



Wondimagegne Bekele<sup>1,2</sup>, Abdulai Guinguina<sup>1</sup>, Abiy Zegeye<sup>2</sup>, Addis Simachew<sup>2</sup> and Mohammad Ramin<sup>1,\*</sup>

- <sup>1</sup> Department of Agricultural Research for Northern Sweden, Swedish University of Agricultural Sciences, 901 83 Umeå, Sweden; wondimagegne.bekele@slu.se (W.B.); abdulai.guinguina@slu.se (A.G.)
- <sup>2</sup> Institute of Biotechnology, Addis Ababa University, Addis Ababa P.O. Box 1176, Ethiopia;

abiyze@yahoo.com (A.Z.); addissimachew@gmail.com (A.S.)

\* Correspondence: mohammad.ramin@slu.se; Tel.: +46-(0)72-210 8373

**Simple Summary:** Greenhouse gases (GHG) are the major responsible drivers for global warming and climate change. Methane (CH<sub>4</sub>) is deemed the second most important GHG emitted from anthropogenic sources in terms of global warming potential (GWP) and quantity. Ruminants contribute to approximately one-fourth of all agricultural anthropogenic sources of CH<sub>4</sub> emissions. As such, ample time and resources were committed to developing strategies to reduce CH<sub>4</sub> emission from ruminants and its negative impacts on the environment. This has led to the development of several techniques for measuring and estimating CH<sub>4</sub> emissions from ruminants. This review summarizes state-of-the-art and futuristic technologies for measuring and estimating CH<sub>4</sub> emissions from ruminants, and their strengths and limitations, for easy understanding.

Abstract: This review aims to elucidate the contemporary methods of measuring and estimating methane (CH<sub>4</sub>) emissions from ruminants. Six categories of methods for measuring and estimating CH<sub>4</sub> emissions from ruminants are discussed. The widely used methods in most CH<sub>4</sub> abatement experiments comprise the gold standard respiration chamber, in vitro incubation, and the sulfur hexafluoride ( $SF_6$ ) techniques. In the spot sampling methods, the paper discusses the sniffer method, the GreenFeed system, the face mask method, and the portable accumulation chamber. The spot sampling relies on the measurement of short-term breath data adequately on spot. The mathematical modeling methods focus on predicting CH<sub>4</sub> emissions from ruminants without undertaking extensive and costly experiments. For instance, the Intergovernmental Panel on Climate Change (IPCC) provides default values for regional emission factors and other parameters using three levels of estimation (Tier 1, 2 and 3 levels), with Tier 1 and Tier 3 being the simplest and most complex methods, respectively. The laser technologies include the open-path laser technique and the laser CH<sub>4</sub> detector. They use the laser CH<sub>4</sub> detector and wireless sensor networks to measure CH<sub>4</sub> flux. The micrometeorological methods rely on measurements of meteorological data in line with CH<sub>4</sub> concentration. The last category of methods for measuring and estimating CH<sub>4</sub> emissions in this paper is the emerging technologies. They include the blood CH<sub>4</sub> concentration tracer, infrared thermography, intraruminal telemetry, the eddy covariance (EC) technique, carbon dioxide as a tracer gas, and polytunnel. The emerging technologies are essential for the future development of effective quantification of CH<sub>4</sub> emissions from ruminants. In general, adequate knowledge of CH<sub>4</sub> emission measurement methods is important for planning, implementing, interpreting, and comparing experimental results.

Keywords: ruminant; emission; measurement; enteric methane

## 1. Introduction

The Environmental Protection Agency [1] defines greenhouse gases (GHG) as gases that trap heat in the atmosphere. Greenhouse gases, such as carbon dioxide (CO<sub>2</sub>), methane



Citation: Bekele, W.; Guinguina, A.; Zegeye, A.; Simachew, A.; Ramin, M. Contemporary Methods of Measuring and Estimating Methane Emission from Ruminants. *Methane* 2022, *1*, 82–95. https://doi.org/ 10.3390/methane1020008

Academic Editor: Secundino López

Received: 21 January 2022 Accepted: 7 April 2022 Published: 11 April 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). (CH<sub>4</sub>), water vapor, and nitrous oxide (N<sub>2</sub>O), while others that are synthetic, including chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs) and per-fluorocarbons (PFCs), as well as sulfur hexafluoride (SF<sub>6</sub>), are found in the atmosphere [2]. The main GHGs are CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O [3,4]. Greenhouse gases are major contributors to climate change [5]. According to Rosenstock et al., [6], agricultural systems are a major source of atmospheric GHG emissions, accounting for roughly 30% of total anthropogenic emissions, including indirect emissions associated with land-cover change [7]. Animal agriculture is a major producer of GHGs, equivalent to 14.5% of global emissions, which is approximately the same size as the transportation sector [8,9]. The enteric fermentation process contributes >90% of CH<sub>4</sub> emissions from livestock [10] and contributes 40% to the agricultural GHG emissions [11], which is the major source of GHG emissions from the agricultural sector [12]. Recent figures show that actually, the contribution of enteric fermentation and manure management is below 10% of the total contribution of the agriculture sector (which is around 15%). The remaining 5% relates to the contribution of rice cultivation, manure applied to soils and synthetic fertilizers.

Methane is the second most important anthropogenic GHG in terms of global warming potential (GWP) and quantity [13,14] and is responsible for 20% of the global warming caused by anthropogenic GHG emissions [15]. The global annual CH<sub>4</sub> emission from ruminant livestock is estimated to be between 80 and 95 million tons [16–18]. CH<sub>4</sub> production is also a loss of energy availability to the host ruminant animal, normally representing between 2% and 12% of the total gross energy intake, depending on the level of intake and diet composition [19–21].

There is immense interest to develop an accurate ruminant  $CH_4$  emission of accounting to reduce the negative effects of GHGs on the environment and to evaluate mitigation strategies [22–25]. Several methods have been developed to measure  $CH_4$  emissions from ruminants [26,27]. All methods have different scopes of applications, advantages, and disadvantages, and none of them is perfect in all aspects [26,28]. The measurement methods depend on aim, equipment, knowledge, time, and money available to facilitate researchers and producers to construct and monitor valid  $CH_4$  mitigation strategies [28]. Knowing the advantages and disadvantages of each method will ease the interpretation of experimental results [29]. Therefore, the objective of this review is to present the contemporary methods of measuring and estimating  $CH_4$  emission from ruminants, as well as emphasize their advantages and disadvantages.

#### 2. Widely Used Methods

#### 2.1. Respiration Chambers (Direct Measurements)

Respiration chambers (RC) have been used for studying the energy metabolism of animals and CH<sub>4</sub> energy losses of ruminants for more than 100 years [28,30,31]. The principle of the RC technique relies on measuring CH<sub>4</sub> concentrations released from enteric fermentation (nasal and rectum) in gas samples and the total volume of air removed from the RC [4,28,32,33]. The chamber method uses only a few animals for continuous monitoring, usually over a course of 24 h periods, for 3–7 days [26,31]. Changes in O<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> contents are calculated from the gas flow, and changes in gas concentrations between the air inlet and outlet are measured using gas analyzers, infrared (IR) photoacoustic monitors, or gas chromatography systems [24,34]. Respiration chambers provide an accurate reference method used for research purposes [26].

There are two types of RC: closed-circuit and open-circuit [35]. While the closed-circuit systems are these days almost never used, the open-circuit chambers are currently the most commonly used, with varying degrees of complexity [31,32]. Gas recovery is an essential routine maintenance task while performing RC experiments. Thresholds for the chamber temperature, relative humidity, CO<sub>2</sub> concentration, and ventilation rate are <27 °C, <90%, <0.5%, and 250–260 L/min, respectively [24].

Chambers need to be routinely calibrated and demonstrate gas recovery rates of close to 100%, both before and after each experimental deployment [36,37]. However, in practice,

it is estimated that the average recovery value is 98.1% [5]. Respiration chambers have low animal-to-animal variations and good refinement in CH<sub>4</sub> measurements. They are suitable for studying the differences between treatments for mitigation strategies and are still regarded as the "gold standard" method for measuring individual animal CH<sub>4</sub> emissions [24,33,37]. However, RC use is technically demanding, and only a few animals can be monitored at the same time [38]. The chamber method has both high investment and labor costs [26]. Animals' behavior is supposed to be affected by the artificial environment created by the method, and it is not suitable for free-ranging animals [28]. Nevertheless, RCs are the most appropriate for providing continuous and accurate data on air composition over an extended period of time [24].

