip files was an increase of 25%. All 43 sets of coefficients were applied to all 43 trip files. The best set of coefficients improved the average PV of the trip files by 35%. Performing detection threshold sensitivity analysis, the best DCM coefficients resulted in a decrease in the false reporting rate by 67% and 75.3% for 10 and 1 Hz peaks, respectively. The best detection threshold for the LI-7700 peaks at 10 Hz was 5.2 ppmv. Due to the observance of other mobile methane system's detection thresholds, the detection threshold should remain between 2.5 ppmv and 3.5 ppmv.

An ANN was created as a function fitting network with 10 nodes and 10,000 iterations. Using the holdout cross validation ratio of 70% training, all the trip files were split into training and validation data. The PV of the training data improved by 75.6% and the PV of validation data improved by 68.3%. The total PV increased by the initial detection thresholds of 2.7 ppmv and 2.6 ppmv for 10 Hz and 1 Hz LI-7700 peaks resulted in decreases of the false negative rate by 51.3% and 75.7% but created false positives.

Performing detection threshold sensitivity analysis, the best detection thresholds resulted in a decrease in the false reporting rate by 48.3% and 77.9% for 10 and 1 Hz peaks, respectively. The best detection thresholds were 3.5 ppmv and 3.3 ppmv.

At 2 Hz, the DCM was trained and resulted in an increase of the average PV by 10.7%. An ANN trained and resulted in an increase of the validation data by 97.9%. The 2 Hz ANN increased the detection

threshold. The 2 Hz data was shown to create false positives and increase the number of false negatives and thus limited the up sampling ability of the UGGA.

Using the reconstruction results, both the DCM and ANN produced improvements to the PV. The DCM required different coefficients to optimize both PV and detection thresholds; however, the ANN improved the validation set for both the PV and detection thresholds. At 1 Hz peaks, the ANN improved the average PV by 72.6% while reducing false negatives by 80.7%.

To apply signal reconstruction without the LI-7700, the UGGA was not required to be normalized, reconstructed, and denormalized. Instead, the reconstruction was applied the methane signal reported by the UGGA after time alignment. Figure 45 displays denormalized methane responses of the LI-7700, the initial UGGA and the UGGA reconstructed by the ANN. Using the reconstruction methods, a post-processing application was created for future works.

Figure 45: Methane Responses by the LI-7700, the initial UGGA, and the UGGA Reconstructed by the ANN.

7. Post-Processing

Using MATLAB[®], an application (app) called *Mobile Methane* was created to simplify processing trip data after collection. Once completed, the application created a Google[®] Earth Map file (.kmz) for a visual representation of the data collected with a MATLAB[®] workspace file (.mat) saving important variables. This ease of access was designed for a simplified and user friendly processing. Note, such an application could prove beneficial in identifying possible sources of methane emissions if wind direction can be estimated and locations of natural gas sites can be mapped respective to the driving trace.

7.1 MATLAB[®] Application (App)

MATLAB[®]'s application designer allowed for the design and implementation of data presentation for the mobile methane detection into a seamless application. Using Scimitar's *Mobile Methane* setup (valid .xml parameter tree), data were processed in the *Mobile Methane*. While data were not required to be collected using Scimitar's *Mobile Methane* setup, the data must be labelled similarly with similar units in Microsoft Excel.

For machines using MATLAB[®], the user can install and execute the *Mobile Methane* app. By selecting the apps tab and running *Mobile Methane*, the initial startup window appears, as displayed in Figure 46. There are a few options to perform in *Mobile Methane* with a dialog box to view and receive messages from the app. The dialog box, denoted "Reports", begins with instructions on how to use *Mobile Methane*. Any user unfamiliar with the app is able to read the reports and begin processing *Mobile Methane* data. As shown, Figure 46 contains 3 options, "Create Mobile Methane", "Load Mobile Methane", or "Apply .mat to Create Mobile Methane" and the choice of file type. The app requires the choice between an excel file (.xls) or Scimitar file (.tz) on the main app window before any operation is performed.

Figure 46: Mobile Methane App Main Window.

“Create Mobile Methane” is the basis for *Mobile Methane*. After pressing the run button, the app prompts questions, via a new window, asking the user’s preferences. It begins by asking if the user would like to perform a KML package including a KML file creation and UGGA Reconstruction. A KML file creation attempts to plot all data of the trip to Google® Earth. UGGA reconstruction attempts to reconstruct the UGGA’s original signal to the LI-7700’s signal. If the user declines to perform a KML package, then the user is prompted to select the KML package pieces individually.

The app prompts the user to determine if they are processing multiple files combined, multiple files separated, or a single file. Multiple files combined is a combination of all the files into single trip file with a name combining all the trip files. Multiple files separated processes multiple files using the initial user prompts. If a multiple files option is selected but the user only selects a single file, then *Mobile Methane* processes the file as if the user selected single file option.

Next, the user is asked the frequency for reconstruction at either 1 Hz, 2 Hz, 5 Hz or 10 Hz. The 5 Hz and 10 Hz reconstruction frequencies were added to *Mobile Methane* for future use that may implement a

higher frequency methane analyzer. Once ready, a file selector appears asking for the files desired with the extension selected earlier.

Because *Mobile Methane* was used to process all trip data, reconstruction methods and options are available to the user's discretion. If reconstruction was selected, then the user is prompted to indicate the reconstruction method, number of derivatives. The reconstruction methods consist of the DCM and ANN. The maximum number of derivatives available is four.

After reconstruction, if the KML file creation was selected, then the user is prompted to enter the detection threshold desired. The default detection threshold is 3 ppmv. A Google® Earth mapping, if selected, and a MATLAB® workspace save file are saved with the name of the file. This allows the user to see the mobile methane detection path and review the data file.

“Load Mobile Methane” requires a MATLAB® workspace save file previously created. If there is not a MATLAB® workspace file available, *Mobile Methane* fails. If there is an available MATLAB® workspace file, then the app prompts the user to select a file with the extension .mat. Using the MATLAB® workspace window, data from the processed *Mobile Methane* MATLAB® workspace file appears. It contains data on reconstruction, mapping, user inputs, and sampling distance. The reconstruction data consists of the method chosen information, the reconstructed points, the coefficients or network of the method, and the PV breakdown. Mapping consists of all the data used for Google® Earth map creation. Sampling distance data contains various sampling frequency limitation data. All the data saved were used for comparisons.

“Apply .mat to Create Mobile Methane” allows the user to take a processed *Mobile Methane* MATLAB® workspace file and apply its training data to another *Mobile Methane* trip file. This combines the steps of both “Create Mobile Methane” and “Load Mobile Methane”. Following the same initial steps as *Create Mobile Methane*, the app requires all the same prompts except reconstruction-based prompts. Using the MATLAB® workspace file, the app imports the reconstruction options and applies them to the new file.

Instead of training the new file based on itself, the app simply reconstructs the new file using the completed training coefficients or signal defined in the MATLAB® workspace file. If reconstruction was not attempted in the MATLAB® workspace file chosen, then *Mobile Methane* fails. Once completed, the app creates a Google® Earth file, if selected, and a MATLAB® workspace file using the full name of the original file with the addition of ‘_tr_’ and the last 3 characters from the MATLAB® workspace file. This allows the user to know which file trained the newly created *Mobile Methane*.

7.2 Google® Earth Mapping

After the *Mobile Methane* app processes a file, a Google® Earth file is created. Contained in the Google® Earth file is the data of the newly processed file shown visually in Google® Earth.

Once the Google® Earth file is open, the user is taken to an overview the route, as shown in Figure 47. This window displays the full route for the viewer with the route options in the left window called *Places*. Using the *Places* window, the user has access to nine selectable routes under the file consisting of fast, slow, and reconstructed systems. When initially loaded, the LI-7700 concentration is displayed. Due to being selectable, the user can view multiple routes at the same time if desired.

Figure 47: Overhead Display of Google® Earth Mapping.

The methane concentration, wind direction, and path are plotted for fast, slow, and reconstructed routes.

The fast route plots the data recorded from the LI-7700 and WindMaster at the points recorded by the EVK-M8U, while the slow route plots the UGGA and WindSonic at the points recorded by the BU-353S4. The reconstructed route plots the attempted reconstruction of the UGGA with the WindSonic and BU at the reconstructed frequency.

Each data set contains a selectable wind direction, methane concentration, and the path. This allows better viewing due to multiple routes overlaying on each other. Figure 48 shows the fast route's LI-7700 concentration. The methane concentrations of the LI-7700, UGGA, and reconstructed UGGA are mapped as displayed in Figure 48. The maximum point in the file is always red while any points below the detection threshold implemented are blue. After changing selections, Figure 49 shows the wind direction arrows of the 1 Hz route. The wind direction data from the WindMaster and WindSonic in each route is similar to Figure 49. The wind arrow only depicts direction, as wind speed is noted in the description; however, Google® Earth does not depict wind arrows at locations where the limiting equations were violated.

Figure 48: Methane Concentration Mapped onto the Vehicle Route.

Figure 49: Wind Direction Mapped onto the Vehicle Route.

Due to multiple points laying near or occasionally on top of each other, each point in all the data sets has a description point. To access the description, click on a point in the route desired and a text box appears depicting the qualitative data for the points. Figures 48 and 49 contain examples of the description box.

Mobile Methane's implementation allows the user to input the file, select choices, and let the app process the data. Any data required is saved for later use and the path is mapped onto a Google® Earth file.

7.3 Post-Processing Review

Using MATLAB® and Google® Earth, the reconstruction of the UGGA was simplified. A MATLAB® application processed the trip data, reconstructed the UGGA and created a Google® Earth File. In Google® Earth, the trip was visible as a path, methane concentration, and wind direction for the fast, slow, and reconstructed systems. Using the limiting equation and detection thresholds defined earlier, the elevated methane plumes with proper wind conditions were displayed for convenient methane detection. With the simplification in post-processing, the requirements and recommendations of its implementations can be determined.

8. Conclusions, Recommendations, and Future Applications

8.1 Conclusions

While natural gas may yield lower CO₂ from combustion compared to coal and petroleum, methane is a potent greenhouse gas with a GWP of 28 over 100 years [95]. To combat methane emissions, researchers have worked on improving methane detection processes. The application of two mobile methane detection systems were compared in the ability to identify methane plumes near atmospheric levels.

Various analyzers and sensors were reviewed and included FID, FTIR, OGI, IR, MOS, catalytic bead sensors, and spectroscopy techniques. After review, the methane analyzers selected for each system were the LI-7700 and the UGGA, which represent nearly the state-of-the-art in both open- and closed-path approaches. The open-path WMS at 10 Hz of the LI-7700 and the closed-path OA-ICOS at 1 Hz of the UGGA allowed for near atmospheric levels of detection. Each system consisted of a methane analyzer, a sonic anemometer, and a GPS. Both systems were deployed simultaneously in the Morgantown, WV surrounding area for a total of 15 hours.

During initial field testing, it was apparent that the LI-7700 and the UGGA reported different methane concentrations. After time alignment, the UGGA reported lower concentrations (by up to 94.6%) and had a smeared methane response when compared to the LI-7700. Using the statistics of the data recorded by both systems a performance value (PV) was defined to quantify the comparison between the methane responses. The average PV of the initial data set was 0.512, with 3 ppmv was defined as the initial detection threshold for determining methane sources. Of the 363 plumes, the UGGA had a false negative rate of 40.2%. This meant that the slower, closed-path system would have “missed” 40% of possible plumes detected by a fast, open-path analyzer. The initial data led to the investigation of the limitations of the systems.

Each system was observed with respect to geospatial, wind, and peak limitations. Geospatial limitations were associated with GR and required a speed limit if a certain GR was required. Because of the influence of sampling frequency, the LI-7700’s GR was a tenth that of the UGGA. The wind limitations consisted of the wind error calculation in the correction of wind speed during vehicle speeds. It was determined that the 33.9% and 22.6% of the moving data for the fast system and slow system could not determine the wind direction quadrant. The peak limitations observed the effect of the detection threshold. Using a sensitivity analysis, the best detection threshold was determined to be 2.6 ppmv for 1 Hz, but the UGGA still reported a false negatives rate of 24.3%. As a reminder, a false negative meant that the UGGA did not identify a plume based on a given threshold even though the open-path system did identify a possible plume.

