

# Sensors and Methods for Measuring Greenhouse Gas Emissions from Different Components of Livestock Production Facilities

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## Abstract

Greenhouse gas monitoring on a broader scale is necessary to ensure that a cap-and-trade system is effective, reduces measurement uncertainty, and detects fraudulent or illegal activities. The recent strict air quality regulation in livestock production facilities has accelerated the need for accurate on-farm determination of greenhouse gas (GHG) emission rates (ERs) from livestock operations in the United States under a wide range of production, management, and climate conditions. The estimation of GHG emissions from different ground-level sources or at a property line is a very complicated process, and such measurements require multidirectional expertise including engineering, micrometeorology, agronomy, applied physics, and chemistry. Accurate measurement of gaseous concentration from an emitting source is a prerequisite and of paramount importance for estimating emissions rates (ERs) using any micro-meteorological and sampling device-based method. This paper provides an overview of the state-of-the-art sensors and analyzers used to measure GHG concentrations. Sensor and analyzer selection and their performance in the laboratory and field were discussed. In addition, protocols for data quality control (QC) and quality assurance (QA) when deploying sensors in the area for long-term use were also discussed. In addition, the preparation of measurement systems, coupling of air samplers with sensing systems for measuring gaseous concentrations, and uncertainties inherent to such measurement methods as a whole to estimate ERs were discussed in this paper.

## Keywords

Flux-Chamber, Spectroscopic Techniques, Separation Techniques, Uncertainty, Open-Path FTIR, CRDS, TDLAS

## 1. Introduction

Animal manure and associated manure management processes at confined livestock operations (CLOs) emit a considerable amount of greenhouse gases (GHGs). Among the confined animal production systems, swine and ruminant livestock operations, especially dairy cows and beef cattle, contribute to the production of GHGs including methane ( $\text{CH}_4$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), and carbon dioxide ( $\text{CO}_2$ ). Greenhouse gases are emitted from all the major components of the livestock production cycle that contaminate the atmosphere and contribute to the greenhouse effect. Measurements of gaseous emissions are extremely important to identify the emission sources in stationary agricultural operations, quantify the emission rates, compare the emission rates among sources, and evaluate the effectiveness of mitigation activities. The characterization and quantification of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  emitted from livestock operations are important because these gases are believed to play a major role in the increase of the Earth's temperature. Continuously increasing livestock production will place additional strains on the environment and natural resources, necessitating the development of appropriate approaches that allow for increased animal production while posing no or minimal environmental risks.

Main sources of GHG emissions from the animal production facilities are feed production (silage pile, feed mill), farm machinery operations (tractors, loaders, and irrigation pumps), fertilizer and liquid manure (chemicals, manure slurry), enteric fermentation (for ruminants, not regulated), manure management (solids separator, composting yard, loafing pen, open lot, retention pond, feedlot pens, opened and covered lagoons, deep pit slurry storage, etc.), processing plants (slaughtering and packaging, distribution), and exhausts from covered lagoons and livestock and poultry production barns, and a ruminant's stomach produces methane through enteric fermentation, from bacterial degradation of organic matter in the manure, and from anaerobic decay of volatile solids in storage lagoons and settling basins. The concentration of  $\text{CH}_4$  in the atmosphere is approximately 1.8 ppm by volume with a global warming potential (GWP) of 25, which indicates that  $\text{CH}_4$  is 25 times more effective at trapping heat in the atmosphere than  $\text{CO}_2$  by weight (IPCC 2006). The GWP is expressed as a relative index to standardize emissions of GHGs for comparing how effectively each gas traps heat in the atmosphere. At CLOs,  $\text{CO}_2$  is released from the use of fertilizers in crop/pasture production, fossil fuel used to run farm machinery and feed processing operations, the loss of trees for crop production on land adjacent to the operation, and carbon loss from the soil for feed production. Nitrous oxide is produced in soils through microbial processes of nitrification and denitrification and is released from manure and urine excreta, from fertilizer and manure slurry applied for crop/pasture production, and from the aerobic and anaerobic degradation of livestock manure and wastewater in lagoons and dry manure piles. The amount of these gaseous emissions from livestock varies by animal type and growth stage due to different diets, feed conversion mechanisms, manure han-

dling and agricultural practices, and climatic conditions.

During the last two hundred and fifty years, human activities, including increased agricultural production, have increased the global atmospheric concentration of GHGs, namely CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O, by 36%, 148%, and 18%, respectively. Total GHG emissions in the US have increased by 14.7% from 1990 to 2006. All agricultural sources of GHG emissions combined were estimated to have generated 454 Tg (10<sup>12</sup> g) of CO<sub>2</sub> equivalents in the U.S. during 2006. Overall, the livestock sector contributes approximately 9% of total anthropogenic CO<sub>2</sub> emissions, 37% of CH<sub>4</sub> emissions, and 65% of N<sub>2</sub>O emissions (Ekpenkhio & Orobator, 2021). The combined emissions expressed in CO<sub>2</sub> equivalents amount to about 18% of anthropogenic GHG emissions. The US Environmental Protection Agency (USEPA) has started regulating GHGs emitted from stationary sources, including manure management from CLOs. Therefore, it is important to obtain accurate estimates of GHG emissions from various ground level area sources (GLASs) at CLOs to devise source-specific abatement strategies and improve emission inventories. When released into the environment through exhaust, gaseous emissions from animal barns, particularly swine housings with deep pits, dairy housing with an inbuilt lagoon, covered liquid and solid manure storages, and poultry barns, accounted for a significant portion of GHG emissions. As a result, emission measurement methods differ according to the source categories described below:

- Silage piles, feed mill premises, pen surfaces, open-lots, loafing pens, settling basins, open lagoons, retention ponds, composting areas, and liquid or dry manure applied crop or pastureland are examples of ground level area sources where GHG gas is produced.
- Exhaust ports of animal housings/barns and covered sources (covered lagoons and other manure management operations) with mechanical ventilation.

The main purpose of this article is to provide farmers or general users with a brief idea of the state of the art of the measurement methods, including sensors and sensing techniques, for quantifying greenhouse gas emissions with sufficient accuracy from different ground-level sources in livestock production facilities. The outlines of the topics are presented sequentially, described, and discussed in the flow-chart below (Figure 1).

### Spectral Properties of Greenhouse Gases

Gases in the atmosphere absorbing and emitting radiation within the thermal infrared range are termed “greenhouse gases”. This process is the primary cause of the greenhouse effect, as gases trap heat in the atmosphere. Greenhouse gases produce spectral features in the infrared region of the electromagnetic spectrum, and different greenhouse gases absorb in different parts of the IR window (Figure 2). Table 1 presents the ambient GHG concentrations, lifetime of the gases, spectrum with wavenumbers at which the molecules of the GHGs absorb infrared

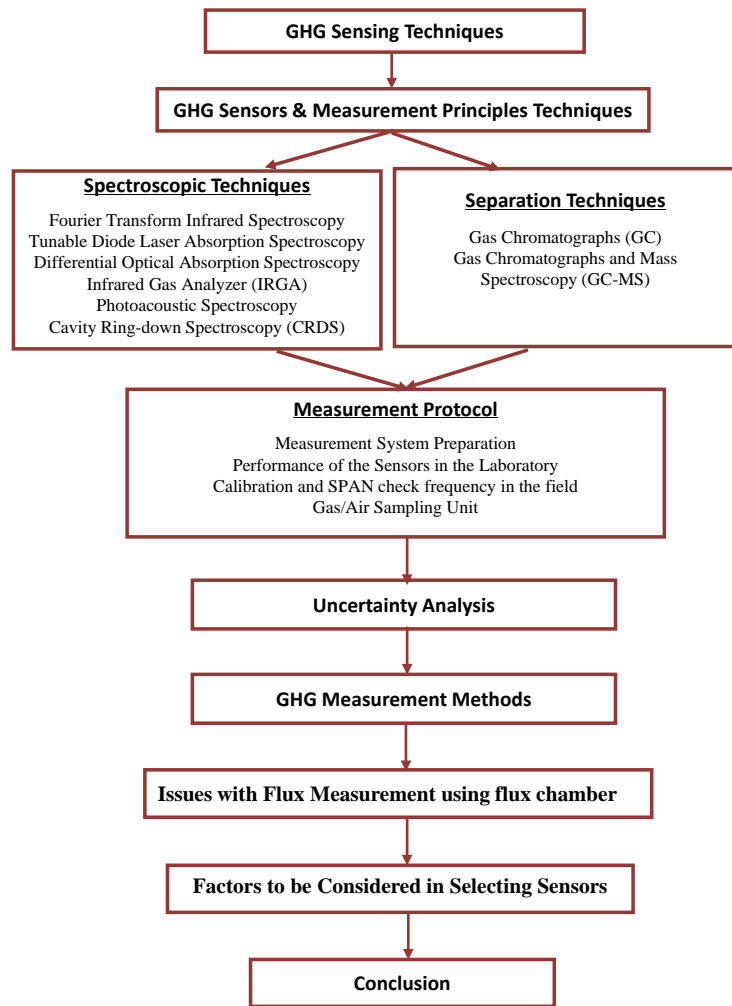


Figure 1. Outlines of the topics described and discussed sequentially.