#### 2.2. In Vitro Incubation (Indirect Measurements)

The basic principle of the in vitro technique is incubating feed under gas-tight culture bottles involving natural rumen microbes under an anaerobic environment [24,28]. The gas measuring technique has been widely used for evaluating the nutritive value of feeds and simulating ruminal fermentation of feed and feedstuffs [32,39]. In this technique, feedstuffs are incubated for a specific time frame (2, 4, 8, 24, 48, 72, 96 and/or 144 h) with a mixture of reducing solution, buffer, and rumen fluid at 39 °C [4]. In the meantime, the total gas production and CH<sub>4</sub> are measured [28]. Blank samples with no feedstuffs are also run to correct for the amount of background gas produced.

The method requires access to fresh rumen fluid from fistulated animals, collected by esophageal tubing on intact animals or from slaughtered animals [4]. The method is ideal to screen different feedstuffs within a short time (1–4 weeks) in a controlled environment [4,28]. One way of determining the kinetic parameter of total gas production is by using the nonlinear curve fitting procedure in GenStat and SAS [24,40]. Syringes; Rusitec; closed vessel batch fermentation and fully automated systems have been used for CH<sub>4</sub> determination [41–44]. The method allows as many replications in one batch to discern differences among treatments [28]. The result of this technique can serve as input to optimize larger and more expensive in vivo experiments [4]. However, the system can only simulate the ruminal fermentation of feed. Furthermore, under normal conditions, the system lacks to capture the thriving environment of rumen microorganisms in the tested feedstuffs [28].

# 2.3. The Sulfur Hexafluoride (SF<sub>6</sub>) (Direct Measurements)

The sulfur hexafluoride tracer method was first developed at Washington State University [45] and described in 1993–1994 by [19]. It is a widely used technique to measure enteric CH<sub>4</sub> emissions [37]. The technique provides a direct measurement of the CH<sub>4</sub> emission of individual animals [24]. The purpose of the SF<sub>6</sub> technique is to investigate how much CH<sub>4</sub> does the penned as well as free-ranging and grazing animals produce over a given period (24h feeding cycle) [4,31,46]. SF<sub>6</sub> is a non-toxic, physiologically inert, and stable gas that is easy to detect, even in minute amounts [4,32,47]. In addition, SF<sub>6</sub> gas mixes with rumen air in the same way as CH<sub>4</sub> [28].

The principle behind this method is that from the rumen, the SF<sub>6</sub> gas release rate is determined in order to calculate the CH<sub>4</sub> emission measurement [19,33,48]. The SF<sub>6</sub> gas release rate could be achieved by placing an SF<sub>6</sub> filled permeation tube in a 39 °C water bath. Once the release rate is known and reaches stability, the permeation tube will be placed in the rumen of the study animals [28].

The sampling apparatus consists of a small brass permeation tube placed in the rumen and a lightweight "yoke", fitted with a collection PVC canister, a halter and capillary tubing in which an air-evacuated canister draws air at a slow and steady rate from near the animal's nostrils [4,28,32,45,46]. Eructated gas samples release both SF<sub>6</sub> and CH<sub>4</sub> from their nostrils, and some of this is sucked into the canister (along with air surrounding the animal) [4,46]. The ratio of CH<sub>4</sub>:SF<sub>6</sub> in the canister is used to determine the daily CH<sub>4</sub> emission with each gas corrected for background concentration. The concentration of SF<sub>6</sub> and CH<sub>4</sub> in the canister is determined by gas chromatography [32], in conjunction with the pre-determined SF<sub>6</sub> permeation rate of the tubes [31,48,49]. Samples are advised to be taken over 24 h intervals, over a minimum period of five sequential days, with background air samples collected alongside animals at the same time [31]. The following equation is used to determine CH<sub>4</sub> emission using the SF<sub>6</sub> technique [33].

 $CH_4 (g/day) = SF_6 (g/day) \times ([CH_4]c - [CH_4]b) / ([SF_6]c - [SF_6]b)$ 

where  $[CH_4]c$  and  $[SF_6]c$  are the concentrations of  $CH_4$  and  $SF_6$  in the canister, respectively; while  $[CH_4] b$  and  $[SF_6] b$  are the  $CH_4$  and  $SF_6$  concentrations in the background air, respectively [33].

In theory, the SF<sub>6</sub> technique is recommended for grazing cattle involving large herds (n > 50), [32,50]. Furthermore, it can also be employed under more controlled conditions where the intake is measured and/or regulated [24]. The duration of collection of each sample is regulated by altering the length and/or diameter of the capillary tube [19,28].

## 3. Spot Sampling Methods

Collecting adequate short-term breath data for measurements of emission are the essence of spot sampling methods [26]. The methods use spot measurement of exhaled CH<sub>4</sub> at milking or during feeding. Such methods are usually automated, non-invasive and non-intrusive, allowing a high throughput of animals [31]. Adequate data provide a repeatable estimate of emission rate and scale up from a short-term emission rate to CH<sub>4</sub> emissions for the whole day [32].

## 3.1. Sniffer Method

The idea of the sniffer method was first gestated by Garnsworthy et al. [51]. This method is based on short-duration continuous breath analysis of exhaled air from the feed troughs in automatic milking systems (AMS) or concentrate feeders (CF) [26]. To collect air eructed by animals during milking, a sample inlet is inserted in the feed manager of an autonomous milking system [51]. The sniffer method sample analysis is based on continuous sampling of air in the manager using data recorders to monitor  $CH_4$  and  $CO_2$  concentrations near the animal's muzzle [33]. This method provides an estimate of total daily emissions by individual animals on-farm [31]. It also provides hundreds of repeated measurements over prolonged periods [37]. However, studies using the sniffer method have shown, a high between-animal coefficient of variation (CV) as compared to the RC and flux method [26,52–54]. In addition, with this method,  $CH_4$  and  $CO_2$  concentrations are highly influenced by the distance of the animal's head from the point of sampling, which is not an issue with total-air sampling [55].

#### 3.2. GreenFeed

GreenFeed<sup>®</sup> (GF) is a patented, commercially available gas-flux quantification system (C-lock Inc., Rapid City, SD, USA) that combines an automatic feeding system with measures of CH<sub>4</sub>, CO<sub>2</sub>, airflow, and the detection of head position during each animal's visit to the unit [24,26,56]. The GF method is based on the idea that many short-term CH<sub>4</sub> emission samples from an individual animal, taken several times throughout a day, can be aggregated to estimate an animal's average daily CH<sub>4</sub> emission across several days/weeks/months [31]. The system measures CH<sub>4</sub> emissions from non-confined cattle and sheep and records short-term data (3–6 min) repeatedly over 24 h by attracting animals to the unit using a "bait" of pelleted concentrate [4,24]. This method uses a similar principle for measuring gas emissions as for respiration chambers (flux method) [26]. What makes the (GF) method special is that there are sensors that measure the concentration of CH<sub>4</sub> released from the animal's mouth during the several minutes that the animal is feeding [4]. The head sensor also detects if the head of the cow is in the correct position before using the exhaled CH<sub>4</sub> concentration values for further calculations of the flux.

The GF system is embedded with automatic baiting, measurements of airflow and gas concentrations, electronics, communication devices, and a gas tracer device. Animal visits result in a feed reward and measurement of CH<sub>4</sub> emission after a specified time has elapsed between visits (determined by the investigator) [28,31,33]. Daily CH<sub>4</sub> emissions are estimated from multiple short-duration visits to the feed station over 1–2 weeks [4]. Daily CH<sub>4</sub> emission CH<sub>4</sub> (L/min) is calculated using the volumetric airflow rate (Fair (i)) adjusted to STP and corrected for the capture rate.