The UGGA was shown to require a correction method to detect methane reported by the LI-7700. The SIT, IFFT, ANN, and DCM reconstruction methods were investigated to correct the UGGA to match the LI-7700’s methane response at 1 Hz. The DCM and ANN were investigated to reduce the number of false negatives reported by the UGGA while removing the LI-7700 from operation.

The DCM was trained using linear least squares for each trip and resulted in an average PV of 0.644. The coefficients created from each trip were applied to all trip files. The best average PV of the coefficient

application was 0.692. A total of 42 of the 43 sets of DCM coefficients resulted in a decrease in false negative rate for the detection threshold of 2.6 ppmv, but all sets yielded unacceptable false positives rates. A detection threshold sensitivity analysis determined that the best trip coefficients resulted in a false reporting rate decrease of 75.3% for the LI-7700 at 1 Hz.

A function fitting ANN was created with 10 nodes, 10,000 training iterations, and 70% training holdout cross validation. The ANN was trained and improved the PV of the validation data by 68.3%. The ANN reduced the false negative rate by 75.7% for 2.6 ppmv detection threshold at 1 Hz LI-7700 peaks. The creation of false positives at the initial detection thresholds by the ANN led to detection threshold sensitivity analysis. The threshold of 3.3 ppmv resulted in a decrease of 24 false negatives and increase of 2 false positives for the LI-7700's peaks at 1 Hz. The optimal detection threshold of the validation data reduced the UGGA to report only two false negatives with the LI-7700 peaks at 1 Hz.

Table 17 shows each detection threshold's results for the DCM and ANN with the initial UGGA for methane detection for 1 Hz LI-7700 peaks. Observing the initial detection threshold, the sensitivity analysis optimized detection threshold, the DCM optimized detection threshold, and the ANN optimized detection threshold, the ANN had the lowest false negative and false reporting rate for 3, 2.6, and 3.3 ppmv detection thresholds. The DCM reported the lowest false negative and false reporting rate for 3.4 ppmv.

Table 17: Results of Each Detection Threshold of the Initial UGGA, UGGA Reconstructed by DCM, and UGGA Reconstructed by ANN for 1 Hz LI-7700 Peaks.

Detection Threshold	UGGA system	False Negative Rate	False Reporting Rate
3 ppm	Initial UGGA	0.309	0.083
	DCM UGGA	0.188	0.072
	ANN UGGA	0.103	0.033
2.6 ppm	Initial UGGA	0.243	0.077
	DCM UGGA	0.199	0.099
	ANN UGGA	0.078	0.096
3.4 ppm	Initial UGGA	0.341	0.077
	DCM UGGA	0.037	0.019
	ANN UGGA	0.049	0.017
3.3 ppm	Initial UGGA	0.341	0.08
	DCM UGGA	0.059	0.028
	ANN UGGA	0.047	0.017

A 2 Hz reconstruction was investigated for the DCM and ANN. The DCM resulted in a 10% PV improvement and the ANN resulted in a 97.9% PV improvement. The ANN was subjected to detection threshold sensitivity analysis. The 2 Hz ANN created false positives and increased the false negatives. Up sampling to perform reconstruction was limited to the highest sampling frequency of the analyzers.

An application was created to process the mobile methane data. Using MATLAB®, the application reconstructed the UGGA signal to match the LI-7700 and created a Google® Earth map displaying the methane concentrations and wind direction at the sampled location. The application allowed for the implementation of the UGGA without the LI-7700.

Of the reconstruction methods, the UGGA reconstructed with the ANN increased the PV of the validation set by 68.3%. After detection sensitivity analysis, the false negatives of the ANN validation set decreased by 9 compared to the LI-7700 peaks at 1 Hz. The application of the ANN allowed for the UGGA to be implemented with improved detection threshold capabilities.

8.2 Recommendations

The implementation of a closed-path methane detection system had errors that require correction. The methane analyzer sampling method and frequency, vehicle speed, and other components defined the ability in methane source attribution.

The LI-7700, an open-path methane analyzer, displayed a sharp methane response compared to the UGGA. Its implementation in mobile methane systems was limited by mounting and interference effects associated with open-path analyzers. In cases without these concerns, the open-path analyzer presents the best option for mobile methane detection; however, if mounting or interference issues are presented, then the open-path analyzer cannot be implemented without loss of data. The LI-7700 is capable of up to 40 Hz, but sampling frequency of the GPS limits the application in mobile methane detection.

The UGGA, a closed-path methane analyzer, displayed a response delay and a smearing effect compared to the LI-7700. With time alignment, a corrected closed-path methane analyzer did not encounter the interference effects associated with open-path operation. The use of a closed-path methane analyzer required a post processing correction to reduce the false negatives reported.

If a closed-path analyzer is used for methane detection, an external correction should be applied to time align and improve the methane response signal. Without correction, the closed-path analyzer reports lower values compared to the open-path analyzer. The ANN reconstructed the UGGA's signal by improving both the PV and detection threshold. An ANN under the correct conditions, can be created and trained for signal reconstruction of a closed-path methane analyzer. To confirm that other closed-path analyzers operate similarly to the UGGA, the analyzers must be deployed compared to an open-path analyzer. Atherton et al. and Brantley et al. deployed a UGGA that will experience the same sampling limitations due to their OA-ICOS [17, 84]. Phillips et al., Jackson et al., Eapi et al., Fischer et al., Rella et al., Albertson et al., Brantley et al., and Weller et al. deployed various Picarro methane analyzers that operate on cavity ringdown spectroscopy [14–16, 19–22, 24]. The Picarro methane analyzers should

experience similar sampling limitations due to its closed-path operation and its relation to OA-ICOS.

Other works may have underreported methane concentrations or missed methane plumes due to the implementation of a closed-path analyzer.

Vehicle speed and sampling frequency are the major components in the GR between points. The closed-path analyzer at 1 Hz created sampling location inaccuracies in geospatial limitations due to the response delay. Time alignment is required with the implementation of a closed-path analyzer.

With the 1 Hz UGGA, the recommended vehicle speed is 36 kph. Methane analyzers with a lower sampling frequency than 1 Hz will yield higher geospatial uncertainty in sampling location than the UGGA. Los Gatos Research currently produces a methane analyzer that samples at 20 Hz frequency [72]. A GPS and anemometer would be required to operate at 20 Hz to prevent linear interpolation of data. The higher sampling frequency methane analyzer would allow for higher vehicle speeds at the GR of 10 m.

For a continuation of this work, a closer analysis into the combined effects of vehicle speed, sampling rate, and methane responses is required. Due to the vehicle speed forcing a flow over the sampling line of a closed-path methane analyzer, the analyzer may experience inaccuracies due to an increase of pressure in the cell. Future works should monitor cell pressure for its effects on the methane response through sampling, mounting, and operating conditions. Cell pressure could be used as a metric for the removal of data when it varies dramatically.

The recommendations of a mobile methane system present the suggestions after conclusions were drawn. For implementing the mobile methane detection, these recommendations pose as guides and points to consider for researchers working in this area.

8.3 Future Applications

There are other applications that could be implemented with the mobile methane detection system. The applications consist of two major categories, leak quantification and ethane detection. Leak quantification

consists of potential methods of indirect quantification methods that may be implemented from the system. Details of each topic include the overview with the requirements and adaptations required of the mobile methane system.

8.3.1 Leak Quantification

Leak quantification is the next progression following leak detection. Given the same vehicle setup, determining the rate of the leak is imperative in determining the severity of the leak. *Mobile Methane* simply determines the sampled location, not the leak source location. Using an indirect quantification method, such as Other Test Method 33a (OTM 33a), or Eddy Covariance, calculation of leak rates could be determined.

8.3.1.1 OTM 33a

OTM33a was a project sponsored by the EPA in order to create a top-down methane quantification method [21]. Using a vehicle mounted system, OTM 33a attempts to quantify the leak rate. OTM 33a begins by mapping the detected methane with wind direction along the vehicle path. After a leak is determined to be downwind, OTM 33a begins trying to discover the leak by applying gaussian dispersion techniques. With knowledge of the leak, OTM 33a gives a leak rate from the source.

OTM33a's implementation would not be a difficult one. The inner workings of OTM 33a could be coded into *Mobile Methane*. Because the app only maps moving data to the Google® Earth file, the stationary data could be applied with OTM 33a if the leak criteria was met. Despite this, OTM 33a's execution on may be limited without further research. Using leak testing and an adaption of OTM 33a, a modified OTM 33a could be paired with a mobile methane detection system for leak detection and quantification.

8.3.1.2 Eddy Covariance

The eddy covariance method is meteorological technique that observes the fluxes of the gas desired. Many environmental scientists deploy these in search of CO₂ and methane effects from the environment. The fluxes in eddy covariances are the small changes in the atmosphere over the course of a set period of

time. By performing long sampling periods, the average of a section of time provides a snapshot of the environmental effects.

Eddy covariance has been attempted for source detection of CO₂ [96]. By observing the background meteorological effects over a long period of time, the background effects could be removed for source location and quantification. Long periods of time usually consist of days at a time with half an hour averaging at a minimum.

Mobile methane detection with eddy covariance is limited due to having to expose the sensors for a long period of time. If the background knowledge of the site was available via an eddy covariance setup near the leak, then mobile methane detection could be deployed for around half an hour for potential source detection. Using the mobile methane detection equipment already deployed, a simple coding of the eddy covariance method would allow for stationary data to be observed. Completing a drive by the site could indicate where to position the vehicle for eddy covariance.

8.3.2 Ethane Detection

Natural gas's composition is primarily methane, but the next largest component is ethane. Ethane is a hydrocarbon extracted from natural gas for its conversion to plastics [97, 98]. Despite its other applications, ethane is still used as a fuel in natural gas.

Because ethane's sources vary from methane, ethane detection indicates natural gas leaks. Ethane's creation consists only of anthropogenic sources. This varies from methane, which consists of both anthropogenic sources and biological sources. With multiple sources, not all methane sources are contributed to natural gas equipment however coexistence of ethane and methane is attributed to natural gas.

With ethane's uses and its distinguishing source ability, ethane analyzers provide insight to potential natural gas leaks [99]. The market for methane and ethane analyzers currently only consists of closed-path ethane analyzers [100]. An open-path analyzer provides sharp signal that does not experience averaging

impulse responses upon it. A methane/ethane analyzer's application to *Mobile Methane* would allow for instantaneous ethane detection.

Using the LI-7700 paired with methane/ethane analyzer, an ethane signal could be recreated. Ethane could be discovered if the UGGA was replaced with a methane/ethane analyzer. Using a method such as IFFT or SIT, an accurate reconstruction could create an instant open-path signal of ethane. Reconstruction using IFFT allows for a signal that is easily invertible to recreate an ethane signal.

An adaption of *Mobile Methane*'s code would simply require reconstruction to be performed, inverted, then applied to ethane. While the apps base operation is methane detection, it could be extended to include ethane.

References

- [1] EIA, “United States remains the world’s top producer of petroleum and natural gas hydrocarbons,” *EIA*. [Online]. Available: <https://www.eia.gov/todayinenergy/detail.php?id=36292>.
- [2] EIA, “U.S. Natural Gas Gross Withdrawals,” *EIA*, 2019. [Online]. Available: <https://www.eia.gov/dnav/ng/hist/n9010us2A.htm>.
- [3] EIA, “How much natural gas does the United States have, and how long will it last?,” *EIA*, 2018. [Online]. Available: <https://www.eia.gov/tools/faqs/faq.php?id=58&t=8>.
- [4] EIA, “How much carbon dioxide is produced when different fuels are burned?,” *EIA*. [Online]. Available: <https://www.eia.gov/tools/faqs/faq.php?id=73&t=11>.
- [5] EIA, “Energy-related CO₂ emissions from natural gas surpass coal as fuel use patterns change,” *EIA*. [Online]. Available: <https://www.eia.gov/todayinenergy/detail.php?id=27552>.
- [6] EPA, “Understanding Global Warming Potentials,” *EPA*. [Online]. Available: [https://www.epa.gov/ghgemissions/understanding-global-warming-potentials#Learn why](https://www.epa.gov/ghgemissions/understanding-global-warming-potentials#Learn%20why).
- [7] G. Myhre *et al.*, “Anthropogenic and Natural Radiative Forcing. In: Climate Change 2013: The Physical Science Basis.,” *Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA. 659, 2013.
- [8] EPA, “Overview of Greenhouse Gases,” *EPA*. [Online]. Available: <https://www.epa.gov/ghgemissions/overview-greenhouse-gases>.
- [9] R. A. Alvarez, S. W. Pacala, J. J. Winebrake, W. L. Chameides, and S. P. Hamburg, “Greater focus needed on methane leakage from natural gas infrastructure,” *PNAS*, vol. 109, no. 17, pp. 6435–6440, 2012.
- [10] X. Zhang, N. P. Myhrvold, and K. Caldeira, “Key factors for assessing climate benefits of natural gas versus coal electricity generation,” *Environ. Res. Lett.*, vol. 9, no. 11, 2014.
- [11] S. Coburn *et al.*, “Regional trace-gas source attribution using a field-deployed dual frequency comb spectrometer,” *Optica*, vol. 5, no. 4, p. 320, 2018.

