Revista ION e-ISSN: 2145-8480 ISSN-L: 0120-100X DOI: https://doi.org/10.18273/revion.v37n2-2024003

System for Quantifying Methane, Carbon Dioxide, and Hydrogen Sulfide Emissions in Low-Cost Digesters Inoculated with Horse Manure

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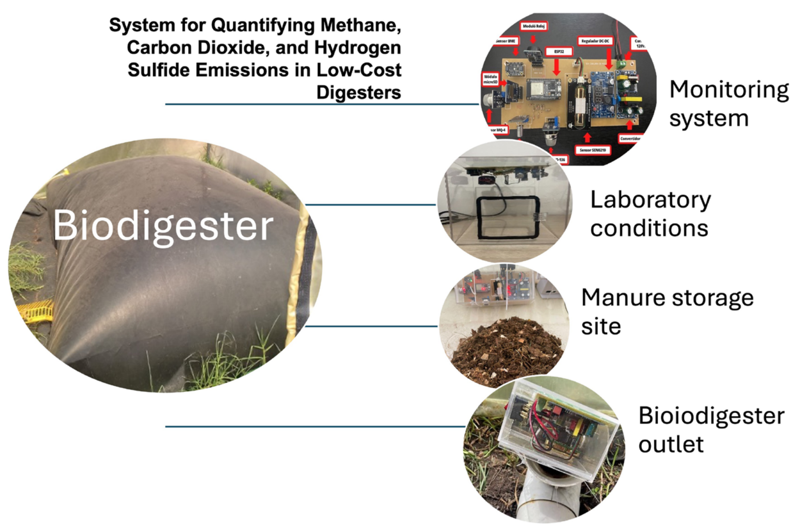
Fecha recepción: 4 de julio de 2024
Fecha aceptación: 15 de agosto de 2024

Graphical abstract



Abstract

Methane CH_4 and carbon dioxide CO_2 are the primary gases produced during anaerobic digestion AD, followed by what is referred to as "other gases," a highly variable group depending on the type of organic matter being digested. However, one of the most notable and common gases is hydrogen sulfide (H_2S), a gas that, while not a greenhouse gas, is well-known for its corrosive effects and its impact on health and the environment [1].

To quantify gas emissions associated with the treatment of horse manure at the Cavalry Canton of the National Army of Colombia, a direct monitoring system was implemented. Over 45 days, measurements of CH_4, CO_2, and H_2S were conducted using sensors such as the MQ-4, TGS 2611, SEN 0219, and MQ-136, respectively. The measurement ranges of the instruments used were: (200 – 10,000 ppm, 500 – 12,500 ppm, 0 – 5,000 ppm, and 0 – 200 ppm), with detection levels of: (10 ppm, 0.1 – 0.65 ppm, 40 ppm, 30 ppm). These instruments were placed in three key scenarios: the manure storage site, the biodigester outlet, and under controlled laboratory conditions. The objective was to generate a detailed analysis of the behavior of these emissions.

As a result, theoretical estimates of CH_4 and CO_2 equivalents were calculated for the Cavalry Canton. These theoretical estimates were compared with the data obtained from the monitoring and showed reductions ranging from 8 to 87% for CH_4, 58 to 67% for CO_2, and 33 to 65% for H_2S. These figures highlight the effectiveness of the implemented system in detecting gas emissions of interest from horse manure management, significantly contributing to environmental sustainability.

***Keywords**: Greenhouse gases; Temperature control; Organic waste; Horse manure; Monitoring.*

Cita: Acuña Monsalve Y, Mecón Rodríguez LS, Molina D. System for Quantifying Methane, Carbon Dioxide, and Hydrogen Sulfide Emissions in Low-Cost Digesters Inoculated with Horse Manure. rev. ion. 2024;37(2):37-47. doi:10.18273/revion.v37n2-2024003

Sistema para cuantificar la emisión de metano, dióxido de carbono y ácido sulfhídrico en digestores de bajo costo inoculados con estiércol equino

Resumen
El metano CH_4 y el dióxido de carbono CO_2 son los dos principales gases producidos en la DA, teniendo luego como tercer producto a la clasificación conocida como “otros gases”, que es un grupo muy variable de acuerdo al tipo de materia orgánica que se esté utilizando en la digestión anaerobia; sin embargo, uno de los gases que más se destaca y es común es el ácido sulfhídrico (H_2S), un gas que aunque no es de efecto invernadero es bastante conocido por su corrosión y efectos en la salud y el ambiente [1].

Con el fin de cuantificar la emisión de gases asociadas al tratamiento del estiércol equino en el Cantón de Caballería Del Ejército Nacional de Colombia se implementó un sistema de monitoreo directo. Durante un período de 45 días, se realizaron mediciones en términos de CH_4, CO_2 y H_2S utilizando sensores como el MQ-4, TGS 2611, SEN 0219, y MQ-136, respectivamente, el rango de medición de los instrumentos utilizados fue de: (200 – 10 000 ppm, 500 – 12 500 ppm, 0 – 5 000 ppm y 0 – 200 ppm), y el nivel de detección de: (10 ppm, 0,1 - 0,65 ppm, 40 ppm, 30 ppm). Estos instrumentos se ubicaron en tres escenarios clave: el lugar de almacenamiento del estiércol, la salida de un biodigestor y en condiciones controladas de laboratorio. El objetivo fue generar un análisis detallado del comportamiento de estas emisiones.