CH4 (L/min) = Cp(i) 
$$\times$$
 ([CH4]c(i) - [CH4] b(i))  $\times$  Fair(i) /106

where Cp(i) is the fractional capture rate of air at time i;  $[CH_4]c(i)$  and  $[CH_4]b(i)$  are the concentrations of captured gas (ppm) and background gas of CH<sub>4</sub> (ppm), respectively, at time i; and Fair(i) is the volumetric airflow rate (L/min) measured on a dry-gas basis at time i. [26,33]. The system provides comparable estimates to those produced both by RC and SF<sub>6</sub> techniques [24,57]. The measurements with sufficient duration (at least 3 min), and 30 observations were enough to obtain reliable CH<sub>4</sub> emission data, regardless of how many times per day the measurements were obtained [37,58]. For measuring CH<sub>4</sub> emissions from individual animals, GF is a more cost-effective method than both SF<sub>6</sub> and RC, both indoors and in pastures [31,37].

## 3.3. Face Mask Method

The principle of face mask (FM) for spot samplings of respiratory exchange and CH<sub>4</sub> emissions is based on animals trained to stay in sternal recumbency for 30 min measurement periods taken every 2–3 h with up to 7 measurements per day [59,60]. The method has been used to measure emissions from cattle, sheep, and goats [31]. The principle of this method is similar to RC in terms of measuring gas exchange and changes in the exhaled CH<sub>4</sub> concentration. It includes a mass flow controller, gas sampling unit, and CH<sub>4</sub> emission analyzer attached to each face mask, where gas measurements are corrected for differences in humidity, lag time, drift, and CH<sub>4</sub> emission (mL/min) for each period [61]. The FM method is comparatively cheaper and simpler than SF<sub>6</sub> or RC. Its mobility provides access to measure multiple locations to collect CH<sub>4</sub> emissions [62]. However, the number of measurements presented had a marked impact on animal behavior, as access to food and water was restricted during measurement periods. The FM method was also considered too laborious and interest in using the method to measure enteric CH<sub>4</sub> from ruminants has faded [61].

## 3.4. Portable Accumulation Chambers

A portable accumulation chamber (PAC) system is essentially an airtight box without airflow [31,33]. The PAC consist of a clear polycarbonate box that has an opening at the bottom and that is sealed by achieving close contact with flexible rubber matting [24]. The method uses a portable air sampler and analyzer unit based on transform IR detection [32]. In this technique, PAC traps all exhaled gases during 2 h of sampling, during which oxygen is depleted, and a single measurement of CH<sub>4</sub> is taken at the end of the sampling [55,63].

One of the advantages of the PAC system is to facilitate easy access to emission measurements on grazing conditions, something not possible with immobile open-circuit chambers [24]. It allows for screening a large number of ruminants for an efficient  $CH_4$  emission measurement [24]. However, the time of measurements relative to feeding and any postprandial changes in  $CH_4$  emission is a potential source of variation in these measurements and thus, should be accounted for when the method is used [31].

#### 4. Models to Estimate CH<sub>4</sub> Emission

Mathematical modeling has been used as an alternative approach to estimating  $CH_4$  emissions [64,65]. Mathematical modeling can be defined as the use of equations to describe or simulate processes in a system and assumes to reasonably represent the behavior of a system [66,67]. Models have a pivotal role in ruminant nutrition, from quantifying nutrient uti-

lization, setting feeding standards, and estimating CH<sub>4</sub> emissions [68]. Models can be classified as; (i) empirical vs. mechanistic, (ii) dynamic vs. static, (iii) deterministic vs. stochastic, and (iv) continuous vs. discrete [3]. Models used to estimate enteric CH<sub>4</sub> emission are mainly categorized into two principal groups: statistical (empirical) or/and dynamic mechanistic models (simulation-based model) [32,65,69].

Simple empirical (statistical) models estimate CH<sub>4</sub> emission from data, such as animal parameters (weight, breed, age), and feed data, such as (nutrient composition and/or digested nutrients) [32,69]. Statistical models have been commonly used for inventory purposes [37]. Ramin and Huhtanen [29], suggested that feed intake is the main determinant of total CH<sub>4</sub> emission. Changes in CH<sub>4</sub> emissions from empirical models have limited scope; they can be evaluated only in relation to changes in animal parameters or feed characteristics [33,64]. Dynamic mechanistic models, on the other hand, predict CH<sub>4</sub> emissions using mathematical descriptions of rumen's fermentation biochemistry [33,69]. Recently, an integrated farm system model has emerged, which is a process-based whole-farm simulation technique [32,70] that incorporates soil processes, crop growth, tillage, planting and harvest operations, feed storage, feeding, herd production, manure storage, and economics [69].

Model development often uses data derived from experiments conducted with animals in respiration chambers [28]. Thus far, available data suggested that mechanistic models are superior to empirical models in accurately predicting  $CH_4$  emissions from animals, having the predictive potential of 70% vs. 42–57% for mechanistic and empirical models, respectively [69].

The Intergovernmental Panel on Climate Change (IPCC) and Food and Agricultural Organization [71], have also developed and issued a standard model for calculating cattle CH<sub>4</sub> emissions. The objective of the IPCC guidelines is to provide "good practice" by promoting high-quality inventories [72]. There are three levels of IPCC estimation methods, Tiers 1, 2, and 3, where Tier 1 is the simplest and most straightforward of the three methods, and Tier 3 is more complex and data-dependent. The three methods are based on the proportion of the cow's gross energy intake excreted as CH<sub>4</sub>. The Tier 1 method is simple so that any country can estimate emissions with limited data and information. The Tier 2 method uses the same methodological approach and equations as Tier 1, but with country-specific emission factors instead of global or continental default values provided by the IPCC. The Tier 3 level uses higher-order estimation methods that typically include complex models, national inventory measurement systems, and highly disaggregated activity data [73,74]. However, the IPCC models are limited due to the fact that there are no models are available to predict CH<sub>4</sub> emissions from tropical cattle, buffaloes, sheep and goats [33].

# 5. Laser Technologies to Measure Enteric CH<sub>4</sub> Emission

#### 5.1. The Laser CH<sub>4</sub> Detector (Direct Measurements)

The use of lasers for gas detection has traditionally been used in environmental monitoring, air-quality monitoring, security, and health care [75]. A laser CH<sub>4</sub> detector (LMD) is used to monitor exhaled air CH<sub>4</sub> concentrations in the air between the laser device and the animal's nose or mouth [37,76]. The LMD method is based on IR-absorption spectroscopy to establish the CH<sub>4</sub> concentration measurement [75]. It allows measurements of CH<sub>4</sub> emissions from the same animals repeatedly in their normal environments [33]. Measurements of CH<sub>4</sub> concentration are taken manually by a portable apparatus approximately 1–3 m from the animal [31]. The technique is similar to automated measurements of CH<sub>4</sub> concentration in exhaled air samples during milking or feeding, except here, measurements are taken from the animals' nostrils [51]. The advantages of LMD over the traditional enteric CH<sub>4</sub> measurement techniques are that the LMD is a non-invasive, non-contact technique, with a fast response, and enables real-time measurements [75]. The author [75] concluded that LMD reflects a strong agreement between those recorded in the indirect open-circuit respiration calorimetric chambers [75]. However, the LMD technique is affected by factors, such as temperature, wind velocity, the proximity of other animals, humidity, and atmospheric pressure [33,37]. In a recent review by Sorg [77], it was suggested that the LMD method could be an alternative in situations where other methods are not suitable for use.

## 5.2. Open-Path Laser (Direct Measurements)

Open-path laser is a novel method for quantifying  $CH_4$  emissions during feeding. It is currently been used to measure enteric  $CH_4$  emissions from herds of animals [24]. The concept of this technique relies on lasers and wireless sensor networks that send beams of light from the herds of animals to an open-path tunable diode detector to analyze  $CH_4$  from grazing animals by IR-absorption spectroscopy [78,79]. The laser comprises upwind and downwind paths for the predominant wind direction of the herd. The herd acts as a surface source or, when individual animals can be fitted with GPS collars, individual animals are treated as point sources. By combining the micrometeorological data, the method possibly measures whole-farm  $CH_4$  emissions across several pastures [24]. However, wind directions, surface roughness, or periods of unfavorable atmospheric conditions (fog, rain, waves, heat, etc.) are a particular concern for the application of this technique [80].