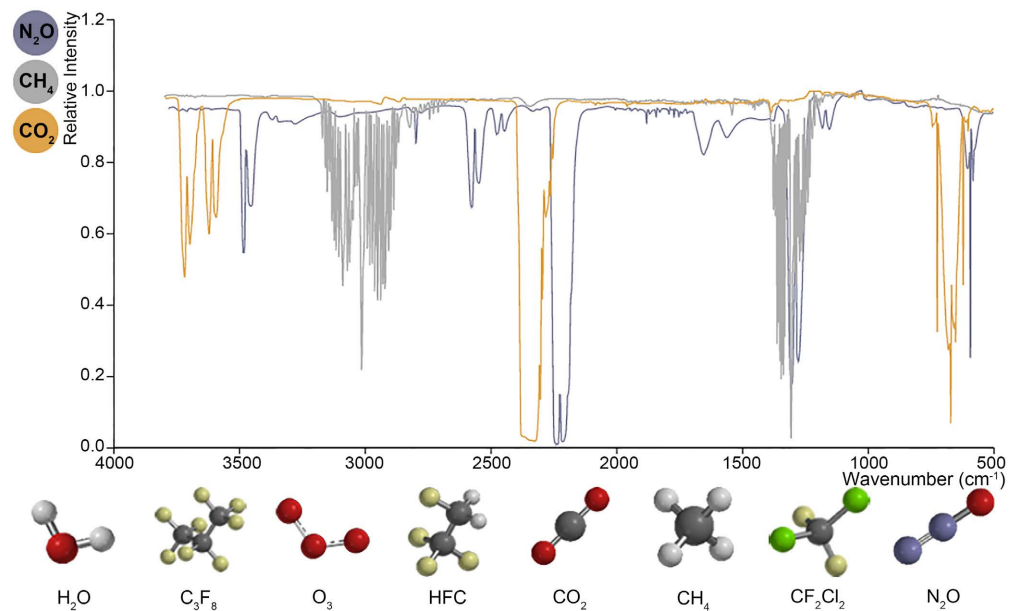


Figure 2. IR window of Greenhouse gases (adapted from Thompson et al., 2019; Schwartz, 1997).

**Table 1.** GHG concentrations, lifetimes, the spectrum at which the molecules of the GHGs absorbs IR and radiative efficiencies.

Gas type	Chemical Formula	MW (g·gmol <sup>-1</sup> )	Ambient <sup>1</sup> concentration (ppm)	Lifetime (years)	GWP	Absorption band (cm <sup>-1</sup> )		Radiative Efficiency (W·m <sup>-2</sup> ·ppb <sup>-1</sup> )
						Central	Band interval	
Carbon dioxide	CO <sub>2</sub>	44.01	~379	5 - 200	1	2526	2000 - 2400	1.4 × 10 <sup>-5</sup>
Methane	CH <sub>4</sub>	16.04	~1.7	12	25	3030	2500 - 3200	3.7 × 10 <sup>-4</sup>
Nitrous Oxide	N <sub>2</sub> O	44.01	~0.3	114	310	2222	2100 - 2300	3.03 × 10 <sup>-3</sup>

MW = Molecular weight; GWP = Global Warming Potential; <sup>1</sup>IPCC, 2007. <https://applets.kcvs.ca/IRWindows/IRWindows.html>; <http://www.ces.fau.edu/nasa/module-2/how-greenhouse-effect-works.php>.

(IR), and radiative efficiencies. In general, CO<sub>2</sub> is variable and regularly travels into and out of the atmosphere through four major processes, such as respiration, photosynthesis, and the burning and decomposition of organic materials. The atmospheric gas is inflated with CO<sub>2</sub> through the burning of fossil fuels (coal, natural gas, and oil), solid waste, trees, and wood products. However, CO<sub>2</sub> is removed from the atmosphere as it is absorbed by plants during the biological carbon cycle. In excess of fossil sources such as the production and transport of coal, natural gas, and oil, the anaerobic decomposition of agricultural biomass and industrial residue, including municipal solid waste, emits CO<sub>2</sub> to the atmosphere. Similarly, N<sub>2</sub>O is emitted during agricultural (land applications of manure and inorganic fertilizer) and industrial activities, as well as during the combustion of fossil fuels and municipal solid waste. Nitrifying and denitrifying bacteria convert a portion of applied inorganic fertilizers, such as NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, into N<sub>2</sub>O. Additionally, internal combustion engines used in agricultural operations also produce nitrous oxide. Methane is 30 times stronger than CO<sub>2</sub> as an absorber of infrared radiation and is produced when bacteria decompose organic plant and animal matter under anaerobic conditions.

The principal GHGs are CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emitted from agricultural sources with a smaller molecular weight when they are in the gas phase. Each gas molecule has an inherent and fundamentally characteristic absorption band that shows a clear distinction among gaseous species in the mid-infrared region. This wavelength region ranged approximately from 2 to 15 μm and was referred as the “molecular footprint region,” which is not in the range of human vision but can be felt as heat (Neftel et al., 2006). When the right wavelength of radiation strikes the absorbing gases, the light is absorbed by the gas molecules and either re-emitted at slightly longer wavelengths or the molecule undergoes non-radiative thermal decay. Thus, the greenhouse effect is caused by this dispersion of light and heat. However, in the IR spectral range, the main concern for data accuracy is the interference due to the overlapping of the gas IR spectra. Thus, it is to be noted that the sensitivity of the detector is in jeopardy when two or more gases interfere with each other, meaning that two or more gases are absorbed at the same wavelength. Therefore, a sensor with the capability of compensating for interfering compounds can be a criterion for selection.

Due to the unique absorption wavelengths of target gases, the densities or gas concentrations are easily measured through molecular absorption. After selecting a suitable device coupled with a target absorption filter corresponding to the targeted gas and its surrounding environment, the optical spectroscopic method is by far the most optimal for high-speed response and high-accuracy gas measurement. A few widely used GHG sensors and sensing systems are described and discussed in the following subsections.

## 2. GHG Sensors and Measurement Principles

### 2.1. Sensing Techniques

The performance of analytical instruments or sensors, such as detection limits, percent analyte recoveries, calibration equations coupled with data quality control, and assurance (QA/QC) protocols, is critical for generating valid authentic gas concentration data. Gases at trace levels can be measured using different sensing techniques. GHGs can be measured using non-destructive infrared spectroscopy (NDIR), Cavity Ring-Down spectroscopy (CRDS), quantum cascade laser spectrometers (QCL), gas chromatography (GC), gas chromatography mass spectroscopy (GC-MS), tunable diode laser absorption spectroscopy (TDLAS) technologies, open path Fourier transform infrared radiation (OP-FTIR) technologies, photo acoustic spectroscopy (PAS) and solid-state electrochemical technologies. Instruments with mass spectrophotometers have a very rapid response, can detect many gases at one time, exhibit linear responses over a wide range of concentrations, and are very accurate and stable (Johnson & Johnson, 1995). Inherently, mass spectrophotometers, TDLs, and OP-FTIRs are expensive. Despite their relative affordability, solid state electrochemical sensors require frequent calibration due to their unstable nature. The shelf lives of those sensors vary from 12 - 18 months. In this section, a few commonly but widely used techniques and instruments for measuring GHGs are discussed.

### 2.2. Spectroscopic Techniques

Spectroscopy refers to the study of the interaction between radiation and matter as a function of wavelength, which measures light that is emitted, absorbed, or scattered by materials and is widely used to identify, and assess the concentration or amount of a given chemical (atomic, molecular, or ionic) species contained in it. A plot of the spectral response of a compound as a function of wavelength is referred to as a "spectra." All spectroscopic techniques work according to the Beer-Lambert absorption law. This law states that the absorption of light is proportional to the concentration of the absorbing species, the line strength, and the path length of the absorption. In other words, when a molecule absorbs external energy (such as photons in light), it is excited and moves from a lower to a higher energy level. When the molecule returns to its lower energy level, it either emits a photon or releases heat, or both, following the Beer-Lambert absorption law (Zhao et al., 2012). Depending on the radiation source used to

illuminate the sample and/or the type of detection method, there are various spectroscopic technique types. The instrument used for such measurements is called a spectrometer or spectrophotometer. The IR sensors are of two types, namely, broadband and laser/single band specific to a target trace gas. The broadband thermal system uses interference filters to select a wavelength band specific to a target gas of interest while screening or blocking the rest. Typically, Fourier transform infrared spectrometry (FTIR) uses a broadband IR source and makes a scan through the entire IR region. In the laser-based system, a laser ray is tuned to the distinctive absorption line of a particular trace gas. The TDLAS, CARDS, and QTL are laser based and specific to a single target gas, whereas the FTIR, OP-FTIR, PAS, and LiCor 820 use a broadband IR spectrum. Several commonly used ones will be briefly discussed.

