

Meta-analysis of GHG Mitigation Potentials of the Application of Anaerobic Digestion in Dairy Farms

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Abstract

Dairy farms can apply anaerobic digestion (AD) as a manure management system, while producing renewable energy. Ultimately, this can reduce greenhouse gas (GHG) emissions. There is much research work that has quantified the changes in emissions due to AD. However, important methodologies such as the Intergovernmental Panel on Climate Change (IPCC) Guidelines, rely only on a small sample of the accumulated scientific findings in the field. This thesis improves the robustness of these methodologies by applying data-driven techniques to estimate values of the energy output of AD systems and their consequent effect in GHG emissions.

For this purpose, meta-analyses techniques are applied to mathematically combine metrics from 155 non-standardised research publications (i.e. with different boundaries, scopes and functional units). As a first step, a novel database is created by systematically searching for relevant articles and assessing them against defined criteria. The database is divided in two parts. Given that the offset of GHGs is highly dependent on the energy output of AD system, empirical methane yields (i.e. key metric of AD performance) are collected in Part I of the database. GHG released from different farm activities are input to Part II of the database. To quantify the change in emissions from these activities, standard baseline and AD scenarios are defined.

The second step of the meta-analysis consists of applying uni- and multi-variate tests to the database. For Part I, methane yields are analysed in terms of type of digesters. From the batch digesters, new maximum methane yields are proposed based on the combined results of 42 peer reviewed articles. These results offer better estimates than default values of methane yields from the 2007 Guidelines of the IPCC, which only consider two studies. For continuously stirred tank digesters and semi-continuous digesters lower methane yields are revealed. Multi-variate analysis of methane yields together with operating conditions and manure composition, enable the identification of clusters. These groups of variables can be useful to build potential AD scenarios in dairy farms.

For Part II of the database, relative changes in emissions between the activities in the standardised baseline and AD scenarios, are examined. It is found, through meta-analysis, that replacing raw manure by anaerobically-treated manure (i.e. digestate) in storage tanks and for field-application, mitigates baseline emissions by 38.7% and 6.9%, respectively. These relative changes can be used to estimate emissions from digestate, being more specific and evidence-based than the current methodology from the IPCC. In addition, relative changes found for offset of fossil fuels by biogas generated in the AD scenarios indicate a reduction of baseline emissions by 9.0%. Only methane leaks from digesters significantly increase the baseline emissions (by 7.4%).

Finally, results found by meta-analyses of methane yields and changes in emissions are applied to four dairy farm case studies. The work presented in the case studies demonstrates the benefits of enhancing the robustness of methods to estimate the effect of AD on GHG emissions from dairy farms.

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Nomenclature

Abbreviations

AD	: Anaerobic digestion.
CHP	: Combined heat and power.
CSTR	: Continuously stirred tank reactor.
CDM	: Clean Development Mechanism.
DB	: Davies-Bouldin Index.
GHG	: Greenhouse gas.
IPCC	: Intergovernmental Panel of Climate Change.
PFR	: Plug-flow reactor.
UASB	: Up-flow anaerobic sludge blanket.
VS	: Volatile solids.

Symbols

$\{a, b, c, d, n\}_{\mathrm{i}}$	: Coefficients for chemical reactions and polynomial expressions.
B_0	: Maximum methane yield $[m^3_{CH4} \cdot kg^{-1}_{VS}]$.
$\{c_i\ ,\ \lvert C_i\rvert\}$	: Centre and size of cluster C_i.
COD	: Chemical oxygen demand $[kg \cdot m^{-3}]$.
$\{d(x,c_i), D(c_i,c_j)\}$	: Distances between datapoint x and centres $\{c_i,c_j\}$.
DM	: Dry matter content $[wt.\%]$.
$\dot{E}$	: Annual power consumption $[GJ \cdot yr^{-1}]$.
EF	: Emission factor $[kg_{GHG} \cdot f.u.^{-1}]$.
$\{F_{ON}, F_{PRP}\}$	: Manure added/deposited by animals on soil $[kg \cdot yr^{-1}]$.
$\{GHG, CH_4, CO_2, N_2O\}_{Op}$	: Greenhouse gases emitted from operation unit "Op" $[kg \cdot yr^{-1}]$.
GWP_i	: Global warming potential of gas "i" $[kg_{CO2e} \cdot kg_i^{-1}]$.
$\hat{H}_i$	: Specific molar enthalpy of gas "i" $[kJ \cdot mol^{-1}]$.
$\{HHV, LHV\}$	: Higher/lower heating value $[kJ \cdot mol^{-1}]$.
HRT	: Hydraulic retention time $[d]$.
$\{M_i, M, M^*\}$	: Mean of sample "i", obtained by fixed-/(*)random-effect model.
MCF_i	: Methane conversion factor for system "i" $[\%]$.
MS_i	: Fraction of manure handled in system "i".
$\dot{n}$	: Molar flow $[mol \cdot yr^{-1}]$.
$N_2O - N_{\{input,OS,PRP\}}$	: Emissions from nitrogen input to soil, managed organic soils or urine/dung from grazing animals $[kg_{N2O-N} \cdot yr^{-1}]$.
$\{N, N_i, N_c\}$	: Size of sample, case "i" or dairy cattle herd.
$\{N_{ex}, N_{rate}\}$	: Nitrogen excretion $[kg_N \cdot hd^{-1} \cdot yr^{-1}]$ or $[kg_N \cdot kg^{-1} \cdot yr^{-1}]$.
OLR	: Organic loading rate $[kg_{VS} \cdot m^{-3} \cdot d^{-1}]$.
Q	: Heterogeneity of sample for random-effect model.
$\dot{Q}_d$	: Thermal power needed for the digester $[kJ \cdot yr^{-1}]$.
$\{r_i, r_{max}, r^{\pm}\}$	: Rank of the ith term and highest rank of sample (positive or negative denotes if it corresponds to ranks of positive or negative differences).
R_{ij}	: Similarity measure between clusters "i" and "j".
$\{RC,RC^*\}_{Op,i}$	: Global and local relative change of GHG "i" in operation unit "Op".
s_i	: Standard deviation of sample "i".

S_i	: Dispersion measurement of cluster "i".
$\{T, T_d, T_s\}$	: Temperatures, digester operation (d) and input slurry (s) [K].
T^2	: Variability between sample and population means.
TAM	: Typical animal mass [kg].
TKN	: Total Kjeldahl nitrogen [$kg \cdot m^{-3}$].
$\{U, U_{red}\}$	: Matrix (or reduced matrix) of eigenvectors for covariance matrix.
$\{u^{(i)}, u_j\}$	: Column "i" of matrix "U" or eigenvectors of covariance matrix.
$\{V, Z\}$	: Covariance and principal component matrices.
$\{V_i, V_i^*, V_M, V_{M*}\}$	: Variance of case "i" or mean "M", for fixed/(*)random-effect models.
VS_{Ex}	: Annual volatile solids excreted by cattle [$kg_{DM} \cdot hd^{-1} \cdot yr^{-1}$].
$\{W_0, W_A, W_B\}$	: Standard distribution of non-parametric statistic tests.
$\{w_+, w_-, w_A, w_B\}$	: Sum of positive/negative ranks or ranks of A/B (Wilcoxon's tests).
$\{W_i, W_i^*\}$	: Weight of sample "i" for fixed-/(*)random-effect models.
$\{x_{i,j}^{(k)}, x_{j,i}^*\}$	: ith data point from sample "j" allocated to cluster "k"(*centred).
Y_{CH4}	: Methane yield [$m_{CH4}^3 \cdot kg_{VS}^{-1}$].
$Z_{C/100}$	: Critical value for confidence interval of 95%.

Greek Symbols

η_i	: Fraction of power conversion in process "i".
Δ	: Change in variable.
$\Delta\hat{H}_f{}^0$	: Standard molar enthalpy of formation [$kJ \cdot mol^{-1}$].
μ	: Mean of population.
σ	: Standard deviation of population.
ρ	: Spearman test rho.

Operation unit (Op) subscripts

AD	: Anaerobic digestion scenario.
B	: Baseline scenario.
B*	: Standard baseline scenario.
Bo	: Anaerobic digestion scenario with condensing boiler.
CHP	: Anaerobic digestion scenario with combined heat and power unit.
E:	: Enteric fermentation.
El	: Electricity consumption/production.
El*	: Consumption of electricity produced on-site.
F	: Field-application of manure/digestate.
F1	: Field-application of manure as management system.
F2	: Manure deposited by grazing animals to fields.
Fe	: Offset of inorganic fertilisers by digestate.
FF	: Offset of fossil fuels by biogas.
L	: Leaks from digester.
NG	: Natural gas consumed.
S	: Storage of manure/digestate.
Th	: Thermal power produced/consumed.

Table of Contents

Acknowledgements ii

Abstract ii

1 Introduction and background 1

1.1 Can AD change GHG emissions? . . . 2

1.2 Methods to determine GHG emissions from dairy farms . . . 7

1.3 IPCC methodology applied in dairy farms . . . 11

1.4 Methane yields (Y_{CH4}) for AD of dairy cattle manure . . . 15

1.5 Meta-analysis to improve robustness of results . . . 18

1.5.1 Benefits of meta-analysis . . . 20

1.5.2 Steps for meta-analysis . . . 22

2 Research approach 23

2.1 Scenarios to evaluate the changes in emissions . . . 24

2.2 Specific research questions and thesis outline . . . 26

2.3 Contribution of the work . . . 31

3 Database of the AD of dairy cattle manure 33

3.1 Methodology for database development . . . 35

3.1.1 Criteria for selection . . . 35

3.1.2 Article search . . . 36

3.1.3 Structure of the database . . . 39

3.2 Results and discussion . . . 42

3.2.1 Articles selected for Part I-Methane Yields . . . 42

3.2.2 Articles selected for Part II-GHG Emissions . . . 48

3.3 Summary and final remarks for the chapter 52

4 Meta-analysis of methane yields **54**

4.1 Mathematical methods 56

4.1.1 Y_{CH4} distributions for meta-analysis 56

4.1.2 Meta-analysis models 57

4.1.3 Comparing distributions of Y_{CH4} 59

4.1.4 Multi-variate analysis 59

4.2 Results and discussion 64

4.2.1 Variables available according to digester type 64

4.2.2 Batch digesters 65

4.2.3 Continuous digesters 70

4.2.4 Semi-continuous digesters 74

4.2.5 Maximum methane yields (B_0) 79

4.3 Summary of the chapter 83

5 Effect of AD on GHG emissions from dairy farms. **85**

5.1 Normalisation of variables to relative changes 86

5.2 Statistical methods 88

5.3 Results and discussion 90

5.3.1 Relative changes according to method of emission estimation 90

5.3.2 Relative changes of specific GHGs 92

5.3.3 Relative changes for operation units 94

5.4 Summary and final remarks of the chapter 105

6 Case studies **108**

6.1 Assessment method 110

6.1.1 Questionnaire for dairy farms 110

6.1.2 GHGs from baseline scenarios 112

6.1.3 GHGs from AD-scenarios . . . 115
6.1.4 AD-Boiler scenario . . . 119
6.1.5 AD-CHP scenario . . . 121
6.2 Case Study I: Dairy Farm in the United Kingdom . . . 123
6.2.1 Baseline emissions from English farm . . . 124
6.2.2 Emissions shared by both English AD scenarios . . . 126
6.2.3 Emissions from AD-boiler scenario . . . 127
6.2.4 Emissions from AD-CHP scenario . . . 129
6.3 Case Study II: Dairy Farms in Guatemala . . . 131
6.3.1 Baseline emissions from Guatemalan farms . . . 132
6.3.2 Emissions shared by both Guatemalan AD Scenarios . . . 136
6.3.3 AD-Boiler Scenario . . . 137
6.3.4 AD-CHP Scenario . . . 139
6.4 Discussion . . . 142
6.4.1 Comparing the English and Guatemalan farms . . . 143
6.4.2 Comparing the IPCC methodology and application of meta-analysis . . . 147
6.5 Summary and concluding remarks of case studies . . . 150

7 Conclusions **154**
7.1 Concluding remarks . . . 154
7.2 Recommendations and future work . . . 156
7.3 Limitations . . . 157

Appendix A Published articles **177**

Appendix B Example calculation of relative changes **206**

Appendix C Example of answered questionnaire **212**

Chapter 1

Introduction and background

This thesis improves existing methodologies to quantify the effect of anaerobic digestion (AD) of cattle manure on the emissions of methane (CH_4), nitrous oxide (N_2O) and carbon dioxide (CO_2) from dairy farms. For this purpose, the work brings together the cumulative scientific findings in the research literature regarding methane yields (Y_{CH4}, key metric for the estimation of energy production) and the changes in greenhouse gas (GHG) emissions. To achieve robust estimates of these indicators, meta-analysis techniques are applied over systematically-selected literature [1–150]. This consequently achieves more evidence-based estimates of methane yields and relative changes in emissions. The meta-analysis findings converge in a unique methodology, which enables a robust estimation of the GHG emissions in baseline (i.e. business-as-usual) and AD scenarios.

This chapter contextualises the work of the thesis. Section 1.1 shows a broad overarching perspective of the application of AD for dairy cattle manure and its relation to GHG emissions. A requirement to improve the estimation methods is to first understand how GHG emissions are calculated for dairy farms in the existing literature. Therefore, Section 1.2 presents common methodologies applied over dairy farms with and without AD. Thereafter, focus is given to the Intergovernmental Panel on Climate Change (IPCC) Guidelines [151], which are the most frequent base for emission estimation found in the literature.

In Section 1.4, Y_{CH4} is presented as a key vector of the AD performance, which is widely

reported in the field. It is proposed to provide refine values of this metric to reach more evidence-based estimations of CH_4 emissions and energy production from AD systems. The estimation of yields and changes in GHGs promoted by AD systems is found in multiple (and sometimes contrasting) results in the literature. Therefore, Section 1.5 presents meta-analysis as a means to provide clarity in the research of AD technologies by statistically synthesising scientific findings from different sources.

1.1 Can AD change GHG emissions?

There is currently a worldwide challenge to reduce GHG emissions and mitigate climate change. Ideally, all countries would utilise resources in a sustainable manner (ecological footprint lower than 1.8 hectares per person [152]) while achieving a human development index above 0.800 [153], as represented by the shaded area in Figure 1.1[1]. However, developed nations are found to have a high human development index at large ecological cost (mainly in the top region of Figure 1.1), and developing countries have low ecological impact (i.e. left of Figure 1.1) but need to increase their national welfare. In this context, the creation and implementation of renewable energy systems are promising to fuel the world's development at a low carbon cost.

Biomass-to-energy processes correspond to one kind of renewable energy systems. The conversion of biomass produces fuels which are considered CO_2-neutral as they recycle atmospheric carbon [154]. This is because the combustion of biomass cannot emit more CO_2 than that captured through photosynthesis (and/or fed to livestock). Conversely, combustion of fossil fuels increases GHG in the atmosphere as these belong to a geological cycle. Therefore, only the use of external fossil fuels in the production of bio-energy can contribute to atmospheric GHGs [155, 156].

Uncertainties in the availability of biomass (e.g.: energy crops, livestock manure), and their specific yields to energy, give rise to large variation in the predictions of potential biomass contribution to the energy supply (100 $EJ \cdot yr^{-1}$ to 400 $EJ \cdot yr^{-1}$ for 2050) [157]. For example, in 1998 biomass was reported to present the highest potential among all the renewable energy sources to

[1] Guatemala and the United Kingdom are marked in Figure 1.1 because dairy farms from these countries are utilised as case studies of Chapter 6.

diminish GHG emissions [158]. Conversely, a review of seventeen studies in 2003, Berndes et al. [157] concluded that bioenergy is still not sufficiently analysed to establish whether it is an attractive option for climate change mitigation. These contrasting results have continued to exist in the field today, where general conclusion on environmental benefits of bioenergy systems are pending.

Within biomass-to-energy systems, AD is a established technology that has been implemented for waste treatment since the 1880s in Europe [159]. This process has become an attractive bioenergy system for treatment of livestock waste as it can potentially tackle two sectors that contribute important GHG emissions: agriculture and energy. The agricultural sector is responsible for 37% of the global CH_4 emissions and 65% of the global N_2O emissions [160]. For energy production, the combustion of fossil fuels emits for 90.5% of total global CO_2 emissions [161]. In this context, and as response to increasing environmental policies [159, 162], research on AD has markedly

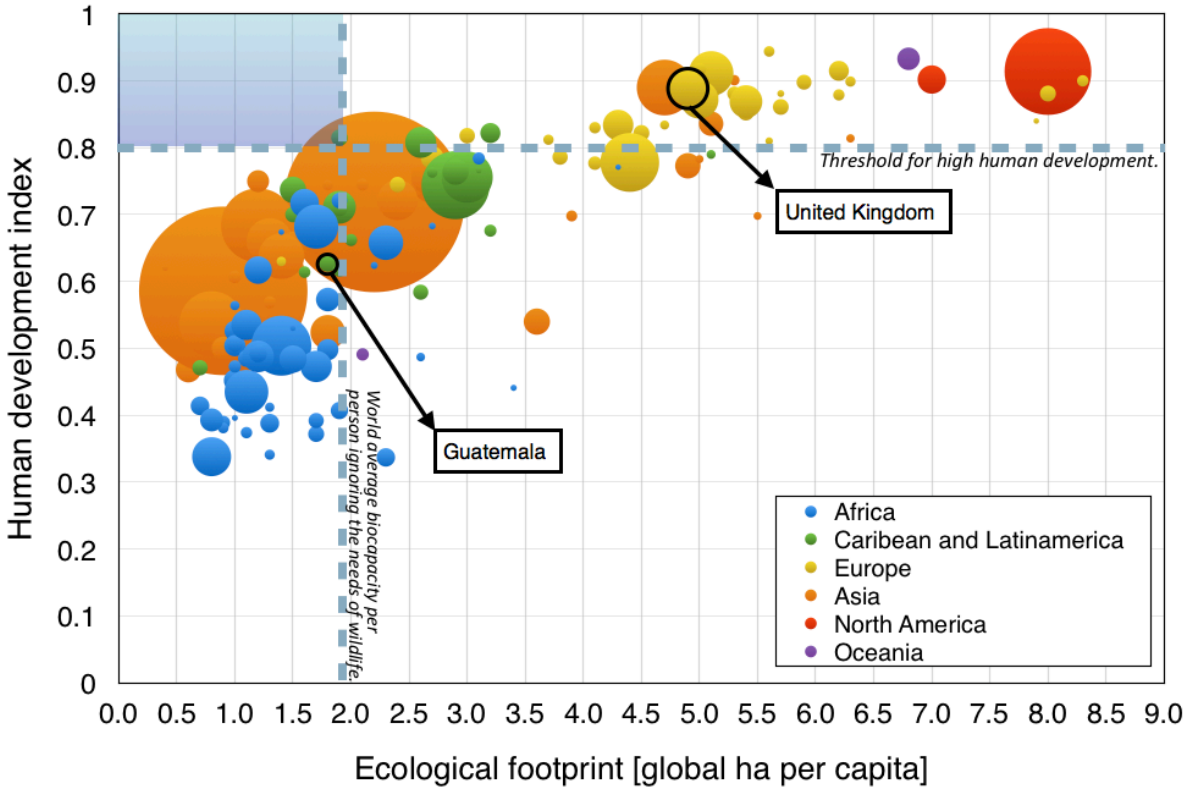

Figure 1.1: Bubble plot for countries according to their ecological footprint and human development index. Size of bubbles is given proportional to the population. Shaded area corresponds to sustainable ecological footprint and superior human development. Data from the United Nations Development Report [153] and the World Wildlife Fund and Global Footprint Network and Living Conservation [152].

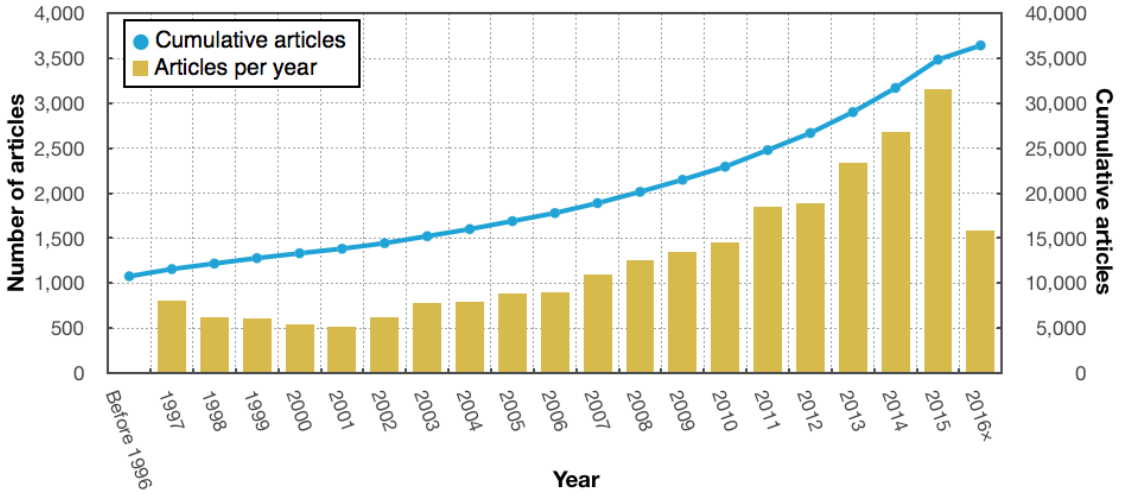

Figure 1.2: Publications covering AD in the last 20 years (source: www.sciencedirect.com, search words: "Anaerobic digestion"). *2016 includes articles from January to March of that year.

developed in the last 20 years, as shown in Figure 1.2.

The dairy sector is reported to contribute 4% of global anthropogenic GHG emissions [163]. Within these emissions, CH_4 from dairy farms have been reported to be the highest among livestock farms (35.5% of their total CH_4 emissions), for example, in a study of agricultural emissions in the fast-growing city of Beijing [138]. These emissions include CH_4 from enteric fermentation, which cannot be controlled by AD. However, using this process for manure management can contribute to the mitigate of fugitive CH_4 from stored and land-applied manure [159].

The application of AD as an organic waste treatment (minimising odours and waste volume) is based on a biochemical process [164, 165]. AD consists of a series of reactions carried out by microorganisms that result in biogas (mixture of CH_4 and CO_2). These require volatile solids (VS) in organic matter as input. The bacterial activity is a function of multiple variables such as temperature (typical mesophilic operating condition: 303-308 K), alkalinity (pH), moisture content and carbon/nitrogen ratio [166–168]. Therefore, the feedstock to the digester is an important factor which affects the CH_4 output [4, 169, 170].

Contrary to energy crops for AD, the application of this technology as manure management offers the following benefits; i) it is continuously available during the year (i.e. not season dependent); ii) it does not present a threat to food price as manure is a secondary product from food

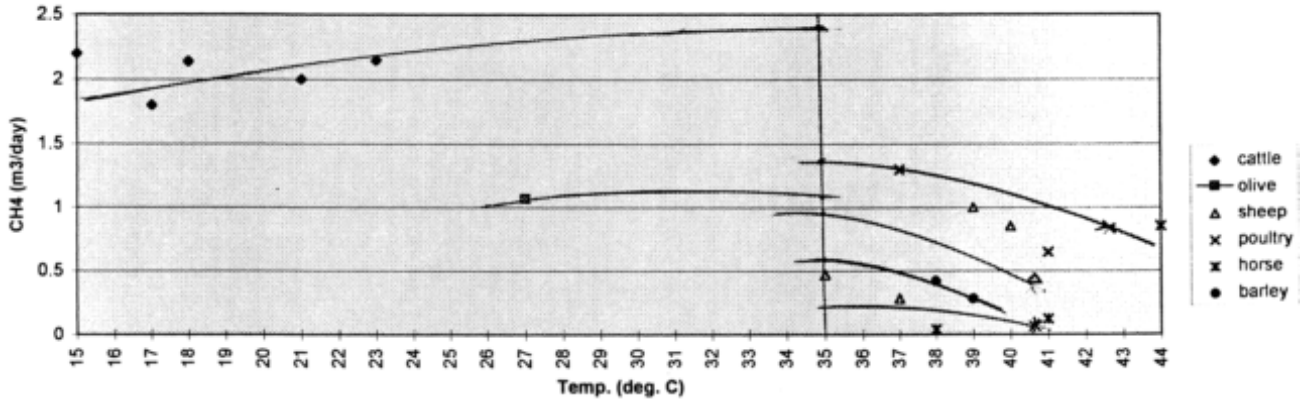

Figure 1.3: CH_4 production from AD of different feedstocks as function of digester temperature, reproduced from Hammad et al. [171].

production (e.g. not competing with milk and/or meat) and; iii) it extends the life-cycle of crops (e.g. grass) fed to livestock. Furthermore, energy systems based on crops have shown higher environmental impact with respect to manure-based pathways due to the intensive cultivation [145]. Compared to other feedstocks, the AD of cattle manure presents high potentials for the production of CH_4, as presented in Figure 1.3 (from Hammad et al. [171]).

The biomass material in the feedstock to digesters can be classified according to its organic composition such as lipid, protein and carbohydrate content [172]. A scheme of the main pathways for AD of these organic substances is proposed by Angelidaki et al. [169] and shown in Figure 1.4. As presented in Figure 1.4, CH_4 is produced in parallel to CO_2 by conversion of acetic acid via methanogenisis. Other gases, such as hydrogen (H_2), hydrogen sulphide (H_2S) and water (H_2O) are only present in small amounts ($\leqq$ 2vol.%) [172]. The gas mixture of CH_4 and CO_2 produced by AD is known as biogas and has typical volumetric composition of 65% CH_4 [159]. However, the detailed production and compositions of biogas are dependent on the Y_{CH4} of the feedstock[2] and the specific technology in place.

The combustion of the CH_4 (i.e. with global warming potential (GWP) of 25 $kg_{CO2e} \cdot kg_{CH4}^{-1}$) in the biogas releases carbon neutral CO_2 and usable energy [159, 172]. Thereafter, CH_4 from biogas offers a sustainable replacement of CH_4 from natural gas. The amount of useful energy that can be extracted from that CH_4 and its consequent offset of emissions, depend on the efficiency of the

[2]Section 1.4 examines this metric specifically for the AD of dairy cattle manure.

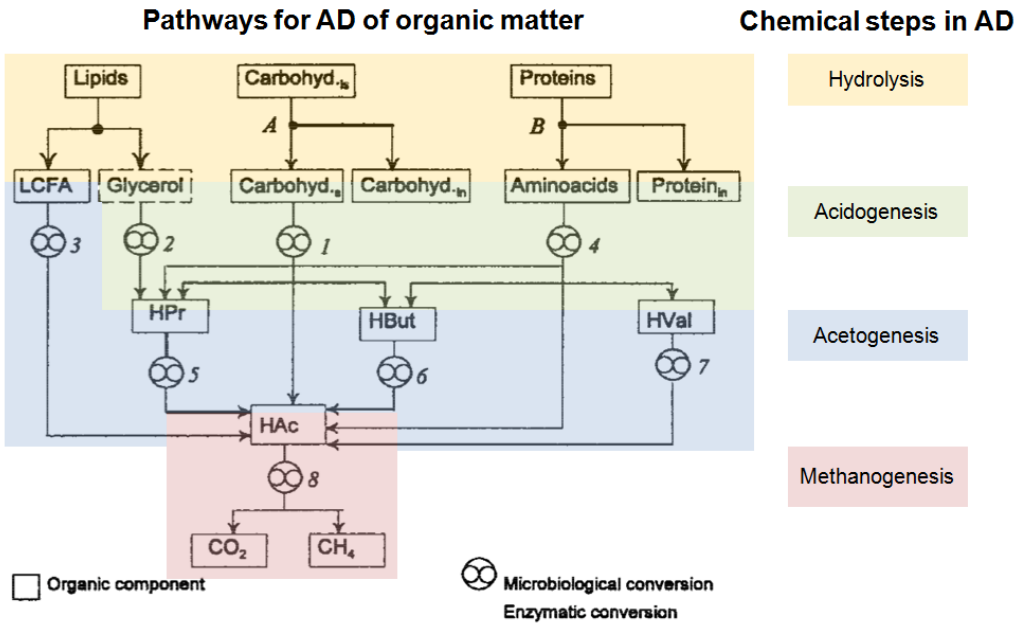

Figure 1.4: Steps in the organic matter anaerobic degradation reproduced from Angelidaki et al. [169]. LCFA: Long-chain fatty acids; HPr: Propionic acid; HBut: Butyric acid; HVal: Valerate; HAc: Acetic acid. Chemical steps on right added by author.

combustion technology in place. High-efficient and common combustion units are combined heat and power (CHP) generation [173, 174] and condensing boilers. Both are suitable for small-scale dairy farm operation [175] and can generate thermal power to heat digesters [175–177][3].

Additionally to biogas, AD offers farmers a management system for the excess nutrients in livestock manure (i.e. nitrogen and carbon species). AD can create another profitable product [178–180], which is the solid residue from the process and is called digestate. Digestate can be applied over crop fields replacing inorganic fertilisers or untreated manure. By replacing inorganic fertilisers, digestate can offset their high-embodied carbon [136, 181]. Compared to raw manure, digestate is reported to enhance fertiliser value of cattle manure because its nutrients are more suitable for crop uptake [182, 183]. There are also hygienic benefits from the digestate as it decreases the presence of infectious pathogens in comparison to the application of fresh manure to soils [184–186]. In terms of emissions, digestate potentially reduces CH_4 released with respect to untreated manure because it requires the collection of manure and removes part of its

[3]Refer to Chapter 6 for details on efficiency, calculation of energy production and of emission offsets.

VSs [14, 20, 120, 121, 123, 126, 131, 133, 141, 146]. After AD, thus, the storage of digestate has less carboneous species than the raw organic waste. The latter is reported [131] as an important source of GHG decrease by using AD.

Considering the above observations in the literature, it is possible to affirm that the implementation of AD for manure management in dairy farms holds the potential to reduce GHG emissions by i) converting high global warming CH_4 to CO_2; ii) generating energy that substitutes fossil fuels and; iii) producing digestate that replaces untreated manure and/or mineral fertilisers. Assuming that leaks from the digesters are minimised, thus, do not trade-off the mitigations of GHGs, the answer to the question in the title of this section "Can AD change GHG emissions?" seems to be answered. However, much more interesting question arises: "How much does AD change GHG emissions?" (i.e. with respect to non-AD/initial scenarios). This is the centre research question of this thesis, particularly, for the AD application in dairy farms. By building upon existing research, the answer to the key question is searched throughout this thesis by meta-analysis techniques. These enable the integration of evidence observed and reported by different authors in multiple scientific works. The combination of multiple findings increases the robustness of evidence, thus, enhanced estimations arise for the impact of AD on GHG emissions.

1.2 Methods to determine GHG emissions from dairy farms

Given the urgency to reduce anthropogenic GHG emissions (i.e. due to its relation to climate change), methodologies to estimate the changes in carbon footprint by implementing mitigation technologies are of great relevance. In this context, the effect of AD over GHG emissions from dairy farms are found, for example, within life-cycle analyses [16, 144, 146, 148, 150, 163, 187–191] and projects of the Clean Development Mechanism (CDM) [192–194]. Although much information is available, it is challenging to compare results given the different approaches. For example, the diversity in estimation methods is reflected in the multiple online carbon calculators [195–197].

This section introduces the underlying common methodologies to estimate GHG emissions

found in the existing literature. Typical methods to quantify overall GHG emissions from dairy farms are first presented. Thereafter, some frequent methods utilised for direct measurement of CO_2, CH_4 and/or N_2O are introduced.

In terms of procedures to determine and report carbon footprints from dairy farms (with and without AD systems), there are two frequent methods identified in the literature, as follows:

- The GHG Protocol Initiative 2011 [198]. This initiative is a partnership from the World Resource Institute and the World Business Council for Sustainable Development. Several important organisations (e.g. United States Environmental Protection Agency and the Climate Registry [199]) have adopted and implemented the GHG Protocol for GHG programmes and registries. The methods are based on the IPCC [151] and ISO standards, particularly focused on the evaluation of CO_2, CH_4, N_2O, hydrofluorocarbons, perfluorocarbons and sulphur hexafluoride of products and human activities. The GHG Initiative facilitates the implementation of its Protocol by providing models for specific sectors, for example, for the production of aluminium, iron and nitric acid. In its Protocol it is recommended to report direct emissions (scope 1), indirect emissions (scope 2) and optionally indirect emissions from other sources (scope 3). As an example of scope 3 emissions, Franchetti and Apul [200] indicate downstream emissions from management of solid waste and wastewater. Therefore, it should be noted that, although this protocol is widely applied for farm carbon footprints, the inclusion of emissions from manure after undergoing AD is not clearly mandatory.

- The Guidelines for National GHG Inventories from the IPCC [151]. Although these Guidelines are for country-scale inventories, their application for case studies is commonly found in the literature [20, 42, 123, 130, 131, 133, 134, 136] and considered to be the base for most standards and tools [200]. For example, the United States Environmental Protection Agency utilises these Guidelines specifically to quantify CH_4 emissions from manure-related systems [201]. The IPCC Guidelines [151] have three methods (hereafter referred to as "Tiers") for the estimation of emissions from livestock manure. The application of a specific Tier methodology depends on: i) the importance of the sector for national GHG inventories and; ii) the level of details available from the farms. For example, the Tier 1 methodology re-

quires the livestock population (N_c), animal specie/category (i.e. "dairy cattle" for this work) and climate region/temperature, while supplying default emission factors (EF). The Tier 2 methodology, requires animal characteristics (e.g. weight), specifications on the manure management practice (e.g. 50% of the manure is directed to an AD and the rest spread on crop fields). From this information, EFs per animal category are calculated. If information is missing to complete a Tier 2 assessment, default parameters are given in the guidelines. Finally, the Tier 3 methodology encourages countries to develop their specific EFs.

Other protocols such as the standards from the ISO 14000 certification are also utilised as base for life-cycle assessments. However, their specific standard to evaluate carbon footprints (ISO/TS 14067:2013 [202]) is only from 2013. Thus, the literature implementing this standard is less available than the IPCC Guidelines and/or GHG Protocol, mentioned above. Based on the initial ISO 14000 certification, the British Standards Institute 2011 reports the Publicly Available Specification (PAS 2050) for carbon footprint of products [200]. Although, the PAS 2015 offers more specific methods than the initial ISO protocol, it is found that the application of the former is not common in the research literature.

Although all previous protocols are applied to quantify GHG emissions from dairy farms, their application can be very different depending on system boundaries (e.g. cradle-to-grave, cradle-to-gate), functional units ([f.u.], e.g. emissions per litre of milk produced, annual tons of manure excreted by livestock and hectare of slurry-application) and assumptions (e.g. efficiencies, yields, farm-related operations). Therefore, even when similar studies focus on determining the effect of AD over GHG emissions, it is difficult to quantitatively compare results and draw general conclusions. This is a gap, which is addressed by meta-analysis techniques in this thesis.

In terms of methods found for determining the direct emissions from specific dairy farm activities, these are mostly associated with experimental work. In this respect, there are particularly two methods identified to be repeatedly reported to quantify the emissions from untreated manure and/or digestate:

- Chamber techniques to measure CO_2, CH_4 and/or N_2O fluxes directly emitted from organic residues [121, 149, 203–206]. This empirical setup for measuring GHG emissions is com-

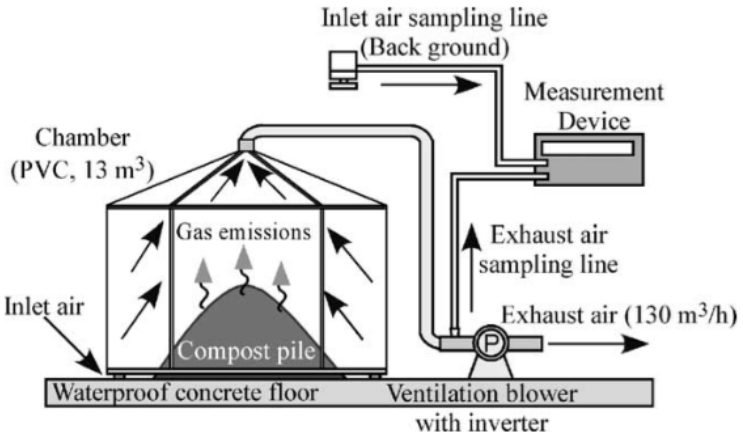

Figure 1.5: Typical experimental setup for measurement of GHG emissions from organic residues using the dynamic chamber technique, reproduced from Fukumoto et al. [203].

monly implemented at pilot scale. It consists of an enclosed space where the organic substrate is placed. The chamber has a continuous vertical circulation of a purge gas to evacuate the GHG of interest (see Figure 1.5 reproduced from Fukumoto et al. [203]). In this way GHGs released from organic waste are directed to a measuring device for sampling.

- Soil incubation. This experimental technique consists of incorporating organic residues (e.g. digestate, compost or untreated manure) to soil in strictly controlled and thus, reproducible procedure. In particular, several studies in the literature [117, 118, 129, 137, 139, 207] utilise laboratory scale soil incubation to measure GHG emissions while fixing soil mass, moisture, pH and/or temperature.

Another experimental setup markedly present in the literature for analysis of AD of dairy cattle manure is the biochemical potential tests. This is revised in Section 1.4, as it is utilised for determining maximum yield potential of a substrate, rather than emissions.

1.3 IPCC methodology applied in dairy farms

Most methods in the literature [20, 42, 123, 130, 131, 133, 134, 136] evaluate the carbon footprint of dairy farms based on the IPCC guidelines [151]. To illustrate the application of these guidelines, this section presents the recommended equations to estimate emissions from dairy farm activities which can be affected by the implementation of AD[4]. The calculations presented in this section correspond to the Tier 2 methodology of the IPCC Guidelines. These are adapted to assess exclusively the CH_4 and N_2O emissions from farms with only dairy cattle.

CH_4 emissions from manure management. To estimate the annual CH_4 released into the atmosphere from untreated manure, the Tier 2 adapted calculation is [151]:

$$\underset{[kg\cdot yr^{-1}]}{CH_{4,i}} = (N_C \cdot VS_{Ex}) \cdot \left[B_0 \cdot 0.67 \cdot \frac{MCF_i}{100} \cdot MS_i \right] \tag{1.1}$$

where N_C is the number of dairy cattle in the farm, VS_{Ex} is the annual volatile solids excreted by dairy cattle in $kg_{VS} \cdot hd^{-1} \cdot yr^{-1}$, B_0 is the maximum methane potential for manure from dairy cattle in $m^3_{CH_4} kg^{-1}_{VS}$, 0.67 is the density of CH_4 at standard conditions (in $kg \cdot m^{-3}$), MCF_i corresponds to the methane conversion factors for manure management system "i", MS_i is the fraction of manure handled in the "i" system. If default values are required for B_0, VS_{Ex}, MCF_i and MS_i these can be found in Table 10.A-4 of the IPCC Guidelines [151]. The latter two depend on the manure management system in place, which are categorised by the IPCC (Table 10.18 of the Guidelines [151]) and can be separated according to the dairy farm activities as shown Table 1.1.

Particularly, for CH_4 emitted from storage tanks of digestate, the IPCC suggests to utilise MCF_i values in Equation 1.1 equivalent to liquid storage (Formula 1, Table 10.17 [151]) if there is no gas tight covers. This indicates that specific EFs for CH_4 emissions from digestate are not available. A gap is therefore identified given that AD changes the composition of untreated manure, thus, the emissions from digestate are expected to be different from the original substrate.

In terms of CH_4 leaks from operating digesters ($CH_{4,L}$), the IPCC method recommends to

[4]Emissions from enteric fermentation are, therefore, not considered in this section (i.e. not affected by the implementation of AD).

Table 1.1: Selected[a] manure management systems according to IPCC (Table 10.18 [151]).

Operation unit[b]	**System defined in the IPCC Guidelines.**
Storage of manure/digestate.	Dry lot.
	Liquid/Slurry.
	Uncovered anaerobic lagoon.
	Pit storage below animal confinements.
Field-application of manure/digestate.	Pasture/Range/Paddock.
	Daily spread.
	Solid storage.
Digester operation	Anaerobic digester.

[a]Other systems are not affected by AD, thus not mentioned.

[b]Defined for this work (details in Chapter 3).

calculate these assuming that 10% of the produced CH_4 is lost. Considering that the potential production of CH_4 can be calculated based on Equation 1.1 (assuming maximum CH_4 conversion, $MCF_L = 1$), the digester leaks can be estimated as:

$$CH_{4,L}[kg_{CH4} \cdot yr^{-1}] = N_C \cdot VS_{Ex} \cdot B_0 \cdot 0.67 \cdot 0.10 \tag{1.2}$$

It is observed that for the calculation of CH_4 emissions from manure or digestate handling, the metric which is associated to the performance of the AD of dairy manure is the yield to CH_4. In particular, the maximum methane yield (B_0) depends on the manure composition. However, there are different protocols to determine the B_0[5] and the default values in the IPCC Guidelines are based on a limited sample size. Therefore, part of the meta-analysis of this research work supplies more evidence-based B_0.

N_2O emissions from manure management. N_2O emissions from storage of raw manure are not specified in this section as: i) they are considered negligible, having emissions factors of 0 or 0.02 in the IPCC Guidelines (Table 10.21 [151]) and; ii) there is evidence to suggest that there is no changes in these emissions attributable to AD [6].

In terms of other farm activities, direct N_2O emissions released from field application of slurries are considered because they are an important by-product of nitrification and denitrification [208,

[5]These procedures are covered in Section 1.4.

[6]Furthermore, the meta-analysis results in Section 5.3.3.2 indicate no significant difference in the emissions of N_2O between stored manure and digestate.

209] occurring in cattle manure applied on fields. The specific sources, according to the IPCC, are nitrogen input to the soil ($N_2O - N_{input}$), managed organic soils ($N_2O - N_{OS}$) and urine/dung inputs by grazing animals ($N_2O - N_{PRP}$). The summarising equation found in the IPCC Guidelines to account for these source is Equation 11.1 [210]:

$$\underset{[kg \cdot yr^{-1}]}{N_2O_F} = \frac{44}{28} \cdot ([N_2O - N_{input}] + [N_2O - N_{OS}] + [N_2O - N_{PRP}]) \tag{1.3}$$

where the fraction $\frac{44}{28}$ is used for conversion of N_2O-N emissions to N_2O for reporting purposes (in $kg_{N2O} \cdot kg^{-1}_{N2O-N}$) [210]. To reduce Equation 1.3 for the application of interest it is assumed that nitrogen in crop residues on field and minerals in the soil (before field-application of slurries) are not affected by AD. Thus, emissions from crops and soil are not accounted. Implementing these assumptions, reduces the first term of Equation 1.3 in the IPCC Guidelines [210], $N_2O - N_{input}$, to the following expression:

$$\underset{[kg \cdot yr^{-1}]}{N_2O - N_{input}} = (F_{ON} \cdot EF_{F1}) \tag{1.4}$$

where EF_{F1} is the emission factor of value 0.01 $kg_{N2O-N} \cdot kg^{-1}_{N\,input}$ (Table 11.1 [210]) and F_{ON} is the annual amount of animal manure or organic nitrogen added to soil (other than by grazing animals) in $kg_N \cdot yr^{-1}$. The latter is estimated assuming that no manure is available for feed, fuel or construction (i.e. all for field application) as follows:

$$F_{ON} = N_C \cdot N_{ex} \cdot MS_{F1} \tag{1.5}$$

where Nex is the annual average nitrogen excretion per dairy cow in $kg_N \cdot hd^{-1} \cdot yr^{-1}$ and MS_{F1} is the fraction of manure applied to field from the total manure excreted by cattle. It should be noted that the IPCC Guidelines consider the application of animal manure, sewage, compost and other organic amendments. Thus, estimates for N_2O emission from digestate applied for soil amendment are not specified.

The second term of Equation 1.3 depends on the soil type, thus, it is not affected by AD and are not accounted in this work. Finally, for $N_2O - N_{PRP}$ emissions in Equation 1.3, the deposit of grazing cattle is considered and can be estimated as:

$$\underset{[kg \cdot yr^{-1}]}{N_2O - N_{PRP}} = (F_{PRP} \cdot EF_{F2}) \tag{1.6}$$

where EF_{F2} ($EF_{3PR,CPP}$ in Table 11.1 of the Guidelines [210]) is the emission factor for dairy cattle and is 0.02 $kg_{N2O-N} \cdot kg_N^{-1}$. F_{PRP} is the annual amount of urine and dung nitrogen deposited by grazing animals and estimated as (Equation 11.5 of Guidelines [210]):

$$F_{PRP} = N_C \cdot N_{ex} \cdot MS_{F2} \tag{1.7}$$

where MS_{F2} is the fraction of annual dairy cattle excretion deposited on pasture, range and paddock.

From the above expressions for $N_2O - N_{input}$ and $N_2O - N_{PRP}$, Equation 1.3 is simplified to:

$$\underset{[kg \cdot yr^{-1}]}{N_2O_i} = \frac{44}{28} \cdot N_C \cdot N_{ex}(MS_{F1} \cdot EF_{F1} + MS_{F2} \cdot EF_{F2}) \tag{1.8}$$

It is noted that the expression includes as first term the fraction of manure applied on fields as part of a management system and the second term is the fraction corresponding to grazing animal. Only the EFs vary between both terms, and from their values it is observed that the the field-application by animals emits more N_2O (by unit of applied nitrogen).

Another important observation of the IPCC methodology is that whilst EFs are readily available (for different Tier methods) for untreated manure systems, they are not for AD scenarios. In particular, CH_4 and N_2O estimations are not specific for storage or field-application of digestate. This is a gap that is addressed by the meta-analysis of the changes in GHG emissions in Chapter 5.

1.4 Methane yields (Y_{CH4}) for AD of dairy cattle manure

Previous sections highlight the importance of methane yields (Y_{CH4} or maximum yield B_0) for the estimation of CH_4 emissions (Equation 1.1) from manure management systems and energy production from AD systems. Therefore, to accurately assess dairy farm emissions, it is necessary to have Y_{CH4} based on strong evidence. As a first step to review how studies in the literature approach the estimation of Y_{CH4} in the dairy sector, this metric is defined (at normal conditions, 273 K, 101.3 kPa) as:

$$Y_{CH4}[m^3_{CH4} \cdot kg^{-1}_{VS}] = \frac{Amount\,of\,CH_4\,produced}{Amount\,of\,VS\,fed\,to\,digester} \tag{1.9}$$

where the denominator corresponds to the VS in the raw manure used as input feedstock for the digester. To determine Y_{CH4}, modelled and experimental work is found in the literature.

Within the modelled work, white-box models are based on chemical and physical fundamentals [169, 211, 212]. These models, for example, serve to determine rate-limiting steps of AD. Some white-box models found in the literature for AD of dairy manure focus on the optimisation of Y_{CH4} through the identification of microbial communities involved [213–215]. More recent approaches have included the genetic analysis of bacterial consortiums [16]. However, a limitation is the large number of parameters required to input to these models and that are often not readily available for continuous AD operations [4]. Thus, although their application for understanding AD microbiology is very valuable, direct application in AD systems requires major computational resources. For example, specifically for livestock manure, Garcia-Ochoa et al. [216] reported a high precision kinetic model. The model relies on the online data-acquisition of an AD plant with continuous elemental analysis.

Black-box models are more dominant [50, 65, 67, 71, 117, 217–220] to predict Y_{CH4}. They are based on determining correlations with respect to input variables to the AD systems. For example, there are black-box models that estimate Y_{CH4} based on organic composition (i.e. fat, protein, carbohydrate and content in the raw manure) [67, 220] or chemical oxygen demand (COD) [117, 221]. For cattle manure, Otero et al. [71] reported that organic matter conversion can be estimated

using its activation energy obtained through thermogravimetric techniques. Another black-box model, from Linke et al. [50], presents Y_{CH4} as function of hydraulic retention time (HRT).

Grey-box models combine a partial theoretical structure with input data. This is the case of an important theoretical model for maximum Y_{CH4} (B_0) which is the Buswell's equation (1930s) [217, 218]. The equation is based on the elemental chemical composition of a substrate undergoing AD and the stoichiometry of the degradation reaction [217, 218]:

$$\begin{aligned} C_nH_aO_bN_c + \left(n - \tfrac{a}{4} - \tfrac{b}{2} + \tfrac{3c}{4}\right) H_2O \\ \rightarrow \left(\tfrac{n}{2} + \tfrac{a}{8} - \tfrac{b}{4} - \tfrac{3c}{8}\right) CH_4 + \left(\tfrac{n}{2} - \tfrac{a}{8} + \tfrac{b}{4} + \tfrac{3c}{8}\right) CO_2 + cNH_3 \end{aligned} \tag{1.10}$$

where $\{n, a, b, c\}$ are stoichiometric coefficients used for balancing the equation. Although the Buswell's equation is still commonly applied for dairy cattle manure [65, 219] to predict the maximum Y_{CH4}, experimental values are lower because not all-organic material converts to biogas (e.g. non-degradable solids, inhibition of reaction and/or higher selectivity to new biomass instead of biogas). Thus, utilising theoretical Y_{CH4} can over-estimate CH_4 production for AD scenario.

Within experimental works to determine B_0 from a particular biomass, the biochemical methane potential test is commonly reported in the literature[7]. The test consists in mixing the organic substrate of interest with an inoculum in a batch system, measuring the production of biogas and quantifying the cumulative methane produced from the system until its production ceases. The most common methodology followed to perform biochemical methane potential tests is that from Owen et al. [222]. However, there is no standard procedure agreed upon in the research literature [219], hence different inoculum, temperature conditions, types of digesters are reported with limited comparability [221]. In this respect, Stroemberg et al. [223] reports the elimination of systematic errors caused by the experimental conditions of biochemical methane potential tests. The authors include standardisation of environmental factors which affect the gas measurements[8].

An important source of B_0 for dairy farm assessments (e.g. life-cycle-analysis of milk) are the IPCC Guidelines. In general, these recommend to use B_0 default value 0.24 $m^3_{CH4} \cdot kg^{-1}_{VS}$ for de-

[7]Results from meta-analysis of Y_{CH4} in Chapter 4 will shows the number of cases to support this.

[8]The diverse procedures for biochemical methane potential test are an indication that the random-effect model for meta-analysis of B_0 is preferable to the fixed-effect model (see Chapter 4).

Table 1.2: Methane yield (Y_{CH4}) for dairy cattle farm manure.

Experimental details	$Y_{CH4}\,[m^3_{CH4}/kg_{VS}]$	[Ref.]
0.001 m^3, batch digester, 311 K, (Austria)[a].	0.137 0.132 0.166 0.143 0.126 0.159	[4]
0.002 m^3, batch digester, 308 K, (Finland)[b].	0.233 0.204	[115]
3×10^{-4} m^3, CSTR[c] digester, 308 K, (Austria).	0.340	[121]
0.02 m^3, CSTR digester, 308 K, (Finland).	0.100	[228]
0.018 m^3, CSTR digester, 308 K.	0.240	[115][b]
0.12 m^3, CSTR, 308-310 K.	0.220	[115][b]
0.002 m^3, CSTR, (no temperature reported).	0.107	[115][b]

[a] Values differ due to different diets for dairy cattle considered in experiments [4]. [b] Values differ due to different retention times in digesters [115]. [c] CSTR is continuously-stirred tank reactor/digester.

veloped nations and 0.13 $m^3_{CH4}\cdot kg^{-1}_{VS}$ for developing countries (i.e. regions of the world). These values arise from the works of Safley [151, 224] and Morris et al. [151, 225] and are based on the diet of dairy cattle in 1976-1992. A re-assessment of these values is essential to capture more recent findings and increase the sample size with respect to that of the IPCC. Furthermore, work in the literature [226, 227] show markedly different outcomes of B_0 with respect to these important Guidelines. In this respect, Matulaitis et al. [226] reports that methane production for cattle manure are from 13% to 36% lower than the default values recommended for Europe in the IPCC Guidelines. Similarly, Chung et al. [227] discusses the underestimation of CH_4 emissions by following the prescribed IPCC methodology in dairy farms in New Zealand. Amon et al. [121] is also a critic of the default values of the IPCC B_0, which they describe to not comprehensively include the wide variation of yields. Additionally, the latter work also presents gaps in the default CH_4 conversion factors from the Guidelines, which are only based on expert judgement [121], rather than clear scientific methods.

In the case of experimental work measuring Y_{CH4} different than the biochemical methane po-

tential test, further diversity in methods and results are found. As an example of this, Table 1.2 presents Y_{CH4} of AD of dairy cattle manure from different sources. Observing this sample from the literature, a large range in Y_{CH4} yields is observed (0.100 to 0.340 m^3_{CH4}/kg_{VS}), but an underlying tendency is difficult to identify given the different experimental conditions.

Meta-analysis can facilitate the collection of information and its mathematical integration, necessary to draw more robust conclusions from a larger sample than that of Table 1.2. There is abundant literature covering Y_{CH4} from different research perspectives. By combining the findings from different authors, better estimates of CH_4 emissions and energy potentials of AD systems can be achieved. Therefore, the following section presents meta-analysis as a technique to systematically and numerically bring together evidence in the literature to provide robust values for Y_{CH4} and the changes in GHG emissions from dairy farms caused by AD.

1.5 Meta-analysis to improve robustness of results

To increase the robustness of methods to estimate GHGs from dairy farms, this work incorporates cumulative (and systematically selected) evidence from research literature to existing methods. In particular, the procedures to estimate the effect of AD of cattle manure over GHGs. In this context, meta-analysis techniques are utilised throughout the thesis to answer to the question "How much does AD change GHG emissions [from dairy farms]?" (as introduced in Section 1.1). The estimation of these emissions is found in multiple results in the literature [120, 121, 134, 136, 183, 188, 190, 191, 229–236]. It is, however, difficult to compare the diverse methodologies, units of measurements and/or system boundaries to provide general conclusions on the true mitigation potential of AD in dairy farms. To contribute clarity in the research of AD, meta-analysis can synthesise the quantitative findings in the literature. Therefore, the key issue of this thesis is to numerically combine the reported evidence to provide a more robust methodology, thus, a better assessment of dairy farms implementing AD.

Meta-analysis techniques are traditionally from the medical sciences. The first systematic synthesis of research findings by Karl Pearson in 1904 [237] determined that vaccination was inef-



Figure 1.6: The hierarchy of evidence (based on Jonas [241] and Rosner et al.[242]).

fective against typhoid fever by combining different trials. More formally, in 1976, Gene Glass [238, 239] presented the practical steps for a cumulative and systematic analysis of scientific results, which he named meta-analysis. From then, meta-analysis has been widely accepted and recognised as a higher-level of evidence in scientific findings (as presented in Figure 1.6). Today, in the "Era of the big data" [240], there is a continuous growth in availability and storage of information. Therefore, powerful statistical tools as meta-analysis can enable comprehensive numerical synthesis of increasing datasets.

In closer relation to this thesis, meta-analyses are reported in the literature for life-cycle indicators. For example, the Journal of Industrial Ecology published the special issue (2012) "Meta-Analysis of Life Cycle Assessments" [243]. Therein contained are meta-analyses that evaluate the emissions of low-carbon energy systems such as: solar [244, 245], wind [246] and nuclear [247]. A major project that also examines the application of meta-analysis for environmental aspects of energy systems from the National Renewable Energy Laboratory [248–250]. It initiated in 2012 and is called the Life-Cycle Analysis Harmonisation Project. The latter performs meta-analyses of wind, solar, geothermal, ocean, hydropower, coal, natural gas and nuclear forms of energy. However, bioenergy systems such as AD are still not included.

For life-cycle indicators of bioenergy systems, more qualitative (i.e. literature reviews [182, 183, 251]) and semiquantitative analyses are reported [249]. Within the limited meta-analyses in the field, a pioneering work is that of Farrell et al. [252]. In that work, six conflicting studies

are combined to identify that corn ethanol provides modest (≈13%) GHG emission reductions compared to conventional petroleum. Others [253–255] have also applied meta-analysis to the bio-energy sector to quantify GHG emissions, but to the author's knowledge no GHG meta-analysis has covered AD in dairy farms. Only one meta-analysis [256] exist for AD of dairy manure, however, it focus on different aspects of the process (i.e. microbial communities). Thus, the application of meta-analysis for GHG emissions is a novel contribution to the field.

To further highlight the advantages of meta-analysis with respect to other works in the literature, Sections 1.5.1 presents the key benefits with respect to other types of research works. Thereafter, Section 1.5.2 present basic step to perform a meta-analysis.

1.5.1 Benefits of meta-analysis

This section shows the main benefits of applying meta-analysis as a tool to make more robust estimates in statistics and, particularly, to quantify the effect of AD on GHG emissions from dairy farms. Meta-analysis presents advantages which are identified with respect to null-hypothesis tests, individual studies and literature review, as follows:

- **Null-hypothesis tests.** In statistics, null-hypothesis tests measure how likely results can be provided by chance (e.g. from a standard distribution) or can be attributed to a phenomena of interest. P-values are output of these test and will indicate if a null-hypothesis is rejected or not [257]. Applying null-hypothesis tests to the key issues of this thesis, would provide an answer to the question "Can AD change GHG emissions from dairy farms?" (see Section 1.1). Conversely, meta-analysis outputs numerical results answering to the more interesting question "How much does AD [in dairy farms] affect GHG emissions?". Meta-analysis quantifies an effect size (e.g. GHG emissions), errors and confidence intervals, rather than only reporting P-values to showing if there is an effect or not [257, 258].

- **Individual studies.** The benefits of increasing by meta-analysis is described by Hunt in the book "How Science Takes Stock. The Story of Meta-Analysis" [239], as follows:

  > "Known as meta-analysis, it is a means of combining the numerical results of studies with disparate, even conflicting, research methods and findings; it enables researchers to discover the consistencies in a set of seemingly inconsistent findings and to arrive at conclusions more accurate and credible than those presented in any one of the primary studies." (Hunt 1997)

  In the case of the effect of AD in dairy farms on GHG emissions, there is increasing evidence found in the literature that addresses this topic (see Section 1.1). These works may approach similar research questions, but not necessarily use the same methodologies. Meta-analysis can convert primary data into comparable metrics and reconcile results of individual articles and methods.

- **Literature reviews.** These type of cumulative studies largely report qualitative assessments of the literature. In particular, for biogas generation from dairy farms, qualitative reviews are dominant [182, 183, 251, 259]. Literature reviews have the disadvantage (with respect to meta-analysis) of not presenting replicable methodologies for the selection of primary sources. Thus, the inclusion of articles in a literature review does not comply with the scientific method and can be subject to an author's biased view. Meta-analysis can provide un-biased reproducible results by detailing a systematic search(es) of articles and methods to extract, standardise and combine numerical results.

1.5.2 Steps for meta-analysis

There are five main steps to perform a meta-analysis, as identified by Hunt [239], as follows:

1. **Formulate problem.** This step comprises setting the key issue addressed by meta-analysis and its scope. For this thesis the key issue to address by meta-analysis is the quantification of changes in GHG emissions as a consequence of AD implementation for manure treatment in dairy farms (see Section 1.1).

2. **Collection of primary sources.** The systematic search of studies is an essential step in meta-analysis. The challenge is to provide reproducible findings (e.g. articles) from the search of an increasing literature. To support this within the academic literature, today's on-line search engines (e.g. ISI Web of Knowledge and Google Scholar) can provide reliable and reproducible findings.

3. **Evaluate the data.** Following the systematic finding of works, it is necessary to select those related to the key issue of the meta-analysis. For this, the definition of criteria is required to assess and select primary sources. Thereafter, the extraction and organisation of the relevant data is carried out. The development of databases are key in this step to enable efficient access to the data in the mathematical processing-steps to follow.

4. **Synthesise the data.** This step comprises the standardisation and numerical combination and analysis of the data collected. Standardisation is required to enable results from different studies to be combined in common distributions. The analysis of those distributions (e.g. by meta-analysis models or cluster analysis) enables the interpretation of general sources of agreement or differences, identification of tendencies, outliers, among others.

5. **Present the findings.** The report of meta-analysis methods and results is essential to allow researchers to build upon the findings and/or replicate them. As for most scientific work, this step displays the work and is the tangible contribution to the research field.

These meta-analysis steps are utilised to improve the estimates of GHG emissions from dairy farms (with and without AD). The following section presents the application of these steps within the roadmap of the thesis to answer specific research questions.

Chapter 2

Research approach

This Chapter presents the research approach of the thesis, which address the issues observed in Chapter 1. As presented in the previous chapter, existing estimates of the energy output (i.e. methane yields, Y_{CH4}) and GHG emissions from dairy farms can be enhanced by meta-analysis. In fact, the robustness of default values of Y_{CH4} in the main GHG-estimation methodology (IPCC Guidelines) can be considerably improved by expanding the sample size (i.e. only two studies are considered in the Guidelines) through meta-analysis, which can bring together the abundant evidence in the literature. Another important aspect shown in Chapter 1 is that the emissions from digestate (i.e. anaerobically treated manure) are not strongly addressed in GHG reporting protocols and farm assessments, although evidence suggests that they are markedly different than those emissions from raw manure.

Chapter 2 builds on these observations and gives an overview of the methodology (and structure) of the thesis. Given that the key issue is to improve existing methodologies to quantify the effect of AD over emissions, the first step is to determine how to measure this effect. Section 2.1 addresses this by considering that the effect of AD over emissions is quantified as the change in emissions between standardised baseline and AD scenarios. In particular, this section defines dairy activities (i.e. operation units) in the scenarios which change their emissions due to the implementation of AD. Thus, the boundaries of each scenario are defined. In addition, the importance of the methane yield within the scenarios is highlighted, as a key metric for the calculation of CH_4

emissions (from both scenarios) and production. Having an overview of how the effect of AD is evaluated in the meta-analysis, the second step is to develop a systematic (i.e. reproducible) search to collect academic articles reporting emissions from the standard baseline and AD scenarios[1]. The statistical tests that follows (in the third step) tackle the specific research questions of the thesis. Therefore, Section 2.2 introduces these specific research question, explains their rationale and, ultimately, the roadmap to address them throughout the thesis is set. Ultimately, the answers to these questions (i.e. the output of the meta-analyses) converge in a novel methodology to estimate the change in emissions in dairy farms. The application of that methodology is presented in four case studies (Chapter 6).

The final section of this chapter (Section 2.3) shows how answering those specific questions result in contributions to the field (i.e. author's publications).

2.1 Scenarios to evaluate the changes in emissions

To enable the evaluation of the effect of AD over GHG emissions while being able to compare results from different articles, two scenarios and seven operation units are defined (see Figure 2.1). The baseline scenario (Figure 2.1, red box) represent typical farm activities and are used as a reference to estimate the changes in emissions once AD is in place. Complete baselines are conformed by the emissions from three operation units: storage and field application of untreated manure and; energy consumption for dairy activities. The AD-scenarios (Figure 2.1, blue box) take into account the AD operation plant, power generation and digestate management.