## 6. Micrometeorological Methods

Micrometeorological methods are based on gas-flux measurements in the free atmosphere and the corresponding emission rates of animals [28,81]. The methods rely on concomitant measurements of wind velocity and  $CH_4$  concentration [32]. For gas analysis, Fourier Transform Infrared (FTIR) spectroscopy is integrated into the system. However, there are differences in the measurement techniques and the calculation of emission rates. Some of the techniques available for emission measurements include mass balance, vertical flux, and Lagrangian dispersion analyses [81]. An advantage of these techniques is that it is possible to study animals within their normal production setting and the measurements can be made on a potentially large number of animals [81]. In addition, the methods can incorporate the measurement of footprint over larger areas [32]. It was confirmed that micrometeorological methods could give similar values of  $CH_4$  emission compared to open-circuit respiration chambers [28,82]. It is, however, not possible to detect emissions from indoor-housed animals as well as from individual animals by using micrometeorological methods [33].

## 7. Emerging Technologies to Measure CH<sub>4</sub> Emission from Ruminant

## 7.1. Blood CH<sub>4</sub> Concentration Tracer

This methodology is an emerging and future technology where the quantification of  $CH_4$  is accessed from a blood sample from the jugular (vein). The method uses  $SF_6$  gas introduced into the rumen by an intraruminal bolus. Enteric  $CH_4$  is absorbed across the rumen wall, transported in the bloodstream to the pulmonary artery, and respired by the lungs [24,83]. The method provides a little more than a "snapshot" of  $CH_4$  concentration at the time of sampling [24].

## 7.2. Infrared (IR) Thermography

Infrared thermography is the process of using a thermal image to detect radiation coming from an object, converting it to temperature and displaying an image of the temperature distribution [84]. Ian [85], examined the use of IR thermography to measure CH<sub>4</sub> emissions using a thermal imaging camera to record flank temperatures on cattle. The difference in temperature between the left and right flanks is believed to be indicative of the heat of fermentation in the rumen, and hence CH<sub>4</sub> emission. A moderate correlation value relationship was found, ranging between r = 0.35 to 0.53, post-feeding between CH<sub>4</sub> emissions and temperature variations [85,86]. However, the postprandial period (100–300 min or 300–442 min after a meal) is the best period to assess CH<sub>4</sub> using IR thermography [85,87]. The system is an emergent technology to measure emissions from the body surface of an animal, which is a simple procedure, non-invasive, and relatively inexpensive [85].

#### 7.3. Intraruminal Telemetry

A telemetry approach is used to measure the concentration of  $CH_4$ ,  $CO_2$ , and hydrogen gas in the rumen using an intraruminal device. The method encompasses miniaturized IR sensors and a wireless network platform [88]. The system is ideal to measure real-time data. However, the unfavorable rumen environment can cause corrosion of electrical circuits in electronic devices [33]. This technology is still in its exploratory stages [24].

## 7.4. Eddy Covariance (EC) Technique

Eddy covariance is a popular micrometeorological method currently being used to directly observe the exchanges of gas, energy, and momentum between ecosystems and the atmosphere [89]. The application of the EC technique to quantify  $CH_4$  fluxes and other tracer gases was made possible with the development of fast-response and field-deployable optical sensors [25]. The method requires the knowledge of animal numbers and their location within the footprint and a model to interpret the relationship between the calculated flux and the emission rate of point sources within the footprint [90]. Under the current technical conditions, minor fluctuations of air mass and energy flux on several time scales (hour, day, season, and year) can be measured [89]. The EC method was successfully applied to measure  $CH_4$  and  $CO_2$  flux data to estimate  $CH_4$  emissions from grazing cattle [6,25]. This method uses footprint calculations to estimate cattle emissions and interpret the relationship between the EC-derived flux and emissions occurring at the animal locations [90,91]. However, one of the practical challenges to measuring tracer gases using the EC technique is the high cost of fast-response instrumentation and the challenge of changes in wind direction, surface roughness, and atmospheric stability conditions [25,90].

#### 7.5. Carbon Dioxide as a Tracer Gas

The use of  $CO_2$  as a tracer gas is used in a newly developed approach for quantifying CH<sub>4</sub> emissions from cattle [28]. The technique uses equations for estimating animal heat production [92]. The premise is that feed intake is assumed to translate to heat production [93] and there is a close correlation between heat and  $CO_2$  production [94]. This method requires knowledge about the intake, energy content, and heat increment of the ration consumed [24]. The method uses the ratio of  $CH_4$ :CO<sub>2</sub> in exhaled breath to calculate enteric CH<sub>4</sub> emission [95]. The calculated CH<sub>4</sub> emission from this method was similar to values derived from the SF<sub>6</sub> tracer technique [32]. The analysis of  $CH_4$  and  $CO_2$  can be conducted with portable FTIR equipment [28]. As a consequence, the  $CO_2$  technique produces a higher level of variability than the RC method, with the coefficient of determination (R2) being 0.4 between the two methods, making it unsuitable for precise measurements of  $CH_4$  emission in dairy cows [24,96]. In addition, the  $CO_2$  technique does not capture the variation in CH<sub>4</sub> emission between efficient and non-efficient cows, as shown by [97]. The analysis of RC data indicated a large bias between the low and high-efficiency cows [97]. The method overestimated CH<sub>4</sub> from efficient cows and underestimated it from inefficient cows. However, the method can easily be applied to many animals, making it possible to reduce the standard error of means from experiments [28,97].

#### 7.6. Polytunnel

A tunnel system for measuring CH<sub>4</sub> release from grazing systems was first conceptualized by the Institute of Grassland and Environmental Research, UK [98]. The system is the simplest method in which animals are housed under controlled conditions [24]. Essentially, polytunnels consist of one large inflatable or tent type tunnel made of heavy-duty polyethylene fitted with end walls and large diameter ports. Air is drawn through the internal space at speeds of up to  $1 \text{ m}^3/\text{s}$  [98]. The system consists of (i) a large polythene tunnel, (ii) two small wind tunnels used to blow air into, and draw air from the larger tunnel, (iii) an apparatus to measure and record the concentration of CH<sub>4</sub> in the air entering and leaving the tunnel and (iv) apparatus to monitor and record airspeed and temperature [99]. This allows test animals to express normal grazing behavior, including diet selection over the forages confined within the polytunnel space [24]. This technique can be used to measure  $CH_4$  in individual or small groups of animals under semi-normal grazing conditions. This approach is easier to use and transport, but it is difficult to maintain the temperature and humidity inside the tunnel [33].

# 8. Pros and Cons of Various Methods for Measuring and Estimating CH<sub>4</sub> Emissions from Ruminants

Various methods exist for measuring and estimating CH<sub>4</sub> emissions [28]. Every method has its advantages and limitations (Table 1), and no single method is appropriate for reliable monitoring of CH<sub>4</sub> emissions in all situations [33].

Table 1. Pros and cons of various methods for measuring and estimating CH<sub>4</sub> emissions from ruminants.