### **2.2.1. Fourier Transform Infrared Spectroscopy (FTIR)**

Fourier transform infrared spectroscopy (FT-IR) is widely used to simultaneously quantify the concentrations of multiple GHGs. Additionally, FTIR spectroscopy is a measurement technique that allows recording and on-board processing of infrared spectra with a research-grade high resolution of 0.001 to 25  $\text{cm}^{-1}$ . The FTIR transformation is basically a mathematical manipulation that relates a signal, curve, or algebraic function to its frequency content and thus transforms a spectral signal from the time domain to the frequency domain. The basis for the operation is how various compounds absorb energy at various wavelengths. In this technique, an infrared light beam is split into two different paths and guided through an interferometer (where the wavelength information characteristics of a particular compound are extracted) and then through the sample (or vice versa). The interferometer's infrared light distribution is modified by a moving mirror inside the device. The light passes through the sample, and the transmitted signal, known as an interferogram, is recorded by a detector that represents light output as a function of mirror position. This spectral signature is merely raw data, which can be processed and enhanced using an algorithm referred to as the Fourier transformation technique to get the actual spectrum. The interferogram is manipulated by built-in software and fitted to a spectral library in order to identify and quantify the pollutant by comparing it to the spectra of known samples (Shao & Griffiths, 2007). Currently, different types of FT-IR spectrometers exist, such as dual-path FTIR, long-path (LP/FTIR), and open-path (OP/FTIR) analyzers. Additionally, benchtop and backpack-style portable FTIR units are also available.

Open-path Fourier transform infrared spectroscopy (OP-FTIR) is a versatile technology that allows multiple pollutants in open spaces to be measured and quantified simultaneously over a distance (an "open path") that ranged from 0.1 m to several kilometers and at concentrations as low as parts per billion (ppb) levels, making it a useful measurement tool for agricultural sources (Hu et al., 2014; Bjorneberg et al., 2009). The most widely used technique to measure gaseous emissions from livestock operations is OP-FTIR. An optical signal detec-



tion device or receiver and an emitter telescope are the main components of open-path sampling. The emitter's source light, which is either ultraviolet (UV) or infrared (IR), is beamed in one direction over a certain distance (100 - 750 m depending on technology) to the receiver or detector (Figure 3). Generally, FTIR involves collecting infrared light that has traveled through or been reflected by sample materials, and analyzing this collected light for the absorbance characteristics of the sample materials. The OP-FTIR measurements, independent of type, do not require frequent calibration. In place of a calibration technique, OP-FTIR systems utilize well maintained databases of reference spectra against which collected data are compared to identify and quantify concentrations of species of interest. This can be used for measuring gas concentrations from integrated sources both upwind and downstream of a facility. The OP-FTIR technique is capable of real-time measuring and monitoring the concentration of multiple gases over relatively long paths without altering ambient climatic conditions (Bjorneberg et al., 2009; Russwurm & Childers, 2002).

Pollutants such as GHGs have been successfully monitored using OP-FTIR spectrometry at large animal production facilities (Bjorneberg et al., 2009; Todd et al., 2010). Previous research has shown that the concentrations of target gases reported by OP-FTIR methods are very close and comparable to those measured by conventional point monitoring methods (Childers et al., 2001; Bjorneberg et al., 2009; Russwurm et al., 1991; Carter Jr. et al., 1992). An OP-FTIR spectrometer was used to measure ammonia ( $\text{NH}_3$ ), methane, and nitrous oxide concentrations over the pens, wastewater storage pond, and composting area on a 700-cow open-lot dairy in Idaho (Bjorneberg et al., 2009). Measured average  $\text{CH}_4$  concentrations over the pens, storage pond, and composting area ranged from 2.07 to 2.80 ppm, 1.87 to 2.15 ppm, and 1.71 to 1.76 ppm, respectively. Average  $\text{N}_2\text{O}$  concentrations ranged from 0.31 to 0.33 ppm for all areas. They also mentioned that the emissions estimated using these methods were similar to the published data.

### 2.2.2. Tunable Diode Laser Absorption Spectroscopy (TDLAS)

The TDLASs are designed to focus on single absorption wavelengths specific to a compound of interest in the gaseous state, are capable of achieving low detection limits, and are virtually interference-free. The open-path tunable diode lasers (OP-TDLAS) are generally used in atmospheric pollutant studies such as fence

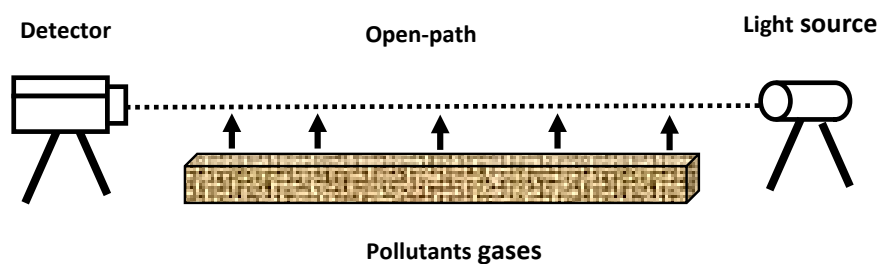


Figure 3. Schematic of open-path sampling (according to Amon et al., 1997).



line monitoring, process line/tank leak detection, industrial gas purity applications, and monitoring and control of combustion processes. The TDLs can also be in enclosed cells where the gas to be measured is drawn into a fixed-length cell at a specified rate and pressure. The multi-pass type of cell capable of allowing light to travel before being measured facilitates near-continuous measurements. Thus, it greatly improves the detection limits of the instrument by reducing pressure, controlling temperature, and increasing path length. The TDLAS technology works based on tunable diode laser absorption spectroscopy, where gaseous molecules are subject to characteristic absorption caused by molecular vibration in the 1 - 2  $\mu\text{m}$  near-infrared region. A laser, with its inherent monochromatic light emission, is used to excite the atoms or molecules. It has a high sensitivity and real-time measurement capability for gas concentrations at the ppm level and lower. It is capable of measuring gas and particle concentrations simultaneously while remaining unaffected by coexisting substances such as gases, dust, or raindrops. A typical TDLAS sensor has the following complements, as shown in **Figure 4** (Mitsubishi Heavy Industries Ltd., 2004).

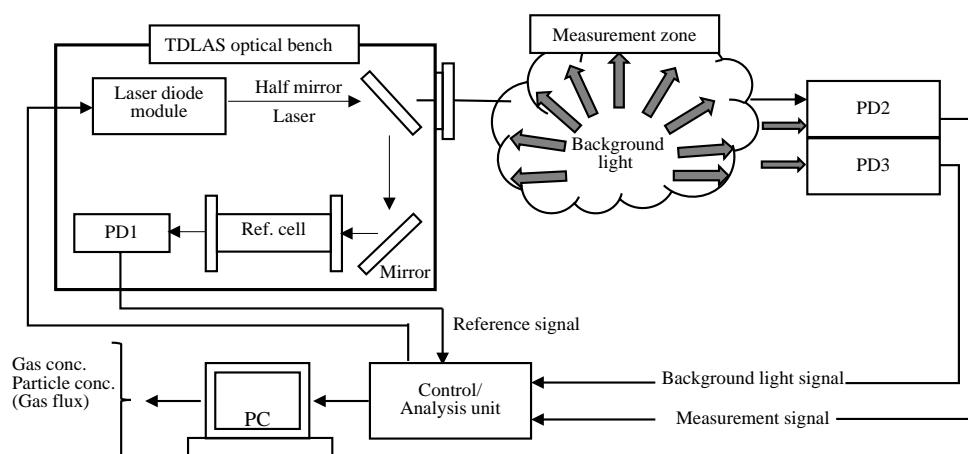
**1) Light source:** a distributed-feedback type (MQW-DFB) InGaAs(P) laser diode (LD) featuring a strained multi-quantum well structure for the oscillation of near-infrared region light at room temperature, and which emits monochromatic light in response to specific species of gas.

**2) Detector:** InGaAs photodiodes (PD) for the measurement of laser light intensity.

**3) Reference cell:** used for calibration and laser wavelength stabilization, which is done through the introduction of a standard gas at a known concentration and constant pressure.

**4) Measurement unit:** Obtains information on concentration by modulating the laser wavelength and separating out signals synchronized with the frequency of the modulated wavelength from among the optical signals received.

**5) LD driver unit:** used to set the temperature and current of the laser diode, as well as the oscillation wavelength of the laser.



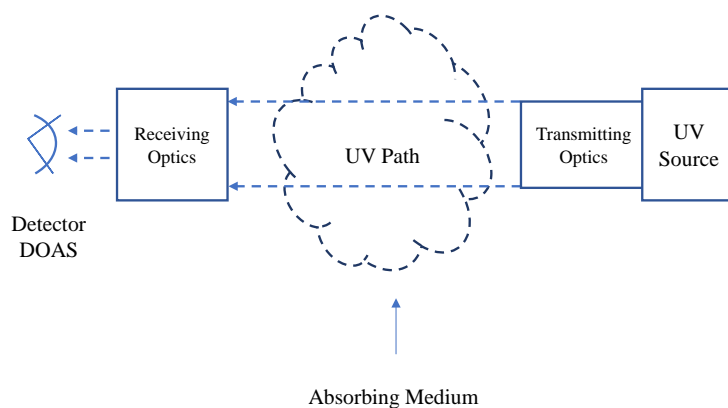
**Figure 4.** Schematic diagram of TDLAS monitoring system (adapted from the Mitsubishi Heavy Industries Ltd., 2004).

The TDLAS technology monitors GHG (CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O) emissions in the vicinity of sources and in the general atmosphere. This instrument was employed to measure GHG emission rates at CLOs. Loh et al. (2008) used an open-path tunable near infrared diode laser coupled with backward lagrangian stochastic (BLS) model of atmospheric dispersion to estimate summer CH<sub>4</sub> ER data for two Australian feed yards. The methane emission rates (ERs) reported were 146 and 166 g hd<sup>-1</sup> d<sup>-1</sup> for Victoria and Queensland, respectively.