There are indirect emissions related to the milking and farm operation unit (Figure 2.1, block A.) which form part of both scenarios. In the baselines, energy is imported from different sources (e.g. electricity grid, on-site combustion of fossil fuels), depending on the article. In this work, the emissions from energy requirements are estimated based on the consumption of natural gas.

In the AD scenarios, additional energy is required for the operation of pumps, mixing and heating of the digester (Figure 2.1, block D.), electricity and/or thermal power is generated (Figure

[1]Details of the systematic search are provided in Chapter 3.

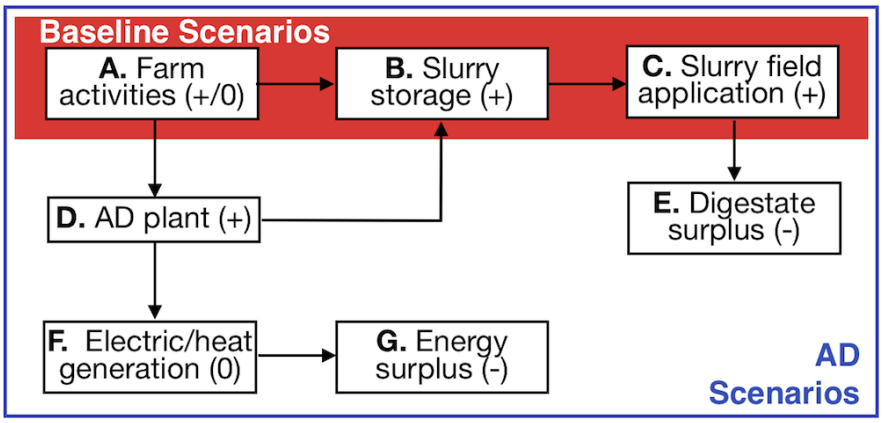

Figure 2.1: Block diagram of material paths for the baseline scenarios (red box) and AD scenario (blue box) through operation unit (black boxes). The signs in the operation units indicate if the process: directly emits GHGs ('+'); can offset GHGs outside the scenario boundaries ('-') or; is considered to have carbon neutral emissions ('0').

2.1, block F.) and surplus energy can be exported (Figure 2.1, block G.). The energy produced and used for farm activities (Figure 2.1, blocks A. and E.) is considered carbon neutral[2] and the export energy, is assumed to replace that energy from natural gas (Figure 2.1, block G.), thus having negative emissions. If papers do not report surplus energy for the AD-scenario, these are calculated by mass and energy balances. Conversely, if not enough energy is produced in the AD scenario to cover milking, farm activities and/or digester requirements, it is assumed to be imported as for the baseline scenario. A final indirect emission source is the operation unit describing digestate surplus for export (Figure 2.1, block E.). This can also allow negative emissions due to the replacement of high embodied-carbon mineral fertilisers [181].

Direct emissions arise from storage (Figure 2.1, block B.) and field application (Figure 2.1, block C.) of slurries in both scenarios. The emissions from these operation units are used to determine changes in GHG emissions when replacing untreated slurry by digestate. Direct missions from the digester (leaks) are also accounted (Figure 2.1, block D.).

Transport is not considered because studies that compare transport emissions from both scenarios are expected to be scarce because the distances from farm to fields are irrespective of the slurry type (untreated or digested). Moreover, a preliminary examination of the articles found in

[2]Bio-energy processes are considered carbon neutral because they are fuelled by renewable sources. Therefore, the CO_2 emitted is part of a shorter carbon cycle, with respect to that from the combustion of fossil fuels. Section 1.1 introduces to this benefit bio-energy systems.

the literature shows that emissions from transport are only reported for individual scenarios. For example, Fantin et al. [188] included transport emissions for a typical baseline dairy farm and the work by Poeschl et al. [260] report transport emissions from an AD-scenario.

The central aspect in this thesis of the scenarios is the AD plant operation unit. Given that the performance of the digesters will dictate the offset of fossil fuels, a key indicator of that performance is considered: the methane yield. In addition, this metric is essential for the estimation of emissions from untreated slurries (baseline scenario, blocks B. and C.). However, as presented in Chapter 1, the IPCC Guidelines only used a small sample size (and updated sources) to provide Y_{CH4}. Therefore, as a preliminary step, the assessment through meta-analysis of these Y_{CH4} is considered.

2.2 Specific research questions and thesis outline

The thesis objective is segmented in specific research questions in this section. It is herein explained, how each chapter of this work addresses these specific questions. Given that the general objective of the thesis is to improve the current methodologies to quantify the effect of AD of cattle manure on GHG emissions from dairy farms, this chapter introduces different methods to determine Y_{CH4} and GHGs from dairy farms in the literature. Additionally, the Chapter covers the potentials of meta-analysis techniques to improve these estimates. Following the above, a first challenge for the application of meta-analysis, is to systematically collect results from the literature in a reproducible and non-biased manner. This issue raises the first specific research question to address:

What is the best data structure to capture the required information for the meta-analysis?

Chapter 3 answers this question by providing a structured methodology to create a novel database. Databases of life-cycle inventories (e.g. Ecoinvent, EioLCA), are not utilised because they are based on pre-established fixed parameters (e.g. AD technology, operation temperature, Y_{CH4}). In addition, the output values from these sources are reported without robust confidence intervals. Given that there is no pre-existing specific database for the Y_{CH4} of dairy cattle manure and car-

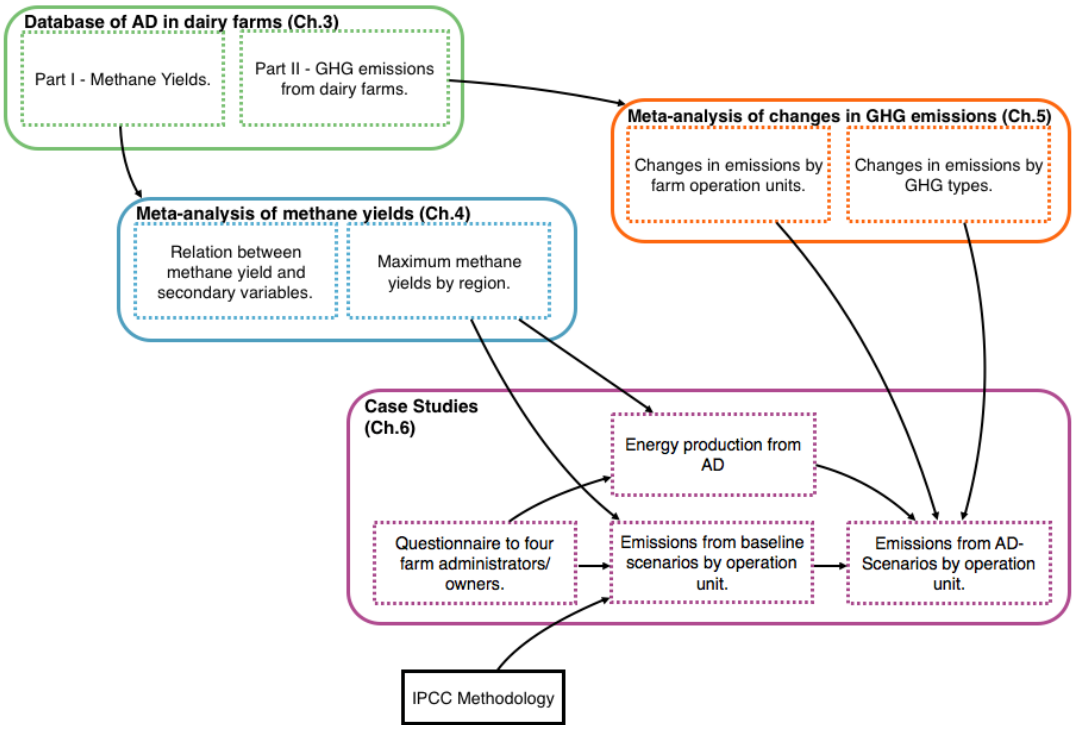

Figure 2.2: Flow diagram of the research work of this thesis according chapter outcomes.

bon footprint of AD scenarios in dairy farms, one is compiled in Chapter 3. For this, relevant information is extracted from selected research papers.

To select articles of interest for the database, four criteria are first defined in Chapter 3 and a systematic on-line search for scientific publications is carried out by utilising keywords. To filter articles, steps are presented to assess them against the defined criteria. The structure of the database is provided in Chapter 3 to organise the findings from different authors.

The developed database consists in two parts: the first part (Part I) is specific to Y_{CH4} of dairy cattle manure and secondary variables describing the manure compositions and AD system performance and; in the second part (Part II) estimates and measurements of GHGs emissions from dairy farm activities (i.e. operation units) are collected from the literature for standardised baseline and AD scenarios. Thereafter, the application of meta-analysis techniques differs for both parts of the database (see Figure 2.2). Thus, the meta-analysis of Part I is carried out in Chapter 4 and that of Part II in Chapter 5.

The difference in units of measurements, operation conditions of experimental setups, manure composition and digester types result in non-comparable Y_{CH4} in Part I of the database. Similarly for Part II, the changes in emissions from reference scenarios to AD scenarios utilise diverse scopes, system boundaries and functional units. The range of approaches, makes it challenging to draw general conclusions from the works in the database.

In order to enable the combination of results from different articles, thus, increasing the sample size, it is necessary to numerically process the information collected in the database. The meta-analysis of Chapter 4 addresses the difference in Y_{CH4} by standardising to comparable units of measurements because this variable is widely reported in common dimensions. Conversely, GHG emissions are reported utilising different functional units and system boundaries of the analysis. Therefore, to transform functional units to a standard measurement (i.e. as for Y_{CH4}), embedded data in the articles is required, yet not often available. In order to overcome this issue, emissions are first categorised according to standardised baseline and AD scenarios, by farm activity conserving the original units of measurements from the articles. Thereafter, given that the interest of this work is to quantify the changes in GHG emissions, the emissions are normalised to relative change percentages with respect to standardised baselines. The methodology to carry out this normalisation is presented in Chapter 5 and is based on response ratios utilised in the environmental assessment from other authors [261, 262].

Once the information is collected in the database and standardised, it can be combined and statistically analysed with meta-analysis statistical techniques. For Part I of the database, the meta-analysis of Y_{CH4} responds to the following question:

What are robust values for methane yields?

This research question is addressed in Chapter 4. To reach robust estimates of Y_{CH4} (i.e. which can be utilised for the estimation of CH_4 emission from dairy farms), the Y_{CH4} collected in Part I of the database are first categorised by digester type. This is an essential step because different reactors (i.e. batch, continuous and semi-continuous) are governed by markedly different aspects in terms of design and operation. Thereafter, fixed- and random-effect meta-analyses models are applied over the subgroups of Y_{CH4} according to digester type. It is of particular interest to evaluate

the maximum Y_{CH4} from batch digesters, because the IPCC Guidelines provide default value based on non-updated cases and limited sample size. In fact, these IPCC values are categorised according to world region, which may not be in the best interest for predicting Y_{CH4}, given the globalisation in animal feed.

In order to provide clarity on the differences and similarities in the Y_{CH4} found in the literature, these are combined with secondary variables describing operation conditions and manure composition. Multi-variate analysis of principal components and of clusters enables the identification of common groups found for Y_{CH4}.

After analysing results for the meta-analysis of Y_{CH4} which affects specifically emissions from manure management and offset of fossil fuels, discussion develops towards a holistic perspective of the effect of AD on emissions from dairy farms. This is approached by the meta-analysis of Part II of the database which addresses the following specific research question:

What are robust factors to determine the GHG emissions from dairy farm activities when implementing AD?

Having compiled Part II of the database, categorised emissions by operation units and scenarios; and standardised the changes in emissions between scenarios, it is possible to bring the literature together in a numerical manner. To determine robust values of the changes in GHG emissions as a consequence of implementing AD, Chapter 5 applies meta-analysis techniques over the distributions of relative changes.

As opposed the meta-analysis models of Chapter 4 for Y_{CH4}, Chapter 5 utilises a semi-quantitative approach. This is because GHG emissions reported in the literature are usually based on single measurements or estimates (i.e. sample size (N_i) and standard deviation (s_i), which are required for meta-analysis models, are not available). Therefore, the application of traditional fixed- and random-effect models for meta-analysis, is not possible.

To assess the changes in emissions from baseline to AD scenarios, Chapter 5 uses non-parametric tests to determine: i) how significant the changes in emissions are; ii) if changes are correlated between GHGs and; iii) which are the best estimates for the relative changes.

Having determined robust values for Y_{CH4} and relative changes according to operation units, results are finally brought together to address the key research issue of the thesis: the improvement of methodologies to evaluate the emissions from baseline and AD scenarios of dairy farms. For this, Chapter 6 presents a unique and specific methodology which utilises the findings of meta-analyses and is based on the IPCC Guidelines as a framework to evaluate emissions. To illustrate how the IPCC-based methodologies can be improved by incorporating Y_{CH4} determined in Chapter 4 and relative changes from Chapter 5, the steps to assess the energy production from AD and its consequent changes in GHG emissions are presented.

To show that the methodology can be applied among vastly different real-world dairy farms, are chosen from contrasting realities. The collection of required information to apply the methodology was carried out by applying a structured questionnaire four farm owners or administrators: one from a developed country (England) and the other three are from a developing nation (Guatemala). The answered questionnaires allow the construction of the standardised baseline and AD scenarios, thus, to quantify the changes in GHG emissions. Ultimately, the case studies examine how the methodology to evaluate the effect of AD on emissions applies in real-world dairy farms (and using different combustion technology for the biogas).

The discussion of the case study results centres, first, on comparing the application of the designed methodology to the dairy farms from developing and developed nations. This allows the analysis of novel insights in terms of preferable AD scenario. Second, the results obtained by the methodology are compared to unaltered IPCC Guidelines to illustrate in the contribution of the meta-analysis findings in refining the estimations of GHG emissions.

Finally, Chapter 7 presents the summary of the results found for each chapter of this work. Discussion of the limitations is also reported together with contributions and future work related to meta-analysis techniques applied in the bio-energy sector to improve estimation of emissions.

2.3 Contribution of the work

At the time of submission of this thesis there are three peer-reviewed papers published based on the research work herein contained: two journal publications and one conference paper. It should be noted that the co-authors of both journal publications participated exclusively by providing comments for the improvement of the manuscripts. The three articles can be found in the Appendix A.

The author's article in *Biomass & Bioenergy* (Elsevier) *"Meta-analysis of Methane Yields from Anaerobic Digestion of Dairy Cattle Manure"* [263] is the base for the work related to the development and analysis of Part I of the database in Chapters 3 and 4, respectively. This publication provides up-to-date robust values of Y_{CH4} obtained by meta-analysis, which offer a better alternative compared to the defaults in the IPCC Guidelines. These can be applied for assessing dairy farms in terms of GHG emissions and energy potential outputs. The paper also presents the multivariate clusters obtained for Y_{CH4}, operation conditions and manure composition, which can be utilised for the construction of AD scenarios. In particular, these clusters (described in Chapter 4) identify common combinations for ranges of key metrics. Therefore, when evaluating AD systems, numerical assumptions on the operation of these systems can be chosen from the grouped variables. This provides more evidence-based and un-biased underlying set of data than if yields, HRTs, temperatures, among others; were extracted from different and possibly unrelated sources.

Methods and results related to Part II of the database in Chapters 3 and 5, respectively, are published by the author in the article named *"Meta-analysis of Greenhouse Gas Emissions from Anaerobic Digestion Processes in Dairy Farms"* in *Environmental Science and Technology* [264] (American Chemical Society). In that work, novel relative changes are reported to estimate GHG emissions from different operation units of dairy farms with AD systems based on emissions from baselines. These relative changes offer a reliable, simple and strongly evidence-based way to calculate emissions from operation units affected by AD. Furthermore, the article (and associated chapters) includes relative changes of for estimating emissions from handling of digestate, which is not commonly found in farm assessments.

A third journal publication is in preparation to be submitted to the *International Journal of Life Cycle Assessment* (Springer) to report the complete findings of Chapter 6. This planned publication is an extension of the published conference article "Potentials of biogas production and GHG mitigation in Guatemalan dairy farms" [265]. The latter relates to the author's oral presentation at the 2014 IEEE Global Humanitarian Conference in San Jose, California. The conference paper is currently an open access publication on the Digital Library of IEEE Xplore. That work illustrates the application of relative changes for the assessment of emissions from theoretical AD scenarios in current dairy farms. It presents the preliminary results of the Guatemalan case studies in Chapter 6 of this thesis. It should be noted that the third journal publication (in preparation) differs from the conference paper because it incorporates the English case study of Chapter 6 and illustrate the application of Y_{CH4} found by meta-analysis. An important contribution is that it suggests to policy-makers to have in consideration the difference in GHG emissions from developed and developing dairy farms regarding carbon credits from manure handling in baselines. Specifically, by comparing case studies in Chapter 6 it is noted that livestock farms with storage of manure (common practice in developing nations) originate more emissions in their baseline than those without. Hence, these farms can account for more carbon credits when implementing AD. Therefore, policies for carbon mitigations should examine if standardise baselines would avoid incentives to transit to storage of manure (i.e. increasing GHG emissions) prior to the implementation of AD.

In addition to the published work, the research of this thesis contributes the two-part database that is compiled from existing literature exclusive related for the application of AD in dairy farms. Additionally, this is the first work to integrate such numerous cases from the academic literature in the field. This database is publicly available as an online resource (epg.eng.ox.ac.uk/content/anaerobic-digestion) and its development method is published in the journal articles described previously [263, 264].

Chapter 3

Database of the AD of dairy cattle manure

To date there is no specific database of the energy productions or the GHG emissions for AD of dairy cattle manure. In consequence, construction of AD scenarios, for example in life-cycle analysis studies, are commonly based in multiple sources. This chapter looks at rectifying this by systematically collecting primary-source articles (and metrics therein contained) in a two-part database. The Y_{CH4} is examined first (in Part I) because it is a critical value required to quantify potential energy output of AD systems. Part II compiles the results on GHG emissions from dairy farms with and without AD systems. Each part is needed to support the work for Chapters 4 and 5, respectively.

The overview of the research work covered in this chapter is shown in Figure 3.1. As a first step, to ensure reproducibility in the article selection process, four criteria are defined (Section 3.1.1). The second step consists of two structured searches carried out by using keywords. One search focuses on the literature covering Y_{CH4} and the other on GHG emissions from AD systems in dairy farms[1]. The articles identified by the search are thereafter assessed against the criteria (Section 3.1.2). The third step consists of the procedure to extract variables and organise them in the database (Section 3.1.3). The methodology leads to the construction of a two-part database which is publicly available as an on-line resource in the website of the Energy and Power Group of the University of Oxford [266].

[1]As results of this chapter will show (Section 3.3), the two searches are justified as there are only four articles that overlap between selected publications for Y_{CH4} and GHG emissions.

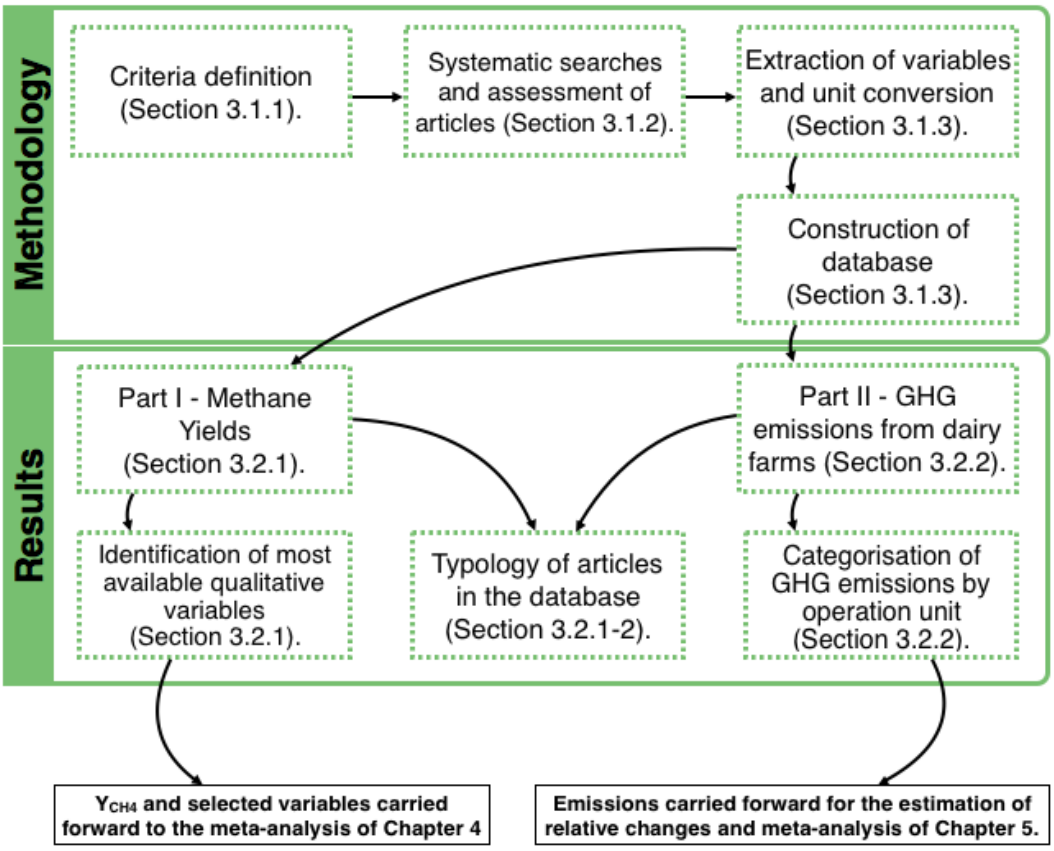

Figure 3.1: Scheme of the research work covered in Chapter 3.

The results for Part I of the database are presented in Section 3.2.1. These identify the operation conditions and slurry-composition variables which are commonly reported simultaneously with Y_{CH4}. Thereafter, secondary variables are selected as a pre-requisite for the multi-variate analysis of Chapter 4. Results for Part II of the database are discussed in Section 3.2.2. For this Part, the availability of emissions in the literature is discussed in terms of operation unit. The latter is the base for the calculation of relative changes and meta-analysis of Chapter 5. For both result parts, the application of criteria and the overview of typology (e.g. year of publication and journal) are discussed.

3.1 Methodology for database development

The systematic collection of metrics for a meta-analysis requires a reproducible methodology. To this end, the following sections (Sections 3.1.1-3.1.2) present the definition and application of specific criteria to select articles from the literature and construct a database. The structural organisation of collected variables is shown in Section 3.1.3.

3.1.1 Criteria for selection

This section presents the criteria defined to select articles that are included in the database. Two systematic searches are carried out to compile the two parts of the database: *Part I-Methane Yields* and *Part II-GHG Emissions*. There are three common criteria that all publications that conform the database must satisfy and in addition, specific criteria applied for each search.

The common criteria for the two searches are:

1. Peer-reviewed scientific publications in the academic literature that report AD of dairy cattle manure.
2. Primary sources and;
3. Available work in English, published in journals indexed in ISI Web of Knowledge [267] to which the author has access[2].

The criteria exclusive for Part I and II of the database are, respectively:

4. Inclusion of specific information:
   (a) Inclusion of experimental data of Y_{CH4} for the AD of interest and;
   (b) Inclusion of numerical data of GHG emissions from two scenarios: with and without an AD system.

The first criterion is defined to ensure quality of the articles and their relevance to AD of dairy cattle manure. Secondary sources are excluded by the second criterion to avoid duplicated values

[2]Accesibility to journals is shown after to not be a great constraint, because the author has access to 4,590 journals in Engineering, 1,699 journals in Agriculture Sciences and 1,152 journals in Environmental Sciences [268], through the subscription of the University of Oxford.

in the database. The third criterion specifies the on-line search-engine that is utilised. The ISI Web of Knowledge is chosen because it contains mainly peer-reviewed journals and a platform with advanced search settings for multiple combination of keywords. Finally, criteria 4.a and 4.b are introduced to ensure that numerical results relevant for the meta-analyses of this work are included. Therefore, the papers selected include quantitative results that allow the study of Y_{CH4} (Part I) and the evaluation of changes in GHG emissions from baseline to AD scenarios (Part II).

3.1.2 Article search

In order to find articles which comply with the criteria, selective keywords are utilised on the search-engine platform of the ISI Web of Knowledge [267]. The language is set to "English" and the year of publication is not constrained. It should be noted that, although China has played an important role in the development of AD plants (e.g. by 2007 it had 26.5 million biogas plants installed [269]), articles written in Chinese are discarded by this criterion. Similarly occurs for

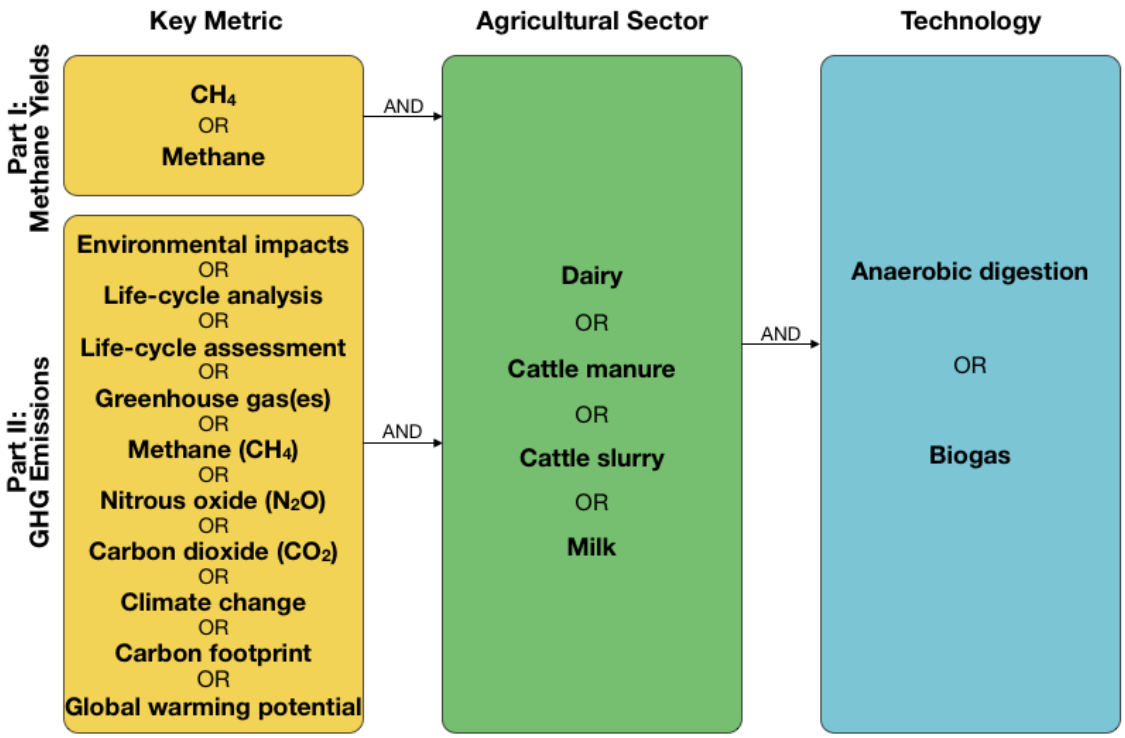

Figure 3.2: Scheme of the combination of logical connectors and keywords for the systematic search of studies in the literature, according to the two parts of the database.

non-English publications from India [270]. This is a marked constraint of the language criterion. However, as a results will show, the selection of English articles in this work markedly contributes in bringing together a large sample size.

Keywords, logical connectors and combinations shown in Figure 3.2 are used as topic input for the search. The keywords aim to identify metric of interest for each Part of the database, agricultural sector and technology presence. To filter articles reporting Y_{CH4} for Part I of the database, a first search uses the keywords in the top yellow block of Figure 3.2[3]. The search is then extended to find articles reporting GHG emissions from dairy farms to form Part II of the database. For this part, the keywords shown in the bottom yellow block of Figure 3.2 are utilised[4]. It should be noted that "methane" and "CH_4" are used in both searches because these keywords can assist to find articles reporting AD system performance (i.e. yields) and/or emissions of this specific GHG.

From the search results, each publication undergoes the two-stage assessment shown in Figure 3.3. In the first stage, the titles and abstracts are reviewed to determine if they are in agreement with the first and second criteria. The first criterion (yellow blocks in Figure 3.3) applied over titles and abstracts discards any publication which is not a research articles (e.g. patent, book chapter) This criterion also eliminates those publications which focus on non-AD processes or different feedstock. There are two exceptions in which articles are not rejected at this stage, although not strictly complying with the specific feedstock:

- If the use of cattle manure is described in the title and/or abstract as feedstock but there is uncertainty on the source (i.e. dairy farm). It is therefore required to assess the complete article to verify if the organic waste is from dairy cattle.
- If co-digestion of manure with another substrate(s) is reported in the title and/or abstract. The publication is not discarded, because articles can include results of control experiments (i.e. mono-digestion). Therefore, the complete article is in need of assessment.

The second criterion (green blocks in Figure 3.3), excludes secondary sources to avoid duplicated values in the database. Therefore, reviews articles which can be identified by titles and/or articles

[3]Based on the last update of Part I of the database (before submission of this thesis) in February 2015.

[4]The last update of Part II of the database corresponds to October 2015. Therefore, more articles are included in this chapter, compared to the associated published work [264] (search: December 2014, details in Section 2.3) .

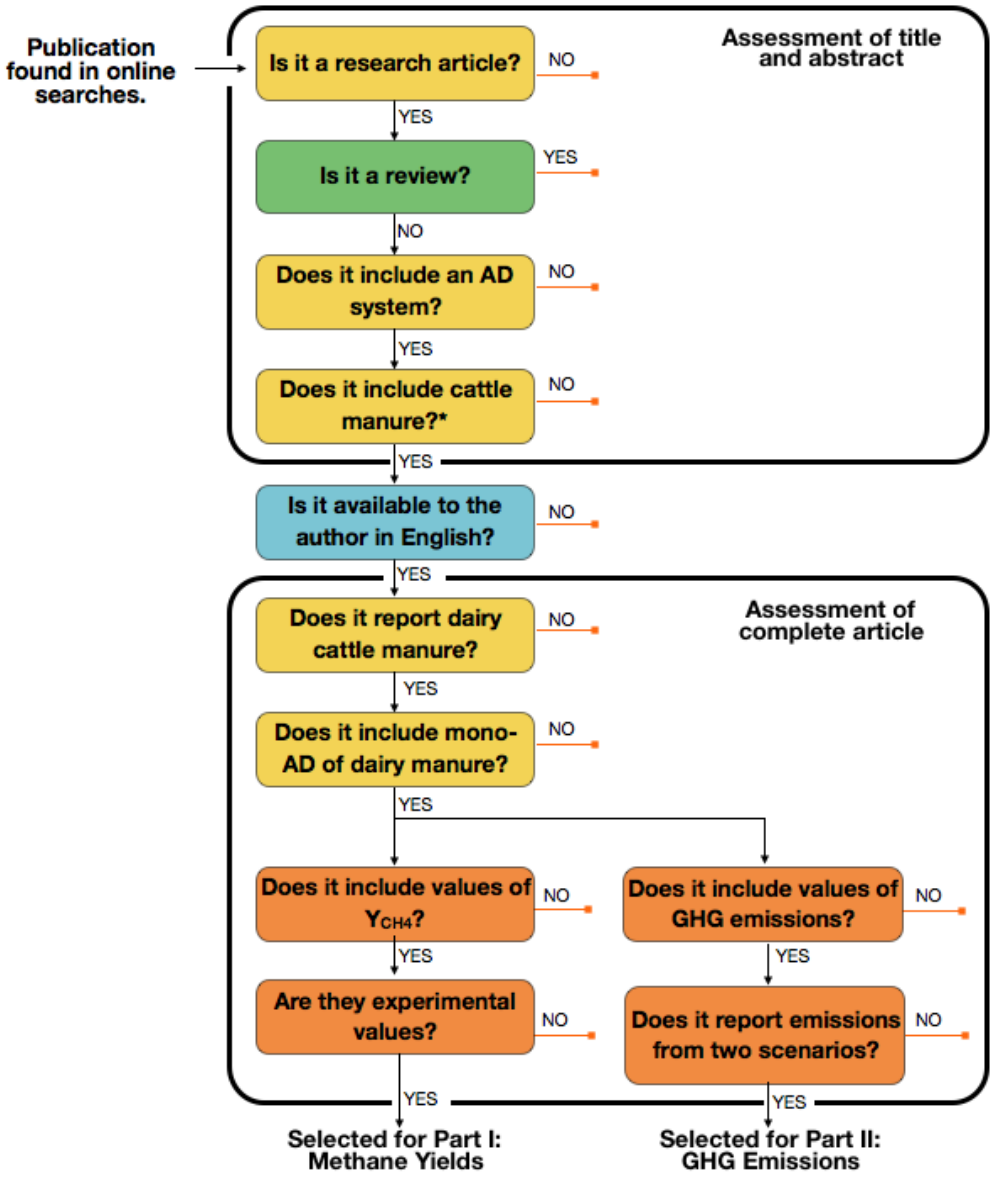

Figure 3.3: Systematic selection of articles for the database applied over publications output by on-line searches. Application of criteria according to colour of boxes: first criterion in yellow; second criterion in green; third criterion in blue and; fourth criterion in orange. Red lines indicates the rejection of a publication. *: Titles and abstract selected in this block are non-specific to dairy manure (i.e. only cattle).

are rejected in the first stage. From the remaining titles and abstracts, articles available to the author are collected (i.e. third criteria, blue block in Figure 3.3).

The second stage of the publication assessment consists of reviewing complete articles against the first and fourth criteria. In particular, as more detailed information on the feedstock is available (i.e. compared to titles and abstracts), the first criterion enables the pre-selection or rejection of

articles, which were previously uncertain due to unclarity in feedstock (see exceptions in the first stage above). Finally, the fourth criterion in applied in the second stage of the assessment as shown by the orange blocks in Figure 3.3. The set of questions for this criterion, focus on selecting papers that include quantitative and empirical results of Y_{CH4} for dairy cattle manure (first search) and GHG emissions from AD and baseline scenarios (second search), in text, tables or figures.

3.1.3 Structure of the database

This section explains the extraction of variables from the selected articles and their consequent arrangement in each part of the database. The two parts of the database are separated as work in the literature does not commonly report experimental measurements of Y_{CH4} together with GHG emissions from AD scenarios. Furthermore, the scopes and structures of the two parts of the database are different. *Part I-Methane Yields* focuses on the AD process itself. Hence, Y_{CH4} is collected together with available secondary variables which allow to characterise the AD system performance. *Part II-GHG Emissions* centres not only on the AD-system, but also on other farm activities (i.e. operation units) which can be affected by AD. To determine the quantifiable effect of AD on each operation unit, in this Part of the database GHG emissions are recorded for a baseline (non-AD) scenario and a corresponding AD scenario.

3.1.3.1 Structure of Part I-Methane Yields

From the output of the first article search and selection process (see Section 3.1.1), Y_{CH4} and secondary variables are extracted to compile Part I of the database. Values of Y_{CH4} are adapted so that all cases correspond to cumulative CH_4 production per kilogram of VS. For the purpose of numerically combining results of different studies conforming Part I of the database, the same conditions and units of measurements must be met. Therefore, Y_{CH4} values are standardised to normal conditions (293 K, 1 atm) and given in "$m^3_{CH4} \cdot kg^{-1}_{VS}$".

When articles report various Y_{CH4} (e.g. profiles across time or measurements at different temperatures), multiple cases are logged into the database. To record differences between cases, secondary variables are also entered to the database (when available). Qualitative secondary variables

are: author(s), journal name, year of publication and location of study (country). If the latter is not available, the location of the first author is used. For quantitative secondary variables, it is required that these specify the AD operation conditions or chemical compositions of untreated or digested slurries. The dominant dimension for each quantitative variable is chosen for statistical use. Numerical data undergoes unit conversion, for example, measurements of COD in articles using units "$mg \cdot L^{-1}$" [5, 17, 18, 32, 36, 52, 64, 74, 87, 108, 271] are converted to "$kg \cdot m^{-3}$" (i.e. units of the International System), as follows:

$$COD^{*} \left[\frac{mg_{COD}}{L_{manure}}\right] \cdot \left[\frac{1\,kg}{1 \times 10^{6}\,mg}\right] \cdot \left[\frac{1{,}000\,L}{1\,m^{3}}\right] = COD \left[kg \cdot m^{-3}\right]$$

where COD^{*} is the value of COD as given in the original unit of measurement "$mg \cdot L^{-1}$" for the example. If a variable is reported in different dimensions (e.g. "$kg_{COD} \cdot kg_{DM}^{-1}$"), underlying data from the original article is utilised to reconcile the units. If insufficient information is available when dimension conversion in needed, the original units of measurements are recorded into the database, but excluded for statistical analysis of Chapter 4.

Articles from a same author are examined in order to not repeat cases in the database. If Y_{CH4} and secondary variables are the same for multiple cases of a single author, cases are merged.

3.1.3.2 Structure of Part II-GHG emissions

The second search and selection process identifies articles which report GHG emissions from scenarios with and without AD systems (see Section 3.1.1). *Part II-GHG Emissions* comprises literature that reports emissions which vary widely, in terms of scope and boundaries. Following the definition of scenarios and operation units described in Section 2.1, a case (tabulated as a row) in Part II of the database is conformed by emissions from different activities (operation units) from baseline and related AD scenarios, determined under the same conditions (e.g. a study of the effect of storage temperature over GHG emissions from untreated and digested slurry would consider each temperature as a case). An example of the structure of the variables in Part II-GHG Emissions is presented in Table 3.1. Two important features should be noted: i) cases in Part II may include multiple or single operation units and; ii) when articles study the effect of different AD systems,

Table 3.1: Example of the organisation of Part II-GHG Emissions of the database

		GHG Emissions [$kg_{CO2e} \cdot f.u.^{-1}$]				
		Operation Unit 1		**Operation Unit 2**		
		Baseline	**AD-Scenario**	**Baseline**	**AD-Scenario**	...
Article "A"	Case 1					
	Case 2					
Article "B"	Case 3					
⋮	⋮					

multiple cases are entered into the database with a common baseline.

The selected articles report emissions of different GHGs (GHG_i, i= CH_4, N_2O or CO_2) per functional unit ($[f.u.]$). To standardise the emissions, these are expressed as carbon dioxide equivalents (CO_{2e}) and calculated, as follows:

$$GHG\,[kg_{CO2e} \cdot f.u.^{-1}] = \sum_i GWP_j \cdot GHG_j \tag{3.1}$$

where GWP_j in "$kg_{CO_{2e}} \cdot kg_j^{-1}$" corresponds to the global warming potential for the emitted gas "j". According to IPCC 2006 [272], GWP_{CH4} is 25 $kg_{CO2e} \cdot kg_{CH4}^{-1}$, GWP_{N2O} is 298 $kg_{CO2e} \cdot kg_{N2O}^{-1}$ and GWP_{CO2} is 1 $kg_{CO2e} \cdot kg_{CO2}^{-1}$, for 100 year time horizon. If a study used different values for GWPs, they are corrected to these specified values. When articles reported different functional units (e.g. emissions per ton of manure for storage and emissions per hectare for field application [14]), the emissions are reconciled by using underlying data.

In addition to the columns presented as example in Table 3.1, Part-II of the database also includes variables describing the typology of the study, as previously described for Part I.

3.2 Results and discussion

This section first presents the output of the two systematic searches for AD articles in the literature and discusses them in terms of criteria application. The database constructed is then characterised by describing overview typology of the papers that conform Parts I and II of the database. For Part I, secondary variables collected are selected based on sample size available so that they can be utilised in multi-variate statistical analysis in Chapter 4. For *Part II-GHG Emissions* the discussion centres on the operation units most reported and that will be utilised for relative change calculations and meta-analysis in Chapter 5.

3.2.1 Articles selected for Part I-Methane Yields

The first search of papers using the word combination for Y_{CH4} (see Figure 3.2), outputs 888 publications. By assessing these papers against the selection criteria, 115 articles (13.0% of the initially found) are chosen for Part I of the database [1–115]. The causes for the high rejection, according to criteria, are shown in Figure 3.4a.

Within the papers rejected by the first criterion, 352 correspond to other feedstocks; 43 co-digest dairy cattle manure with other organic waste, excluding specific Y_{CH4} values of interest; 38 are not research articles and correspond, for example, to patents or book chapters and; 29 articles do not report the production of CH_4 from AD, focusing on different technologies for manure-management systems (e.g. hydrogen production or composting). All articles rejected by the second criteria correspond to review publications. The third criteria discards 14 articles that reported titles and/or abstracts in English, however, their main content is in a different language. In addition, 33 papers (from which 22 correspond to two publishers), are not accessible to the author. Finally, the fourth criteria rejects 178 papers that do not include results on Y_{CH4} of AD process and 31 that use modelled or assumed (i.e. non-empirical) Y_{CH4} values.

Regarding secondary variables that describe the typology of studies, the 115 selected articles are found in 45 scientific journals, of which the main contributors are specified in Figure 3.4b. In relation to the geographic location of the articles comprising Part I of the database (see Figure 3.4c), European and North American work is dominant with 46 articles [3, 4, 8–11, 14, 17–19, 25,

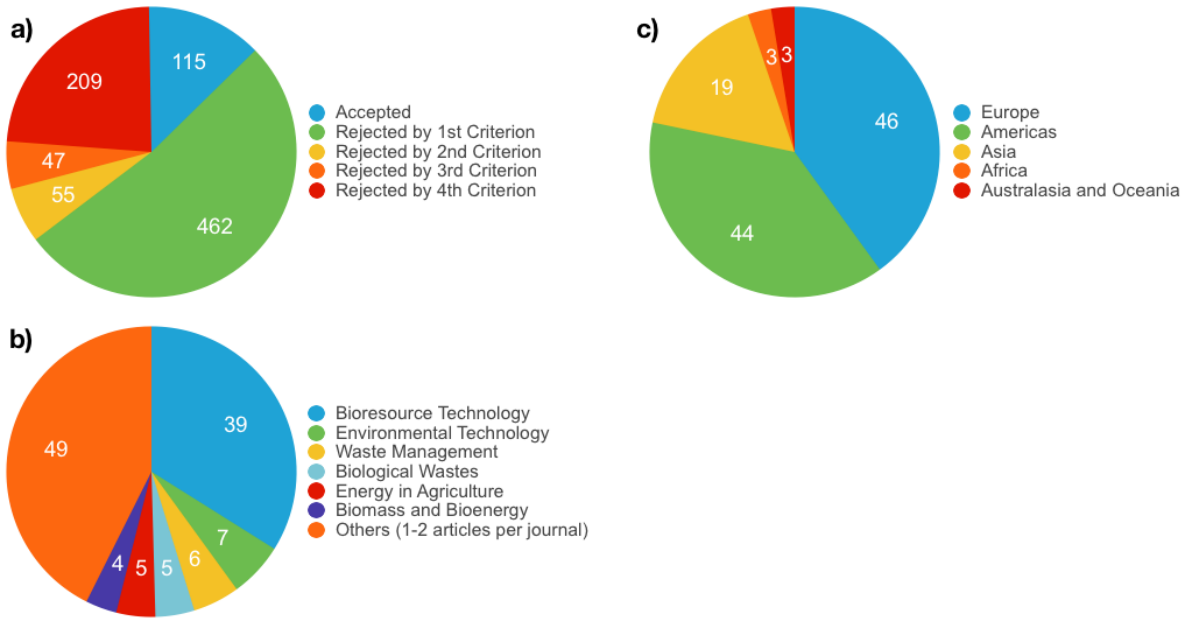

Figure 3.4: Pie-charts for articles in Part I of the database. Classification according to: a) filtering criteria; b) scientific journals where published and; c) continents.

34, 38, 41, 42, 50, 60, 61, 65–67, 71–73, 76, 78–83, 85, 89–91, 93, 95–97, 101–104, 113–115] and 44 articles [6, 12, 13, 15, 16, 23, 24, 26, 29–33, 35, 37, 39, 40, 44, 45, 49, 51, 53–59, 62–64, 69, 74, 84, 86, 87, 92, 94, 98–100, 108, 109, 111], respectively. For other continents markedly fewer articles are found to report Y_{CH4}: 19 for Asia [1, 2, 5, 7, 21, 36, 43, 46–48, 52, 68, 77, 88, 105–107, 110, 112], 3 for Africa [22, 27, 28] and 3 for Oceania [20, 70, 75]. The categorisation of cases conforming Part I of the database according to world regions is of particular interest when comparing results of meta-analysis (Chapter 4) to the default maximum Y_{CH4} of the IPCC (see Section 4.2.5).

With respect to year of publication, the literature covering AD in dairy farms (and specifically Y_{CH4}) is increasing as shown in Figure 3.5. Results indicate that from 2007 to 2014 an average of 10 publication per year report Y_{CH4} of dairy cattle manure. Before 2007 only two articles per year on average contain experimentally-measured Y_{CH4} of this waste. This increase is expected because, although AD is a mature technology (i.e. implemented for waste treatment since 1880s in Europe [159]), today it is being re-visited as a mean to reduce carbon emissions in the context of international agreements. In addition, it is observed that the increase in publication begins the

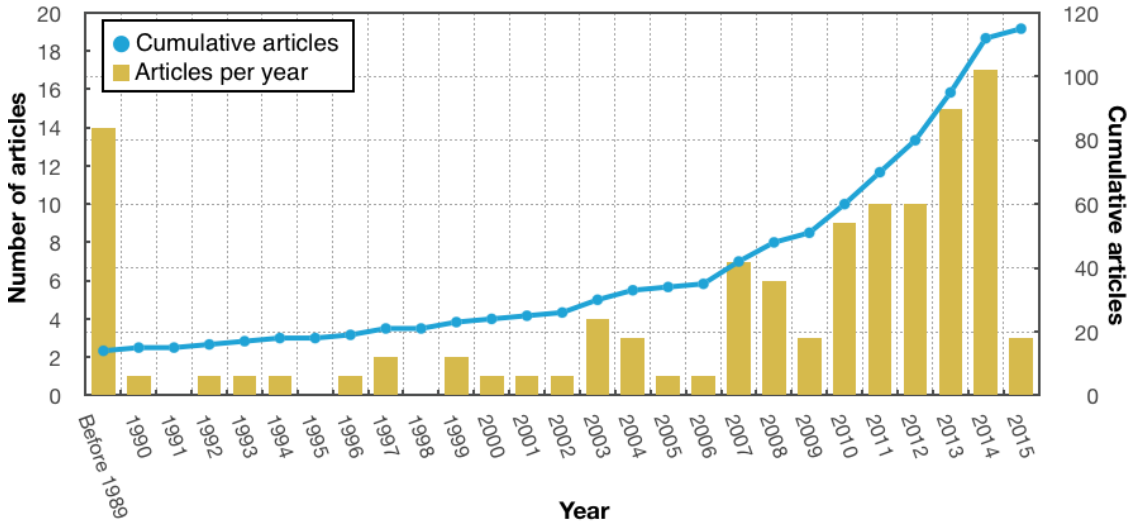

Figure 3.5: Articles in Part I of the database according to year of publication. The year 2015 only includes publication until February.

same year of the global financial crisis (2007-8), which could be related to dairy farms seeking to diversify their income activities.

From the selected papers 2,181 cases are extracted and conform the *Part I- Methane Yields*. To avoid duplicates, repeated cases found in five of the articles [53, 55–58], are entered once. From the cases in the database, 2,161 are selected from 95 articles [1, 2, 4–7, 9–16, 19, 21, 22, 24, 26, 27, 29–44, 46, 49–51, 53–60, 62–67, 70, 71, 73, 74, 76–84, 86–104, 107–115]. The remaining 20 articles [3, 8, 17, 18, 20, 23, 25, 27, 45, 47, 48, 52, 61, 68, 69, 72, 75, 85, 105, 106] report single cases from which 16 are identified as control experiments in co-digestion studies.

The quantitative secondary variables that are identified for the cases from the selected articles are summarised in Table 3.2. It should be noted that articles which report multiple cases commonly have constant values for some of the secondary variables. For example, articles that report CH_4 production across time in batch digester will have multiple cases differing in Y_{CH4} and time, but with the same working volume and input composition.

It is observed that secondary variables describing operational conditions are the most found in Part I of the database. On average, each of the operation variables in Table 3.2, is found in 76.3% of cases. For secondary variables that correspond to slurry composition, as expected, more information is available for the characterisation of raw manure with respect to digestate. This can

be attributed to the interest in predicting Y_{CH4} based on composition.

Based on the available material in the literature, the meta-analysis of Chapter 4 concentrates on the most numerous variables presented in Table 3.2. Therefore, the operation variables carried forward are: time (or HRT), working volume, temperature and OLR. The stages of the digesters are not considered because they are commonly specified as "multi-stage" or "single-stage", which can be treated as qualitative information, rather than numerical. From the secondary variables describing slurry composition the following are selected: input pH, input dry matter (DM), input VS, input COD and total Kjeldahl nitrogen (TKN).

Table 3.2: N. of cases and articles specifying variables in Part I of the database

Variables	N. of Cases	N. of Articles	Reference(s)
Methane Yield (Y_{CH4})	2,181 (100%)	115 (100%)	[1–115]
Operation conditions			
Time[b]	1,962 (89.9%)	104 (89.5%)	[1–9, 11, 13–19, 21–46, 48–59, 61, 63–67, 69–73, 76, 77, 79–86, 88–100, 102–115]
Working volume	2,141 (98.2%)	107 (93.0%)	[1–16, 19–22, 26–71, 73–92, 94–100, 102–115]
Temperature	2,097 (96.1%)	108 (93.9%)	[1, 2, 4, 6–19, 21, 22, 25–37, 39–63, 65–115]
Organic loading rate (OLR)	693 (31.8%)	51 (44.3%)	[2, 5, 9, 12, 15–20, 24–27, 34, 37, 39, 42, 49, 50, 52–59, 62]
			[63, 69, 75, 76, 78, 81, 82, 85–87, 89, 90, 92, 94, 97, 99, 100, 103, 110, 112, 114, 115]
Stages of digester	1,425 (65.3%)	82 (70.4%)	[1, 3–5, 7–11, 13–16, 21–32, 34–38, 40–44, 46, 47, 51–55, 57, 58, 60–62, 65–67]
			[68, 69, 71, 75, 77–83, 85, 87–90, 93–96, 98, 101, 102, 104–109, 111, 112, 115]
Chemical composition of input slurry			
pH	1,314 (60.2%)	63 (53.9%)	[4–8, 10–14, 17–19, 21, 25, 29, 30, 32, 35, 37, 41–43, 45–48, 51, 52, 60, 61, 64]
			[68, 69, 71, 72, 74, 79–83, 85–89, 91, 92, 94, 95, 97–99, 104–110, 113, 114]
Density	11 (0.5%)	6 (5.2%)	[8, 17, 18, 60, 72, 112]
DM mass fraction	1,793 (82.2%)	95 (82.6%)	[1–6, 8–10, 12–14, 16, 19, 21, 25, 27–42, 44–49, 51–59]
			[60–63, 65–70, 72–74, 76, 79–91, 93–99, 101, 102, 104–115]
VS mass fraction	1,816 (83.3%)	102 (87.8%)	[1–3, 5, 6, 8–14, 17–21, 24, 25, 27–42, 44–65, 68–77, 79–97, 99, 101–115]
COD	1,150 (52.7%)	51 (44.3%)	[3, 5, 6, 8, 14, 17, 18, 25, 27, 29, 30, 32–34, 36, 40, 41, 44, 45, 49, 51, 52]
			[53–61, 64, 70, 72–74, 80–83, 85–87, 90, 99, 108, 109, 111, 113–115]
Biological oxygen demand	39 (1.8%)	8 (7.0%)	[14, 17, 18, 44, 74, 75, 93, 99]
Organic nitrogen	1 (0.05%)	1 (0.9%)	[25]
Total nitrogen	283 (13.0%)	23 (20.0%)	[25, 27, 35, 38, 43, 48, 60, 61, 65, 66, 71, 72, 74, 76, 77, 84, 85, 88, 90–93]
			[95, 96, 111, 115]

[a]Percentage of cases/articles that report secondary variable with respect to all cases for that type of digester.

[b]Time for batch and hydraulic retention time (HRT) for continuous and semi-continuous digesters, respectively.

Secondary Variables	N. of Cases	N. of Articles	Reference(s)
Chemical composition of input slurry (continuation)			
Ammonia content	1,132 (51.9%)	59 (51.3%)	[5, 11, 14, 17–19, 25, 27, 28, 30, 32, 35–37, 40–42, 45, 49, 52–61, 65, 66, 72] [68, 76, 77, 79, 81, 82, 84–87, 90–97, 101, 104, 105, 109–111, 113–115]
Total Kjeldahl nitrogen (TKN)	1,198 (54.9%)	35 (30.4%)	[5, 13, 14, 19, 25, 28, 32, 34, 36, 37, 40–42, 45, 49, 53–59, 80, 82, 83] [86, 87, 94, 105–110, 114]
C/N ratio	181 (8.2%)	16 (13.9%)	[2, 3, 25, 48, 64, 72, 77, 85, 88, 91, 102–107]
Chemical composition of output slurry			
pH	442 (20.3%)	51 (44.3%)	[2, 5–7, 11, 14, 15, 17–19, 21, 28, 30, 34, 35, 37, 42, 43, 45–48, 51, 60] [64, 69, 71, 74, 81, 86–95, 97–101, 103–105, 108, 110, 114, 115]
Density	2 (0.1%)	2 (1.7%)	[17, 18]
DM mass fraction	388 (17.7%)	35 (30.4%)	[2, 5, 12, 14, 16, 31–34, 37, 45, 49, 53–59, 115] [69, 70, 73, 74, 76, 81, 86, 87, 90, 99, 103, 104, 108, 110, 114]
VS mass fraction	465 (21.3%)	46 (40.0%)	[5, 11, 12, 14, 15, 18, 21, 23, 30–34, 37, 45, 48, 49, 53–59] [63, 69–71, 73, 74, 76, 81, 86, 87, 90–92, 94, 99, 103–105, 108, 110, 114, 115]
COD	353 (16.2%)	32 (27.8%)	[5, 14, 18, 30, 32–34, 36, 45, 49, 53–59, 64, 70, 73, 81, 86, 87] [80, 82, 90, 99, 108, 111, 114, 115, 273]
Biological oxygen demand	29 (1.3%)	7 (6.1%)	[14, 17, 18, 74, 75, 93, 99]
Nitrogen content	16 (0.7%)	8 (7.0%)	[60, 61, 71, 76, 90, 92, 111, 115]
Ammonia content	442 (20.3%)	42 (36.5%)	[5, 11, 14, 17, 18, 30, 32, 34, 37, 39–42, 45, 49, 53–61, 74, 76, 81, 86, 87] [89–93, 97, 101, 103–105, 110, 114, 115]
Total Kjeldahl nitrogen (TKN)	332 (15.2%)	24 (20.9%)	[5, 6, 14, 19, 32, 34, 37, 41, 45, 49, 53–59, 81, 86, 87, 94, 108, 110, 114]
C/N ratio	2 (0.1%)	1 (0.9%)	[104]

[a]Percentage of cases/articles that report secondary variable with respect to all cases for that type of digester.

[b]Time for batch and hydraulic retention time (HRT) for continuous and semi-continuous digesters, respectively.

3.2.2 Articles selected for Part II-GHG Emissions

The second systematic search in the literature is carried out to find relevant articles that report GHG emitted in baseline and AD scenarios from dairy farms. By using the word combination shown in Figure 3.2 for this part of the database, 1,144 articles are output. The papers are assessed against the selection criteria and 40 articles [14, 16, 20, 42, 75, 116–150] (3.5% of the initially found) are chosen to compile the database *Part II-GHG Emissions.*

According to criteria used to filter articles (see Figure 3.6a), the first criterion rejects 594 articles (51.9% of the total output papers) because these are not specific to the field of study. Particularly, 325 articles correspond to the AD of different feedstock and 78 report dairy manure co-digested with other substrate(s) (e.g. food waste [111], whey [220], waste from milk process [108, 274–276], slaughter houses [277]). The remaining 260 articles rejected by the first criterion, focus on different technology (43 papers) or do not correspond to research articles (61 papers). For the second criterion, 80 papers are discarded because they are reviews. The assessment of papers against the third criterion filters out 18 articles which are not in English and 33 which are not available to the author [5]. Finally, the fourth criterion discards 380 of the articles (33.2% of the

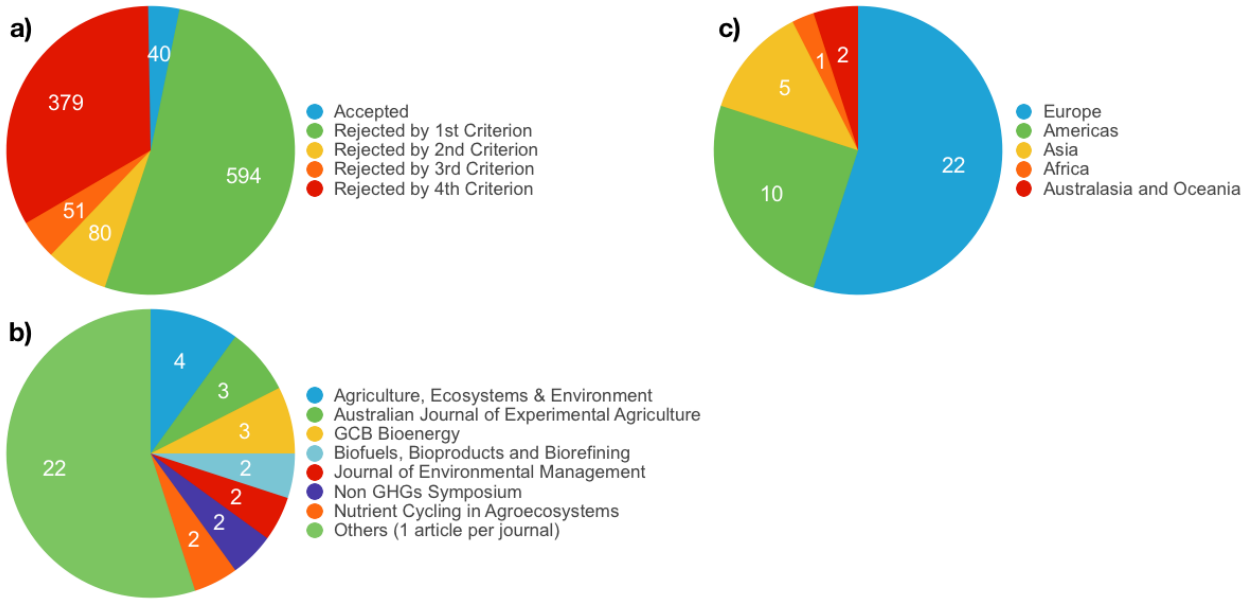

Figure 3.6: Pie-charts for articles in Part II of the database. Classification according to: a) filtering criteria; b) scientific journals where published and; c) continents..

[5]The 33 papers not available, are the same articles not found for Part I of the database.

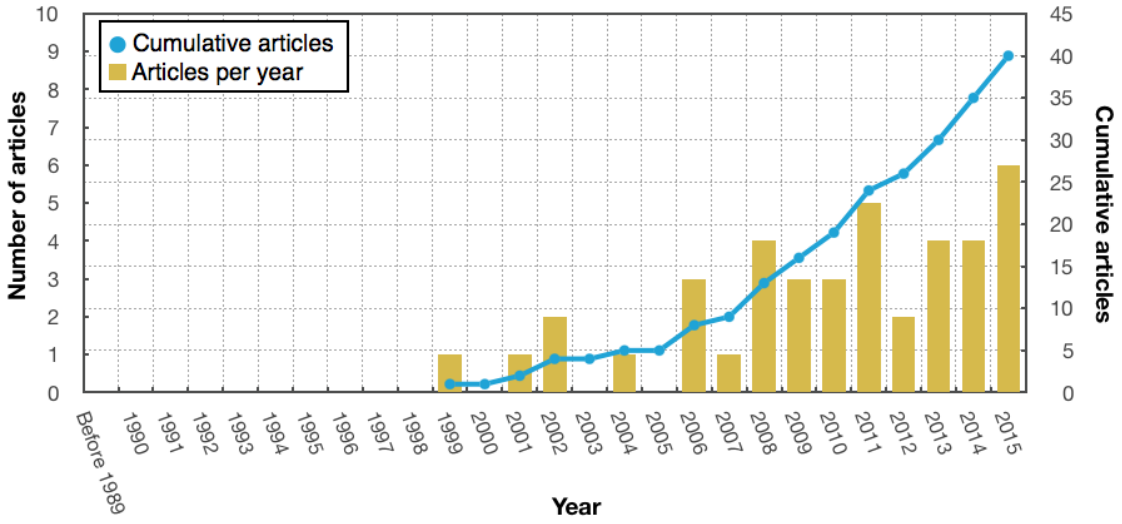

Figure 3.7: Articles in Part II of the database according to year of publication. The year 2015 includes publication until October.

search output). These are rejected because, although focusing on the AD of dairy manure, they are not specific to emissions. In particular, 32 of these articles only study emissions from one scenario, thus, cannot be used for the estimation of relative changes (analysis of Chapter 5).

The 40 articles selected to develop the database (Part II) are found in 29 journals. The largest contributor to Part II of the database, in terms of number of articles, is the journal *Agriculture, Ecosystems & Environment* with four publications (see Figure 3.6b).

From the selected publications, 22 (55.0%) correspond to studies of European dairy farms, as shown in Figure 3.6c. This is expected because in Europe AD has a large trajectory (since 1880s) [159] and, as part of the current emission targets [278, 279] it plans to limit GHG releases. Therefore, European cases generally report baseline scenarios (complying with the fourth criteria) in order to quantify changes in emissions when implementing AD systems.

The profile in Figure 3.7 (blue lines) show the progress of the selected articles in terms of time of publication. It is observed that, although the publication date is not constrained in the search, all of the selected articles have been published after 1998. This can be due to environmental agreements, particularly the Kyoto Protocol (signed in 1997) [279, 280], which drove research on GHG emissions. The first paper to report emissions from baseline and AD-scenarios is the work from Petersen et al. [116]. In that publication, the authors carry out experimental measurements for

GHG emissions from different scenarios. Empirical work is found to be followed by model-based papers, beginning in 2002 (Van Dooren et al. [119]). Within these, the IPCC methodologies (i.e. Tier 1 and Tier 2) were first applied for dairy farms with AD systems in 2008 (Craggs et al. [20] and Hishinuma et al. [123]). This is expected because the IPCC Guidelines for National GHG Inventories [151] only included the emissions from AD systems in 2006 and only anaerobic ponds were in the previous guideline version of 1996 [281].