Catego	ories	Pros	Cons
Widely Used	d Methods		
Respiration chamber		Provides the most accurate and precise measurements of emissions, including CH <sub>4</sub> from ruminal and hindgut fermentation.	Expensive to construct and maintain. Use is technically demanding. Not suitable for examining effects of grazing management; restricts normal animal behavior and movement.
In Vitro Incubation		Can be used as a first approach to test potential feedstuffs and additives under controlled conditions. Less expensive and time-consuming than respiration chambers.	May not represent whole animal (in vivo) emissions.
Sulfur Hexafluoride Tracer Technique (SF <sub>6</sub> )		Applicable for large numbers of individual animals. Allows the animal to move about freely, suitable for grazing systems.	$SF_6$ is a highly potent GHGs with GWP 22800. A great risk of equipment failure and more labor-intensive than respiration chambers. Does not measure hindgut $CH_4$ emissions.
1. Spot samplir	ng methods		
Sniffer n	nethod	Provides hundreds of repeated measurements over prolonged periods.	High between-animal CV compared to RC or flux.
Green	Feed	Provides comparable estimates to respiratory chamber and $SF_6$ techniques.	Requires the use of a feed "attractant" to lure the anima to the facility, which alters measurement results. Does not measure hindgut CH <sub>4.</sub>
Face mask	c method	When compared to other techniques such as SF <sub>6</sub> or RC, it is far less expensive and simpler.	Restricted measurement periods and access to food and water. FM technique was considered also too laborious.
Portable Accumulation Chambers		Designed to measure large numbers of animals for genetic screening of relative CH <sub>4</sub> emission.	Similar in cost to open-circuit respiration chambers, but with much shorter measurement time. Comparability with respiration chambers unclear.
2. Modeling		Applicable in cases where measurements are not possible. Inexpensive to use once developed; eliminates need for CH <sub>4</sub> measurement; easy for predicting national or global emissions; they are easy to apply.	Since the models are trained on experimental data, their applicability is limited. Developed empirical models are mainly related to the range of intake in the dataset used to develop the equations. Models cannot be used to study between-animal variation. Although many models with different characteristics exist for predicting CH <sub>4</sub> emission from ruminants, most of them require the use of feed intake which is difficult to obtain on a large thereby hindering their use.
3. Laser techno	logies		
Open Pat	th Laser	Measures CH <sub>4</sub> emissions from herds of animals and facilitates whole-farm measurements across a number of pastures.	Expensive. Requires sensitive instrumentation to analyze CH <sub>4</sub> concentration; dependent on environmental factors and the location of test animals.

	Categories	Pros	Cons
	The laser CH <sub>4</sub> detector	Non-invasive, non-contact technique, fast response, and enables real-time measurements.	Affected by factors, such as temperature, wind velocity proximity of other animals, humidity, and atmospheric pressure.
4.	Micrometeorological methods	Ideal for measuring animal emissions, without altering animal behavior; measurements can be made on a potentially large number of animals.	Individual animals, as well as indoor confined animals cannot be measured. Hardly to use during evaluation of CH <sub>4</sub> abatement. The accuracy and precision of measuring CH <sub>4</sub> varied with surrounding weather, e.g., wind speed and landscape. This method is generally costly.
5.	Emerging technologies		
Blood CH <sub>4</sub> Concentration tracer		Potential to measure large number of animals.	The method provides little more than a "snapshot" of ${\rm CH}_4$ concentration. Destructive method during collection of blood sample.
Infrared Thermography		Simple procedure, non-invasive and relatively inexpensive.	No direct relationship was reported between temperature in any specific part of the body and CH <sub>4</sub> emission.
Intraruminal Telemetry		Ideal to measure real-time data.	The electronic circuit of an electric gadget corrodes inside the rumen due to the tough rumen environment.
Eddy covariance (EC) technique		Successfully applied to measure CH <sub>4</sub> and CO <sub>2</sub> flux data to estimate CH <sub>4</sub> emissions from grazing cattle.	The high cost of fast-response instrumentation and the challenge with changes in wind direction, surface roughness, and atmospheric stability conditions. Interpretation of the EC flux as an animal emission rate is challenging. EC measurements of point-source emissions may be biased because of cattle movement. When measured during daylight, the EC is more effective than when measured at night.
Carbon dioxide as a tracer gas		Can be easily applied to many animals.	Has a higher day-to-day variation unsuitable for precision measurements. Overestimate CH <sub>4</sub> from efficient cows and underestimated it from inefficient cows.
Polytunnel		Suitable for measuring CH <sub>4</sub> emission from the small group of grazing animals. This is portable and easy to operate.	It is difficult to control the temperature and humidity inside the tunnel.

# Table 1. Cont.

## 9. Conclusions

To date, quite a lot of ruminant  $CH_4$  measurement and estimation methods are available in the literature. Knowing the advantages and disadvantages of each method helps us to fine-tune experimental designs based on the cost, suitability, and availability of methods of measuring and estimating  $CH_4$  emission. The choice of the technique should primarily be driven by the objective of the experiment; but obviously, other considerations also come into play. In situations where  $CH_4$  cannot be measured directly, it could be estimated reliably by the use of empirical or mechanistic models available in the literature.

Author Contributions: Conceptualization and writing of the draft manuscript, W.B.; writing—review and editing, A.Z., A.G., A.S. and M.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

# References

- 1. EPA (United States Environmental Protection Agency): Greenhouse Gas Emissions. 2017. Available online: https://www.epa.gov/ghgemissions/overview-greenhouse-gases (accessed on 10 September 2020).
- NOAA (National Oceanic and Atmospheric Administration): Greenhouse Gases. 2020. Available online: https://www.ncdc. noaa.gov/monitoring-references/faq/greenhouse-gases.php (accessed on 10 September 2020).
- Alemu, A.W.; Dijkstra, J.; Bannink, A.; France, J.; Kebreab, E. Rumen stoichiometric models and their contribution and challenges in predicting enteric methane production. *Anim. Feed Sci. Technol.* 2011, 166–167, 761–778. [CrossRef]
- 4. Okpara, M.O. Methane Emissions in Ruminants: Perspectives on Measurement and Estimation Methods. *Russ. Agric. Sci.* 2018, 44, 290–294. [CrossRef]
- 5. Li, D.H.; Kim, B.G.; Lee, S.R. A respiration-metabolism chamber system for measuring gas emission and nutrient digestibility in small ruminant animals. *Rev. Colomb. Cienc. Pecu.* **2010**, *23*, 444–450.
- Rosenstock, T.S.; Rufino, M.C.; Chirinda, N.; van Bussel, L.; Reidsma, P.; Butterbach-Bahl, K. Scaling Point and Plot Measurements of Greenhouse Gas Fluxes, Balances, and Intensities to Whole Farms and Landscapes. In *Methods for Measuring Greenhouse Gas Balances and Evaluating Mitigation Options in Smallholder Agriculture*; Rosenstock, T., Rufino, M., Butterbach-Bahl, K., Wollenberg, L., Richards, M., Eds.; Springer: Cham, Switzerland, 2016. [CrossRef]
- Vermeulen, S.J.; Campbell, B.M.; Ingram, J.S.I.I. Climate change and food systems. Annu. Rev. Environ. Resour. 2012, 37, 195–222.
   [CrossRef]
- Gerber, P.J.; Steinfeld, H.; Henderson, B.; Mottet, A.; Opio, C.; Dijkman, J.; Falcucci, A.; Tempio, G. Tackling Climate Change through Livestock—A Global Assessment of Emissions and Mitigation Opportunities; Food and Agriculture Organization of the United Nations (FAO): Rome, Italy, 2013; pp. 1–139. Available online: http://www.fao.org/3/i3437e/i3437e00.htm (accessed on 25 June 2021).
- Kristiansen, S.; Painter, J.; Shea, M. Animal Agriculture and Climate Change in the US and UK Elite Media: Volume, Responsibilities, Causes and Solutions. *Environ. Commun.* 2020, 15, 153–172. [CrossRef] [PubMed]
- 10. Food and Agriculture Organization of the United Nations. Available online: http://faostat.fao.org/ (accessed on 4 March 2019).
- 11. Tubiello, F.N.; Salvatore, M.; Rossi, S.; Ferrara, A.; Fitton, N.; Smith, P. The FAOSTAT database of greenhouse gas emissions from agriculture. *Environ. Res. Lett.* **2013**, *8*, 015009. [CrossRef]
- 12. Steinfeld, H.; Gerber, P.; Wassenaar, T.D.; Castel, V.; Rosales, M.; Rosales, M.; de Haan, C. *Livestock's Long Shadow: Environmental Issues and Options*; Food and Agriculture Organization: Rome, Italy, 2006; ISBN 978-9251055717.
- 13. Martin, C.; Rouel, J.; Jouany, J.P.; Doreau, M.; Chilliard, Y. Methane output and diet digestibility in response to feeding dairy cows crude linseed, extruded linseed, or linseed oil. *J. Anim. Sci.* **2008**, *86*, 2642–2650. [CrossRef] [PubMed]
- Olivier, J.G.; Schure, K.M.; Peters, J.A.H.W. Trends in Global CO<sub>2</sub> and Total Greenhouse Gas Emissions; PBL Netherlands Environmental Assessment Agency: The Hague, The Netherlands, 2018. Available online: https://www.pbl.nl/en/publications/trends-inglobal-co2-and-total-greenhouse-gas-emissions-2018-report (accessed on 5 November 2019).
- 15. Nisbet, E.G.; Dlugokencky, E.J.; Manning, M.R.; Lowry, D.; Fisher, R.; France, J.; Michel, S.E.; Miller, J.; White, J.W.; Vaughn, B.; et al. Rising atmospheric methane: 2007–2014 growth and isotopic shift. *Glob. Biogeochem. Cycles* **2016**, *30*, 1356–1370. [CrossRef]
- 16. Beauchemin, K.A.; Kreuzer, M.; O'Mara, F.; McAllister, T.A. Nutritional management for enteric methane abatement: A review. *Aust. J. Exp. Agric.* 2008, *48*, 21–27. [CrossRef]
- 17. Beauchemin, K.A.; McGinn, S.M.; Benchaar, C.; Holtshausen, L. Crushed sunflower, flax, or canola seeds in lactating dairy cow diets: Effects on methane production, rumen fermentation, and milk production. *J. Dairy Sci.* 2009, *92*, 2118–2127. [CrossRef]
- 18. Patra, A.K. Trends and Projected Estimates of GHG Emissions from Indian Livestock in Comparisons with GHG Emissions from World and Developing Countries. *Asian-Australas. J. Anim. Sci.* **2014**, 27, 592–599. [CrossRef] [PubMed]
- 19. Johnson, K.; Huyler, M.; Westberg, H.; Lamb, B.; Zimmerman, P. Measurement of methane emissions from ruminant livestock using a sulfur hexafluoride tracer technique. *Environ. Sci. Technol.* **1994**, *28*, 359–362. [CrossRef] [PubMed]
- 20. Johnson, K.A.; Johnson, D.E. Methane emissions from cattle. J. Anim. Sci. 1995, 73, 2483–2492. [CrossRef]
- 21. McGinn, S.M.; Turner, D.; Tomkins, N.; Charmley, E.; Bishop-Hurley, G.; Chen, D. Methane Emissions from Grazing Cattle Using Point-Source Dispersion. *J. Environ. Qual.* 2011, 40, 22–27. [CrossRef]
- 22. Kebreab, E.; Clark, K.; Wagner-Riddle, C.; France, J. Methane and nitrous oxide emissions from Canadian animal agriculture: A review. *Can. J. Anim. Sci.* 2006, *86*, 135–157. [CrossRef]
- Castelan-Ortega, O.A.; Ku-Vera, J.C.; Estrada-Flores, J.G. Modeling methane emissions and methane inventories for cattle production systems in Mexico. *Atmósfera* 2014, 27, 185–191. [CrossRef]
- Goopy, J.P.; Chang, C.; Tomkins, N. A Comparison of methodologies for measuring methane emissions from ruminants. In *Methods for Measuring Greenhouse Gas Balances and Evaluating Mitigation Options in Smallholder Agriculture*; Rosenstock, T., Rufino, M., Butterbach-Bahl, K., Wollenberg, L., Richards, M., Eds.; Springer: Cham, Switzerland, 2016. [CrossRef]
- 25. Prajapati, P.; Santos, E.A. Estimating Herd-Scale Methane Emissions from Cattle in a Feedlot Using Eddy Covariance Measurements and the Carbon Dioxide Tracer Method. *J. Environ. Qual.* **2019**, *48*, 1427–1434. [CrossRef] [PubMed]
- 26. Huhtanen, P.; Cabezas-Garcia, E.H.; Utsumi, S.; Zimmerman, S. Comparison of methods to determine methane emissions from dairy cows in farm conditions. *J. Dairy Sci.* 2015, *98*, 3394–3409. [CrossRef]
- 27. Hill, J.; McSweeney, C.; Wright, A.-D.G.; Bishop-Hurley, G.; Kalantar-Zadeh, K. Measuring Methane Production from Ruminants. *Trends Biotechnol.* **2016**, *34*, 26–35. [CrossRef]