In Queensland and Alberta, feedlots emit on average 166 and 214 g CH<sub>4</sub> hd<sup>-1</sup> d<sup>-1</sup> using the same methods. Average daily CH<sub>4</sub> emissions were estimated to be 323 g hd<sup>-1</sup> d<sup>-1</sup> for a large beef feedlot in western Canada using TDLAS and an inverse dispersion model (Van Haarlem et al., 2008). In a New Mexico dairy, methane concentration over three interconnected lagoons (total area of 1.8 ha) was measured using open path laser spectroscopy (Todd et al., 2010). Methane concentrations over the lagoons ranged from 3 to 12 ppm, with an average of 5.6 ppm. The average ER for methane was calculated to be 0.211 kg head<sup>-1</sup> d<sup>-1</sup>. The ability to analyze multiple compounds simultaneously and continuously is a significant advantage of OP-FTIR. The long path length monitoring also facilitates in obtaining more comprehensive data than the conventional multiple- and single-point monitoring methods. However, it required high technical skills, and this technology is very expensive when compared with other methods. An OP-TDLAS system is a little different than OP-FTIR in that the gas plume under investigation passes through the path between the laser source (TDLAS) and retroreflectors and measures the average concentration of a target compound within that path length. An OP-TDLAS system is less expensive than a comparable OP-FTIR. However, the TDLAS technique is able to measure one to three gases at a time using gas specific lasers, with increasing potential error with each addition. In contrast, FTIR systems are able to measure multiple compounds simultaneously (Thoma et al., 2005).

### 2.2.3. Differential Optical Absorption Spectroscopy (DOAS)

The typical application of DOAS is to quantify gaseous concentrations over an optical path in the atmosphere under investigation. This technology was extensively used for NH<sub>3</sub>, and fluxes were estimated when used with airflow characterization methods including tracer gas, inverse modeling, and aerodynamic gradient. It was also for estimating greenhouse gases (CO<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>O) along with reactive species such as NH<sub>3</sub>, NO, SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub> from livestock barns, manure storage, and crop/pasture fields (Leytem et al., 2011b; Hu et al., 2014; Volten et al., 2012). The system consisted of a DOAS spectrometer, a light source (usually tungsten or halogen), and a telescopic conduit to guide and receive light. For passive DOAS, the light source is the sun, for active DOAS, an artificial light source is used (Figure 5). Measurements are based on the absorption of light at characteristic wavelengths of the target gases. The DOAS instrument detects a gas by measuring its absorption in the mid-ultraviolet spectrum (200 - 235 nm). The NH<sub>3</sub> detection limit for this instrumentation is a few ppb (2 ppb)



**Figure 5.** Bistatic configuration of UV-DOAS system (adapted from the USEPA, 2018).

and facilitates high precision measurements that are also faster (Hu et al., 2014; Rumburg et al., 2008).

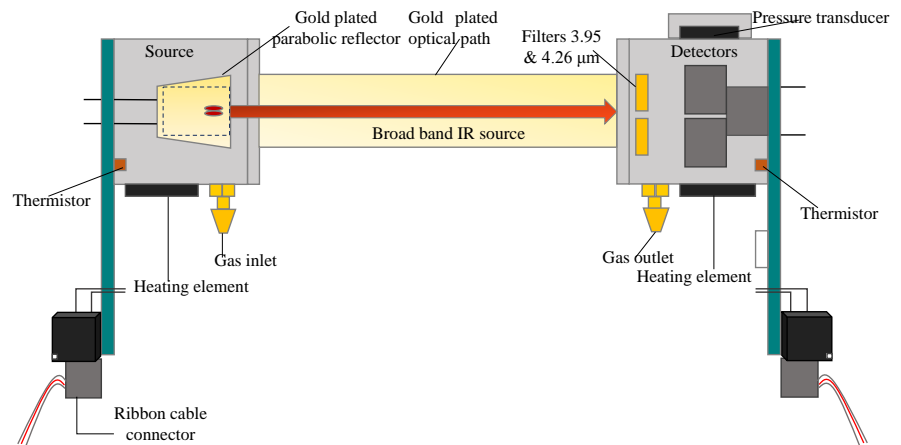
According to the Beer-Lambert law, the intensity of the light detected at a particular wavelength determines the concentration of the target gas as shown in the equation.

$$I_{\lambda} = I_{0,\lambda} \times e^{-(\alpha_{i,\lambda} \times C_i + \epsilon_M + \epsilon_R) \times L} + S(\lambda) \quad (1)$$

where  $I$  and  $I_0$ , ( $W \cdot sr^{-1}$ ) are the intensities of the wavelength radiation incident on the receiver and emitted by the radiation source, respectively;  $i$ , ( $m^2 \cdot g^{-1}$ ) is the absorption cross-section of gas  $i$  at wavelength;  $C_i$  ( $g \cdot m^{-3}$ ) is the concentration of the gas in the gaseous compound;  $L$  (m) is the length of the optical path; and  $\epsilon_M$  and  $\epsilon_R$  are the extinction coefficients per unit of the optical path Volten et al. (2012) used a DOAS to measure  $NH_3$  concentration in the atmosphere close to a livestock farm with an accuracy of  $0.15 \mu g \cdot m^{-3}$  (215 ppb) over a path length of 100 m. They recognized that the device provided fast response, required low maintenance, and measured interference-free  $NH_3$  concentrations up to at least  $200 \mu g \cdot m^{-3}$  (287 ppm). Similarly, Rumburg et al. (2008) used DOAS in conjunction with two area source tracer ratio techniques to measure  $NH_3$  fluxes of  $2919 g/cow^{-1} \cdot h^{-1}$  from downwind of a milking cow.

#### 2.2.4. Infrared Gas Analyzer (IRGA)

Trace gases found in the Earth's atmosphere get excited at specific wavelengths found in the infrared region of the electromagnetic spectrum. An infrared gas analyzer measures these trace gases by determining the absorption of an emitted infrared light source through a certain air sample. The main components of an infrared sensor are an infrared light source, a sample chamber or light tube, and filters housed in a wavelength sample chamber (Figure 6). In this technique, the gas concentration measurement is based on the difference between the absorption of infrared radiation passing through two gas sampling cells. The reference cell is filled with a gas at a known concentration, and the sample cell is used for the determination of the unknown sample gas concentration. The gas concentration is measured electro-optically by its absorption of a specific wavelength in



**Figure 6.** Schematic diagram of Li-820 showing system components. (adapted from <https://www.licor.com/env/support/LI-820/topics/theory.html>)

the infrared range. When an infrared beam of a certain wavelength resonates with the molecular bond of a gas molecule, energy is absorbed by the molecule and then passes through a detection cell to the detection element. This loss of energy is converted to display the concentration of the gas by onboard electronics. These analyzers measure the gas concentration in a steady gas stream. Thus, to identify trace gases and measure their concentrations, it is required to pass the pollutant gases through an analyzer using a pump. The IRGA is capable of measuring the concentrations of NO, SO<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub> and O<sub>2</sub> components in sample gas. There are two basic types of infrared gas analyzers, such as dispersive and non-dispersive, that are widely used to measure trace gases. A grating or prism type optical device to spread the light spectrum over an area containing the wavelength of interest is used in a dispersive IRGA. On the other hand, discrete optical band-pass filters are used in a non-dispersive type IRGA, which is commonly known as a non-dispersive infrared (NDIR) system.

A model of an infrared gas analyzer (IRGA) is widely used in the field of agriculture, including, soil CO<sub>2</sub> flux, CO<sub>2</sub> sequestration, growth chambers, greenhouse control, etc.

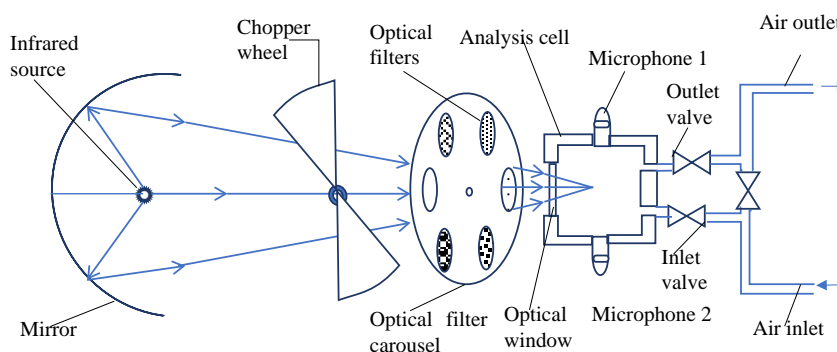
Patrick et al. (2007) used an infrared gas analyzer (IRGA) model Licor LI-820 (Biosensor, Lincoln, NE) to determine how leaf, soil, and ecosystem fluxes of CO<sub>2</sub> and H<sub>2</sub>O are affected by a few precipitation events, as well as how an increase in summer precipitation affects leaf, soil, and ecosystem CO<sub>2</sub> and H<sub>2</sub>O fluxes within a sotol grassland near Big Bend National Park. Borhan and Hao (2007) used the same IRGA (LI-820, Biosensor, Lincoln, NE) for measuring CO<sub>2</sub> concentration inside greenhouses with a measuring accuracy of 2.5% of the reading.