Regarding GHG emissions found in the 40 selected articles, Table 3.3 summarises these in accordance to operation units. It is observed that the most reported operation units correspond to storage and field application of slurry, with 32 [14, 16, 20, 42, 75, 119–126, 130–136, 138, 140–150] and 30 articles [14, 116–122, 126, 127, 129–131, 133–146, 148–150], respectively. In particular, there are 2 articles [124, 125] which only report emissions associated with storage, 7 articles [116–118, 127, 129, 137, 139] exclusive to field application and 4 articles [14, 121, 126, 149] which report only emissions from these two farm activities. This results in 13 articles (33% of those in Part II of the database) which compare direct emissions from untreated and digested manure, without including digester leaks or indirect emissions from offset of fossil fuels and/or inorganic fertilisers. Moreover, no article is exclusive in reporting emissions from the latter operation units. There are 12 articles [120, 123, 128, 131, 133, 136, 141–145, 150] which account for leaks from digesters. For indirect emission, 26 of the articles [16, 20, 42, 75, 119, 122, 123, 128, 130–136, 138, 140–148, 150] quantify emissions due to offset of fossil fuels by biogas. Eight of these articles [42, 122, 128, 131, 133, 136, 140, 150] correspond to those reporting emissions from the replacement of inorganic fertilisers by slurries. All articles reporting these three operation units also include GHG released from storage or field application.

The above observation for different operation units found in the database, identify two main groups of research for GHG emissions from AD systems in dairy farms. The first group corresponds to articles studying direct emissions from different slurries. These are mostly based on experimental measurements of GHG emissions. The second group includes a broader amount of operation units and can be more associated with life-cycle-assessment studies.

Table 3.3: Emissions reported in the articles of Part II of the database according to operation unit.

First author and year	[Ref]	Anaerobic digester	Storage	Field application	Offset of fossil fuel	Offset of mineral fertilisers[a]
1. Petersen 1999	[116]			✓		
2. Clemens 2001	[117]			✓		
3. De Boer 2002	[118]			✓		
4. Van Dooren 2002	[119]		*	**	**	
5. Sommer 2004	[120]	✓	✓	✓		
6. Amon 2006	[121]		✓	✓		
7. Clemens 2006	[14]		✓	✓		
8. Weiske 2006	[122]		**	**	**	**
9. Park 2007	[75]		*		**	
10. Craggs 2008	[20]		✓		**	
11. Hishinuma 2008	[123]	**	✓		✓	
12. Sakamoto 2008	[124]		✓			
13. Zhang 2008	[125]		✓			
14. Chianese 2009	[126]		✓	✓		
15. Moeller 2009	[127]			✓		
16. Pathak 2009	[128]	✓			*	*
17. Cayuela 2010	[129]			✓		
18. Cornejo 2010	[130]		*	*	**	
19. Michel 2010	[131]	✓	✓	✓	✓	✓
20. Boadzo 2011	[132]		*		✓	
21. Hamelin 2011	[133]	✓	✓	✓	✓	✓
22. Kaparaju 2011	[42]		✓		✓	✓
23. Marañón 2011	[134]		*	*	✓	
24. Unal 2011	[135]		*	*	✓	
25. De Vries 2012	[136]	**	✓	✓	✓	✓
26. Schouten 2012	[137]			✓		
27. Coats 2013	[16]		**		**	
28. Liang 2013	[138]		*	*	**	
29. Thomsen 2013	[139]			✓		
30. Zhang 2013	[140]		**	**	✓	✓
31. Aguirre-Villegas 2014	[141]	✓	✓	✓	✓	

[a]Inorganic fertilisers replaced by untreated slurry (baseline scenario) or digestate (AD scenario). ✓: Emissions from baseline and AD scenarios for this operation unit are reported. *: Article assumes zero emissions from this operation unit in the AD scenario. **: Emissions are included in (at least one) scenario(s), but the individual breakdown for each GHG contribution and/or for this operation unit are not specified.

(Continuation of Table 3.3).

First author and year	[Ref]	Anaerobic digester	Storage	Field application	Offset of fossil fuel	Offset of mineral fertilisers[a]
32. Battini 2014	[142]	✓	✓	✓	✓	
33. Dieterich 2014	[143]	**	✓	**	✓	
34. Zhang 2014	[144]	✓	*	✓	✓	
35. Agostini 2015	[145]	✓	✓	✓	**	
36. Aguirre-Vellegas 2015	[146]		✓	**	✓	
37. Manning 2015	[147]		✓		✓	
38. Rivas-Garcia 2015	[148]		**	**	✓	
39. Rodhe 2015	[149]		✓	✓		
40. Styles 2015	[150]	✓	✓	✓	✓	✓

[a]Inorganic fertilisers replaced by untreated slurry (baseline scenario) or digestate (AD scenario). ✓: Emissions from baseline and AD scenarios for this operation unit are reported. *: Article assumes zero emissions from this operation unit in the AD scenario. **: Emissions are included in (at least one) scenario(s), but the individual breakdown for each GHG contribution and/or for this operation unit are not specified.

The total cases conforming this part of the database is 142 which is a larger amount than the articles selected as 21 publications provide multiple conditions and/or studied farms. The statistical analysis of the GHG emissions collected for these cases in the database is presented in Chapter 5[6].

3.3 Summary and final remarks for the chapter

The construction of a novel database specific to AD of dairy cattle manure is presented in this chapter and the overview of its results. Two sets of keywords are utilised in online searches to identify possible articles of interest. The first search is specific for Y_{CH4} and outputs 888 articles. The second, focuses on articles reporting GHG emissions from dairy farms with and without AD systems, resulting in 1,144 scientific publications. The papers found are assessed against four defined criteria to determine if they should be included in the database. The first criteria rejects the most articles (~52% in both searches) because it discards different feedstock, technologies and non-research works.

[6]Chapter 5 is based on the author's published work "Meta-analysis of GHG emissions from anaerobic digestion processes in dairy farms" [264], which uses an earlier version of Part II of the database. In that publication only 30 articles were available (search in December 2014), which are a subgroup of the articles presented in this chapter.

After the selection of articles useful for this work, a novel two-part database is constructed from 155 papers. *Part I- Methane Yields*, is conformed by 2,181 cases extracted from 115 articles from the first search. These cases are conformed by empirical Y_{CH4} measurements, qualitative information on the articles and quantitative variables describing operation conditions of AD systems and the input manure composition. *Part II-GHG emissions* contains 40 articles which yield 142 cases. These cases are mainly constructed from life-cycle assessments of different scenarios in dairy farms. Part II of the database is developed in accordance to GHG emissions (CH_4, N_2O and/or CO_2) categorised by operation units (i.e. farm activities) in defined scenarios.

This database is an unprecedented combination of two types of publications, those on energy performance of AD systems and and those of that study the relation of AD to changes in GHG emissions. It is found that there is a stratified literature in terms of energy output of AD and its environmental consequences. This is indicated by the fact that only five articles [14, 16, 20, 42, 75] contribute to both parts of the database. In addition, markedly fewer articles and cases is found for Part II. These differences can relate to shorter time-frame of publication of articles in Part II (from 1999 onwards) in comparison to those in Part I (publications since 1984). More work on Y_{CH4} is expected because the energy output of AD, affects not only the changes in GHG emissions, but also other aspects of the process (e.g. economic).

The development of Parts I and II of the database in this chapter is a preliminary step for Chapters 4 and 5, respectively. Chapter 4 considers a subgroup of Part I of the database which comprises only those cases which express Y_{CH4} in "$m^3_{CH4} \cdot kg^{-1}_{VS}$" (the most common unit of measurement found) or can be converted to this unit of measurement. For multi-variate analysis, this chapter carries forward the following operation conditions they are: time (or HRT), working volume, temperature and OLR; and for composition of manure (input) these are: pH, DM, VS, COD and TKN.

The GHG emissions collected in Part II of the database are carried forward to Chapter 5 in accordance to scenarios, operation unit and GHG type. Emissions are normalised to relative changes in order to enable comparison between different operation units and cases.

Chapter 4

Meta-analysis of methane yields

The quantification of changes in GHG emissions by implementing AD in dairy farms is strongly dependent on the yield to methane (Y_{CH4}) of manure. Y_{CH4} is essential to estimate the energy production that, in consequence, can replace the use of fossil fuels. Additionally the maximum Y_{CH4} (B_0) is commonly used to estimate emissions related to leaks of digesters and CH_4 emissions from manure management systems. The selection of a Y_{CH4} value is therefore critical for the construction of scenarios in life-cycle studies of products from livestock farms.

Given the increasing literature covering AD of dairy manure, life-cycle assessments commonly utilise Y_{CH4} from different sources. More standardised approaches apply default maximum Y_{CH4} values from the IPCC Guidelines for National GHG Inventories [151]. However, the latter method reports values of Y_{CH4} for dairy manure which only consider two publications: Morris in 1976 [225] for developed countries and Safley et al. in 1992 [224] for developing nations (see Section 1.4).

This chapter addresses these issues by providing robust Y_{CH4} values based on the meta-analysis of the larger and more updated (up to 2015) sample collected in Part I of the database. The challenge of combining inter-study quantitative results is to infer general characteristics of the database structure considering differences in operation conditions, slurry compositions and units of measurements. Therefore, the most reported secondary quantitative variables selected from Chapter 3 are used to identify underlying sources of similarities and variations of AD systems, with particular

attention to the Y_{CH4}. This, in turn, can contribute to a better categorisation of yields, according to operation of digesters and composition of input manure, rather than the regional categories from the IPCC.

The methods of this chapter begin by presenting uni-variate statistical tests to characterise Y_{CH4} distributions constructed from Part I of the database (Section 4.1.1). In order to quantitatively combine the distributions of Y_{CH4} and determine novel effect sizes, the mathematical steps to carry out meta-analysis models is then presented in Section 4.1.2. Thereafter, to enable a comprehensive examination of the relation between Y_{CH4} and secondary quantitative variables, Section 4.1.4 shows the mathematical background of multi-variate statistics.

Given that some of these secondary variables are intrinsically related to specific types of digesters (e.g. HRT to continuous or semi-continuous digesters), the analysis of Y_{CH4} in the result section is segmented to batch, continuous and semi-continuous reactors. Multi-variate structure between key variables related to the performance of AD systems is examined. Correlations and clustering of principal components are discussed in terms of sources of similarities and variations. The discussion finally compares results from meta-analysis models applied over B_0 to default values of the National Guidelines for GHG emissions of the IPCC [151].

It should be noted that this chapter comprises the main results from the author's work in Biomass & Bioenergy titled "Meta-analysis of methane yields from anaerobic digestion of dairy cattle manure" [263].

4.1 Mathematical methods

Scientific clarity is needed to provide robust Y_{CH4} values of dairy cattle manure and to understand its diversity in the literature. To address the first issue, meta-analysis models are utilised in this work to produce strong evidence-based Y_{CH4} means and confidence intervals. The section begins by explaining the construction and characterisation of distribution of Y_{CH4} collected in Part I of the database. Thereafter, the mathematical transformations of the standardised data to produce meta-analysis results, are presented. To establish the extent to which meta-analysis outputs represent the primary Y_{CH4} distributions from the database (and also how they compare to IPCC default values [151]), Section 4.1.1 describes the selection and application of Wilcoxon-Signed rank test.

In order to examine reasons behind the range of Y_{CH4} found in the literature, secondary variables describing AD operation conditions and manure composition are considered. As a first step to achieve this, bi-variate correlations are analysed between Y_{CH4} and each secondary quantitative variables (Section 4.1.4.1). Thereafter, given the large number of variables in the database, principal component analysis is utilised for dimension-reduction (Section 4.1.4.2). Cluster analysis is then applied over the first two principal components to evaluate associations between multi-variate results and to examine underlying structure in the database (Section 4.1.4.3).

4.1.1 Y_{CH4} distributions for meta-analysis

Having standardised variable in Part I of the database to common units of measurements (see Section 3.1.3), the Y_{CH4} cases are combined to construct uni-variate distributions.

These are represented by box plots in the results of this chapter[1]. In these graphical representation, upper and lower sides of boxes correspond to first and second interquartile ranges. Therefore, the inter-quartile ranges are illustrated by the lengths of the boxes and can be utilised to examine the dispersion of a variable. Lines which cross the box represent medians of the distributions.

To further characterise the distributions, normality is assessed because it is necessary to identify if parametric or non-parametric tests are applicable for letter statistical tests. The Shapiro-Wilk test [282] is chosen because it has been reported to have better power properties (i.e. complies

[1]Box plots are also used in Chapter 5 for relative changes of GHG emissions from Part II of the database.

with critical value at smaller sample size) in comparison to other common normality tests such as Kolmogorov-Smirnov, Lilliefors and Anderson-Darling [283].

The null-hypothesis of the Shapiro-Wilk test is that the sample comes from a normally-distributed population. Therefore, a low P-value (<0.05) will indicate that the latter is rejected, hence, the distribution is statistically (and significantly) different from normality. The Shapiro-Wilk statistic is calculated for an ordered sample, $x_1 < x_2 < ... < x_n$, as follows [283]:

$$(Shapiro-Wilk)_{Statistic} = \frac{\left(\sum_{i=1}^{n} a_i x_i\right)^2}{\sum_{i=1}^{n} (x_i - M)^2} \tag{4.1}$$

where x_i is the ith data point of the distribution, M is its median and $a_i = (a_1, \ldots, a_n) = \frac{W_0^T V^{-1}}{\sqrt{(W_0^T V^{-1} V^{-1} W_0)}}$. For the latter, $W_0 = (W_1, \ldots, W_n)^T$ are the expected values from a standard normal distribution and V is the covariance matrix ($n \times n$ matrix) of those values calculated as:

$$V = \frac{1}{n-1} \sum_{i=1}^{n} (x)(x)^T \tag{4.2}$$

4.1.2 Meta-analysis models

As presented in Section 1.5, meta-analysis offers a robust numerical combination of evidence from multiple studies to estimate novel effect sizes. In this chapter, the effect size of interest is the mean Y_{CH4} value (M_j) of different distributions "j" [2]. It should be noted that M_j is the statistical estimation of the mean of a larger population of yields (μ). To obtain M_j, two traditional meta-analysis models are applied: the fixed-effect and the random effect models [257].

As a first step, both models require the distribution's mean (M_i), s_i and sample size (N_i) of each case "i" in the database. Therefore, those cases which do not provide one or more of these metrics, are excluded from the meta-analysis. The calculation steps undertaken to evaluate the new Y_{CH4} values of this work, are presented in Table 4.1 [257].

The main assumption of the fixed-effect model is that each case "i" is estimating a unique

[2]For Chapter 5 the effect size of interest is the relative change of GHGs emitted in AD scenarios, with respect to standardised baselines.

Table 4.1: Calculations for meta-analysis models [257].

Steps for calculation	**Fixed-Effect**	**Random-Effect**
1. Variance of case "i"	$V_i = s_i^2/N_i$	$V_i = s_i^2/N_i$
2. Initial weight of case "i"	$W_i = 1/V_i$	$W_i = 1/V_i$
2. Measure of heterogeneity	n.a.	$Q = \sum W_i M_i^2 - \frac{(\sum W_i M_i)^2}{\sum W_i}$
3. Std. deviation of sample	n.a	$T^2 = \frac{Q-(k-1)}{W_i - \sum W_i^2 / \sum Wi}$
4. Variance of case "i"[a]	As above.	$V_i^* = V_i + T^2$
5. Weight of case "i"[a]	As above.	$W_i^* = 1/V_i^*$
6. Mean of sample	$M = \sum W_i M_i / \sum W_i$	$M^* = \sum W_i^* M_i / \sum W_i^*$
7. Variance of sample	$V_M = 1/\sum W_i$	$V_{M*} = 1/\sum W_i^*$
8. Std. deviation	$\sqrt{V_M}$	$\sqrt{V_{M^*}}$
9. Confidence interval (CI)	$\left[M \mp z_{C/100}\sqrt{V_M}\right]$	$\left[M^* \mp z_{C/100}\sqrt{V_{M^*}}\right]$

[a]For the fixed-effect model, case variances and weights are calculated in Steps 1-2.

k: number of cases; $z_{C/100}$: critical value for confidence interval of 95%
(assumed 1.96 from [257]).

underlying μ. In this model M is calculated as a weighted average of the means (M_i) of each case (see Table 4.1). In turns, the weights (W_i) will represent the contribution of each case and are based on the case sample size and its precision. Thus, cases with larger N_i and smaller s_i are weighted more heavily.

In the random-effect model each case is assumed to be estimating means from different populations (μ_i). These μ_i have a distribution with an overall mean μ and standard deviation τ. To account for this, the model first calculates the variability of M_i with respect μ_i (T^2) by measuring the heterogeneity (Q) of the cases. Second, the model utilises these T^2 values to estimate weights of each case and, as shown in Table 4.1, the final steps are similar to those of the fixed-effect model. The final mean from this model is named M^*, to distinguish it from the mean of the random-effect model M.

4.1.3 Comparing distributions of Y_{CH4}

To evaluate the significance of the differences between two distributions, the Wilcoxon rank-sum test [284, 285] is used. This test is chosen because it is a non-parametric test, which is required as normality cannot be assumed. The null-hypothesis of the Wilcoxon rank-sum test is that two distributions ("A" and "B") correspond to a same population. The P-value is calculated by applying the following steps [284, 285]:

1. The data points of the two distributions are ranked, as if they conformed only one distribution (e.g. the smallest data point of both distributions will have rank 1).

2. The sum of the ranks for individual distributions is calculated (w_A and w_B).

3. Standard distribution of rank-sums (W_A) are utilised to determine if w_A (or w_B) comply with the null-hypothesis. If the distribution "A" is significantly greater than "B", the ranks for each data point of A will be unusually high. From this, the P-value is defined as the probability that $W_A \geq w_A$. Similarly, if the distribution "A" is significantly smaller than "B", the P-value is the probability of $W_A \leq w_A$. For a two-tailed tests, the probabilities are added for $W_A \geq w_A$ and $W_A \leq w_A$. P-values of less than 5% are considered to reject the null-hypothesis.

4.1.4 Multi-variate analysis

The difference in Y_{CH4} found in the literature is analysed in terms of secondary variables describing operation conditions and manure composition. For this, in Section 4.1.4.1 the application of Spearman Rank test is explained to examine correlation between bi-variate combinations of Y_{CH4} and secondary variables. Thereafter, to identify underlying structure of Y_{CH4} with respect to multiple secondary variables, principal component calculations (Section 4.1.4.2) and clustering by the k-means algorithm are presented (Section 4.1.4.3).

4.1.4.1 Bi-variate correlation examination

To assess the correlation between secondary variables and Y_{CH4}, a non-parametric test is required as no underlying distribution can be assumed. The Spearman Rank test satisfies this condition for determining monotonic correlations between paired samples [286, 287]. It is preferred over the Pearson non-parametric test because the latter, only evaluates linear relationship between two variables [287].

The first step of the Spearman test consists in ranking the data points of the samples from variables "A" and "B" separately (e.g. the rank "1" corresponds to the smallest values in each variable). As a second step, the difference between the ranks of each pair is calculated. Thereafter, the rho of the Spearman test is computed as follows:

$$\rho = 1 - \frac{6\sum(r_{ai} - r_{bi})^2}{r_{max}(r_{max}^2 - 1)}$$

where r_{ai} and r_{bi} are the ranks for the data points contained in samples "A" and "B", respectively, and r_{max} is the highest rank.

The sign of Spearman's rho is an indicator of positively or negatively correlated variables. The magnitude of absolute value of rho, will indicate the strength of the correlation as presented in Table 4.2.

Table 4.2: Correlation levels between two variables.

Absolute value of Spearman's rho	**Strength of correlation**
0.00 to 0.19	very weak
0.20 to 0.39	weak
0.40 to 0.59	moderate
0.60 to 0.79	strong
0.80 to 1.00	very strong

4.1.4.2 Principal component analysis

Given the multiple combinations between secondary variables and Y_{CH4} collected in Part I of the database, reducing the dimensionality of the database can enable the examination of underlying structure. For this purpose, principal component analysis is used. This is an unsupervised pattern-recognition technique based on projecting data points of variables on to planes, which in turns have lower dimensions than the original database [288]. The dimension reduction enables the synthesis and visualisation of the multi-variate database structure.

A recommended pre-processing procedure is centring and scaling the variables so that the influence of high magnitude variables is reduced [288]. To centre, the mean of a sample of variable "i", the mean (M_j) is subtracted from each data point $x_{j,i}$. The new $x_{j,i} - M_i$ values will therefore have mean zero. Thereafter, scaling of the each observation is carried out as follows:

$$x^*_{j,i} = \frac{x_{j,i} - M_i}{s_i} \tag{4.3}$$

where $x^*_{j,i}$ is the centred and scaled data point calculated from the original data point $x_{j,i}$.

Thereafter, principal component reduces the n-dimensions of the original set of variables assembled in the (centred and scaled) matrix "x" to k-dimensions ($n < k$). The first step of this is to determines the covariance matrix V (see Equation 4.2). The second step is to compute the Eigenvectors (u_j) of the covariance matrix. For this purpose, singular value decomposition is utilised. This method is preferred over the Eigen of the covariance matrix because it has better numerical stability [289, 290]. The singular value decomposition will output three matrices so that the matrix V can be expressed as

$$V = UPQ^T \tag{4.4}$$

where U is a $n \times n$ matrix, which contains the Eigenvectors in each column (i.e. $u^{(i)} = u_j$). To

reduce the dimensions, the first k-columns of the U matrix are extracted to a matrix (U_{red}):

$$U = \begin{bmatrix} | & | & & | & & | \\ u^{(1)} & u^{(2)} & \dots & u^{(k)} & \dots & u^{(n)} \\ | & | & & | & & | \end{bmatrix} \tag{4.5}$$

$$U_{red} = \begin{bmatrix} | & | & & | \\ u^{(1)} & u^{(2)} & \dots & u^{(k)} \\ | & | & & | \end{bmatrix} \tag{4.6}$$

The coordinates of the observations with respect to the principal component axis (i.e. principal component scores) is finally calculated as:

$$Z = U_{red}^T x \tag{4.7}$$

First and second principal components are presented by score plots in the result section (Section 4.2) of this chapter. On these graphical representations red arrow show the loading of each original variable. The loading, in turns, is an indication of the influence of the original variables over the principal component.

4.1.4.3 K-means cluster-analysis

Clusters of multi-variate data points hold the potential to identify differences in AD performances (i.e. Y_{CH4}), given diverse operation conditions and manure composition. Therefore, the most often used clustering algorithm (k-means [291]) is applied over the first two principal components as a means to identify underlying structure.

K-means is a partional clustering method which requires as an input a position of centroids (to be optimised) and the number of clusters (k). Thereafter, two iterative steps determine the clusters. In the first, each data point x is allocated to the closest cluster "C_i". The second step is to recalculate (i.e. move) the centroid as the mean of data points in each clusters. These steps are repeated until no further changes of data point allocation is found. The minimisation algorithm (J) can therefore

be represented as:

$$J = \frac{1}{m}\sum_{i=1}^{m} ||x^{(i)} - c_i||^2 \tag{4.8}$$

where $x^{(i)}$ is the data point assigned to cluster "C_i" and c_i is the centre of cluster C_i. In the first iterative step J is minimised by varying $x^{(i)}$, and in the second step J is minimised with respect to c_i.

To avoid local optimisation of the final centroid positions, 100 random initialisations are utilised for each k-means run. To determine the number of clusters, the Davies-Bouldin Index (DB Index) is utilised. This cluster evaluator is chosen because it does not depend on the number of clusters and the cluster algorithm [291]. To calculate the DB Index, the dispersion measurement (S_i) of a cluster "i" (C_i) and similarity measure between clusters C_i and C_j (R_{ij}) are defined, respectively, as:

$$S_i = \left(\frac{1}{|C_i|}\sum d^p(x, c_i)\right)^{1/p}, \; p > 0 \tag{4.9}$$

$$R_{ij} = \frac{S_i + S_j}{D^t(c_i, c_j)} \tag{4.10}$$

where $|C_i|$ is the number of data points in cluster C_i, c_i is the centre of cluster C_i, $d(x, c_i)$ is the p-norm distance between the data point x (in cluster C_i) and c_i; and $D^t(c_i, c_j)$ is the t-norm distance between the centres c_i and c_j. For this work the Euclidean distance is used for $d^p(x, c_i)$ and $D^t(c_i, c_j)$, therefore, $p = t = 2$. The DB Index is then calculated as follows:

$$DB\ Index = \frac{1}{k}\sum_{i=1}^{k} \underset{j \neq i}{max} R_{ij} \tag{4.11}$$

where k is the number of clusters and is varied between 2 and 10. The lowest DB Index obtained from the latter, determines the number of clusters input to k-means.

4.2 Results and discussion

The results in this section first introduces to the secondary variables available in Part I of the database according to the types of digesters. Sections 4.2.2 to 4.2.4 report the meta-analysis results of Y_{CH4} for batch, continuous and semi-continuous AD systems. Y_{CH4} and its relation to secondary variables are examined by uni- and multi-variate analysis for these different types of digesters. In the last Section 4.2.5, meta-analysis of B_0 is discussed to improve those currently used by the IPCC.

4.2.1 Variables available according to digester type

From the cases in Part I of the database 2,147 (98.1%) can be classified according to the digester type as: batch, continuous and semi-continuous. Table 4.3 summarises the secondary quantitative variables found in Part I, categorised by these digester types.

It is observed that the cases in Part I of the database present different secondary variables. These are reported in accordance to the specific objectives of each article and types of digesters. For example, for batch and semi-continuous cases the time and HRT, respectively, are specified in less cases than the temperature. However, for continuous digesters, the opposite occurs. In order to improve the consistency in reporting the performance of AD systems in the research literature, it is recommended to follow standardised protocols such as the Environmental Protection Agency Guidelines [201]. The implementation of standardised protocols to report specifications on AD systems (and composition of inlet substrate) would allow the selection of a larger sample size for the multi-variate analysis of this work. This is reflected in the exclusion of cases which report Y_{CH4} in units of measurements that cannot be reconciled to "$m^3_{CH4} \cdot kg^{-1}_{VS}$".

Table 4.3: Cases in the database[a] (percentages[b]) reporting secondary quantitative variables according to digester type.

Secondary Variables	[Units]	Batch	Continuous	Semi-continuous
Operation conditions				
Time[c,d]	$[d]$	1,260 (97.0%)	326 (97.3%)	332 (64.7%)
Working volume	$[m^3]$	1,286 (99.0%)	311 (92.8%)	513 (100%)
Temperature	$[^{\circ}C]$	1,288 (99.1%)	291 (86.9%)	509 (99.2%)
Organic loading rate (OLR)[c]	$[kg_{VS} \cdot m^{-3} \cdot d^{-1}]$	n.a.	277 (82.7%)	377 (73.5%)
Chemical composition				
pH	n.a.	785 (60.4%)	115 (34.3%)	348 (67.8%)
DM mass fraction	$[\%\, wt.]$	1,078 (83.0%)	232 (69.2%)	470 (91.6%)
VS mass fraction	$[\%\, DM]$	1,063 (81.8%)	231 (69.0%)	505 (98.4%)
Chemical oxygen demand (COD)	$[kg \cdot m^{-3}]$	653 (50.3%)	183 (54.6%)	304 (59.3%)
Total Kjeldahl nitrogen (TKN)	$[kg \cdot m^{-3}]$	726 (55.9%)	159 (77.3%)	303 (59.1%)

[a]Cases are defined in Section 3.1.3. It should be noted that an article can present multiple cases. [b]Percentage of cases that report secondary variable with respect to all cases for that type of digester. [c]Time for batch and HRT for continuous and semi-continuous digesters. [d] Utilises days in units of measurement because this is more common in experimental work than years.

4.2.2 Batch digesters

Batch reactors are the most reported in the literature for the AD of dairy cattle manure with 1,299 cases. From these, 1,144 cases from 54 articles report Y_{CH4} in the unit of measurement of interest (or can be converted to it). Digesters operated as batch reactors are loaded at the beginning of the experiment (or cycle) and only biogas is extracted during the AD process. The yields from these digesters result in non-normal distribution (Shapiro's P= 3.06×10^{-33}), median 0.124 $m^3_{CH4} \cdot kg^{-1}_{VS}$ and inter-quartile range 0.235 $m^3_{CH4} \cdot kg^{-1}_{VS}$. Low median is due to the presence of cases at low operation times, where the AD process is only beginning. In fact, 19 articles used for this distribution report profiles of Y_{CH4} against time, which indicate that multiple cases represent initial stages of CH_4 production.

To observe underlying structure of the Y_{CH4} from batch digester, results from principal component analysis and their subsequent cluster analysis are shown in Figures 4.1 and 4.3 for operational and composition variables, respectively. For the former, 42 studies report simultaneously Y_{CH4},

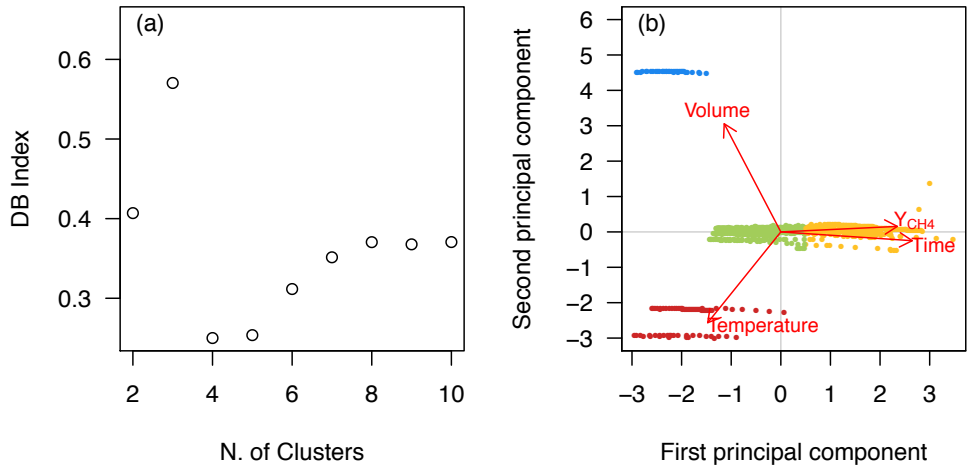

Figure 4.1: K-means clustering for first and second principal components of Y_{CH4} from batch digesters and operation variables: a) evaluation of DB Index for 2 to 10 clusters (see Eq. 4.11) and; b) clusters (each one in a different colour).

digester volume, temperature and operation time, yielding 1,104 cases. The first two principal components of Figure 4.1a retains 61.6% of the variance. The first principal component is highly dependent on Y_{CH4} and time of operation, while the contrary is observed for the second principal component.

The directions of the Y_{CH4} and time of residency vectors are similar. Thus, high Y_{CH4} is associated with longer digestion times, as expected. Higher correlation is also expected (Spearman's rho= 0.411, P-value= 2.2×10^{-16}), but not achieved due to the presence of overlapping profiles (i.e. see biplot of Y_{CH4} over time in Figure 4.2a). Individual profiles of Y_{CH4} are observed to reach asymptotic maximums. This is due to the decrease in the available organic material to be anaerobically digested. As time advances in batch digesters, bacterial population growth is limited by the availability of nutrients and therefore, these profiles are associated with Monod's equation [292].

With respect to the digester volume, the Y_{CH4} vector show opposite direction (with respect to the first principal component axis), which can be attributed to these variables presenting poor (and negative) correlations (Spearman's rho= -0.135, P-value= 4.68×10^{-6}). It is unexpected that the temperature vector is opposite to the Y_{CH4}, with respect to the first principal component axis. Much work (e.g. Umetsu et al. 293 and Kaparaju et al. 41) have reported an increase of Y_{CH4} with raise of temperature, however, the batch digesters collected in the database show a weak, and

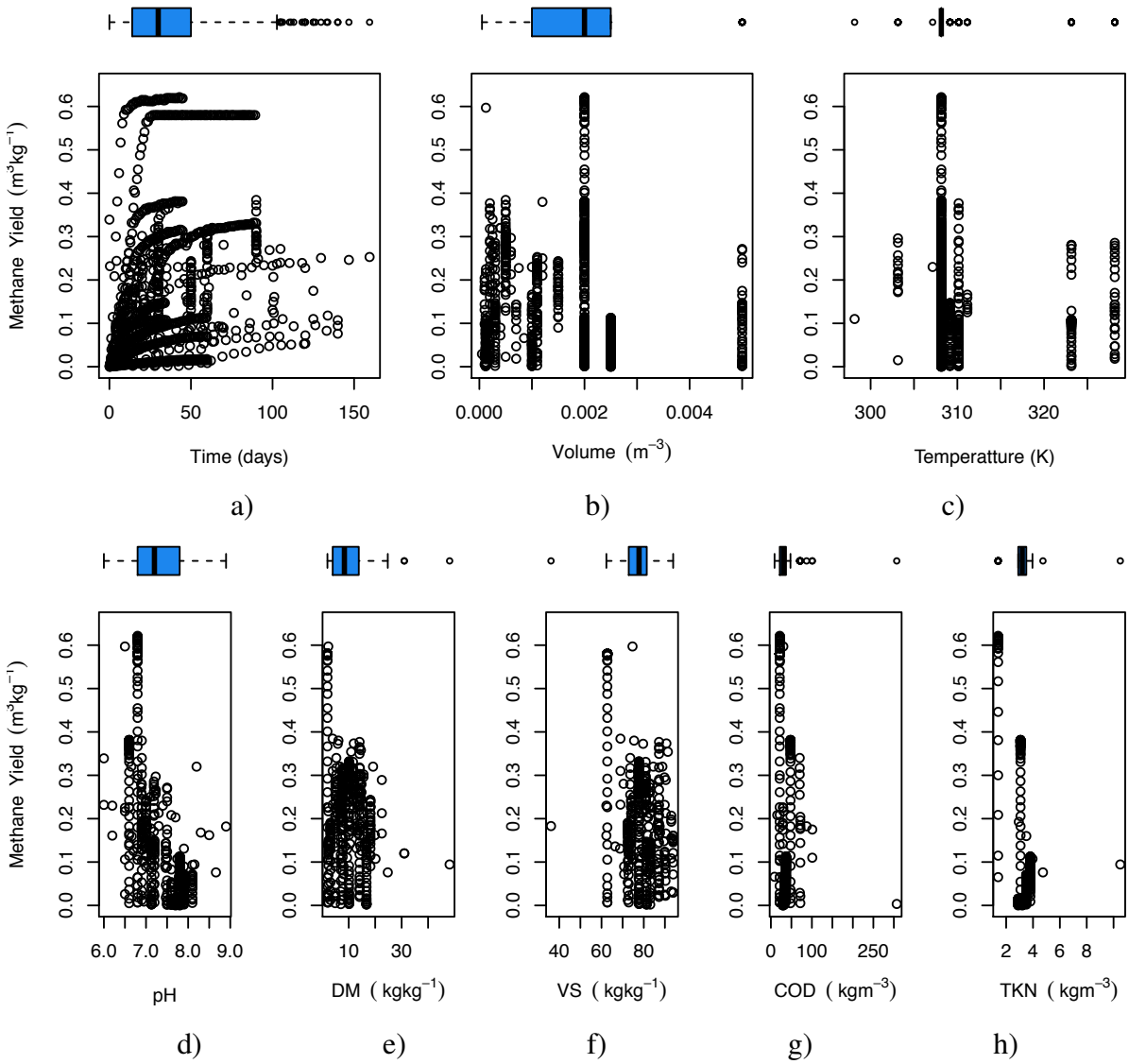

Figure 4.2: Y_{CH4} from batch digesters with respect to secondary variables and (top of each scatter-plot) the box plot showing the distribution of the secondary variables. Spearman-correlation results (from "a" to "h"): rho= 0.411, -0.135, -0.263, -0.696, -0.361, -0.457, -0.261 and -0.082; P-values= 2.2×10^{-16}, 4.7×10^{-6}, 2.2×10^{-16}, 1.0×10^{-97}, 6.3×10^{-18}, 1.6×10^{-27}, 2.5×10^{-9} and 0.131.

inverse correlation (Spearman's rho= -0.263, P-value= 2.2×10^{-16}). This could be explained by batch digesters achieving B_0 independently of operation temperature as long as enough retention time is allowed.

In accordance to the position of the cases in the biplot, four clusters result from the k-means algorithm (DB Index= 0.25 in Figure 4.1a). All clusters extend across the first principal component, while being less affected by the second principal component. The red cluster of Figure 4.1b,

corresponds to small digesters (0.30×10^{-4} to 0.002 m^3) operating at the highest temperatures for batch digesters in Part I of the database (323 K and 328 K). This cluster is conformed by 73 cases from seven articles. The blue cluster of Figure 4.1b, represents large digesters (0.850 m^3) operating at 308 K. This cluster of 34 cases is conformed by the data reported in only one article [6]. The blue and red clusters correspond to the lowest Y_{CH4} obtained for batch digesters with B_0 0.19 and 0.29 $m^3_{CH4} \cdot kg^{-1}_{VS}$, respectively. The green and yellow clusters of Figure 4.1b correspond to the most common values for digester volumes (1×10^{-4} to 0.005 m^3) and temperatures (298 to 311 K). These clusters are conformed by 653 (from 31 articles) and 344 cases (from 24 articles), respectively. The main difference between these groups is the time of reaction. In particular, the green cluster represents experiments carried out at lower retention times (up to 69 days) than those in the yellow cluster (up to 160 days). In agreement with this, the centroid of the green cluster corresponds to a lower Y_{CH4} (~0.05 $m^3_{CH4} \cdot kg^{-1}_{VS}$) than that of the yellow cluster (~0.32 $m^3_{CH4} \cdot kg^{-1}_{VS}$). An interesting case in the yellow cluster is that of Zeeman et al. [113] which, although outside the main group of cases, shows high Y_{CH4} (0.11 $m^3_{CH4} \cdot kg^{-1}_{VS}$) for low operation temperature (298 K).

For secondary variables describing initial compositions, 4 studies report simultaneously Y_{CH4}, pH, DM mass fraction, VS mass fraction and COD values, yielding 108 cases. The first two principal components of these variables are shown in Figure 4.3b and retains 74.8% of the variance. The variables that most affect the first principal component (51.8% of variance) are VS, DM and COD. These variables relate to the available organic matter to be digested, thus, their vectors in Figure 4.3b are in similar direction. DM and COD present weak negative correlations with respect to Y_{CH4} resulting in Spearman's rho of -0.361 for DM (P-value= 6.3×10^{-18}) and -0.261 for COD (P-value= 2.5×10^{-9}), respectively. VS shows a moderate monotonic function (Spearman's rho= -0.457, P-value= 1.6×10^{-27}). The second principal component is more affected by pH and Y_{CH4}. These vectors show a strong negative correlation (Spearman's rho= -0.696, P-value= 1.0×10^{-97}), which is reflected in the opposite direction of their vectors in Figure 4.1b. This is an expected result because high pH content (e.g. ammonia in the slurry) can inhibit the methanogenic activity [228].

Eight clusters result (DB Index= 0.13, see Figure 4.3a) from the k-mean applied to the principal components of composition variables for batch digesters. The cases align in diagonals which

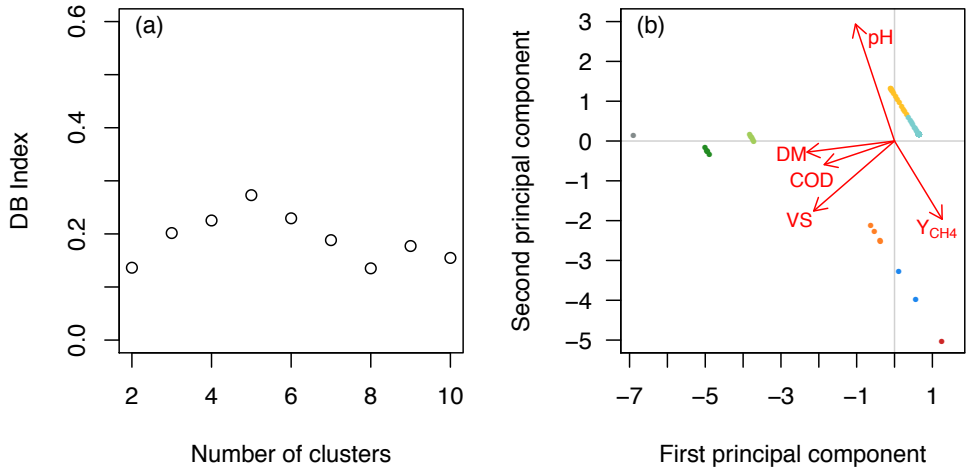

Figure 4.3: K-means clustering for first and second principal components of Y_{CH4} from batch digesters and variables describing slurry composition: a) evaluation of DB Index for 2 to 10 clusters and; b) clusters (each one in a different colour).

could suggest that other cluster algorithms are preferable (e.g. density-based). The particular large amount of clusters for this score-plot could be due to overlapping data in each diagonal, which can affect the DB Index optimisation [294]. The lines which arise from the cases are parallel with slope value -1.56. In the case of the yellow and light blue clusters, these align having pH 6.8, DM mass fraction 1.9%, VS mass fraction 62.7% and COD 21 $kg \cdot m^{-3}$. The Y_{CH4} for these clusters ranges from 0 to 0.33 $m^3_{CH4} \cdot kg^{-1}_{VS}$ and their intercept is 1.17. The orange, blue and red clusters (bottom right of Figure 4.3b) are aligned with an intercept -3.09. The cases in these clusters, have a fixed value for pH (6.5), DM mass fraction (2.3%), VS mass fraction (74.7% (dry matter)) and COD (30.3 $kg \cdot m^{-3}$). The red cluster corresponds to a case from the work of Pandey et al. [74], who attribute the high results for Y_{CH4} to differences in the inocula utilised (i.e. granular sludge from digester processing potato starch). However it is considered to be an outlier in this meta-analysis because it reports 1.67 $m^3_{CH4} \cdot kg^{-1}_{VS}$ for Y_{CH4}, which markedly exceeds the theoretical value (0.469 $m^3_{CH4} \cdot kg^{-1}_{VS}$ by Buswell's equation [65, 218]).

The light green cluster has pH 6.9, DM mass fraction 5.3%, VS mass fraction 73.6% (dry matter) and COD 70.3 $kg \cdot m^{-3}$, with Y_{CH4} ranging from 0.26 to 0.33 $m^3_{CH4} \cdot kg^{-1}_{VS}$. The parallel that crosses this cluster has an intercept -5.78. The final cluster corresponds to a single case from Pabon-Pereira et al. [72] (dark green cluster in Figure 4.3b). This has pH 6.9, DM mass fraction

10.5%, VS mass fraction 86.7% (dry matter) and COD 29.2 $kg \cdot m^{-3}$ (Y_{CH4} range= 0.14 to 0.23 $m^3_{CH4} \cdot kg^{-1}_{VS}$). If the same slope was repeated for this case, the intercept is -10.6. Overall, increase in the organic matter content of the slurry, it is observed that the lines shift to the left of Figure 4.3b. However, the increase of these variables presents no correlation with the range of Y_{CH4} in each aligned group. This is also observed in the low correlations (i.e. Spearman rho values) between Y_{CH4} and DM mass fraction, VS mass fraction and COD.

4.2.3 Continuous digesters

For these digesters cattle manure is fed continuously into the reactor while streams of biogas and digestate (products) are removed. Continuous digesters are less found in the database in comparison to batch systems. There are 335 cases for continuously-operated digesters, from which 331 (from 38 articles) are used because Y_{CH4} can be expressed as "$m^3_{CH4} \cdot kg^{-1}_{VS}$". If these continuous digester cases were considered in a single distribution, this would result in in a non-normal distribution (Shapiro's P= 4.56×10^{-30}) with median 0.137 $m^3_{CH4} \cdot kg^{-1}_{VS}$. However, there are markedly different types of continuous digesters. Specific subcategories that are found and analysed in this section are: continuously-stirred tank reactors (CSTRs), fixed-film reactors, plug-flow reactors (PFRs) and up-flow anaerobic sludge blanket (UASB). The distribution of Y_{CH4} for these digesters are shown as green box plots in Figure 4.4. The orange box plot correspond to distribution of Y_{CH4} which are jointly reported with N_i and s_i, thus, can be used for meta-analysis. The results from meta-analyses models are also presented in Figure 4.4 (fixed-effect model: red circles and random-effect model: yellow circles).

There are 241 cases (from 35 articles) in the database that report Y_{CH4} from CSTR. These present a non-normal distribution of Y_{CH4} (Shapiro's P= 2.91×10^{-5}) and has median 0.141 $m^3_{CH4} \cdot kg^{-1}_{VS}$. As expected, this distribution is significantly lower (Wilcoxon's P= 2.97×10^{-16}) from the B_0 of batch digesters. This is due to significantly lower HRTs in continuous digesters compared to residency time in batch digesters (Wilcoxon's P<2.2×10^{-16}). From this distribution, 12 cases report Y_{CH4} with N_i and s_i (orange box plot in Figure 4.4). This subgroup is non-significantly different from the distribution of all Y_{CH4} reported for CSTR (Wilcoxon's P= 0.143). Therefore,

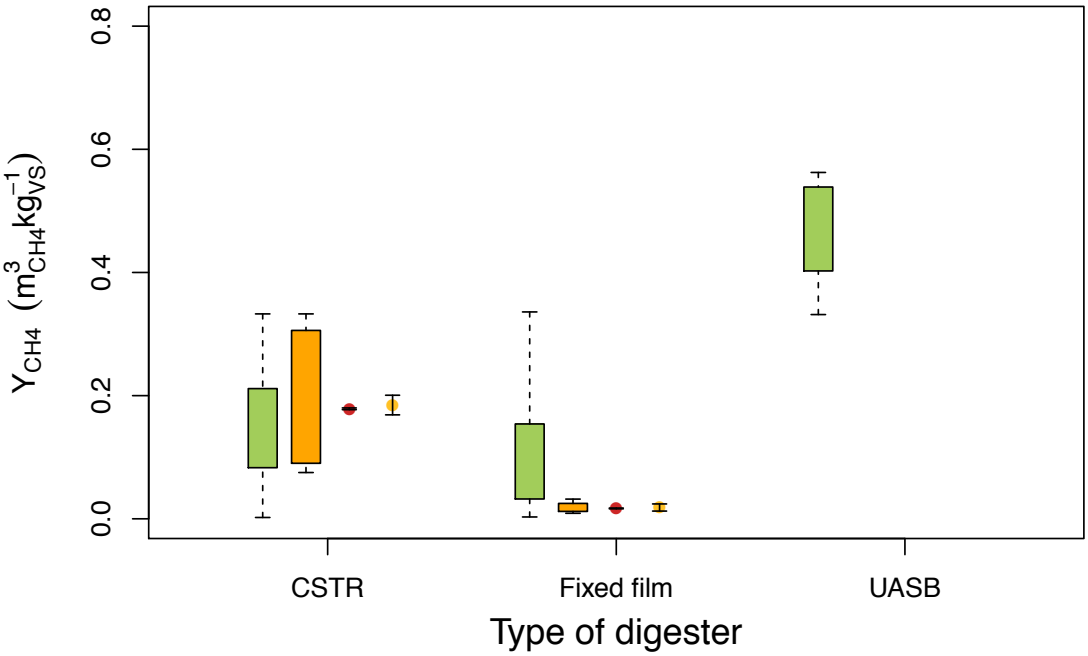

Figure 4.4: Y_{CH4} of dairy cattle manure for three types of continuous digesters in Part I of the database. Green box plot: Y_{CH4} for continuous digesters; orange box plot: Y_{CH4} which are reported together with s_i and N_i; red circles: results from fixed-effect model and; yellow circles: results from random-effect model.

meta-analysis models applied over this subgroup are representative of the literature data. A mean 0.179±0.001 $m^3_{CH4} \cdot kg^{-1}_{VS}$ results for the fixed-effect model and 0.190±0.016 $m^3_{CH4} \cdot kg^{-1}_{VS}$ for the random-effects model.

Multi-variate analysis is carried out for CSTRs because these are the most numerous cases reported for continuous digesters. Score-plots for operation variables associated with CSTR are shown in Figure 4.5b. From 23 articles which report the operation variables of Table 4.3, 173 cases are extracted and used for principal component analysis. The first principal component of Figure 4.5b corresponds to 43.2% of the variance and is highly dependent on Y_{CH4}, organic loading rate (OLR) and volume. Contrary to batch digesters, the volume and temperature vectors are in the same direction as the Y_{CH4} with respect to the first principal component. These both variables show a strong positive correlation with respect to Y_{CH4} (Spearman's rho 0.71 for volume and 0.69 for temperature). The second principal component retains 26.8% of the variance and is mostly influenced by the HRT and OLR. A positive moderate correlation is found, between the Y_{CH4} and

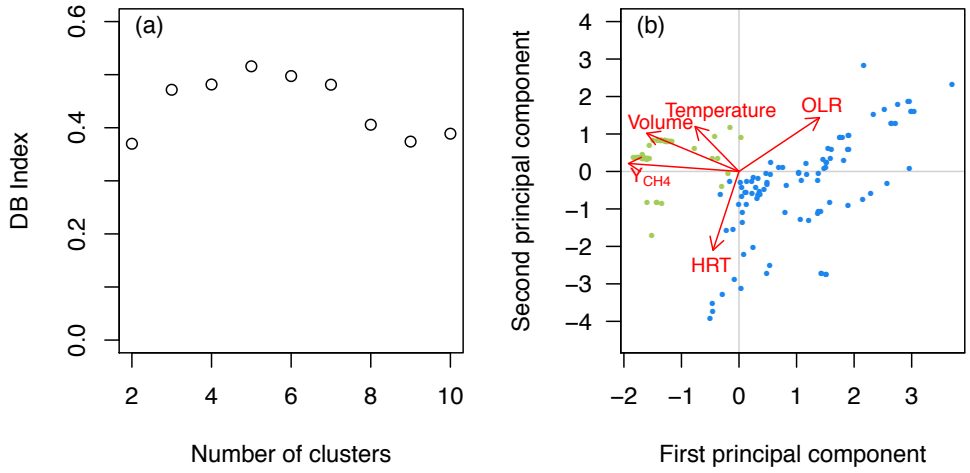

Figure 4.5: K-means clustering for first and second principal components of Y_{CH4} from CSTR digesters and operation variables: a) evaluation of DB Index for 2 to 10 clusters and; b) Clusters (each one in a different colour).

HRT (Spearman's rho= 0.435, P-value: 2.7×10^{-16}). At lower HRT (< 40 days), Y_{CH4} exhibits a larger range (0.002 to 0.333 $m^3_{CH4}\cdot kg^{-1}_{VS}$), while presenting more stable values thereafter. These observations are similar to the asymptotic profiles for Y_{CH4} and retention time in batch digesters (see biplot of Figure 4.6). With respect to the OLR, the Y_{CH4} is in opposite direction having a Spearman's rho of -0.45 (P-value: 5.2×10^{-11}). This is an expected result because increasing OLR (i.e. lowering the retention times) can wash-out bacterial cultures reducing the digester performance [23].

Two clusters are output from the application of k-means to the principal components of Figure 4.5b (DB Index= 0.37 from Figure 4.5a). The blue cluster is conformed by 95 cases from 16 articles. This cluster groups cases of CSTR in a larger range of HRT (0 to 128 days) and OLR (0.12 to 34.4 $kg_{VS}\cdot m^{-3}\cdot d^{-1}$), compared to the green cluster (HRT: 8 to 69 days and; OLR: 0.12 to 6.6 $kg_{VS}\cdot m^{-3}\cdot d^{-1}$). The digesters operating within the blue cluster also have lower temperatures (383 to 328 K) and result in lower Y_{CH4} (maximum 0.220 $m^3_{CH4}\cdot kg^{-1}_{VS}$). For the green cluster, 78 cases (from 11 articles) are observed in Figure 4.5b. The Y_{CH4} from cases in this cluster range from 0.115 to 0. 333 $m^3_{CH4}\cdot kg^{-1}_{VS}$. In general, these cases operate at higher temperatures (35 to 328 K) in larger digesters (up to 1.5 m^3) than those in the blue cluster (up to 0.23 m^3).

With regards to the composition variables (see Table 4.3), it is found that there are insufficient

cases of CSTR digesters in the literature for dairy cattle manure to perform principal component analysis. However, there are enough cases for bi-variate analysis between Y_{CH4} and each composition variable (Figure 4.6). The variables most correlated with Y_{CH4} are found to be the pH (Spearman's rho= -0.685, P-value= 2.0×10^{-15}) and nitrogen content of untreated manure (i.e. TKN, Spearman's rho= 0.605, P-value= 7.8×10^{-13}). The strong correlation between pH and Y_{CH4} is in agreement with the findings for batch digesters. However, high correlation between TKN and Y_{CH4} is unexpected because higher nitrogen in ammonia has been reported to inhibit AD [228]. For variables related to organic material in the input slurry, only weak correlations are found with respect to Y_{CH4}: DM (Spearman's rho= 0.188, P-value= 0.018), VS (Spearman's rho= -0.338, P-value: 2.5×10^{-5}) and COD (Spearman's rho= 0.48, P-value= 1.9×10^{-8}).

Fixed-film reactors are the second most found for continuous digesters collected in the database (N= 81, from five articles). The Y_{CH4} for this digester type (green box plot in Figure 4.4) is non-normally distributed (Shapiro's P= 3.3×10^{-14}) and has median 0.103 $m^3_{CH4}\cdot kg^{-1}_{VS}$. From these Y_{CH4}, eight cases from the work of Lo et al. [55] are the only to report N_i and s_i (orange box plot Figure 4.4). The fixed-effect meta-analysis model applied over these eight cases results in Y_{CH4} of 0.017±0.001 $m^3_{CH4}\cdot kg^{-1}_{VS}$. For the random-effect model, the mean Y_{CH4} is 0.018±0.006 $m^3_{CH4}\cdot kg^{-1}_{VS}$. However, the means obtained by meta-analysis should be used with caution as the distribution of the eight cases in the subgroup is significantly different (Wilcoxon's P= 3.94×10^{-4}) from the Y_{CH4} in the 81 cases for all fixed-film reactors in the database.

For the remaining continuous digesters, insufficient cases are found for the application of meta-analysis models. A single case is found to report experimental Y_{CH4} of dairy cattle manure in dimensions of interest for PFR (N= 1). Thus, the latter is omitted from Figure 4.4. For UASB digesters, there are eight cases which report experimental Y_{CH4} and correspond to the work of Rico et al. [81]. The distribution of these digesters is normal (Shapiro's P= 0.58) and has median 0.484 $m^3_{CH4}\cdot kg^{-1}_{VS}$ (see Figure 4.4). The mean of these cases exceeds the theoretical value (0.469 $m^3_{CH4}\cdot kg^{-1}_{VS}$ by Buswell's equation [65, 217]. However, they do not present a significant difference (Wilcox's P= 1). Therefore differences in Y_{CH4} could be attributed to chemical compositions or longer biomass retention time (i.e. formation of bacterial consortia and organic substrate).

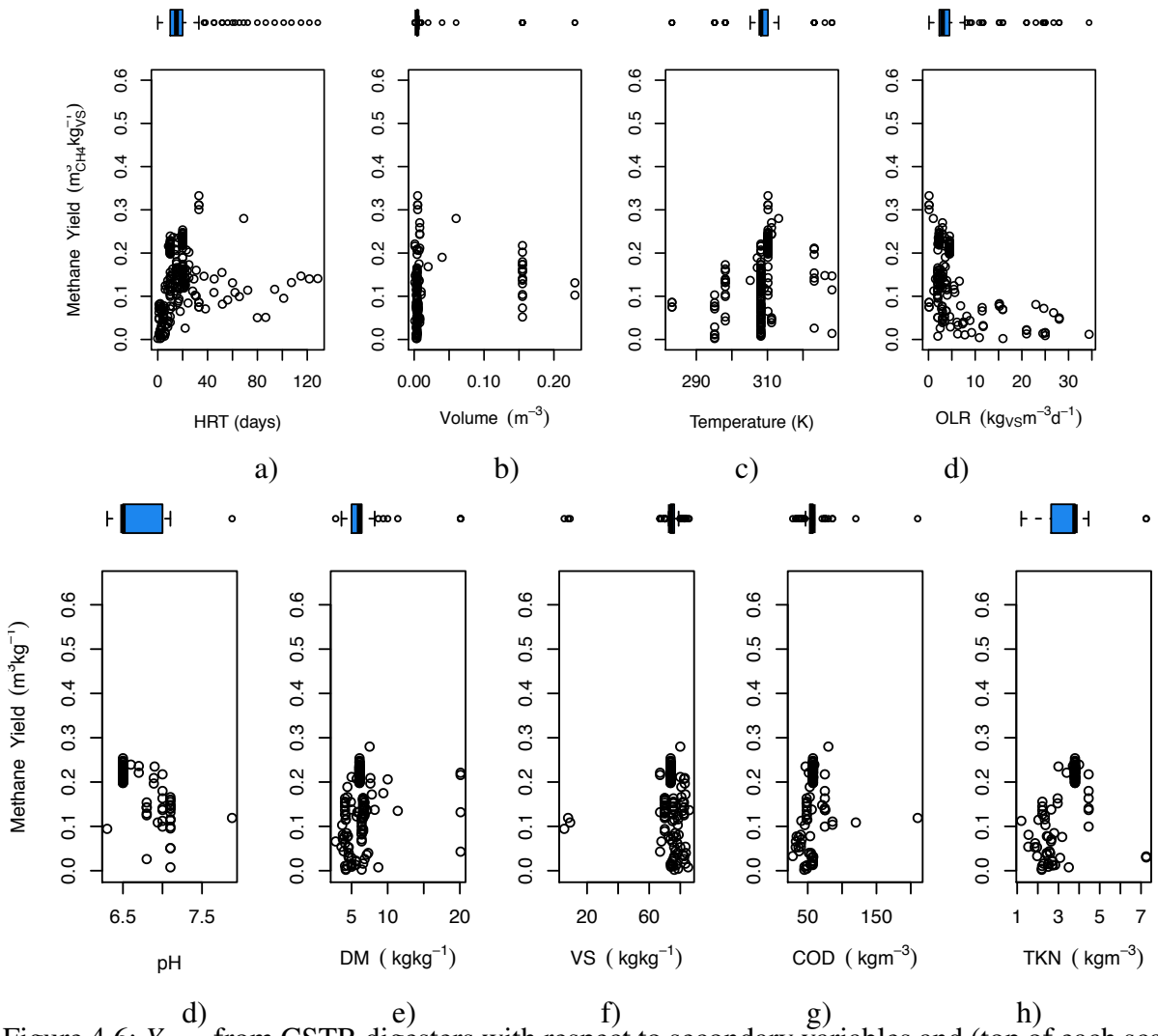

Figure 4.6: Y_{CH4} from CSTR digesters with respect to secondary variables and (top of each scatter-plot) the box plot showing the distribution of the secondary variables. Spearman-correlation results (from "a" to "h"): rho= 0.372, 0.673, 0.582, -0.423, -0.685, 0.188, -0.338, 0.480 and 0.605; P-values= 4.9×10^{-9}, 2.2×10^{-16}, 2.2×10^{-16}, 1.8×10^{-9}, 2.0×10^{-15}, 1.8×10^{-2}, 2.5×10^{-5}, 1.9×10^{-8} and 7.7×10^{-13}.

4.2.4 Semi-continuous digesters

For semi-continuous digesters the input and/or output of digesters are discontinuous (i.e. hybrid of batch and continuous reactors). There are 513 of these cases identified in this work, from which 443 (from 26 studies) are used.

One type of semi-continuous digester corresponds to AD lagoons. These usually accumulate manure periodically, but are discharged sporadically (e.g. when the digestate is needed as bio-fertiliser). There are 96 cases identified in the database for lagoon digesters from three articles.

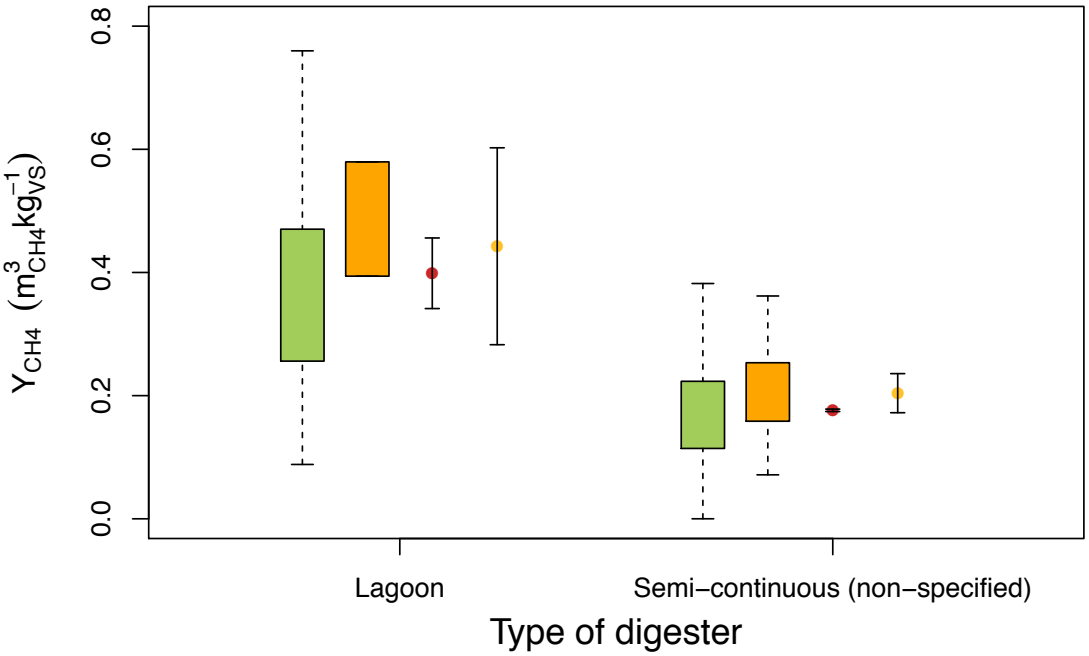

Figure 4.7: Y_{CH4} of dairy cattle manure for semi-continuous digesters in Part I of the database. Green box plot: Y_{CH4} for continuous digesters; orange box plot: Y_{CH4} which are reported together with s_i and N_i; red circles: results from fixed-effect model and; yellow circles: results from random-effect model.

The high variability in loading/discharging rates and operation temperature for AD lagoons results in a large interquartile range of 0.214 $m^3_{CH4} \cdot kg^{-1}_{VS}$ (see green box plot in Figure 4.7). The Y_{CH4} for these semi-continuous digesters presents a non-normal distribution (Shapiro's P= 2.84×10^{-6}) and median 0.345 $m^3_{CH4} \cdot kg^{-1}_{VS}$. Higher performance of lagoons with respect to batch digesters is attributed by the authors of these cases [20, 75, 273], to degradation of accumulated organic matter on the bottom of lagoons. Thus, more VS are available to be converted to CH_4, than the measured at the inlet to the AD lagoons. From the above, it is suggested that for future work, measurements of VS fed to lagoon digesters are standardised.