- Storm, I.M.L.D.; Hellwing, A.L.F.; Nielsen, N.I.; Madsen, J.O. Methods for Measuring and Estimating Methane Emission from Ruminants. *Animals* 2012, 2, 160–183. [CrossRef]
- Ramin, M.; Huhtanen, P. Development of equations for predicting methane emissions from ruminants. J. Dairy Sci. 2013, 96, 2476–2493. [CrossRef] [PubMed]
- Armsby, H.P. The Principles of Animal Nutrition; J. Wiley & Sons: New York, NY, USA, 1903. Available online: http://hdl.loc.gov/ loc.gdc/scd0001.00008948185 (accessed on 10 September 2020).
- Hammond, K.J.; Waghorn, G.C.; Hegarty, R.S. The GreenFeed system for measurement of enteric methane emission from cattle. *Anim. Prod. Sci.* 2016, 56, 181–189. [CrossRef]
- 32. Brouček, J. Methods of methane measurement in ruminants. Slovak J. Anim. Sci. 2014, 47, 51-60.
- Patra, A.K. Recent Advances in Measurement and Dietary Mitigation of Enteric Methane Emissions in Ruminants. *Front. Vet. Sci.* 2016, 3, 39. [CrossRef]
- Hellwing, A.L.F.; Lund, P.; Weisbjerg, M.R.; Brask, M.; Hvelplund, T. Technical note: Test of a low-cost and animal-friendly system for measuring methane emissions from dairy cows. J. Dairy Sci. 2012, 95, 6077–6085. [CrossRef]
- Wainman, F.W.; Blaxter, K.L. Closed-Circuit Respiration Apparatus for the Cow and Steer. In Proceedings of the 1st Symposium in Energy Metabolism, Principles, Methods and General Aspects, Copenhagen, Denmark, 15–19 September 1958; pp. 80–84.
- 36. Gerrits, W.; Labussière, E.; Reynolds, M.C.; Kuhla, B.; Lund, P.; Weisbjerg, M.; Dijkstra, J. Letter to the Editor: Recovery test results as a prerequisite for publication of gaseous exchange measurements. *Dairy Sci.* **2018**, *101*, 4703–4704. [CrossRef]
- Hristov, A.; Kebreab, E.; Niu, M.; Oh, J.; Bannink, A.; Bayat, A.; Boland, T.; Brito, A.; Casper, D.; Crompton, L.; et al. Symposium review: Uncertainties in enteric methane inventories, measurement techniques, and prediction models. *J. Dairy Sci.* 2018, 101, 6655–6674. [CrossRef]
- 38. McGinn, S.M.; Chen, D.; Loh, Z.; Hill, J.; Beauchemin, K.A.; Denmead, O.T. Methane emissions from feedlot cattle in Australia and Canada. *Aust. J. Exp. Agric.* 2008, *48*, 183–185. [CrossRef]
- Rymer, C.; Huntington, J.A.; Williams, B.A.; Givens, D.I. In vitro cumulative gas production techniques: History, methodological considerations and challenges. *Anim. Feed Sci. Technol.* 2005, 123–124, 9–30. [CrossRef]
- 40. Payne, R.W.; Murray, D.A.; Harding, S.A. *An Introduction to the GenStat Command Language*, 14th ed.; VSN International: Hemel Hempstead, UK, 2011.
- 41. Blümmel, M.; Ørskov, E.R. Comparison of in vitro gas production and nylon bag degradability of roughages in predicting feed intake in cattle. *Anim. Feed Sci. Technol.* **1993**, *40*, 109–119. [CrossRef]
- Bhatta, R.; Tajima, K.; Takusari, N.; Higuchi, K.; Enishi, O.; Kurihara, M. Comparison of sulfur hexafluoride tracer technique, rumen simulation technique and in vitro gas production techniques for methane production from ruminant feeds. *Int. Congr. Ser.* 2006, 1293, 58–61. [CrossRef]
- 43. Navarro-Villa, A.; O'Brien, M.; Lopez, S.; Boland, T.M.; O'Kiely, P. Modifications of a gas production technique for assessing in vitro rumen methane production from feedstuffs. *Anim. Feed Sci. Technol.* **2011**, *166–167*, 163–174. [CrossRef]
- Pellikaan, W.F.; Hendriks, W.H.; Uwimana, G.; Bongers, L.J.G.M.; Becker, P.M.; Cone, J.W. A novel method to determine simultaneously methane production during in vitro gas production using fully automated equipment. *Anim. Feed Sci. Technol.* 2011, 168, 196–205. [CrossRef]
- DeRamus, H.A.; Clement, T.C.; Giampola, D.D.; Dickison, P.C. Methane emissions of beef cattle on forages: Efficiency of grazing management systems. J. Environ. Qual. 2003, 32, 269–277. [CrossRef] [PubMed]
- 46. Zimmerman, P.R. System for Measuring Metabolic Gas Emissions from Animals. U.S. Patent 5265618, 30 December 1993.
- 47. Johnson, K.; Huyler, M.; Pierce, C.S.; Lamb, B.; Zimmermann, P. The use of SF6 as an inert gas tracer for use in methane measurements. *J. Anim. Sci.* **1992**, *70*, 302.
- 48. Harper, L.A.; Denmead, O.T.; Freney, J.R.; Byers, F.M. Direct measurements of methane emissions from grazing and feedlot cattle. *J. Anim. Sci.* **1999**, 77, 1392–1401. [CrossRef]
- Williams, S.R.O.; Moate, P.J.; Hannah, M.C.; Ribaux, B.E.; Wales, W.J.; Eckard, R.J. Background matters with the SF6 tracer method for estimating enteric methane emissions from dairy cows: A critical evaluation of the SF6 procedure. *Anim. Feed Sci. Technol.* 2011, 170, 265–276. [CrossRef]
- 50. McSweeney, C. Measuring Methane in the Rumen under Different Production Systems as a Predictor of Methane Emissions. CCH.6210 Final Report. 2015. Available online: https://www.mla.com.au/ (accessed on 20 March 2019).
- 51. Garnsworthy, P.C.; Craigon, J.; Hernandez-Medrano, J.H.; Saunders, N. On-farm methane measurements during milking correlate with total methane production by individual dairy cows. *J. Dairy Sci.* **2012**, *95*, 3166–3180. [CrossRef]
- Yan, T.; Mayne, C.S.; Gordon, F.G.; Porter, M.G.; Agnew, R.E.; Patterson, D.C.; Ferris, C.P.; Kilpatrick, D.J. Mitigation of enteric methane emissions through improving efficiency of energy utilization and productivity in lactating dairy cows. *J. Dairy Sci.* 2010, 93, 2630–2638. [CrossRef]
- 53. Zimmerman, S.; Brito, A.; Huhtanen, P.; Johnson, K.; Michal, J.; Pereira, A.; Pineras, C.; Utsumi, S.; Waghorn, G.; Zimmerman, P. Measurement and evaluation of enteric CH<sub>4</sub> emissions and variability in production systems. *Adv. Anim. Biosci.* **2013**, *4*, 518.
- 54. Bell, M.J.; Saunders, N.; Wilcox, R.; Homer, E.; Goodman, J.; Craigon, J.; Garnsworthy, P. Methane emissions among individual dairy cows during milking quantified by eructation peaks or ratio with carbon dioxide. J. Dairy Sci. 2014, 97, 6536–6546. [CrossRef] [PubMed]