Como resultado se calcularon estimaciones teóricas de CH_4 y CO_2 equivalentes para el Cantón de Caballería. Estas estimaciones teóricas se compararon con los datos obtenidos del monitoreo realizado y se encontraron reducciones entre el 8 a 87 % para CH_4, 58 a 67 % para CO_2 y 33 a 65 % para H_2S. Estas cifras resaltan la eficacia del sistema implementado para detectar las emisiones de gases de interés derivadas de la gestión de estiércol equino, ofreciendo una contribución significativa a la sostenibilidad ambiental.

Palabras clave: *Gases de efecto invernadero; Control de temperatura; Desechos orgánicos; Estiércol equino; Monitoreo.*

Sistema para quantificar emissão de metano, dióxido de carbono e sulfeto de hidrogênio em biodigestores de baixo custo inoculados com esterco de cavalo

Resumo
O metano CH_4 e o dióxido de carbono CO_2 são os dois principais gases produzidos na AD, sendo o terceiro produto classificado como “outros gases”, que é um grupo muito variável dependendo do tipo de matéria orgânica utilizada na digestão anaeróbica; Porém, um dos gases que mais se destaca e é comum é o sulfeto de hidrogênio (H_2S), gás que, embora não seja um gás de efeito estufa, é bastante conhecido por sua corrosão e efeitos à saúde e ao meio ambiente [1].

Para quantificar a emissão de gases associada ao tratamento de dejetos eqüinos no Cantão Caballería do Exército Nacional da Colômbia, foi implementado um sistema de monitoramento direto. Durante um período de 45 dias, foram feitas medições em termos de CH_4, CO_2 e H_2S usando sensores como MQ-4, TGS 2611, SEN 0219 e MQ-136, respectivamente, a faixa de medição de os instrumentos utilizados foram: (200 – 10 000 ppm, 500 – 12 500 ppm, 0 – 5000 ppm e 0 – 200 ppm) e o nível de detecção: (10 ppm, 0,1 - 0,65 ppm, 40 ppm, 30 ppm). Esses instrumentos foram localizados em três cenários principais: o local de armazenamento de esterco, a saída de um biodigestor e em condições laboratoriais controladas. O objetivo era gerar uma análise detalhada do comportamento dessas emissões.

Como resultado, foram calculadas estimativas teóricas dos equivalentes de CH_4 e CO_2 para o Cantão de Caballería. Estas estimativas teóricas foram comparadas com os dados obtidos no monitoramento realizado e foram constatadas reduções entre 8 a 87 % para CH_4, 58 a 67 % para CO_2 e 33 a 65 % para H_2S. Estes números destacam a eficácia do sistema implementado para detectar emissões de gases de interesse provenientes da gestão do dejeto equino, oferecendo uma contribuição significativa para a sustentabilidade ambiental.

Palavras-chave: *Gases de efeito estufa; Controle de temperatura; Resíduos orgânicos; Estrume equino; Monitoramento.*

Introduction

In the 2022 climate change assessment report, the IPCC (Intergovernmental Panel on Climate Change) highlights the AFOLU sector (Agriculture, Forestry, and Other Land Use) as a significant source of greenhouse gas emissions, representing approximately 23 % of global anthropogenic emissions between 2010-2019 [2]. Globally, manure management generates around 230 million tons of CO_2 equivalent annually.
Colombia, as the third-largest country in terms of greenhouse gas emissions from agriculture, contributes 65 Mt of CO_2 equivalent [3]. In the context of the Cavalry Canton in Bogotá, which houses around 100 equine specimens, the challenge is to manage these animals' feces. At present, a portion of the feces is utilized to feed a biodigester within the canton, while the remainder is collected by a waste management company. During storage and the anaerobic process in the biodigester, gases such as CH_4, CO_2, and H_2S are emitted.
Some previous studies have addressed greenhouse gas detection at the industrial level, such as in the dairy industry with implementations in Canada, the Netherlands, and Japan. However, there are no similar reports related to equine feces. Therefore, the concentration of CH_4, CO_2, and H_2S emitted by the spontaneous decomposition of these feces is not reliably reported.
Given this, during this research, a monitoring system was implemented over a period of 45 days to measure the concentration of CH_4, CO_2, and H_2S in different scenarios: the manure storage site, the biodigester outlet, and under controlled laboratory conditions. The second stage focused on calculating CH_4 and CO_2 equivalent emission factors for the Cavalry Canton without implementing any treatment. Finally, in the third phase, the potential for transforming equine manure using a low-cost tubular digester and its contribution to reduce greenhouse gas emissions was evaluated.