From the 96 cases, only two (from two articles [75, 273]) can be used for meta-analysis models. These are presented as the orange box plot in Figure 4.7. The Y_{CH4} from these cases are non-significantly different from the distribution of all lagoon digesters (Wilcoxon's P= 0.297). The fixed-effect model results in a mean 0.400 ± 0.057 $m^3_{CH4} \cdot kg^{-1}_{VS}$ (see red circles in Figure 4.7). This is in great agreement with the case from Safley et al. [273] because the sample size of Y_{CH4} from

that case is 93, whereas, the case from Park et al. [75] has a sample size of seven. For the random-effect model a mean of 0.440±0.160 $m^3_{CH4} \cdot kg^{-1}_{VS}$ is obtained.

There are 347 cases in Part I of the database (from 23 articles) that include Y_{CH4} from other non-specified semi-continuous digester (also shown in Figure 4.7). Their distribution is non-normal (Shapiro's P< 2.2×10^{-16}) with median 0.173 $m^3_{CH4} \cdot kg^{-1}_{VS}$. A subgroup of 27 of these cases (from five articles) are utilised for meta-analysis models. The fixed-effect model results in a mean 0.176±0.001 $m^3_{CH4} \cdot kg^{-1}_{VS}$ and for the random-effect model 0.204±0.032 $m^3_{CH4} \cdot kg^{-1}_{VS}$.

There are 98 cases from 15 articles in the database that specify all operation variables of Table 4.3 and Y_{CH4}, for semi-continuous digesters (non-specific, i.e. AD lagoons analysed previously are excluded). These cases undergo principal component analysis and the resulting score-plot are presented in Figure 4.9b. With the exception of the volume vector, it is observed that according to the variables directions (red arrows of Figure 4.9b), the semi-continuous digesters are in closer agreement to the batch digesters than the continuous digesters. In fact, it is observed that the studies utilising semi-continuous digester are classified as such because of the feeding procedure, however, the overview of many systems corresponds to dynamic states, rather than stationary (i.e. continuously operated digesters).

The first principal component represents 43.7% of the variance and the second 27.8%. The first principal component is highly dependent on OLR and Y_{CH4}, exhibiting a weak correlation (Spearman's rho= -0.262; P-value= 1.0×10^{-5}). The second principal component is mostly affected by the volume and temperature. The direction of the Y_{CH4} vector is opposite (along the first principal component axis) to the digester temperature. This show a weak and inverse correlation which is further indicated by the Spearman's rho value -0.162 (P-value= 2.6×10^{-3}). The volume of digesters also presents a weak negative correlation to the Y_{CH4} (Spearman's rho= -0.250, P-value= 2.5×10^{-6}). Regarding the HRT and Y_{CH4} vectors, these have similar direction, with respect tot the first principal component. These variables exhibit a moderate positive correlation (spearman's rho= 0.242, P-value= 5.1×10^{-6}) and follow similar patterns than those observed for batch digesters (i.e. asymptotic curves, see Figure 4.8a).

Three clusters are found (minimum DB Index= 0.33, Figure 4.9a) for semi-continuous digesters

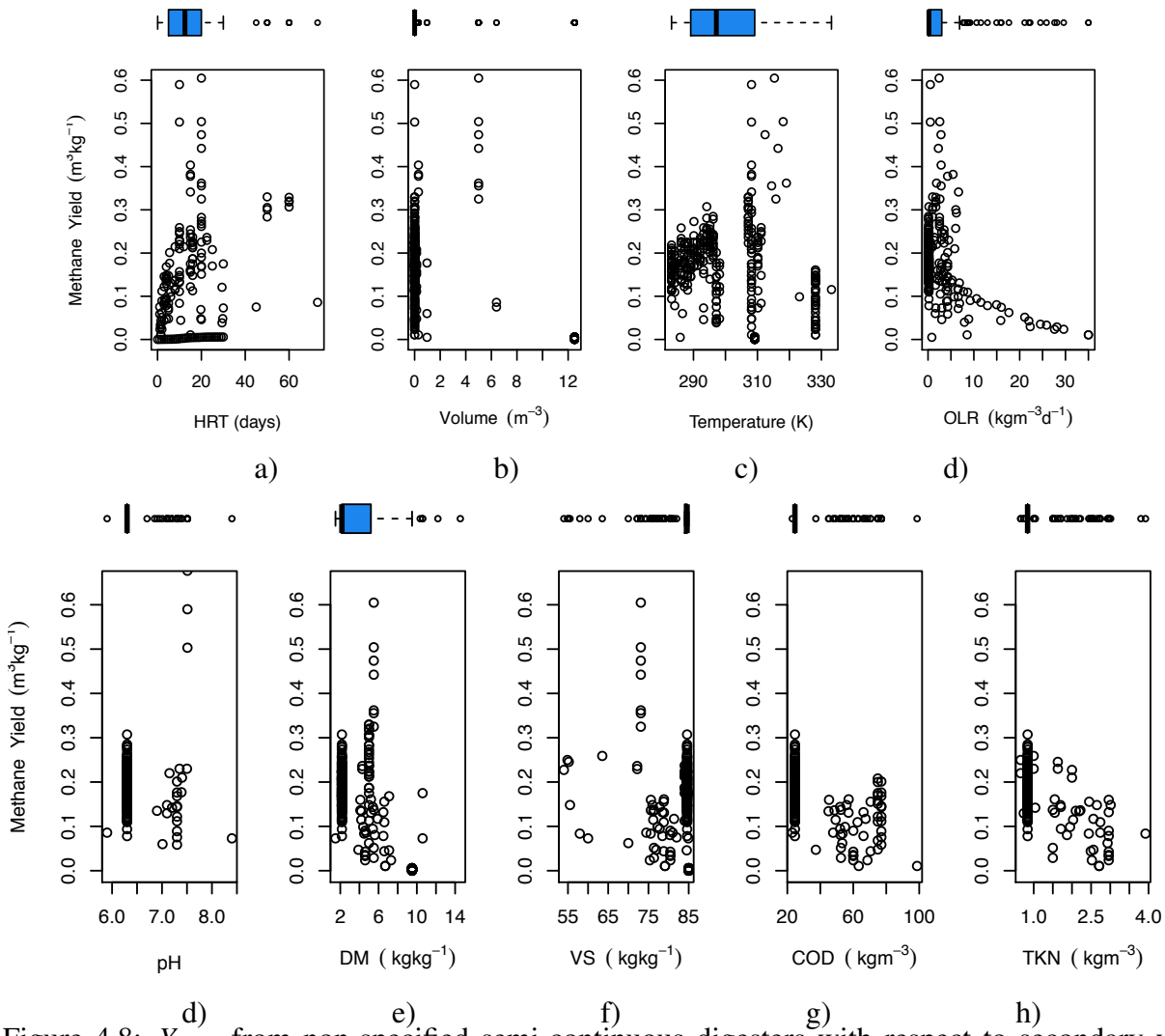

Figure 4.8: Y_{CH4} from non-specified semi-continuous digesters with respect to secondary variables and (top of each scatterplot) the box plot showing the distribution of the secondary variables. Spearman correlation results (from "a" to "h"): rho= 0.343, -0.250, -0.162, -0.262, -0.060, -0.354, -0.284, -0.542 and -0.485; P-values= 5.1×10^{-6}, 2.5×10^{-6}, 2.6×10^{-3}, 1.0×10^{-5}, 0.413, 2.8×10^{-9}, 3.5×10^{-6}, 2.2×10^{-16} and 1.6×10^{-13}.

and presented in Figure 4.9b. The red clusters comprises 28 cases from three different articles of Lo et al. [55, 57, 58]. It is observed that all cases in the cluster operate at thermophilic conditions (328 K) and volume 0.003 m^3. The differences in principal components for this cluster are due to changes in OLR (2.07 to 35 $kg_{VS}\cdot m^{-3}\cdot d^{-1}$) and HRT (1 to 15 days). The Y_{CH4} range is the lowest among those in Figure 4.9b, from 0.011 to 0.161 $m^3_{CH4}\cdot kg^{-1}_{VS}$. The blue cluster comprises 57 cases from 13 articles. These cases exhibit higher Y_{CH4} than the red cluster, with centroid at approximately 0.262 $m^3_{CH4}\cdot kg^{-1}_{VS}$. This is attributed to higher HRT (1 to 60 days) and lower OLR

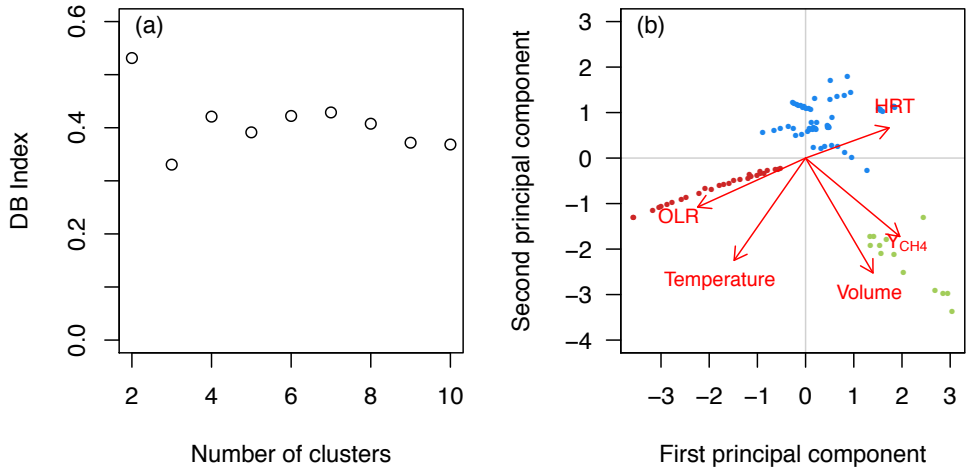

Figure 4.9: K-means clustering for first and second principal components of Y_{CH4} from semi-continuous digesters and operation variables: a) evaluation of DB Index for 2 to 10 clusters and; b) clusters (each one in a different colour).

(0.4 to 8.87 $kg_{VS} \cdot m^{-3} \cdot d^{-1}$. The semi-continuous digesters of the blue cluster operate at the lowest range of temperature (293 to 310 K), which is consistent with psychrophilic and mesophilic conditions. The volumes of the digesters in this cluster covers a large range (between 0.4×10^{-4} m^3 and 0.3 m^3), suggesting that this operation variable is not affecting the principal components describing AD performance. The green cluster of Figure 4.9b corresponds to 13 cases from two articles. The Y_{CH4} are the highest found for the semi-continuous digesters, with centroid at approximately 0.77 $m^3_{CH4} \cdot kg^{-1}_{VS}$. This exceeds batch performances, which could suggest the presence of lagoons which, as discussed previously, have been identified to have higher performances due to organic material accumulated in the bottom of digesters. The OLR (0.5 to 2.9 $kg_{VS} \cdot m^{-3} \cdot d^{-1}$) and HRT (10 to 20 days) is not markedly different from the other clusters. The temperatures of the digesters in the green cluster are between 308 and 318 K (mesophilic conditions). This suggests that temperature is a key factor in the separation of the three clusters.

As for continuous digesters, there are insufficient cases in the database to perform principal component analysis over composition variables of interest. Considering bi-variate analysis some moderate correlations can be found between Y_{CH4} and secondary variables describing initial composition of the dairy cattle manure. The strongest correlations between Y_{CH4} and a secondary composition variable for semi-continuous digesters is with COD (Spearman's rho= -0.542, P-value=

2.2×10^{-16}) and TKN (Spearman's rho= -0.482, P-value= 1.6×10^{-13}). This interesting result supports the well-known work of Angelidaki et al. [228], which reports that an increase in ammonia (containing nitrogen) can suppress CH_4 production in AD of livestock waste. However, it should be noted that Sterling et al. [92] have reported that only steep increases in ammonia can inhibit AD, while gradual increases could enhance the AD performance. The latter is not evidenced in the results of this work.

Other composition variables of interest are less or only weakly correlated to Y_{CH4}: pH (Spearman's rho= -0.06, P-value= 041), DM (Spearman's rho= -0.354, P-value= 2.8×10^{-9}) and VS (Spearman's rho= -0.284, P-value= 3.5×10^{-6}).

4.2.5 Maximum methane yields (B_0)

This section considers the B_0 of dairy cattle manure (i.e. obtained from batch essays). These values are interesting to study separately from other cases because they can be utilised to quantify potential energy output and environmental benefits of AD systems. In terms of databases, only one other is found in the literature specifically for B_0. This is reported in the work by Chynoweth et al. [295] and includes municipal wastes, woody feedstocks, among others; but it does not include B_0 of dairy cattle manure. Another weakness of that database is that it is developed in a non-reproducible manner (i.e. not compiled systematically). In terms of meta-analysis in the literature covering maximum yields, the most similar work is that from Daemmgen et al. [296]. They inspected the available B_0 and *MCF* in literature. However, the authors only covered German and Austrian slurries, without systematically selecting and synthesising the findings. Thus the systematical review and meta-analysis of B_0 for all regions described in the IPCC Guidelines [151], is a novel approach.

Much experimental work to determine B_0 is based on the methodology described by Owen et al. [222]. However, it should be noted that there is little agreement in the use of this or any standard protocol [219]. This results in difficulties to identify the differences between AD systems. In particular, an essential issue to consider when comparing B_0 from different AD systems is to report the temperature and pressure at which the experiments are carried out (i.e. as reported by

Marti-Herrero et al. [297]). In order to estimate robust B_0 values, this section utilises the B_0 samples collected in Part I of the database. Novel effect sizes are obtained by meta-analysis models. Results are compared against the B_0 default values from the IPCC methodology [151], in accordance to the world regions of the latter.

The IPCC Guidelines provide two default B_0 for AD of dairy cattle manure. For Europe, Oceania and North America the default B_0 is 0.24 $m^3_{CH4} \cdot kg^{-1}_{VS}$ and is based on the work of Morris [151, 225]. For other regions of the world the default value 0.13 $m^3_{CH4} \cdot kg^{-1}_{VS}$ is based on the work of Safley et al. [151, 224]. A revision of these values is needed because they only consider a reduced amount of literature (from 1976 and 1992) and excludes the last thirteen years of research which, according to the findings of this work (Chapter 3), accounts for the fraction of 87.5% of published articles in the field. Furthermore, the B_0 of the original work is based on the diet of dairy cattle which are also in need of update.

The B_0 values from the IPCC are shown as blue circles in Figure 4.10. It should be noted that

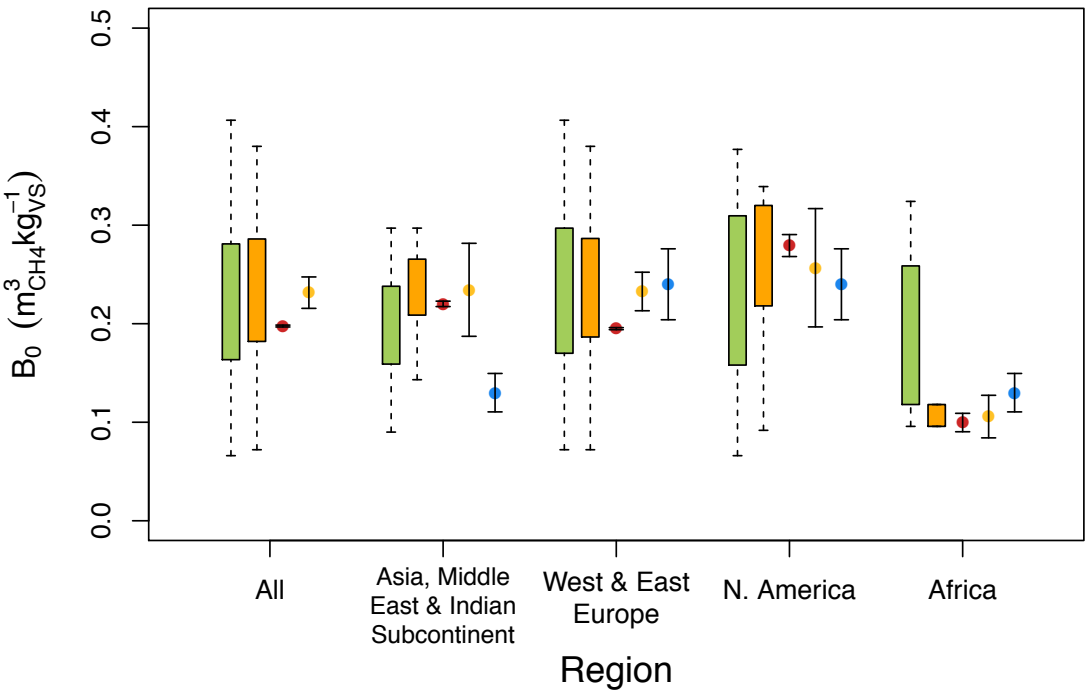

Figure 4.10: B_0 from batch test according to regions. Blue circles: IPCC default values[151]; green box plot: all B_0 in the developed database; orange box plot: B_0 in database which are reported with s_i and N_i; red circles: results from fixed-effect model and; yellow circles: results from random-effect model.

these default Y_{CH4} are not considered in the subgroup for meta-analysis because the original sources [224, 225] are published in books (i.e. not research articles as required by the first criterion).

From Part I of the database, 799 cases are identified (from 42 articles) as either biochemical potential tests or determination of B_0 in similar batch conditions (i.e. measuring cumulative CH_4 production until no increase is observed). For articles reporting Y_{CH4} against time, the B_0 of each profile is extracted. In the 42 articles, 143 cases are identified as B_0 measurements. The distribution of B_0 are represented by the green box plots of Figure 4.10. For all the regions defined in the IPCC Guidelines, experimental results (in comparable units of measurements) are found for B_0, except Oceania and Latin America (i.e. omitted in Figure 4.10). As expected, these are significantly higher than the Y_{CH4} distribution for all batch cases (Wilcoxon's P= 9.67×10^{-10}).

It is observed in Figure 4.10, that the B_0 values from the IPCC with their corresponding error bars ($\pm$15%), are within the distribution of B_0 found in the database. In fact, only the region comprising "Asia, Middle East & Indian Subcontinent" show a significant difference (Wilcoxon's P-values in Table 4.4) between its B_0 distribution and the IPCC value. This can be attributed to developments in feeding of dairy cattle in that region, because the IPCC default values are based on the livestock diets prior to 1992 [224]. Similar observations occur for African experiments (60% of the cases are greater than the default IPCC value). However, the sample size is not large enough (N= 5) to prove a significant difference. Europe and North America present the larges samples of B_0 (see Table 4.4), as expected from the origin of the articles identified in Section 3.2.1.

Although most regional B_0 values from IPCC are non-significantly different from those in the database, results indicate that other means and error bars can better represent the findings of the literature. Therefore novel effect sizes and confidence intervals are examined by applying fixed- and random effect models of meta-analysis.

The meta-analysis models require cases which report B_0 together with specific N_i and s_i are selected. There are 53 cases from 21 studies which comply with this and are selected. The distributions of this subgroup of B_0 is shown in Figure 4.10 (orange box plots). Results show that the means of these distributions differ with the IPCC default value between 0.01 and 0.13 $m^3_{CH4} \cdot kg^{-1}_{VS}$. In particular, the subgroup distributions for "Asia, Middle East & Indian Subcontinent" is again the

Table 4.4: Wilcoxon's P-values between default B_0 values from IPCC and B_0 from database of this work, according to region of the world.

B_0 **group**	**Asia, Middle East & Indian Subcontinent**	**West & East Europe**	**North America**	**Africa**
All B_0 in database	0.023 (38)	1.000 (76)	0.908 (24)	0.571 (5)
Subgroup B_0 [a]	0.033 (7)	0.916 (36)	0.474 (8)	0.400 (2)

[a]Subgroup of "All B_0" which report specific N_i and s_i, thus, can be used for meta-analysis models. Numbers of cases of B_0 in database in parenthesis.

only significantly different (p<0.05) (i.e. as for green box plot of Figure 4.10).

The results of fixed-effect and random-effect models are also shown in Figure 4.10 in red and yellow circles, respectively. The means obtained by the random-effect models are found to be in best agreement with the distribution of the subgroup of B_0 cases (i.e. cases reporting N_i and s_i), with differences between 0.001 and 0.026 $m^3_{CH4} \cdot kg^{-1}_{VS}$. The means for this model are 0.232±0.016, 0.234±0.047, 0.233±0.020, 0.257±0.060 and 0.106±0.022 $m^3_{CH4} \cdot kg^{-1}_{VS}$ for all regions, Asia/Middle East & Indian Subcontinent, West/East Europe, North America and Africa, respectively. For the fixed-effect model the means are 0.198±0.001, 0.220±0.003, 0.195±0.001, 0.279±0.011, 0.100±0.009 $m^3_{CH4} \cdot kg^{-1}_{VS}$, for the same regions mentioned above, respectively. This results in differences from 0.010 to 0.040 $m^3_{CH4} \cdot kg^{-1}_{VS}$ between the means of the fixed-effect model and those of the subgroup of B_0 cases. The random-effect model is expected to show better results because it assumes a distribution of B_0, rather than a fixed value. This is more representative of the high heterogeneity of the samples, which arise from different experimental set-ups. Therefore, it is preferable to adopt the results of B_0 from the random-effect model to estimate the potential CH_4 production from AD of dairy manure.

Compared to the IPCC default values, the random-effect meta-analysis model provides more robust values of B_0 (i.e. based on larger sample size, more updated cases and considers the heterogeneity of cases). Therefore, the means and confidence intervals of B_0 obtained by this model are suggested to replace those in the current IPCC Guidelines. Furthermore, it is recommended to apply this meta-analysis model for the estimation of B_0 of other digestible feedstock. This would provide better IPCC-default B_0 values, with stronger evidence-base (i.e. larger sample integration).

4.3 Summary of the chapter

This chapter presents a meta-analysis of Y_{CH4} of dairy cattle manure based on Part I of the novel database compiled. The systematic review of 115 articles (2,181 cases) shows that the report of operation conditions and slurry composition does not generally follow standardised protocols. The latter are strongly recommended in order to provide insights of the differences in performance of AD systems.

Meta-analysis models are applied over Part I of the database according to digester type (batch, continuous or semi-continuous). This methodology enables numerical combination and synthesis of experimental results to date. Most cases (N= 1,299) are reported for batch digesters and meta-analysis results in a mean Y_{CH4} of 0.230±0.016 $m^3_{CH4} \cdot kg^{-1}_{VS}$. CSTR (the most reported continuously-operated digester in the literature, N= 241), results in mean of 0.190±0.016 $m^3_{CH4} \cdot kg^{-1}_{VS}$ (random-effect model). Other continuous digesters, such as fixed-film, plug-flow and UASB require further cases for the application of meta-analysis. For non-specified semi-continuous digesters (N= 347), the mean calculated by the random-effect model is 0.204±0.032 $m^3_{CH4} \cdot kg^{-1}_{VS}$ (N= 27). Research on Y_{CH4} from lagoon digesters is recommended to be carefully reported because many of these systems are observed to not account for degradable material in bottom of lagoons.

Multi-variate analysis identifies clusters for Y_{CH4} and operation conditions (i.e. temperature, volume, time/HRT, OLR) or feedstock composition (i.e. pH, DM, VS, COD, TKN). This can contribute to the construction of AD scenarios by providing ranges of variables that are commonly grouped. Batch digesters form four clusters, while two clusters are identified for CSTR and three for semi-continuous digesters. For variables describing manure composition, batch digesters present eight clusters, while CSTR and semi-continuous digesters have insufficient cases. A moderate positive correlation is observed for Y_{CH4} of all digester types with respect to time (or HRT) (Spearman's rho: 0.343-0.410). Volume and temperature also exhibit positive moderate correlation with the Y_{CH4} in CSTRs and weak effect in batch and semi-continuous digesters. The strongest correlations found between Y_{CH4} and secondary variables result for pH in batch and CSTR, respectively (Spearman's rho: -0.685 and -0.696). For manure composition, only batch digesters present suffi-

cient cases for principal component and results in eight clusters. The multi-variate clusters found in the database indicate combinations of operation conditions (and feedstock composition) found in the literature. These can be helpful when making assumptions in the construction of AD scenarios. For example, in life-cycle-assessments it is often found that assumptions on AD variables are made from different sources. Instead, the clusters found in this work offer metrics for different variables which are more likely to be combined in practical cases. In addition, the sizes of these clusters can give insights on the expected confidence intervals for different digesters.

Meta-analysis applied over B_0 is a reliable form to correct the out-of-date IPCC default values. This method has a greater sample size (i.e. based on more articles than the current IPCC Guidelines). In particular, markedly higher Y_{CH4} results from the meta-analysis are obtained for Asia, Middle East and Indian Subcontinent than the IPCC guidelines. For Africa, the meta-analysis Y_{CH4} are noted to be lower than the IPCC values, but a larger sample size is required to prove a significant difference. The application of these statistically-estimated Y_{CH4} provides stronger evidence of bioenergy potentials from the dairy sector in accordance to continent. This methodology should be extended to other digestible feedstock of those guidelines for more robust evidence of literature results.

Chapter 5

Effect of AD on GHG emissions from dairy farms.

The emissions from AD scenarios in dairy farms has been widely reported through case studies in the literature. However, it is difficult to compare results between works because there are differences in system boundaries, functional units ($[f.u.]$, e.g. kilogram of CO_2-equivalent emissions per litre of milk produced or per ton of manure) and AD technologies. Consequently, overall conclusion have not been derived from the literature and underlying mitigation potentials of AD are not completely unveiled.

To overcome the different approaches found in the literature, meta-analysis can systematically integrate quantitative results. In particular, to address the diversity in scopes, Chapter 3 shows how GHG emissions reported in the literature are compiled in Part II of the database in accordance to farm activity (i.e. operation units defined in Section 3.1.3). To enable the combination of results reported with dissimilar functional units, this chapter defines relative changes between emissions from baseline and AD scenarios as the primary metric. Relative changes can be normalised with respect to global GHG emissions from baseline scenarios or the local operation unit under question (see Section 5.1).

To assess the overall effect of AD on emissions from dairy farms, non-parametric tests are introduced in Section 5.2. The Wilcoxon Signed Rank test is chosen to evaluate if AD systems

significantly change the GHG emissions of baseline scenarios. For examining correlations between emissions the Spearman Rank test is utilised (Section 4.1.4.1) and to determine the best estimates of relative changes the adaptive Kernel estimator is applied.

The distribution of relative changes are summarised in box plots in the result section of this chapter. These are discussed in terms of methodology to determine emissions (Section 5.3.1), specific GHG type (Section 5.3.2) and farm operation units (Section 5.3.3). Correlations and level of significance between scenarios are discussed to ultimately quantify the effect of applying AD over GHG emissions in dairy farms.

It should be noted that the main results of this chapter are based on the published work in Environmental Science and Technology "Meta-analysis of Greenhouse Gas Emissions from Anaerobic Digestion Processes in Dairy Farms" [264][1].

5.1 Normalisation of variables to relative changes

Relative change is chosen as key metric because it is related to response ratios which, in turns, have been identified as a successful mean to quantify ecological indicators in meta-analysis [261, 262]. Relative change reconciles differences in functional units of the original articles by non-dimensionalising the difference in emissions between baselines and AD-scenarios. Thus, it is independent of the unit of measurement of the original articles.

As a pre-requisite step for the calculation of relative changes, each case collected in Part II of the database presents separately the GHG emissions from a baseline (reference with no AD system) and an AD scenario (see Section 3.1.3). This chapter builds upon the operation units and GHG types from those scenarios to calculate relative changes. In particular, two types of relative changes are calculated. The first type corresponds to the difference in emissions of scenarios (or operation units), with respect to global emissions from standardised baseline scenarios (GHG_{B*}).

[1]Some results of this chapter are different than the mentioned publication because there have been articles and cases added to Part II of the database during its update in October 2015 (i.e. seven months after the published work).

These relative changes are denoted "$RC_{GHG,Op}$" and are calculated as follows:

$$RC_{GHG,Op}[\%] = \left(\frac{GHG_{Op,AD} - GHG_{Op,B}}{GHG_{B*}} \right) \times 100 \tag{5.1}$$

where GHG_{B*} accounts for the sum of emissions from storage, field application and use of fossil fuel in farm activities in the baseline scenario (as presented in Section 3.1.3). $GHG_{Op,AD}$ corresponds to the emissions in the AD scenario from the operation unit "Op" and similarly $GHG_{Op,B}$ from the corresponding operation unit in the baseline scenario. "Op" is "L" for digester leaks, "S" for storage of slurries, "F" for field-application of slurries, "FF" for offset of fossil fuels and "Fe" for offset of inorganic fertilisers. In the case of sources of emissions that only exist for the AD scenario (e.g. leaks from the digester), the value of $GHG_{Op,B}$ (for Op= L) is zero. It should be noted that GHG_{B*}, $GHG_{Op,AD}$ and $GHG_{Op,B}$ have the same units of measurement for each case in the database.

The second relative change used in this work normalises the difference in emissions according to a specific operation units. This relative change can be more useful in combining cases which do not comply with standard baseline scenarios (i.e. required for the global relative change). In particular, this type of relative change is utilised for comparing emissions from slurries (i.e. raw and digested) in storage and after field application. The local relative changes (denoted as "$RC^{*}_{Op,GHG}$") are calculated as follows:

$$RC^{*}_{GHG,Op}[\%] = \left(\frac{GHG_{Op,AD} - GHG_{Op,B}}{GHG_{Op,B}} \right) \times 100 \tag{5.2}$$

where $GHG_{Op,B}$ and $GHG_{Op,AD}$ are the GHG emissions released from the untreated manure and digestate, respectively, in the operation unit "Op".

For both types of relative changes utilised, negative values indicates less GHG emissions from an AD scenario with respect to its baseline. Relative changes which are less than -100% indicate that more GHG emissions are eliminated (by offsets) than those emitted in the baseline scenario. Conversely, positive relative changes indicate higher emissions from AD scenarios. Examples of the calculation of relative changes can be found in the Appendix B.

5.2 Statistical methods

The distributions of the relative changes are represented as box plots for discussion and analysis. Similar to other meta-analysis [262], relative changes are not weighted so that each case has the same level of impact on the distributions. As for the meta-analysis of Chapter 4, normality is assessed by the Shapiro-Wilk test [282, 290]. The dispersion of the relative changes is examined by analysing outliers and interquartile ranges. Outliers are defined as those cases which present relative changes more then 1.5 interquartile distant from the box plots (first or third quartile). If present, the statistical analysis of the relative change distribution is carried out with and without the outlier(s).

Because the distributions of relative changes of emissions are found to be mainly non-normal, statistical analysis is based on the non-parametric tests. Non-parametric statistic tests are applied, first, to assess the overall effect of AD on emission and, second, to examine the relation between relative change in emissions.

To evaluate the significance of the changes in GHG emissions from baseline to AD scenarios it is necessary to numerically compare the distribution of relative changes to zero (i.e. value of relative change in which both scenarios have the same GHG emissions). For this purpose the Wilcoxon Signed Rank test is chosen [284, 290]. The null hypothesis of this non-parametric test is that two paired distributions ("A" and "B") belong to the same underlying population. In this case the distribution "B" is considered to be a vector of zero values, with length equal to that of sample "A" (i.e. to pair each value in "A" to zero). The following steps are carried out to determine the test statistic and P-value [284, 285]:

1. The difference between data points of "A" and "B" distributions is calculated. Because the samples in this work (distribution "A") are paired with zero (distribution "B"), these differences are equal to the values or relative changes in distribution "A" ($x_i - 0$).

2. The absolute value of the differences previously calculated ($|x_i - 0|$) are ranked. The lowest difference is assigned rank "1".

3. The sum of ranks are computed separately for positive (w_+) and negative differences (w_-),

respectively, as:

$$w_+ = \sum_i r_i^+ \text{ and } w_- = \sum_i r_i^-$$

where r^+ and r^- correspond to the ranks of the positive and negative differences, respectively.

4. The test statistic is selected as the smallest sum of ranks ($min(w_+, w_-)$) for two-tailed test, which is preferred because it is unknown if distribution "A" will be greater or lower than zero.

5. Standard distribution of the sum of the ranks (W_0) are utilised to determine the P-value of the test. This is defined as the probability that $W_0 \geq min(W_\pm)$. If this probability should be less than 5%, then there is a significant difference between the distribution "A" and zero.

To examine the correlations between relative changes (i.e. from different operation units and GHGs), the Spearman Rank test is chosen [285, 286]. Its selection rationale and mathematical implementation is presented previously in Section 4.1.4.

To identify the best estimate of relative changes, two-dimension density distributions are examined by the adaptive kernel estimator (modified from Bishop et al. [298]). This test adjusts bin-bandwidths in accordance to density of datapoint (i.e. relative changes for this chapter). The optimum bandwidth is used to form continuous probability distributions.

5.3 Results and discussion

Robust estimations of the overall quantitative effects of AD over GHG emissions in dairy farms are currently unavailable. In consequence, diverse methods for calculating emissions from scenarios with this technology are found, for example, in life-cycle assessments. To solve this, so far this work has systematically collected values of GHG emissions in Part II of the database (Chapter 3) and reconciled differences in functional units by non-dimensionalising to relative changes (Section 5.1). The next step consists of numerically combining relative changes to find best universal estimates and is covered in this section.

As an introduction to the results, Section 5.3.1 first illustrates the different methods found in the literature to determine GHG emissions from dairy farm scenarios. In particular, relative changes obtained from experimental measurements, models based on IPCC and models from independent researchers are compared and discussed. Relative changes are then categorised by type of GHG in Section 5.3.2 to identify the overall changes of CO_2, N_2O and CH_4 from baseline to AD scenarios. Thereafter, Section 5.3.2 assesses the changes emission of these GHGs according to the operation units. The best estimates for relative changes are reported in the latter sections based on non-parametric statistics and kernel distribution estimator.

5.3.1 Relative changes according to method of emission estimation

Three main groups of methodologies to determine the GHG emissions from dairy farms are found in Part II of the database: experimental measurements, models from independent researchers and models based on IPCC guidelines [151]. For empirical results, no case account simultaneously for emissions from all operation units needed to compile baseline and AD scenarios (e.g. a complete baseline scenario includes energy consumption of dairy activities, storage and field application of untreated slurry, as defined in Section 3.1.3). In this respect, experimental works focus on measuring the GHG emissions of specific operation units (analysed individually in Section 5.3.3). Therefore, relative changes for complete scenarios can be calculated only model results collected in Part II of the database.

The modelled emissions yield 38 cases (from 12 papers [122, 131, 133, 134, 136, 140–142, 144–146, 150] of the database). The box plots of these relative changes are shown in Figure 5.1. IPCC-based result published in the literature show overall reductions of emissions due to the implementation of AD processes. This is a significant change with respect to baseline scenarios (Wilcoxon's P= 2.87×10^{-5}). The median of the relative changes shows a reduction in emissions by -73.2%. For other models reported in the literature, significant reductions of GHG emissions are also found. This result is supported by the median of -11.8% and its significant differences with respect to zero (Wilcoxon's P= 6.1×10^{-5}). The extraction of the outliers does not affect the significance of the reductions.

When comparing the two box plots of Figure 5.1 three main observation are found. First, most of the model cases (23 cases from 10 articles [131, 133, 134, 136, 141, 142, 144–146, 150]) have estimated GHG emissions based on the IPCC methodology [151]. This is expected because the latter is an international guideline recommended for nations to estimate their GHG inventories. Thus, the IPCC methods are more established than any individual model. Second, the IPCC-based

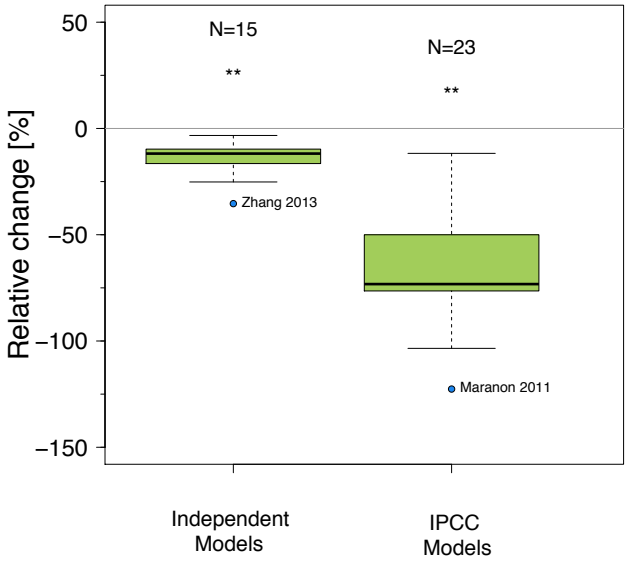

Figure 5.1: Box plot for the relative changes of total GHG emissions according to methodology used to determine emissions. Upper and lower sides of boxes: first and third quartile; line through the box: median; ○: outliers (>1.5 interquartile range); N= number of cases; positive values: emissions with AD are higher; negative values: emissions with AD are lower; n.s.: not significantly different from zero (Wilcoxon Signed Rank test P>0.05); **: P<0.01; *: P<0.05; Z-values: 0.298 and -0.250.

models show a larger interquartile range (26.4%) with respect to independent models (6.8%). This could be attributed to one independent model being dominant in the latter category (i.e. Weiske et al. [122] presents 14 cases). Thus it is expected that there is consistency and agreement in the findings of a single article. Third, cases based on IPCC methods, estimate more reductions than independent models. This could imply an over-estimation of mitigation potentials of AD systems. Therefore, to provide more detailed understanding of the effect of AD over GHGs, relative changes are analysed in the following sections according to specific GHG and operation units.

5.3.2 Relative changes of specific GHGs

The box plot of relative changes for overall GHGs and specifically CH_4, CO_2 and N_2O emissions with respect to each of their baseline emissions, are presented in Figure 5.2. It should be noted that some cases report individual contributions of multiple GHGs while other report emissions of complete scenarios without specifying GHG type. Therefore, the cases (N) of "All GHGs" in Figure 5.2 does not necessarily correspond to the sum of the cases of individual GHGs.

Results in Figure 5.2 indicate that total GHG emissions are significantly reduced by applying AD (median= -41.43%, Wilcoxon's P= 8.04×10^{-8}). However, not all specific GHGs show a significant decrease in emissions.

For CH_4 emissions, it is observed that the cases collected in the database are more focused on that released from storage of untreated slurry and digestate, than overall scenario emissions. CH_4 presents non-significant differences between baseline and AD scenarios (median= -35.4%, Wilcoxon's P= 0.088). This non-significant difference in emissions is an unexpected result because after the digestion process, less VS are available in the solid residue to be converted into CH_4. It is observed in Figure 5.2 that the box plot of CH_4, only includes negative relative changes. Furthermore, only two overlapping cases from Battini et al. [142] present positive relative changes and correspond to outliers. Therefore, it is recommended to exclude the outliers for the analysis. This would shift the median of the distribution to -36.0% and would result in significant decrease of CH_4 emissions with respect to baseline scenarios (Wilcoxon's P= 3.5×10^{-3}). If the outlier is not excluded results could suggest that CH_4 leaks from the digester are similar in magnitude to the

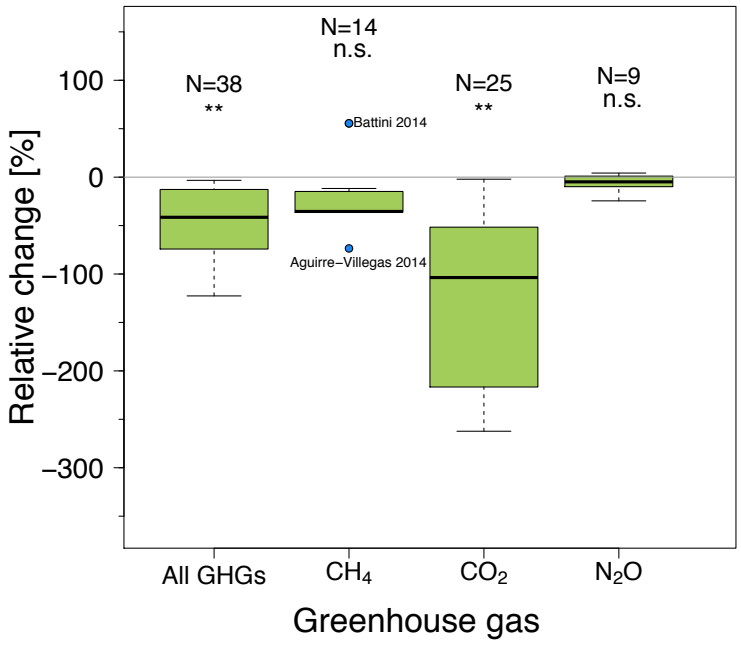

Figure 5.2: Box plots for the relative changes of overall and specific GHGs. Z-values (respectively from left to right on the box plot): 0.134, -0.440, 0.248 and 0.058.

emissions reduced from storage. In order to elucidate how CH_4 emissions from leaks compare to those from storage, Sections 5.3.3.1 and 5.3.3.2 analyse these operation units separately.

CO_2 is the gas most mitigated by implementing AD systems (median= -103.6%, Wilcoxon's P= 1.30×10^{-5}). This is explained by the negative CO_2 emissions from AD scenarios that account for the offset of fossil fuel energy and mineral fertilisers. For this reason, this GHG is the only that can present relative changes lower than -100%. Dispersion is observed by the large interquartile range (165.0%) and this high level of variation is mainly attributed to differences in the assumed values of Y_{CH4} and different CO_2 sources in baselines.

Emissions of N_2O are simultaneously reported with complete baseline scenarios for only 9 cases (see Figure 5.2). This distribution of relative changes shows a non-significant reduction of N_2O (median= -4.9%, Wilcoxon's P= 0.107). The small interquartile range (10.9%) and absence of outliers suggest that the articles that report N_2O and baseline emissions are in close agreement. However, a larger sample size is available for local relative changes, with particular attention to emissions after field-application of raw manure and digestate (N= 27). This difference in sample size for relative changes of N_2O are evidence of the need of a closer inspection of sources of

emissions. Consequently, the increase of sample size can enhance the robustness of conclusions.

5.3.3 Relative changes for operation units

Section 5.3.1 shows that from 142 cases in Part II of the database 36 present emissions from complete baseline and AD scenarios. It is noted that much of this literature covers GHG emissions from specific sources in dairy farms. The categorisation of emissions by sources can solve the difference in boundaries of works, thus, enabling their comparison. Therefore, in this section relative changes are estimated and analysed in accordance to emitting farm activity (i.e. operation units). This conducts to a detailed quantification of the effect of AD over farm emissions.

The distributions of global relative changes by operation unit are presented in Figure 5.3. These correspond to the change in emissions caused by AD, with respect to standardised baseline scenarios ($B*$, see definition in Section 5.1). In the sections, these distributions are analysed. Local relative changes are also reported to compare the emissions from untreated and digested slurries.

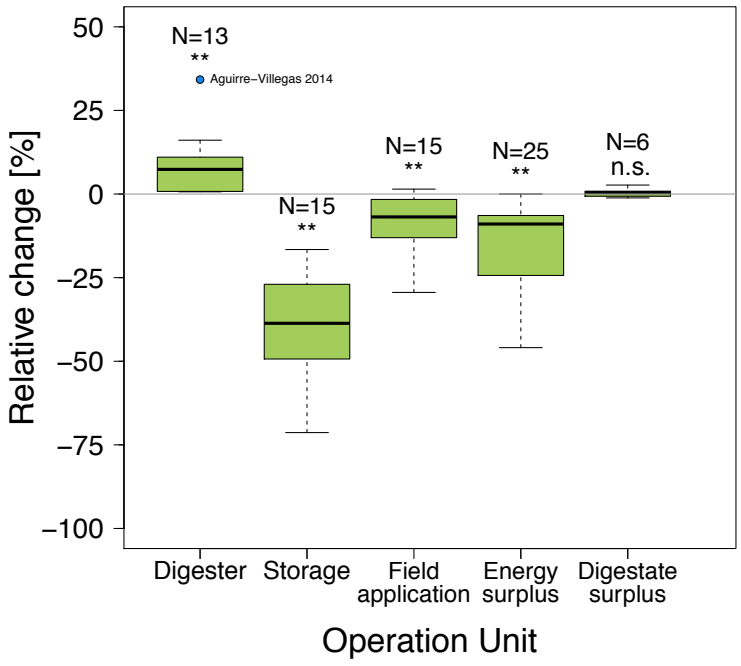

Figure 5.3: Box plot for the global relative changes of emissions according to operation units with respect to baseline. Z-values (respectively from left to right on the box plot): -0.122, 0.027, 0.222, 0.510 and -0.003.

5.3.3.1 Leaks from AD system

There are 11 papers [120, 123, 128, 131, 133, 136, 141, 142, 144, 145, 150] which consider emissions from the operating digesters in Part II of the database[2]. Two of these articles [123, 136] include digester leaks in AD scenarios but do not detail the individual contribution of this operation unit. Therefore, they are omitted from the discussion of this section. The remaining nine papers [120, 128, 131, 133, 141, 142, 144, 145, 150] specify emissions from digesters, mainly focusing on leaks of CH_4 (i.e. CO_2 emissions are reported by Michel et al.[131], Aguirre-Villegas [141] and Hamelin et al. [133], while N_2O emission are solely reported by the former).

To estimate CH_4 losses articles assume that a range from 1% to 10% of the produced (and captured) CH_4, is leaked. The highest assumption of 10% is found in the work of Pathak et al. [128], which follows the IPCC default value [151]. The higher leaks are expected for the cases from that article because it studies a family size digester with exposed areas of slurry in the inlets (i.e. as opposed to a biogas plant that would minimise leaks). However, it is not possible to compare the global relative change from this case to other farms because it does not comply with the emissions of complete baseline scenarios. Similar occurs for the cases from the work of Sommers et al. [120]. Therefore, the distribution of relative changes for this operation unit (Figure 5.3) is conformed by cases from the seven remaining articles [131, 133, 141, 142, 144, 145, 150].

All cases in Figure 5.3 for digester operation assume that leaks are lower than 10% of the produced CH_4 (i.e. IPCC default value). This is because they are based on IPCC guidelines which allow to report less CH_4 losses from digesters if there is supporting evidence. In particular, five of the papers [133, 142, 144, 145, 150] in the distribution assume that 1.0% of the CH_4 produced is released to the atmosphere. Only Michel et al. [131] and Aguirre-Villegas et al. [141] assume higher losses of 1.8% and 2.4%, respectively. Thus, all cases in the box plot of this operation unit are an indication that the default IPCC-value is an overestimation of leaks from digesters. In addition to the cases in the database, fewer leaks from the digesters are also evidenced in the work of Flesch et al. [235] (i.e. not included in meta-analysis because it does not report a reference

[2]In the published work related to this chapter [264] (search in August 2013) only six of these articles report emissions from the digester. Thus, the update of Part II of the database (October 2015) has affected numerical results for this operation unit.

scenario as baseline). They determined experimentally that 3.1% of the CH_4 produced in a digester is leaked.

The first box plot (left side) of Figure 5.3 shows the median relative change of 7.4%. This corresponds to the percentage of the baseline emissions which is increased due to leaks from the digester. The change in emissions is significantly different to zero (Wilcoxon's P= 1.65×10^{-3}), which implies that there are sufficient cases to conclude that fugitive emissions from digesters raise the carbon footprint of baseline dairy activities. Furthermore, there appears to be agreement on the increase of GHG emissions, as shown by the low interquartile range (10.2%).

There are two cases in the distribution which are of particular interest because, as mentioned previously, they assume higher losses of CH_4 produced: one from Aguirre-Villegas [141] and one from Michel et al. [131]. The former corresponds the outlier case in the distribution of digester in Figure which corresponds to a case from Aguirre-Villegas et al. [141]. If this outlier is excluded from the distribution the median shifts to 6.6% and there is still a significant increase in emissions caused by this operation unit (Wilcoxon's P= 2.52×10^{-3}). If the case of Michel et al. [131] is eliminated from the distribution, the same median and Wilcoxon's P-value are obtained. Excluding both cases would result in a median of 5.8% with significant increase in emissions (Wilcoxon's P= 3.84×10^{-3}). Therefore, the inclusion of these cases does not markedly affect the observation of leaks significantly increasing emissions from baseline scenarios. Furthermore, if these cases are adapted to assume a loss of 1% of the produced CH_4, the significant increase in emissions remains (Wilcoxon's P= 1.66×10^{-3}) with shift of the median to 6.1%.

As final element of discussion for this operation unit, it is interesting to observe how the relative changes of digester leaks are affected by correcting the Y_{CH4} from original articles to those determined in Chapter 4 by meta-analysis. This correction of Y_{CH4} is recommended because: i) the value obtained by meta-analysis informs on the range (confidence interval) of the Y_{CH4} and; ii) any possible biased selection of a Y_{CH4} value is reduced because meta-analysis is a reproducible and systematic procedure (see methodology of Chapter 3).

From the six articles presented for this operation unit, two [133, 145] report Y_{CH4} values, which are assumed from the literature. These articles provide three cases which utilise CSTRs for the

Table 5.1: Global relative change in emissions caused by digester leaks with respect to baseline scenario for articles which report Y_{CH4} values.

Use of original article		Relative change [%] correction by meta-analysis result[a]	Ref.
Y_{CH4} [$m^3_{CH4} \cdot kg^{-1}_{VS}$]	Relative change [%]		
0.231	1.99	1.64±0.13	[133]
0.220	5.81	5.02±0.42	[145]
0.220	14.5	12.5±1.05	[145]

[a]This Y_{CH4} is obtained for CSTR in Section 4.2.3 of this work and corresponds to 0.190±0.016 $m^3_{CH4} \cdot kg^{-1}_{VS}$. Relative changes are modified assuming no changes in baseline emissions.

AD process. The assumed Y_{CH4} in those articles and their consequent relative changes are presented in Table 5.1. Compared to yields obtained by random-effect meta-analysis for CSTRs (i.e. 0.190±0.016 $m^3_{CH4} \cdot kg^{-1}_{VS}$, see Section 4.2.3), the assumed Y_{CH4} in original articles are out of the confidence interval. This suggests that leaks from the digesters are overestimated in the two articles. In fact, correcting the relative changes to the Y_{CH4} of the meta-analysis results in lower relative changes for this operation unit (see Table 5.1).

In addition the overall range of the relative changes of the three cases in Table 5.1 is reduced by 0.5% with the application of the Y_{CH4} from meta-analysis. The latter indicates that the robust Y_{CH4} values, can contribute in reducing overall uncertainties when calculating changes in emissions from digester leaks. Therefore, bringing together the findings of Chapter 4 with emissions found for this operation unit can be applied for the standardisation of leaks reported for AD systems in the literature and enable more adequate inter-study comparison.

5.3.3.2 Storage of slurry

From the papers in the database, nine articles [131, 133, 136, 141, 142, 144–146, 150] specify data on the GHG emissions from storage tank of slurries and from all the operation units in standardised baseline scenarios (Figure 5.3)[3]. These articles yield 15 cases which are sufficient to determine that the emissions of this operation unit have a significant effect over the emissions of baseline scenarios (median= −38.7%, Wilcoxon's P= 6.10×10^{-5}). To understand in more detail the effect of AD over this operation unit, it is interesting to categorise the relative changes by type of

[3]In the update of Part II of the database (October 2015) more articles have been found for this operation unit. Therefore, distribution of global and relative change in the published work related to this chapter [264] (based on search in August 2013) have been accordingly modified.

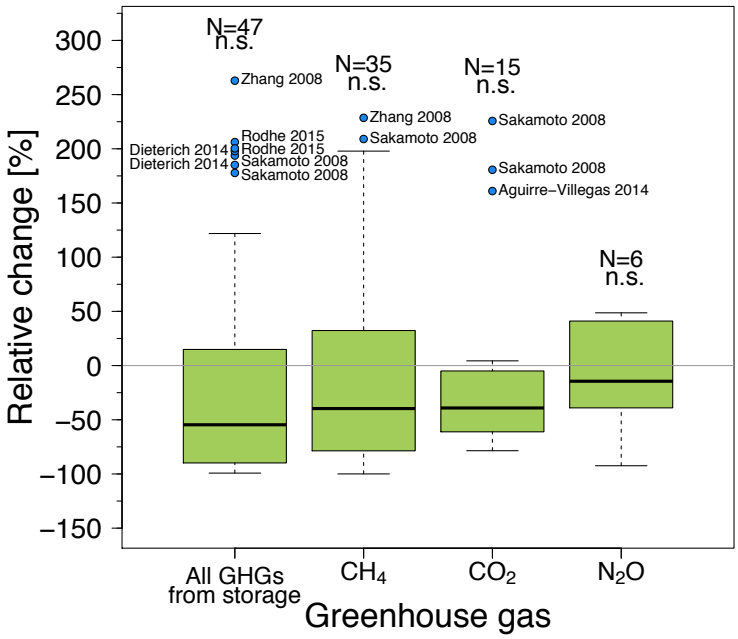

Figure 5.4: Box plots for the relative changes of GHG emissions from storage of digestate, with respect to storage of untreated slurry. Z-values: -0.399, -0.357, -0.410 and -0.051.

GHG. For this purpose, there are more cases which compare emissions from storage of digestate and untreated slurry, with respect to those which present emissions of complete baseline scenarios. Therefore, the local relative changes of this operation unit are utilised to assess the specific effects of AD on CH_4, CO_2 and N_2O.

In the database, 47 cases (from 19 articles [14, 20, 42, 120, 121, 123–126, 131, 133, 136, 141–143, 145, 146, 149, 150]) report emissions from stored untreated and digested slurries. Local relative changes for this operation unit (calculated by Equation 5.2) are presented in Figure 5.4. These relative changes show a non-significant change in GHG emissions (median= −54.6%, Wilcoxon's P= 0.119). However, removing the outliers results in a significant reduction in emissions (median= −64.1%, Wilcoxon's P= 5.05×10^{-5}).

Specifically for CH_4, 35 cases (see second box plot of Figure 5.4) from 13 articles [14, 20, 120, 121, 123–126, 131, 133, 141, 143, 146] report emissions from the storage of slurries. A non-significant change in emissions is obtained for the CH_4 cases (median= −39.7%, Wilcoxon's P= 0.518). This observation remains if outliers are excluded (median= −41.7%, Wilcoxon's P= 0.186). The non-significant change in CH_4 emissions from stored slurries is a highly unexpected result be-

cause 26 of the 35 cases (from 11 of the 13 articles), report mitigations[4]. A reduction of this GHG is anticipated because, during AD, organic matter is degraded, resulting in a solid substrate with lower potential for CH_4 formation [14, 121]. The non-significant change in emissions is due to the positive relative changes calculated from Sakamoto et al. [124], Dieterich et al. [143] and Zhang et al. [125]. In particular, the cases from Sakamoto et al. [124] could be removed from the distribution because of markedly different experimental conditions. In that work the digestate is extracted directly from the bulk of an operating digester and not the outlet. This could explain an increase in the bacterial population but insufficient HRT, which could delay the methanogenic phase to the storage period. Accordingly, results of Clemens et al. [14] show that increasing the HRTs (from 26 to 56 days) results in reduction of CH_4 emissions from stored digestate with respect to untreated manure. As consequent of incomplete HRTs, the four cases from Sakamoto et al. [124] show an increase in CH_4 emissions from stores by 96–209%. If this work was excluded from the distribution, significant reductions in CH_4 emissions would result (median= -54.5%, Wilcoxon's P= 0.044, interquartile range= 52.6%). The same does not occur when eliminating the cases from Dieterich et al. (median= -38.0%, Wilcoxon's P= 0.334) or Zhang et al. (median= -41.67, Wilcoxon's P= 0.186).

Comparing CH_4 emissions to other GHGs, it is found that CO_2 and N_2O emissions are less reported in the literature for this operation unit. Reduced research on CO_2 emissions can be explained by it being often considered carbon neutral in bioenergy systems. However, this meta-analysis includes the changes in emissions of CO_2 because these can potentially indicate the carbon-sink capacity of the digestate compared to the untreated slurry, as studied by Smith et al. [299]. In particular, 15 cases from three articles [124, 125, 141] are found to compare CO_2 emissions from unprocessed and digested dairy manure. It is observed that these local relative changes present the smallest interquartile range of the operation unit (56.2%). For these cases, non-significant differences are obtained for CO_2 emissions (median= -39.1%, Wilcoxon's P= 0.359). This is due to three outliers in the distribution. If these are excluded a significant mitigation of CO_2 emissions is obtained (median= -48.0%, Wilcoxon's P= 9.77×10^{-4}). Two outliers are cases the work of Sakamoto

[4]It should be noted that cases from Zhang et al. [125] result in positive and negative relative changes.

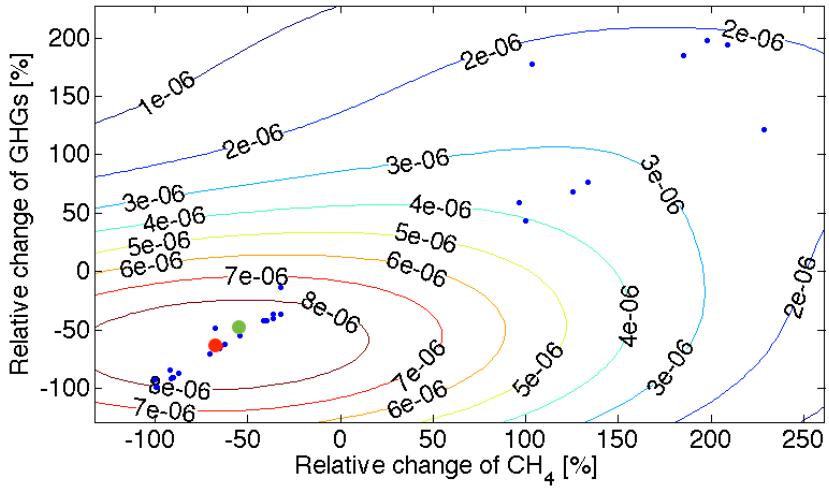

Figure 5.5: Storage CH_4 and total GHG local relative changes between digestate and untreated slurry (blue dots). Contour plots (lines) are adaptive Kernel probability distribution. Red circle: median estimate (CH_4= -54.5% and GHG= -48.4%); green dot: best estimate (CH_4= -65.1% and GHG= -64.1%).

et al. [124]. As discussed for CH_4emissions these cases should not be considered in the distribution because of particularly different experimental methods. However, if the cases from Sakamoto et al. are excluded, non-significant change in emissions remain for the distribution (median= -55.0%, Wilcoxon's P= 0.067). Similarly, eliminating the cases from Aguirre-Villegas et al. [141] (source of the third outlier) no change in significance of the difference between emissions occurs (median= -40.0%, Wilcoxon's P= 0.135).

For emissions of N_2O from storage of digestate and raw slurry, five papers [14, 121, 123, 133, 141] yield six cases (Figure 5.4). The cases present large dispersion as shown by the interquartile range of 80.13%. The reduced sample size and dispersion of cases can be explained by the difficulty to measure low generation of N_2O from both raw and digested manure [14]. Low emissions of N_2O are expected because stored slurries contain neither nitrate nor nitrite which produce N_2O [131]. The combination of the above observations result in non-significant effect of AD process over N_2O emissions from storage (median= -14.5%, Wilcoxon's P= 0.844).

As discussed above, the articles that report emissions from storage of digestate mainly focus on CH_4. Consequently, a high correlation (Spearman's Rho= 0.97, $P< 2.20 \times 10^{-16}$) between local relative changes (i.e. with respect to untreated slurry) of CH_4 and all GHGs for storage is obtained

(N= 31; see Figure 5.5), and these local relative changes have similar medians and interquartile ranges (CH_4= 111.0%; total GHGs from storage= 104.7%). In accordance to the Kernel density distribution for these local relative changes, the best estimations for reduction of CH_4 and GHGs from storage are −65.1% and −64.1%, respectively.

5.3.3.3 Field application of slurry

Emissions from field application of untreated slurry and digestate together with standardised baseline scenarios are specified in nine papers [131, 133, 136, 141, 142, 144–146, 150]. These articles yield 15 cases (see Figure 5.3) with an overall significant reduction of emissions (median= −6.9%, Wilcoxon's P= 4.27×10^{-4}, interquartile range= 11.5%).

Similar to emissions from storage of slurries, this operation units utilises local relative changes to quantify the effect of AD over specific GHGs. These relative changes are presented in Figure 5.6. There are 20 articles [14, 116–118, 120, 121, 126, 127, 129, 131, 133, 136, 137, 139, 141, 142, 144, 145, 149, 150] which report 42 cases of emissions from digestate and untreated slurry. Results indicate that GHG emissions from digestate after field application are significantly less (median= −34.8%, Wilcoxon's P= 1.63×10^{-3}) than from untreated slurry.

Six of the papers compare emissions of CH_4 from field-applied slurries (N= 8)[14, 118, 121, 126, 141, 142]. This GHG is the only to present non-significant differences between emissions of untreated manure and digestate (median= 20.5%, Wilcoxon's P= 0.362, interquartile range= 79.3%). This is attributed to aerobic conditions after soil incorporation of slurries, that limit CH_4 formation for both materials.

Five papers [129, 133, 137, 139, 141] specify CO_2 emissions after field application (N= 7). Most of these articles study the effect of slurry treatment on carbon sequestration of soils [129, 137, 139]. In this respect, changes in emissions of CO_2 from this operation unit could be a new source of carbon credits. Results indicate that AD significantly reduces CO_2 emissions of slurry in this operation unit by −52.3% (Wilcoxon's P= 0.016). By eliminating the outlier, lower relative change of CO_2 is obtained (median= -54.5%, Wilcoxon's P= 0.031). Hamelin et al [133] attributes less CO_2 emissions from digestate, to the decrease (by 15%) of soil carbon pool. This occurs

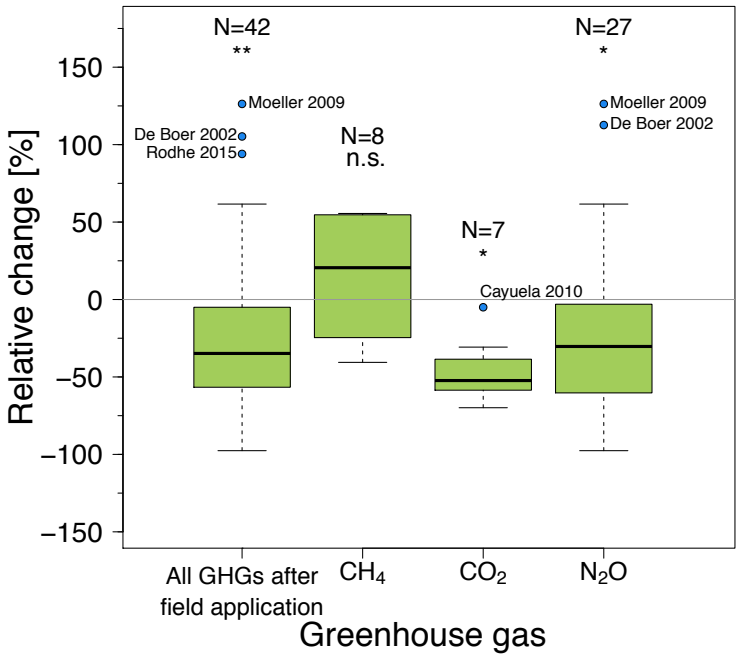

Figure 5.6: Box plots for the local relative changes of GHG emissions from field application of digestate with respect to those from untreated slurry. Z-values: -0.198, 0.149, -0.295 and -0.114.

because the AD process removes easily biodegradable organic matter from the slurry [139].