- [12] ARPA-E, “MONITOR,” *ARPA-E*. [Online]. Available: <https://arpa-e.energy.gov/?q=programs/monitor>.
- [13] Stanford School of Earth Energy and Environmental Sciences, “Mobile Monitoring Challenge,” *Stanford University*. [Online]. Available: <https://methane.stanford.edu/>.
- [14] N. Phillips *et al.*, “Mapping urban pipeline leaks: Methane leaks across Boston,” *Environ. Pollut.*, vol. 173, pp. 1–4, 2013.
- [15] R. B. Jackson *et al.*, “Natural gas pipeline leaks across Washington, DC,” *Environ. Sci. Technol.*, vol. 48, no. 3, pp. 2051–2058, 2014.
- [16] G. R. Eapi, M. S. Sabnis, and M. L. Sattler, “Mobile measurement of methane and hydrogen sulfide at natural gas production site fence lines in the Texas Barnett Shale,” *J. Air Waste Manag. Assoc.*, vol. 64, no. 8, pp. 927–944, 2014.
- [17] E. Atherton *et al.*, “Mobile measurement of methane emissions from natural gas developments in northeastern British Columbia, Canada,” *Atmos. Chem. Phys.*, vol. 17, no. 20, pp. 12405–12420, 2017.
- [18] SCAQMD, “Mobile Methane Measurement Surveys.” [Online]. Available: <https://www.aqmd.gov/home/news-events/community-investigations/aliso-canyon-update/air-sampling/mobile-methane-measurement-surveys>.
- [19] C. W. Rella, T. R. Tsai, C. G. Botkin, E. R. Crosson, and D. Steele, “Measuring emissions from oil and natural gas well pads using the mobile flux plane technique,” *Environ. Sci. Technol.*, vol. 49, no. 7, pp. 4742–4748, 2015.
- [20] J. D. Albertson *et al.*, “A Mobile Sensing Approach for Regional Surveillance of Fugitive Methane Emissions in Oil and Gas Production,” *Environ. Sci. Technol.*, vol. 50, no. 5, pp. 2487–2497, 2016.
- [21] H. L. Brantley, E. D. Thoma, W. C. Squier, B. B. Guven, and D. Lyon, “Assessment of methane emissions from oil and gas production pads using mobile measurements,” *Environ. Sci. Technol.*, vol. 48, no. 24, pp. 14508–14515, 2014.
- [22] Z. D. Weller *et al.*, “Vehicle-Based Methane Surveys for Finding Natural Gas Leaks and Estimating Their Size: Validation and Uncertainty,” *Environ. Sci. Technol.*, vol. 52, pp. 11922–11930, 2018.

- [23] L. Tao, K. Sun, D. J. Miller, D. Pan, L. M. Golston, and M. A. Zondlo, “Low-power, open-path mobile sensing platform for high-resolution measurements of greenhouse gases and air pollutants,” *Appl. Phys. B Lasers Opt.*, vol. 119, no. 1, pp. 153–164, 2015.
- [24] J. C. Von Fischer *et al.*, “Rapid, Vehicle-Based Identification of Location and Magnitude of Urban Natural Gas Pipeline Leaks,” *Environ. Sci. Technol.*, vol. 51, no. 7, pp. 4091–4099, 2017.
- [25] D. R. Caulton *et al.*, “Quantifying uncertainties from mobile-laboratory-derived emissions of well pads using inverse Gaussian methods,” *Atmos. Chem. Phys.*, vol. 18, no. 20, pp. 15145–15168, 2018.
- [26] Picarro Inc, “Picarro Drive,” *Picarro Inc.* [Online]. Available: <https://naturalgas.picarro.com/overview#drive>.
- [27] ABB, “MobileGuard.” [Online]. Available: <https://heathus.com/wp-content/uploads/MobileGuard.pdf>.
- [28] Earth System Research Laboratory, “Trends in Atmospheric Methane,” *NOAA*. [Online]. Available: https://www.esrl.noaa.gov/gmd/ccgg/trends_ch4/.
- [29] I. G. McWilliam and R. A. Dewar, “Flame Ionization Detector for Gas Chromatography,” *Nature*, vol. 181, p. 760, 1958.
- [30] W. K. Cheng, T. Summers, and N. Collings, “THE FAST-RESPONSE FLAME IONIZATION DETECTOR,” *Prog. Energy Combust. Sci.*, vol. 24, pp. 89–124, 1998.
- [31] Horiba, “OBS-ONE GS Unit,” *Horiba*. [Online]. Available: https://www.horiba.com/en_en/products/detail/action/show/Product/obs-one-gs-unit-28/.
- [32] Sensors, “SEMTECH FID and DUAL FID Specifications.,” *Sensors*. .
- [33] D. A. Skoog, F. J. Holler, and S. R. Crouch, “Chapter 16 An Introduction to Infrared Spectrometry,” in *Principles of Instrumental Design Seventh Edition*, C. Learning, Ed. 2017, pp. 398–411.
- [34] D. A. Skoog, F. J. Holler, and S. R. Crouch, “Chapter 17 Applications of Infrared Spectroscopy,” in *Principles of Instrumental Design Seventh Edition*, Cengage Learning, Ed. 2017, pp. 412–436.
- [35] FLIR, “Infrared Cameras for Gas Leak Detection,” *FLIR*, 2017. [Online]. Available: https://www.flir.com/globalassets/imported-assets/document/17-2691-ins-ogi-gf-series-family-brochure_revise_final_v2_lwrez.pdf.

- [36] T. Dinh, I. Choi, Y. Son, and J. Kim, "Sensors and Actuators B : Chemical A review on non-dispersive infrared gas sensors : Improvement of sensor detection limit and interference correction," *Sensors Actuators B. Chem.*, vol. 231, pp. 529–538, 2016.
- [37] V. DiVenere, "The Electromagnetic Spectrum," *Columbia University*. [Online]. Available: http://www.columbia.edu/~vjd1/electromag_spectrum.htm.
- [38] D. A. Skoog, F. J. Holler, and S. R. Crouch, "Chapter 7 Components of Optical Instruments," in *Principles of Instrumental Design*, Cengage Learning, 2017, pp. 148–195.
- [39] B. Daham *et al.*, "Application of a Portable FTIR for Measuring On-road Emissions," *SAE Tech. Pap.*, 2005.
- [40] A. R. Korb, P. Dybwad, W. Wadsworth, and J. W. Salisbury, "Portable Fourier transform infrared spectroradiometer for field measurements of radiance and emissivity," *Opt. Soc. Am.*, vol. 35, no. 10, pp. 1679–1692, 1996.
- [41] MKS, "MultiGas 2030-HS High Speed (5 Hz) FTIR Gas Analyzer," *MKS*. [Online]. Available: <https://www.mksinst.com/f/multigas-2030-hs-ftir-continuous-gas-analyzer>.
- [42] ARCOptix, "FT-IR Rocket," *ARCOptix*. [Online]. Available: http://www.arcoptix.com/IR_infrared_spectrometer.htm.
- [43] A. P. Ravikumar, J. Wang, M. McGuire, C. S. Bell, D. Zimmerle, and A. R. Brandt, "' Good versus Good Enough? ' Empirical Tests of Methane Leak Detection Sensitivity of a Commercial Infrared Camera," *Environ. Sci. Technol.*, vol. 52, pp. 2368–2374, 2018.
- [44] A. P. Ravikumar, J. Wang, and A. R. Brandt, "Are Optical Gas Imaging Technologies Effective For Methane Leak," *Environ. Sci. Technol.*, vol. 51, pp. 718–724, 2016.
- [45] Y. Zeng and J. Morris, "Detection limits of optical gas imagers as a function of temperature differential and distance," *J. Air Waste Manag. Assoc.*, vol. 69, no. 3, pp. 351–361, 2018.
- [46] Rebellion Photonics, "PORTABLE METHANE DETECTION SYSTEM," *ARPA-E*. [Online]. Available: <https://arpa-e.energy.gov/?q=slick-sheet-project/portable-methane-detection-system>.
- [47] X. Liu *et al.*, "A Survey on Gas Sensing Technology," *Sensors*, vol. 12, no. 7, pp. 9635–9665, 2012.
- [48] NET, "IRNET-P," *NET*. [Online]. Available: <http://www.nenvitech.com/wp-content/uploads/2018/06/DS3706-IRNET-P-32-methane-Rev-8.pdf>.

- [49] Edinburgh Sensors, “Gascard NG,” *Edinburgh Sensors*. [Online]. Available: <https://edinburghsensors.com/products/oem/gascard-ng/>.
- [50] Dynamet, “Dynamet MSH,” *Dynamet*. [Online]. Available: https://www.dynamet.com/_webedit/uploaded-files/All Files/Data/tds0123.pdf.
- [51] A. Dey, “Materials Science & Engineering B Semiconductor metal oxide gas sensors : A review,” *Mater. Sci. Eng. B*, vol. 229, pp. 206–217, 2018.
- [52] C. Wang, L. Yin, L. Zhang, D. Xiang, and R. Gao, “Metal Oxide Gas Sensors: Sensitivity and Influencing Factors,” *Sensors*, vol. 10, pp. 2088–2106, 2010.
- [53] Winsen, “Flammable Gas Sensor (Model: MQ-4,” *Winsen*. [Online]. Available: <https://cdn.sparkfun.com/datasheets/Sensors/Biometric/MQ-4 Ver1.3 - Manual.pdf>.
- [54] J. E. Thompson, “Crowd-sourced Air Quality Studies: A Review of the Literature & Portable Sensors,” *Trends Environmental Anal. Chem.*, vol. 11, pp. 23–34, 2016.
- [55] NET, “NP-18SHM & NP-18SHP,” *NET*. [Online]. Available: <http://www.nenvitech.com/wp-content/uploads/2016/04/DS3347-rev.-2-NP-18SHM-NP-18SHP-.pdf>.
- [56] Los Gatos Research, “GHG Analyzer Travels Anywhere,” *Los Gatos Research*. [Online]. Available: <https://www.ecotech.com/wp-content/uploads/2015/03/LGR-UltraPortable-GGA-Datasheet.pdf>.
- [57] LI-COR, “LI-7700 Manual,” *LI-COR*. [Online]. Available: <https://www.licor.com/documents/18warrx05laaa1zo9s0pepmjk0cgism3>.
- [58] Los Gatos Research, “Ultra-Portable Greenhouse Gas Analyzer User Manual,” *Los Gatos Research*, 2014. [Online]. Available: <https://www.ecotech.com/wp-content/uploads/2015/03/UltraPortable-GGA-User-Manual-Rev-1.01.pdf>.
- [59] R. Di Capua, F. Offi, and F. Fontana, “Check the Lambert – Beer – Bouguer law : a simple trick to boost the confidence of students toward both exponential laws and the discrete approach to experimental physics Check the Lambert – Beer – Bouguer law : a simple trick to boost the confidence of,” *Eur. J. Phys.*, vol. 35, 2014.
- [60] D. F. Swinehart, “The Beer-Lambert Law,” *J. Chem. Educ.*, vol. 39, no. 7, pp. 333–335, 1962.
- [61] J. A. Silver, “Frequency-modulation spectroscopy for trace species detection: theory and comparison among experimental methods,” *Appl. Opt.*, vol. 31, no. 6, pp. 707–717, 1992.