Methodology

During the initial phase of this research, a review of greenhouse gas emissions was conducted, identifying CH_4, CO_2, and H_2S as the primary contributors. Based on this identification, sensors that integrated the system during the 45-day monitoring period in the three scenarios where the concentrations of these gases were measured were selected: the manure storage site, the biodigester outlet, and under controlled laboratory conditions. For each scenario, the system consisted of four sensors: TGS2611 and MQ-4 for CH_4, SEN 0219 for CO_2, and MQ-136 for H_2S with a measurement range of (200 – 10,000 ppm, 500 – 12,500 ppm, 0 – 5000 ppm, and 0 – 200 ppm) and detection levels of (10 ppm, 0.1 – 0.65 ppm, 40 ppm, 30 ppm).
The second phase of this research involved calculating CH_4 and CO_2 emission factors following the guidelines established by the Intergovernmental Panel on Climate Change (IPCC) [4]. For estimating CH_4 emissions from manure, the IPCC establishes three levels, each depending on the waste production rate per animal, the number of animals, and how it is treated. Of the three levels, the one that best suited the context of the research was Level 1. This is a simplified method that only requires data on livestock population by species/category and climate region or temperature, in combination with the IPCC's default emission factors to estimate emissions [4].

Equation 1 illustrates the calculation of CH_4 emissions from manure management, following the Level 1 methodology.

$$CH_{4\,Manure} = \Sigma_{(T)} \frac{(EF_{(T)} * N_{(T)})}{10^6} \quad (1)$$

Where:
$CH_{4Manure}$ = CH_4 emissions from manure management for a defined population ($GgCH_4{*}yr^{-1}$).

$EF_{(T)}$ = emission factor for the defined livestock population.

$N(T)$ = number of heads of the species/category of livestock.

T = species/category.

Regarding CO_2 emissions estimation, the IPCC proposes an equation to find the CO_2 equivalent emissions of CH_4.

$$CO_{2\,Manure} = CH_{4\,Manure} * GWP \quad (2)$$

Where:
$CO_{2\,Manure}$ = CH_4 emissions in CO_2eq from manure management ($GgCO_2eq{*}yr^{-1}$).
GWP = global warming potential over a 100-year time horizon.

Finally, in the third phase of this research, an analysis was conducted to evaluate the potential for transforming equine manure using a low-cost tubular digester, with the primary objective of analyzing its contribution to reducing greenhouse gas emissions. In this context, a detailed analysis of the organic matter input into the biodigester was performed, characterizing it through parameters such as total solids (TS), volatile solids (VS), and chemical oxygen demand (COD). This characterization is crucial as there is a direct correlation between the percentages of contaminant load removal and biogas production [5]. Moreover, the results obtained from the installed monitoring system were assessed to determine the effectiveness of the digester in reducing greenhouse gas emissions within the specific context of the canton.

Results

Manure Storage Location

The results obtained from the monitoring system at the manure storage location show a directly proportional relationship with ambient temperature. It was noted that higher temperatures were associated with increased emissions, while lower temperatures resulted in reduced emission levels. Figure 1 clearly illustrates this behavior, where methane emissions at the manure storage site varied from a minimum of 2.07 to a maximum of 21.36 ppm of CH_4, with peak concentrations identified in a temperature range between 10 and 15 °C.

Carbon dioxide CO_2 emissions at the manure storage site, like methane emissions, are the result of the decomposition process of organic matter present in the manure. Their generation is directly linked to the bacterial consortium present in the feces, which is sensitive to temperature variations. During the storage period, the most significant emissions were recorded in a temperature range between 5 and 24 °C, with concentrations ranging from 950 to 2167 ppm of CO_2, as illustrated in Figure 2.

Regarding hydrogen sulfide emissions, the research results revealed concentrations in the storage scenario ranging from 0.58 to 0.63 ppm, recorded in a temperature range between 15 and 22 °C, as shown in Figure 3. These findings indicate that during the storage period of equine manure, hydrogen sulfide emissions were produced at relatively low levels, showing some stability in concentrations across the evaluated thermal range.