The mechanisms that produce N_2O are highly sensitive to oxygen availability, soil moisture content, and carbon content in the slurry [117, 127, 137]. These variable conditions result in the large interquartile range (57.3%; see Figure 5.6) for the local relative changes of N_2O emissions. It is found that the median relative changes results in a significant decrease by 30.3% (Wilcoxon's P= 0.017). If the outliers are extracted, further mitigation of N_2O is found (median= -36.0%, Wilcoxon's P= 6.98×10^{-4}). The emission mitigation can be mainly attributed to denitrification processes, which have been reported to be the dominant mechanism in N_2O formation [116, 137, 208]. Denitrification occurs in anoxic conditions created when: (i) high water content in the soil restricts oxygen transport [300], and (ii) carbon in the organic substrate reacts with the available oxygen [117]. AD can reduce these denitrifying processes with respect to untreated manure because it lowers the organic carbon content. Consequently, less carbon promotes aerobic conditions or is available for the metabolism of denitrifying bacteria. For these reasons, the carbon content in soils plays a key role in denitrification. This mechanism could explain the outlier of De Boer et al. [118] (see Figure 5.6), in which high amount of carbon is locally available after digestate application,

thus increasing denitrification and N_2O emissions, with respect to the untreated manure.

To a less extent, N_2O is also liberated as an intermediate of nitrification [14, 129]. Nitrification reactions convert ammonium (NH_4^+) in the manure or digestate into NO_3^-. The NO_3^- can then take part in denitrification reactions [14, 129]. Because AD reduces the organic material, the NH_4 proportion increases and consequently nitrification activity is enhanced. This is the explanation of Moeller et al. [127] for their unusual results (second outlier in the N_2O distribution of Figure 5.6). The author report an increase in emissions after AD because digestate has higher NH_4^+ content than raw slurry and, additionally, the water content of the soil is below the field capacity.

N_2O is the GHG most reported for this operation unit; thus, the local relative changes of total GHG emissions after field application exhibit a strong correlation with the local relative changes of this GHG (Spearman's Rho= 0.93, P= 1.02×10^{-12}, see Figure 5.7). Results from the Kernel distribution indicate that the best estimate for local relative change of N_2O and total GHGs from field applied slurries is −33.1% for both relative changes.

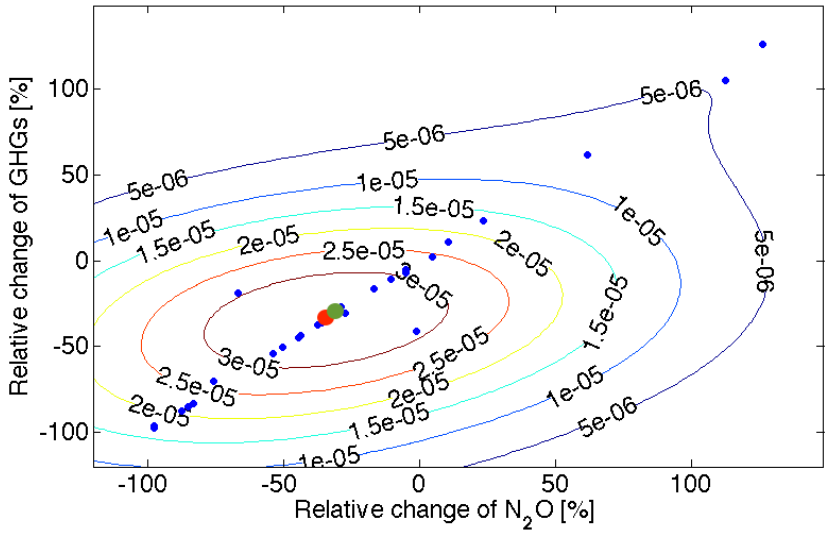

Figure 5.7: Local relative changes for field N_2O and total GHG emissions between digestate and untreated slurry (blue dots). Contour plots (lines) are adaptive Kernel probability distribution. Red star: median estimate (N_2O= -30.2% and GHG= -30.7%); green dot: best estimate (N_2O= GHG= -33.1%).

5.3.3.4 Energy surplus

The estimation of fossil fuel offsets and their negative emissions depend on the energy sources used in baseline scenarios (e.g. embodied carbon of national grids). Therefore, to enable comparison between cases, it is assumed that surplus energy in the AD scenarios is exported to replace electricity from natural gas (see Section 3.1.3.2), as approached by other authors [301, 302].

In the database, twelve [122, 131, 133, 134, 136, 140–142, 144–146, 150] papers (N= 25) report the offset of emissions due to replacement of fossil fuels by biogas and also comply with the baseline scenario definition. Overall, the relative changes of this operation unit indicates that the offset of fossil fuels significantly reduces the emissions with respect to the baseline scenarios (median= −9.0%, interquartile range= 17.9% and Wilcoxon's P= 5.96×10^{-8}). This implies that there is sufficient evidence in the literature that suggests that baseline emissions can be neutralised and excess energy could further mitigate off-site emissions (i.e. from natural gas combustion).

Although, no outliers are present (see Figure 5.3) in the relative change distribution, there is a large interquartile range (17.9%) indicating little agreement in the quantification of fossil fuel offset in the literature (i.e. even if the same fuel is assumed). This could be explained by the differences in Y_{CH4} assumed in the different AD systems and operation conditions. However, there are only seven cases (from three European articles [133, 134, 145]) which indicate this key variable of the AD process. None of these experimentally determined the Y_{CH4} of their feedstock. It is found that the assumed values for yields used by Hamelin et al. [133] and Agostini et al. [145] (0.231 and 0.22 $m^3_{CH4} \cdot kg_{VS}$, respectively), are in agreement with the yields for European cases determined by the random-effect model in Chapter 4 (0.233±0.020 $m^3_{CH4} \cdot kg_{VS}$). Marañón et al. [134], however, under estimates the production of biogas (Y_{CH4}= 0.185 $m^3_{CH4} \cdot kg_{VS}$). Following the above observations, to enable comparison between studies, it is recommended to report Y_{CH4} utilised for case studies (as Chapter 6 will show). Furthermore, the yields obtained by meta-analysis of this work are suggested as a means to avoid bias selection of this variable from the literature.

It should be noted that although this operation unit (Figure 5.3) is related to the offset of CO_2, it exhibits markedly different relative changes than total CO_2 emissions (median= -103.6%, Figure 5.2). This is explained by the different relative changes utilised. In this section global relative

changes are calculated with respect to complete baseline emissions, while the analysis of Figure 5.2 presents changes in CO_2 emissions with respect to baseline emissions of only this GHGs. Given that the baseline emissions of CO_2 are significantly less than total baseline emissions (i.e. only the latter considers CH_4 from storage of manure), the relative changes of this operation unit is expected to be less than the local CO_2 relative changes.

5.3.3.5 Digestate surplus for export

The offset of mineral fertilisers by digestate is considered as an operation unit in seven papers [42, 128, 131, 133, 136, 140, 150]. Five of these [131, 133, 136, 140, 150] (N= 6) also report the emissions of the complete baseline scenarios. An interesting observation is that all latter articles also include the offset of fossil fuels from energy replacement.

The relative changes of for this operation unit are also presented in Figure 5.3. The median (+0.4%, interquartile range= 2.3%) presents a non-significant increase with respect to the baseline standardised emissions (Wilcoxon's P= 0.590). The value is positive due to higher offsets of inorganic fertilisers in the baseline scenarios by utilising untreated manure. More emissions from the AD-scenario are expected because the slurry decreases as a result of carbon extraction (i.e. as CH_4 and CO_2). Consequently, more mineral fertilisers are needed to compensate for less-available biosolids in the AD scenario. The non-significant result and small sample size are indicators of more research required to quantify the offsets of mineral fertilisers by digestate and by untreated manure, together with emissions from complete baseline scenarios.

5.4 Summary and final remarks of the chapter

This chapter quantifies the effect of AD over CH_4, CO_2 and N_2O emissions from dairy farms by meta-analysis techniques. For this, 40 articles collected in Part II of the database ([14, 16, 20, 42, 75, 116–150], see Chapter 3) are systematically integrated. The increased sample size enhances the robustness of evidence, in comparison to the individual articles of the database. Therefore, results provide insights on general agreements, sources of variation and gaps in the literature of this field.

To enable inter-study comparison and overcome differences in system boundaries and func-

tional units, emissions are standardised to global relative changes (i.e. with respect to total standardised baseline scenarios) and local relative changes (i.e. with respect to specific emissions in baselines). Thereafter, non-parametric tests are applied given the dominant non-normal distributions of relative changes, to identify statistical difference of AD with respect to baseline scenarios, correlations and best estimation for changes in emissions.

Results first indicate that global relative changes for complete scenarios are available for independent and IPCC-based models. Comparing the distribution of relative changes of these methods shows that the latter generally estimate higher mitigation potentials of AD systems. No empirical results are found for complete AD and baseline scenarios for further comparison. However, much experimental work is found for specific GHGs emissions and their sources (i.e. operation units).

In reference to the relative changes of specific GHG emissions from overall scenarios, it is found that AD significantly decreases CH_4 by 36.0% (excluding outliers, interquartile range= 22%) and CO_2 by 103.6% (interquartile range= 165%). The latter median indicates that more offsets occur than the CO_2 emissions in baseline scenarios. For overall N_2O emissions, no significant change is observed (median= -4.9% and interquartile range= 10.9%).

With respect to global relative changes for operation units, the negative emissions from biogas replacing fossil fuels are the mitigations most compared against baseline scenarios in the literature (median= -9.0% and interquartile range= 17.9%). In contrast, it is found that negative emissions from replacing inorganic fertiliser by digestate are scarcely reported with emissions from reference scenarios (non-significant, median= +0.4% and interquartile range= 2.3%). The only operation unit which shows to significantly increase emissions from dairy farms is the digester due to leaks (median= +7.4% and interquartile range= 10.2%). Empirical work is recommended to measure these fugitive emissions and compare them against emissions from complete (standardised) baseline scenarios. For storage and field application of slurries, significant changes in emissions of -38.7% (interquartile range= 22.3%) and -6.9% (interquartile range= 11.5%), respectively, are determined.

Most work on the latter operation units has compared specific emissions from untreated and digested slurries, rather than utilising a baseline scenario (i.e. local relative changes). In particular,

extensive research on changes in CH_4 emissions for storage of slurries show a median relative change of -54.5% (interquartile range= 52.6%, excluding the article of Sakamoto et al. [124], which is found to have markedly different experimental conditions). Articles comparing emissions from field-application of slurries mainly cover N_2O emissions, which show a median reduction of 30.3% (interquartile range= 57.3%). It should be noted that although the interquartile ranges of the latter two relative changes are large, the median obtained for those distributions are suggested to be utilised to estimate emissions from storage and field-application of digestate, as they are heavily evidence-based (i.e. as no other emission estimation methodology, to the author's knowledge).

It is expected that the quantification of the effects of AD on GHG emissions from dairy farms of this chapter can meaningfully contribute in determining more accurate carbon footprints, for example, within life-cycle assessments and CDM projects. The median global relative changes provide a simple and reliable estimation method for emissions from AD scenarios if the baseline emissions are known (e.g. calculated by IPCC methodologies). Furthermore, local relative changes offer an estimation method of direct emissions from digestate of cattle manure (i.e. its storage and field-application), which is not closely addressed in the IPCC Guidelines [151]. To illustrate the application of the findings, relative changes are used for estimation of emissions from theoretical AD scenarios of four case studies in Chapter 6.

Chapter 6

Case studies

This chapter illustrates the application of the Y_{CH4} of Chapter 4 and relative changes of Chapter 5 to assess the production of renewable energy and mitigation of GHG emissions in markedly different dairy farms; one from a developed country (England) and three from a developing country (Guatemala).

For the English farm, AD is a promising option to diversify profitable activities (i.e. energy production) while lowering ecological footprint (4.9 ha per capita in the United Kingdom [303]). Furthermore, the search for new income sources for English dairy farms is of particular interest given the current low price of milk in the United Kingdom [304]. In another developed country (United States) there is an increase interest in dairy farms to implement AD associated with power generation and its association with organic farming [178].

The application of AD in the Guatemalan three cases could contribute to providing off-grid energy. In Guatemala, electricity is unavailable for more than 16% of the population (3.1 million people) [305] and a national natural gas grid is only expected for 2017 for industrial use [306]. The energy poverty reflects in the Guatemalan low human development index which is 0.628. This is lower than the threshold of higher human development (0.800 [153]). Therefore, AD is a means to confront energy scarcity in Guatemala while managing highly available livestock waste in rural zones[1]. In addition, it should be noted that AD systems have been carried out in Guatemala within

[1] The research of the three Guatemalan farm shown in this chapter is based on the peer-reviewed conference article

the CDM mainly in the palm oil industry[307–310]. However, the AD of dairy cattle manure in Guatemala has not been explored under this perspective. The use of CDM funds could incentivise the application of AD in dairy farms, by allowing local communities to overcome initial construction costs [311].

To evaluate the consequences of AD in terms of energy production and GHG emission changes over the case studies, baseline and AD scenarios are established for each farm. The chapter comprises three scenarios of cattle manure management for each farm: i) a baseline scenario that considers typical existing farm practices; ii) an AD scenario which combusts the methane (CH_4) produced in a condensing boiler (AD-boiler); and iii) an AD scenario which combusts the CH_4 in a combined heat and power unit (AD-CHP). The scenarios are evaluated in terms of power production/consumption and GHG emissions.

The construction of the scenarios is based on the information collected in a structured questionnaire (Section 6.1) to owners or administrators of the farms. Thereafter, the assessment of the baseline and AD scenarios are carried out by following the methodology also presented in Section 6.1.

Results are presented in Sections 6.2 and 6.3 for the English and Guatemalan farms, respectively, according to scenarios. The discussion of the energy and GHG aspects of the scenarios are combined with the information collected by the questionnaire, providing insights of the preferable AD-combustion technology. Therefore, Section 6.4.1 discusses the differences in the application of AD for these dairy farms. Ultimately, the most beneficial scenario is proposed for the farms as a system which could meaningfully effect activities and the surrounding community. Final remarks in Section 6.4.2 discuss the results in terms of the effect of meta-analysis results over the GHG estimations.

"Potentials of biogas production and GHG mitigation in Guatemalan dairy farms" [265].

6.1 Assessment method

This section explains the assessment of the energy production/use and the emissions from baseline and AD scenarios of case studies. The methodology is based on the data provided in Table 6.1. It should be noted that the CO_2 emitted from storage tanks or field-applied manure is excluded from the table due to lack of forced aeration and because biogenic CO_2 is assumed carbon neutral. Also, given that results in Chapter 5 indicate that there is insufficient evidence in the literature of significant changes in emissions, offsets of mineral fertiliser by digestate are excluded. To carry out the assessment, a first step is to collect information on the farm operations by performing interviews to farm owners or administrators, based on a structured questionnaire (Section 6.1.1). Thereafter, the baseline emissions of Table 6.1 must be addressed by following the steps of Section 6.1.2. The next steps are the calculations of the energy production and the emissions from AD scenarios as presented in Section 6.1.3. Ultimately, the assessment of scenarios and completions of Table 6.1, enables the estimation of changes in emissions as follows[2]:

$$\triangle GHG_j\,[kg_{CO2e} \cdot yr^{-1}] = (GHG_{Op,AD}) - (GHG_{Op,B}) \tag{6.1}$$

where "Op" corresponds to an emitting operation unit detailed in Table 6.1. All emissions are standardised to "$kg_{CO2e} \cdot yr^{-1}$" by using GWP_j for gas "j" ($kg_{CO2e} \cdot kg_{GHG}^{-1}$) utilising the values from the IPCC Guidelines [272] (as presented in Equation 3.1).

6.1.1 Questionnaire for dairy farms

Quantitative and qualitative information from the four dairy farms is necessary to construct baseline and AD scenarios, as well as to understand the differences in resulting emissions. To collect the required data, a structured questionnaire is developed and applied to owners or farm administrators of the case studies[3]. The questionnaire covers the following quantitative points:

[2]Enteric fermentation is common for both scenarios. Therefore, Equation 6.1 for this operation unit results in zero changes in emissions. These emissions are therefore discussed only in terms of individual scenarios, considering they are main contributors of GHG emissions in dairy farms.

[3]Four owners or administrators answered the questionnaire for this work (in person or through on-line platform, see Appendix C). One for each case study.

Table 6.1: Summary of GHG emission calculations from the three scenarios.

Operation units and GHGs	**Emissions from scenarios**		
	Baseline (Step, Eq.)	**AD Scenarios (Step, Eq.)**	
Ent. fermentation (E)			
CH_4 emissions[a]	$CH_{4,E,B}$ (St. 1, Eq. 6.2)	$CH_{4,E,AD}$ (St. 7, Eq. 6.2)	
Storage (S)			
CH_4 emissions	$CH_{4S,B}$ (St. 2, Eq. 1.1)	$CH_{4S,AD}$ (St. 8, Eq. 6.7)	
Field-application (F)			
CH_4 emissions	$CH_{4F,B}$ (St. 3, Eq. 1.1)	$CH_{4F,AD}$ (St. 9, Eq. 6.8)	
N_2O emissions	$N_2O_{F,B}$ (St. 4, Eq. 1.8)	$N_2O_{F,AD}$ (St. 10, Eq. 6.9)	
Digester leaks (L)			
CH_4 emissions	0	$CH_{4L,AD}$ (St. 11, Eq. 6.10)	
Electricity (El)		**AD-Boiler (Bo)**	**AD-CHP (CHP)**
Import (from grid)	$CO_{2El,B}$ (St. 5, Eq.6.4)	$CO_{2El,Bo}$ (St. 14a, Eq. 6.4)	$CO_{2El,CHP}$ (St. 15b, Eq. 6.18)
Export (to grid)	0	0	$CO_{2El,CHP}$ (St. 15b, Eq. 6.18)
On-site generation[b]	$CO_{2El*,B}$ (St. 6, Eq. 6.5)	$CO_{2El*,Bo}$ (St. 14a, Eq. 6.5)	$CO_{2El*,CHP}$ (St. 15a, Eq. 6.18)
Thermal energy (Th)			
Export	0	$CO_{2Th,Bo}$ (St,. 16a, Eq. 6.15)	$CO_{2Th,CHP}$ (St. 17b, Eq. 6.20)
On-site generation.	$CO_{2Th,B}$ (St. 6, Eq. 6.6)	$CO_{2Th,Bo}$ (St. 16a, Eq. 6.15)	$CO_{2Th,CHP}$ (St. 17b, Eq. 6.20)

[a]Enteric fermentation is not affected by AD, therefore these emissions are the same for baseline and AD scenarios.
[b]Applicable to farms that use on-site electricity (El*) generators which combust fossil fuels.

- Herd size (N_C): To provide information regarding the scale of the farm. It is used for the estimation of CH_4 from enteric fermentation and manure management system and; N_2O from field-applied slurries, according to Tier 2 methodology of the IPCC [151]. Additionally the herd size is used to standardise the emissions from farms for comparative purposes.

- Annual milk production: Also utilised to provide understanding of the scale of the farm and to standardise the emissions from farms for comparative purposes.

- Annual electricity consumption: For the estimation of energy requirements from baseline scenarios and their associated emissions.

- Annual consumption of fossil fuels on farm site: Also used to calculate the emissions from energy use in baseline scenarios. In addition this point identifies which fossil fuels are used, which in turns allows to select their corresponding EFs.

To assess the differences between scenarios and assist the decision-making process in determining the best scenario for English and Guatemalan farms, the following qualitative information is

also collected in the questionnaire:

- Location: Required for identifying local temperatures. In turns, these affect the baseline emissions, according to the IPCC methodologies.
- Milking procedure: Serves to identify differences in equipment and milking practices which affect the dairy farm performance (i.e. energy used per litre of milk).
- Description of the manure management: Necessary to estimate direct emissions associated with the handling of untreated manure. In particular, this is needed for baseline emissions calculated by the methodology of the IPCC [151].
- Knowledge and interest in AD: To incorporate feasibility aspects in the assessment of AD systems.
- Local options to export products from the AD process: to discard scenarios in case there products cannot be useful.

The completed questionnaires provide the required data from the case study farms in order to quantify the changes in emissions from a baseline scenario to AD scenarios ($\triangle GHG_i$ in Equation 6.1).

6.1.2 GHGs from baseline scenarios

This section presents the steps to complete the emissions from operation units in baselines, as shown in Table 6.1. Baselines are established for each farm as a reference to assess the effects of implementing AD on GHG emissions and energy use. To estimate these emissions, calculations are based on the guidelines from the IPCC [151]. In particular, Y_{CH4} values found by the meta-analysis of Chapter 4 are utilised as replacement to the default IPCC values. The emissions of electricity consumed from national grids, when available, and/or the combustion of fossil fuels on-site for electricity generation are also included in the assessment.

Step 1: Emissions from enteric fermentation. In accordance to the IPCC Guidelines [151] (Tier 1 methodology) enteric fermentation releases CH_4 ($CH_{4,E,B}$) into the atmosphere directly from the cattle. These, can be estimated as follows:

$$CH_{4,E,B}[kg \cdot yr^{-1}] = EF_E \cdot N_C \tag{6.2}$$

where EF_E refers to the default emission factor associated with enteric fermentation of dairy cattle and can be found in Table 10.11 of the IPCC Guidelines [151], according to world region. This EF has an accuracy between 30 and 50% (Section 10.3.4 [151]), thus an average 40% is considered for error calculation in the case studies. N_C corresponds to the number of cattle in the dairy farm, which is known by the questionnaire (Section 6.1.1).

Step 2: CH_4 emissions from storage of manure. For CH_4 emissions from untreated manure in storage tanks ($CH_{4,S,B}$), Equation 1.1 is used. Values for volatile solid excretion rate (VS_{Ex}), required for Equation 1.1 can be found in Table 10A-4 of the IPCC Guidelines [151]. The MCFs and the MS_S are also found in the latter Table. These depend on the manure management systems in place and the local temperature of the case study. The IPCC categorises manure management systems in Tables 10.18 and 10.21 of the Guidelines [151]as (for storage of untreated manure): “Solid storage”, “Dry lot”, “Liquid/Slurry”, “Uncovered anaerobic lagoon” or “Pit storage below animal confinements”. The local temperature can be obtained from national weather offices (e.g. MetOffice for the United Kingdom [312]).

For the B_0 needed in Equation 1.1, median values from Chapter 4 found in Figure 4.10 are chosen, according to the world region. For error calculation, the uncertainty of B_0 is given by the confidence interval calculated from the random-effect meta-analysis model. If not available (e.g. Latin America has insufficient cases for the meta-analysis of Chapter 4), the median B_0 of the region which is in closest agreement in terms of human development index is chosen.

Step 3: CH_4 emissions from field-application of manure. As for storage, CH_4 emissions from field-applied manure are calculated by using Equation 1.1. Values for N, $\dot{VS}$ and B_0 required

in the latter equation are specified in Step 2. For MCF_F and MS_F in this operation unit, it is necessary to define the field-application method in accordance to the manure management system considered from Table 10.18 of the IPCC Guidelines [151] and the responses to questionnaires. The alternatives found for field-application of manure are: "Pasture/Range/Paddock" and "Daily spread". The fractions of manure managed by each system "i" ($MS_{F,i}$) is that which best reflects the farm practice and values for MCF_i are found in Table 10A-4 of the IPCC Guidelines [151].

Step 4: N_2O emissions from field-application of manure. To estimate N_2O emissions from field-application of untreated manure, Equation 1.8 is used (based on Equation 11.1 from the IPCC methodology [210]). For that equation the EFs for N_2O from managed manure (EF_{F1}, i.e. "Daily spread") and that deposit on field by grazing animals (EF_{F2}, i.e. "Pasture/Range/Paddock") are obtained from Table 11.1 of the IPCC Guidelines [210]. MS_{F1} and MS_{F2} are obtained from the answered questionnaire. The annual average nitrogen excretion per cow required for Equation 1.8 is calculated as follows:

$$N_{ex}[kg_N \cdot hd^{-1} \cdot yr^{-1}] = TAM \cdot N_{rate} \tag{6.3}$$

where TAM is the typical animal mass and can be found in Table 10A-4 of the IPCC Guidelines [151], if not available. N_{rate} is the nitrogen excretion rate, which can be selected from Table 10.19 IPCC Guidelines [151].

Step 5: Emissions from grid electricity consumption. Emissions associated with electricity consumption depend on the electricity grid to which the dairy farm is connected. It is assumed that the farms are connected to national grids to with emission factors "EF_{El}". Therefore, the emissions from the import of electricity from grids ($CO_{2,El,B}$ in Table 6.6) is determined as follows:

$$CO_{2,El,B}[kg \cdot yr^{-1}] = EF_{El} \cdot \dot{E}_{El,B} \tag{6.4}$$

where $\dot{E}_{El,B}$ corresponds to the annual electricity consumption from the national grid in "$GJ \cdot yr^{-1}$" (i.e. known from the answered questionnaire). The EFs can be obtained, for example, from the International Energy Agency [313]. These value should be used with caution as they commonly

consider the average national mix of generation.

Step 6: Emissions from on-site combustion of fossil fuels. The emissions from the combustion of fossil fuels for electricity or thermal power generation are considered for the baseline scenario. These emission depend on the EF of the specific fossil fuel utilised. The sum of the emissions from fossil fuels combusted for electricity generation will result in $CO_{2,El*,B}$ of Table 6.1 and are estimated for fossil fuel "i" as:

$$CO_{2,El*,B}[kg \cdot yr^{-1}] = \sum_i (EF_{El*,B} \cdot \dot{E}_{El*,B})_i \tag{6.5}$$

where the emission factors ($EF_{i,B}$) can be found in T-1.4 of the IPCC Guidelines [272]. The subscript $El*$ is utilised to distinguish electricity produced on-site by combustion of fossil fuels, to that from grid (El).

Similarly, the total emissions from fossil fuels combusted for thermal power ($CO_{2,Th,B}$ in Table 1.1) is calculated as:

$$CO_{2,Th,B}[kg \cdot yr^{-1}] = \sum_i (EF_{Th,B} \cdot \dot{E}_{Th,B})_i \tag{6.6}$$

6.1.3 GHGs from AD-scenarios

This section presents the calculations to estimate the emissions from the AD-Boiler and AD-CHP scenarios, as shown in Table 6.1. First, the common emissions for both scenarios are presented (i.e. enteric fermentation, storage tanks, field-application of digestate and digester leaks) in Steps 7 to 11. In particular, these steps illustrate how relative changes (from Chapter 5) are applied over baseline results to obtain CH_4 and N_2O emissions (i.e. not specified in the IPCC methodology). Second, the calculations related to the operation of the theoretical digester are presented in Steps 12 and 13. For this, energy potentials are calculated by assuming the B_0 determined in the meta-analysis of Chapter 4 and by utilising mass and energy balances. The methodology is common

for both AD scenarios until Step 7 (inclusive). Thereafter, the specific emissions related to energy consumption (i.e. import and export) are calculated separately for the AD-boiler (Steps 14a to 16a) and AD-CHP (Steps 14b to 16b) scenarios. In these final steps, negative emissions arise from the generation of thermal power generated assumed to offset natural gas and production of electricity, which is assumed to replace consumption of national grids.

Step 7: Emissions from enteric fermentation. The enteric fermentation is not affected by the AD of cattle manure. Consequently they are estimated as for the baselines utilising Equation 6.2 ($CH_{4,E,B} = CH_{4,E,AD}$ in Table 6.1).

Step 8: CH_4 emissions from storage of digestate. Following the GHGs emitted from operation units in Table 6.1, AD scenarios also include emissions from handling of digestate. In particular, as for untreated manure in baselines, stored digestate releases CH_4 emissions. The estimations of these emissions is as follows:

$$CH_{4,S,AD}[kg \cdot yr^{-1}] = CH_{4,S,B} \cdot \left(\frac{RC_{CH_4,S}}{100} + 1 \right) \tag{6.7}$$

where $CH_{4,S,B}$ are the CH_4 emissions for this operation unit and GHGs in the baseline. $RC_{CH4,S}$ is the local relative change for storage found in Chapter 5. From Figure 5.4 $RC_{CH4,S}$ corresponds to -55%, which is the median excluding cases from Sakamoto [124] (see explanation for this in Section 5.3.3.3).

Step 9: CH_4 emissions from field-application of digestate. CH_4 emitted from field-application of digestate ($CH_{4,F,AD}$) are estimated as:

$$CH_{4,F,AD}[kg \cdot yr^{-1}] = CH_{4,F,B} \cdot \left(\frac{RC^*_{CH_4,F}}{100} + 1 \right) \tag{6.8}$$

where the local relative change for CH_4 in this operation unit ($RC^*_{CH_4,F}$) is 20% (corresponding median in the box plot of Figure 5.6). It should be noted that this relative change presents a non-significant difference with respect to baseline emissions.

Step 10: N_2O emissions from field-application of digestate. N_2O emitted from field-application of digestate ($N_2O_{F,AD}$) are estimated as:

$$N_2O_{F,AD,}[kg \cdot yr^{-1}] = N_2O_{F,B} \cdot \left(\frac{RC^*_{N_2O,F}}{100} + 1 \right) \tag{6.9}$$

where the local relative change for N_2O in this operation unit ($RC^*_{N_2O,F}$) is -30% based on the corresponding median of Figure 5.6.

Step 11: CH_4 emissions from digester leaks. The operation of digesters release direct emissions due to leaks of biogas. The estimation of leaks from digesters in the AD scenarios ($CO_{2e,D,L}$) is as follows:

$$CO_{2e,L}[kg \cdot yr^{-1}] = \frac{RC_L}{100} \cdot CO_{2e,B*} \tag{6.10}$$

where $CO_{2e,B*}$ corresponds to the baseline emissions, as defined in Sections 3.1.3.2 and 5.1 (i.e. without enteric fermentation)[4]. RC_L corresponds to the global relative change found by the meta-analysis of operation units (see Figure 5.3) and is 7.4%.

Step 12: CH_4 production. The theoretical digester of the AD scenarios is assessed in terms of its potential methane production (Step 12) and its heat requirement to operate at mesophilic conditions (308 K, Step 13). To estimate the emissions associated with the offset of fossil fuels, it is necessary to first calculate the CH_4 production ($CH_{4,Prod}$). This is similar to Equation 1.1 from the IPCC protocol, as follows:

$$\begin{matrix} CH_{4,Prod} \\ [kg \cdot yr^{-1}] \end{matrix} = 0.67 \cdot N_C \cdot VS_{Ex} \cdot B_0 \tag{6.11}$$

where B_0 is obtained from the meta-analysis of Chapter 4. VS_{Ex} is given in Table 10A-4 [151] and N_C is collected by the questionnaire of Section 6.1.1. It should be noted that the CO_2 in the bio-

[4]Namely, $B*$ is the sum of emissions from fossil fuel consumption, storage of untreated manure and its field application in corresponding baseline scenario.

gas would increase with higher methane production, as expected for constant biogas composition. However, that CO_2 emission is not quantified because it is considered to be carbon neutral.

Step 13: Simplified estimation of thermal power for digester. The thermal power needed for the digester ($\dot{Q}_d$) is quantified in this step. It should be noted that the thermal power used for the digester is assumed carbon neutral (i.e. supplied by the combustion of biogas). Namely, these emissions are not accounted as negative because they do not replace conventional energy sources of the baselines (or outside the boundaries of the farms).

To quantify $\dot{Q}_d$, the typical mesophilic operation temperature of 308 K [159, 172] is assumed. At this condition, Marañón et al. [134] reports a range of 1.6×10^{-2} to 2.5×10^{-2} $GJ\cdot kg_{CH4}^{-1}$ needed to heat digesters fed with dairy cattle manure. The mean conversion factor of 2.04×10^{-2} $GJ\cdot kg_{CH4}^{-1}$ from Marañón et al. [134] is used as a simplified estimate for this analysis, as follows:

$$\dot{Q}_d[GJ\cdot yr^{-1}] = 2.04\times10^{-2}\cdot CH_{4Prod} \tag{6.12}$$

It should be noted that the later is a conservative estimate (i.e. over estimate of heat required by digester) if:

i) the average local temperatures in the case studies are equal or higher than the work of Marañón et al. (286 K) and/or;

ii) the case study herd size is larger than the work of Marañón et al. (herd sizes: 28, 36, 52 and 90 livestock units, for four farms)

The first condition would imply that less energy is required by the digester of a case study to reach the operation temperature than the work of Marañón et al. [134]. The second condition is in accordance of AD being an economy of scale [314, 315]. As a consequence of this, thermal power could be better utilised in larger digesters (i.e. more efficient use of biogas) than the thermal power used in the work of Marañón et al.

Having the energy requirements of the baseline and the digester, the energy available to export (i.e. and offset fossil fuels) is determined separately for the AD-boiler and AD-CHP scenarios.

Step 13 (alternative): Thermal power for digester. For cases which do not satisfy the conditions of the simplified estimation of $\dot{Q}_d$ (step 7), an alternative approach is presented. To establish the thermal power input to the digester, an energy balance is performed. It is assumed that heating of water in the cattle manure dominates the heat balance. Therefore, the inputs to the balance are water, CH_4 and CO_2. The energy balance over the digester is expressed in terms of the individual species as follows:

$$\dot{Q}_d[kJ \cdot yr^{-1}] = \dot{n}_{out,CH4} \cdot \hat{H}_{CH4}(T_d) + \dot{n}_{out,CO2} \cdot \hat{H}_{CO2}(T_d)$$
$$- \dot{n}_{out,H2O} \cdot \hat{H}_{out,H2O}(T_d) - \dot{n}_{in,H2O} \cdot \hat{H}_{H2O}(T_s)$$

where temperature values for the water inlet (T_s) are based on maximum and minimum local annual averages. To calculate $\dot{Q}_d$ using Equation (6.1), the specific enthalpies of each component ($\hat{H}_i$) are expressed by the integration of heat capacities:

$$\hat{H}_i(T_s)\,[kJ \cdot mol^{-1}] = \Delta\hat{H}_f^0 + \int_{298}^{T_s} a_i + b_i T + c_i T^2 + d_i T^3 \, dT \tag{6.13}$$

where 298 is the temperature at the reference state (101 kPa), T_s is the temperature of the inlet stream, $\Delta\hat{H}_f^0$ is the molar heat of formation, and $\{\text{a,b,c,d}\}_\text{i}$ are constant parameters of gas "i" (Table B.2 Felder [316]). The temperature of the produced biogas was considered to be equal to mesophilic operating temperature (308 K) of the digester (i.e. as for CSTRs).

6.1.4 AD-Boiler scenario

To combust the biogas, the AD-boiler scenario is established for its high efficiencies ($\simeq$90% respect to the higher heating value (HHV)) and suitability for small-scale operations [175]. In this scenario, biogas is converted only to heat in a condensing boiler (i.e. no electricity generation). Therefore, the emissions from electricity consumption are estimated as for the baselines ($CO_{2El,Bo} = CO_{2El,B}$ in Table 6.1). The following steps are specific to the AD-boiler scenario and are the continuation of common Steps 1 to 7 for both AD scenarios.

Step 14a: Emissions from electricity consumption (AD-boiler scenario). The AD-boiler scenario is assumed to consume the same electricity than for the baseline scenario, because the condensing boiler only produces thermal power. Consequently, the emissions associated with electricity from national grids and combustion of fossil fuels for on-site electricity generation are estimated as for the baselines utilising Equation 6.4 ($CO_{2,El,B} = CO_{2,El,Bo}$ and $CO_{2,El*,B} = CO_{2,El*,Bo}$ in Table 6.1).

Step 15a: Thermal power generation (AD-boiler scenario). The energy from the biogas is released by the combustion of CH_4 in the boiler. Complete combustion (stoichiometric) is assumed. However, it should be noted that equilibrium reactions such as the dissociation of CO_2 and water-gas shift reaction, are also present and effect the composition of the combustion products (i.e. presence of carbon monoxide and hydrogen) [317]. A condensing boiler extracts the heat of evaporation of water contained in the flue gas [318, 319]. Therefore, the HHV of CH_4 is used to estimate the total thermal power produced in the AD-boiler scenario [175]:

$$\dot{E}_{Th,Bo}\,[GJ \cdot yr^{-1}] = \eta_{Th,Bo} \cdot HHV_{CH4} \cdot CH_{4,Prod} \tag{6.14}$$

where $\eta_{th,boiler}$ is the fraction of chemical power (combustion reaction) converted to thermal power in the condensing boiler and is 90% based on the HHV ($55.6 \times 10^{-3} GJ \cdot kg_{CH4}^{-1}$ [316]).

Step 16a: Emissions associated with thermal power generation (AD-boiler scenario). By combining the $\dot{E}_{Th,B}$ (Step 5 of the baseline emissions), $\dot{Q}_d$ (Step 7) and $\dot{E}_{Th,Bo}$ (Step 8) emissions associated with thermal power import or export can be estimated. It is assumed that export of thermal power will displace CO_2 emissions from the combustion of natural gas. Therefore, the latter have negative emission and are estimated as:

$$CO_{2Th,Bo}[kg \cdot yr^{-1}] = (\dot{E}_{Th,B} + \dot{Q}_d - \dot{E}_{Th,Bo}) \cdot EF_{NG} \tag{6.15}$$

where the emission factor of natural gas "EF_{NG}" is 69.3 $kg_{CO2e} \cdot GJ^{-1}$ (Table 1.4). $CO_{2Th,Bo}$ of Equation 6.15 results in positive emissions, if there is insufficient thermal energy produced by the condensing boiler to supply the dairy farm activities and digester requirements.

Step 16a (alternative): Estimation of emissions associated with thermal power generation (AD-boiler scenario). The emissions associated with the use of conventional sources in this scenario can also be estimated by utilising the global relative change presented in Figure 5.3 (RC_{Off}= -8.9±8.9%). This relative change is adequate for the AD-boiler scenario as it is standardised to replace natural gas (i.e. no electricity generation as occurs in the AD-CHP scenario). However this value should be utilised with caution as it is an overall synthesis of emission changes, but not specific for condensing boiler technology. In consideration of the above, the emissions are estimated as:

$$CO_{2,Th,Bo} = \frac{RC_{Off}}{100} \cdot CO_{2e,B*} + CO_{2e,Th,B*} \tag{6.16}$$

6.1.5 AD-CHP scenario

The AD-CHP scenario is chosen because CHP is feasible and commonly applied in biogas plants [159, 177, 320] producing electricity and useful thermal energy to heat digester(s). The emissions associated with this sustainable energy production are estimated in the following steps. It should be noted that these are the continuation of common Steps 1 to 7 for both AD scenarios.

Step 14b: Electricity generation (AD-CHP scenario). The electrical energy that can be produced from the CH_4 contained in the biogas by combusting it in an CHP unit is estimated as:

$$\dot{E}_{El,CHP}\,[GJ \cdot yr^{-1}] = \eta_{el} \cdot LHV_{CH4} \cdot CH_{4,Prod} \tag{6.17}$$

where LHV is the lower heating value (50.1 $MJ \cdot kg_{CH4}^{-1}$ [316]), η_{el} is the fraction of chemical power to electricity in the CHP unit, and is assumed to be 36% (based on LHV) for small scale CHP units

[159, 176].

Step 15b: Estimation of emissions associated with electricity generation (AD-CHP scenario). The excess electricity is used to estimate the exportable power that would offset emissions (i.e. negative emissions) from the use of national grids:

$$CO_{2El,CHP}[kg \cdot yr^{-1}] = (\dot{E}_{El,B} - \dot{E}_{El,CHP}) \cdot EF_{El} \tag{6.18}$$

where $\dot{E}_{EL,B}$ is the annual electricity consumption in the baseline and EF_{EL} is the national emission factor of the electricity grids and can be obtained from the International Agency of Energy [313]. If there is insufficient electricity produced in the AD-CHP scenario to supply the requirements of the baseline, Equation 6.18 will result in positive emissions. For these cases, priority is given to the replacement of grid electricity over on-site generators.

Step 16b: Estimation of thermal power generation (AD-CHP scenario). The reported CHP efficiencies for biogas are over 80% based on the LHV [175–177]. The thermal power generated by the CHP process is, therefore, estimated as:

$$\dot{E}_{Th,CHP}[GJ \cdot yr^{-1}] = \eta_{th} \cdot LHV_{CH4} \cdot CH_{4,Prod} \tag{6.19}$$

where η_{th} is fraction of power converted to thermal power in the CHP unit. Based on the LHV, η_{th} is 50% [176].

Step 17b: Emissions associated with thermal power generation (AD-CHP scenario). Similar to the AD-boiler scenarios offset of emissions are estimated by assuming the offset of natural gas. The latter has negative emission estimated as:

$$CO_{2Th,CHP}[kg \cdot yr^{-1}] = (\dot{E}_{Th,B} + \dot{Q}_d - \dot{E}_{Th,CHP}) \cdot EF_{NG} \tag{6.20}$$

Table 6.2: Calculations for changes in emissions according to Equation 6.1 for each operation unit.

GHG and operation unit	Change in emissions (Eq. 6.1)
CH_4 from storage of slurries	$CH_{4,S,AD} - CH_{4,S,B}$
CH_4 from field-application of slurries	$CH_{4,F,AD} - CH_{4,F,B}$
N_2O from field-application of slurries	$N_2O_{F,AD} - N_2O_{F,B}$
Digester CH_4 leaks	$CH_{4,S,AD} - 0$
CO_{2e} from electricity consumption[a]	$CO_{2,El,CHP} - CO_{2,El,B} - CO_{2,El*,B}$
CO_{2e} from thermal energy consumption[b]	$CO_{2,Th,AD} - CO_{2,Th,B}$

[a]Only the AD-CHP scenario is presented in the calculation, because the AD-boiler and baseline scenario consume the same electricity. [b]AD in the Equation can be "Bo" (i.e. for the AD-boiler scenario) or "CHP" for the AD-CHP scenario.

If there is insufficient thermal energy produced by the CHP unit, positive emissions will result from Equation 6.20 because thermal energy from conventional sources would be required to be imported.

It should be noted that relative changes from Chapter 5 for offset of fossil fuels are not utilised for this scenario because they assume that power generated replaces only natural gas (i.e. not carbon embodied in the consumption of electricity from national grids). This is not the case of this scenario in which electricity is also produced. Thus, the energy and mass balances above are more specific to the combustion technology of the scenario.

Step 18: Calculation of changes in emissions for both AD scenarios. As a final step, the changes in emissions are estimated for each operation unit by utilising Equation 6.1. These calculations are specified, according to the nomenclature of Table 6.1, in Table 6.2.

6.2 Case Study I: Dairy Farm in the United Kingdom

This section presents the emissions and energy use/production for baseline and AD scenarios of the English case study. For this, a theoretical AD plant for dairy cattle manure in Mapledurham Estate, Oxfordshire (United Kingdom) is considered (see geographic location in Figure 6.1).

According to the questionnaire response, this dairy farm produces 4.7 million litres of milk from 500 Holstein cattle. The livestock diet consists of Justina maize harvested within the 729 ha farm site. The cattle manure is stored on site (diluted with water, i.e. "Liquid/Slurry" in the



Figure 6.1: Location of English dairy farm used for case study (red circle), reproduced from Google Maps [322].

IPCC Guidelines Intergovernmental Panel on Climate Change National Greenhouse Gas Inventories Programme [151]) and spread on the maize fields as nutrient source (i.e. "Daily spread" in the IPCC Guidelines [151]). Therefore, the manure deposit by animal on grassland ("Pastures/Range/Paddock") is minimised (i.e. $MS_3 \approx 0$ in Equation 6.3). As reported in a previous assessment of the farm [321], the power required for dairy operations is 1.1 $TJ \cdot yr^{-1}$ of electricity from the English grid and 39 $GJ \cdot yr^{-1}$ of thermal power from natural gas.

In order to complete the energy and emission assessment of the scenarios for this case study, the methodology of Section 6.1 is carried out. To perform the calculations therein (Equations 6.2 to 6.20), Table 6.3 presents the information selected from the literature, specific to this case study.

6.2.1 Baseline emissions from English farm

The emissions according to operation unit are shown in Table 6.4. The baseline of Mapledurham Estate releases 1,203±90 $ton_{CO2e} \cdot yr^{-1}$ from operation units which can be changed by AD. If the emissions from enteric fermentation are accounted, total GHGs emitted are 2,660±679 $ton_{CO2e} \cdot yr^{-1}$. Thus, direct emissions from livestock contribute 55% of total baseline emissions and increase the uncertainty from 7% to 25%. The latter is due to the use of Tier 1 methodology for estimation of enteric emissions, which implements a highly uncertain emissions factor EF_E (see

Table 6.3: Required information to estimate emissions from English case study (Eqs. 6.2 to 6.20).

Eq.	Variable	Value	Unit	Source
6.2	EF_E	117±47	$kg_{CH4} \cdot hd^{-1} \cdot yr^{-1}$	Table 10.11 [151]
6.2, 1.1, 1.8, 6.11	N	500	hd	Questionnaire (Section 6.1.1)
1.1	VS_{Ex}	1,862	$kg_{VS} \cdot hd^{-1} \cdot yr^{-1}$	Table 10A.4 [151]
1.1	B_0	0.230±0.016	$m^3_{CH4} \cdot kg^{-1}_{VS}$	Ch. 4 (this work)
1.1	MCF_S	22	%	Table 10A.4 [151][a]
1.1	MS_S	1	n.a.	Questionnaire (Section 6.1.1)
1.1	Temp	286[b]	K	[312]
6.3	MS_{F1}	1	n.a.	Questionnaire (Section 6.1.1)
1.1	MCF_{F1}	0.1	%	Table 10A.4 [151][a]
6.3	EF_{F1}	0.01	$kg_{N2O-N} \cdot kg^{-1}_N$	Table 11.1 [210]
6.3	MS_{F2}	0	n.a.	Questionnaire (Section 6.1.1)
6.3	N_{rate}	0.1752	$kg_N \cdot kg^{-1}_{animal} \cdot yr^{-1}$	Table 10.19 [151]
6.3	TAM	600±60	kg	Table 10A-4 [151]
1.8	Nex	105±11	$kg_N \cdot hd^{-1} \cdot yr^{-1}$	Calculated from Eq. 1.8
6.15 & 6.20	EF_{NG}[e]	0.4	$kg_{CO2e} \cdot kWh^{-1}$	Table-[313]
6.18	EF_{El}[e]	131±8	$kg_{CO2e} \cdot GJ^{-1}$	[323]

[a]Liquid/Slurry for storage. [b]Average temperature values for United Kingdom is considered (minimum 280 K and maximum 292 K). [c]Daily spread for field-application.[d]Pasture/Range/Paddock for field-application is not applicable. [e]Energy sources identified by the questionnaire.

Table 6.4: Summary of GHG emission from the three scenarios in the English case study.

	Emissions from scenarios ($ton_{CO2e} \cdot yr^{-1}$)		
GHGs from operation units	**Baseline (B)**	**AD Scenarios**	
Enteric fermentation (E)			
CH_4 emissions	(+) 1,460±590	(+) 1,460±590	
Storage of slurries (S)			
CH_4 emissions	(+) 790±55	(+) 360±25	
Field-application of slurries (F)			
CH_4 emissions	(+) 3.6±0.2	(+) 4.3±0.3	
N_2O emissions	(+) 250±25	(+) 172±17	
Digester leaks (L)			
CH_4 emissions	0	(+) 89±6	
Electricity (El)		**AD-Boiler (Bo)**	**AD-CHP (CHP)**
Import (from grid)	(+) 144±9	(+) 144±9	0
Export (to grid)	0	0	(-) 190±24
On-site generation	0	0	0
Thermal energy (Th)			
Export	0	(-) 470±33	(-) 70±5
On-site combustion of fossil fuels.	(+) 15.6	0[a]	0[a]

[a]Combustion of biogas to supply heat to the digester is assumed carbon neutral.

Table 6.3).

CH_4 emissions from stored manure are 790±55 $ton_{CO2e} \cdot yr^{-1}$ (~30% of total baseline emissions) and CH_4 released after field application is estimated to be 3.6±1.0 $ton_{CO2e} \cdot yr^{-1}$ in the baseline. The difference in CH_4 emissions from stored and field-applied manure is attributed to the dissimilar oxygen availability. For stored manure, CH_4 formation is enhanced because anaerobic conditions are dominant in the bulk of tanks (i.e. only surface at storage level can promote oxygen exchange). Conversely, the application of slurries over fields by spraying techniques (i.e. creating droplets which jointly increase the contact surface) promotes oxygen reactions. These aerobic conditions favour CO_2 formation instead of CH_4.

N_2O is only considered to be emitted from field-application of manure in the baseline. These emissions are estimated to be 250±25 $ton_{CO2e} \cdot yr^{-1}$ (~9% of total baseline emissions). Compared to CH_4 from field-applied slurries, greater contribution of N_2O emissions are found. This is explained by the nitrification of urine in the manure, which is promoted by aerobic conditions [324] and the higher GWP of the latter GHG.

The use of electricity from the English grid to meet the dairy requirements emits 144±9 $ton_{CO2e} \cdot yr^{-1}$. This electricity is directed to milk production and manure management. In particular, the dairy farm has an ice-making machine to cool the milk, vacuum pumps to extract the milk, rotating platform for milking of cattle, pumps for the collection of manure for storage and lighting [321]. The emissions from the combustion of natural gas are associated with space heating and are 15.6 $ton_{CO2e} \cdot yr^{-1}$.

6.2.2 Emissions shared by both English AD scenarios

The emissions from theoretical AD scenarios are shown in Table 6.4 according to operation units. Emissions from the replacement of untreated manure by digestate (i.e. storage and field-application of slurry) and from digester leaks are common for both AD-boiler and AD-CHP scenarios (Steps 7 to 13 in methodology).

For storage, CH_4 emissions from stored manure in the baseline scenario are replaced by those from digestate stored in the AD scenarios. The CH_4 emissions from stored digestate are 430±80

$ton_{CO2e} \cdot yr^{-1}$ less than the emissions from stored manure in the baseline.

For field-application, given the non-significant changes in CH_4 emissions, no observable differences between emissions of this GHG from baseline and AD scenarios are found (0.74±0.05 $ton_{CO2e} \cdot yr^{-1}$, n.s.). However, reduction of N_2O from applying digestate as fertiliser instead of untreated manure are observed. In the AD scenarios the digestate applied over fields emits 172±17 $ton_{CO2e} \cdot yr^{-1}$ (343±34 $kg_{CO2e} hd^{-1} yr^{-1}$), which corresponds to a reduction of 80±7 $ton_{CO2e} \cdot yr^{-1}$ (150±15 $kg_{CO2e} hd^{-1} yr^{-1}$) with respect to the baseline scenario.

The digester is the only operation unit to increase emissions due to CH_4 leaks, as expected from the results of relative changes (Section 5.3.3.1). This contributes 89±6 $ton_{CO2e} \cdot yr^{-1}$ to the AD scenarios.

With respect to energy production, the application AD in Mapledurham Estate holds the potential to produce 143±10 $ton_{CH4} \cdot yr^{-1}$. This is equivalent to 286±20 $kg_{CH4} \cdot hd^{-1} \cdot yr^{-1}$ when standardising by the herd size. Given this CH_4 production, the application of Equation 6.12 results in 2,930±204 $GJ \cdot yr^{-1}$ of heat required for the operation of a theoretical digester at 308 K. To supply this heat to the digester, the combustion of the CH_4 produced is considered. The amount of useful energy that can be extracted from the CH_4 in the biogas and the consequent offset of emissions, depend on the efficiency of the combustion technology in place. Therefore, the two AD scenarios of interest in this chapter (AD-boiler and AD-CHP) are discussed in the following Sections 6.2.3 and 6.2.4, together with total scenario emissions.

6.2.3 Emissions from AD-boiler scenario

Figure 6.2 presents the results of the changes in emissions of the AD-boiler scenario with respect to the baseline (from Equation 6.1). The total emissions of this scenario are 300±90 $ton_{CO2e} \cdot yr^{-1}$ without considering enteric fermentation and 1,760±680 $ton_{CO2e} \cdot yr^{-1}$ with that operation unit. If the English case study transitions from the current manure management practice to the AD-boiler scenario the potential change in emissions is -900±80 $ton_{CO2e} \cdot yr^{-1}$ (i.e. parameters specified in Table 6.3). This corresponds to a reduction by ~75% of the emissions from operation units which can be affected by AD (i.e. not enteric fermentation). Standardising these

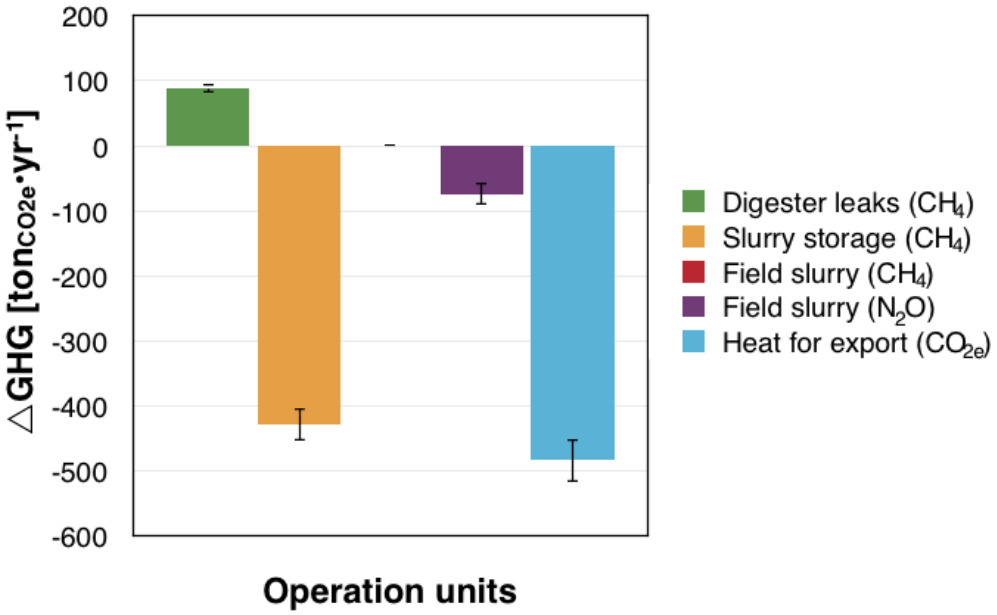

Figure 6.2: Changes in emissions with respect to baseline scenario. Error bars are based on the ranges of default parameters from the IPCC methodology and interquartile range of B_0(see Table 6.3).

changes in emissions by herd size results in mitigations of 1,800±150 $kg_{CO2} \cdot hd^{-1} \cdot yr^{-1}$ for this English dairy farm.

The generation of carbon neutral CH_4 through AD, which can replace natural gas as fuel for the condensing boiler, is the main source of emission reduction. The thermal power generated in the AD-boiler scenario is directed towards the internal farm use or to export. Figure 6.3 presents the thermal power output for the AD scenarios in the English case study using different biogas combustion technologies. The potential gross thermal power generation from the AD-boiler system in Mapledurham Estate is 7,200±500 $GJ \cdot yr^{-1}$ (14.4±1.0 $GJ \cdot hd^{-1} \cdot yr^{-1}$). When subtracting the heat to operate the digester, 4,260±300 $GJ \cdot yr^{-1}$ are obtained. This heat is available for farm consumption (replacing the use of natural gas) and/or export (green bars in Figure 6.3). Given that the baseline scenario only consumes 39 $GJ \cdot yr^{-1}$, there is sufficient thermal power to supply the farm and export 4,220± 300 $GJ \cdot yr^{-1}$. The internal use of the thermal energy would therefore offset the 15.6 $ton_{CO2e} \cdot yr^{-1}$ from the consumption of natural gas in the baseline scenario. The export of heat would offset 470±30 $ton_{CO2e} \cdot yr^{-1}$.

The AD-boiler, as for the baseline scenario, does not produce electricity. Therefore, this scen-

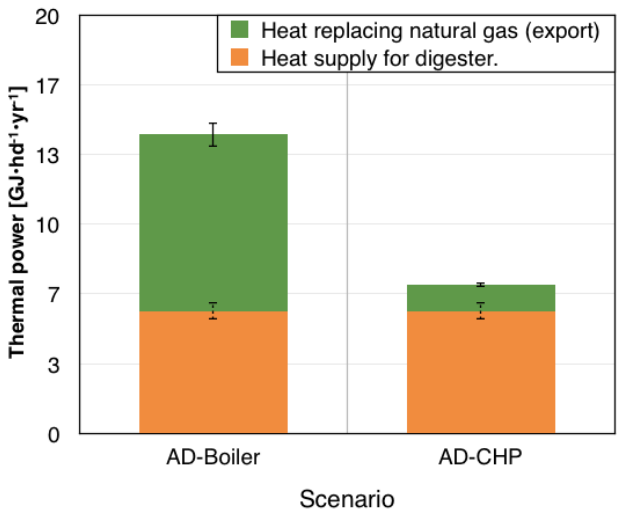

Figure 6.3: Thermal power production in English dairy farm with AD-Boiler and AD-CHP. Error bars correspond to ranges in parameters of the IPCC methodology [151] and the confidence determined by meta-analysis for B_0 (Chapter 4).

ario imports electric power from the English grid to supply the required 1,100 $GJ \cdot yr^{-1}$ for the dairy operations. The consumption of electricity from this source is thus equivalent to that of the baseline scenario (144±9 $ton_{CO2e} \cdot yr^{-1}$, in Table 6.4).

6.2.4 Emissions from AD-CHP scenario

CHP was chosen as a technology to evaluate the use of biogas as it has been reported to be convenient in generating electrical power while supplying heat to the digester [159]. The results of GHG emissions from the AD-CHP scenario are presented in Figure 6.4. The total emissions from operation units which are susceptible to AD (i.e. those different to enteric fermentation in Table 6.4) are 365±76 $ton_{CO2e} \cdot yr^{-1}$. The difference in emissions with respect to the baseline scenario is -840±70 $ton_{CO2e} \cdot yr^{-1}$ which corresponds to 70% reduction of the emissions from the baseline scenario. Normalised by herd size, the emissions change 1,670±110 $kg_{CO2e} \cdot hd^{-1} \cdot yr^{-1}$. If emissions from enteric fermentation are accounted, the AD-CHP scenario releases 1,825±760 $ton_{CO2e} \cdot yr^{-1}$ and the AD only decreases emissions by 31% of those from the baseline.

The generation of renewable electricity in this scenario is the second most important source of emission mitigation. The implementation of the theoretical AD-CHP scenario in Mapledurham Estate plant has the estimated potential of generating 2,590±180 $GJ \cdot yr^{-1}$ of electric power for

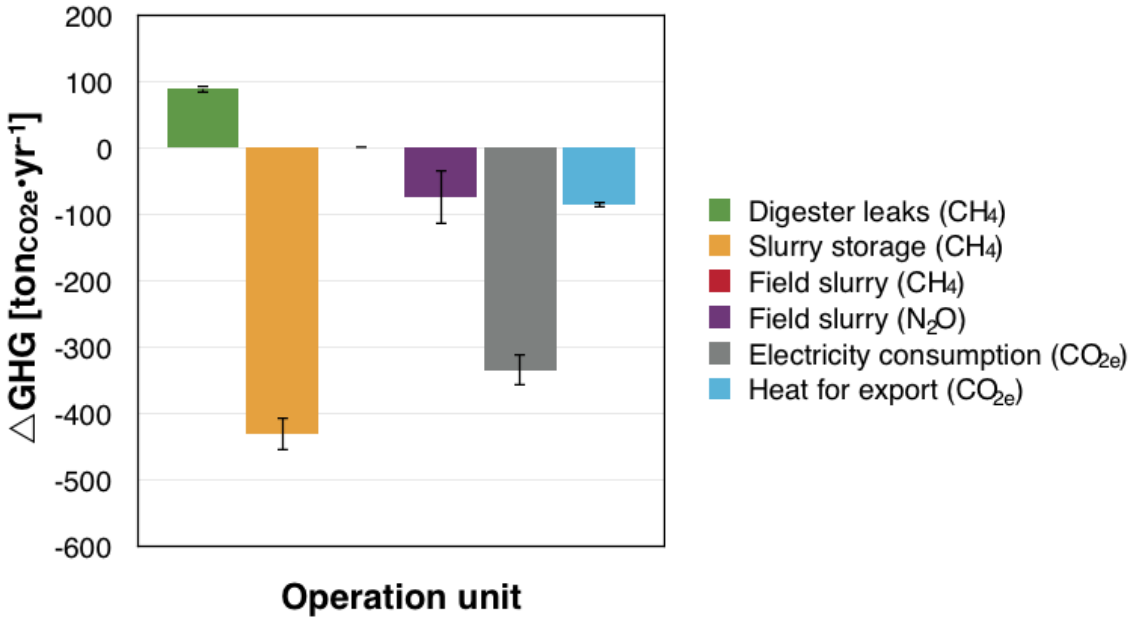

Figure 6.4: Changes in emissions from AD-CHP scenario in the English case study. Error bars relate to ranges of default parameters from the IPCC methodology and B_0 confidence interval as determined by meta-analysis.

the Y_{CH4} of 0.230±0.016 $m^3_{CH4} \cdot kg^{-1}_{VS}$. This electric power can be used internally to supply the requirements of the dairy activities and excess power is assumed to be exported. The electricity used for the dairy operations displaces 144±9 $ton_{CO2e} \cdot yr^{-1}$, that otherwise would be provided by the English grid. There is an excess of electric power to export of 1,450±180 $GJ \cdot yr^{-1}$. This available electricity, that can replace grid electricity, holds the potential of offsetting 190±24 $ton_{CO2e} \cdot yr^{-1}$.

The thermal power produced and used in the AD-CHP scenario holds the potential to generate 3,590±250 $GJ \cdot yr^{-1}$ (see Figure 6.3). This is sufficient to supply heat to the digester and to the farm. In fact, after subtracting the required heat for the digester (2,940±200 $GJ \cdot yr^{-1}$) and for the baseline scenario (39 $GJ \cdot yr^{-1}$) there are 630±46 $GJ \cdot yr^{-1}$ remaining and available for export (light blue bars in Figure 6.4). These changes in emissions from this operation unit contribute the least reductions from activities in the AD-CHP scenario.

For the English farm, there is infrastructure available for the export of electricity and/or thermal power. Therefore, the implementation of an AD system could make available low-cost power to farm and surrounding community. In addition, the dairy farms holds the potential to offset emissions which could generate carbon credits for trading. In terms of the latter benefit the AD-



Figure 6.5: Location of Guatemalan dairy farms used for case studies [325]. Red circle indicates highly remote rural area and green circles indicate neighbouring urban area.