- [62] D. R. Herriott and H. J. Schulte, "Folded Optical Delay Lines," *Appl. Opt.*, vol. 4, no. 8, p. 883, 1965.
- [63] LI-COR, "LI-7700 Specifications*," *LI-COR*. [Online]. Available: https://www.licor.com/env/products/gas_analysis/LI-7700/specifications.html.
- [64] D. McDermitt *et al.*, "A new low-power, open-path instrument for measuring methane flux by eddy covariance," *Appl. Phys. B Lasers Opt.*, vol. 102, no. 2, pp. 391–405, 2011.
- [65] A. O'Keefe and D. A. G. Deacon, "Cavity ring-down optical spectrometer for absorption measurements using pulsed laser sources," *Rev. Sci. Instrum.*, vol. 54, no. 2544, 1988.
- [66] Picarro Inc, "Picarro G2301," *Picarro Inc.* [Online]. Available: https://www.picarro.com/support/library/documents/co2_ch4_and_h2o_gas_concentration_analyzer_g2301_data_sheet.
- [67] A. O'Keefe, "Integrated cavity output analysis of ultra-weak absorption," *Chem. Phys. Lett.*, vol. 293, no. 5, pp. 331–336, 1998.
- [68] A. O'Keefe, J. J. Scherer, and J. B. Paul, "cw Integrated cavity output spectroscopy," *Chem. Phys. Lett.*, vol. 307, pp. 343–349, 1999.
- [69] D. Herriot, H. Kogelnik, and R. Kompfner, "Off-Axis Paths in Spherical Mirror Interferometers," *Appl. Opt.*, vol. 3, no. 4, pp. 523–526, 1964.
- [70] PEER, "QCL Whispering Gallery Mode Sensor," *PEER*. [Online]. Available: <http://www.peeri.org/OV/qclWGM.htm>.
- [71] I. Leifer, C. Melton, M. Gupta, and B. Leen, "Mobile Monitoring of Methane Leakage," *Gases Instrum.*, no. July/August, pp. 20–24, 2014.
- [72] LGR, "Fast Methane Analyzer," *LGR*. [Online]. Available: http://www.lgrinc.com/documents/LGR_FMA_Datasheet.pdf.
- [73] S. W. Smith, "Chapter 5: Linear Systems," in *The Scientist and Engineer's Guide to Digital Signal Processing*, 1998, pp. 87–106.
- [74] S. W. Smith, "Chapter 6: The Delta Function and Impulse Response," in *The Scientist and Engineer's Guide to Digital Signal Processing*, 1998, pp. 107–122.
- [75] S. W. Smith, "Chapter 7: Properties of Convolution," in *The Scientist and Engineer's Guide to Digital Signal Processing*, 1998, pp. 123–140.

- [76] GILL, “WindMaster & WindMaster Pro Sonic Anemometer User Manual,” *GILL*. [Online]. Available: <http://gillinstruments.com/data/manuals/WindMaster-and-Windmaster-Pro-Manual.pdf>.
- [77] U-blox, “NEO-M8U Data Sheet,” *U-Blox*, 2018. [Online]. Available: https://www.u-blox.com/sites/default/files/NEO-M8U-04B_DataSheet_%28UBX-15015679%29.pdf.
- [78] GILL, “WindSonic User Manual,” *GILL*, 2006.
- [79] GlobalSat, “GPS Mouse User’s Guide V1.0.” [Online]. Available: https://www.globalsat.com.tw/ftp/download/GMouse_Win_UsersGuide-V1.0.pdf.
- [80] LI-COR, “LI-7500A/RS Open-path CO₂/H₂O Gas Analyzer,” *LI-COR*. [Online]. Available: <https://www.licor.com/env/support/LI-7500RS/topics/specifications.html>.
- [81] LI-COR, “LI-200R Pyranometer,” *LI-COR*. [Online]. Available: <https://www.licor.com/env/products/light/pyranometer.html>.
- [82] ICP-DAS, “PET-7019Z,” *ICP-DAS*. [Online]. Available: http://www.icpdas.com/products/Remote_IO/pet-7000/pet-7019.htm.
- [83] Omega, “Barometric Pressure, Temperature, Humidity Virtual Recorder,” *Omega*. [Online]. Available: https://www.omega.com/das/pdf/IBTX_IBTHX.pdf.
- [84] H. L. Brantley, E. D. Thoma, W. C. Squier, B. B. Guven, and D. Lyon, “Assessment of methane emissions from oil and gas production pads using mobile measurements,” *Environ. Sci. Technol.*, vol. 48, no. 24, pp. 14508–14515, 2014.
- [85] Picarro Inc, “G2132-i Isotope Analyzer.” [Online]. Available: https://www.picarro.com/products/g2132_i_isotope_analyzer.
- [86] B. Ganesan and N. N. Clark, “Relationships Between Instantaneous and Measured Emissions in Heavy Duty Applications,” *SAE Trans. J. FUELS Lubr.*, vol. 110, no. 724, pp. 1798–1806, 2016.
- [87] M. R. Madireddy and N. N. Clark, “Sequential inversion technique and differential coefficient approach for accurate instantaneous emissions measurement,” *Int. J. Engine Res.*, vol. 7, no. 6, pp. 437–446, 2006.
- [88] S. W. Smith, “Chapter 8: The Discrete Fourier Transform,” in *The Scientist and Engineer’s Guide to Digital Signal Processing*, 1998, pp. 141–168.
- [89] van M. Gerven, “Computational Foundations of Natural Intelligence,” *Front. Comput. Neurosci.*, vol. 11, no. 112, 2017.

- [90] H. P. Gavin, "The Levenberg-Marquardt algorithm for nonlinear least squares curve-fitting problems," 2019. [Online]. Available: <http://people.duke.edu/~hpgavin/ce281/lm.pdf>.
- [91] D. Ajtay and M. Weilenmann, "Compensation of the Exhaust Gas Transport Dynamics for Accurate Instantaneous Emission Measurements," *Environ. Sci. Technol.*, vol. 38, no. 19, pp. 5141–5148, 2004.
- [92] M. R. Madireddy and N. N. Clark, "Attempts to enhance the differential transient emissions from heavy-duty vehicles of Engine Research," *Int. J. Engine Res.*, vol. 10, no. 1, pp. 65–70, 2008.
- [93] K. K. Dobbin and R. M. Simon, "Optimally splitting cases for training and testing high dimensional classifiers," *BMC Med. Genomics*, vol. 4, no. 1, p. 31, 2011.
- [94] V. Gholami, K. W. Chau, F. Fadaee, J. Torkaman, and A. Ghaffari, "Modeling of groundwater level fluctuations using dendrochronology in alluvial aquifers," *J. Hydrol.*, vol. 529, no. March 2019, pp. 1060–1069, 2015.
- [95] IPCC, "Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. [S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller." Cambridge University Press. Cambridge, United Kingdom 996 pp., 2007.
- [96] J. L. Lewicki *et al.*, "Detection of CO₂ leakage by eddy covariance during the ZERT project's CO₂ release experiments," *Energy Procedia*, vol. 1, no. 1, pp. 2301–2306, 2009.
- [97] EIA, "Hydrocarbon Gas Liquids Explained," EIA, 2018. [Online]. Available: https://www.eia.gov/energyexplained/index.php?page=hgls_uses.
- [98] The Essential Chemical Industry-online, "Ethene (Ethylene)," *The Essential Chemical Industry-online*, 2017. [Online]. Available: <http://www.essentialchemicalindustry.org/chemicals/ethene.html>.
- [99] T. I. Yacovitch *et al.*, "Mobile Laboratory Observations of Methane Emissions in the Barnett Shale Region," *Environ. Sci. Technol.*, vol. 49, no. 13, pp. 7889–7895, 2015.
- [100] D. Kim-hak, D. Fleck, J. Yiu, Z. Lin, and G. Lucic, "Fugitive Methane Emission Identification and Source Attribution: Ethane-to- Methane Analysis using a Portable Cavity Ring-Down Spectroscopy Analyzer," *Picarro*. [Online]. Available: <https://www.picarro.com/sites/default/files/EGU-AGU 2017 Ethane-Methane Poster.pdf>.

Appendices

Appendix I: UGGA Methane Calibration

The UGGA required calibration prior to operation. On December 12, 2018, the UGGA was internally calibrated at 101.3 ppmv methane. To perform calibration, the 101.3 ppmv methane bottle and Teflon line were required. Using a T fitting, a separate line was used to prevent a pressured system, where excess methane could vent to the atmosphere. Using the internal computer of the UGGA, the UGGA's calibration steps were performed. Figure 50 depicts a section of the UGGA's calibration screen with the time and date of the last calibration.

Figure 50: The Calibration of the UGGA.

Appendix II: Calibration Certificates

All the calibrated equipment was used for either burst testing or calibration. The calibration certificates of the gas bottles used are supplied. In addition, the calibration certificate of the gas divider is also provided. Figure 51 depicts the 101.3 ppmv of methane calibration certificate. The 101.3 ppmv methane had an uncertainty of 0.9%. Figure 52 is the ultra-zero air calibration certificate. The ultra-zero air bottle had an error less than 0.1 ppmv of methane. Figure 53 shows the calibration sheet used for the STEC SGD-710C gas divider. The gas divider had an uncertainty of 0.048 liters per minute. Figure 54 depicts the gas divider verification check sheet. The gas divider has a maximum error less than 1%.

EPA Protocol Gas Mixture

Customer: Wilson Supply
CGA: 590
Customer PO#: 144705-1
Cylinder #: EB0067295

Reference#: 091518CL-BB
Certification Date: 09/20/2018
Expiration Date: 09/20/2026
Pressure, psig: 2000

Method: This standard was analyzed according to EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, Procedure G1 (May 2012).

Components	Requested Concentration	Certified Concentration	Expanded Uncertainty	Assay Dates
Methane	100ppm	101.3ppm	0.9%	9/20/18
Air	Balance	Balance	-	-

Reference Standard	Cylinder #	Concentration	Expanded Uncertainty	Expiration Date
Methane/ GMI5	EB0026425	95.0ppm	0.7%	01/25/23
Methane/ SRM	FF23127	98.23ppm	0.5%	06/01/18

Instrument/ Model	Serial Number	Last Date Calibrated	Analytical Method
Cow-Mac/ 23-500	K35606	9/20/2018	Flame Ionization Detector

These mixtures were prepared gravimetrically using a high load high sensitivity electronic scale. Prior to filling the scale is verified for accuracy throughout the target mass range against applicable NIST traceable weights. We certify that the weights are calibrated to ASTM E617-97 Echelon 1 tolerances.

This report states accurately the results of the investigation made upon the material submitted to the analytical laboratory. Every effort has been made to determine objectively the information requested. However, in connection with this report, Global Calibration Gases LLC shall have no liability in excess of the established charge for this service. Assayed at Global Calibration Gases LLC, Sarasota, Florida. No correction required for interfering gases.

The calibration results published in this certificate were obtained using equipment and standards capable of producing results that are traceable to National Institute of Standards and Technology (NIST) and through NIST to the International System of Units (SI). The expanded uncertainties, if included on this certificate, use a coverage factor of $k=2$ to approximate the 95% confidence level of the measurement, unless otherwise noted. If uncertainties are not included on this certificate, they are available upon request. This calibration certificate applies only to the item described and shall not be reproduced other than in full, without written approval from the calibration facility. Calibration certificates without signatures are not valid. This calibration meets the requirements of ISO/IEC 17025:2005. Do not use this standard when cylinder pressure is below 100 psig.

Produced by:
Global Calibration Gases LLC
1090 Commerce Blvd N.
Sarasota, Florida 34243 USA
PGVP Vendor ID: N22018

Principal Analyst: Kathy Walker
Date: 9/20/2018

Principal Reviewer: Kathy Walker
Date: 9/20/2018

Figure 51: 101.3 ppmv Methane Bottle Calibration Certificate.