### 2.2.5. Photoacoustic Spectroscopy

With photoacoustic spectroscopy (PAS), the measurement principle is based on the photoacoustic infrared detection method that can measure accurately and reliably almost any gas that absorbs infrared light. The PAS has become a po-

werful technique to quantify concentrations of gases simultaneously at the parts per billion (ppb) level or even better. In the PAS technique, excited molecules of gases undergo a non-radiative (thermal) decay to the ground state in response to infrared light. A pressure modulation that can be picked up by microphones is produced by the generated temperature modulation. A measurement of the generated microphone signal as a function of the wavelength allows the identification of the absorbing molecules or atoms (Michaelian, 2010; Neftel et al., 2006). The general working principle of the PAS system (INNOVA 1412, AirTech Instruments A/S, Ballerup, Denmark) is shown in Figure 7. As the name implies, the PAS monitor can automatically measure multiple gases with a single instrument, hence the name multi-gas monitor. When gas samples are drawn from ambient air around the analyzer, the measurement time is  $\sim 30$  s for one gas or water vapor and  $\sim 120$  s if five gases plus water vapor are measured. The measurement time is configurable on the monitor. Increasing the length of the sampling tube increases the time required to pump in a new air sample and therefore increases the measurement time. The PAS requires less frequent calibration as compared with NO<sub>x</sub> analyzers. However, this measurement system is relatively expensive.

A most widely used PAS is a multi-gas INNOVA system (Models 1412 and 1312, Innova AirTech Instruments A/S, Ballerup, Denmark), which has been using to measure GHG emissions (NH<sub>3</sub>, CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O) from livestock production facilities, including swine and poultry (Leytem et al., 2011b; Leytem et al., 2011a; Sun et al., 2008; Osada et al., 1998). The gas selectivity with this system is achieved using five pre-selected optical filters arranged in a carousel to measure the concentration of up to 5 component gases and water vapor in any air sample. In a multi-gas PAS monitoring system, the target gases are irradiated by intermittent infrared light. The gas molecules absorb some of the light energy transmitted by the optical filter and convert it into an acoustic signal. Two microphones mounted in the cell wall measure this acoustic signal, which is directly proportional to the concentration of the monitored gas present in the cell. CO<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub>, and N<sub>2</sub>O concentrations were continuously measured in a mechanically ventilated swine barn using another brand of PAS (Multi-gas Monitor



**Figure 7.** Schematics of the INNOVA multigas PAS (adapted from the LumaSense Technology, INNOVA 1412, AirTech Instruments Product Datasheet).

Type 1302; Brüel & Kjaer Sound & Vibration Measurement A/S, Naerum, Denmark) at the inlet air, inside the barn, and in the exhaust ducts of each experimental barn (Osada et al., 1998; Costa & Gurino, 2009). The detection limits of CH<sub>4</sub>, N<sub>2</sub>O, NH<sub>3</sub>, and CO<sub>2</sub> for both PAS models were presented in Table 2 (listed a few commercially available trace-gas analyzers widely used in GHG concentration measurements).

### 2.2.6. Cavity Ring-Down Spectroscopy (CRDS)

The CRDS is a laser-based absorption spectroscopy technique that has been widely used to quantify the concentration of compounds in air samples that absorb light at specific wavelengths (Wheeler et al., 1998). Recently, the PICARRO brand greenhouse gas analyzer with the CRDS principle enabled gases to be monitored in seconds or less at ppb and ppt levels. This analyzer is rugged, easy to set up, facilitates months or years of calibration-free operation, and ensures the

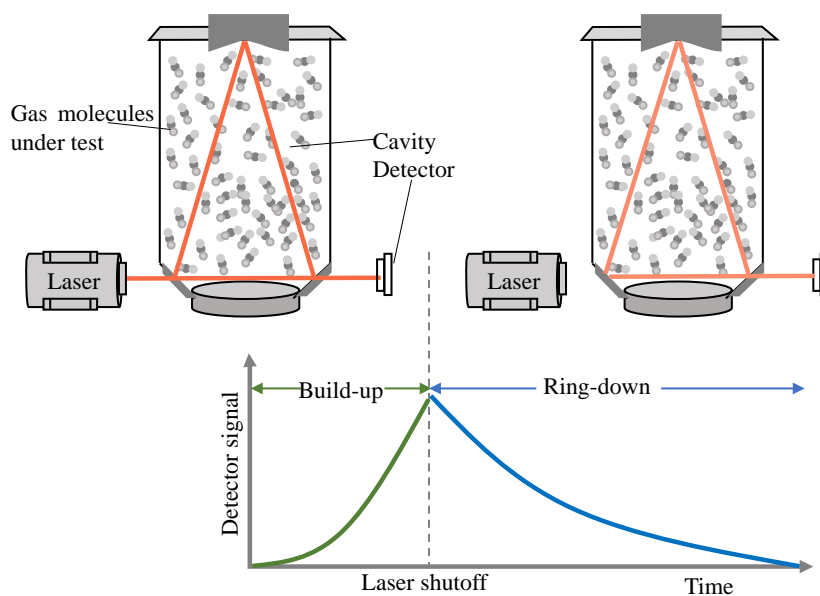
**Table 2.** Commercially available trace-gas analyzers widely used in the GHGs concentrations measurement from livestock operations.

Manufacturer	Model	Principle	Detection limit/Sensitivity (ppm or %)				Response time (s)	Remarks Measurement range (ppm)
			CO <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub> O	NH <sub>3</sub>		
Multigas monitor								
Brüel & Kjaer	Model 1302	PAS <sup>1</sup>	1.5 ppm	0.39 ppm	0.03 ppm	0.2 ppm	-	-
INNOVA <sup>2,5</sup>	1412/1312	PAS <sup>2</sup>	1.5 ppm	0.4ppm	0.03ppm	0.1 ppm	26 s	5 - 4000 ppm CO <sub>2</sub> 0.4 - 5000 ppm CH <sub>4</sub> 0.03 - 300 ppm N <sub>2</sub> O
PICARRO	G2301	CRDS	25 ppb	0.22 ppb	-	-	<3 s	0 - 1000 ppm CO <sub>2</sub> 0 - 20 ppm CH <sub>4</sub> 0% - 7%V H <sub>2</sub> O
Campbell Sci	TGA200A	TDLAS	0.3 ppm	7 ppb	1.5 ppb	-	-	-
Boreal laser Edmonton, Alberta, Canada	GasFinder 2 <sup>7</sup>	OP-TDLAS	-	0.3 - 0.6 ppm per 100 m	-	5.32 ppm per m	1 s	-
Boreal laser Edmonton, Alberta, Canada	GasFinder2 <sup>5</sup> Bomem MB100-2E	OP-FTIR	1.6 ppm per 100 m	4 ppb per 100 m	0.3 ppb per 100 m	0.4 ppb per 100 m	-	-
AirSentry FTIR 5 - 1000 m path	AirSentry FTIR <sup>6</sup>	OP-FTIR	43.7 ppb 300 m path	11.7 ppb 300 m path	6.3 ppb 300 m path	0.7 ppb 300 m path	Near real time	ppb to % level
MIDAC		OP-FTIR	<10%	<10%	<10%			
SRI	8610C	GC <sup>3</sup>	993 ppb	131ppb	21 ppb	-	-	5000 ppm CO <sub>2</sub> 1000 ppm CH <sub>4</sub> 50 ppm N <sub>2</sub> O
Agilent <sup>4</sup>	6280	GC <sup>4</sup>	-	0.01 ppm	0.005 ppm	-	-	-
Li-Cor	820	NDIR	<3%	-	-	-	-	0 - 20,000

<sup>1</sup>Osada et al. (1998); <sup>2</sup>Leytem et al. (2011b); <sup>3</sup>Borhan et al. (2011a); <sup>4</sup>Zhu et al. (2014); CRDS = Cavity Ring-Down Spectroscopy; <sup>5</sup>Leytem et al. (2013); <sup>6</sup>Bai et al. (2022); <sup>7</sup>Todd et al. (2010).

highest quality measurements. In CRDS, the beam from a single-frequency laser diode is directed to illuminate a high-finesse optical cavity/resonator, which is defined by two or more highly reflective (typically 99.9% reflectivity) concave mirrors positioned at both ends of a high-finesse measurement cavity with wavelengths within the range of interest (Wheeler et al., 1998). Picarro analyzers use a three-mirror cavity to support a continuous traveling light wave, as shown in Figure 8. Comparatively speaking, this offers a better signal-to-noise ratio than a two-mirror cavity that accommodates a standing wave. The cavity quickly fills with circulating laser light when the laser is turned on. One of the mirrors' small amount of light leakage is detected by a quick photodetector, which then generates a signal that is directly proportional to the cavity's intensity. The light intensity inside the cavity gradually leaks out and decays to zero in an exponential manner as it bounces between the mirrors (about 100,000 times), because the mirrors have slightly less than 100% reflectivity (99.99%). The laser is then turned off to make it possible to measure the light intensity that is escaping from the cavity exponentially.

The photodetector measures this decay, or “ring down,” in real-time, and the mirrors' reflectivity alone determines how long it takes for the ring down to occur (for an empty cavity). Light is bounced back and forth between the mirrors thousands of times during this decay, resulting in an effective path length on the order of tens of kilometers (Wheeler et al., 1998). If a gas that absorbs light is placed in the cavity, the amount of light decreases faster. A CRDS measures how long it takes for the light to decay to  $1/e$  of its initial intensity, and calculating the concentration of the absorbing substance in the gas mixture in the cavity can be done using this “ring-down time.” Advantages of CRDS include high sensitivity due to the multi-pass nature of the detection, immunity to shot-to-shot



**Figure 8.** Schematic of Picarro CRDS analyzer showing how a ring down measurement is carried out (adapted from the Picarro CRDS Product Datasheet, 2022).



variations in the laser intensity, and high throughput (Stelmaszczyk et al., 2009; Wheeler et al., 1998).