Table 6.5: Quantitative information collected by questionnaire for Guatemalan case study farms.

					Energy consumption $[GJ \cdot yr^{-1}]$		
Farm	**Location**	**Average Temp. [K]**	**Dairy cattle** $[hd]$	**Milk produced** $[L \cdot yr^{-1}]$	**Grid electr.** $(\dot{E}_{El,B})$	**Diesel** $(\dot{E}_{Di,B})$	**Petrol** $(\dot{E}_{Pe,B})$
A	Petén	299[a]	600[b]	55,000	0[d]	52	71
B	Santa Rosa	294[a]	370[c]	260,000	15	45	22
C	Escuintla	294[a]	350	91,250	151	45	0

[a]Average temperature by Guatemalan regions [326]. [b]Of which 60 are milked annually. [c]Of which 150 are milked annually. [d]Off-grid electricity from petrol generator.

boiler scenario is preferable as it mitigates more GHGs with respect to the baseline than the AD-CHP scenario.

6.3 Case Study II: Dairy Farms in Guatemala

This section presents the potential energy production and changes in emissions caused by AD scenarios in three Guatemalan case studies, which are labelled A, B and C (geographic location in Figure 6.5). To follow the assessment method of Section 6.1, details collected by the questionnaire are given in Table 6.5 for each Guatemalan farm. Other parameters utilised to carry out the steps in the methodology are shown in Table 6.6. It should be noted that B_0 in Table 6.6, is based on the

meta-analysis for African countries given that: i) insufficient cases are available in the literature to carry out a meta-analysis of B_0 for Latin America; ii) the IPCC Guidelines use the same B_0 default values for Latin America and Africa and; iii) Guatemalan development is similar to most African countries (see development index in Figure 1.1), hence, it is assumed that cattle feed (and consequently its manure) is similar.

Another observation of Table 6.6 is that, for the three Guatemalan cases resources are unavailable for the implementation of storage tanks ($MS_S = 0$) and the controlled spreading of untreated slurry over fields as a source of nitrogen ($MS_{F1} = 0$). Therefore, MCF and MS presented in Table 6.5 reflect no infrastructure for slurry management and all manure is considered to be deposit by grazing animals over fields. This corresponds to "Pasture/ Range/ Paddock" in the IPCC classification [151]. The absence of storage tanks in baselines implies that the implementation of AD in Guatemalan farms would also require a new form to collect cattle manure. It is assumed that for the AD scenarios cattle would be housed, given the difficulty to collect manure from pastures and that housing is a dominant practice in the literature Weiske et al. [122], Michel et al. [131], Monteny et al. [327]. The baseline and AD scenarios for the Guatemalan case studies are presented in the following sections.

6.3.1 Baseline emissions from Guatemalan farms

The total emissions from the case study farms are 1,510±480, 930±290 and 890±280 $ton_{CO2e} \cdot yr^{-1}$ for farms A, B and C, respectively (see Tables 6.7, 6.8 and 6.9). Enteric fermentation is the main source of emissions for all farms. These contribute ~71% of the baseline emissions. Therefore, if excluding these emissions (i.e. because they are not affected by AD) total emissions for farms A, B and C result in 426±44, 260±30 and 260±30 $ton_{CO2e} \cdot yr^{-1}$, respectively. Similar emissions for farm B and C are observed given their proximity in herd size. However, the emissions by source vary, thus, results by operation units are discussed.

Manure deposit on field by grazing animals emit only low amount of CH_4 (1.0-1.5% of total farm emissions), but high emissions of N_2O (~26% of total farm emissions). The low CH_4 contribution is explained by manure piles over pastures which are under aerobic conditions (i.e. promoting

Table 6.6: Required information to estimate emissions from Guatemalan case studies.

Eq.	Variable	Value	Unit	Source
6.2	EF_E	72±29	$kg_{CH4} \cdot hd^{-1} \cdot yr^{-1}$	Table 10.11 [151]
1.1	VS_{Ex}	1,059	$kg_{VS} \cdot hd^{-1} \cdot yr^{-1}$	Table 10A.4 [151]
1.1	B_0	0.110±0.022[b]	$m^3_{CH4} \cdot kg^{-1}_{VS}$	Ch. 4 (this work)
1.1	MS_S	0	n.a.	Questionnaire (Section 6.1.1)
1.1	MCF_S	n.a.	n.a.	Ch. 4
1.1 & 1.8	MS_{F1}	0	n.a.	Questionnaire (Section 6.1.1)
1.1 & 1.8	MS_{F2}	1	n.a.	Questionnaire (Section 6.1.1)[a]
1.1	MCF_{F2} (A)	2.0	%	Table 10A.4 [151][a]
1.1	MCF_{F2} (B, C)	1.5	%	Table 10A.4 [151][a]
1.8	EF_{F2}	0.02	$kg_{N2O-N} \cdot kg^{-1}_N$	Table 11.1 [210]
6.3	N_{rate}	0.1752	$kg_N \cdot kg^{-1}_{animal} \cdot yr^{-1}$	Table 10.19 [151]
6.3	TAM	400±40	kg	Table 10A-4 [151]
1.8	Nex	70±7	$kg_N \cdot hd^{-1} \cdot yr^{-1}$	Calculated from Eq. 1.8
6.15 & 6.20	EF_{NG}	0.4	$kg_{CO2e} \cdot kWh^{-1}$	[313]
6.18	EF_{El}[c]	91±11	$kg_{CO2e} \cdot GJ^{-1}$	Average 2008-10 [313]
6.5	EF_{Diesel}[c]	74.1	$kg_{CO2e} \cdot GJ^{-1}$	Table 1.4 [272]
6.5	EF_{Petrol}[c]	69.3	$kg_{CO2e} \cdot GJ^{-1}$	Table 1.4 [272]

[a]Pasture/Range/Paddock for field-application. [b]B_0 for African countries (i.e. insufficient Latin American cases are available for the meta-analysis of Chapter 4).[c]Energy sources identified by the questionnaire.

Table 6.7: Summary of GHG emission from the three scenarios in the Guatemalan case study "A".

	Emissions from scenarios ($ton_{CO2e} \cdot yr^{-1}$)		
GHGs and operation units.	**Baseline (B)**	**AD Scenarios**	
Enteric fermentation (E)			
CH_4 emissions	(+) 1,080±430	(+) 1,080±430	
Storage of slurries (S)			
CH_4 emissions	0	0	
Field-application of slurries (F)			
CH_4 emissions	(+) 23±5	(+) 28±6	
N_2O emissions	(+) 390±40	(+) 275±27	
Digester leaks (L)			
CH_4 emissions	0	(+) 32±3	
Electricity (El)		**AD-Boiler (Bo)**	**AD-CHP (CHP)**
Import (from grid)	0	0	0
Export (to grid)	0	0	(-) 65±15
On-site generation	(+) 9.0	(+) 9.0	0
Thermal energy (Th)			
Export	0	(-) 154±31	(-) 24±5
On-site combustion of fossil fuels.	0	0[a]	0[a]

[a]Combustion of biogas to supply heat to the digester is assumed carbon neutral.

Table 6.8: Summary of GHG emission from the three scenarios in the Guatemalan case study "B".

	Emissions from scenarios ($ton_{CO2e} \cdot yr^{-1}$)		
GHGs and operation units.	**Baseline (B)**	**AD Scenarios**	
Enteric fermentation (E)			
CH_4 emissions	(+) 670±270	(+) 670±270	
Storage of slurries (S)			
CH_4 emissions	0	0	
Field-application of slurries (F)			
CH_4 emissions	(+) 11±2	(+) 13±3	
N_2O emissions	(+) 240±24	(+) 170±17	
Digester leaks (L)			
CH_4 emissions	0	(+) 19±2	
Electricity (El)		**AD-Boiler (Bo)**	**AD-CHP (CHP)**
Import (from grid)	(+) 1.4±0.2	(+) 1.4±0.2	0
Export (to grid)	0	0	(-) 40±9
On-site generation	(+) 4.9	(+) 4.9	0
Thermal energy (Th)			
Export	0	(-) 95±19	(-) 15±3
On-site combustion of fossil fuels.	0	0[a]	0[a]

[a]Combustion of biogas to supply heat to the digester is assumed carbon neutral.

Table 6.9: Summary of GHG emission from the three scenarios in the Guatemalan case study "C".

	Emissions from scenarios ($ton_{CO2e} \cdot yr^{-1}$)		
GHGs and operation units.	**Baseline (B)**	**AD Scenarios**	
Enteric fermentation (E)			
CH_4 emissions	(+) 630±250	(+) 630±250	
Storage of slurries (S)			
CH_4 emissions	0	0	
Field-application of slurries (F)			
CH_4 emissions	(+) 10±2	(+) 12±2	
N_2O emissions	(+) 230±23	(+) 160±17	
Digester leaks (L)			
CH_4 emissions	0	(+) 19±2	
Electricity (El)		**AD-Boiler (Bo)**	**AD-CHP (CHP)**
Import (from grid)	(+) 14±2	(+) 14±2	0
Export (to grid)	0	0	(-) 27±9
On-site generation	(+) 3	(+) 3	0
Thermal energy (Th)			
Export	0	(-) 90±18	(-) 14±3
On-site combustion of fossil fuels.	0	0[a]	0[a]

[a]Combustion of biogas to supply heat to the digester is assumed carbon neutral.

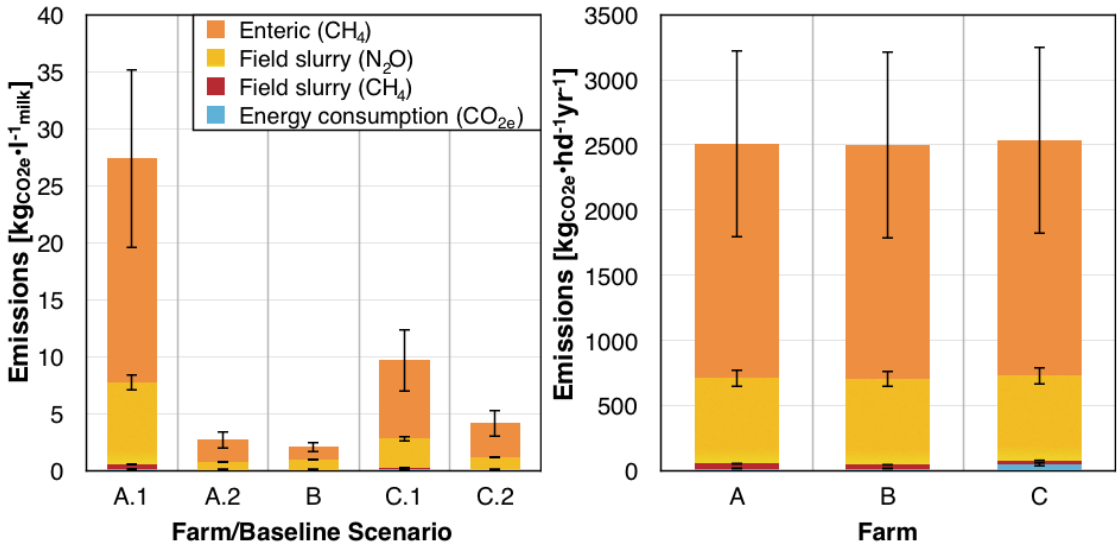

Figure 6.6: Emissions from Guatemalan baseline scenarios normalised by (a) farm and annual milk production and; (b) herd size. Error bars correspond to ranges in default parameters of the IPCC methodology and confidence intervals of the B_0 (i.e. meta-analysis in Chapter 4).

CO_2 formation). Therefore, anaerobic conditions which support CH_4 production only occur in the bulk of animal residues on pastures. The high contribution of N_2O emissions to field-applied slurries is explained (i.e. as for the English farm) by favourable aerobic conditions for denitrification and the high GWP_{N2O} of this GHG.

Consumption of electricity and fossil fuels in all Guatemalan case studies is mainly for domestic use as cattle are milked manually and, given the tropical conditions, no thermal energy is required for heating houses. This results in 0.5-2.0% of the dairy farm emissions attributed to energy consumption. Differences between Guatemalan farm emissions arise from the number of households on-site and the energy sources. Farms A and B have one household on-site, while Farm C has ten. Farm A, the largest in terms of herd size, obtains electricity by generators because grid electricity is unavailable. Conversely, Farms B and C consume mainly grid electricity, having diesel and petrol generators as well (see Table 6.5).

To discuss and compare the Guatemalan farms, the emissions from the baseline scenarios are normalised by milk production and herd size as presented in Figure 6.6 a) and b), respectively. Emissions by litre of milk of Farm A and C are presented as two sub-scenarios: A.1-2 and C.1-2. The first sub-scenarios (A.1 and C.1) represent the current farm situation in which only a fraction

of the total dairy cows are milked (see Table 6.5). Therefore, the milk production is lower than the farm potential and emissions account for non-milked cattle. The reason for these farms to maintain large herd size in reproductive age is that additionally to milk production they produce meat and livestock for trade. For the sub-scenarios A.2 and C.2 the milk production is based on the theoretical milking of all dairy cattle on-site. In the latter sub-scenarios for baselines, the emissions per litre of milk produced are in closer agreement with results from the literature (~1.3 $kg_{CO2} \cdot L_{milk}^{-1}$ [188]). However, this level of milk production is currently unsuitable for the farm as manual milking takes place, human resources are limited given the isolated locations (markedly remote for Farm A) and the product distribution is not consolidated. In addition, Farm A does not have grid electricity access to implement automated milking procedures. This can be an incentive for off-grid electricity generation as discussed in the AD-CHP scenario (Section 6.3.4).

Emissions normalised with respect to the number of cattle are shown in Figure 6.6b. Because the farm emissions are strongly dependent on the herd size (N_C in Equations 1.1, 1.8 and 6.2), this normalisation results in similar values (2,510±800 $kg_{CO2e} \cdot hd^{-1} \cdot yr^{-1}$ with enteric fermentation and 718±81$kg_{CO2e} \cdot hd^{-1} \cdot yr^{-1}$ without this operation unit). Differences are attributed to electricity and fossil fuels consumption because these are dependent on different domestic uses as explained above. Additionally to this, the *MCF* value in Equation 1.1 varies from 1 to 2% depending on the local annual average temperature (T-10A.4 of IPCC Guidelines [151]).

6.3.2 Emissions shared by both Guatemalan AD Scenarios

Tables 6.7, 6.8 and 6.9, present the emissions for AD-boiler and AD-CHP scenarios for all Guatemalan farms. It is observed that these scenarios have common emissions from those operation units which are not related to energy production. The first of these operation units is enteric fermentation, which has emissions equal to the baseline scenarios.

The emissions from digestate applied on field is also shared by both AD scenarios. These emissions replace those from manure deposit by grazing animals. For the parameters specified in Table 6.6, the N_2O offset in this operation unit accounts for -115±13 $ton_{CO2e} \cdot yr^{-1}$ for farm A and -70±7 $ton_{CO2e} \cdot yr^{-1}$ for farms B and C. For CH_4 released from field-applied slurries, changes

Table 6.10: Theoretical digester for the Guatemalan case studies.

	Unit	Farm A	Farm B	Farm C
CH_{4Prod}	$[ton \cdot yr^{-1}]$	47± 9	29±6	27±5
$\dot{Q}_d$	$[GJ \cdot yr^{-1}]$	960±190	590± 120	560±110

in CH_4 emissions are inconclusive given the non-significant relative changes obtained by meta-analysis (Section 5.3.3.2).

CH_4 leaks from the digester increase the emissions of baseline scenario when implementing a theoretical AD system in both boiler and CHP scenarios. The emissions released from digesters are 32±3 $ton_{CO2e} \cdot yr^{-1}$ for Farm A and 19±2 $ton_{CO2e} \cdot yr^{-1}$ for both Farms B and C. Because these emissions are calculated by applying the relative change determined in Section 5.3.3.1, this operation unit increases the emissions of standardised baseline scenarios (i.e. excluding enteric fermentation) by 7.4% in all case studies.

The methane productions from each Guatemalan dairy farm and the energy requirements of the theoretical digester are also common for AD-boiler and AD-CHP scenarios. For the case study farms, AD holds the potential to produce 27 to 47 $ton \cdot yr^{-1}$ of CH_4 (see Table 6.10) that otherwise would not be available or would be provided from fossil fuel sources. Expressed by unit of livestock, the produced CH_4 is 78±16 $kg_{CH4} \cdot hd^{-1} \cdot yr^{-1}$ for the three farms. The supply of heat to operate the digester is considered to come from the combustion of the CH_4 in the produced biogas. This required thermal energy is presented in Table 6.10 according to Guatemalan farm. The following Sections 6.3.3 and 6.3.4 examine the energy production and use by combusting the biogas in a condensing boiler and CHP unit, respectively, together with the analysis of the consequent changes in GHG emissions.

6.3.3 AD-Boiler Scenario

Figure 6.7 presents the results of the changes in emissions of the Guatemalan AD-boiler scenarios with respect to the baseline. Total emissions for farms A, B and C from this scenario, respectively, are 190±67, 113±41 and 118±41 $ton_{CO2e} \cdot yr^{-1}$ without considering enteric fermentation. Therefore, the AD-boiler scenarios avoid 240±47, 150±30 and 140±30 emissions from the baseline scenarios of the three farms. These changes in emissions correspond to a decrease by 54

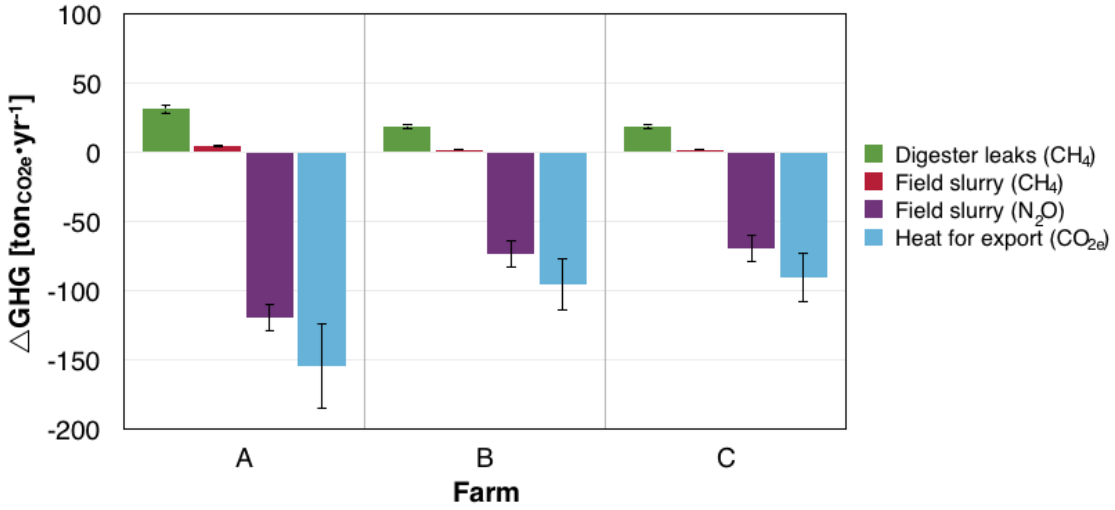

Figure 6.7: Changes in GHG emissions by the application of AD with condensing boiler to the Guatemalan dairy farm. Error bars are based on default parameters from the IPCC methodology [151] and B_0 confidence intervals from meta-analysis.

to 58% of those from the baselines. By standardising the changes in emissions of Figure 6.7, the Guatemalan farms result in reductions of 400±80 $kg_{CO2} \cdot hd^{-1} \cdot yr^{-1}$. If enteric fermentation is included, the total emissions for the farms in this scenario are 1,270±497, 783±311 and 748±291 $ton_{CO2e} \cdot yr^{-1}$ for farms A, B and C, respectively. The latter would result in decreases with respect to the baseline emissions by 15 to 16%.

The biogas is assumed to replace natural gas as fuel for the condensing boiler. Figure 6.8 presents the thermal power outputs for the AD-boiler scenarios of the three Guatemalan farms, normalised by herd size. The potential gross thermal power generation from these scenarios is 2,340±470 $GJ \cdot yr^{-1}$, 1,450± 290$GJ \cdot yr^{-1}$ and 1,370 ± 270 $GJ \cdot yr^{-1}$ for Farms A, B and C, respectively. This corresponds to energy production per animal of 3.9±0.8 $GJ \cdot hd^{-1} \cdot yr^{-1}$. For all case studies, the condensing boiler produces sufficient thermal power to meet the digester heating requirements. Subtracting the thermal power required for the digester, results in the potential exportable thermal power of 1,390±280 $GJ \cdot yr^{-1}$, 860±170 $GJ \cdot yr^{-1}$ and 810±160 $GJ \cdot yr^{-1}$ for Farms A, B, and C, respectively. The export of heat would offset 150±30, 95±20 and 90±18 $ton_{CO2e} \cdot yr^{-1}$ for farms A to C, respectively, assuming the replacement of thermal power from natural gas.

Although the AD-boiler scenario is capable of generating thermal energy for export, the use

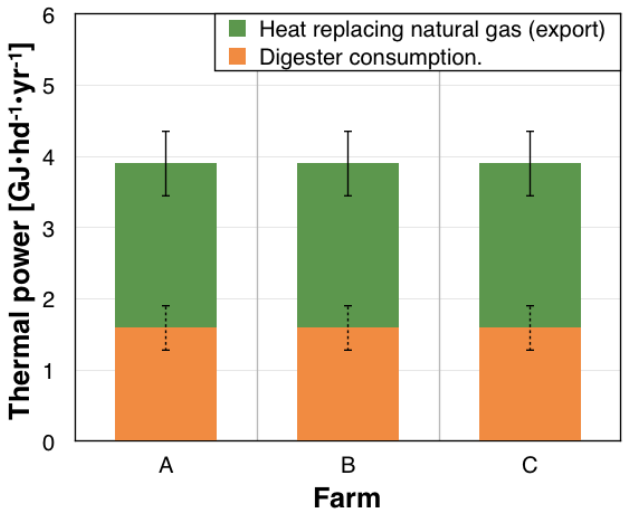

Figure 6.8: Thermal power production/use in Guatemalan dairy farms with theoretical AD-Boiler scenarios. Error bars are based on the ranges in default parameters of the IPCC methodology [151] and confidence intervals determined for B_0 by meta-analysis.

of such energy presents challenges. Domestic heating of neighbouring communities is unlikely, because the tropical weather of Guatemala diminishes this need. Consequently, the offset of emissions is highly dependent on the use of that net heat. The produced heat could be used on-site if a pasteurisation process took place. However, for this to be applied in these farms, access to reliable electricity is a key factor.

The AD-boiler does not produce electricity, thus, this scenarios is assumed to consume and/or produce electricity as for the baseline scenario.

6.3.4 AD-CHP Scenario

The changes in GHG emissions of the AD-CHP scenario with respect to the baseline scenario are presented in Figure 6.9. It is found that the AD-CHP scenarios emit 1,330±490, 810±300 and 780±290 $ton_{CO2e} \cdot yr^{-1}$ from farms A, B and C, respectively. Extracting the enteric fermentation (i.e. only considering the operation units which are affected by AD), results in emissions from this scenario of 250±60, 150±34 and 150±36 $ton_{CO2e} \cdot yr^{-1}$ for farms A to C. Therefore, the emissions from standardised baseline (i.e. without enteric fermentation) are reduced between 42 and 43%.

The main GHG and operation to contribute to reduction is N_2O from field-application of slurries. Details of this and other shared operation unit for AD scenarios are presented in Section

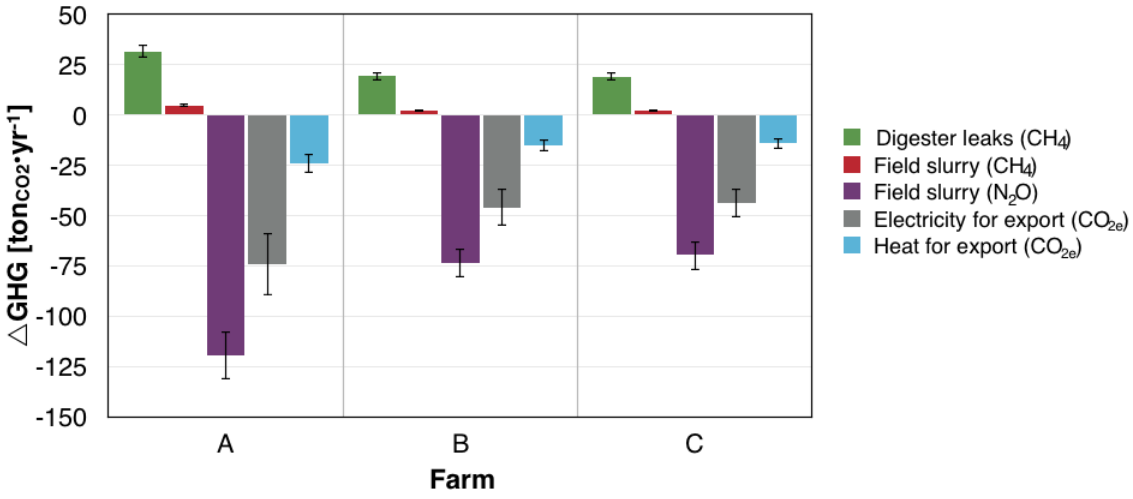

Figure 6.9: Results of GHG emissions AD-CHP scenarios for Guatemalan farms. Error bars are based on range of default parameters of the IPCC methodology [151] and confidence intervals determined for B_0 by meta-analysis.

6.3.2.

The generation of electricity in the AD-CHP scenario is the second contributor to emission reductions. Figure 6.10 presents electric power outputs of this scenario expressed by herd size for the three Guatemalan farms. The implementation of an AD-CHP has the estimated potential of generating 845±169 $GJ \cdot yr^{-1}$, 521±104 $GJ \cdot yr^{-1}$ and 493±99 $GJ \cdot yr^{-1}$ of electric power for Farms A, B and C, respectively. The electric power can be used on-site or exported to the Guatemalan grid.

The dairy activities consume 15 to 40% of the generated electricity (as shown in Figure 6.10). The use of renewable electricity on-site would therefore offset 9, 6 and 15 $ton_{CO2e} \cdot yr^{-1}$ from the baselines of Farms A, B and C, respectively. It is observed that although Farms B and C are similar in herd size, the electricity for export markedly differs. This is due to the higher domestic use of electricity in Farm C, as ten houses are in the later and only one in Farm B.

The available electric power to export ranges from 300±99 $GJ \cdot yr^{-1}$ for farm C to 720±169 $GJ \cdot yr^{-1}$ for farm A. The export of electricity holds the potential to offset 27±9 $ton_{CO2e} \cdot yr^{-1}$ (Farm C) to 65±15 $ton_{CO2e} \cdot yr^{-1}$ (Farm A). As an alternative to export electricity, this could be used on-site to improve the milking process. For example, the implementation of refrigeration, rotating platform for milking and manure pumps could increase the production, imitating the installations

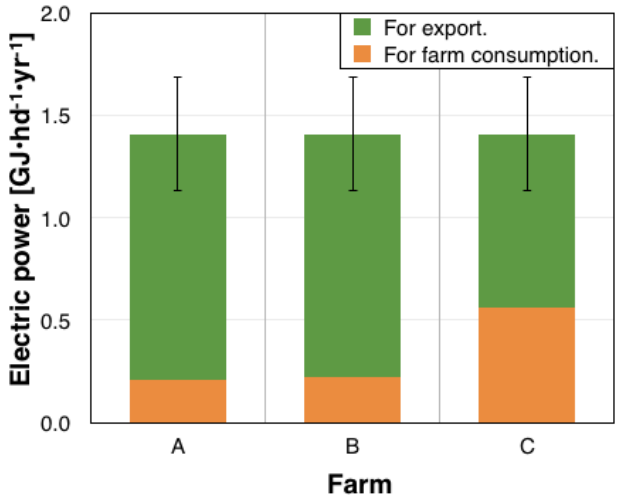

Figure 6.10: Electric power production/use in Guatemalan dairy farms with theoretical AD-CHP system. Error bars are based on ranges of the default parameters of the IPCC methodology [151] and confidence interval of B_0 determined by meta-analysis.

of developed countries (i.e. the case study from the United Kingdom). Therefore, the AD-CHP scenario can increase the farm activities and, for Farm A, bring electricity to an off-grid location thus, promoting the rural welfare. In a survey covering similar aspects to this work, to a developing world country (Kenya) [22] results found that the main use of biogas was for cooking and lighting. Thus, this is in agreement with preference for AD-CHP scenario in farms with no electricity.

The production of thermal heat that replaces fossil fuels in the AD-CHP scenario is the third contributor to the reduction of GHG emissions from the Guatemalan baselines. Figure 6.11 presents the thermal power production and use for the AD-CHP scenario normalised by herd size. As expected, the thermal power generation per livestock unit is similar for all farms (2.0±0.4 $GJ \cdot hd^{-1} \cdot yr^{-1}$) due to the common IPCC methodology. This results in the farms generating thermal energy from 684±137 $GJ \cdot yr^{-1}$ (Farm C) to 1,173±235 $GJ \cdot yr^{-1}$ (Farm A). Compared to thermal power generated in the AD-boiler scenario, these amount correspond to ~50%, because the LHV of CH_4 is used instead of the HHV and the efficiency to heat is less for a CHP unit ($\eta_{TH,CHP}$= 50% and $\eta_{Th,Bo}$= 90%, see Eqs. 6.14 and 6.19). The thermal power generated in the AD-CHP scenario is sufficient to supply heat to the digester. However, the overlapping error bars of Figure 6.9 indicate that this may not always be the case. Therefore, insulation of digesters is a key factor to avoid heat losses and maintain the operation conditions. If the digester is heated in this way, the

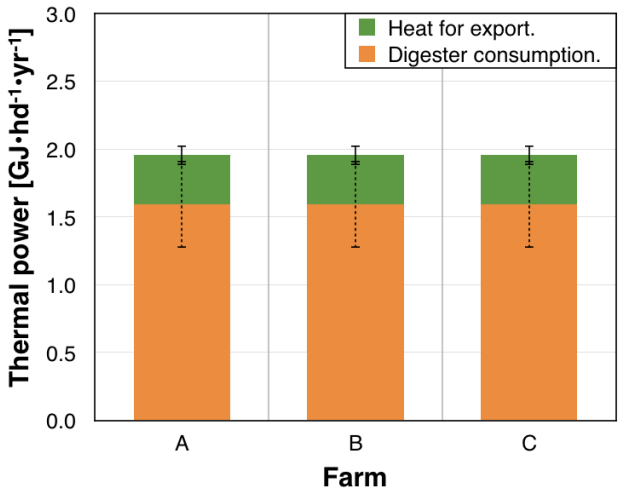

Figure 6.11: Thermal power production/use in Guatemalan dairy farms with theoretical AD-CHP system. Error bars are based on ranges of the default parameters of the IPCC methodology [151] and confidence interval of B_0 determined by meta-analysis.

net thermal energy remaining for export corresponds to 218±44, 135± 27 and 127±26 $GJ \cdot yr^{-1}$ for farms A, B and C, respectively. Consequently, Farm A offsets 24±5 $ton_{CO2e} \cdot yr^{-1}$, Farm B 15±3 $ton_{CO2e} \cdot yr^{-1}$ and Farm C 14±3 $ton_{CO2e} \cdot yr^{-1}$ by export of thermal power.

Although the AD-boiler scenario mitigates more GHGs, the uncertainty in the use of thermal heat particularly for farm A, suggests that the AD-CHP scenario is the most suitable technology for that case study. In the latter scenario thermal energy generated in combination with electricity, could jointly improve the milking activities, for example, by introducing on-site pasteurisation. Additionally, the AD-CHP scenario holds the potential to provide electricity access to rural communities and increase their quality of life, while the heat required by the digester could still be met. Given that Farms B and C are in less rural areas it is recommended to evaluate the export of thermal power for its use in local industrial processes (e.g. sugar and/or textiles production).

6.4 Discussion

To provide insights on the implementation of the meta-analysis results over markedly different dairy farms, emissions obtained for case studies are compared in Section 6.4.1. Thereafter, to assess the contribution of the Y_{CH4} and relative changes found by the meta-analyses of Chapter 4 and 5, respectively, the emissions determined for the case studies are compare to those from default IPCC

Table 6.11: Comparative photographs of dairy farm facilities.

	English farm	**Guatemalan Farm A**[a]
Milking process	 Rotating platform.	 Manual milking.
Milk storage	 Refrigeration tank.	 Plastic containers for milk.
Cattle management	 Confined cattle.	 Livestock on pastures.

[a]Photographs courtesy of Andrés Chicol MSc.

methodology Intergovernmental Panel on Climate Change National Greenhouse Gas Inventories Programme [151] (Section 6.4.2).

6.4.1 Comparing the English and Guatemalan farms

As presented in the results of Sections 6.2-6.3, the transition from common farm practices (baseline scenarios) to the implementation of theoretical AD plants affects GHGs emissions. These changes differ between farms as they depend on the sources of GHGs in the baselines and the assumptions made for the estimation of emissions from the AD scenarios. To compare emissions from the English and Guatemalan case studies in this section, these are standardised by herd size.

Main differences in the changes of emissions arise from the baseline scenarios. The English dairy farm produces milk in an industrial manner (i.e. supplying important national food chains),

while the Guatemalan farms have manual-based processes. Photographs of the milk production are shown in Table 6.11 for the English case study and Guatemalan farm A. It is observed that although these farms are comparable in herd size, the milking systems are very dissimilar.

For overall baseline emissions, the English farm releases on average 2,800 $kg_{CO2e} \cdot yr^{-1} \cdot hd^{-1}$ more emissions than the Guatemalan farms. The emissions from enteric fermentation are an important contributor to the marked difference in emissions from the English and Guatemalan case studies. This is due to the EFs assumed in Equation 6.2, which depend on cattle feed. The difference in EFs results in the English farm emitting 1,125 $kg_{CO2e} \cdot yr^{-1} \cdot hd^{-1}$ more than the Guatemalan farm from enteric fermentation.

Within the operation units affected by AD, the storage of untreated manure causes the English case study to emit more than any Guatemalan farm (1,577$\pm$447 $kg_{CO2e} \cdot yr^{-1} \cdot hd^{-1}$). This is because no storage exists for the baselines of Guatemalan case studies (i.e. cattle spend most time on pastures with no manure collection system). In accordance to these observations, storage of manure is reported in the literature [14, 42, 121, 188] as more common in developed countries than developing countries. Consequently, the implementation of AD systems in the English dairy farm would reduce emissions from an important additional source (storage of slurry has a local relative change in emissions: -55% according to findings in Section 5.3.3.2).

From a carbon credit perspective, the latter could incentivise farm owners in developing countries to implement storage tanks (or anaerobic lagoons with no CH_4 recovery) before AD. This would establish an interim business-as-usual scenarios with storage tanks which emit more GHGs. Consequently, after the implementation of AD, more carbon credits could be claimed by farms with storage tanks than farms without. This observation raises an interesting question for debate: should baselines be standardised for the estimation of carbon credits when implementing AD scenarios? A positive aspect of standardising baselines is that it eliminates the questionable advantage in terms of carbon credits, of farms which initially emit more GHGs in baselines (i.e. with storage tanks). For example, the Indian CDM project "Bagepalli CDM Biogas Program" [328] does not have manure storage in the baseline. Therefore, it focuses only on the mitigation of GHGs by replacing non-sustainable energy sources by biogas. Similar to the Guatemalan case studies, this project does not

benefit from emitting less GHGs in the baselines than if it had storage. Conversely, many other CDM projects [192, 193, 329] claim the reduction in emissions from storage in tanks or lagoons. There are also negative aspects of the standardisation of baselines. In particular, standard baselines would not necessarily accurately quantify real manure management practices in dairy farms. For example, the English case study includes storage tanks in its baseline which allows the dairy farm to comply with local regulations for manure management [330]. In this way, that farm provides a more controlled return of nutrients from the cattle sheds to crops. If baselines were standardised by excluding storage tanks, emissions from farms which follow good-practices, would not be accounted. Contrary, if all baselines included storage tanks, farm would account for non-existing emissions in baselines.

In terms of the emissions from untreated slurries applied over fields, the Guatemalan farm exceeds N_2O emissions of the English by 160 $kg_{CO2e} \cdot hd^{-1} \cdot yr^{-1}$. Differences are attributed to the higher EFs for the manure deposit by grazing animals in the Guatemalan cases compared to the systematic application of slurry in the English case study (EFs in Tables 6.3 and 6.6). Similarly, for CH_4 emissions from this operation unit, Guatemalan farms emits 32 ± 19 $kg_{CO2e} \cdot hd^{-1} \cdot yr^{-1}$ more than the English case study. An intriguing aspect is that, although Guatemalan farms emit more N_2O and CH_4 from field-application of untreated manure (680 ± 8 $kg_{CO2e} \cdot hd^{-1} \cdot yr^{-1}$), this is still less than the emissions from storage tanks in the English baseline ($1{,}580 \pm 110$ $kg_{CO2e} \cdot hd^{-1} \cdot yr^{-1}$).

Considering the energy consumption in the baseline scenarios, the English farm emits significantly more emissions than any Guatemalan farm. Compared to Farm C (i.e. the Guatemalan farm with highest energy consumption), the English case study exceeds its emissions by 270 $kg_{CO2e} \cdot hd^{-1} \cdot yr^{-1}$. These differences are expected as there is: i) higher consumption of electricity in the English farm due to the more specialised equipment for milking and manure management and; ii) higher embodied energy in the UK grid (see Table 6.3), which is the principal source of energy for the English farm. The use of natural gas for space heating only contributes an additional 31.2 $kg_{CO2e} \cdot hd^{-1} \cdot yr^{-1}$ to the emissions of the English farm (i.e. not applicable in Central America due to climate conditions).

With regards to the AD scenarios, the potential biogas production of the English dairy farm

exceeds that of the three Guatemalan farms by 208±34 $ton_{CH4} \cdot yr^{-1}$. This is expected because higher B_0 and $\dot{VS}$ values for the English case study are utilised in Equation 6.11. The IPCC, in turns, is based on differences in animal feed according to world region. As a consequence of the higher production of biogas by the English farm, this also presents higher offsets of emissions from fossil fuels in the AD-scenarios.

The AD-boiler scenarios result in the most reduction of GHGs for the English and the Guatemalan farms. In this scenario, the English farm would reduce up to 710±120 $kg_{CO2e} \cdot hd^{-1} \cdot yr^{-1}$ more than the Guatemalan farms due to higher B_0, thus, more production of biogas and export of thermal power. The English farm has the additional advantage of already having installations for the combustion of natural gas, which can be adapted for biogas (i.e. biogas can be upgraded to higher CH_4 content to use the same combustion technology). Conversely, there are challenges for the use of the thermal power produced by the AD-boiler scenarios in Guatemalan farms. Space heating is inessential in the latter. Moreover, for Farm A there are no gas networks currently installed in the area. Therefore, it is difficult to export the thermal power to neighbouring communities. Given that the Guatemalan farms B and C are close to industrial areas (e.g. sugar and textile), it is recommended to asses the export of thermal energy for local processes.

The theoretical AD-CHP scenario in the English case study mitigates 130±18 $kg_{CO2e} \cdot hd^{-1} \cdot yr^{-1}$ more emissions than the Guatemalan farms, in terms of thermal power export. For replacement of grid electricity by that produced in the CHP unit, the English farm also exceeds the offsets of the Guatemalan case studies (i.e. by 544±67 $kg_{CO2e} \cdot hd^{-1} \cdot yr^{-1}$). The latter difference results by the combination of: i) higher CH_4 produced per animal in the English case study and; ii) the more carbon intensive English electricity grid (see Table 6.3). Regardless of the better performance of this scenario in the English case study, there are other benefits of this scenario which make it more preferable for one Guatemalan farm. In particular for farm A, which has similar herd size than the English farm, but no access to electricity, the implementation of AD-CHP could enable off-grid electricity access. In turns, this could increase the milk production (i.e. it only produces milk from 10% of the available dairy cattle), while producing sufficient thermal energy to operate

the digester(s) at mesophilic conditions.

6.4.2 Comparing the IPCC methodology and application of meta-analysis

This section compares the results obtained by applying the B_0 and relative changes determined in the meta-analyses of this work, against the default IPCC methodology [151]. Emissions are analysed by scenarios and operation units.

For baseline scenarios, B_0 determined by meta-analysis affects the estimation of CH_4 from stored and field-application of manure. Storage of manure is only present in the English case study. For that case, the results using the B_0 from the meta-analysis ($0.230\pm0.016\ m^3_{CH4} \cdot kg^{-1}_{VS}$ random-effect model) result in $790\pm55\ ton_{CO2e} \cdot yr^{-1}$ (see Table 6.4). If instead the default B_0 of the IPCC methodology is used in Equation 1.1 ($0.24\pm0.04\ m^3_{CH4} \cdot kg^{-1}_{VS}$ in Step 2) the emissions from storage of manure in the baseline result in $820\pm140\ ton_{CO2e} \cdot yr^{-1}$. Therefore, the application of the B_0 determined by meta-analysis is within the range reported by the IPCC methodology[5]. However, the B_0 from this work decreases the estimated CH_4 emissions from stored manure and reduce the uncertainty in that value. This is a highly important results given that an increase sample size is more certain than the recommended by these international guidelines.

For CH_4 from manure applied (or deposit) over fields, Table 6.12 shows the emissions estimated by utilising the B_0 from this work and those from the default IPCC values. It is observed that B_0 from meta-analysis result in lower median emissions for this operation unit. However, considering these are non-significantly different from the IPCC estimates.

Table 6.12: CH_4 emissions from field-applied manure estimated by using B_0 from meta-analysis (this work) and default IPCC method.

	Estimated emissions ($ton_{CO2e} \cdot yr^{-1}$)	
Case Study	**This work**	**IPCC**
English Farm	3.5±0.2	3.7±0.6
Guatemala Farm A	23±5	28±4
Guatemala Farm B	11±2	13±2
Guatemala Farm C	10±2	12±2

[5]For discussion of the differences in B_0 from meta-analysis and IPCC values refer to Section 4.2.5.

Table 6.13: Estimates of leaks from the digester according to methodology.

Case study	This work		IPCC default[a]
	Emissions $[ton_{CO2e} \cdot yr^{-1}]$	**Fraction of $CH_{4,Prod}$[%]**	$[ton_{CO2e} \cdot yr^{-1}]$
English	89±6	2.4%	380±60
Guatemalan A	32±3	2.8%	140±20
Guatemalan B	19±2	2.8%	85±13
Guatemalan C	19±2	3.0%	80±13

[a]Leaks estimated as 10% fraction of $CH_{4,Prod}$, B_0 and GWP_{CH4} from the IPCC methodology [151].

For the AD scenarios, the meta-analysis results from Chapter 5 contribute relative changes in emissions. These are used to estimate the emissions from: digester leaks, storage of digestate and field-application of digestate. For the estimation of leaks from digesters, the IPCC methodologies assume that 10% of the produced CH_4 is lost (Table 10A-4 [151]). This results in the leaks presented in Table 6.13. It is observed that, in accordance to the findings of Section 5.3.3.1, the IPCC method results in higher digester leaks than those found by relative changes. In particular, the leaks from this work suggest that only 2.4 to 3.0% of the produced CH_4 is leaked. The latter values are recommended to replace the 10% default value of the IPCC as they are based on evidence from the systematic literature review of Chapter 5. Another article in the literature [331] (not included in the meta-analysis because they do not comply with all criteria) also reports that 3-4% of the produced CH_4 is leaked from the digester.

The estimation of GHG emissions from stored and field-applied digestates is addressed in the IPCC methodologies within generalised equations (see Section 1.3). Therefore, the relative changes of this work provides more specific and evidence-based estimates of CH_4 emissions from digested cattle manure. In the English case study (see Table 6.4) the reduction in emissions due to the replacement of manure by digestate in storage tanks account for 430±30 $ton_{CO2e} \cdot yr^{-1}$. This corresponds to a reduction by 54% of the emissions from stores, which would not be accounted by following the IPCC method. Furthermore, this reduction in emissions accounts for 47% of total mitigations in the AD-boiler scenario and 51% in the AD-CHP scenario.

The CH_4 emissions after field application of digestate are also omitted in the IPCC methods. Given that the meta-analysis of this work (Section 5.3.3.3) indicates non-significant changes in CH_4 emissions between digestate and untreated slurry for this operation unit, the estimation of

Table 6.14: Estimates of $CH_{4,Prod}$ according to B_0 source ($ton_{CH4} \cdot yr^{-1}$).

Case study	This work	IPCC default
English	143±10	150±25
Guatemalan A	47±9	55±8
Guatemalan B	29±6	34±5
Guatemalan C	27±5	32±5

this GHG released after field-application of digestate is suggested to follow the calculations as for untreated manure. Conversely, the N_2O from field-applied digestate is significantly different than from untreated manure (Section 5.3.3.3). However, there are no specific EFs in the IPCC method to account for this difference. In particular the IPCC guidelines [151] indicate the use of Equation 11.3 for emissions from "applied organic nitrogen fertiliser", which is detailed as: applied animal manure, sewage sludge, compost or "*other organic amendments of regional importance to agriculture (e.g., rendering waste, guano, brewery waste, etc.)*"[151]. By not considering the significant change in N_2O emissions between untreated and digested manure, an important source of mitigation is omitted. In particular, for the English case study of this chapter -78±8 $ton_{CO2e} \cdot yr^{-1}$ would not be accounted. For the combined three Guatemalan farms, 255±26 $ton_{CO2e} \cdot yr^{-1}$ would be omitted.

In terms of energy production from the AD scenarios, the application of B_0 from meta-analysis (results from Chapter 4) is used to estimate the biogas potential (i.e. $CH_{4,Prod}$ in Equation 6.11, Step 12). The $CH_{4,Prod}$ estimates of this work and those obtained by applying the IPCC methodology are presented in Table 6.14. For the English case study, the meta-analysis results conduct to 5% less emissions than the IPCC guidelines. Similarly, for the Guatemalan estimates of this work, $CH_{4,Prod}$ is ~15% less with respect to the IPCC method. These differences are expected given that B_0 values from meta-analysis are 5 and 15% less than the default B_0 in the IPCC methodology [151], respectively, for the English and Guatemalan farms.

The application of the global relative change for the offset of fossil fuels (-9.0% determined in Section 5.3.3.4) is examined and compared to those obtained in this chapter for each AD scenario. It is found that for the English case study the application of this relative change would estimate a reduction by 110±15 $ton_{CO2e} \cdot yr^{-1}$ (for both AD scenarios). For the Guatemalan farms the

changes in emissions would be -38±4 $ton_{CO2e} \cdot yr^{-1}$ for farm A, -24±2 $ton_{CO2e} \cdot yr^{-1}$ for farm B and -23±3 $ton_{CO2e} \cdot yr^{-1}$ for farm C. These offsets are in closer agreement with the estimates of AD-CHP scenarios, expected from the determination of relative changes which is based mainly on cases which specify the use of CHP in Part II of the database (N= 12).

6.5 Summary and concluding remarks of case studies

This chapter develops a robust methodology to determine the mitigation potential of the use of AD on dairy farms. It enhances existing techniques because it uses the maximum methane production determined in Chapter 4 and relative changes established in Chapter 5. The chapter then presents the case studies of four dairy farms: one English and three Guatemalan. In particular, three scenarios for each farm are assessed: baseline, AD with condensing boiler (AD-boiler) and AD with CHP unit (AD-CHP).

From a questionnaire responded by the farm administrators or owners; and using a step-by-step methodology based on IPCC Guidelines [151], the emissions from the baseline scenarios are estimated. It is found that enteric fermentation is the main contributor of GHGs with 71 to 72% of baseline emissions for Guatemalan farms and 55% for the English farm. Unfortunately, these emissions cannot be mitigated by AD technology. For those operation units which can be affected by AD, markedly different baseline scenarios become evident for the English and the Guatemalan farms due to the nature of their development. Specifically for the English case study, storage of manure follows enteric emissions with 30% of total baseline emissions. The latter operation unit is not available in the Guatemalan farms due to limited resources. It is pointed out that this important difference between baseline scenarios could result in undesirable incentives as farms without manure storage tanks could prefer to first transition to scenarios with storage of manure, consequently increasing their carbon footprint, but enabling the claim of more carbon credits when AD is implemented. This is the case for all Guatemalan case studies, which do not currently have storage of manure in the baselines, thus N_2O emissions from field-applied represent the second most important contributor ~26% of baseline emissions. Another important difference in baselines is the consumption of energy which contributes 6% of the baseline emission in the English case

study while only 1-2% in Guatemalan farms. This is mainly attributed to the milking systems which is automated in the former and manual in Guatemalan cases.

For the AD scenarios, an important contribution of this chapter is the novel application of local relative changes to quantify emissions from digestate handling. Currently, the IPCC methodology only allows to report N_2O emissions from organic nitrogen application which locates digestate within a broader category. Similarly, CH_4 from stored digestate is assumed to be as for liquid slurry if no gas tight covers are installed. Thus, this chapter provides a simple and robust estimation methodology for emissions from storage and field-application of digestate.

Results from the application of global relative change indicate that leaks from the digesters significantly increase emissions from baselines. In this respect, an intriguing observation is that the estimation of leaks for all case studies is significantly lower with respect to the default IPCC methodology. The analysis shows that the IPCC Guidelines suggestion of 10% losses from the produced CH_4 should be corrected to 2.4-3.0%.

Energy and mass balances are performed for the theoretical AD of cattle manure. The English case study holds a higher potential of CH_4 production from the AD system ($CH_{4,Prod}$= 290±20 $kg_{CH4} \cdot hd^{-1} \cdot yr^{-1}$) with respect to the Guatemalan cases ($CH_{4,Prod}$= 78±20 $kg_{CH4} \cdot hd^{-1} \cdot yr^{-1}$). This is expected given the higher yield of European farms found by meta-analysis (B_0 for Western Europe is 0.230±0.016 $m^3_{CH4} \cdot kg^{-1}_{VS}$ and B_0 for Guatemalan case studies is 0.110±0.020 $m^3_{CH4} \cdot kg^{-1}_{VS}$). In consequence there are also higher offsets in the English case study due to replacement of conventional sources of energy by renewable biogas.

For the AD-boiler scenario, 14±1 $GJ \cdot hd^{-1} \cdot yr^{-1}$ of thermal power is produced the English case study and 3.9±0.8 $GJ \cdot hd^{-1} \cdot yr^{-1}$ for the Guatemalan farms. This is sufficient to heat the digester to 308 K while excess thermal power is available to export from all AD-boiler scenarios. In terms of electricity, the same import than the baseline scenarios is necessary for the AD-boiler scenario. Overall, the English farm offsets 900±76 $ton_{CO2e} \cdot yr^{-1}$ for this scenario. The Guatemalan case studies have the potential of jointly offsetting ~520 $ton \cdot yr^{-1}$ with respect to the baseline scenarios.

For the AD-CHP scenario, 7.2±0.5 $GJ \cdot hd^{-1} \cdot yr^{-1}$ of gross thermal power is estimated to be generated in the English case study and 2.0±0.4 $GJ \cdot hd^{-1} \cdot yr^{-1}$ for the Guatemalan farms.

Therefore, as for the AD-boiler scenario sufficient thermal energy is available for the heating of the digester. Additionally, electric power would be available for the English case study (5.2±0.4 $GJ \cdot hd^{-1} \cdot yr^{-1}$) and for the Guatemalan case studies (1.4±0.3 $GJ \cdot hd^{-1} \cdot yr^{-1}$). For Guatemalan farms this could significantly contribute to an increase the performance of milk production. For example, the implementation of automated milking systems (i.e. rotating platform and pumps) would allow to milk more cows in Farms A and C, which are currently not reaching their full milk production potential. This scenario would offset 840±70 $ton \cdot yr^{-1}$ of emissions in the English case and jointly for all Guatemalan cases 240±45 $ton \cdot yr^{-1}$, with respect to the baselines.

It should be noted that the offset in emissions obtained in these case studies are low in comparison to other AD systems reported as projects for the CDM (1,400 to 136,000 $ton \cdot yr^{-1}$ [332]). This is mainly due to the case studies of this chapter having less available feedstock for AD than those in CDM projects. For example the combined Guatemalan cases have 1,320 cattle, while the smallest CDM project found [333] is for AD of swine manure which considers 2,418 livestock (offset 1,415 $ton \cdot yr^{-1}$). Therefore, to increase offsets, the combination of multiple farms or co-digestion of different animal waste could be an applicable approach considering that total Guatemalan cattle inventory is approximately 3.4 million heads [334] (2012). Consequently, the GHG mitigation could be more attractive for carbon credits commercialisation in that country.

In terms of preferable scenarios, it should be noted that different motivations to apply AD are observed. For the English case study electricity and thermal power are already available. Therefore, considering that the reduction of GHG emissions can diversify profitable farm activities by entering the carbon credit market, the best alternative is the AD-boiler scenario. This interest to implement AD is recently reported [147] for dairy farmers in California (United States), which have indicated that the large initial cost of AD is markedly traded-off by the social benefits of this technology.

Conversely for Guatemalan farms, AD-boiler scenario is challenging because there are no obvious uses for surplus thermal power (i.e. no need for space heating). For farm A, the application of the AD-CHP scenario is preferable as it would bring electricity to an off-grid location improving the welfare of the community (e.g. contributing to local economy, producing more milk). By utilising this renewable energy system, an increase in human development index would be expected

at lower ecological cost than the current baseline scenario. For farms B and C, it is suggested to study alternatives for the export of thermal power to neighbouring industries, thus expanding the boundaries of the energy and emission assessments of this chapter.

Chapter 7

Conclusions

The key research issue addressed by this thesis is to develop an improved methodology to determine the GHG emissions from dairy cattle manure with and without the use of AD. This chapter presents the key findings of the thesis as concluding remarks in three sections. Section 7.1 presents an overview of how the key findings of the research work improves the estimation of GHG emissions of interest. This is presented with respect to the specific research questions set in the Chapter 2 (Research Approach). Thereafter, key recommendations emerge to improve the existing estimation methodologies. The latter are presented in Section 7.2 together with suggested future work in the field. Finally, Section 7.3 poses limitations of the meta-analyses of this thesis.

7.1 Concluding remarks

This thesis develops novel meta-analyses to improve the estimates of GHG emissions from AD scenarios applied in dairy farms. This section presents the answers to the specific research questions of the Research Approach (Chapter 2), which were posed to achieve the meta-analysis.

Having highlighted the potential benefits of meta-analysis to quantify Y_{CH4} and the changes in GHGs emissions in Chapter 1, the first step set in the Research Approach is to address the key question "**What is the best data structure to capture the required information for the meta-analysis?**". To collect and organise numerical results of key metrics from the literature and comply with the scientific method, the thesis presents a systematic search and selection of articles

in the literature by defining four specific criteria. Thereafter, results of interest are extracted and organised in a novel two-part database. Part I focus on the experimental Y_{CH4} results and also collects secondary variables related to operation conditions and manure composition. Part II of the database is conformed by GHG emissions from dairy farms with baseline and AD scenarios. The latter are categorised by operation units to reconcile system boundaries and identify specific changes in emissions according to farm activities. As a result, a novel database specific to energy performance and GHG changes in dairy farms (i.e. due to AD of cattle manure), is developed and made publicly available.

Robust values of methane yields have been provided by the meta-analysis of Chapter 4. This answers to the second specific research question (i.e. "**What are robust values for methane yields?**"). These values have been achieved by the the mathematical application of meta-analysis techniques over Y_{CH4} and secondary variables collected in Part I of the database. In particular, fixed- and random-effect meta-analysis models reveal Y_{CH4} values that are recommended to be used for the estimation of CH_4 emissions from dairy farms. In particular, uni-variate analysis of the maximum Y_{CH4} should replace those from the IPCC, as a larger and more updated sample is considered in the meta-analysis results. The random-effect model is preferred over the fixed-effect model because it assumes an underlying distribution of the Y_{CH4} population. The overall mean estimated by the random-effect model is $0.230 \pm 0.016\ m^3_{CH4} \cdot kg^{-1}_{VS}$. Lower Y_{CH4} are obtained when extending this analysis to CSTR and semi-continuous digesters. With respect to multi-variate analysis, underlying structure in the relation between secondary variables (describing AD operation and slurry composition) and Y_{CH4}, are examined. The identification of multi-dimensional clusters, based on principal component analysis, enables grouping of variables (and their ranges), which can be useful when construction AD scenarios for dairy farms.

Chapter 5 presents the meta-analysis of Part II of the database to determine the consequences of AD on GHG emissions from operation units in dairy farms. This responds the specific research question "**What are robust factors to determine the GHG emissions from dairy farm activities when implementing AD?**". The standardisation of baseline and AD scenarios, allow to generate robust relative change percentages. In turns, the estimation of relative changes for different articles

enable inter-study combination and comparison. Thus, diverse functional units in the literature are overcome with this metric. The analysis of the combined relative changes results in estimations of the mitigation potentials of specific GHGs and farm activities (i.e. operation units). Novel relative changes for manure management result from the analysis. In particular, the replacement of raw manure by digestate (i.e. anaerobically digested manure) in storage tanks decreases emissions by 38.7%. Similarly, field-application of digestate decreases emissions of baseline scenarios by 6.9%. For other farm activities, mitigation of baseline emissions by 9.0% are obtained for offset of energy from fossil fuel, +0.4% (n.s.) for offset of organic fertilisers and +7.4% for leaks from digesters.

The final chapter of this thesis brings together the findings of the meta-analyses of Y_{CH4} and relative changes, addressing directly the key issue of the thesis: the improvement of methodologies to quantify the effect of AD over GHG emissions from dairy farm. For this purpose, Chapter 6 presents a detailed methodology to estimate emissions based on the inclusion of the thesis results in the IPCC Guidelines. The methodology provides a unique estimation for emissions from storage and field-application of digestate in the AD scenarios, by the use of relative changes. Additionally, the application of relative changes for estimation of leaks from the digester results in lower emissions than those predicted by the IPCC methods. In terms of energy production, the Y_{CH4} from meta-analysis provide more robust estimations than the IPCC default values. The application of the methodology in four existing dairy farms as case studies (one English and three Guatemalan) indicates how valuable the findings from meta-analysis are to evaluate baselines and AD scenarios with more evidence-based primary inputs.

7.2 Recommendations and future work

Given that this research work has shown unique improvements on the existing methodologies for emissions estimation from dairy farms, recommendations arise from the results. This section presents these recommendations divided in two groups: i) the continuation of work presented in this thesis and; ii) the extension of the research in the future to a broader scope.

With regards to the continuation of this work, the following recommendation is made:

- The regular maintenance of the database to incorporate new primary sources. By continuing

the update, the database can accumulate the methane yields and GHG emissions from the field, building upon the structure developed in this thesis.

In terms of expanding this research to future work, it is recommended to:

- Examine the available literature on Y_{CH4} of different feedstocks also included in the IPCC Guidelines (e.g. beef cattle, buffalo, swine). If there is sufficient evidence, the meta-analysis techniques of this thesis is suggested to be applied. This could improve the robustness of the default Y_{CH4} IPCC values. This would not only achieve more robust emission estimates, but also provide better assumptions to calculate energy outputs.

- Analyse the Y_{CH4} of the co-digestion of dairy manure with other substrates. Although different feedstocks are out of the scope of this work, the systematic review of the literature suggests that there is sufficient research work to extend the database and meta-analysis to co-digestion of manure with other agricultural, municipal, and/or agro-industrial wastes. Co-digestion could increase the Y_{CH4} in the AD process because organic co-substrates would contribute raw carbonaceous species for CH_4 formation. Thus, co-digestion would improve the energy output and increase the environmental benefits of AD.

- Examine other life-cycle indicators in dairy farms which are affected by AD (e.g. water footprint, acidification and eutrophication). Similarly to this work, if there is abundant evidence found in the literature relative changes could quantify the differences between baselines and the AD scenarios. Furthermore, this would enable the identification of trade-offs between different environmental metrics.

7.3 Limitations

There are certain limitation of the research work of this thesis that should be considered. These are mainly related to the database development and are highlighted as follows:

- An important constrain arises from the article selection criterion (Chapter 3) which sets the language of publications for inclusion in the database to English (i.e. within the domain of

the author). It should be noted that, although abundant evidence for Y_{CH4} of dairy cattle manure and GHG emissions from dairy farms exists in the research literature in English, there are other languages in which AD has strongly developed. The latter is particular valid for Chinese and Indian scientific journals.

- Manual selection and assessment of articles for their inclusion in the database is also a limitation because it is difficult to maintain the database updated with the most recent research work. Therefore, the meta-analyses of Chapters 4 and 5 synthesise the literature available until the last updated version of the database of Chapter 3. To capture the dynamism of the field, on-line automated assessment and the extraction of relevant information from selected articles to conform the database is an interesting challenge.

- Given the large sample size used for the meta-analyses, there is underlying difficulties to normalise all fluctuations of different articles. For the meta-analysis of Y_{CH4} the random-effect model reconciles these differences as it assumes a distribution of underlying population medians. However, the application of such model is not possible for relative changes given that articles do not commonly present the N_i and their s_i (i.e. required for meta-analysis models). Therefore, the semi-quantitative meta-analysis of relative changes explains the sources of variations between cases, by analysing outliers and inter-quartile ranges.

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Appendix A

Published articles

Potentials of biogas production and GHG mitigation in Guatemalan dairy farms.

Nicole D. Miranda*, Andrés Chicol** and Malcolm McCulloch*

***Abstract*—This work presents results of a survey of case studies to quantify the potential energy production and GHG emission changes of anaerobically digesting (AD) cattle manure in three Guatemalan dairy farms. Livestock inventory and energy consumption data were collected and used to define three scenarios for each farm: baseline, AD with condensing boiler (AD-boiler) and AD with combined heat and power unit (AD-CHP). The estimated emissions account for enteric fermentation, manure/digestate handling, import/export of thermal energy and electricity and use of fossil fuels for transport. The AD systems result in a production of 100±37 $kg_{CH4} \cdot head^{-1} \cdot yr^{-1}$. If this CH_4 is combusted in the AD-boiler scenarios, 5.00±1.59 $GJ \cdot head^{-1} \cdot yr^{-1}$ of thermal energy is generated and emissions from baseline scenarios are offset by 600±280 $kg_{CO2e} \cdot head^{-1} \cdot yr^{-1}$. The generated heat is sufficient to operate digesters (308 K) and export 2.90±0.62 $GJ \cdot head^{-1} \cdot yr^{-1}$. Challenges are found to use that thermal power because domestic heating is inessential. AD-CHP is found to be more suitable because it produces sufficient thermal energy for the digesters (2.50±0.80 $GJ \cdot head^{-1} \cdot yr^{-1}$) while generating electric power (1.80±0.57 $GJ \cdot head^{-1} \cdot yr^{-1}$). This scenario could promote the welfare of neighboring communities by making sustainable electricity available. AD-CHP could offset 400±320 $kg_{CO2e} \cdot head^{-1} \cdot yr^{-1}$ from the baselines.**

***Index Terms*—Anaerobic digestion, biogas, dairy farm, GHG, Guatemala.**

NOMENCLATURE

AD	: Anaerobic digestion.
B_0	: Maximum methane producing capacity [m^3_{CH4}/kg_{DM}].
CHP	: Combined heat and power.
$\dot{E}$	: Annual electric or thermal energy consumption [$GJ \cdot yr^{-1}$].
ECR	: Emission change ratio [non-dimensional].
EF_i	: Emission factor for energy from source "i" [$kg_{CO2e} \cdot GJ^{-1}$].
EF_3	: Emission factor from manure over pastures for N_2O [$kg_{N2O-N} \cdot head^{-1} \cdot yr^{-1}$].
GHG	: Greenhouse gas.
GWP	: Global warming potential [$kg_{CO2e} \cdot kg^{-1}_{GHG}$].
HHV	: Higher heating value [$GJ \cdot kg^{-1}$].
LHV	: Lower heating value [$GJ \cdot kg^{-1}$].
MCF	: Methane conversion factor for manure management system [%].
N	: Herd size [head].
Nex	: Annual average N excretion per dairy. cow [$kg_N \cdot head^{-1} \cdot yr^{-1}$].
VS	: Volatile solids [$kg_{DM} \cdot head^{-1} \cdot day^{-1}$].