Certificate of Analysis

Certification Date: 28 November 2016
Product: Air Ultra Zero
Expiration Date: 28 November 2024
Lot Number: 3156A-01T5

Purity Specification

Oxygen	19.5%-23.5%
Carbon Monoxide	< 1.0 ppm
Carbon Dioxide	< 1.0 ppm
Moisture	< 3.0 ppm
Total Hydrocarbons	< 0.1 ppm

The calibration results published in this certificate were obtained using equipment and standards capable of producing results that are traceable to National Institute of Standards and Technology (NIST) and through NIST to the International System of Units (SI). The expanded uncertainties, if included on this certificate, use a coverage factor of $k=2$ to approximate the 95% confidence level of the measurement, unless otherwise noted. If uncertainties are not included on this certificate, they are available upon request. This calibration certificate applies only to the item described and shall not be reproduced other than in full, without written approval from the calibration facility. Calibration certificates without signatures are not valid. This calibration meets the requirements of ISO/IEC 17025:2005.

Jeff Lynn

Figure 52: Ultra Zero Air Bottle Calibration Certificate.

HORIBA Instruments
5900 Hines Drive
Ann Arbor, MI 48108

Certificate of Calibration

Certificate Number: 1861930-020218

The calibration was performed using reference standards which have traceability to the International System of Units (SI) through the United States National Institute of Standards and Technology (NIST). This calibration is accredited under the laboratory's ISO/IEC 17025 accreditation issued by the ANSI-ASQ National Accreditation Board. Refer to certificate and scope of accreditation ACT-1312. The calibration was performed using the procedure number stated below.

Customer: West Virginia University
Customer Address: One Waterfront Place
Morgantown, WV 26506

Manufacturer: STEC
Description: Gas Divider
Condition Received: See attached
Cal Procedure: WI-QM-B-010

Part Number: SGD-710C
Serial Number: 1861930
Condition Returned: Passed
Uncertainty: +/- 0.048 L/min
Recommended Re-calibration Due: 02/02/19
Lot Number: 32-401022004-1

Date Calibrated: 02/02/18
Calibration Gas: Zero N₂

Standards Traceability

Mfr./Model Number	Serial #	Test Number	Cal. Date	Due Date
Fluke / 3E4	1016+	PHC4504.0005	07/20/17	07/20/18
Fluke / 3E4	1015+	PHC4504.0005	07/20/17	07/20/18
Fluke/Molbox 1+	448+	PHC4504.0006	07/19/17	07/19/18

Service Technician: *Bryant Tipton*

QA Manager: *Don Therman*

Date: 02/02/18

Date: 02/02/18

This certificate may not be reproduced, except in full, without the written approval of HORIBA. The calibrated system is operating within the specification. The recommended calibration cycle implies system usage in normal, non extreme, environmental conditions. The uncertainty is calculated at a 95% confidence interval with a coverage factor of k=2. This certificate is issued under the authority of: HORIBA Instruments, 2890 John R Road, Troy, MI 48063.

F-QM-108
Revision Date: 1/22/2016

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Issue Date: 2/6/2010
Revision Level: C

Figure 53: STEC SGD-710C Gas Divider Calibration Certificate.

SGD-A10, SGD-710 GAS DIVIDERS VERIFICATION CHECK SHEET

CUSTOMER: WVU DATE: 02/02/18

MODEL: SGD-710C SERIAL NUMBER: 1861930

CUT PT.	COMP A MIXTURE GAS	COMP B DILUTANT GAS	TOTAL FLOW POINT	MIXTURE FLOW %	%POINT ERROR >2.0%	STATUS
0	0.0000	4.0193	4.0193	0.000	0.000	Pass
10	0.3965	3.6067	4.0032	9.905	0.963	Pass
20	0.7970	3.2051	4.0021	19.915	0.429	Pass
30	1.2003	2.8038	4.0041	29.977	0.077	Pass
40	1.5957	2.3982	3.9939	39.953	0.117	Pass
50	1.9909	2.0045	3.9954	49.830	0.342	Pass
60	2.3877	1.6028	3.9905	59.835	0.276	Pass
70	2.7824	1.2066	3.9890	69.752	0.358	Pass
80	3.1772	0.8053	3.9825	79.779	0.277	Pass
90	3.5789	0.4044	3.9833	89.848	0.170	Pass
100	3.9927	0.0000	3.9927	100.000	0.000	Pass
100	3.9912	0.0000	3.9912	100.000	0.000	Pass
90	3.5399	0.3957	3.9356	89.946	0.060	Pass
80	3.1437	0.7950	3.9387	79.816	0.231	Pass
70	2.7477	1.1885	3.9362	69.806	0.278	Pass
60	2.3523	1.5825	3.9348	59.782	0.365	Pass
50	1.9641	1.9683	3.9324	49.947	0.107	Pass
40	1.5892	2.3579	3.9271	39.958	0.105	Pass
30	1.1808	2.7417	3.9223	30.100	-0.331	Pass
20	0.7828	3.1340	3.9168	19.986	0.072	Pass
10	0.3912	3.5167	3.9079	10.010	-0.105	Pass
0	0.0000	3.8976	3.8976	0.000	0.000	Pass

STD. DEV. 0.0393 LPM

MIXTURE GAS INLET PRESSURE TO DIVIDER: 21.0 PSIG
(At 100% CUTPOINT)

DILUTION GAS INLET PRESSURE TO DIVIDER: 17.0 PSIG
(AT 0.0% CUTPOINT)

OUTLET FLOW FROM GAS DIVIDER: 4.00 LPM

Figure 54: STEC SGD-710C Gas Divider Verification Check Sheet.

Appendix III: Create Google® Earth File

Given the data set inputs, the MATLAB® script called kml.m creates a Google® Earth map of the data.

Original codes developed by Dr. Marc Besch, Mr. Robert Heltzel, and Mr. Zachary Luzader were reviewed and used as a foundation for this code. To make operational for the field testing data collected, the code was edited to account for errors with file creation and description display. In addition, mapping of the wind direction was implemented for possible source detection.

```
% Dakota Oliver
% West Virginia University
% Original: Jul 2014 by Marc Besch and Robert Heltzel
% Updated: November 2018
%-----
% 3-D KML File Generator for Methane Monitoring
% Input Data Should be at 1 Hz

%% defined outside script
% the variables Data and Data_Descript must have the same column length

% Data = [longitude, latitude, methane];
% Data_Descript = [U wind, V wind, W wind, wind speed, wind direction (North aligned), vehicle speed];

% also, an arrow must be in the same folder as the script ran and titled
% arrow.png

%% Define Global and Default Variables/Values:
% -----
Set.DownScale = 0;
Set.MaxDataPoints = 600000;
Dim3 = size(Data);
% Route
Set.Route.LineColor = 'ff0000ff';
Set.Route.LineWidth = 2.0;
Set.Route.AltMode = 'clampToGround';
% If 3-D Data is Used
Set.Data.On = 1;
Set.Data.Scale = 100;
Set.Data.Mode = '3D';
Set.Data.LineColor = 'ff000000';
Set.Data.LineWidth = 8.8;
Set.Data.Unit = 'ppm';
Set.Data.Descript = 'Licor Methane';
Set.Data.Precision = '%4.2f';
Set.Data.ColorBin = 64; % Number of colorbins (depending on colormap)
Set.Data.Transparency = 1; % Transparency => 0-fully transparent, 1-fully opaque
% Document Information
Set.Docu.author = 'Dakota Oliver';
Set.Docu.url = 'http://www.wvu.edu';
```

```

Set.Docu.visibility = 1;
Set.Docu.open = 1;
Set.Docu.description = '';
Set.Docu.LookAt.longitude = 'Data_(1,1)';
Set.Docu.LookAt.latitude = 'Data_(1,2)';
Set.Docu.LookAt.altitude = 10000;
Set.Docu.LookAt.heading = 0;
Set.Docu.LookAt.tilt = 20;
Set.Docu.LookAt.range = 40000;
% Style Information
% Normal Data
Set.Style.Data.Normal.Label.color = 'ff00ffff';
Set.Style.Data.Normal.Label.scale = 0;
Set.Style.Data.Normal.Line.width = 5;
Set.Style.Data.Normal.Icon.scale = 0;
% Highlight Data
Set.Style.Data.Highlight.Label.color = 'ff00ffff';
Set.Style.Data.Highlight.Label.scale = 0.75;
Set.Style.Data.Highlight.Line.width = 10;
Set.Style.Data.Highlight.Icon.scale = 0;
% Route Data
Set.Style.Route.color = Set.Data.LineColor;
Set.Style.Route.width = Set.Data.LineWidth;
% Folder Information
% Route
Set.Folder.Route.styleUrl = '#routestyle2';
Set.Folder.Route.tessellate = 1;
Set.Folder.Route.altitudeMode = 'clampToSeaFloor';
% Data
Set.Folder.Data.styleUrl = '#datastyle2';
Set.Folder.Data.Line.tessellate = 1;
Set.Folder.Data.Point.altitudeMode = 'relativeToGround';
Set.Folder.Data.Line.altitudeMode = 'relativeToGround';
Set.Folder.Data.Line.extrude = 1;
%% Generating vector with color information for input data:
% -----
% Scaled data parameter:
for i = 1:length(Data(:,3))
    if Data(i,3) < lowmet
        Data(i,3) = lowmet;
    end
end
Data(:,4) = Data(:,3)*(Set.Data.Scale/max(Data(:,3)));
clear i
% Evaluating min/max data:
Set.Data.Min = min(Data(:,4));
Set.Data.Max = max(Data(:,4));
% Converting Matlab colormap into hexadecimal format for (Google Earth):
cmap_rgb3 = single(round(colormap('Jet')*255));
close(gcf);
cmap_hex3 = cell(length(cmap_rgb3),1);
for i=1:length(cmap_rgb3)
    temp = dec2hex(cmap_rgb3(i,:));
    cmap_hex3{i,1} = [temp(3,:),temp(2,:),temp(1,:)]; % BGR (Google Earth)
    clear temp;
end

```



```

clear i cmap_rgb;
% Converting transparency information into hexadecimal format:
alpha3 = dec2hex(Set.Data.Transparency*255);
% Binning data and assign color information:
% Set the limits of the colors with a linearly spaced vector starting
% with the minimum scale and ending with the maximum scale with the same
% number of bins as colors
Limit3 = linspace(Set.Data.Min,Set.Data.Max,(Set.Data.ColorBin+1));
% Set the Bin to a zero matrix with the same # of columns as data points
% and the same # of rows as colors + 1 additional for sum
Bin3 = zeros(Dim3(1),Set.Data.ColorBin+1);
% Scan through the number of bins
for i=1:1:(length(Limit3)-1)
    % Temporary row of zeros
    Temp3 = zeros(Dim3(1),1);
    Temp3(Data(:,4)>=Limit3(i)) = 1;
    Bin3(:,i) = Temp3;
end
clear i;
Bin3(:,(Set.Data.ColorBin+1)) = sum(Bin3(:,1:(Set.Data.ColorBin+1)),2);
Set.Data.Color = cell(Dim3(1),1);
for i=1:1:Dim3(1)
    Set.Data.Color{i} = [alpha3,cmap_hex3{Bin3(i,(Set.Data.ColorBin+1))}];
end
clear i;
%% Defining 'kml'- Structure:
% ----- %
Para3.File.PreInfo = {'<?xml version="1.0" encoding="utf-8"?>'; ...
    '<kml xmlns="http://earth.google.com/kml/2.1" xmlns:gx="http://www.google.com/kml/ext/2.2"
xmlns:kml="http://www.opengis.net/kml/2.2">'; ...
    '<Document>'};
Para3.File.PostInfo = {'</Document>'; ...
    '</kml>'};
% KML Format for Document Info
%-----
Para3.Document.Info = [{'<name>',Set.TripName,'</name>']; ...
    ['<visibility>',sprintf('%1.0',Set.Docu.visibility),'</visibility>']; ...
    ['<open>',sprintf('%1.0',Set.Docu.open),'</open>']; ...
    ['<description>',Set.Docu.description,'</description>']; ...
    '<LookAt>'; ...
    ['<longitude>',sprintf('%f',eval(Set.Docu.LookAt.longitude),'</longitude>']; ...
    ['<latitude>',sprintf('%f',eval(Set.Docu.LookAt.latitude),'</latitude>']; ...
    ['<altitude>',sprintf('%f',Set.Docu.LookAt.altitude),'</altitude>']; ...
    ['<heading>',sprintf('%1.0f',Set.Docu.LookAt.heading),'</heading>']; ...
    ['<tilt>',sprintf('%1.0f',Set.Docu.LookAt.tilt),'</tilt>']; ...
    ['<range>',sprintf('%1.0f',Set.Docu.LookAt.range),'</range>']; ...
    '</LookAt>'; ...
    ['<author><name>',Set.Docu.author,'</name><uri>',Set.Docu.url,'</uri></author>']];
% KML Format for Route Settings
%-----
Para3.Style.Route = {'<Style id="routestyle2">'; ...
    '<LineStyle>'; ...
    ['<color>',Set.Style.Route.color,'</color>']; ...
    ['<width>',sprintf('%1.1f',Set.Style.Route.width),'</width>']; ...
    '</LineStyle>'; ...
    '</Style>'};