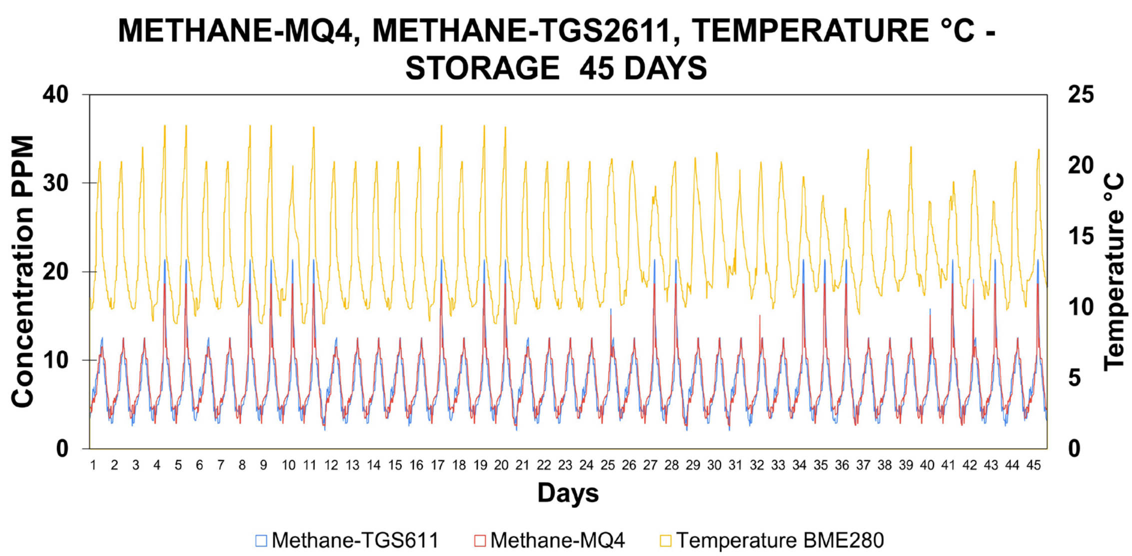


Figure 1. Methane emissions CH_4 at the manure storage site throughout the monitoring period.

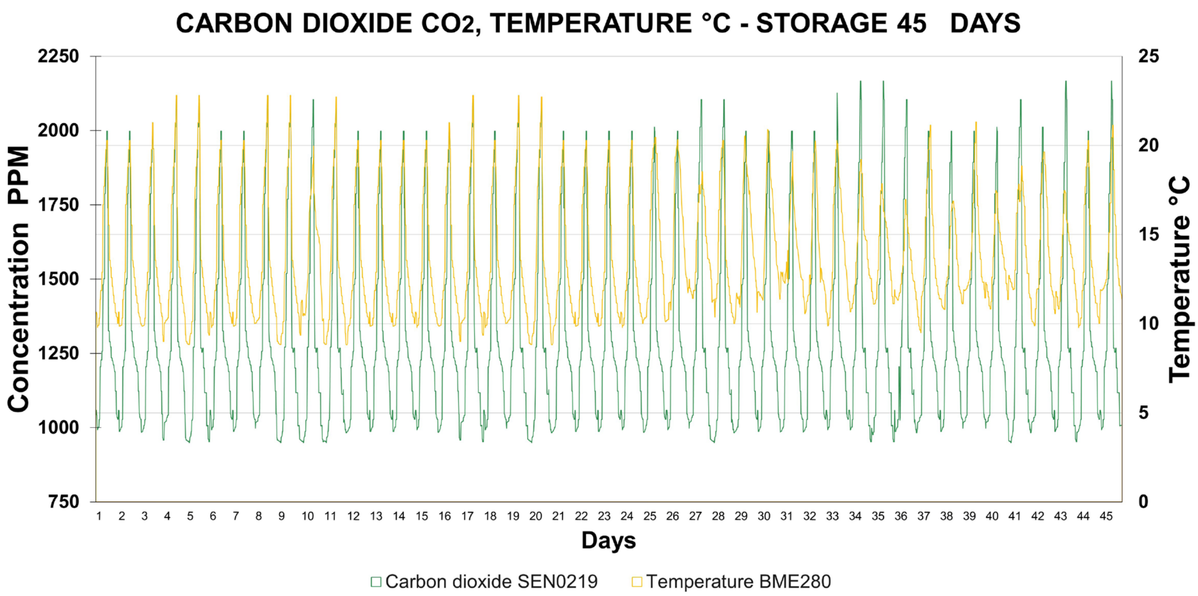


Figure 2. Carbon dioxide CO_2 emissions at the manure storage site throughout the monitoring period.

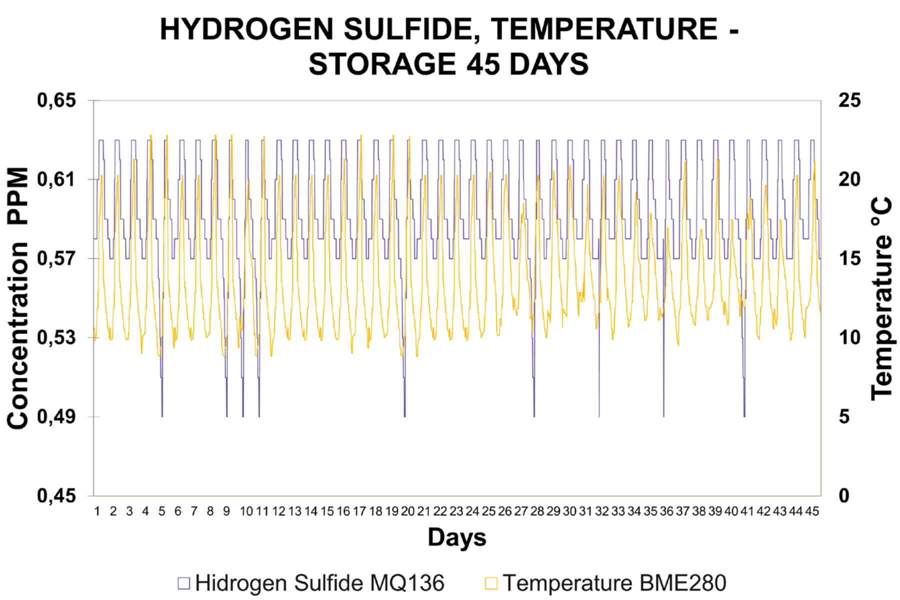


Figure 3. Hydrogen sulfide H_2S emissions at the manure storage site throughout the monitoring period.