Greek terms

η	: Fraction of power conversion.
ρ	: Density at standard conditions.
Δ	: Change or difference.

Subscripts

AD	: Anaerobic digestion scenarios.
B	: Baseline scenario.
Bo	: Boiler.
D	: Digestate.
Ds	: Diesel.
d	: Digester.
E	: Enteric fermentation.
El	: Electric energy.
j	: Emitting item to specify.
M	: Manure.
P	: Petrol.
Prod	: Produced.
Th	: Thermal energy.
NG	: Natural gas.

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I. INTRODUCTION

Anaerobic digestion (AD) is a technology that allows proper management of animal waste, contributing to the protection of human health and the environment, while making green power available. This work analysis the potentials of producing renewable energy and of GHG mitigation by the AD of dairy cattle manure in three farms in Guatemala. The study compares three scenarios of cattle manure management for each farm: i) baseline scenario that considers typical farm practices; ii) AD scenario which combusts the methane (CH_4) produced in a condensing boiler (AD-boiler) and; iii) AD scenario which combusts the CH_4 in a combined heat and power unit (AD-CHP). The scenarios are evaluated in terms of power production/consumption and greenhouse gas (GHG) emissions.

Agricultural activities release 65% of the global nitrous oxide (N_2O) emissions and 37% of the total world CH_4 emissions [1]. AD has the potential of diminishing the carbon footprint of farms as it extracts CH_4 from organic residues (i.e.: manure, crop waste) and makes this CH_4 available for renewable energy generation [2]. In developing nations, where agriculture is an important fuel of the economy, access to thermal and electric power are fundamental for economic development and welfare improvement. Particularly, in Guatemala a national gas grid is only expected for 2017 for industrial use [3] and electricity is unavailable for more than 16% of the population (3.1 million people) [4]. Consequently, Guatemalan human development index is 0.568, which is lower than the threshold of higher human development 0.800 [5]. AD is a practical mean to confront the energy poverty in Guatemalan rural zones while managing highly available livestock waste.

The AD process consists of a series of biochemical reactions that convert volatile solids (VS) in organic matter to biogas (mixture of CH_4 and carbon dioxide (CO_2)). The resulting solid digestate can be used as bio-fertiliser for growing crops which offsets embodied carbon of inorganic fertilisers [6]. Furthermore, application of digestate as a fertiliser has been reported to decrease up to 90% the CH_4 emissions compared to the application of untreated manure on crop fields [7].

The biogas produced by AD is a source of CH_4 that can be used to generate electrical power and/or heat. The CO_2 produced by the combustion of CH_4 in the biogas has a rapid recycle period in comparison to that CO_2 emitted from fossil fuel processes [8]. For

this reason, the CO_2 generated from biomass is generally considered carbon neutral. Therefore, the use of biogas in the developing world can contribute to a sustainable development.

AD systems have been carried out in developing countries within the framework of the Clean Development Mechanism (CDM) [9]. This mechanism incentives developed nations to achieve their emission reduction targets by investing in clean technologies in developing countries. Consequently, developing countries grow in a more sustainable manner and the international investment can promote economical growth. Guatemala has hosted AD projects within the CDM and these have been carried out mainly in the palm oil industry [10]–[13]. However, the AD of livestock manure has not been explored under this perspective in that country.

In this work, three typical dairy farms from Guatemala are taken as case studies. Inventory data on the farm operations are obtained by a structured survey. To evaluate the consequences of AD in terms of energy generation and GHG emission changes, baseline scenarios are established for each farm.

The emissions from the baseline scenarios relate to typical Guatemalan manure handling and energy consumption. CH_4 and N_2O are emitted from manure deposit by grazing livestock and are estimated in accordance to the Guidelines from the IPCC [14]. Electricity, when available, is assumed to come from the Guatemalan grid. Consumption of fossil fuels on-site for energy generation is also accounted in the emissions using corresponding conversion factors.

For the theoretical AD systems, mass and energy balances are performed to process the manure from the dairy farms. To account for reduction in emissions of CH_4 and N_2O when replacing untreated manure with digestate, a meta-analysis was carried out using available data from the literature.

To combust the biogas, the AD-boiler scenario was established for its high efficiencies ($\simeq$90% respect to the higher heating value (HHV)) and suitability for small-scale operations [15]. The AD-CHP scenarios were chosen because CHP is commonly applied in biogas plants [2], producing electricity and useful thermal energy to heat digester(s). The reported CHP efficiencies for biogas are over 80% of the lower heating value (LHV) [15], [16].

For the AD-boiler and AD-CHP scenarios thermal power generated was assumed to offset the use of natural gas, therefore, having negative emissions. In similar way, electric power produced by the AD-CHP scenarios displace the use of electricity from the Guatemalan grid. By comparing emissions from baselines and both AD scenarios, changes in the carbon footprint of the dairy farms are calculated.

The discussion of the energy and GHG aspects of the scenarios combined with the collected survey information provide insights into the preferable AD-combustion technology. Ultimately, the most beneficial scenario is proposed as a system which could meaningfully effect the farm activities and surrounding community.

II. Methodology

Three Guatemalan farms labelled A to C (details are given in Table I) are considered as case study for this analysis. Information on the farm operations was obtained by developing and applying a structured questionnaire to owners and/or administrators. The collected data was used to estimate potential energy outputs and the GHG emissions of theoretical AD scenarios. The questionnaire covers the following points:

- Herd size.
- Annual milk production.
- Milking procedure (i.e. manual or with rotating platform).
- Manure management system.
- Access to grid electricity.
- Annual electricity consumption.
- Annual consumption of fossil fuels on farm site.
- Knowledge and interest in anaerobic digestion.
- Possibility of exporting AD products.

The completed questionnaires allow to quantify the potential changes in emissions from baseline scenarios to the postulated AD scenarios ($\triangle GHG_i$) as follows:

$$\triangle GHG_j = (AD - Scenario)_j - (Baseline)_j \quad (1)$$

Where "j" corresponds to emitting item detailed in Table II. For the baseline scenarios, GHG emissions from manure management (enteric fermentation and field application of manure) are estimated utilising IPCC methodology [14]. The GHG associated to energy use (electricity and fossil fuels) are estimated using emission factors from the literature [17].

For the AD scenarios, emissions from field applied digestate are calculated based on a meta-analysis approach. The renewable energy generated and available to export is considered to offset (negative emissions) the use of conventional sources (Guatemalan grid for electricity and/or natural gas for thermal energy).

Table II presents the summary of GHG emissions that are accounted in this analysis. The equations to determine those emissions are presented in the Methodology Sections II-A and II-B. All emissions are standardised to $[kg_{CO2e} \cdot year^{-1}]$ by using global warming potentials (GWP_i) for emitted gas "i" ($kg_{CO2e} \cdot kg_{GHG}^{-1}$). GWP_{CH4} is taken to be 25 and GWP_{N2O} is 298 $kg_{CO2e} \cdot kg_{GHG}^{-1}$ [18].

Table I
Inventory and energy consumption in case study farms.

Farm	Location	Dairy cattle [head]	Annual energy use $[GJ \cdot yr^{-1}]$ Electricity ($\dot{E}_{El,B}$)	Diesel ($\dot{E}_{Di,B}$)	Petrol ($\dot{E}_{P,B}$)
A	Petén	600[a]	16[b]	52	55
B	Santa Rosa	370[c]	15	45	22
C	Escuintla	350	151	45	0

a: Of which 60 are milked annually. b: Off-grid electricity from petrol generator. c: Of which 150 are milked annually.

Table II
Summary of GHG emission $[kg \cdot yr^{-1}]$ calculations from the three scenarios.

Emission item	Baseline (B)	AD Scenarios	
A. Enteric fermentation.			
A1. CH_4 emissions	(+) $CH_{4,E}$	(+) $CH_{4,E}$	
B. Field application.			
B1. CH_4 emissions	(+) $CH_{4,M}$	(+) $CH_{4,D}$	
B2. N_2O emissions	(+) N_2O_M	(+) N_2O_D	
C. Fuel for transport.			
C1. Diesel	(+) $CO_{2,Ds,B}$	(+) $CO_{2,Ds,AD}$	
C2. Petrol	(+) $CO_{2,P,B}$	(+) $CO_{2,P,AD}$	
D. Grid electricity.		**AD-boiler**	**AD-CHP**
D1. Consumption	(+) $CO_{2,El,B}$	(+) $CO_{2,El,Bo}$	0
D2. Export	0	0	(-) $CO_{2,El,CHP}$
D3. Produced and used.	(+) $CO_{2,P,B}$[a]	(+) $CO_{2,P,B}$[a]	0
E. Fuels for thermal energy.			
E1. Consumption.	0	0	0
E2. Export.	0	(-) $CO_{2,Th,Bo}$	(-) $CO_{2,Th,CHP}$

a: Only applicable to farm A that uses petrol generator for electricity.

A. Baseline scenarios

A baseline is established for each farm as a reference to assess the effects of implementing AD on energy production, GHG emissions and energy use. The baselines are defined in accordance to the data collected in the questionnaires and that is summarised in Table I. In these scenarios emissions arise from enteric fermentation, manure

Table III
EMISSION FACTORS ACCORDING TO ENERGY SOURCE.

i	Energy source	EF_i	Unit	Reference
El	National electric grid	79.44	$[kg_{CO2e}/GJ]$	[17]
Ds	Diesel	74.10	$[kg_{CO2e}/GJ]$	T-1.4 [14]
P	Petrol	69.30	$[kg_{CO2e}/GJ]$	T-1.4 [14]
NG	Natural gas	69.30	$[kg_{CO2e}/GJ]$	T-1.4 [14]

deposit over fields by grazing cattle, electricity consumption and fossil fuel consumption.

In accordance to the IPCC Guidelines [14] (Tier 1 methodology), enteric fermentation releases CH_4 ($CH_{4,E}$) into the atmosphere can be estimated as follows:

$$CH_{4,E}[kg \cdot yr^{-1}] = EF_E \cdot N \tag{2}$$

Where EF_E refers to the emission factor associated to enteric fermentation of dairy cattle in Latin America and is 72 $[kg_{CH4} \cdot head^{-1} \cdot yr^{-1}]$ (Table 10.11 and Eq. 10.19 [14]).

In the three farms manure is deposited over fields by grazing cattle. Due to unavailable resources, manure storage tanks and controlled spreading of untreated slurry over fields as a source of nitrogen, have not been implemented. For this reason, the manure management system usage is considered be 100% deposit over "Pasture/ Range/ Paddock", in the IPCC classification [14]. This manure handling has associated CH_4 and N_2O emissions. The formation of CO_2 is excluded because any CO_2 formed from biomass was assumed to be neutral due to the fast carbon cycle to which this CO_2 relates, in contrast to fossil fuel sources.

The CH_4 and N_2O emissions were estimated using the Tier 2 methodology [14]. CH_4 is the result of anaerobic condition in the bulk of cattle dung heaps on the fields [7]. The annual CH_4 released into the atmosphere is calculated as:

$$\underset{[kg\,yr^{-1}]}{CH_{4,M}} = N \cdot VS \cdot 365 \cdot B_0 \cdot \rho_{CH4} \cdot \frac{MCF}{100} \tag{3}$$

Where N is the number of dairy cattle in the farm, VS is the daily volatile solid excreted by dairy cattle in $[kg_{DM} \cdot head^{-1} \cdot day^{-1}]$, 365 are the days in a year, B_0 is the maximum methane producing capacity for manure from dairy cattle in $[m^3_{CH_4} kg^{-1}_{DM}]$, ρ_{CH4} is the density of CH_4 at standard conditions, MCF corresponds to the methane conversion factors for manure management system and represents the degree to which B_0 is achieved [%].

The N_2O emitted from untreated manure on pastures is a by-product of nitrification and denitrification [19]. The annual emissions of this GHG are estimated as (Eq. 11.1 and Eq. 11.5 [14]):

$$\underset{[kg \cdot yr^{-1}]}{N_2O_M} = \frac{44}{28} \cdot (N \cdot Nex \cdot EF_M) \tag{4}$$

Where Nex is the annual average nitrogen excretion per dairy cow in $[kg_N \cdot head^{-1} \cdot yr^{-1}]$ and EF_M is the emission factor for N_2O from nitrogen in urine and dung in $[kg_{N2O-N} \cdot ha^{-1} \cdot yr^{-1}]$.

The values in Eqs. 3 and 4 that relate to manure composition are assumed to be the default values of the IPCC (T-10A.4 and T-11.1 **[14]**) for the manure management (S) "Pasture/ Range/ Paddock" and climate region "Latin America".

The emissions from the combustion of diesel and petrol for transport in baseline scenarios are estimated as:

$$CO_{2,Ds,B} = EF_{Ds} \cdot \dot{E}_{Ds,B} \tag{5}$$

$$CO_{2,P,B} = EF_P \cdot \dot{E}_{P,B} \tag{6}$$

Where the emission factors are specified in Table III and the annual energy consumption from petrol and diesel for the transport in the dairy farms are detailed in Table I.

The emissions from the consumption of electricity from the grid connection were determined using the emission factor in Table III (EF_{El}) as follows:

$$CO_{2,El,B}[kg \cdot yr^{-1}] = EF_{El} \cdot \dot{E}_{El,B} \tag{7}$$

Where $\dot{E}_{El,B}$ corresponds to the annual electricity consumption from the national grid in $[GJ \cdot yr^{-1}]$ and is specified for each farm in Table I. The value for emission factor of electricity should be used with caution as it considers the average Guatemalan annual mix of generation. It should be noted that Farm A consumes electricity generated on site because it does not have grid access. Therefore, emissions from electricity consumption in that baseline scenario use the emission factor of petrol (EF_P, Table III) instead of EF_{EL} used in Farms B and C.

Thermal energy is not required for space heating in the baseline scenarios because of the tropical conditions in the Guatemalan dairy farms.

B. AD-Scenarios

The emissions from the AD scenarios raise from enteric fermentation, the field application of digestate, transport in the farms and offset of conventional energy sources (considered negative emissions). The enteric fermentation is not affected by the AD of cattle manure and consequently they are estimated as for the baselines utilising Eq. 2. For the emissions from digestate after field application, a meta-analysis approach is carried out because specific emission factors are not detailed in the IPCC methodology (Section II-B1). The transport within the Farm is assumed to not be affected by the AD systems, therefore these emissions are estimated as for the baselines ($CO_{2,Ds,AD} = CO_{2,Ds,B}$ and $CO_{2,P,AD} = CO_{2,P,B}$ in Table II). To estimate the emissions from the offset of conventional energy sources (thermal energy from NG and electricity from Guatemalan grid) CH_4 generated from theoretical digesters ($CH_{4,Prod}$) is calculated. Two combustion technologies are then assessed with respect to the energy output and emission changes: AD-boiler and AD-CHP scenarios (Section II-B2).

1) Emissions from digestate after field application. : The CH_4 and N_2O emissions from digestate after soil application were calculated as:

$$CH_{4,D}[kg \cdot yr^{-1}] = ECR_{CH_4} \cdot CH_{4,M} \tag{8}$$

$$N_2O_D[kg \cdot yr^{-1}] = ECR_{N_2O} \cdot N_2O_M \tag{9}$$

Where $CH_{4,M}$ and N_2O_M have been estimated for the baseline scenarios (Eq. 3 and 4) and $ECR_{i=CH4 or N2O}$ is defined as the emission change ratio of gas "i".

To estimate ECR_{CH4} and ECR_{N2O} articles found in the literature that compare CH_4 and N_2O emissions from untreated and digestate cattle manure were collected. Due to limited scientific publications specific to Central America, the articles selected report emissions from field applied manure or digestate in dairy farms worldwide. The studies meet the following criteria: i) they are peer-reviewed scientific publications to ensure quality; ii) they correspond to primary sources to avoid duplicates and; iii) they include numerical data of GHG emissions for untreated slurries and their digestate so that quantitative results allow the evaluation of changes in GHG emissions. The articles may include multiple cases, each of which is considered separately.

From 14 selected articles [7], [20]–[32] 6 cases are found for CH_4 and 24 cases for N_2O. For each case a corresponding ECR_i was estimated ($GHG_{i,D}/GHG_{i,M}$) and the distributions of Fig. 1 are obtained. A $ECR_i < 1$ indicates that the digested manure emits less gas "i" than its untreated manure.

To assess if the ECR_i value is significantly different from one (value in which emissions from untreated and digested manure are

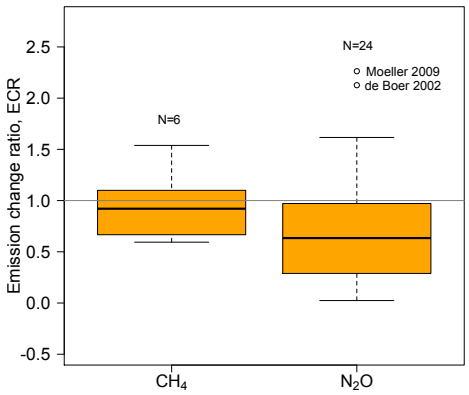


Figure 1. Box plots for the emission change ratio (*ECR*) of greenhouse gas emissions from field application. Upper and lower sides of boxes: first and third quartile; line through the box: median; ○: outliers (more than 1.5 interquartile range); N: number of cases; $ECR > 1$ indicate that emissions with AD are higher than baseline.

equal), the Wilcoxon Signed Rank tests was applied over the median of the distributions. For p-values<0.05 the null hypothesis is rejected, thus, it is found that the emissions from digested is significantly different from untreated manure [33].

For CH_4, it is expected to observe less emissions from digestate, because volatile solids have been extracted during the AD process. However, in the aerobic conditions after field application CH_4 formation is limited for both untreated and digested manure [7]. As a result of this, the median ECR_{CH4} is 0.92 (interquartile range= 0.36) and is not significantly different from one (Wilcoxon's P=0.787). Consequently, CH_4 emissions from untreated and digested manure after field application are statistically equivalent.

Emissions of N_2O are the most reported from soil application of untreated and digested manure because it holds a high GWP and because N_2O formation is favoured in aerobic conditions. The mechanisms that produce N_2O are also highly dependent on soil moisture content and organic carbon in the slurry [25], [26], [28]. The variation in these parameters result in the large interquartile range (0.62) shown in Fig. 1 for the ECR_{N2O} and in the presence of outliers [25], [32].

Regarless of this high dispersion in the ECR_{N2O} distritubion, a significant decrease (median= 0.63, Wilcoxon's P= $2.11x10^{-2}$) in N_2O emissions with the implementation of AD is found in the literature. AD holds the potential to reduces denitrification with respect to untreated manure because it lowers the organic carbon content and consequently, less carbon is available as energy source for the metabolism of denitrifying bacteria [34], [35].

2) Operation of theoretical digester : To estimate the output energy from the AD-boiler and AD-CHP scenarios, it is necessarily to first calculate the potential CH_4 production (CH_{4Prod}) by AD of the available cattle manure. This was calculated similarly to Eq. 3 from the IPCC protocol, as follows:

$$\underset{[kg\ yr^{-1}]}{CH_{4,Prod}} = 365 \cdot 0.67 \cdot N \cdot VS \cdot Y_{CH4} \tag{10}$$

Where the default range for methane yield (Y_{CH4}) according to those guidelines is 0.11 to 0.15 $m^3_{CH4} \cdot kg^{-1}_{DM}$. As a reference for the analysis, a specific yield of 0.14 $m^3_{CH4} \cdot kg^{-1}_{DM}$ is estimated from the work from Amon et al. [36]. That study is chosen as it corresponds to cattle manure from dairy farms which are fed only hay and grass, similar to the Guatemalan cows in the case studies.

In order to establish the heat input to the theoretical digesters ($\dot{Q}_d$) typical mesophilic operation temperature of 308 K [2], [37] is assumed. Maranon et al. [38] reports a range of $1.6x10^{-5}$ to $2.5x10^{-5}$ $TJ/kg_{CH4Produced}$ needed to heat digesters for dairy cattle manure. By using this range a conservative estimation for $\dot{Q}_d$ is obtained for the Guatemalan farms because: i) the average temperature in Guatemala (293 K) is higher than that study (286 K) which implies that less energy would be required to reach the operation temperature and; ii) the dairy farms considered in the work of Maranon et al. [38] are smaller (herd sizes: 28, 36, 52 and 90 livestock units) and because AD has been suggested to be an economy of scale [39], [40], heat losses could be better reduced in larger digesters. The median $20.1\,GJ/kg_{CH4,Prod}$ from Maranon et al. [38] is used as the best estimate for this analysis. Therefore, the heat required for the digester is calculated as:

$$\dot{Q}_d[GJ \cdot yr^{-1}] = 2.01x10^{-2} \cdot CH_{4Prod}$$

It should be noted that although the thermal power used for the digester is carbon neutral, it is not accounted as negative emissions because it is not replacing conventional energy sources present in the baseline scenarios.

3) Energy output from the AD-boiler scenarios : The energy from the biogas is released by the combustion of CH_4. Complete combustion (stoichiometric) was assumed. However, equilibrium reactions such as the dissociation of CO_2 and water-gas shift reaction, are also present and effect the composition of the combustion products (i.e. presence of carbon monoxide and hydrogen) [41].

Biogas can be converted to heat in a condensing boiler, however, these scenarios do not produce electricity and therefore, emissions from electricity consumption exist as for the baseline ($CO_{2,El,Bo} = CO_{2,El,B}$ in Table II).

A condensing boiler extracts the heat of evaporation of water contained in the flue gas [42], [43]. Therefore, the higher heating value (HHV) of CH_4 is used to estimate the potentially useful thermal energy [15]:

$$\dot{E}_{Th,Bo}[GJ \cdot yr^{-1}] = \eta_{Th,Bo} \cdot HHV_{CH4} \cdot CH_{4,Prod} \tag{11}$$

where $\eta_{Th,Bo}$ is the fraction of chemical power (combustion reaction) converted to thermal power in the condensing boiler and is 90% based on the HHV ($55.6x10^{-3}\,GJ \cdot kg^{-1}_{CH4}$ [44]).

The offset of CO_2 emissions due to export of thermal energy from the AD-boiler scenarios can then be estimated as:

$$CO_{2,Th,Bo}[kg \cdot yr^{-1}] = (\dot{E}_{Th,Bo} - \dot{Q}_d) \cdot EF_{NG} \tag{12}$$

Where it is assumed that the excess (export) heat is replacing the use of natural gas (NG).

4) Energy output from the AD-CHP scenarios : The implementation of CHP plants to extract energy from biogas has been explored as a feasible alternative [16]. The theoretical AD-CHP scenarios are analysed for the Guatemalan dairy farm case studies. The electrical energy that can be produced from the CH_4 contained in the biogas can be estimated as:

$$\dot{E}_{El,CHP}[GJ \cdot yr^{-1}] = \eta_{El} \cdot LHV_{CH4} \cdot CH_{4,Prod} \tag{13}$$

where LHV is the lower heating value ($50.1x10^{-3}\,GJ \cdot kg^{-1}_{CH4}$ [44]), η_{El} is the fraction of chemical power to electricity in the CHP unit and is assumed to be 36% (based on LHV) for small scale CHP units [2], [45]. The excess electricity with respect to the baseline, was then used to estimate the export that would offset the Guatemalan grid:

$$CO_{2,El,CHP}[kg \cdot yr^{-1}] = (\dot{E}_{El,CHP} - \dot{E}_{El,B}) \cdot EF_{El} \tag{14}$$

Where values used for annual energy consumption in the baseline and emission factor of the Guatemalan electricity grid can be found in Tables I and III.

The thermal power generated by the CHP process is estimated as:

$$\dot{E}_{Th,CHP}[GJ \cdot yr^{-1}] = \eta_{Th,CHP} \cdot LHV_{CH4} \cdot CH_{4,Prod} \tag{15}$$

where $\eta_{Th,CHP}$ is fraction of power converted to thermal power in

the CHP process. Based on the LHV, $\eta_{Th,CHP}$ is 50% [45]. Similar to the AD-boiler scenarios offset of emissions were estimated based on the available heat to export that was assumed to replace natural gas:

$$CO_{2,Th,CHP}[kg \cdot yr^{-1}] = (\dot{E}_{Th,CHP} - \dot{Q}_d) \cdot EF_{NG} \quad (16)$$

III. Results and Discussion

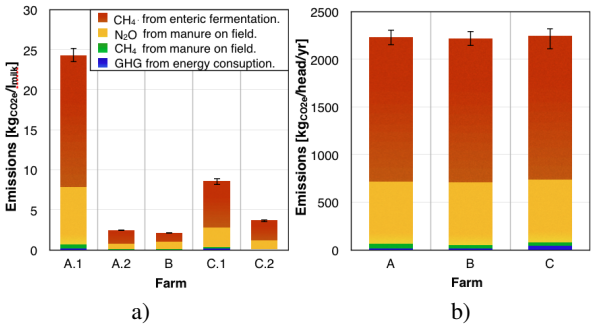
A. Baseline scenarios

The total emissions from the case study farms are 1340±50, 820±30 and 790±30 $ton_{CO2e} \cdot yr^{-1}$ for farms A, B and C, respectively. This corresponds to 2230±80 $kg_{CO2e} \cdot head^{-1} \cdot yr^{-1}$ for all the baseline farms. Enteric fermentation is the main source of emissions for all farms, contributing ~67% of the total GHGs.

Manure deposit on field by grazing animals emit only low amount of CH_4 (1-2% of total farm emissions), but high amount of N_2O (~31% of total farm emissions). The low CH_4 contribution is explained by aerobic conditions that promote CO_2 formation. Therefore, CH_4 is only produced in the bulk of manure piles over pastures. An intriguing aspect observed is that CH_4 from stores is avoided in these baselines. This is a major difference with dairy farms from developed countries [7], [20], [46], [47], in which CH_4 emissions from stores has been identified as the most important source of GHGs (up to 60%) [23]. The high level of N_2O emitted from soils is explained by favourable aerobic conditions for denitrification and high GWP_{N2O}.

In all case studies the consumption of electricity and fossil fuels is mainly for domestic use as cattle are milked manually. This implies that only 1-2 % of the dairy farm emissions are due to energy requirements. Differences arise from the number of households on-site and energy sources. Farms A and B have one household on-site, while Farm C has ten. Farm A obtains electricity by using a petrol generator because grid electricity is unavailable. Conversely, Farms B and C consume grid electrify (see Table I). As expected for tropical conditions, no thermal energy is required for heating houses. However, the availability of cheap thermal energy could increase the farm activity, for example, for using it for on-site pasteurisation.

To discuss and compare farms, the emissions from the baseline scenarios are normalised by milk production and herd size as presented in Fig. 2a and 2b, respectively. Emissions by litre of milk of Farm A and C are presented as two sets: A.1-2 and C.1-2. Sets A.1 and C.1 represent the current farm situation in which only a fraction of the total dairy cows are milked (see Table I). Therefore, the milk production is lower than the potential of the farms and emissions account for non-milked cattle. The reason for these farms to maintain large herd size in reproductive age is that additionally to milk production they produce meat and livestock for trade. For A.2 and C.2 sets the potential milk production is considered based on the theoretical milking of all dairy cattle. In these cases, the emissions per milk are in closer agreement with results from the literature (~1.3 kg_{CO2}/l_{milk} [46]). However, this level of milk production is currently unsuitable for the farm as manual milking takes place, human resources are limited given the isolated locations and the product distribution is not consolidated. In addition, Farm A does not have grid electricity access to implement automated milking procedure. This is a further incentive for off-grid electricity generation as discussed in the AD-CHP scenario.



a) b)

Figure 2. Emissions from baseline scenarios of farms, normalised by milk production (a) and by herd size (b). Error bars correspond to ranges in default parameters of the IPCC methodology [14].

Table IV
Theoretical digester for the case study farms.

	Unit	Farm A	Farm B	Farm C
CH_{4Prod}(x1000)	$[kg \cdot yr^{-1}]$	60± 21	38±14	34±14
$\dot{Q}_d$	$[GJ \cdot yr^{-1}]$	1200±820	750± 500	710± 480

Normalising the carbon footprint with respect to the number of cattle (Fig. 2b) results, as expected, in similar values between Farms (2230±80 $kg_{CO2e} \cdot head^{-1}$). Differences are attributed to electricity and fossil fuels consumption because these are dependent on different houses on-site and electricity sources, as explained above. An additional source of variation is the MCF value in Eq. 3 which varies from 1 to 2% depending on the average annual temperature in the farms location (T-10A.4 [14]).

B. Theoretical digesters

The two aspects of the theoretical digesters that are analysed are the heat requirement to operate at 308 K and the potential methane production. It should be noted that the CO_2 in the produced biogas would be increased with higher methane production, as expected for constant biogas composition. However, that CO_2 emission is not quantified because it is considered to be carbon neutral.

The thermal energy needed to operate the digesters are presented in Table IV. The supply of this heat is considered to come from the combustion of the CH_4 produced.

For the case study farms, AD holds the potential to produce 34±14 to 60±21 $ton \cdot yr^{-1}$ of CH_4 (see Table IV) that otherwise would not be available or would be provided from fossil fuel sources. Expressed by unit of livestock the produced CH_4 is 100±37 $kg_{CH4} \cdot head^{-1} \cdot yr^{-1}$ for the three farms. The amount of useful energy that can be extracted from the CH_4 in the biogas and the consequent emission offset depends on the efficiency of the combustion technology. Therefore, the AD-boiler and AD-CHP scenarios are discussed in the following sections II-B3 and II-B4.

C. AD-Boiler Scenarios

The AD-boiler only produces thermal power, therefore, these scenarios import electricity as for their associated baselines. Fig. 3 presents the thermal power outputs for the AD-boiler scenarios of the three Guatemalan farms, normalised by herd size. The potential gross thermal power generation from these scenarios is 2900±1100 $GJ \cdot yr^{-1}$, 1800± 700$GJ \cdot yr^{-1}$ and 1700 ± 660 $GJ \cdot yr^{-1}$ for Farms A, B and C, respectively. This corresponds to an emission per animal of 5.00±1.59 $GJ \cdot head^{-1} \cdot yr^{-1}$. Sources of variation (up to 35%) are explained by the range of methane yield and default parameters in the IPCC methodology [14].

For all cases, the condensing boiler produces sufficient thermal power to meet the digester heating requirements. Subtracting the thermal power required for the digester, gives the estimated potential exportable thermal power of 1800±370 $GJ \cdot yr^{-1}$, 1100±220 $GJ \cdot yr^{-1}$ and 1000±220 $GJ \cdot yr^{-1}$ for Farms A, B, and C, respectively.

Fig. 4 presents the results of the changes in emissions of the AD-boiler scenario with respect to the baseline. The reduction of emissions in these scenarios result in 600 ± 280 $kg_{CO2} \cdot head^{-1} \cdot yr^{-1}$. It is observed that there are two main sources of GHG emission offsets:

1. The avoided emissions from manure deposit on the field in the baseline scenario. For the best estimate of methane yield, the N_2O

offset accounts for 42% of the total displaced emissions for all farms. Approximately 1% of the changes in emission can be attributed to the reductions in CH_4 from field application. This value is low because the meta-analysis showed insignificant changes in emissions between the untreated and digested manure deposit on field.

2. The biogas is assumed to replace natural gas as fuel for the condensing boiler. This accounts for 52% of the total displaced GHG emissions in the AD-boiler scenario. Although the AD-boiler scenario is capable of generating thermal energy for export, the use of such energy presents challenges. Consequently, the offset of emissions is highly dependent on the use of that net heat. Domestic heating of neighbouring communities is unlikely, because the tropical weather of Guatemala diminishes this need. The produced heat could be used on-site if a pasteurisation process took place. However, for this to be applied in these farms, access to electricity is a key factor. Therefore the AD-CHP scenario is analysed in the following section.

D. AD-CHP scenario

CHP was chosen as a technology to evaluate the use of biogas as it has been reported to be convenient in generating electrical power while supplying heat to the digester [2]. Fig. 3 presents the thermal power production and use for the AD-CHP scenario for the case study dairy farms normalised by herd size of the farms. As expected, the thermal power generation per livestock unit is similar for all farms (2.50±0.8 $GJ \cdot head^{-1} \cdot yr^{-1}$) because the common IPCC methodology was used. This results in the farms generating thermal energy from 900±330 $GJ \cdot yr^{-1}$ in farm C to 1500±520 $GJ \cdot yr^{-1}$ in Farm A. Compared to thermal power generated in the AD-boiler scenario, these amount correspond to ~50%, because the LHV of CH_4 is used instead of the HHV and the efficiency to heat is less for a CHP unit ($\eta_{TH,CHP}$ = 50%) than for a boiler ($\eta_{Th,Bo}$= 90%, see Methodology Eqs. 11 and 15).

For the best estimate of methane yield of 0.14 $m^3_{CH4} \cdot kg^{-1}_{DM}$, the thermal power generated is sufficient to supply heat to the digester. However, the overlapping error bars of Fig. 3 indicate that this may not always be the case. Therefore, insulation of digesters is a key factor to avoid heat losses and maintain the operation conditions.

Fig. 6 presents the electric power outputs of this scenario expressed by herd size. The implementation of an AD-CHP has the estimated potential of generating 1100±410 $GJ \cdot yr^{-1}$ (35±13kW), 700±250 $GJ \cdot yr^{-1}$ (22±8 kW) and 600±240 $GJ \cdot yr^{-1}$ (19±8kW) of electric power for Farms A, B and C, respectively.

There is the potential to export electric power because the farms only consume up to 24% (Farm C) of the generated electricity. The available electric power to export ranges from 500±87 $GJ \cdot yr^{-1}$ for farm C to 1100±410 $GJ \cdot yr^{-1}$ for farm A. It is observed that although Farms B and C are similar in herd size, the electricity for export differs. This is attributed to the higher domestic use of electricity in Farm C, as ten residence houses are in the later and only one in Farm B.

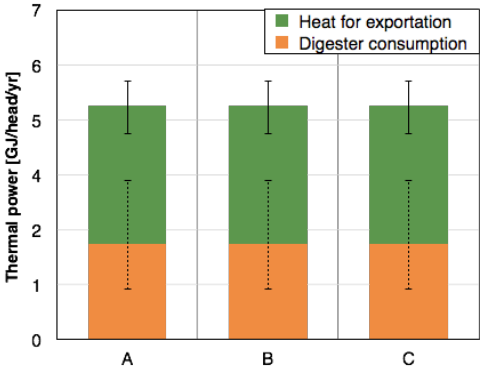


Figure 3. Thermal power production/use in Guatemalan case study farms with theoretical AD-boiler scenarios. Best estimate for methane yield is used (0.14 $m^3_{CH4} \cdot kg^{-1}_{DM}$). Error bars correspond to ranges in default methane yields and parameters of the IPCC methodology [14].

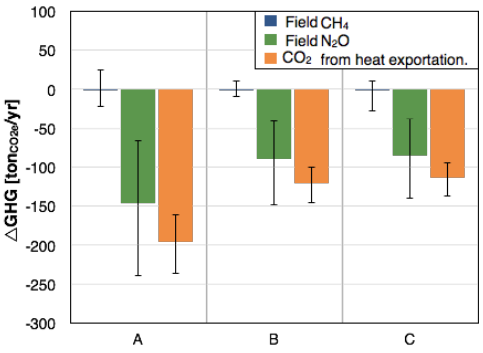


Figure 4. Offsets of GHG emissions by AD-boiler scenarios for each farm. Error bars relate to ranges of default parameters from the IPCC methodology [14] and interquartile ranges of *ECR* from the meta-analysis.

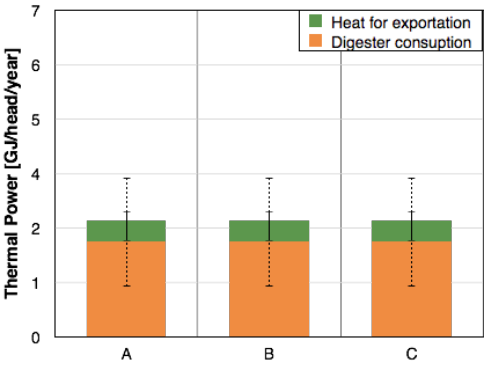


Figure 5. Thermal power production/use in Guatemalan case study farms with theoretical AD-CHP scenarios. Best estimate for methane yield is used (0.14 $m^3_{CH4} \cdot kg^{-1}_{DM}$). Error bars correspond to ranges in default methane yields and parameters of the IPCC methodology [14]. Solid-line error bars relate to the heat available for exportation and the dashed-line error bars to the digester consumption.

As an alternative to export electricity, this could be used on-site in the the milking process. As a reference, an English farm similar in herd size to Farm A (500 dairy cattle) consumes 1100 $GJ \cdot yr^{-1}$ in dairy activities, including refrigeration, rotating platform for milking and manure pumps [48], [49]. Therefore, the AD-CHP scenario holds the potential of increasing the farms activity and, for Farm A, bringing electricity to off-grid location can promote rural community welfare.

The offset of GHG emissions of the AD-CHP scenario respect to the baseline scenario is presented in Fig. 7. The three displacement of GHG emissions observed are:

1. Such as for the AD-boiler scenario, the emissions from manure deposit on the field are avoided. The CH_4 emissions from digestate applied on soils is not significantly different from its corresponding untreated slurry. Therefore, the change in emissions are also insignificant. The N_2O emissions reductions account for 55 to 60% of the total changes in GHG emissions of this scenario.

2. The export thermal heat would offset 17000 to 30000 $GJ \cdot yr^{-1}$ (11-12% of total offsets). As for the AD-boiler scenario, the use of this thermal power is challenging, however, in combination with the available electricity generated in this scenario, implementation of

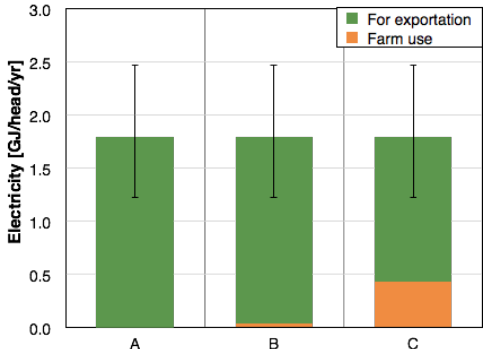


Figure 6. Electric power production/use in Guatemalan case study farms with theoretical AD-CHP scenario. Best estimate for methane yield is used (0.14 $m^3_{CH4} \cdot kg^{-1}_{DM}$). Error bars correspond to ranges in default methane yields and default parameters of the IPCC methodology [14].

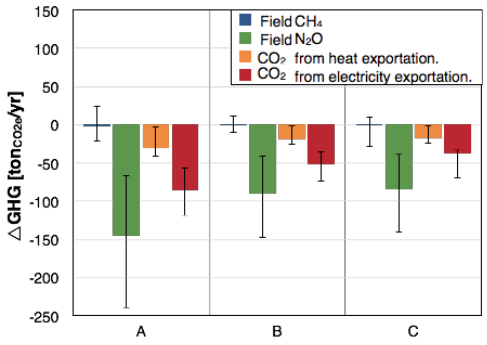


Figure 7. Offset of GHG emissions by AD-CHP scenarios for each farm. Error bars relate to ranges of default parameters from the IPCC methodology [14] and interquartile ranges of *ECR* from the meta-analysis.

more automated milking process could be achieved.
2. Excess generation of electric power that can be used on-site or exported, and that otherwise would be provided by the Guatemalan grid or fossil fuel generation. The export of electricity holds the potential of offsetting 38000 $kg_{CO2} \cdot yr^{-1}$ (Farm C) to 85000 $kg_{CO2e} \cdot yr^{-1}$ (Farm A). The total displacement of GHG emissions by the carbon neutral electricity generated from the AD-CHP scenario corresponds to 27-32% of the total offsets for this scenario.

When comparing scenarios it is found that the AD-boiler scenario holds the potential to offset a total of 600±280 $kg_{CO2e} \cdot head^{-1} \cdot yr^{-1}$ and the AD-CHP 400±320 $kg_{CO2e} \cdot head^{-1} \cdot yr^{-1}$. Although, in terms of emission reduction the AD-boiler scenario is superior, the uncertainty in the consumption of that thermal heat suggests that the AD-CHP scenario is a more suitable technology to implement. Additionally the latter has the potential to give electricity access to rural communities and increase their quality of life, while the heat required by the digester could still be met.

IV. Conclusions

The analysis accounts for the power generation and offset of GHG emissions of three Guatemalan dairy farms (A, B and C) in the transition from the common farm practices (baseline scenarios) to the implementation of theoretical AD plants. The yield 0.14 $m^3_{CH4} \cdot kg^{-1}_{VS}$ was used as the best estimate for the case studies. Two AD scenarios are established to analyze the alternatives of extracting the energy from the methane produced: AD-boiler and AD-CHP. CO_2 emitted was assumed carbon neutral if the source is biomass.

From a questionnaire responded by the farm administrators, using the IPCC methodology [14], the emissions from the baseline scenarios are estimated 2230±80 $kg_{CO2e} \cdot head^{-1} \cdot yr^{-1}$. From these, ~67 % correspond to CH_4 enteric fermentation and ~31% to N_2O from manure deposit by grazing cows on fields. CH_4 emissions from manure over fields and emissions from energy consumption contributed only 2-3% of the baseline emissions.

The AD systems can produce 100±37 $kg_{CH4} \cdot head^{-1} \cdot yr^{-1}$ operating digesters at mesophilic condition (308 K), which would consume 2.1±0.6 $MJ \cdot head^{-1} \cdot yr^{-1}$.

In the AD-boiler scenarios, the combustion of this CH_4 generates 5.00±1.59 $GJ \cdot head^{-1} \cdot yr^{-1}$ of thermal energy, leaving 2.90±0.62 $MJ \cdot head^{-1} \cdot yr^{-1}$ to be exported. The use of that exported heat is difficult for these dairy farms because they are in isolated areas and domestic heating for neighbouring communities is unnecessarily given the Guatemalan weather. If the thermal heat to export would replace the use of natural gas, 600±280 $kg_{CO2e} \cdot head^{-1} \cdot yr^{-1}$ would be offset in the AD-boiler scenario.

The AD-CHP scenario seems as a scenario from which Guatemalan farms can benefit further. If the CH_4 produced in digesters was combusted in CHP units 2.50±0.80 $GJ \cdot head^{-1} \cdot yr^{-1}$ of thermal energy would be produced and would be sufficient to supply digesters. Additionally, 1.80±0.57 $GJ \cdot head^{-1} \cdot yr^{-1}$ of electric power would be generated. This would cover the complete electric consumption of the farms. Up to 24% (0.40±0.14 $GJ \cdot head^{-1} \cdot yr^{-1}$) of the generated electricity would be used on-site (Farm C). The excess electric power (≥1.40±0.43 $GJ \cdot head^{-1} \cdot yr^{-1}$) could be used for export and could be used to increase the performance of milk production. For example, the implementation of automated milking systems (i.e. rotating platform and pumps) would allow to milk more cows in Farms A and C, which are currently not reaching their full milk production potential. This scenario would offset 400±320 $kg_{CO2e} \cdot head^{-1} \cdot yr^{-1}$ of emissions, with respect to the baseline.

The three case study farms can jointly mitigate up to 1160 $ton_{CO2e} \cdot yr^{-1}$ for the AD-boiler scenario or 950 $ton_{CO2e} \cdot yr^{-1}$ for the AD-CHP scenario. These values are low in comparison to other AD systems within the CDM (1802 to 136000 $ton_{CO2e} \cdot yr^{-1}$ [9]), because they consider only 1320 cows and no CH_4 reductions from storage of untreated manure. However, the total Guatemalan cattle inventory is approximately 3.4 million heads [50] (2012). Therefore, the combination of multiple farms and/or animal waste (co-digestions) could be an applicable approach to maximise offsets and produce renewable energy by AD. Consequently, the GHG mitigation could be attractive for carbon credits commercialisation. In this respect, a preliminarily cost of CO_2 abatement would range between 2-12 $\$_{USD} \cdot ton^{-1}_{CO2e}$ (based on 0.16 $\$_{USD} \cdot ton^{-1}_{sludge}$ from the Mexican case study reported by Pena et al. [51]). However, in practice electricity generation (0.10-0.27 $\$_{USD} \cdot kWh^{-1}$ price in Guatemala [52]) can be sold, decreasing the cost of carbon offsets. The production of that renewable off-grid energy by AD systems is crucial for the upgrade of these farms and can be used for the development of neighbouring communities. This technology therefore not only offers an alternative to diminish ecological footprint but most importantly can contribute in improving the quality of life of people living in rural Guatemalan areas.

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Research paper

Meta-analysis of methane yields from anaerobic digestion of dairy cattle manure

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ABSTRACT

This work presents a novel meta-analysis for methane yields from anaerobically digesting dairy cattle manure. A database is compiled from 115 articles (2181 cases) by systematically assessing the academic literature. Y_{CH_4} and secondary variables collected in the database describe performance, operation conditions of digester and manure composition. Inputs to the database are normalised to enable inter-study uni- and multi-variate analysis, according to different types of digesters.

Most cases (N = 1299) are reported for batch digesters and meta-analysis results in a mean Y_{CH_4} of 0.230±0.016 m^3kg^{-1}. CSTR (N = 241), results in mean of 0.190±0.016 m^3kg^{-1} (random-effect model). Other continuous digesters, such as fixed-film, plug-flow and UASB require further cases for the application of meta-analysis. For non-specified semi-continuous digesters (N = 347), the mean calculated by the random-effect model is 0.204±0.032 m^3kg^{-1} (N = 27).

With respect to multi-variate analysis of operation conditions, batch digesters form four clusters, while two clusters are identified for CSTR and three for semi-continuous digesters. For variables describing manure composition, batch digesters present eight clusters, while CSTR and semi-continuous digesters have insufficient cases. The strongest correlations found for these secondary variables (Spearman's rho: −0.685 and −0.696) result for pH and Y_{CH_4} in batch and CSTR, respectively.

Maximum Y_{CH_4} estimated by meta-analysis are proposed to replace the default IPCC values because they are based on a larger sample size and integrate updated literature. In particular, markedly higher Y_{CH_4} are obtained for Asia, Middle East and Indian Subcontinent than those in the IPCC guidelines.

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1. Introduction

This meta-analysis examines the methane yields (Y_{CH_4}) found in the literature for anaerobic digestion (AD) of dairy cattle manure. The dairy sector is responsible for 4% of global anthropogenic greenhouse gas (GHG) emissions [1]. To reduce the carbon footprint of milk-producing farms, AD has been proposed as a mitigating technology. AD converts the volatile solids (VS) in cattle manure to biogas (CH_4 and CO_2 mixture) and digestate [2]. Consequently, GHG emissions are decreased by: i) avoiding high global warming CH_4 from manure management systems; ii) generating renewable energy that substitutes fossil fuels and; iii) producing digestate that replaces mineral fertilisers. In order to quantitatively predict these benefits, assumptions on the performance of AD processes are critical [3].

In this respect, Y_{CH_4} is a metric widely utilised in mass and energy balances to calculate the CH_4 production. The Y_{CH_4} corresponds to the CH_4 formed by unit of VS and is defined as follows:

$$Y_{CH_4}\left[m^3kg^{-1}\right] = \frac{CH_{4,output}}{VS_{input}} \quad (1)$$

Theoretical, modelled and experimental values of Y_{CH_4} are available in the literature. Theoretical estimates commonly use the Buswell equation [4,5] which is based on the chemical composition and stoichiometry of degradation reactions. However, actual Y_{CH_4} are less than theoretical values because not all organic material converts to biogas (e.g. non-degradable solids, inhibition of reaction and/or generation of new bacteria). Thus, utilising theoretical

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Y_{CH_4} can over-estimate CH_4 production for AD scenarios. For models of Y_{CH_4} (e.g. ADM1 [6] and Linke et al. [7]), validations are based on experimental work with limited AD operation conditions. Therefore, increasing the sample size of experimental results can provide a more robust source of validation. Although, empirical values of Y_{CH_4} are available in multiple (and increasing) publications, it is challenging to integrate results differing in operation conditions, slurry compositions and units of measurements. This work addresses this by applying meta-analysis techniques to systematically review and numerically combine the research on Y_{CH_4} in the dairy sector.

Meta-analysis has traditionally developed in the medical sciences but in recent years has been applied in the bio-energy sector [8,9]. For biogas generation from dairy farms, qualitative reviews are dominant [10–12]. Only two meta-analysis [13,14] exist for AD of dairy manure, however, they are focused on different aspects of the process (i.e. microbial communities [13] and the effects over farm emissions [14]). Additionally, to the authors' knowledge, this is the first work to integrate such numerous cases from the academic literature in the field.

The aim of this meta-analysis is to quantitatively combine Y_{CH_4} measurements to enable a comprehensive understanding of this metric with respect to operational and composition variables. For this purpose, two main steps are carried out: creating a specific database and statistically analysing the collected information. A database is compiled because no specific dataset is available for the entire literature reporting Y_{CH_4} of AD in dairy farms. Research articles are found by using particular keywords and applying defined criteria (Section 2.1). The Y_{CH_4} are extracted from the selected work and entered to the database together with secondary variables (i.e. specifying operation and/or manure composition). In order to enable numerical combination, units of measurements for all variables are standardised (Section 2.2). To analyse the variables compiled in the database, uni- and multi-variate tests are introduced in Sections 2.3–2.4.

In the Results and Discussion section, key aspects of the database are first described (Section 3.1). Thereafter, Y_{CH_4} are discussed in terms of digester type (i.e. batch, continuous or semi-continuous). Multi-variate structure between key variables related to the performance of different AD systems is examined. Correlations and clustering of principal components are discussed in terms of sources of similarities and variations. The discussion finally compares results of meta-analysis models applied over maximum Y_{CH_4} to the default values of the National Guidelines for GHG emissions of the Intergovernmental Panel of Climate Change (IPCC [15], i.e. widely used to predict CH_4 emission from manure management systems).

2. Methods

This section first presents the methodology to develop the novel database of Y_{CH_4} for AD of dairy cattle manure. Second, the mathematical background for the statistical analysis of the variables in the database is introduced. All statistical calculations are performed in R v.3.0.2.

2.1. Article selection

A systematic search of articles in the academic literature is carried out to compile the database of Y_{CH_4} of dairy cattle manure and secondary variables. The selection of articles is based on the following four criteria:

i) scientific publications in the academic literature that have been peer-reviewed and are in the field of AD;
ii) primary sources;
iii) available work in journals in English to which the authors have access and;
iv) inclusion of experimental data of Y_{CH_4} for AD of dairy cattle manure.

The first criterion is defined to ensure quality results in articles that potentially report Y_{CH_4} values. The ISI Web of Knowledge platform [16] is used because it contains mainly peer-reviewed journals. The publication language is set as "English" and the publication year is not constrained. It should be noted that, although China has played an important role in the development of AD plants (e.g. by 2007 it had 26.5 million biogas plants installed [17]), articles written in Chinese are discarded by this criterion. Similarly occurs for publications from India [18]. This is significant constraint of the language criterion. However, as results will show, the selection of English articles in this work markedly contributes in bringing together a large sample size.

Keywords, logical connectors and combinations shown in Fig. 1 are used for the search of articles. The keywords aim to identify technology presence, agricultural sector and the metric of interest for this meta-analysis.

From the search results, titles and abstracts are used for a first filtering step. They are assessed to determine if studies report mono-digestion of dairy cattle manure and are primary sources (i.e. the latter corresponds to the fulfilment of the second criteria). Secondary sources are excluded to avoid duplicated values in the database. Therefore, review articles are rejected in this step. In addition, articles from a same author are verified to not repeat cases in the database.

From the titles and abstracts, articles available to the authors are collected (i.e. third criteria). The final filter step consists of selecting papers that include quantitative and empirical results (in text, tables or figures) of Y_{CH_4} for dairy cattle manure, thus, complying with the fourth criteria.

2.2. Database input

Y_{CH_4} are extracted from the selected articles to compile the database. Values of Y_{CH_4} are adapted so that all cases correspond to cumulative CH_4 production per kilogram of VS. Y_{CH_4} values are standardised to normal conditions (20 °C, 101.3 kPa) and given in "$m^3\ kg^{-1}$" (i.e. volume of methane produced per mass of VS fed to digester.

When articles report various Y_{CH_4} (e.g. profiles across time or measurements at different temperatures), multiple cases are logged into the database. To record differences between cases, secondary variables are also entered to the database (when available). Qualitative secondary variables are: author name, journal name, year of publication and location of study (country and/or continent). If the latter is not available, the location of the first author is used. For quantitative secondary variables, the first column of Table 1 shows those that are found most frequently in the literature for AD of dairy cattle manure, thus, used in this work. These variables specify AD operation conditions and chemical compositions of the undigested slurries (i.e. before entering the digester). The units of measurements for secondary quantitative variables are also presented in Table 1. If a variable is reported in different dimensions, underlying data from the original article is utilised to reconcile the units. If insufficient information is available when dimension conversion is required, the original units of measurements are recorded into the database, but the variable is excluded for numerical analysis.

To ensure that comparable experiments are combined, the results are presented separately according to type of digester (batch,

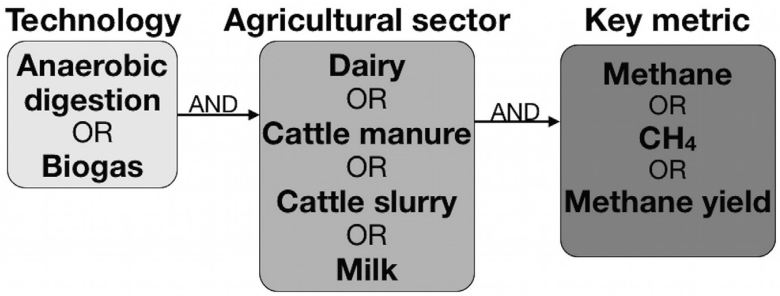

Fig. 1. Keywords and logical connectors used for search of articles for the database.

Table 1
Number of cases (fraction of cases[a]) reporting secondary quantitative variables according to digester type.

Secondary variables	[Units]	Batch	Continuous	Semi-continuous
Operation conditions				
Time[b]	[d]	1260 (97.0%)	326 (97.3%)	332 (64.7%)
Working volume	[m^3]	1286 (99.0%)	311 (92.8%)	513 (100%)
Temperature	[$^\circ C$]	1288 (99.1%)	291 (86.9%)	509 (99.2%)
Organic loading rate (OLR)	[$kg{\cdot}m^{-3}s^{-1}$]	n.a.	277 (82.7%)	377 (73.5%)
Chemical composition				
pH	n.a.	785 (60.4%)	115 (34.3%)	348 (67.8%)
Dry matter (DM)	[$kg{\cdot}kg^{-1}$]	1078 (83.0%)	232 (69.2%)	470 (91.6%)
Volatile solids (VS)	[$kg{\cdot}kg^{-1}$]	1063 (81.8%)	231 (69.0%)	505 (98.4%)
Chemical oxygen demand (COD)	[$kg{\cdot}m^{-3}$]	653 (50.3%)	183 (54.6%)	304 (59.3%)
Total Kjeldahl nitrogen (TKN)	[$kg{\cdot}m^{-3}$]	726 (55.9%)	159 (77.3%)	303 (59.1%)

[a] Fraction of cases that report secondary variable with respect to total cases of specific digester (in %) for that type of digester.
[b] Time for batch and hydraulic retention time (HRT) for continuous and semi-continuous digesters, respectively.

continuous and semi-continuous) and differences are discussed.

2.3. Uni-variate analysis

Having the variables standardised to the required unit of measurement, normality of the distributions is assessed by the Shapiro–Wilk test [19]. Inter-quartile ranges (IQRs) are reported to examine the dispersion of the variables of the database. Because of the expected non-normal distributions of Y_{CH_4}, Wilcoxon Signed Rank test [20] is used to evaluate significant differences between distributions.

In order to obtain novel effect sizes (i.e. Y_{CH_4}) that synthesise the literature, meta-analysis models were applied to the distributions from the database. Fixed- and random-effect models are applied given the mean (M_i), standard deviation (s_i) and sample size (N_i) for each case "i". The calculations undertaken to evaluate the new Y_{CH_4} from this work, are summarised in Table 2. The main difference between the models is that the fixed-effect model considers that each case corresponds to a measurement of effect size from a population with unique mean (μ). The estimation of μ is reported as M. For this model, the variance (V_i) is calculated with respect to μ. The random-effect model, in contrast, assumes a distribution of the population, hence multiple μ_i. To account for this, the model measures the variability of M_i with respect μ_i and of μ_i with respect to μ.

2.4. Multi-variate analysis

To assess the overall effect of the secondary variables in Table 1 over the Y_{CH_4}, correlations are examined by using the Spearman Rank test [21]. This test determines ($p < 0.05$) if the relation between variables is monotonic (non-specific to linear relations). This test is chosen because it is a robust method in the presence of outliers.

Table 2
Calculations for two meta-analysis models [52].

Steps for calculation	Fixed-effect	Random-effect
1. Variance of case "i"	$V_i = s_i^2/N$	
2. Initial weight of case "i"	$W_i = 1/V_i$	
2. Measure of heterogeneity	n.a.	$Q = \sum W_i M_i^2 - \frac{(\sum W_i M_i)^2}{\sum W_i}$
3. Std. deviation of sample	n.a	$T^2 = \frac{Q-(k-1)}{W_i - \sum W_i^2/\sum W_i}$
4. Variance of case "i"[a]	V_i	$V_i^* = V_i + T^2$
5. Weight of case "i"[a]	W_i	$W_i^* = 1/V_i^*$
6. Mean of sample	$M = \sum W_i M_i / \sum W_i$	$M^* = \sum W_i^* M_i / \sum W_i^*$
7. Variance of sample	$V_M = 1/\sum W_i$	$V_M = 1/\sum W_i^*$
8. Std. deviation	$\sqrt{V_M}$	$\sqrt{V_{M^*}}$
9. Confidence interval (CI)	$[M \mp z_{C/100}\sqrt{V_M}]$	$[M^* \mp z_{C/100}\sqrt{V_{M^*}}]$

[a] For the fixed-effect model, case variances and weights are calculated in Steps 1–2. k: number of cases; $z_{C/100}$: critical value for confidence interval of 95% (assumed 1.96 from Ref. [52]).

Principal component analysis is combined with cluster-analysis to study the underlying structure of the operation conditions and slurry compositions. This approach is adopted from Brambilla et al. [22]. As a first step, the most reported variables describing AD systems in the literature are identified to undergo principal component analysis. This technique is a unsupervised pattern-recognition method that allows reduction of dimensionality for multivariate datasets [23]. The dimension reduction allows visualisation of the database and synthesis of the data collected from the numerous cases in the database. Results of first and second principal components are presented by score plots.

As a second step, different groups of cases in the database are analysed by applying the most used clustering algorithm (k-means [24]) over the first two principal components. K-means clustering

depends on the initialisation, therefore, experiments are repeated over 100 initial random centroids for 2 to 10 clusters. The number of clusters is defined by selecting the best Davies-Bouldin Index (DB Index) score from the k-means output [24].

3. Results and discussion

This section presents the outcomes of the database development and statistical analyses in five subsections. The first subsection covers results from the application of filtering criteria, general overview of the typology of the papers that conform the database (e.g. year of publication and journal) and introduction to types of digester found in the literature. The second to fourth subsections report the Y_{CH_4} for batch, continuous and semi-continuous AD-systems, respectively. Y_{CH_4} and its relation to secondary variables are examined by uni- and multi-variate analysis for these different types of digesters. In the last subsection, the meta-analysis of maximum CH_4 potentials is discussed to improve those currently used by IPCC.

3.1. Database development

The search of papers using the word combination described in the methods section, outputs 888 publications. By assessing these papers against the selection criteria (i.e. peer-reviewed research articles in the field of interest), 115 articles (fraction equivalent to 13.0% of the initially found) are chosen to construct the database (publicly available on the website of the Energy and Power Group from the University of Oxford: epg.eng.ox.ac.uk/content/anaerobic-digestion). The causes for the high rejection, according to criteria, are shown in Fig. 2a.

Within the papers rejected by the first criterion, 352 correspond to other feedstock; 43 co-digest dairy cattle manure with other organic waste, excluding specific Y_{CH_4} values of interest; 38 are not research articles and are, for example, patents or book chapters and; 29 articles do not assess the production of CH_4 from AD, focusing on different technologies for manure-management systems (e.g. hydrogen production). All articles rejected by the second criteria correspond to review publications. The third criteria discards 14 articles that report titles and/or abstract in English, however, their main content was in a different language. In addition, 33 articles (from which 22 correspond to two journals), are not accessible to the authors. It should be noted that the database includes 45 scientific journals, thus, the third is not an important constraint. The fourth criteria rejects 178 papers that do not include numerical results on Y_{CH_4} of AD process and 31 that use modelled or assumed (i.e. non-empirical) Y_{CH_4} values.

Regarding secondary variables that describe the typology of the studies, the origin and year of publication of the 115 selected articles are shown in Figs. 2b and 3, respectively. It is observed that European and American work is dominant with 46 articles and 44 articles, respectively. For other continents markedly fewer articles are found to report empirical Y_{CH_4} values. The categorisation of cases conforming the database according to world region is of particular interest when comparing results from this meta-analysis to the default maximum Y_{CH_4} of the IPCC (see Section 3.5).