- 55. Hegarty, R.S. Applicability of short-term emission measurements for on-farm quantification of enteric methane. *Animal* **2013**, 7, 401–408. [CrossRef] [PubMed]
- 56. Zimmerman, P.R.; Zimmerman, R.S. Method and System for Monitoring and Reducing Ruminant Methane Production. U.S. Patent US20090288606A, 26 November 2009.
- Hammond, K.; Humphries, D.; Crompton, L.; Kirton, P.; Green, C.; Reynolds, C. Methane Emissions from Growing Dairy Heifers Estimated Using an Automated Head Chamber (GreenFeed) Compared to Respiration Chambers or SF6 Techniques. *Adv. Anim. Biosci.* 2013, 4, 391.
- Arthur, P.F.; Barchia, I.M.; Weber, C.; Bird-Gardiner, T.; Donoghue, K.A.; Herd, R.M.; Hegarty, R.S. Optimizing test procedures for estimating daily methane and carbon dioxide emissions in cattle using short-term breath measures. J. Anim. Sci. 2017, 95, 645–656.
   [CrossRef]
- 59. Washburn, L.E.; Brody, S. Growth and development with special reference to domestic animals. Methane, hydrogen, and carbon dioxide production in the digestive tract of ruminants in relation to the respiratory exchange. *Univ. Missouri. Coll. Agric. Agric. Exp. Stat. Res. Bull.* **1937**, 263, 614.
- 60. Bhatta, R.B.; Nishi, O.; Kurihara, M. Measurement of Methane Production from ruminants. *Asian-Aust. J. Anim. Sci.* 2007, 20, 1305–1318. [CrossRef]
- Oss, D.B.; Marcondes, M.I.; Machado, F.S.; Pereira, L.G.R.; Tomich, T.R.; Ribeiro, G.O.; Chizzotti, M.L.; Ferreira, A.L.; Campos, M.M.; Maurício, R.M.; et al. An evaluation of the face mask system based on short-term measurements compared with the sulfur hexafluoride (SF 6) tracer, and respiration chamber techniques for measuring CH<sub>4</sub> emissions. *Anim. Feed Sci. Technol.* 2016, 216, 49–57. [CrossRef]
- 62. Brosh, A. Heart rate measurements as an index of energy expenditure and energy balance in ruminants: A review. *J. Anim. Sci.* **2007**, *85*, 1213–1227. [CrossRef]
- 63. Goopy, J.P.; Woodgate, R.; Donaldson, A.; Robinson, D.L.; Hegarty, R.S. Validation of a short-term methane measurement using portable static chambers to estimate daily methane production in sheep. *Anim. Feed Sci. Technol.* **2011**, *166–167*, 219–226. [CrossRef]
- 64. Kebreab, E.; Johnson, K.A.; Archibeque, S.L.; Pape, D.; Wirth, T. Model for estimating enteric methane emissions from United States dairy and feedlot cattle. *J. Anim. Sci.* 2008, *86*, 2738–2748. [CrossRef]
- 65. Kumari, S.; Fagodiya, R.K.; Hiloidhari, M.; Dahiya, R.P.; Kumar, A. Methane production and estimation from livestock husbandry: A mechanistic understanding and emerging mitigation options. *Sci. Total Environ.* **2020**, *709*, 136135. [CrossRef] [PubMed]
- 66. Thornley, J.H.M.; France, J. Mathematical Models in Agriculture: Quantitative Methods for the Plant, Animal and Ecological Sciences; Cromwell Press: Trowbridge, UK, 2007; ISBN 9780851990101. [CrossRef]
- 67. Dumas, A.; Dijkstra, J.; France, J. Mathematical modelling in animal nutrition: A centenary review. J. Agric. Sci. 2008, 146, 123–142. [CrossRef]
- 68. France, J.; Kebreab, E. Mathematical Modelling in Animal Nutrition. CABI: Wallingford, UK, 2008. Available online: https://books.google.com.et/books?id=Fs9piuD\_K1YC (accessed on 5 November 2019).
- 69. Kebreab, E.; Tedeschi, L.; Dijkstra, J.; Ellis, J.L.; Bannink, A.; France, J. *Modeling Greenhouse Gas Emissions from Enteric Fermentation*; Advances in Agricultural Systems Modeling; Wiley: New York, NY, USA, 2015. [CrossRef]
- Sejian, V.; Lal, R.; Lakritz, J.; Ezeji, T. Measurement and prediction of enteric methane emission. *Int. J. Biometeorol.* 2011, 55, 1–16. [CrossRef] [PubMed]
- Food and Agriculture Organization of the United Nations (FAO). *Greenhouse Gas Emissions from the Dairy Sector*; FAO: Rome, Italy, 2010. Available online: http://www.fao.org/docrep/012/k7930e/k7930e00.pdf (accessed on 5 July 2019).
- 72. Stephen, M.; Ogle, S.M.; Shannon, S.; Melannie, H.; Leandro, B.; Luanne, S.; du Toit, L.; Jongikhaya, W. Developing National Baseline GHG Emissions and Analyzing Mitigation Potentials for Agriculture and Forestry Using an Advanced National GHG Inventory Software System; Advances in Agricultural Systems Modeling. 2016. Available online: https://doi.org/10.2134/ advagricsystmodel6.2013.0009 (accessed on 10 March 2019).
- 73. International Panel on Climate Change (IPCC). Agriculture, Forestry and Other Land Use. In *Revised IPCC Guidelines for National Greenhouse Gas Inventories*; Chapter, 10; Wiley: New York, NY, USA, 2006; Volume 4.
- 74. Ogle, S.M.; Breidt, F.J.; Easter, M.; Williams, S.; Killian, K.; Paustian, K. Scale and uncertainty in modeled soil organic carbon stock changes for US croplands using a process-based model. *Glob. Chang. Biol.* **2010**, *16*, 810–822. [CrossRef]
- 75. Chagunda, M.G.G. Opportunities and challenges in the use of the Laser Methane Detector to monitor enteric methane emissions from ruminants. *Animal* **2013**, *7*, 394–400. [CrossRef]
- 76. Ricci, P.; Chagunda, M.G.G.; Rooke, J.; Houdijk, J.G.M.; Duthie, C.-A.; Hyslop, J.; Roehe, R.; Waterhouse, A. Evaluation of the laser methane detector to estimate methane emissions from ewes and steers. *J. Anim. Sci.* **2014**, *92*, 5239–5250. [CrossRef]
- 77. Sorg, D. Measuring Livestock CH<sub>4</sub> Emissions with the Laser Methane Detector: A Review. Methane 2022, 1, 38–57. [CrossRef]
- Troy, S.; Rooke, J.A.; Duthie, C.A.; Ross, D.; Hyslop, J.J.; Roehe, R. Measurement of methane from finishing cattle fed either a forage-based or high concentrate diet from both feeder-mounted samplers and respiration chambers. *Adv. Anim. Biosci.* 2013, 4, 551.
- Rey-Sanchez, C.; Bohrer, G.; Slater, J.; Li, Y.-F.; Grau-Andrés, R.; Hao, Y.; Rich, V.I.; Davies, G.M. The ratio of methanogens to methanotrophs and water-level dynamics drive methane transfer velocity in a temperate kettle-hole peat bog. *Biogeosciences* 2019, 16, 3207–3231. [CrossRef]