Biodigester Outlet

Methane emissions at the biodigester outlet site showed significantly lower concentrations compared to those observed in manure storage. Values ranging from 0.54 to 2.57 ppm were recorded, as detailed in Figure 4. This indicates that the anaerobic digestion process applied in the biodigester has a positive impact on reducing methane emissions. This phenomenon is attributed to the effectiveness of the biodigester in treating manure, minimizing the release of greenhouse gases compared to conventional storage.

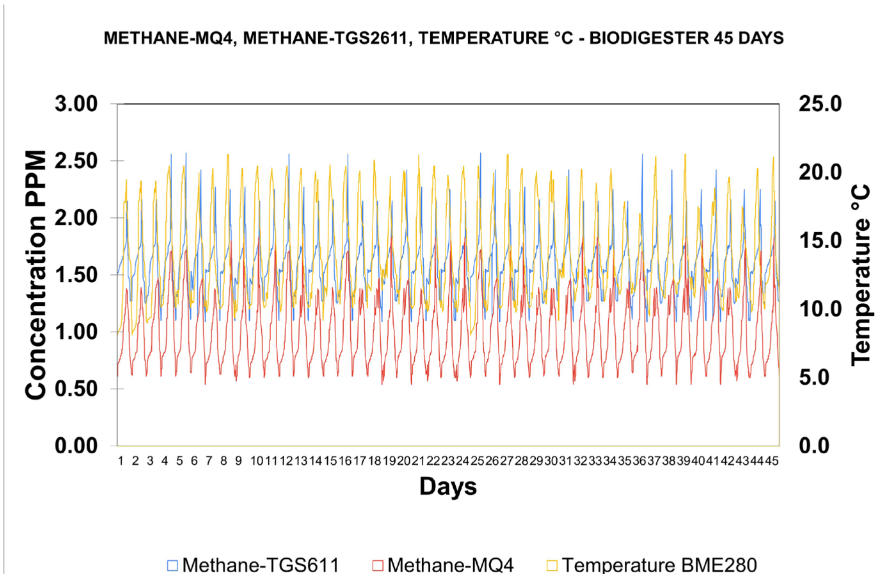


Figure 4. Methane emissions CH_4 at the biodigester outlet throughout the monitoring period.

Monitoring results of carbon dioxide CO_2 at the biodigester outlet revealed emissions in a range of 397 to 694 ppm, as illustrated in Figure 5. Although these figures are relatively low compared to CO_2 emissions at the manure storage site, the fact that elevated CO_2 emissions are still generated highlights the importance of evaluating and improving this tool to minimize environmental impact.

In the biodigester outlet scenario, hydrogen sulfide H_2S concentrations were recorded in a range of 0.20 to 0.33 ppm, as shown in Figure 6. These results contrast significantly with the concentrations observed at the manure storage site, where hydrogen sulfide emissions reached higher levels.

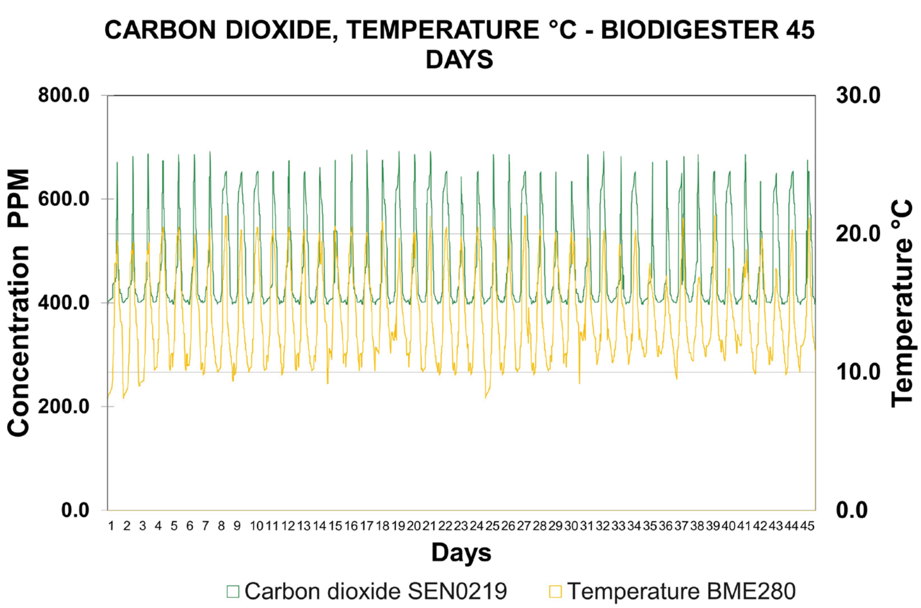


Figure 5. Carbon dioxide CO_2 emissions at the biodigester outlet throughout the monitoring period.