```

% KML Format for Additional Data

```
%-----
Para3.Style.Data = { '<StyleMap id="datastyle2">'; ...
    '<ListStyle>';...
    '<listItemType>checkHideChildren</listItemType>';...
    '</ListStyle>';...
    '<Pair>'; ...
    '<key>normal</key>'; ...
    '<Style>'; ...
    '<IconStyle>'; ...
    ['<scale>',sprintf('%1.2f',Set.Style.Data.Normal.Icon.scale),'</scale>']; ...
    '</IconStyle>'; ...
    '<LabelStyle>'; ...
    ['<color>',Set.Style.Data.Normal.Label.color , '</color>']; ...
    ['<scale>',sprintf('%1.2f',Set.Style.Data.Normal.Label.scale),'</scale>']; ...
    '</LabelStyle>'; ...
    '<BalloonStyle>'; ...
    '<text><![CDATA[<div><small><u>Placemark info:</u></small></div>${description}]]></text>'; ...
    '</BalloonStyle>'; ...
    '<LineStyle>'; ...
    ['<width>',sprintf('%2.1f',Set.Style.Data.Normal.Line.width),'</width>']; ...
    '</LineStyle>'; ...
    '</Style>'; ...
    '</Pair>'; ...
    '<Pair>'; ...
    '<key>highlight</key>'; ...
    '<Style>'; ...
    '<IconStyle>'; ...
    ['<scale>',sprintf('%1.2f',Set.Style.Data.Highlight.Icon.scale),'</scale>']; ...
    '</IconStyle>'; ...
    '<LabelStyle>'; ...
    ['<color>',Set.Style.Data.Highlight.Label.color , '</color>']; ...
    ['<scale>',sprintf('%1.2f',Set.Style.Data.Highlight.Label.scale),'</scale>']; ...
    '</LabelStyle>'; ...
    '<BalloonStyle>'; ...
    '<text><![CDATA[<div><small><u>Placemark info:</u></small></div>${description}]]></text>'; ...
    '</BalloonStyle>'; ...
    '<LineStyle>'; ...
    ['<width>',sprintf('%2.1f',Set.Style.Data.Highlight.Line.width),'</width>']; ...
    '</LineStyle>'; ...
    '</Style>'; ...
    '</Pair>'; ...
    '</StyleMap>'};
Para3.Folder.Data.PreInfo = { '<Folder id="concentration_data_2">'; ...
    '<name>Concentration Data</name>'};
Para3.Folder.Data.PostInfo = { '</Folder>'};
Para3.Folder.Route = { '<Folder id="route_data_2">'; ...
    '<name>Route Coordinates Slow</name>'; ...
    '<Snippet>Trip mapping</Snippet>';...
    '<Placemark>'; ...
    '<visibility>1</visibility>';...
    '<open>0</open>';...['<styleUrl>',Set.Folder.Route.styleUrl,'</styleUrl>']; ...
    '<LineString>'; ...
    ['<tessellate>',sprintf('%1.0f',Set.Folder.Route.tessellate),'</tessellate>']; ...
    ['<altitudeMode>',Set.Folder.Route.altitudeMode,'</altitudeMode>']; ...
    ['<coordinates>',sprintf('%f,%f,%f\n',[Data(:,1:2),zeros(Dim3(1),1)]),'</coordinates>']; ...
```

```

'</LineString>'; ...
'</Placemark>'; ...
'</Folder>'};
Para3.Folder.Data.PreInfo2 = {'<Folder id="Wind_data_2">'; ...
'<name>Wind Data</name>'};
Para3.Folder.Data.PostInfo2 = {'</Folder>'};
%% Generating xml Structure and Export to 'kml'-File:
% ----- %
fid = fopen(file.savefile2,'Wt');
if fid == -1
    Message = 'Warning: File could not be generated => Check kml-file name/path.';
    disp(Message);
    Error.File = Message;
    clear Message;
else
    % Write pre-file information into xml:
    % -----
    for i=1:1:size(Para3.File.PreInfo,1)
        fprintf(fid,'%s \n',Para3.File.PreInfo{i});
    end
    clear i;
    for i=1:1:size(Para3.Document.Info,1)
        fprintf(fid,'%s \n',Para3.Document.Info{i});
    end
    clear i;
    % Write style information into xml:
    % -----
    Style = fieldnames(Para3.Style);
    for j=1:1:length(Style)
        for i=1:1:size(Para3.Style.(Style{j}),1)
            fprintf(fid,'%s \n',Para3.Style.(Style{j}){i});
        end
        clear i;
    end
    clear i;
    % Write route information/coordinates into xml:
    % -----
    for i=1:1:size(Para3.Folder.Route,1)
        fprintf(fid,'%s \n',Para3.Folder.Route{i});
    end
    clear i;
    if (Dim3(2) > 2) && (Set.Data.On == 1)
        for i=1:1:size(Para3.Folder.Data.PreInfo,1)
            fprintf(fid,'%s \n',Para3.Folder.Data.PreInfo{i});
        end
        clear i;
        Format = repmat('%s\n ',1,43); % Data format for gradient/concentration placemark
        for i = 1:length(Data_Descript(:,4))
            HEAD(i) = Data_Descript(i,4);
            if HEAD(i) >= 360
                HEAD(i) = HEAD(i) - 360;
            end
        end
        for i=1:1:Dim3(1)-1
            Para3.Folder.Data.Main = ['<Placemark>', ...
                '<visibility>1</visibility>',...

```



```

        '<open>0</open>',...
        '<name>',[sprintf(Set.Data.Precision,Data(i,3)),Set.Data.Unit],'</name>', ...
        '<Snippet>LGR Methane</Snippet>',...
        '<description><![CDATA[',[sprintf('Longitude: %2.2f deg<br>Latitude: %2.2f deg<br>
',[Data(i,1),Data(i,2)]),Set.Data.Descript,: ',sprintf(Set.Data.Precision,Data(i,3)),Set.Data.Unit,'<br>U wind: ',
sprintf(Set.Data.Precision,Data_Descript(i,1)),' m/s<br>V Wind: ', sprintf(Set.Data.Precision,Data_Descript(i,2)),'
m/s<br>W wind: ',sprintf(Set.Data.Precision,Data_Descript(i,3)),' m/s<br>wind speed:
',sprintf(Set.Data.Precision,Data_Descript(i,4)),' m/s<br>wind direction:
',sprintf(Set.Data.Precision,Data_Descript(i,5)),' theta<br>Vehicle speed:
',sprintf(Set.Data.Precision,Data_Descript(i,5)),' mph' ],']></description>', ...
        '<styleUrl>',Set.Folder.Data.styleUrl,'</styleUrl>', ...),
        '<Style>', ...
        '<LineStyle>', ...
        '<color>',Set.Data.Color{i},'</color>', ...
        '</LineStyle>', ...
        '</Style>', ...
        '<MultiGeometry>', ...
        '<LineString>', ...
        '<tessellate>',sprintf('%1.0f',Set.Folder.Data.Line.tessellate),'</tessellate>', ...
        '<extrude>',sprintf('%1.0f',Set.Folder.Data.Line.extrude),'</extrude>', ...
        '<altitudeMode>',Set.Folder.Data.Line.altitudeMode,'</altitudeMode>', ...
        '<coordinates>',sprintf('%f,%f,%f
%f,%f,%f\n',[Data(i,1:2),Data(i,4),Data(i+1,1:2),Data(i,4)]),'</coordinates>', ...
        '</LineString>', ...
        '<Point>', ...
        '<altitudeMode>',Set.Folder.Data.Point.altitudeMode,'</altitudeMode>', ...
        '<coordinates>',sprintf('%f,%f,%f\n',[Data(i,1:2),Data(i,4)]),'</coordinates>', ...
        '</Point>', ...
        '</MultiGeometry>', ...
        '</Placemark>'];
    fprintf(fid,Format,Para3.Folder.Data.Main);
end
clear i;
for i=1:1:size(Para3.Folder.Data.PostInfo,1)
    fprintf(fid,'%s \n',Para3.Folder.Data.PostInfo{i});
end
end
if (Dim3(2) > 2) && (Set.Data.On == 1)
    for i=1:1:size(Para3.Folder.Data.PreInfo2,1)
        fprintf(fid,'%s \n',Para3.Folder.Data.PreInfo2{i});
    end
    clear i;
    Format = repmat('%s\n',1,43); % Data format for gradient/concentration placemark
    for i = 1:length(Data_Descript(:,4))
        HEAD(i) = Data_Descript(i,4);
        if HEAD(i) >= 360
            HEAD(i) = HEAD(i) - 360;
        end
    end
    for i=1:1:Dim3(1)-1
        Para3.Folder.Data.Main2 = ['<Placemark>',...
            '<visibility>1</visibility>',...
            '<open>0</open>',...
            '<name>',sprintf(Set.Data.Precision,Data_Descript(i,10)),'</name>', ...
            '<description><![CDATA[',[sprintf('Longitude: %2.2f deg<br>Latitude: %2.2f deg<br>
',[Data(i,1),Data(i,2)]),Set.Data.Descript,: ',sprintf(Set.Data.Precision,Data(i,3)),Set.Data.Unit,'<br>U wind: ',

```

```

sprintf(Set.Data.Precision,Data_Descript(i,1)), ' m/s<br>V Wind: ', sprintf(Set.Data.Precision,Data_Descript(i,2)), '
m/s<br>W wind: ',sprintf(Set.Data.Precision,Data_Descript(i,3)), ' m/s<br>wind speed:
',sprintf(Set.Data.Precision,Data_Descript(i,4)), ' m/s<br>wind direction:
',sprintf(Set.Data.Precision,Data_Descript(i,5)), ' theta<br>Vehicle speed:
',sprintf(Set.Data.Precision,Data_Descript(i,5)), ' mph' ],']></description>', ...
    '<Snippet>Wind North Corrected</Snippet>',...
    '<StyleMap>',...
    '<Pair>', ...
    '<key>normal</key>', ...
    '<Style>', ...
    '<IconStyle>',...
    '<scale>.5</scale>',...
    '<Icon>',...
    '<href> image '</href>',...
    '</Icon>',...
    '<heading>',sprintf(Set.Data.Precision,HEAD(i)), '</heading>',...
    '<color>FF00FFFF</color>', ...
    '<IconStyle>',...
    '<BalloonStyle>', ...
    '<text><![CDATA[<div><small><u>Placemark info:</u></small></div>${description}]]></text>', ...
    '</BalloonStyle>', ...
    '<LabelStyle>', ...
    ['<color>',Set.Style.Data.Normal.Label.color, '</color>'], ...
    ['<scale>',sprintf('% 1.2f',Set.Style.Data.Normal.Label.scale), '</scale>'], ...
    '</LabelStyle>', ...
    '</Style>', ...
    '</Pair>', ...
    '<Pair>', ...
    '<key>highlight</key>', ...
    '<Style>', ...
    '<IconStyle>',...
    '<scale>.75</scale>',...
    '<Icon>',...
    '<href> image '</href>',...
    '</Icon>',...
    '<heading>',sprintf(Set.Data.Precision,HEAD(i)), '</heading>',...
    '<color>FF00FFFF</color>', ...
    '<IconStyle>',...
    '<BalloonStyle>', ...
    '<text><![CDATA[<div><small><u>Placemark info:</u></small></div>${description}]]></text>', ...
    '</BalloonStyle>', ...
    '<LabelStyle>', ...
    ['<color>',Set.Style.Data.Highlight.Label.color, '</color>'], ...
    ['<scale>',sprintf('% 1.2f',Set.Style.Data.Highlight.Label.scale), '</scale>'], ...
    '</LabelStyle>', ...
    '</Style>', ...
    '</Pair>',...
    '</StyleMap>',...
    '<Point>', ...
    '<tessellate>',sprintf('% 1.0f',Set.Folder.Data.Line.tessellate), '</tessellate>', ...
    '<altitudeMode>clampToGround</altitudeMode>', ...
    '<coordinates>',sprintf('% f,% f,% f
% f,% f,% f\n',[Data(i,1:2),Data(i,4),Data(i+1,1:2),Data(i,4)]), '</coordinates>', ...
    '</Point>', ...
    '</Placemark>'];
fprintf(fid,Format,Para3.Folder.Data.Main2);

```

```

end
clear i HEAD;
for i=1:size(Para3.Folder.Data.PostInfo2,1)
    fprintf(fid,'%s \n',Para3.Folder.Data.PostInfo2{i});
end
end
% Write post-file information into xml:
% -----
for i=1:size(Para3.File.PostInfo,1)
    fprintf(fid,'%s \n',Para3.File.PostInfo{i});
end
clear i;
% Close 'kml'-file:
% -----
fclose(fid);
end
clear fid;

```

Appendix IV: Initial PVs

Table 18: Initial PVs of the Field Testing Data.