The primary advantage that CRDS has over PAS methods is that the absorption of photons by the analyte is detected directly. Disadvantages include the following: the spectra cannot be acquired quickly due to the monochromatic laser source, analytes are limited both by the availability of tunable laser light at the appropriate wavelength and also the availability of high reflectance mirrors at those wavelengths, and it is more expensive than some alternative spectroscopic techniques as a consequence of the laser systems and high reflectivity mirrors required (Stelmaszczyk et al., 2009).

The spectroscopic techniques discussed so far are referred to as “non-destructive infrared” (NDIR), in which the tested air sample or airstream does not suffer any physical damage and is better suited to real-time analysis without distracting the active operation. The NDIR is a gas concentration measurement method that uses the unique absorption wavelength range of each gas. In contrast, separation, or gas chromatography (GC), is referred to as a destructive technique because, in this device, samples are destroyed after analysis is done. However, GC is considered a highly accurate and precise method for measuring GHGs compared with other methods and is used as a reference method for comparing measurements made with non-destructive optical sensors or devices. The following sub-sections describe and discuss gas measurement with chromatographic technologies.

### 3. Separation Techniques

A popular method of chromatography used in analytical chemistry for separating and analyzing substances that can be vaporized without decomposing is gas chromatography (GC). Most prominent separation techniques are gas chromatography and mass spectrometry. These techniques have the major disadvantage that the chemical composition of the gas sample changes during the course of the analysis (Nefel et al., 2006). However, GC is recognized to be a highly accurate and precise method for measuring GHGs compared with other methods.

#### 3.1. Gas Chromatographs (GC)

Chromatography is a separation technique that divides the components in a mixture using variations in the partitioning behavior between a flowing mobile phase and a stationary phase. A gas chromatograph typically includes a stationary phase, a detector, an injection port, a separation column, a flowing mobile phase, and a data recording system. Mobile phase, or “moving phase,” is a carrier gas (inert gas such as helium and nitrogen) that guides injected compounds along the stationary phase. A column is a tube made of glass or metal that contains a thin layer of liquid or polymer on an inert solid support. Generally, GHGs are measured using a GC system equipped with flame ionization (FID), thermal conductivity (TCD), and electron capture detectors (ECD). In all detec-

tors, GHGs are quantified by comparing the area under the response curves (peak height versus retention time) of a sample to known concentration standards. However, co-elution of two or more compounds is a concern for GC-related erroneous identification. This is a relatively sensitive piece of equipment that was originally only intended for use in laboratories. With the rapid advancement of computer technology, relatively low-cost and portable GCs are available for both laboratory and field uses. Generally, with the GC systems, detection limits are around 50 ppb, 50 ppm, and 30 ppb for CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O, respectively. In addition, the maximum concentrations that can be measured are around 100 ppm for N<sub>2</sub>O and over 5000 ppm for CH<sub>4</sub> and CO<sub>2</sub>.

### 3.2. Gas Chromatographs and Mass Spectroscopy (GC-MS)

Mass spectrometry (MS) is involved with the separation of matter according to atomic and molecular mass. It is most often used in the analysis of organic compounds of molecular mass up to as high as 200,000 Da. The MS was mainly restricted to relatively large volatile compounds until recent years. The GC-MS is an analytical method and consists of GC and MS units that basically combine the features of both gas-liquid chromatography and mass spectrometry to identify different compounds within a sample under testing. This is a relatively sensitive piece of equipment that was originally limited to laboratory settings. Continuous development and improvement of instrumentation and techniques have made mass spectrometry one of the most versatile, sensitive, and widely used analytical methods available today. A single instrument, either GC or MS, alone cannot make an accurate identification of a particular molecule (compound). Co-elution of two or more compounds is a source of erroneous identification in GC. On the other hand, a similar pattern of ionized fragments between two different molecules in a mass spectrometer is a similar concern. Using GC-MS, accurate identification of the compound can be achieved. For analyzing volatile organic compounds (VOCs) or compounds with very low concentration, they can be analyzed with both the GC and GC-MS systems by attaching a concentrator commonly known as Purge and Trap (P&T). The trap is a column of adsorbent material that holds the compounds at ambient temperature. Test air can be drawn into the P&T assembly downstream of the injection port for a specified time period. The trap is then baked, and the sample compounds are injected or introduced to the column of GC or GC-MS.

Before using the GC for analysis, optimize the operational conditions and parameters with a GC and a GCMS, and allow enough time for temperature stabilization. These include setting up carrier gas flow, detector sample and reference cell flow rates, and column and detector temperatures according to the manufacturer's specifications to provide good resolution and a minimum analysis time. Also, test the performance of the GC before sample analysis by verifying the detector linearity over the range of suspected sample concentrations with at least three points per analyte of interest. With GC, standard curves (calibration

equations) are generally developed from 3 to 5 four known concentration levels of each standard, with five to seven replicates at each concentration. Then, regressions between the sensor's responses (peak areas for GC, absorption or reflectance for NDIR sensors, etc.) and different concentration levels of each compound through the origin are used to interpolate the total concentration of compounds found in real world (laboratory and field) samples. The selection of the concentration range should bracket the expected average sample concentration under investigation. In general, it is recommended to perform the calibration check before and after each day's sample analyses using the procedures delineated in Method EPA 18. The quality of the standards and the standard curve is dependent on the care taken in their preparation and analysis. Checks should be used for all analyses to ensure that laboratory techniques and procedures are working properly. According to USEPA guidelines, Method Detection Limits (MDLs) were determined (USEPA, 1995). In the analysis of a given sample in a given matrix containing an analyte, the minimum detection limit (MDL) refers to the concentration of the analyte that can be measured and reported with 99.99% confidence that the concentration exceeds zero. MDL is a measure of how well a measurement can be repeated in analysis. The MDL is calculated as the product of the standard deviation of seven replicates and the Student's *t* value at the 99% confidence level. For seven replicates (6 degrees of freedom), a *t* value of 3.14 was used. MDLs as shown in the following Equation (2):

$$\text{MDL} = \text{Student's } t \text{ value} \times \text{Standard Deviation} \quad (2)$$

It is crucial to choose the right sampling techniques and protocols to create enough air volumes from a variety of sources in livestock production facilities to enable and prepare for emission analysis. The sections that follow describe and discuss various strategies for producing accurate and reliable GHG emission data.

## 4. GHG Measurement Protocol

### 4.1. Measurement System Preparation

Similar to GC, other sensing systems (sensors and analyzers) such as NDIR, UV, Chemiluminescence, and FTIR for measuring gaseous compounds should be assembled, and the whole monitoring system should be set up by following the manufacturer's written instructions. In addition, sampling equipment used to draw air samples from the source to the sensors, including plumbing, multiplexers (multiple sources for one sensor), flux generators, real-time data logging, etc., coupled with a particular measuring protocol, should be prepared, and pre-conditioned before starting a real measurement. **Table 2** listed a few commercially available trace-gas analyzers that are commonly used in measuring GHG concentrations from livestock operations.

### 4.2. Performance of the Sensors in the Laboratory

The calibration and measurement stability of a gas analyzer is another important

consideration for making reliable field measurements. Therefore, the performance assessment of detectors and sensors itself is a critical step and prerequisite to generating valid data using a continuous gas monitoring (CGM) system. However, the quality control (QC) and quality assurance (QA) requirements mainly depend on the operating period, analyte or compound types, and condition of the environment under investigation. Among the QC/QA protocol, zero and span checks (weekly or even daily), quarterly performance audits, and annual zero alignment checks are strongly recommended in order to assure the proper functioning of the CGM system and the accuracy of the CGM data generated. Multipoint (3 - 5) calibration, repeating three times at each concentration level for any particular gas and analyzers, is strongly recommended (Borhan et al., 2011b). An accurate gas mixer or a dynamic dilution system can be employed to create serial dilutions or multiple cylinders with different concentrations of calibration gases that can feed the analyzer with a series of concentrations to facilitate multipoint calibration. The performance of the analytical systems, such as method detection limit, accuracy, percent gas recovery, and precision, can be determined from those following an appropriate method.

When measuring in the linear range with an acceptable error of 5%, single-point span calibration should be used. The recommended span gas concentration should be at least 100 times its detection limit, and preferably not more than the highest concentration you expect to measure (INNOVA 1412i). On the other hand, two or multiple-point calibration is recommended when measurement is targeted in the non-linear range, especially when measurement is targeted over a certain dynamic range. The analyzer calibration error check is conducted by introducing calibration gases (single or multipoint, such as zero, midrange, and high range) to the measurement system at any point upstream. The analyzer calibration error check shall be considered invalid if the gas concentration displayed by the analyzer exceeds  $\pm 2\%$  of the span for any of the calibration gases. In the sampling, the system bias can be determined by introducing a known concentration of gas at the calibration valve installed at the outlet of the sampling probe and recording the gas concentration displayed by the analyzer. Then introduce zero gas and record the gas concentration displayed by the analyzer. The analyzer sampling bias error check shall be considered invalid if the gas concentration displayed by the analyzer exceeds  $\pm 5\%$  of the span for any of the calibration gases. During the sampling system bias check, operate the system at the normal sampling rate, and make no adjustments to the measurement system other than those necessary to achieve proper calibration gas flow rates at the analyzer.