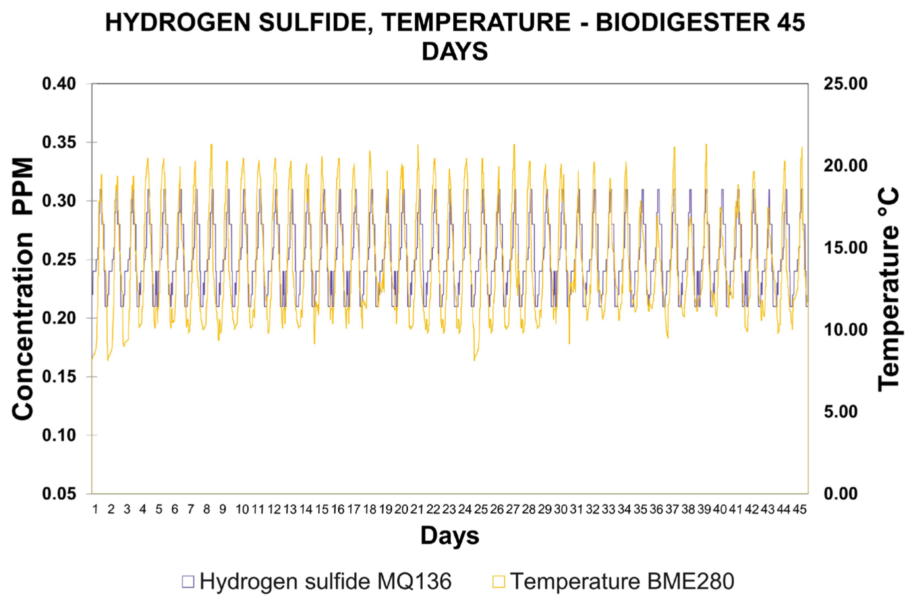


Figure 6. Hydrogen sulfide H_2S emissions at the biodigester outlet throughout the monitoring period.

Controlled Laboratory Conditions

In the third scenario, in the laboratory under controlled conditions, methane production increased progressively over time, facilitated by the device designed to create a hermetic environment. In this closed space, concentrations of CH_4, CO_2 and H_2S, and accumulated more markedly compared to the previous scenarios, as those were semi-open settings. Figure 7 shows that CH_4 production exhibited concentrations ranging from 170 to 2216 ppm. This increase is attributed to the constant temperature of 20 °C in the incubator, providing ideal conditions for the mesophilic and cryophilic bacterial consortium.

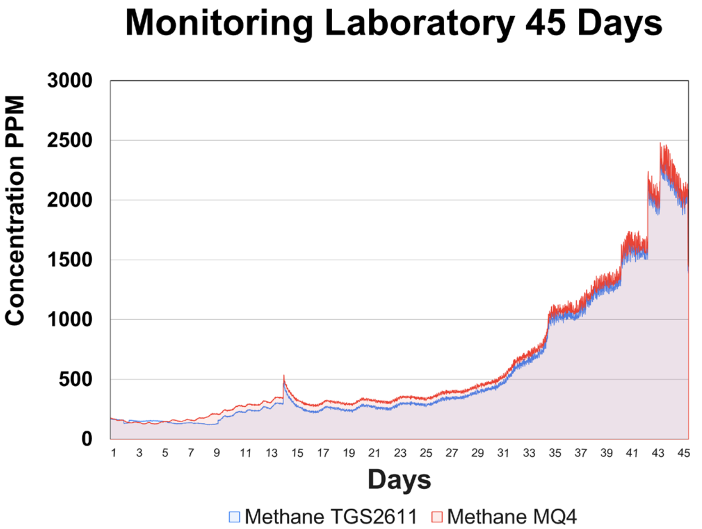


Figure 7. Methane emissions CH_4 under controlled laboratory conditions throughout the monitoring period.

Regarding hydrogen sulfide H_2S emissions in the monitoring system under controlled conditions, as illustrated in Figure 8, concentrations ranging from 0.49 to 1.75 ppm of H_2S were recorded. Emissions show a similar behavior to methane, which is explained by the composition of biogas, where represents less than 1 %, along with CH_4 (50 - 70 %) and carbon dioxide (50 - 30 %) [6]. These results highlight the influence of controlled laboratory conditions on gas generation, providing insight into the behavior of such gas emissions.

The theoretical estimation of CH_4 and CO_2 equivalent emissions for manure management in the Cavalry Canton, the method proposed by the IPCC Tier 1 was used for this calculation. Theoretical results indicate that the annual emission of CH_4 would be 2.69*10 Gg and for CO_2 the equivalent would be 0.08339 Gg. Comparing these values with those obtained from the monitoring system reveals notable differences.