File	UGGA Max (ppm)	LI-7700 Max (ppm)	PE	r ²	SEE	PIE	PV
533	2.771	2.739	0.326	0.615	0.061	0.045	0.687
534	2.840	4.740	0.862	0.533	0.045	0.064	0.372
535	5.292	6.572	0.829	0.737	0.039	0.017	0.466
536	3.489	5.644	0.601	0.430	0.037	0.235	0.455
537	4.821	8.349	0.730	0.417	0.115	0.032	0.405
538	6.666	19.974	0.626	0.278	0.098	0.008	0.414
539	7.013	13.429	0.430	0.361	0.117	0.050	0.542
540	11.404	20.440	0.655	0.333	0.105	0.393	0.375
541	3.272	5.941	0.667	0.310	0.098	0.007	0.403
542	8.924	31.305	0.641	0.274	0.097	0.100	0.394
543	5.573	13.065	0.559	0.329	0.021	0.006	0.468
544	3.243	5.250	0.694	0.502	0.050	0.010	0.456
545	14.396	25.545	0.414	0.606	0.048	0.054	0.636
546	22.451	27.265	0.252	0.672	0.076	0.035	0.747
549	3.698	3.361	0.085	0.981	0.082	0.077	0.939
550	4.737	5.823	0.136	0.929	0.032	0.090	0.893
551	4.412	7.318	0.586	0.602	0.035	0.007	0.549
552	3.431	6.835	0.932	0.323	0.021	0.472	0.217
553	27.358	43.372	0.953	0.739	0.034	0.026	0.401
554	25.668	69.703	0.900	0.703	0.019	0.015	0.417
555	18.909	37.650	0.903	0.666	0.044	0.038	0.400
565	2.910	5.682	0.919	0.285	0.017	0.148	0.246
575	2.481	2.385	0.414	0.478	0.071	0.142	0.582
579	4.743	10.575	0.869	0.439	0.026	0.037	0.339
580	10.329	21.949	0.811	0.467	0.106	0.090	0.373
581	3.522	3.886	0.292	0.706	0.098	0.075	0.733
582	3.182	2.969	0.071	0.877	0.106	0.057	0.912
583	12.001	15.431	0.513	0.743	0.050	0.022	0.636
584	35.819	56.272	0.238	0.629	0.116	0.093	0.733
585	25.656	52.145	0.366	0.640	0.097	0.037	0.675
586	10.195	17.334	0.662	0.359	0.136	0.076	0.415
587	8.568	21.154	0.489	0.551	0.107	0.004	0.582
588	6.372	19.504	0.867	0.338	0.096	0.067	0.301
589	8.021	18.716	0.748	0.315	0.120	0.059	0.356
590	11.413	32.812	0.548	0.328	0.093	0.044	0.469
591	5.163	12.433	0.789	0.355	0.090	0.025	0.353
592	5.874	10.012	0.701	0.546	0.091	0.024	0.466
593	2.765	3.363	0.551	0.379	0.057	0.003	0.490
594	9.762	9.842	0.568	0.939	0.047	0.074	0.669
595	24.195	16.034	0.866	0.473	0.061	0.087	0.346
596	35.789	45.284	0.806	0.746	0.034	0.039	0.479
597	38.126	41.922	0.760	0.793	0.060	0.070	0.516
598	2.727	3.299	0.246	0.669	0.073	0.500	0.698

Appendix V: DCM Self-Training PVs

Table 19: PVs of the Field Testing Data Using DCM and Self-Training.

File	PE	r ²	SEE	PIE	PV
533	0.176	0.828	0.041	0.027	0.843
534	0.825	0.755	0.032	0.028	0.474
535	0.779	0.655	0.046	0.028	0.463
536	0.047	0.842	0.025	0.041	0.915
537	0.561	0.915	0.053	0.066	0.665
538	0.007	0.958	0.025	0.034	0.978
539	0.055	0.771	0.070	0.053	0.884
540	0.526	0.024	0.225	0.599	0.312
541	0.002	0.743	0.077	0.382	0.866
542	0.353	0.853	0.156	0.374	0.719
543	0.299	0.576	0.016	0.007	0.692
544	0.638	0.803	0.032	0.004	0.592
545	0.371	0.921	0.021	0.013	0.774
546	0.060	0.866	0.053	0.004	0.920
549	0.358	0.996	0.021	0.002	0.809
550	0.129	0.980	0.011	0.002	0.924
551	0.540	0.879	0.020	0.012	0.670
552	0.848	0.857	0.010	0.453	0.451
553	0.945	0.932	0.017	0.032	0.472
554	0.871	0.639	0.022	0.017	0.410
555	0.890	0.841	0.030	0.012	0.471
565	0.808	0.273	0.024	0.032	0.314
575	0.266	0.566	0.113	0.077	0.698
579	0.835	0.734	0.018	0.066	0.457
580	0.754	0.264	0.128	0.053	0.336
581	0.312	0.925	0.048	0.002	0.808
582	0.017	0.940	0.073	0.006	0.969
583	0.277	0.817	0.042	0.000	0.789
584	0.000	0.907	0.060	0.005	0.966
585	0.044	0.874	0.057	0.006	0.932
586	0.526	0.701	0.094	0.119	0.603
587	0.021	0.098	0.327	0.159	0.652
588	0.649	0.758	0.059	0.029	0.568
589	0.590	0.444	0.111	0.131	0.477
590	0.329	0.494	0.081	0.051	0.643
591	0.608	0.698	0.062	0.032	0.568
592	0.567	0.051	0.270	0.340	0.328
593	0.198	0.779	0.035	0.005	0.817
594	0.549	0.803	0.065	0.008	0.639
595	0.835	0.314	0.056	0.040	0.313
596	0.786	0.877	0.023	0.034	0.537
597	0.728	0.506	0.092	0.004	0.440
598	0.482	0.464	0.109	0.012	0.554

Appendix VI: Average PVs of the Self-Trained DCM Applied to Remaining Trip Files

Table 20: Average PVs and its components of the Field Testing Data Using DCM Coefficients Created.

File	PE	r ²	SEE	PIE	PV
533	0.474	0.739	0.053	0.071	0.649
534	0.522	0.561	0.075	0.064	0.562
535	0.497	0.415	0.100	0.084	0.522
536	0.495	0.793	0.094	0.229	0.639
537	0.482	0.770	0.052	0.096	0.653
538	0.438	0.716	0.061	0.075	0.659
539	0.513	0.346	0.108	0.592	0.433
540	0.537	0.100	0.178	0.162	0.382
541	0.543	0.600	0.178	0.379	0.529
542	0.561	0.428	0.137	0.234	0.476
543	0.492	0.719	0.057	0.065	0.633
544	0.479	0.671	0.079	0.082	0.621
545	0.461	0.813	0.046	0.071	0.682
546	0.476	0.746	0.073	0.080	0.650
549	0.455	0.750	0.051	0.074	0.663
550	0.456	0.806	0.044	0.078	0.681
551	0.466	0.806	0.045	0.070	0.677
552	0.440	0.815	0.049	0.083	0.692
553	0.479	0.743	0.052	0.071	0.648
554	0.506	0.393	0.104	0.091	0.509
555	0.486	0.709	0.061	0.062	0.634
565	0.539	0.668	0.110	0.129	0.583
575	0.513	0.809	0.111	0.218	0.636
579	0.473	0.766	0.054	0.063	0.660
580	0.523	0.385	0.100	0.071	0.499
581	0.465	0.743	0.059	0.060	0.657
582	0.480	0.729	0.054	0.075	0.642
583	0.495	0.667	0.069	0.081	0.612
584	0.508	0.782	0.050	0.096	0.644
585	0.473	0.730	0.070	0.079	0.645
586	0.484	0.663	0.077	0.120	0.612
587	0.507	0.546	0.107	0.133	0.557
588	0.481	0.734	0.071	0.078	0.643
589	0.509	0.454	0.104	0.137	0.524
590	0.525	0.528	0.084	0.083	0.547
591	0.485	0.685	0.077	0.080	0.623
592	0.504	0.146	0.235	0.384	0.390
593	0.462	0.801	0.049	0.082	0.676
594	0.583	0.147	0.118	0.084	0.383
595	0.633	0.241	0.098	0.126	0.385
596	0.506	0.734	0.055	0.080	0.630
597	0.558	0.204	0.112	0.082	0.416
598	0.531	0.224	0.301	0.504	0.389

Appendix VII: DCM Peak Sensitivity Analysis

Table 21: Detection Thresholds of DCM Reconstruction Coefficients for 2.7 ppmv and 2.6 ppmv with 10 Hz and 1 Hz LI-7700.

Trip Files	10 Hz LI-7700			1 Hz LI-7700		
	False Reporting	False Positive	False Negative	False Reporting	False Positive	False Negative
533	0.099	0.059	0.177	0.047	0.038	0.069
534	0.102	0.059	0.185	0.074	0.077	0.069
535	0.146	0.138	0.161	0.080	0.088	0.059
536	0.094	0.100	0.081	0.096	0.119	0.039
537	0.102	0.067	0.169	0.074	0.077	0.069
538	0.102	0.079	0.145	0.074	0.084	0.049
539	0.121	0.079	0.202	0.091	0.080	0.118
540	0.190	0.209	0.153	0.154	0.180	0.088
541	0.251	0.351	0.056	0.231	0.310	0.029
542	0.314	0.448	0.056	0.209	0.280	0.029
543	0.105	0.067	0.177	0.080	0.077	0.088
544	0.190	0.243	0.089	0.140	0.176	0.049
545	0.099	0.063	0.169	0.072	0.077	0.059
546	0.154	0.188	0.089	0.121	0.153	0.039
549	0.088	0.029	0.202	0.030	0.015	0.069
550	0.085	0.029	0.194	0.033	0.019	0.069
551	0.124	0.071	0.226	0.063	0.057	0.078
552	0.085	0.042	0.169	0.050	0.046	0.059
553	0.099	0.059	0.177	0.047	0.038	0.069
554	0.179	0.188	0.161	0.138	0.165	0.069
555	0.110	0.084	0.161	0.083	0.088	0.069
565	0.110	0.130	0.073	0.105	0.134	0.029
575	0.080	0.079	0.081	0.096	0.123	0.029
579	0.110	0.084	0.161	0.083	0.088	0.069
580	0.165	0.163	0.169	0.127	0.138	0.098
581	0.102	0.084	0.137	0.088	0.103	0.049
582	0.091	0.017	0.234	0.033	0.015	0.078
583	0.113	0.084	0.169	0.085	0.092	0.069
584	0.094	0.042	0.194	0.044	0.019	0.108
585	0.157	0.176	0.121	0.113	0.142	0.039
586	0.118	0.100	0.153	0.094	0.107	0.059
587	0.259	0.360	0.065	0.242	0.318	0.049
588	0.176	0.209	0.113	0.143	0.184	0.039
589	0.193	0.222	0.137	0.152	0.188	0.059
590	0.135	0.113	0.177	0.085	0.088	0.078
591	0.198	0.251	0.097	0.163	0.207	0.049
592	0.077	0.050	0.129	0.069	0.077	0.049
593	0.099	0.059	0.177	0.074	0.077	0.069
594	0.110	0.013	0.298	0.063	0.008	0.206
595	0.124	0.008	0.347	0.080	0.008	0.265
596	0.102	0.059	0.185	0.063	0.057	0.078
597	0.110	0.033	0.258	0.061	0.019	0.167
598	0.154	0.188	0.089	0.121	0.153	0.039

Table 22: The Best False Reporting Rates from 2.5 to 3.5 ppmv for the DCM Coefficients.