### **4.3. Calibration and SPAN Check Frequency in the Field**

Stable responses of the sensing devices with respect to target minimum and maximum concentration values are extremely critical in a gas sensing process. Therefore, the performance of the sensors should be checked at a regular inter-

val. This interval can be a set amount of time, a set number of samples, or both, based on which a known concentration of the sample is run (known as a calibration gas check or span gas check). In real-time sensing, sensors are generally calibrated after a certain time period by plumbing a calibration gas to the sensor inlet when the sample line is kept offline using the distribution control mentioned before. In a discrete sampling, sample containers (cylinders, canisters, tedlar bags, etc.) were randomized prior to analysis. A mean of three measurements from the same sample, or at least duplicate measurements, were made to ensure the sensor's consistent response. A control check standard is introduced in the sampling train and analyzed every 10 - 15 samples. The values measured were within 10% of expected values. When using multiple analyzers, calibration gases can be routed through this manifold to the sample probe through a Teflon line. This makes it conceivable to include every element of the sampling system in calibration and bias checks. The distribution manifold should have the capability to route calibration gases directly to the analyzers to facilitate linearity checks. In the field, all equipment used according to a measurement protocol, including sampling pumps, plumbing, and analytical instruments, is required to be inspected regularly during a field visit (generally twice a week, possibly daily) by the person responsible for the project. The widely practiced frequency for maintenance checks on sensors and sensing systems was twice a week. Standard routine calibration checks are performed twice a week by introducing a particular span gas into the analyzer inlet with a concentration equal to 80% of the expected levels of the environment under investigation.

#### 4.4. Gas/Air Sampling Unit

Gaseous emissions from ground surface sources (open lots, water surfaces, etc.) and exhaust ports (barns and covered waste management structures) must be conditioned (removing water vapor) prior to introduction into the sensors and analyzers to ensure proper and reliable measurement. An air sample is pulled out of the ground and exhaust ducts through a sample line and stainless-steel probe, respectively, and then transported to a gas conditioning system using a sample pump. The clean, dry sample is then transported to a flow distribution manifold or to multiple-way solenoid valves, where the flow of the sample to each analyzer (when multiple analyzers are used to quantify multiple gases) is controlled.

**Table 3** presents summaries of the EPA Federal Reference Methods from Title 40 CFR 60. These reference methods are well documented in the Code of Federal Regulations (CFRs) and are used to determine pollutant levels from a wide variety of sources. They include procedures for selecting measurement system performance specifications and test procedures, quality control procedures, and emission calculations.

The gas analyzer that will be used in each of the chosen methods that use an instrumental measurement technique has performance-based requirements. These

**Table 3.** Summary of emission USEPA ambient air monitoring methods.

Air Pollutant	Reference Method	Principle of Detection	Proposed Analytical Range
CH <sub>4</sub>	EPA 18	GC/FID	0 to 25 ppm
	EPA 3C	GC/TCD	0 to 10 ppm
CO	EPA 10	NDIR-Gas Filter Correlation	0 to 25 ppm
CO <sub>2</sub>	EPA 3A	NDIR	0% to 10%
NO <sub>x</sub>	EPA 20	Chemiluminescence	0 to 25 ppm

performance standards include requirements for calibration drift as well as span, calibration error, sampling system bias, zero drift, response time, and interference response. Each test method planned for use is discussed in more detail in the following subsections and can be consulted when required. The analytical ranges specified in **Table 2** may be modified during testing if the proposed ranges are found to be inadequate.

## 5. Uncertainty Analysis

To develop overall or source-specific abatement strategies with a view to reducing GHG emissions, it is important to learn to collect, analyze, verify, and report genuine data on actual emissions. Therefore, the validation of emission inventories using scientifically convincing emission measurement protocols is extremely important, as are source-related emission estimates and the measurement uncertainty that are feeding emission inventories. Uncertainties in accurate emission rate estimation using both device-dependent and device-independent (microclimatological) methods are generally dependent on sampling protocol errors (air drawing pump and flux generation devices, mass flow meter, and climatological variables (air temperature and humidity, wind speed and direction, solar radiation, and barometric pressure), as well as gas analyzers.

### Taylor Series Uncertainty Analysis

Uncertainty in emission rate measurements can be estimated using the standard “National Institute of Standards and Technology” (NIST) method, also known as the first order Taylor series technique of uncertainty estimation, which indicates the maximum uncertainty expected using a particular set of primary measurements. For example, this analysis can be performed to determine potential errors in the primary measurements discussed above by inserting them into the Taylor series equations. In addition, this analysis can identify which measurement errors contribute the most to emission rates. The total systematic uncertainty in measuring GHG emission rates using the NIST method (Taylor & Kuyatt, 1994) can be calculated using representative measures of uncertainty in each primary measurement. In brief, this method states that when a measured variable,  $Y$ , cannot be measured directly, it is determined by a number of inde-

pendent variable,  $x_1, x_2, x_3, \dots, x_N$ , through a functional relation,  $f$  (Equation (3)):

$$Y = f(x_1, x_2, x_3, \dots, x_N) \quad (3)$$

Each independent variable,  $x_i$ , has an associated uncertainty,  $\omega_i$  where  $i$  ranges between 1 and  $N$  variables. The variable  $\omega_Y$  represents the systematic uncertainty of  $Y$  resulting from the propagation of uncertainties in each independent variable and is calculated as the positive square root of the estimated variance,  $\omega_Y^2$  (Equation (4)):

$$\omega_Y = +\sqrt{\omega_Y^2} \quad (4)$$

where the variance,  $\omega_Y^2$ , is calculated with Equation (5):

$$\omega_Y^2 = (\theta_1 \omega_1)^2 + (\theta_2 \omega_2)^2 + \dots + (\theta_N \omega_N)^2 \quad (5)$$

The sensitivity coefficient,  $\theta_i$ , is the ratio of the change of the result per unit change of a single input parameter (Equation (6)):

$$\theta_i = \frac{\partial Y}{\partial x_i} \quad (6)$$

The contribution of uncertainty from each primary measurement to the overall uncertainty of the result is calculated by dividing the absolute systematic contribution of a single measurement,  $U_i$  by the total absolute systematic uncertainty (Equation (7)):

$$\% \text{ Contribution} = \frac{U_i}{\sum_{i=1}^N U_i} * 100\% \quad (7)$$

where the absolute systematic uncertainty contribution,  $U_i$  of a primary measurement is determined according to Equation (8):

$$U_i = \left( \frac{\omega_i}{2} * \theta_i \right)^2 \quad (8)$$

## 6. Greenhouse Gas Measurement Approaches/Methods

The GHG emission estimation from different ground level sources (GLAS) of manure management in livestock operations such as lagoons (primary and secondary), barns, settling basins, carrols, silage piles, loafing pens, feedlot pens, compost windrows, and crop and pasture land is a very complicated process. Generally, two basic processes, such as device independence and using a sampling device, are widely used to estimate emission from emitting surfaces. There are broadly three main methods, such as device independence, sampling devices, and biochemical reactions, commonly used to quantify gaseous emissions from ground-level sources in livestock production facilities. The device-independent methods commonly referred to as the micrometeorological techniques include atmospheric dispersion modeling such as inverse dispersion and backward Lagrangian stochastic models, flux gradient, boundary layer budgeting, eddy covariance, and relaxed eddy accumulation. These techniques involve a combination

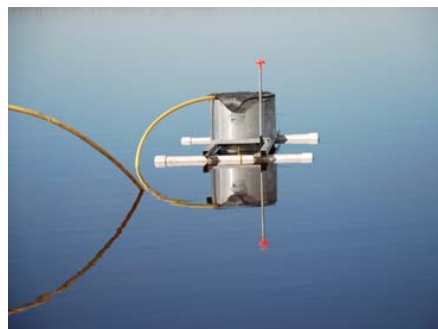


of atmospheric turbulence theory, especially the wind velocity profile (the vertical and horizontal speed of the wind), coupled with local micrometrical data, which also calls for the gas concentrations measured across the plume of the emitted surfaces to estimate the gas emission rate from a surface (McGinn & Beauchemin, 2012; McGinn et al., 2006, 2008; Christensen et al., 1996; Hudson & Ayoko, 2008). Among the biochemical methods, IPCC tiers I and II algorithms, Blaxter and Clapperton algorithms, and mathematical models based on the assumptions of biochemical reactions driven by animal size, feed intake, and feed quality in confined conditions are also being used (Loh et al., 2008; Van Haarlem et al., 2008). When using a sampling device, a chamber or wind tunnel is deployed on an emitting surface under some recommended operating conditions (Figure 9). The devices may be static devices (sealed or vented) or dynamic devices that purged with zero grade air (containment free) at a constant velocity or flow rate. In general, emission rates are estimated as the product of concentration and air flow through the device, and are influenced by climate, animal size and type, device footprint area, and the area and number of animals in the farm (Kienbusch, 1986; Eklund et al., 1985; Gholson et al., 1989; Hudson & Ayoko, 2008; Borhan et al., 2011a). Emission rate estimation is expressed with the following equations:

To be consistent with the reporting of emission rates of different air pollutants by the USEPA, 1995 measured concentration values are generally standardized