- Loh, Z.; Chen, D.; Bai, M.; Naylor, T.; Griffith, D.; Hill, J.; Denmead, T.; McGinn, S.; Edis, R. Measurement of greenhouse gas emissions from Australian feedlot beef production using open-path spectroscopy and atmospheric dispersion modelling. *Aust. J. Exp. Agric.* 2008, 48, 244–247. [CrossRef]
- Harper, L.A.; Denmead, O.T.; Flesch, T.K. Micrometeorological techniques for measurement of enteric greenhouse gas emissions. *Anim. Feed Sci. Technol.* 2011, 166–167, 227–239. [CrossRef]
- Tomkins, N.W.; McGinn, S.M.; Turner, D.A.; Charmley, E. Comparison of open-circuit respiration chambers with a micrometeorological method for determining methane emissions from beef cattle grazing a tropical pasture. *Anim. Feed Sci. Technol.* 2011, 166–167, 240–247. [CrossRef]
- Ramírez-Restrepo, C.A.; Barry, T.N.; Marriner, A.; Lopez-Villalobos, N.; McWilliam, E.L.; Lassey, K.R.; Clark, H. Effects of grazing willow fodder blocks upon methane production and blood composition in young sheep. *Anim. Feed Sci. Technol.* 2010, 155, 33–43. [CrossRef]
- 84. Johannes, L.; Francis, M. Methane emissions from dairy cows: Comparing open-path laser measurements to profile-based techniques. *Agric. For. Meteorol.* **2005**, *135*, 340–345.
- 85. Ian, B. Using Infrared Thermography as a Proxy for Measuring Methane Emissions. MLA (Meat & Livestock Australia); Project Code: B.CCH.1085; University of Melbourne: Parkville, Australia, 2012.
- Montanholi, Y.R.; Odongo, N.E.; Swanson, K.C.; Schenkel, F.S.; McBride, B.W.; Miller, S.P. Application of infrared thermography as an indicator of heat and methane production and its use in the study of skin temperature in response to physiological events in dairy cattle (*Bos taurus*). J. Therm. Biol. 2008, 33, 468–475. [CrossRef]
- Gabbi, A.M.; Kolling, G.J.; Fischer, V.; Pereira, L.G.R.; Tomich, T.R.; Machado, F.S.; Campos, M.M.; da Silva, M.V.G.B.; Cunha, C.S.; Santos, M.K.R.; et al. Use of infrared thermography to estimate enteric methane production in dairy heifers. *Quant. Infrared Thermogr. J.* 2021, 1–9. [CrossRef]
- McSweeney, C. Measuring Methane in the Rumen under Different Production Systems as a Predictor of Methane Emissions. CCH.6210 Final Report. 2015. Available online: https://www.mla.com.au/contentassets/92d46123c2a640268f7a978c1d50c787/b. cch.6210\_final\_report.pdf (accessed on 14 May 2019).
- Shunlin, L.; Xiaowen, L.; Jindi, W. Vegetation production in terrestrial ecosystems. In Advanced Remote Sensing; Meat & Livestock, Australia Limited ABN: Sydney, Australia, 2012; pp. 501–531; ISBN 9780123859549. [CrossRef]
- 90. Coates, T.W.; Benvenutti, M.A.; Flesch, T.K.; Charmley, E.; McGinn, S.M.; Chen, D. Applicability of Eddy Covariance to Estimate Methane Emissions from Grazing Cattle. *J. Environ. Qual.* **2018**, *47*, 54–61. [CrossRef]
- 91. Coates, T.W.; Flesch, T.K.; McGinn, S.M.; Charmley, E.; Chen, D. Evaluating an eddy covariance technique to estimate point-source emissions and its potential application to grazing cattle. *Agric. For. Meteorol.* **2017**, 234–235, 164–171. [CrossRef]
- 92. Brouwer, E. Report of sub-committee on constants and factors. In *Energy Metabolism: Proceedings of the 3rd Symposium Held at Troon, Scotland, May 1964;* European Association for Animal Production: Academic Press: London, UK, 1965; Volume 11, pp. 441–443.
- Pedersen, S.; Sällvik, K. 4th Report from Working Group on Climatization in Animal Houses—Heat and Moisture Production at Animal and House Level. 2002. Available online: http://www.cigr.org/documents/CIGR\_4TH\_WORK\_GR.pdf (accessed on 27 June 2019).
- 94. Pedersen, S.; Blanes, V.; Jørgensen, H.; Chwalibog, A.; Haeussermann, A.; Heetkamp, M.J.W.; Aarnink, A.J.A. Carbon dioxide production in animal houses: A literature review. *Agric. Eng. Int.* **2008**, *10*, 1–20.
- 95. Madsen, J.; Bjerg, B.S.; Hvelplund, T.; Weisbjerg, M.R.; Lund, P. Methane and carbon dioxide ratio in excreted air for quantification of the methane production from ruminants. *Livest. Sci.* **2010**, *129*, 223–227. [CrossRef]
- 96. Hellwing, A.; Lund, P.; Madsen, J.; Weisberg, M.R. Comparison of enteric methane production from the CH4/CO2 ratio and measured in respiration chambers. *Adv. Anim. Biosci.* **2013**, *4*, 557.
- Huhtanen, P.; Bayat, A.R.; Lund, P.; Hellwing, A.L.F.; Weisbjerg, M.R. Short communication: Variation in feed efficiency hampers use of carbon dioxide as a tracer gas in measuring methane emissions in on-farm conditions. *J. Dairy Sci.* 2020, 103, 9090–9095. [CrossRef] [PubMed]
- 98. Lockyer, D.R.; Jarvis, S.C. The measurement of methane losses from grazing animals. Environ. Pollut. 1995, 90, 383–390. [CrossRef]
- Murray, P.; Chadwick, D.; Newbold, C.; Lockyer, D. Measurement of methane from grazing animals—The tunnel method. In Measuring Methane Production from Ruminants; Makkar, H.P., Vercoe, P.E., Eds.; Springer: Dordrecht, The Netherlands, 2007. [CrossRef]