Theoretical data, based on the IPCC Tier 1 method and extrapolated for the entire manure management in the Cavalry Canton, suggest significant annual emissions of methane and carbon dioxide equivalent. Meanwhile, measurements from the monitoring system in specific scenarios (manure storage, biodigester outlet, and laboratory conditions) present lower concentrations of CH_4 and CO_2 equivalent. These values, although valid for specific areas and particular scenarios, are significantly lower than theoretical estimates.

This difference suggests that actual emissions, according to the specific measurements, are lower than theoretical projections. Various factors can explain this difference: such as the spatial variability of emissions in the facility, the efficiency of the biodigester in reducing emissions, and the specific temperature and bacterial consortium conditions in each scenario.

However, although the concentrations measured at the storage site represent only a specific area (6 of 42 m² total), it suggests that total emissions in manure storage could be considerably higher, covering the entire storage space.

Table 1. Results of the physicochemical characterization of the influent and effluent.

Proximate Analysis	Units	Influent	Effluent
DQO	gDQO/L	24.44±0.79	3.92±0.120
ST	g/kg	23.48±1.50	2.10±0.060
SV	g/kg	20.74±1.56	1.10±0.005

The significant reductions in COD (84 %) and VS (95 %) indicate that the organic matter in the manure is effectively degraded during the digestion process. These reductions in COD and VS are indicative of successful organic waste management, directly contributing to the reduction of GHG emissions, such as CH_4, CO_2 and H_2S associated with anaerobic decomposition.

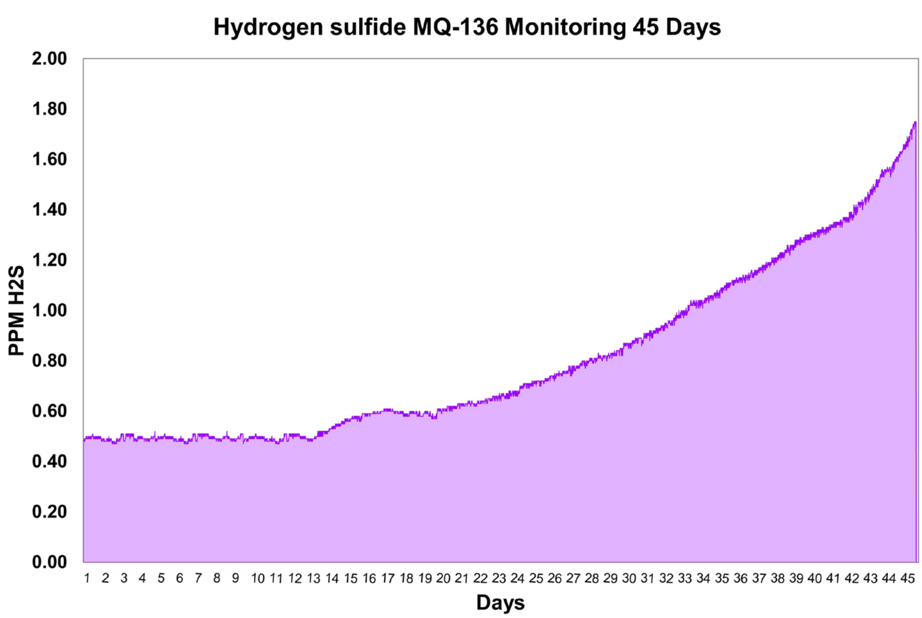


Figure 8. Hydrogen sulfide H_2S emissions under controlled laboratory conditions throughout the monitoring period.

Analysis of Results

A detailed analysis of emissions during the 45-day monitoring period reveals significant patterns, particularly when comparing emissions at the storage site and the biodigester outlet. By implementing two-time frames—day and night—we observed how light conditions affect gas emissions, confirming the direct influence of temperature on this process [6].

As shown in Figure 9, emissions at the storage site significantly increase during the day, with an 85 % increase in CH_4, a 61 % increase in H_2S, and a 99 % increase in CO_2. During the nighttime, average emissions were 4.83 ppm of CH_4, and 9.42 ppm during the day; H_2S, emissions were 0.58 ppm at night and 0.61 ppm during the day, while for CO_2, emissions were 1074 ppm at night and 1506 ppm during the day. These variations suggest a direct relationship between emissions, ambient temperature, and microbial activity. Elevated daytime temperatures accelerate microbial kinetics, increasing the rate at which organic substrates break down into simpler compounds, thus increasing GHG production. This finding supports the direct influence of temperature and sunlight on biological decomposition processes.

In contrast, at the biodigester outlet (Figure 10), CH_4 emissions were 0.43 ppm during the night and 1.76 ppm during the day. For H_2S, concentrations were 0.23 ppm at night and 0.27 ppm during the day, while CO_2 emissions were 408 ppm at night and 523 ppm during the day. These data indicate that the anaerobic digestion process effectively mitigates CH_4, CO_2 and H_2S emissions by capturing the methane produced by the manure for use in biogas combustion. The conversion of methane into CO_2 and water reduces the greenhouse effect impact [6].