(A)



(B)



(C)

**Figure 9.** Photographs showing sampling devices in operation. (A) Flux chamber at feedlot pen (ground surface); (B) Flux chamber at retention pond surface of a feedlot; (C) Flux chamber at compost pile in feedlot.

at 1 atmosphere and 25°C. The equation (9) can be used to convert volumetric concentration (ppm) to mass concentration ( $\mu\text{g}\cdot\text{m}^{-3}$ ) at standard temperature and pressure. Generally, the volumetric concentrations were expressed in parts per billion (ppb) ( $\text{ppb} = 1000 \times C_{\text{ppm}}$ ) and mass concentration in microgram per cubic meter ( $\mu\text{g}\cdot\text{m}^{-3}$ ) as follows:

$$C_{\text{mass}} = \frac{1000 \times (C_{\text{ppm}}) \times MW_p}{24.45} \quad (9)$$

where  $C_{\text{mass}}$  is the concentration of a compound on a mass basis ( $\mu\text{g}\cdot\text{m}^{-3}$ ),  $C_{\text{ppm}}$  is the volumetric concentration of compound (ppm); an ideal gas' volume per mole at standard temperature and pressure is  $24.45 \text{ L}\cdot\text{gmol}^{-1}$ ; and the molecular weight of a compound at standard pressure and temperature is  $MW_p$  ( $\text{g}\cdot\text{mol}^{-1}$ ). To estimate flux measurement from the ground level area sources, an enclosure method where a small area is enclosed by devices (flux chambers or wind tunnels). Sweep air is introduced at a fixed rate and concentration of target compound is measured at an exit point of the devices by an appropriate analyzer. Equation (10) can be used to calculate emission flux ( $EFlux$ ).

$$EFlux = \frac{C_{\text{mass}} \times V_{fc-wt}}{A_{fc}} \quad (10)$$

where  $EFlux$  is the gas emission flux ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{min}^{-1}$ ),  $V_{fc-wt}$  is the flow rate of air supplied to the flux generating devices ( $\text{m}^3 \text{ min}^{-1}$ ),  $A_{fc-wt}$  is the footprint area enclosed in a source ( $\text{m}^2$ ). Finally, emission rates ( $ERs$ ) using flux chamber and wind tunnel can be estimated as follows (Equation (11)):

$$ER = \frac{EFlux \times 1.44}{TNA} \times A_{sc} \quad (11)$$

where  $ER$  is the emission rate ( $\text{g}\cdot\text{hd}^{-1}\cdot\text{d}^{-1}$ ),  $A_{sc}$  is the area of source (GLAS,  $\text{m}^2$ ), and  $TNA$  is the total number of animals.

Again, ground-level area source methods can be divided into source-integrated and source-specific methods. In the source integrated method, pollutant gas concentrations are measured downwind of the sources of a facility and require reverse air dispersion modeling to determine the emission rates of pollutants from the same sources. Thus, the source-integrated method includes emissions from multiple sources (pens, lagoons/retention ponds, compost piles, feed mills, etc.) combined at a given facility. Emissions from specific sources cannot be differentiated in the source integrated measurement. On the other hand, source specific methods measure pollutants' gas concentrations directly at the source by dividing the source into a discrete grid. In the sampling device methods, flux chambers and wind tunnels are deployed on the emitting surfaces under some recommended operating conditions. Two types of flux chambers, e.g., static (sealed or vented) or dynamic (flushed with zero-grade air at a known flow rate) were widely used. The wind tunnels, flux chambers, mass balance, and tracer ratio techniques are widely used source specific emissions measurement techniques, which also fall under non-micrometeorological methods. Few random

grid samplings (8 - 10 samplings) may not accurately represent emission rates from a complex, spatially and temporally heterogeneous source. Concentration measurements of the target gas(es) in the environment under study are required by all emission estimation protocols (device independent and device dependent).

## 7. Issues with Flux Measurement Using Flux Chamber at the Ground Level of the Livestock Facilities

Several difficulties and issues are associated with the use of static and dynamic chambers, but the wind tunnel does not appear to be subject to these problems (Hudson & Ayoko, 2008). There is a slight disturbance of the soil surface in the flux chamber which isolates the emitting surface from external meteorological conditions. Furthermore, the chamber temperature may increase due to solar radiation trapping (Figure 7). Wind speed, ground level surface areas (GLAS), surface temperature and moisture, air temperature and humidity, and a gas leak under the chamber base can all affect emission fluxes from the emission sources (Kienbusch, 1986; Borhan et al., 2011a). During the summer, gas sealing around the flux chamber base on the dry surfaces can be accomplished by compacting manure around it. When sampling over liquid surfaces, the base of the chamber needs to be submerged 2.5 cm below the liquid surface.

A similar insertion depth of 1.5 to 2.5 cm could also be maintained at the loafing pen and walk-way during the winter when the GLAS surface is wet, soft, or semisolid. To minimize soil disturbance, the flux chamber should be placed gently on the source surfaces (Borhan et al., 2011b). Maintaining a sweep air flow rate of  $0.005 \text{ m}^3 \cdot \text{min}^{-1}$  alleviates some of the issues associated with the creation of a microenvironment by avoiding the negative bias associated with stagnant air or insufficient airflow in the chamber (Kienbusch, 1986; Eklund, 1992). Furthermore, steady state conditions in the flux chamber may be established after three to four volumetric exchanges of air in the chamber, at which point air sampling from the chamber can be initiated (Gholson et al., 1989).

On a hot and sunny day, condensation inside the chamber may occur due to high ambient temperatures that enhance evaporation from the foot-print area of the chamber. This moisture accumulation might affect the emission flux of the measured compounds within the flux chamber. Moisture in each air sample may be removed during sampling by a Nafion<sup>®</sup> dryer placed immediately before the sampling pump or analyzer (Borhan et al., 2011b). There is debate about the suitability and accuracy of quantifying pollutant emissions at CLOs and other area sources due to the creation of microenvironments in the chamber and the small measurement footprint relative to the size of the source (Hudson & Ayoka, 2008; Hudson et al., 2009; Zhang et al., 2002; Lindberg et al., 2002). Hudson et al. (2009) compared and reported that odor emissions from a wind tunnel were 60 - 240 times higher than those in a flux chamber (Kienbusch, 1986). Parker et al. (2010, 2013) also demonstrated that water evaporation, wind speed, and temperature would be useful to standardize and compare emission rates from flux

chambers and wind tunnels. They also suggested developing correction factors for each device that depend on the geometry of the wind tunnel and chamber.

## 8. Factors to Be Considered in Selecting Sensors

A properly designed sampling protocol, including the selection of an appropriate air sampler and sensors or analyzers, might make difficult or impossible applications possible to achieve trouble-free operation and reliable data output. The main parameters to consider before selecting a sensor are the types of gases to be measured, the environment in which it will be deployed, expected accuracy levels, data resolution, output and display, portability and compactness, ease of operation and installation, and cost. Each must meet certain criteria to be practical for use in area air quality and safety applications. Commonly, in deciding the type of sensor to be used for a particular application, the following aspects should be considered:

- Begin by researching the problems, defining an objective to be accomplished, listing the expected range of gaseous concentrations to be measured, including the maximum and minimum concentrations, and then comparing the results with instrument specifications that meet the requirements.
- Analyze a sample of air or conduct research to identify background information on gaseous compounds in a target monitoring area that may interfere with the gas under consideration or damage the circuitry and optics of a sensor. They should be certified for safe use in industrially hazardous environments. A major cause of sensor failure is the presence of background gases that the instrument's manufacturers did not take into consideration. In many cases, sensor failure is caused by background gases that were overlooked by the manufacturers of the instrument.
- The sensor should be compact, robust, and portable, with a small, rugged housing that allows it to be easily carried and installed. When deployed in remote areas without power supply, the sensor should be able to operate in both AC (dual voltage, e.g., 120- and 220-volt AC) and DC power with low power consumption.
- The air temperature and humidity ranges in the target environment where the sensor is to be installed should be within the sensor's specifications and suitable for the gases to be monitored. Alternately, those sensors could be housed in an environment-controlled mobile trailer and driven to sampling areas.
- The operation and maintenance of the instruments should be simple enough that an ordinary plant manager with little or no technical knowledge in instrumentation can perform the task with minimal training.
- The sensor should be operable in both stand-alone and computer-aided operation (online monitoring), with an analog output module to log output data externally using a suitable data logger. Additionally, it can be installed in a multi-point system and accomplished by a controller or a computer-controlled

sequencing system.

- In comparison to others, the cost of the instruments and their spare parts should be relatively low. The users also should consider the after-sales service, including technical support from the manufacturer.

## 9. Conclusion

To develop appropriate mitigation strategies for reducing GHG emissions, it is important to learn to collect, analyze, verify, and report real data on actual emissions. Methods and sensors for measuring these emissions from various livestock production systems are currently being developed. However, a solid measurement protocol, starting with selecting sensors for the specific job to be performed, and subsequent protocol, including flux or emission generation, sample conditioning, and conveyance from the source to the detector or sensors, are prerequisites for generating valid data. This article summarizes the spectral characteristics of greenhouse gases and sensing techniques, along with their performance in the laboratory and field, measurement methods including device installation, emission generation, and calibration methods that will guide farmers, students, researchers, engineers, and technicians involved in greenhouse gas measurement.

## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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