Trip File	10 Hz				1 Hz			
	Best False Reporting Rate	Best Detection Threshold	False Positive Rate	False Negative Rate	Best False Reporting Rate	Best Detection Threshold	False Positive Rate	False Negative Rate
533	0.063	3.5	0.008	0.216	0.025	3.5	0.011	0.074
534	0.069	3.5	0.023	0.196	0.036	3.1	0.022	0.077
535	0.072	3.5	0.026	0.196	0.039	3.3	0.032	0.059
536	0.083	3.5	0.083	0.082	0.088	2.9	0.110	0.030
537	0.069	3.5	0.023	0.196	0.033	3.4	0.028	0.049
538	0.061	3.5	0.030	0.144	0.033	3.5	0.039	0.012
539	0.072	3.5	0.026	0.196	0.047	3.3	0.036	0.082
540	0.099	3.5	0.064	0.196	0.069	3.4	0.071	0.061
541	0.107	3.5	0.120	0.072	0.118	3.5	0.149	0.012
542	0.096	3.5	0.105	0.072	0.107	3.5	0.135	0.012
543	0.083	3.2	0.023	0.231	0.047	3.3	0.029	0.106
544	0.091	3.5	0.090	0.093	0.091	3.3	0.115	0.012
545	0.066	3.5	0.026	0.175	0.033	3.5	0.032	0.037
546	0.094	3.5	0.098	0.082	0.088	2.9	0.106	0.040
549	0.066	3.5	0.011	0.216	0.025	3.3	0.014	0.059
550	0.063	3.4	0.011	0.200	0.019	3.4	0.014	0.037
551	0.072	3.5	0.015	0.227	0.030	3.4	0.018	0.073
552	0.055	3.5	0.011	0.175	0.022	3.5	0.018	0.037
553	0.069	3.5	0.008	0.237	0.030	3.5	0.011	0.099
554	0.083	3.5	0.041	0.196	0.055	3.5	0.050	0.074
555	0.063	3.5	0.023	0.175	0.030	3.5	0.028	0.037
565	0.077	3.5	0.075	0.082	0.083	3.5	0.103	0.012
575	0.050	3.5	0.038	0.082	0.055	3.4	0.068	0.012
579	0.066	3.5	0.026	0.175	0.033	3.5	0.032	0.037
580	0.077	3.5	0.030	0.206	0.050	3.5	0.039	0.086
581	0.080	3.5	0.068	0.113	0.069	3.5	0.085	0.012
582	0.074	3.4	0.008	0.250	0.030	3.1	0.007	0.099
583	0.077	3.5	0.038	0.186	0.044	3.5	0.043	0.049
584	0.074	3.3	0.008	0.243	0.030	3.3	0.011	0.094
585	0.091	3.5	0.090	0.093	0.088	2.9	0.106	0.040
586	0.074	3.5	0.045	0.155	0.052	3.5	0.057	0.037
587	0.107	3.5	0.109	0.103	0.107	3.4	0.135	0.012
588	0.096	3.5	0.102	0.082	0.091	2.9	0.110	0.040
589	0.096	3.5	0.075	0.155	0.080	3.5	0.089	0.049
590	0.091	3.5	0.041	0.227	0.055	3.4	0.046	0.085
591	0.099	3.5	0.098	0.103	0.091	3.3	0.115	0.012
592	0.077	2.7	0.050	0.129	0.063	3.1	0.074	0.033
593	0.063	3.5	0.026	0.165	0.033	3.1	0.029	0.044
594	0.105	3.1	0.008	0.333	0.058	3.1	0.007	0.209
595	0.121	2.9	0.000	0.383	0.077	3.1	0.000	0.308
596	0.074	3.5	0.008	0.258	0.036	3.5	0.011	0.123
597	0.088	3.5	0.004	0.320	0.047	3.1	0.007	0.165
598	0.080	3.5	0.071	0.103	0.072	2.9	0.084	0.040

Table 23: The Best False Reporting Rates from 2.5 to 5.5 ppmv for the DCM Coefficients.

Trip File	10 Hz				1 Hz			
	Best False Reporting Rate	Best Detection Threshold	False Positive Rate	False Negative Rate	Best False Reporting Rate	Best Detection Threshold	False Positive Rate	False Negative Rate
533	0.063	3.5	0.008	0.216	0.025	3.5	0.011	0.074
534	0.061	4.6	0.004	0.253	0.028	5.3	0.003	0.158
535	0.063	4.7	0.011	0.244	0.036	4.7	0.020	0.106
536	0.044	4	0.030	0.087	0.044	3.9	0.053	0.013
537	0.066	3.6	0.022	0.188	0.030	5.5	0.007	0.161
538	0.055	4.9	0.011	0.210	0.028	4.1	0.021	0.053
539	0.072	3.5	0.026	0.196	0.041	4.8	0.023	0.127
540	0.069	4.9	0.014	0.259	0.047	4.7	0.027	0.136
541	0.052	5.4	0.042	0.089	0.077	4.6	0.092	0.014
542	0.039	5.2	0.032	0.063	0.061	4.6	0.075	0.000
543	0.069	4.7	0.004	0.293	0.036	5.5	0.010	0.179
544	0.055	4.4	0.026	0.146	0.039	4.1	0.042	0.027
545	0.061	3.8	0.011	0.207	0.028	4.9	0.013	0.098
546	0.044	4.9	0.028	0.099	0.041	4.4	0.048	0.014
549	0.063	3.7	0.007	0.223	0.025	3.3	0.014	0.059
550	0.063	3.4	0.011	0.200	0.019	3.4	0.014	0.037
551	0.072	3.5	0.015	0.227	0.030	3.4	0.018	0.073
552	0.055	3.5	0.011	0.175	0.019	3.6	0.014	0.037
553	0.069	3.5	0.008	0.237	0.028	5.3	0.003	0.158
554	0.069	4.9	0.014	0.259	0.044	4.7	0.027	0.121
555	0.063	3.5	0.023	0.175	0.030	3.5	0.028	0.037
565	0.041	4.2	0.033	0.067	0.052	4.5	0.065	0.000
575	0.041	4.7	0.025	0.098	0.036	4.2	0.042	0.013
579	0.061	3.8	0.026	0.163	0.033	3.5	0.032	0.037
580	0.074	4.7	0.014	0.280	0.047	4.7	0.024	0.152
581	0.055	3.8	0.026	0.141	0.033	3.7	0.032	0.037
582	0.074	3.4	0.008	0.250	0.030	3.1	0.007	0.099
583	0.066	3.6	0.022	0.188	0.036	3.6	0.028	0.062
584	0.074	3.3	0.008	0.243	0.030	3.3	0.011	0.094
585	0.050	4.7	0.028	0.122	0.039	4.2	0.042	0.027
586	0.061	4.7	0.018	0.207	0.039	3.9	0.032	0.063
587	0.055	5.2	0.028	0.150	0.063	5.5	0.065	0.054
588	0.047	4.7	0.028	0.110	0.039	4.2	0.042	0.027
589	0.063	5.2	0.014	0.238	0.052	5.5	0.042	0.107
590	0.069	4.8	0.011	0.268	0.044	4.7	0.024	0.136
591	0.052	4.6	0.029	0.133	0.047	4.4	0.048	0.042
592	0.052	4.6	0.018	0.169	0.041	4.2	0.035	0.067
593	0.055	3.8	0.011	0.185	0.025	3.7	0.014	0.062
594	0.105	3.1	0.008	0.333	0.052	5.3	0.000	0.333
595	0.116	3.8	0.000	0.457	0.063	5.3	0.000	0.404
596	0.074	3.5	0.008	0.258	0.033	5.3	0.003	0.193
597	0.088	3.5	0.004	0.320	0.047	3.1	0.007	0.165
598	0.050	4.9	0.028	0.123	0.047	4.4	0.051	0.028

Appendix VIII: ANN Details

The ANN created during training is shown in Figure 55. The ANN is a function fitting network with 10 nodes. The details of the weights and activation functions used are given in Table 24. The ANN can be recreated using these values.

Figure 55: View of the ANN created.

Table 24: Detailed Values of the Weights of Each Node.

Hidden Layer (tansig activation function)						Output Layer (tansig Activation function)	
Node	Weights 1	Weights 2	Weights 3	Weights 4	Node Bias	Weights	Output Bias
1	0.325	1.732	1.768	-3.36	-0.42	-310	60.92
2	11.57	37.59	-60.3	-30.1	18.89	925.6	
3	22.33	-45.5	-15.9	137.1	-29.3	916.8	
4	1.034	-40.3	29.96	-32.6	-30.3	267.2	
5	-2.35	-10.5	8.156	-5.84	0.372	-105	
6	1.67	8.324	2.706	-14.7	7.768	-62.1	
7	-1.56	-7.79	-3.12	14.32	-7.38	-68.3	
8	-4.56	-5.42	11.94	-16.1	-3.44	99.61	
9	4.491	5.476	-12	15.81	3.597	116.5	
10	-0.26	-1.26	-0.44	1.506	-1.52	-8.3	

Appendix IX: DCM Self Training at 2 Hz PVs

Table 25: PVs of the Field Testing Data Using DCM and Self-Training at 2 Hz.

File	PE	r ²	SEE	PIE	PV
533	0.463	0.207	0.077	0.071	0.468
534	0.800	0.228	0.059	0.034	0.302
535	0.797	0.491	0.040	0.038	0.395
536	0.019	0.056	0.052	0.054	0.653
537	0.576	0.004	0.109	0.421	0.299
538	0.137	0.001	0.126	0.014	0.575
539	0.247	0.121	0.120	0.320	0.525
540	0.548	0.018	0.159	0.403	0.320
541	0.740	0.011	0.263	0.654	0.187
542	0.573	0.000	0.120	0.429	0.298
543	0.590	0.009	0.024	0.495	0.286
544	0.593	0.121	0.074	0.001	0.377
545	0.477	0.222	0.062	0.015	0.473
546	0.696	0.025	0.119	0.917	0.188
549	0.693	0.939	0.075	0.005	0.610
550	0.562	0.793	0.032	0.039	0.625
551	0.754	0.056	0.055	0.419	0.223
552	0.952	0.004	0.034	0.294	0.114
553	0.957	0.575	0.042	0.074	0.336
554	0.901	0.404	0.025	0.049	0.308
555	0.940	0.361	0.064	0.000	0.277
565	0.931	0.106	0.020	0.039	0.189
575	0.512	0.001	0.103	0.906	0.279
579	0.908	0.090	0.028	0.123	0.187
580	0.698	0.011	0.152	0.158	0.265
581	0.297	0.230	0.176	0.576	0.508
582	0.134	0.625	0.193	0.055	0.790
583	0.554	0.501	0.080	0.013	0.530
584	0.038	0.196	0.154	0.030	0.694
585	0.502	0.383	0.132	0.028	0.514
586	0.512	0.000	0.209	0.256	0.348
587	0.047	0.056	0.230	0.042	0.637
588	0.703	0.008	0.161	0.320	0.244
589	0.726	0.001	0.103	0.691	0.189
590	0.665	0.003	0.151	0.209	0.274
591	0.785	0.003	0.115	0.169	0.215
592	0.633	0.027	0.119	0.955	0.218
593	0.595	0.038	0.065	0.068	0.340
594	0.661	0.880	0.041	0.027	0.604
595	0.935	0.213	0.076	0.047	0.223
596	0.896	0.545	0.049	0.028	0.362
597	0.803	0.572	0.074	0.005	0.423
598	0.674	0.411	0.069	0.052	0.430