This analysis highlights the positive impact of anaerobic digestion, as it not only mitigates emissions but also captures and utilizes the generated methane as an energy source. The results show significant reductions, ranging from 8 to 87 % in CH_4, from 58 to 67 % in CO_2, and from 33 to 65 % in , when comparing emissions with untreated storage conditions.

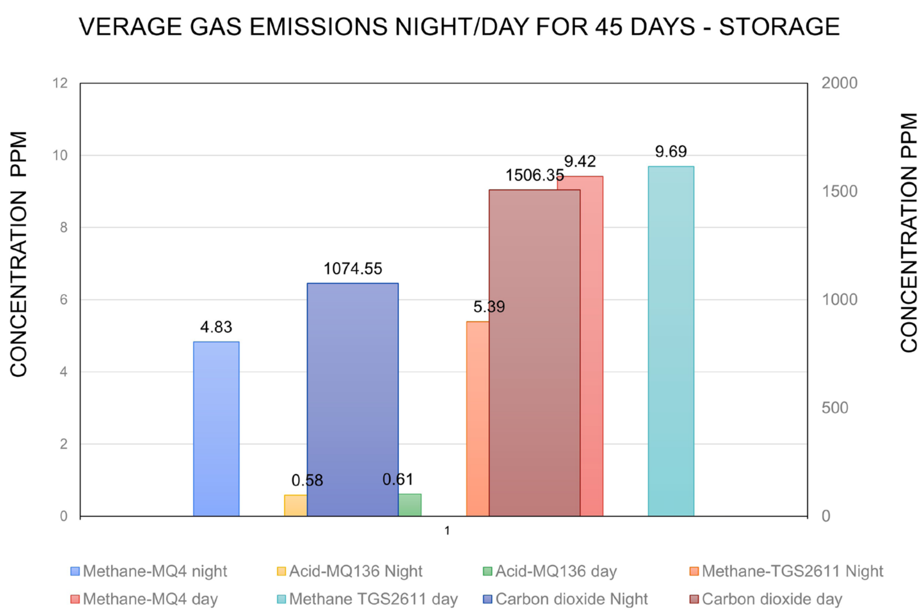


Figure 9. Average emissions of CH_4, CO_2, H_2S over 45 days at the manure storage site.

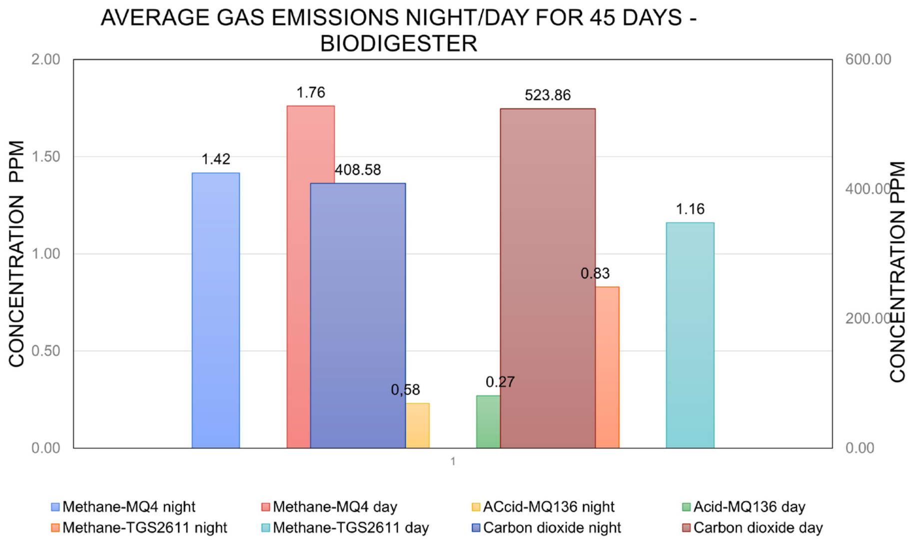


Figure 10. Average emissions of CH_4, CO_2, H_2S over 45 days at the biodigester outlet.

Conclusions

Direct measurements taken at the manure storage site and the biodigester outlet revealed a significant reduction in emitted gas concentrations. Methane decreased by 8 to 87 %, carbon dioxide by 58 to 67 %, and hydrogen sulfide by 33 to 65 %, compared to emissions recorded under untreated storage conditions. This reduction highlights the effectiveness of anaerobic digestion in mitigating GHGs.

Additionally, a directly proportional relationship between emissions and temperature was observed in both scenarios. Emission concentrations increased with higher temperatures and decreased with lower temperatures, aligning with the optimal conditions for microbial activity in the bacterial consortium. This behavior underscores the importance of maintaining ideal thermal conditions (35 - 37 °C) to enhance microbial activity and maximize the efficiency of the anaerobic digestion process.

The project, in essence, contributes to technological advancement by offering an alternative methodology for quantifying GHG emissions—specifically CH_4, CO_2 and H_2S—derived from manure management and biodigester outputs. This proposal stands out by providing a practical alternative to theoretical calculations in small-scale gas estimates, validating the effectiveness of anaerobic digestion as a sustainable alternative for mitigating and utilizing these gases.

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