With respect to year of publication, the literature covering AD of dairy cattle manure is increasing (see Fig. 3). Results indicate that from 2007 to 2014 an average of 10 publication per year reported Y_{CH_4} of dairy cattle manure. Before 2007 only two articles per year

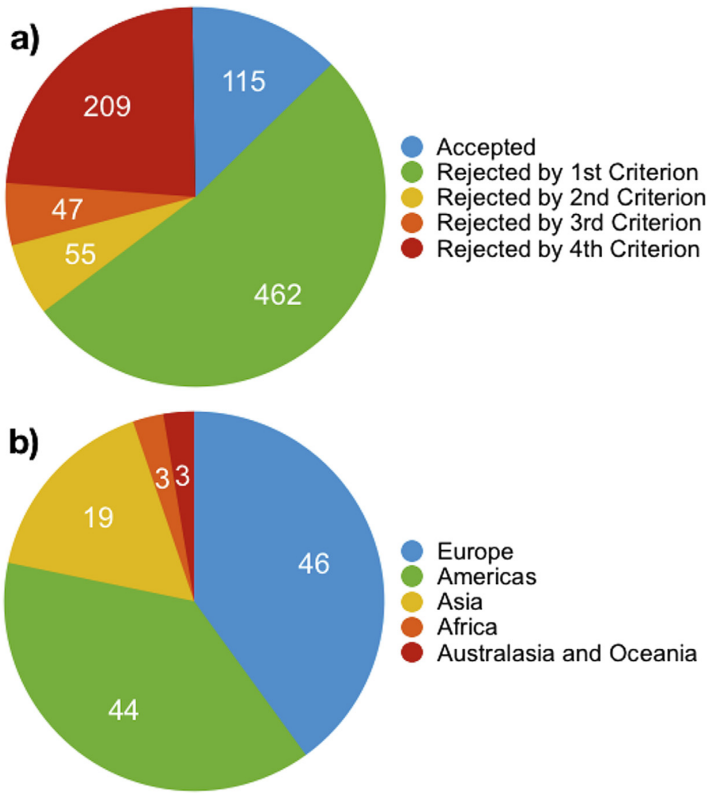

Fig. 2. Pie-charts for articles in the database classified according to: a) filtering criteria and; b) continent.

in average contain experimentally-measured Y_{CH_4} of this dairy waste. This increase is expected because, although AD is a mature technology (i.e. implemented for waste treatment since 1880s in Europe [2]), today it is being re-visited as a mean to reduce carbon emissions in the context of international agreements. In addition, it is observed that the increase in publication begins the same year of the global financial crisis (2007–8), which could be related to dairy farms seeking to diversify their production activities.

From the selected papers 2181 cases are extracted and conform the database. To avoid duplicates, repeated cases found in five of the articles [25–29] are entered once. 2161 of the cases in the database are selected from 95 articles. The remaining 20 articles report single cases from which 16 are identified as control experiments in co-digestion studies.

Table 1 summarises secondary quantitative variables in the database according to digester type. It is observed that the cases in the database report different operation conditions and composition variables, according to the objectives of each article. For example, for batch and semi-continuous cases the time and hydraulic retention time, respectively, are specified in less cases than the temperature. However, for continuous digesters the opposite occurs. In order to improve the consistency in reporting the performance of AD systems in the research literature, it is recommended to follow standardised protocols such as the EPA Guidelines [30]. In consequence, the implementation of standardised protocols to report specifications on AD systems (and composition of inlet substrate) would allow the selection of a larger sample size for the multi-variate analysis of this work.

As presented in Table 1, 2147 of the cases in the database can be classified as: batch, continuous or semi-continuous. The following sections analyse the Y_{CH_4} and secondary quantitative variables separated in these categories. It should be noted that cases which report Y_{CH_4} in units of measurements that cannot be reconciled to "$m^3\ kg^{-1}$", are omitted.

3.2. Batch digesters

Batch reactors are the most reported in the literature for the AD of dairy cattle manure with 1299 cases. From these, 1144 cases from 54 articles report Y_{CH_4} in the units of interest (or can be converted to it). Digesters operated as batch reactors are loaded at the beginning of the experiment (or cycle) and only biogas is extracted during the AD process. The yields from these digesters result in non-normal distribution (Shapiro's P = 3.06×10^{-33}), median 0.124 m^3kg^{-1} and inter-quartile range (IQR) 0.235 m^3kg^{-1}. Low median is due to the presence of cases at low operation times, where the AD process is only beginning. In fact, 19 articles report profiles of Y_{CH_4} against time, which indicate that multiple cases represent initial stages of CH_4 production.

To observe underlying structure of the Y_{CH_4} from batch digester, results from principal component analysis and their subsequent cluster analysis are shown in Fig. 4a–b for operational and composition variables, respectively. For the former, 42 studies report simultaneously Y_{CH_4}, digester volume, temperature and operation time, yielding 1104 cases. The first two principal components of Fig. 4a represent jointly the variance fraction of 61.6%. The first principal component is highly dependent on Y_{CH_4} and time of operation, while the contrary is observed for the second principal component.

The directions of the Y_{CH_4} and time of residency vectors are similar. Thus, high Y_{CH_4} are associated to longer digestion times, as expected. Higher correlation is also expected (Spearman's rho = 0.411, P-value = 2.2×10^{-16}), but not achieved due to the presence of overlapping profiles (i.e. see bi-plots of Y_{CH_4} over time in Supporting Material). Individual profiles of Y_{CH_4} are observed to reach asymptotic maximums. This is due to decrease in the available organic material to be anaerobically digested. As time advances in batch digesters, bacterial population growth is limited by the availability of nutrients and therefore, these profiles are associated to Monod's equation [31].

With respect to the digester volume, the Y_{CH4} vector shows opposite direction (with respect to the first principal component axis), which can be attributed to variables presenting poor (and negative) correlation (Spearman's rho = −0.135, P-value = 4.68×10^{-6}). It is unexpected that the temperature vector is opposite to the Y_{CH4}, with respect to the first principal component axis. Much work (e.g. Umetsu et al. [32] and Kaparaju et al. [33]) have reported an increase of Y_{CH4} with raise of temperature, however, the batch digesters collected in the database show a weak and inverse correlation (Spearman's rho = −0.263, P-value = 2.2×10^{-16}). This could be explained by batch digesters achieving maximum Y_{CH4} independently of operation temperature

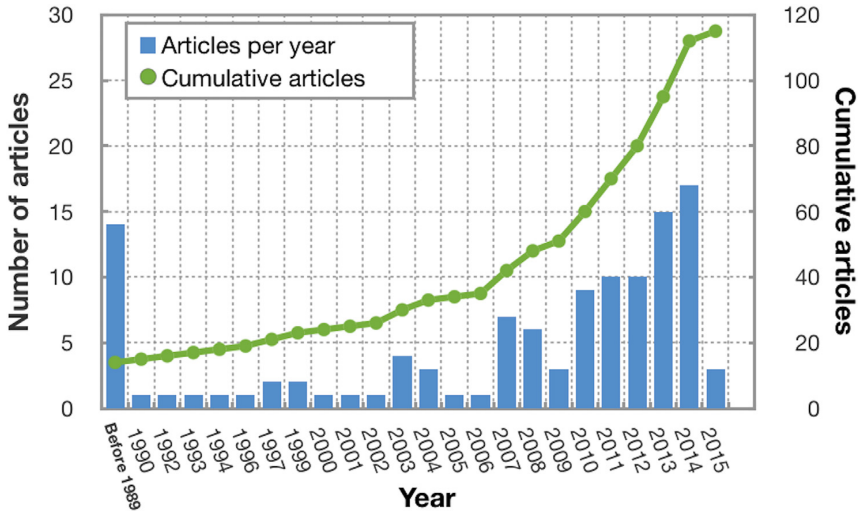

Fig. 3. Articles in the database according to year of publication.

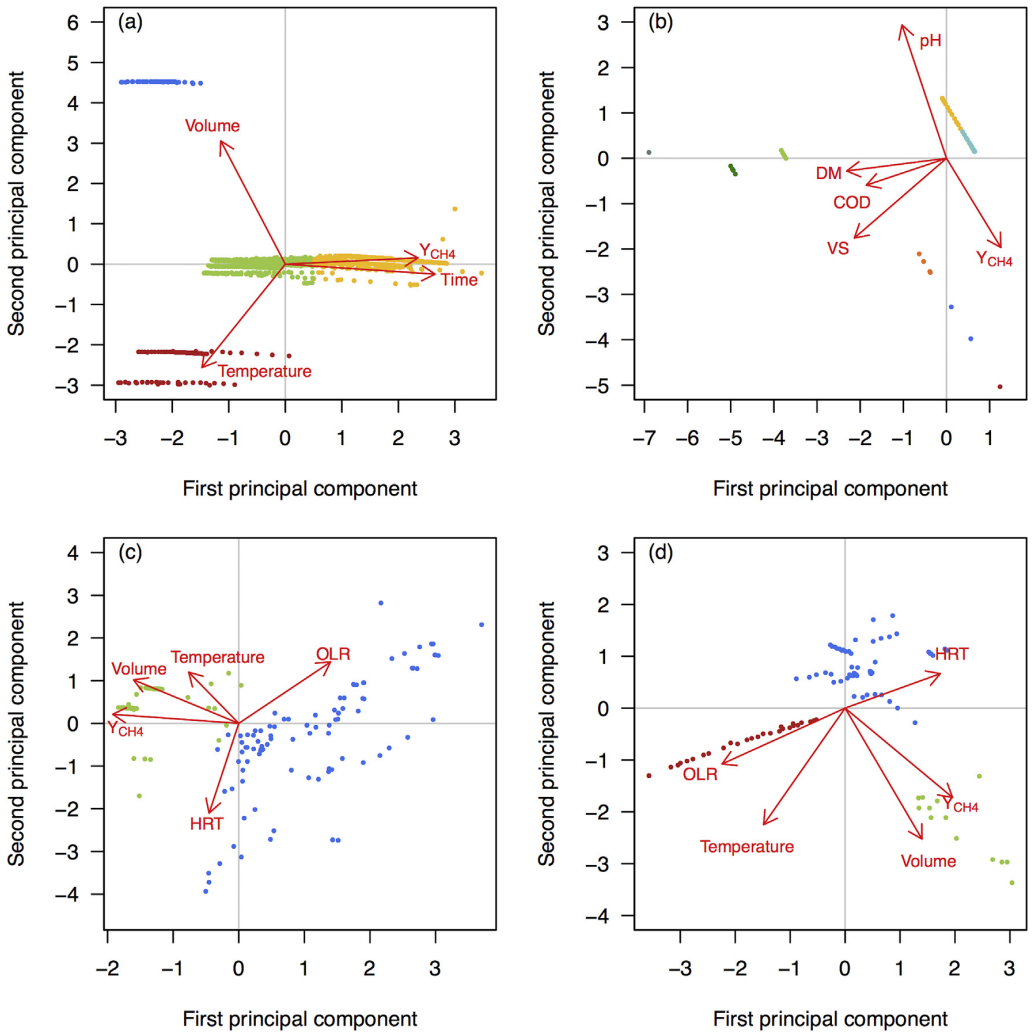

Fig. 4. K-means clusters for first and second principal components of Y_{CH_4} and: a) operational variables for batch; b) composition variables for batch; c) operational variables for continuous and; d) operational variables for semi-continuous digesters. Colours represent different clusters.

as long as enough retention time is allowed.

Four clusters result from the k-means algorithm (DB Index = 0.25), as shown in Fig. 4a. All clusters extend across the first principal component, while being less affected by the second principal component. The red cluster of Fig. 4a, corresponds to small digesters (0.30–2.0 *l*) operating at the highest temperatures for batch digesters in the database (50 °C and 55 °C). This cluster is conformed by 73 cases from seven articles. The blue cluster of Fig. 4a, represents large digesters (850 *l*) operating at 35 °C. This cluster of 34 cases is conformed by the data reported in only one article [34]. Both blue and red clusters correspond to the lower Y_{CH4} obtained for batch digesters with maximums 0.19 and 0.29 m^3kg^{-1}, respectively. The green and yellow clusters of Fig. 4a correspond to the most common values for digester volumes (0.1–5.0 *l*) and temperatures (25–38 °C). These clusters are conformed by 653 cases (from 31 articles) and 344 cases (from 24 articles), respectively. The main difference between these groups is the time of reaction. In particular, the green cluster represents experiments carried out at lower retention times (up to 69 *d*) than those in the yellow cluster (up to 160 *d*). In agreement with this, the centroid of the green cluster corresponds to a lower Y_{CH4} (~ 0.05 m^3kg^{-1}) than that of the yellow cluster (~0.32 m^3kg^{-1}). An interesting case in the yellow cluster is that of Zeeman et al. [35] which, although outside the main group of cases, shows high Y_{CH4} (0.11 m^3kg^{-1}) for low operation temperature (25 °C).

For secondary variables describing initial compositions, only 4 studies report simultaneously Y_{CH4}, pH, DM content, VS content and COD values, yielding 108 cases. The first two principal components of these variables are shown in Fig. 4b and represent the variance fraction of 74.8%. The variables that most affect the first principal component (variance fraction of 51.8%) are VS, DM and COD. These variables relate to the available organic matter to be digested, thus, their vectors in Fig. 4b are in similar direction. DM and COD present weak negative correlations with respect to Y_{CH4} resulting in Spearman's rho of −0.361 (P-value = 6.3×10^{-18}) and −0.261 for COD (P-value = 2.5×10^{-9}), respectively. VS shows a moderate monotonic function (Spearman's rho = −0.457 and P-value = 1.6×10^{-27}). The second principal component is more

affected by pH and Y_{CH4}. These vectors show a strong negatively correlation (Spearman's rho = −0.6960, P-value = 1.0×10^{-97}), which is reflected in the opposite direction of their vectors in Fig. 4b. This is an expected result because high pH content (e.g. ammonia in the slurry) can inhibit the methanogenic activity [36].

Eight clusters result (DB Index = 0.13) from the k-mean applied to the principal components of composition variables for batch digesters. The cases align in diagonals which could suggest that other cluster algorithms are preferable (e.g. density-based). The particular large amount of clusters for this bi-plot could be due to overlapping data in each diagonal which can affect the DB Index optimisation [37]. The lines which arise from the cases are parallel with slope value −1.56. In the case of the yellow and light blue clusters, these align having pH 6.8, DM mass fraction 1.9%, VS dry mass fraction 62.7% and COD 21 $kg{\cdot}m^{-3}$. The Y_{CH4} for these clusters ranges from 0 to 0.33 m^3kg^{-1}. Their intercept is 1.17. The orange, blue and red clusters (bottom right of Fig. 4b) are aligned with an intercept −3.09. The cases in these clusters, have fix value for pH (6.5), DM (mass fraction 2.3%), VS (dry mass fraction 74.7%) and COD (30.3 $kg{\cdot}m^{-3}$). The red cluster corresponds to a case from the work of Pandey et al. [38], who attribute the high results to differences in the inocula utilised (i.e. granular sludge from digester processing potato starch). However, it is considered to be an outlier in this meta-analysis because it reports 1.67 m^3kg^{-1} for Y_{CH4}, markedly exceeding the theoretical value (0.469 m^3kg^{-1} by Buswell's equation [39,5]).

The light green cluster has pH 6.9, DM mass fraction 5.3%, VS dry mass fraction 73.6% and COD 70.3 $kg{\cdot}m^{-3}$, with Y_{CH4} ranging from 0.26 to 0.33 m^3kg^{-1}. The parallel that crosses this cluster has an intercept −5.78. The final cluster corresponds to a single case from Pabon-Pereira [40] (dark green cluster in Fig. 4b). This has pH 6.9, DM mass fraction 10.5%, VS dry mass fraction 86.7% and COD 29.2 $kg\ m^{-3}$ (Y_{CH4} range = 0.14 to 0.23 $m^3\ kg^{-1}$). If the same slope was repeated for this case, the intercept is −10.6. Overall, an increase in the organic matter content of the slurry is observed according to the first principal component. However, the increase of these variables presents no correlation with the ranges of Y_{CH4} in each aligned group. This also is observed by the low correlations (i.e. Spearman rho values) between Y_{CH4} and DM, VS and COD.

3.3. Continuous digesters

Continuous and semi-continuous digesters are less found in the literature in comparison to batch systems. The Y_{CH4} distributions for these types of digesters are shown as green box-plots in Fig. 5. The orange box-plot correspond to distribution of Y_{CH4} which are jointly reported with N_i and s_i, thus, can be used for meta-analysis. The results from meta-analyses models are also presented in Fig. 5 (fixed-effect model: red circles and random-effect model: yellow circles).

The database includes 335 cases for continuous digesters (see Table 1), from which 331 (from 38 articles) are used because Y_{CH4} can be expressed as "$m^3\ kg^{-1}$". For these digesters, dairy cattle manure is fed continuously into the reactor while streams of biogas and digestate (products) are removed. Specific subcategories found for continuous digesters, according to reactor operation are (see Fig. 5): continuously-stirred tank reactors (CSTRs), fixed-film reactors, plug-flow reactors and up-flow anaerobic sludge blanket.

There are 241 cases (from 35 articles) in the database that report Y_{CH4} from CSTR. The distribution of all Y_{CH4} for this digester type (green boxplot in Fig. 5) is non-normal (Shapiro's P = 2.91×10^{-5}) and has a median 0.141 m^3kg^{-1}. As expected this distribution is significantly lower (Wilcox's P = 2.97×10^{-16}) from the B_0 of batch digesters. This is due to significantly lower hydraulic retention times (HRTs) in continuous digeseters compared to residency time in batch digesters (Wilcox's P < 2.2×10^{-16}). From this distribution, 12 cases report Y_{CH4} with N_i and s_i (orange box-plots in Fig. 5). This subgroup is non-significantly different from the distribution of all Y_{CH4} reported for CSTR (Wilcox's P = 0.143). Therefore, meta-analysis models applied over this subgroup are representative of the literature data. The meta-analyses models applied over the latter cases results in Ref. 0.179±0.001 m^3kg^{-1} for fixed-effects and 0.190±0.016 m^3kg^{-1} for random-effects.

Multi-variate analysis is carried out for CSTRs because these are the most numerous cases reported for continuous digesters. Score-plots for operation variables associated with CSTR digesters are shown in Fig. 4c. From 23 articles which report all operation variables of Table 1, 173 cases are extracted and used for principal component analysis. The first principal component of Fig. 4c corresponds to the variance fraction of 43.2% and is highly dependent on Y_{CH4}, OLR and volume. Contrary to batch digesters, the volume and temperature vectors are in the same direction as the Y_{CH4} with respect to the first principal component. These both variables show a strong positive correlation with respect to Y_{CH4} (Spearman's rho = 0.71 for volume and; rho = 0.69 for temperature). The second principal component represents the variance fraction of 26.8% and is mostly affected by the HRT and OLR. A positive moderate correlation (Spearman's rho = 0.435, P-value: 2.7×10^{-16}) is found, between the Y_{CH4} and HRT. At lower HRT (<40 d), Y_{CH4} exhibits a larger range (0.002–0.333 m^3kg^{-1}), while presenting more stable values thereafter. These observations are similar to the asymptotic profiles for Y_{CH4} and retention time in batch digesters (see biplots of Supporting Material). With respect to the OLR, the Y_{CH4} vector is in opposite direction having a Spearman's rho −0.45 (P-value = 5.2×10^{-11}). This is an expected result because increasing OLR (i.e. lowering the retention times) can wash-out bacterial cultures reducing the digester performance [41].

Two clusters are output from the application of k-means to the principal components of Fig. 4c (DB Index = 0.37). The blue cluster is conformed by 95 cases from 16 articles. This cluster groups cases in a larger range of HRT (1–128 d) and OLR (0.12–34.4 $kg{\cdot}m^{-3}d^{-1}$), compared to the green cluster (HRT: 8–69 d and; OLR: 0.12 to 6.6 $kg{\cdot}m^{-3}d^{-1}$). The digesters operating within the blue cluster also have lower temperatures (10–55 °C) and result in lower Y_{CH4} (maximum 0.220 m^3kg^{-1}). For the green cluster, 78 cases (from 11 articles) are observed in Fig. 4c. The Y_{CH4} from cases in this cluster range from 0.115 to 0.333 m^3kg^{-1}. In general, these cases operate at higher temperatures (35–55 °C) and in larger digesters (up to 1500 l) than those in the blue cluster (up to 230 l).

With regards to the composition variables (see Table 1), it is found that there are insufficient cases of CSTR digesters in the literature for dairy cattle manure to perform principal component analysis. However, there are enough cases for bi-variate analysis between Y_{CH4} and each composition variable (see Supplementary Material).

The variables most correlated with Y_{CH_4} are found to be the pH (Spearman's rho = −0.685, P-value = 2.0×10^{-15}) and nitrogen content (i.e. TKN, Spearman's rho = 0.605, P-value = 7.8×10^{-13}) of untreated manure. The strong correlation between pH and Y_{CH_4} is in agreement with the findings for batch digesters. However, high correlation between TKN and Y_{CH_4} is unexpected because higher nitrogen in ammonia has been reported to inhibit AD [36]. For variables related to organic material in the input slurry, only weak correlations are found with respect to Y_{CH_4}: DM (Spearman's rho = 0.188, P-value = 0.018), VS (Spearman's rho = −0.338, P-value: 2.5×10^{-5}) and COD (Spearman's rho = 0.48, P-value = 1.9×10^{-8}).

Fixed-film reactors are the second most numerous continuous digesters collected in the database (N = 81, from five articles). The Y_{CH_4} for this digester type (green boxplot in Fig. 5) is not normally

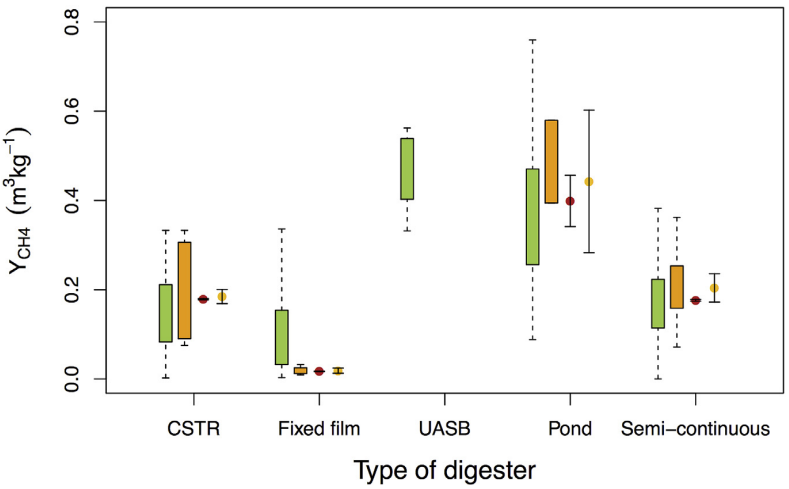

Fig. 5. Y_{CH_4} from different digester types found in the literature. Green box-plot: all Y_{CH4}; orange box-plot: Y_{CH_4} which are reported together with s_i and N_i; red circles: results from fixed-effect model and; yellow circles: results from random-effect model. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

distributed (Shapiro's P = 3.3×10^{-14}) and has median 0.103 m^3kg^{-1}. From these Y_{CH_4}, eight cases from the work of Lo et al. [27] are the only to report N_i and s_i (orange box-plot Fig. 5). The fixed-effect meta-analysis model applied over these eight cases results in Y_{CH4} mean of 0.017±0.001 m^3kg^{-1}. For the random-effect model, the mean Y_{CH_4} is 0.018±0.006 m^3kg^{-1}. However, the means obtained by meta-analysis should be used with caution as the distribution of the eight cases in the subgroup is significantly different (Wilcox's P = 3.94×10^{-4}) from the Y_{CH_4} in the 81 cases for all plug-flow digesters in the database.

For the remaining continuous digesters, insufficient cases are collected for the application of meta-analysis models. A single case is found to report experimental Y_{CH_4} of dairy cattle manure in units of interest for plug-flow reactors (PFRs, N = 1). Thus, the latter is ommited from Fig. 5. For up-flow anaerobic sludge blanket (UASB) digesters, there are eight cases which report experimental Y_{CH_4} and correspond to the work of Rico et al. [42]. The distribution of these digesters is normal (Shapiro's P = 0.58) and has median 0.484 m^3kg^{-1} (see Fig. 5). The mean of these cases, exceeds the theoretical value (0.469 m^3kg^{-1} by Buswell's equation [39,5]). However, they do not present a significant difference (Wilcox's P-value = 1). Therefore, differences in Y_{CH_4} could be attributed to chemical compositions or longer biomass retention time (i.e. bacterial consortia and organic substrate).

3.4. Semi-continuous digesters

For semi-continuous digesters the input and/or output of digesters are discontinuous. There are 513 of these cases identified in this work (Table 1) and 443 of them (from 26 studies) are used.

One type of semi-continuous digester corresponds to AD ponds. These usually accumulate manure periodically but are discharged sporadically (e.g. when the produced bio-fertiliser is needed). There are 96 cases identified in the database for lagoon digesters from three articles. The high variability in loading/discharging rates and operation temperature results in a large IQR of 0.214 m^3kg^{-1} (see Fig. 5). The Y_{CH_4} for lagoon digesters presents a non-normal distribution (Shapiro's P = 2.84×10^{-6}) and median 0.345 m^3kg^{-1}. This median is not significantly different than the theoretical Y_{CH4} (Wilcox's P-value = 0.422). The higher Y_{CH_4} of the lagoon digesters distribution, has been attributed by other authors [43–45] to degradation of accumulated organic matter on the bottom of ponds. Thus, more VS are available to be converted to CH_4, than the measured at the inlet to the AD ponds. From the above, it is suggested that for future work, measurements of VS fed to lagoon digesters are standardised.

From the 96 cases, only two (from two articles [43,44]) can be used for meta-analysis models (orange box-plot in Fig. 5). The Y_{CH_4} of these cases is non-significantly different from the distribution of all lagoon digesters (Wilcox's P = 0.297). The fixed effect model results in a mean 0.400±0.057 m^3kg^{-1} (see red circles of Fig. 5). This is in great agreement with the case from Safley et al. [43], because the sample size of Y_{CH_4} from that case is 93, whereas, the case from Park et al. [44] has a sample size of seven. For the random-effect model a mean of 0.440±0.160 m^3kg^{-1} is obtained.

There are 347 cases in the database (from 23 articles) that include Y_{CH_4} from other non-specified semi-continuous digesters. These cases are grouped and also shown in Fig. 5. Their distribution is non-normal (Shapiro's P < 2.2×10^{-16}) with median 0.173 m^3kg^{-1}. A subgroup of 27 of these cases (from five articles) are utilised for meta-analysis models. For the fixed-effect model a mean 0.176±0.001 m^3kg^{-1} is obtained and for the random-effect model 0.204±0.032 m^3kg^{-1}.

There are 98 cases from 15 articles in the database that specify all operation variables of Table 1 and Y_{CH_4}, for semi-continuous digesters (non-specified, i.e. anaerobic digesters labelled as ponds are excluded). These cases undergo principal component analysis and the resulting score-plots are presented in Fig. 4d. With the exception of the volume vector, it is observed that according to the variables directions (red arrows of Fig. 4d), the semi-continuous digesters are in closer agreement to the batch digesters than the continuous digesters. In fact, it is observed that the studies utilising semi-continuous digesters are classified as such because of the feeding procedure, however, the overview of many systems corresponds to dynamic states, rather than stationary (i.e. continuously operated digesters).

The first principal component represents the variance fraction of 43.7% and the second 27.8%. The first principal component is highly dependent on OLR and Y_{CH_4} and exhibit a weak correlation (Spearman's rho = −0.262; P-value = 1.0×10^{-5}). The second principal component is mostly affected by the volume and temperature. The direction of the Y_{CH_4} vector is opposite (along the first

principal component axis) to the digester temperature. This shows a weak and inverse correlation which is further indicated by the Spearman's rho value −0.162 (P-value = 2.6×10^{-3}). The volume of digesters also presents a weak negative correlation to the Y_{CH_4} (Spearman's rho = −0.250; P-value = 2.5×10^{-6}). Regarding the HRT and Y_{CH_4} vectors, these have similar direction, with respect to the first principal component. These variables exhibit a moderate positive correlation (Spearman's rho = 0.242, P-value = 5.1×10^{-6}) and follow similar patterns than those observed for batch digester (see Supporting Material).

Three clusters are found (DBI = 0.33) for semi-continuous digesters and presented in Fig. 4d. The red cluster comprises 28 cases from three different articles of Lo et al. (see online database). It is observed that all cases in the cluster operate at thermophilic conditions (55 °C) and volume 3 *l*. The differences in principal components for this cluster are due to changes in OLR (2.07–35 $kg{\cdot}m^{-3}d^{-1}$) and HRT (1–15 *d*). The Y_{CH_4} range is the lowest among those in Fig. 4d, from 0.011 to 0.161 m^3kg^{-1}. The blue cluster comprises 57 cases from 13 articles. These cases exhibit higher Y_{CH_4} than the red cluster, with centroid at approximately 0.262 m^3kg^{-1}. This is attributed to higher HRT (1–60 *d*) and, in turns, lower OLR (0.4–8.87 $kg{\cdot}m^{-3}d^{-1}$). The semi-continuous digesters of the blue cluster operate at the lowest range of temperatures (20–37 °C), which is consistent with psychrophilic and mesophilic conditions. The volumes of the digesters in this cluster covers a large range (between 0.04 L and 300 L), suggesting that this operation variable is not affecting the principal components describing AD performance. The green cluster of Fig. 4d corresponds to 13 cases from two articles. The Y_{CH_4} are the highest found for the semi-continous digesters, with centroid at approximately 0.77 m^3kg^{-1}. This exceeds batch performances, which could suggest the presence of lagoons which, as discussed previously (see Fig. 5), have been identified to have higher performance due organic material accumulated in the bottom of digesters. The OLR (0.5–2.9 $kg{\cdot}m^{-3}d^{-1}$) and HRT (10–20 *d*) is not markedly different from the other clusters. The temperatures of the digesters in the green cluster are between 35 and 45 °C (i.e. mesophilic conditions). This suggests that temperature is a key factor in the separation of the three clusters.

As for continuous digesters, there are insufficient cases of semi-continuous reactors in the database to perform principal component analysis over composition variables of interest. Considering bi-variate analysis some moderate correlations can be found between Y_{CH_4} and secondary variables describing initial composition of the dairy cattle manure. The strongest correlations between Y_{CH_4} and a secondary variable is with COD (Spearman's rho = −0.542, P-value = 2.2×10^{-16}) and TKN (Spearman's rho = −0.485, P-value = 1.6×10^{-13}). This interesting result supports the well-known work of Angelidaki et al. [36], which reports that an increase in ammonia (containing nitrogen) can suppress CH_4 production in AD of livestock waste. However, it should be noted that Sterling et al. [46] have reported that only large increases in ammonia can inhibit AD, while gradual increases could enhance the CH_4. The latter is not evidenced in the results of this work. The other composition variables of interest are less correlated or weakly correlated to Y_{CH_4}: pH (Spearman's rho = −0.060, P-value = 0.41), DM (Spearman's rho = −0.354, P-value = 2.8×10^{-9}) and VS (Spearman's rho = −0.284, P-value = 3.5×10^{-6}).

3.5. Maximum methane potentials

This section considers the experimental Y_{CH_4} (B_0) of dairy cattle manure (i.e. obtained from batch essays). These values are interesting to study separately from other cases, because they can be utilised to quantify energy output and environmental benefits of AD systems. Much work is based on the methodology described by Owen et al. [47] to experimentally determine B_0. However, it should be noted that there is little agreement in the use of this or any standard protocol [48]. This results in difficulties to identify the differences between AD systems. In particular, an essential issue to consider when comparing B_0 from different AD systems is to report the temperature and pressure at which the experiments are carried out (i.e. as reported by Marti-Herrero et al. [49]).

The B_0 from the database are used to obtain novel effect sizes by meta-analysis models. Results are compared against the B_0 default values from the IPCC 2006 methodology [15], in accordance to the world regions defined in the latter.

The IPCC Guidelines provide two default values of B_0 from AD of dairy cattle manure. For Europe, Oceania and North America the default B_0 is 0.24 m^3kg^{-1} and is based on the work of Morris 1976 [50,15]. For other regions of the world the default value 0.13 m^3kg^{-1} is based on the work of Safley et al. (1992, [51,15]). A revision of these values is needed because they only consider a reduced amount of literature (from 1976 to 1992) and exclude the last thirteen years of research which, according to the findings of this work (see Fig. 3), accounts for the fraction of 87.5% of published articles in the field. Furthermore, the B_0 of the original work is based on the diet of dairy cattle which are also in need of update.

The B_0 values from the IPCC are shown as blue circles in Fig. 6. It should be noted that these default Y_{CH4} are not considered in the subgroup for meta-analysis because the original sources [51,50] are published in books (i.e. not research articles as required by the first criterion).

From the database, 799 cases (from 42 articles) are identified as either biochemical potential tests or maximum Y_{CH4} determined in similar batch conditions (i.e. measuring cumulative CH_4 production until no increase is observed). For articles reporting Y_{CH_4} against time, the maximum yield of each profile is extracted. In the 42 articles, 143 cases are identified as B_0. The distributions of B_0 are represented by the green box-plots of Fig. 6. For all the regions defined in the IPCC Guidelines experimental results (in comparable units of measurements) are found for B_0 (see number of cases in Table 3), except Oceania and Latin America (i.e. omitted in Fig. 6). As expected, the results for B_0 are significantly higher than the Y_{CH_4} distribution for all batch cases (Wilcox's P = 9.67×10^{-10}).

It is observed in Fig. 6, that the B_0 values from the IPCC with corresponding error bars of 15%, are within the distribution of B_0 found in the database. In fact, only the region comprising Asia, Middle East and Indian Subcontinent shows a significant difference (Wilcox's P-values in Table 3) in B_0 distribution with respect to the IPCC value. This could be attributed to developments in feeding of dairy cattle in that region, because the IPCC default values are based on the dairy diets prior to 1992 [51]). Similar observations are found for African experiments (i.e. the fraction of cases which is greater than the default IPCC value is 60%). However, the sample size is not large enough (N = 5) to prove significant difference. Europe and North America present the largest samples of B_0 (see Table 3), as expected from the origin of the articles identified in Section 3.1.

Although most regional B_0 values are non-significantly different from those in the database from the IPCC default values, results indicate that different means and error bars would better represent the findings of the literature. Therefore novel effect sizes and confidence intervals are examined by applying fixed- and random-effect models of meta-analysis.

The meta-analysis models require cases which report B_0 together with specific N_i and s_i. For this 53 cases from 21 studies are selected. The distributions of this subgroup of B_0 is shown in Fig. 6 (orange box-plots). Results show that the means of these distribution differ with the IPCC default value between 0.01 and 0.13 m^3kg^{-1}. In particular, the subgroup distributions for the Asia,

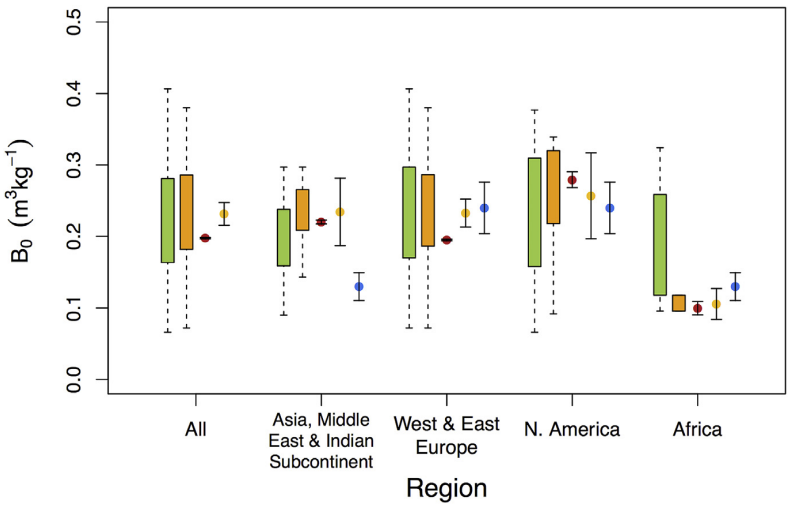

Fig. 6. Maximum Y_{CH_4} (B_0) from batch tests according to regions. Green box-plot: all B_0 in the developed database; orange box-plot: B_0 in database which are reported together with s_i and N_i; red circles: results from fixed-effect model; yellow circles: results from random-effect model and; blue circles: IPCC default values (IPCC 2006, [15]). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
Wilcoxon's P-values between default B_0 values from IPCC and B_0 from database of this work, according to region of the world.

B_0 group	Asia, Middle East & Indian Subcontinent	West & East Europe	North America	Africa
All B_0 in database	0.023 (38)	1.000 (76)	0.908 (24)	0.571 (5)
Subgroup B_0[a]	0.033 (7)	0.916 (36)	0.474 (8)	0.400 (2)

[a] Subgroup of "All B_0" which report specific N_i and s_i, thus, can be used for meta-analysis models. Numbers of cases of B_0 in database in parenthesis.

Middle East & Indian Subcontinent Region is again the only significantly different ($p < 0.05$) from the IPCC value (i.e. as for the green box-plot of Fig. 6, discussed previously).

The results of fixed-effect and random-effect models are also shown in Fig. 6 in red and yellow circles, respectively. The means obtained by the random-effect models are found to be in best agreement with the distributions of the subgroup of B_0 cases (i.e. case reporting N_i and s_i), with differences from 0.001 to 0.026 m^3kg^{-1}. The means for this model are 0.230±0.016, 0.230±0.047, 0.230±0.020, 0.260±0.060 and 0.110±0.022 m^3kg^{-1} for all regions, Asia/Middle East & Indian Subcontinent, West/East Europe, North America and Africa, respectively. For the fixed-effect model the means are 0.198±0.001, 0.220±0.003, 0.195±0.001, 0.280±0.011, 0.100±0.009 m^3kg^{-1}, for the same regions mentioned above, respectively. This results in differences from 0.010 to 0.040 m^3kg^{-1} between the means of the fixed-effect model and those of the subgroup of B_0 cases. The random-effect model is expected to show better results because it assumes a distribution of B_0, rather than a fix value. This is more representative of the high heterogeneity of the samples, which arise from different experimental set-ups. Therefore, it is preferable to adopt the results of B_0 from the random-effect model to estimate the potential CH_4 production from AD of dairy manure.

Compared to the IPCC default values, the random-effect meta-analysis model provides more robust values of B_0 (i.e. based on larger sample size, more updated cases and considers the heterogeneity of cases). Therefore, the means and confidence intervals of B_0 obtained by this model are suggested to replace those in the current IPCC Guidelines. Furthermore, it is recommended to apply this meta-analysis model for the estimation of B_0 of other digestible feedstock. This would provide better IPCC-default B_0 values, with stronger evidence-base (i.e. larger sample integration).

4. Conclusions

This work presents a meta-analysis of methane yield of dairy cattle manure. A novel database is compiled from 115 selected articles (2181 cases). The systematic review of the literature shows that the report of operation conditions and slurry composition does not generally follow standardised protocols. The latter are strongly recommended in order to provide insights of differences in performance of AD systems.

Meta-analysis models are applied over the database according to digester type (batch, continuous or semi-continuous). This methodology enables numerical combination and synthesis of experimental results to date.

Multi-variate analysis identifies clusters for Y_{CH_4} and operation conditions (i.e. temperature, volume, time/HRT, OLR) or feedstock composition (i.e. pH, DM, VS, COD, TKN). This can contribute to the construction of AD scenarios by providing ranges of variables that are commonly grouped.

Meta-analysis applied over maximum Y_{CH_4} is a reliable form to correct the out-of-date IPCC default values. This method has a greater sample size (i.e. based on more articles than the current IPCC Guidelines). Consequently, this work can contribute to more robust estimates of energy production and greenhouse gas mitigation of AD systems in the dairy sector.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.biombioe.2016.01.012.

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Meta-Analysis of Greenhouse Gas Emissions from Anaerobic Digestion Processes in Dairy Farms

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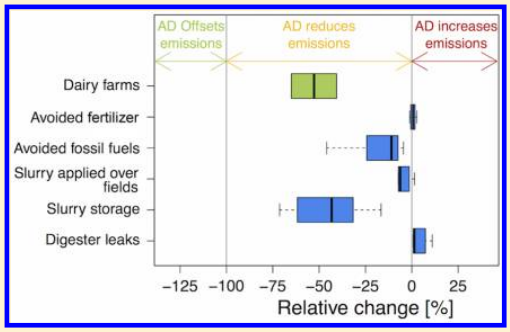
Supporting Information

ABSTRACT: This meta-analysis quantifies the changes in greenhouse gas (GHG) emissions from dairy farms, caused by anaerobically digesting (AD) cattle manure. As this is a novel quantifiable synthesis of the literature, a database of GHG emissions from dairy farms is created. Each case in the database consists of a baseline (reference with no AD system) and an AD scenario. To enable interstudy comparison, emissions are normalized by calculating relative changes (RCs). The distributions of RCs are reported by specific GHGs and operation units. Nonparametric tests are applied to the RCs in order to identify a statistical difference of AD with respect to baseline scenarios (Wilcoxon rank test), correlations (Spearman test), and best estimation for changes in emissions (Kernel density distribution estimator). From 749 studies identified, 30 papers yield 89 independent cases. The median reductions in emissions from the baseline scenarios, according to operation units, are −43.2% (n.s.) for storage, −6.3% for field application of slurries, −11.0% for offset of energy from fossil fuel, and +0.4% (n.s.) for offset of inorganic fertilizers. The leaks from digesters are found to significantly increase the emissions from baseline scenarios (median = +1.4%).



INTRODUCTION

The agricultural sector is responsible for 37% of the global CH_4 emissions and 65% of the global N_2O emissions.[1] Farms with livestock have particularly high emissions due to enteric fermentation and fugitive greenhouse gases (GHGs) from stored and land-applied manure. Therefore, the development of methodologies to estimate the carbon footprint reduction of various farming technologies is of great relevance. In particular, dairy farming has been reported to contribute 4% of global anthropogenic GHG emissions.[2] Anaerobic digestion (AD) is a technology that holds the potential to mitigate these emissions.

The AD process consists of biochemical reactions (typical operating temperatures: 30−35 °C), that convert volatile solids in organic matter to biogas and digestate. The biogas is a mixture of CH_4 (typical volumetric composition: 65%[3]) and CO_2. Traces (<2 vol %) of other gases such as hydrogen, hydrogen sulfide, and water are also present.[3] The combustion of the CH_4 in the biogas releases carbon neutral CO_2 and usable energy.

The solid residue from the AD process, the digestate, can be applied over crop fields replacing inorganic fertilizers or untreated manure. Digestate can lower emissions by the offset of embodied carbon in inorganic fertilizers.[4,5] Additionally, the AD has been reported to enhance the fertilizer value of cattle manure because nutrients in the digestate are more suitable for crop uptake.[6−8] To reduce the carbon footprint of milk-producing farms, AD has a triple benefit of: (i) converting high global warming CH_4 to CO_2; (ii) generating energy that substitutes fossil fuels; and (iii) producing digestate that replaces mineral fertilizers. Consequently, implementing AD offers farmers a management system for their excess nutrients (i.e., nitrogen and carbon species) and can create profitable products.[9−11]

Much work in the literature[5,12−18] evaluates the carbon footprint in dairy farms based on the Intergovernmental Panel on Climate Change (IPCC) guidelines[19] and/or in the context of life-cycle assessments (LCAs). The results vary widely because of differences in system boundaries (e.g., cradle-to-grave, cradle-to-gate), functional units ([f.u.], e.g., emissions per [$liter_{milk}$], [ton_{manure}], [$ha_{application}$]), and assumptions. It is therefore difficult to compare multiple studies. The meta-analysis approach can systematically review and integrate quantitative results in the literature.

A meta-analysis increases the effective sample size by combining results, hence improving the accuracy of GHG

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emissions estimates and allowing the analysis and identification of sources of variation. In the bioenergy sector, meta-analysis has been used to quantify GHG emissions,[20−22] but to our knowledge no such study has covered AD in dairy farms. The review literature on AD for agricultural purposes is predominantly qualitative in nature.[6,8,23−25] The only meta-analysis in this sector concentrated on identifying microbial communities.[26]

Meta-analysis requires an appropriate database of the literature. Life-cycle inventory databases (e.g., Ecoinvent, EioLCA) utilize pre-established parameters (e.g., AD technology, operation temperature, methane yields). Additionally, the output values from these sources are used without reporting confidence intervals. Because there is no pre-existing specific database for the carbon footprint of AD on dairy farms, one is compiled by using the relevant information in selected research papers. To enable the combination of results from different studies, emissions are standardized and relative changes (RCs) in emissions are used as the metric.

Key aspects of the developed database using the methodology presented in this work are described in the Results and Discussion Section. The distributions of RCs are categorized by gas type, relevant qualitative variables, and farm operation units to analyze trends and sources of differences. Correlations and level of significance between scenarios are examined, and the best estimates for the RCs are presented.

METHODOLOGY

The methodology first presents the database creation by systematically filtering articles from the academic literature and extracting relevant information from them according to the sources of emissions. Second, the RCs calculations are presented as the method to standardize the emissions in the literature. Finally, to statistically analyze the distribution of RCs, nonparametric tests are introduced.

Article Selection. The database is developed by a systematic selection of articles to ensure reproducibility. Selected articles meet the following criteria:

(i) peer-reviewed scientific publication in the field of study;
(ii) primary source; and
(iii) inclusion of numerical data of GHG emissions for dairy farms with and without an AD process.

The first criteria is established to obtain high-quality results in the academic literature. The second criteria is applied to avoid duplicates and, consequently, review articles are excluded. The third criteria is introduced to ensure that numerical results are relevant for this meta-analysis.

The ISI Web of Knowledge database[27] is used because it mainly contains peer-reviewed journals. To search for articles on this platform, all publication years and types are selected and the language is set to English. Keywords and logical connector represented in Figure 1 are used as topic input. The keywords aim to identify technology presence, agricultural sector studied, and emission indicators of interest for this meta-analysis. From the search results, titles and abstracts are extracted and first filtered according to the criteria. A final selection step is applied by assessing the complete papers against the criteria. The papers selected include quantitative results that allow the evaluation of changes in GHG emissions from baseline(s) to AD scenario(s). Where articles reported more than two scenarios, multiple cases are entered into the database. A case is defined as the emissions from different activities (operation units) from baseline and related AD scenarios, determined under the same conditions (e.g., a study of the effect of storage temperature over GHG emissions from untreated and digested slurry would consider each temperature as a case). Cases may include multiple or single operation units. In order to identify sources of variation of the cases, additional variables are recorded in the database (details in SI−II, Supporting Information).

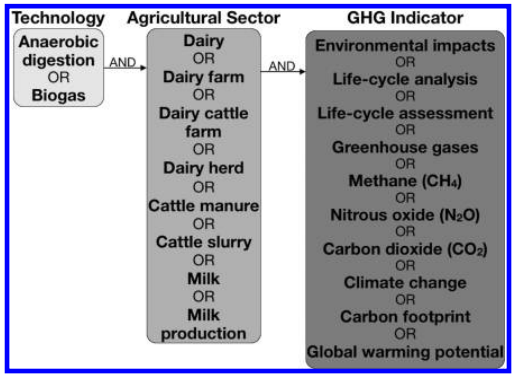

Figure 1. Scheme of the systematic search of studies in the literature by a combination of logical connectors and keywords.

Standardization of Emissions. The selected articles report emissions of different GHGs per functional unit [f.u.] (GHG_i, i = CH_4, N_2O, or CO_2). To standardize the emissions, these are expressed as carbon dioxide equivalents (CO_{2e}) and calculated, as follows:

$$\text{GHG}\ [\text{kg}_{\text{CO}_{2e}}/\text{f.u.}] = \sum_i \text{GWP}_i \times \text{GHG}_i \quad (1)$$

where GWP_i in $[kg_{CO_{2e}} \cdot kg_i^{-1}]$ corresponds to the global warming potential for the emitted gas "i". According to IPCC 2006,[19] GWP_{CH_4} is 25 $[kg_{CO_{2e}} \cdot kg_{CH_4}^{-1}]$, GWP_{N_2O} is 298 $[kg_{CO_{2e}} \cdot kg_{N_2O}^{-1}]$, and GWP_{CO_2} is 1 $[kg_{CO_{2e}} \cdot kg_{CO_2}^{-1}]$, for a 100 year time horizon. If a study used different values for GWPs, they are corrected to these specified values. When articles reported different [f.u.] (e.g., emissions per $[ton_{manure}]$ for storage and emissions per [ha] for field application[28]), the emissions were reconciled by using underlying data.

Scenarios and Operation Units. The database comprises emissions that vary widely, in terms of scope and boundaries. To enable comparison between cases, two scenarios and seven operation units are defined (see Figure 2). The baseline

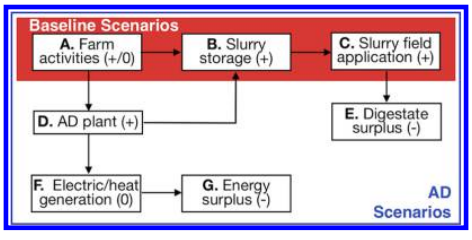

Figure 2. Block diagram of material paths for the baseline scenarios (red box) and AD scenario (blue box) through operation unit (black boxes). The signs in the operation units indicate if the process: directly emits GHGs ("+"); offsets GHGs outside the scenario boundaries ("−"); or has carbon neutral emissions ("0").

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Environ. Sci. Technol. 2015, 49, 5211−5219

scenarios (red box) represent typical farm activities and are used as a reference to estimate the changes in emissions. Standardized baselines are conformed by the emissions from three operation units: storage and field application of untreated manure and energy consumption for dairy activities. The AD scenarios (blue box) take into account the AD operation plant, power generation, and digestate management.

There are indirect emissions related to the milking and farm operation unit (block A) which form part of both scenarios. In the baselines, energy is imported from different sources (e.g., electricity grid, on-site combustion of fossil fuels), depending on the article. In this work, the emissions from energy requirements are estimated on the basis of the electricity generated from natural gas with emission factor 0.1836 $kgCO_{2e}/kWh$.[29] For cases which indicated the consumption of other fossil fuels in dairy activities, the energy requirements were calculated using heating values.[30] Thereafter, the energy was assumed to be delivered as electricity derived from natural gas, with the above emission factor. In the AD scenarios, additional energy is required for the operation of pumps, mixing, and heating of the digester (block D); electricity and/or thermal power is generated (block F), and surplus energy can be exported (block G). It is assumed that energy produced and used for farm activities (blocks A and D) is carbon neutral. The surplus energy is assumed to be exported replacing electricity from natural gas (block G), thus having negative emissions. If papers do not report surplus energy for the AD scenario, these are calculated by energy balances. An example of this calculation can be found in the Supporting Information (SI−I). Conversely, if not enough energy is produced in the AD scenario to cover milking, farm activities, and/or digester requirements, it is assumed to be imported as for the baseline scenario. A final indirect emission source is the operation unit describing digestate surplus for export (block E). This can also allow negative emissions due to the replacement of high embodied-carbon mineral fertilizers.[4]

Direct emissions arise from storage (block B) and field application (block C) of slurries in both scenarios. The emissions from these operation units are used to determine changes in GHG emissions when replacing untreated slurry by digestate. Direct missions from the digester (leaks) are also accounted (block D).

Transport is not considered because data associated with this farm activity can be found in the literature only for individual scenarios. For example, Fantin et al.[31] included transport emissions for a typical baseline dairy farm, and the work by Poeschl et al.[32] reports transport emissions from an AD scenario. Studies that compare transport emissions from both scenarios are expected to be scarce because the distances from farm to fields are irrespective of the slurry type (untreated or digested).

Relative Changes. Relative change (RC) is chosen as a key metric because response ratios have been identified as a successful mean to quantify ecological indicators in meta-analysis.[33,34] RC reconciles differences in [f.u.] of the original articles, by nondimensionalizing the changes in emissions between baselines and AD scenarios.

Two RCs are used in this work, and examples of their calculation can be found in the Supporting Information (SI−I). The first RC corresponds to the change in emissions of scenarios or operation units, with respect to emissions from standardized baseline scenarios (GHG_B). These relative changes are denoted "$RC_{GHG,Op}$" and are calculated as follows:

$$RC_{GHG,Op}\,[\%] = \left(\frac{GHG_{AD,Op} - GHG_{B,Op}}{GHG_B}\right) \times 100 \quad (2)$$

where GHG_B accounts for the sum of emissions from storage, field application, and use of fossil fuel in farm activities in the baseline scenario. $GHG_{AD,Op}$ corresponds to the emissions in the AD scenario from the operation unit "Op" and similarly $GHG_{B,Op}$ from the corresponding operation unit in the baseline scenario. In the case of sources of emissions that only exist for the AD scenario (e.g., leaks from the digester), the value of $GHG_{B,Op}$ (for Op = digester) is zero. It should be noted that GHG_B, $GHG_{AD,Op}$, and $GHG_{B,Op}$ have the same units of measurement ([f.u.]) in the database.

The second relative change used in this work is the relative change in emissions from slurries ($RCS_{GHG,Op}$). These are used to quantify the difference in emissions between untreated and digested slurries. They are calculated as follows:

$$RCS_{GHG,Op}\,[\%] = \left(\frac{GHG_{dig,Op} - GHG_{man,Op}}{GHG_{man,Op}}\right) \times 100 \quad (3)$$

where $GHG_{man,Op}$ and $GHG_{dig,Op}$ are the GHG emissions released from the untreated manure and digestate, respectively, in the operation unit "Op". Because the storage and field-application of slurries are the only two operation units that allow the calculation of both RC and RCS, the results present more detailed analysis on these farm activities.

For both RCs utilized, negative values represent less GHG emissions from an AD scenario with respect to its baseline. RCs less than −100% indicate that more GHG emissions are eliminated (by offsets) than those emitted in the baseline scenario. Conversely, positive RCs indicate higher emissions from AD scenarios.

The distributions of the RCs are obtained and analyzed. Similar to other meta-analysis,[34] RCs are not weighted so that each case has the same level of impact on the distributions. Normality is assessed by the Shapiro-Wilk test.[35,36] Dispersion of the distributions is examined by analyzing outliers and interquartile ranges. Because the distributions of RCs of emissions are mainly non-normal, further statistical analysis is based on the nonparametric test.

Nonparametric Statistical Tests. Nonparametric statistics is applied, first, to assess the overall effect of AD on emission and, second, to examine the relation between some emissions. To evaluate the significance of the changes in GHG emissions (from baseline to AD scenarios), the Wilcoxon Signed Rank test[36,37] is used. It is applied over the median values of RC distributions and zero (value of RC if no difference between scenarios exists). Significant differences between these values (Wilcoxon P-value <0.05) indicate evident changes in the emissions when AD is implemented. This test is also utilized to assess the significant difference between two distributions of RCs.

Correlations between the RC of CH_4 and N_2O for different operation units is examined by using the Spearman Rank test.[36,38] This test is chosen because it is a method that is robust in the presence of outliers.

Two-dimension density distribution of RCs are examined by the adaptive kernel estimator (modified from Bishop et al.[39]). This test adjusts the bandwidth in accordance to the density of the RCs.The optimum bandwidth is used to form continuous probability distribution and outputs the best estimate of RCs.

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Environ. Sci. Technol. 2015, 49, 5211−5219

RESULTS AND DISCUSSION

The results for the meta-analysis first covers key aspects of the database construction and general characteristics of the papers that conform it. The second section presents the distribution of RCs of individual operation units and specific GHGs. The Supporting Information covers results of RCs according to the qualitative variables (SI–II), overall RCs of GHGs with respect to the baselines (SI–III), and kernel distribution plots of interest (SI–IV).

General Aspects of the Database. The search of papers using the word combination described in the methodology, outputs 749 articles. By assessing the papers against the selection criteria, 30 articles[5,12−18,28,40−60] (4% of the initially found) are chosen. The main causes for the high rejection, according to criteria, are the following:

(i) First criteria: 84% of total output papers are not specific to the field and focus on codigestion, experimental measurements of methane yield, bacterial population, and/or different life-cycle-analysis indicator.
(ii) Second criteria: 9% of the papers correspond to reviews and, therefore, are not primary sources.
(iii) Third criteria: 7% of the articles are rejected because they report GHG emissions only for AD scenarios or baselines (i.e., not both scenarios).

From the selected 30 articles, 60% correspond to studies of European dairy farms. This is expected because in Europe AD is a mature technology implemented for waste treatment since the 1880s,[3] and today, it is being revisited as a mean to reduce carbon emissions in the context of European international agreements. Therefore, European cases generally report baseline scenarios (complying with the third criteria) in order to quantify changes in emissions when using AD systems.

Although the publication date is not constrained in the search of articles, 100% of the selected articles have been published after 1998. This could also be explained by environmental agreements, particularly the Kyoto Protocol (signed in 1997),[61,62] which was the motivation for research on GHG emissions.

The profiles in Figure 3 show the progress of methodologies used to determine GHG emissions over time. Papers that measured emissions experimentally from baseline and AD scenarios started in 1999 (Petersen[53]). They are followed by model-based papers, beginning in 2002 (Van Dooren et al.[57]). Articles that use independent models are separated from the IPCC-based papers in Figure 3, because the methodology of the latter is highly established. The IPCC methodologies (i.e., Tier 1 and Tier 2) were first applied for diary farms with AD systems in 2008 (Craggs et al.[15] and Hishinuma et al.[17]). As expected, these models have developed in the latest years because the IPCC Guidelines for National Inventories[19] only include the emissions from digester systems from 2006 (i.e., only anaerobic ponds exist in the previous version of 1996[63]).

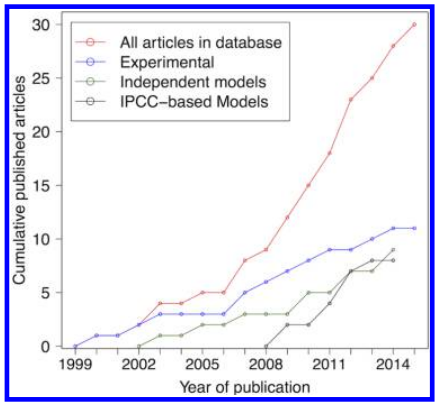

Figure 3. Accumulative number of publications over time according to methodologies.

From the 30 articles, 13 present more than one farm and/or multiple conditions. Therefore, the selected publications yield 87 cases. The developed database is publicly available.[64]

Changes in GHG Emissions from Operation Units. To analyze the specific sources of emissions, RCs of emissions are examined according to the operation units in Figure 2. Table 1 summarizes the operation units reported in the selected papers. From the 87 cases in the database, approximately one-third includes emissions of complete baseline scenarios, while the remaining baseline emissions are from different combinations of the operation units, such as for the AD scenarios.

The distributions of RCs by operation unit are presented in Figure 4. In the following subsections, these distributions are analyzed. RCSs are also reported to compare the emissions from untreated and digested slurries.

Anaerobic Digestion of Slurry. Six papers[13,18,42,46,59,60] report emissions from digesters in the database. These cases mainly focus on leaks of CH_4 (only Michel et al.[13] report CO_2 and N_2O emissions). To estimate these losses, a range from 1% to 10% of the produced (captured) CH_4 is assumed in the original articles. The highest assumption of 10% is found in the work of Pathak et al.,[46] which follows the IPCC default value.[19] Higher leaks are expected for this article because it studies a family size digester with exposed areas of slurry in the inlets (i.e., as opposed to a biogas plant that would minimize leaks). This particular case does not comply with the emissions of baseline scenarios in order to include it in the distribution of RCs of this operation unit.

The IPCC guidelines allow one to report less CH_4 losses from digesters if there is evidence to support it. This is applied in the four articles[13,18,59,60] that yield the eight cases shown in Figure 4 for this operation unit. The distribution of this operation unit presents a low interquartile range (6.6%), and all cases have positive values. The median of 1.4% indicates that this percentage of the baseline emissions is increased due to leaks from the digester. This change in emissions is significantly different to the baseline emissions (Wilcoxon's $P = 0.014$), which implies that there are sufficient cases to conclude that fugitive emissions from digesters alone increase the carbon footprint of the dairy activities. Three of the papers[18,59,60] in the distribution assume that 1.0% of the CH_4 produced is lost. Michel et al.[13] is the only to assume a higher lost (1.8%). However, if this case is adapted to assume a loss of 1% of the produced CH_4, the median of the distribution is not affected.

In the literature, it is found that Flesch et al.[66] determined experimentally that 3.1% of the CH_4 produced in a digester is leaked. However, that work is not included in the database because it does not report a baseline reference scenario. This shows a gap in the literature of empirical measurements of CH_4 leaks from digesters and their comparison to emissions from baseline scenarios. Two additional articles[5,17] in the database include emissions from digesters and baseline but do not specify the individual contribution of this operation unit.

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Environ. Sci. Technol. 2015, 49, 5211−5219

Table 1. Emissions Included in the Articles of the Database According to Operation Units[a]

Study	Anaerobic digester	Storage	Field application	Offset of fossil fuel	Offset of mineral fertilizers
1. Maranon 2011[12]		*	*	✓	
2. Clemens 2006[28]		✓	✓		
3. Amon 2006[40]		✓	✓		
4. De Vries 2012[5]	**	✓	✓	✓	✓
5. Cayuela 2010[41]			✓		
6. Michel 2010[13]	✓	✓	✓	✓	✓
7. Sommer 2004[42]	✓	✓	✓		
8. Cornejo 2010[14]		*	*	**	
9. Moeller 2009[43]			✓		
10. Craggs 2008[15]		✓		**	
11. Kaparaju 2011[16]		✓		✓	✓
12. Weiske 2006[44]		**	**	**	**
13. Clemens 2001[45]			✓		
14. Hishinuma 2008[17]	**	✓		✓	
15. Pathak 2009[46]	✓			*	*
16. Chianese 2009[47]		✓	✓		
17. Schouten 2012[48]			✓		
18. Thomsen 2013[49]			✓		
19. Zhang 2013[50]		**	**	✓	✓
20. Park 2007[51]		*		**	
21. Boadzo 2011[52]		*		✓	
22. Petersen 1999[53]			✓		
23. Sakamoto 2008[54]		✓			
24. Unal 2011[55]		*	*	✓	
25. Hamelin 2011[18]	✓	✓	✓	✓	✓
26. Liang 2013[56]		*	*	**	
27. Van Dooren 2002[57]		*	**	**	
28. De Boer 2002[58]			✓		
29. Battini 2014[59]	✓	✓	✓	✓	
30. Zhang 2014[60]	✓	*	✓	✓	

[a]Inorganic fertilizers replaced by untreated slurry (baseline scenario) or digestate (AD scenario). Check mark: Emissions from baseline and AD scenarios for this operation unit are reported. *: Article assumes zero emissions from this operation unit in the AD scenario. **: Emissions are included in (at least one) scenario(s), but the individual breakdown for each GHG contribution and/or for this operation unit are not specified.

Storage of Slurry. From the papers in the database, four articles[5,13,18,59] specify data on the GHG emissions from stores and from all the operation units in standardized baseline scenarios (Figure 4). These articles yield 5 cases which are insufficient to determine if the emissions of this operation unit have a significant effect over the emissions of baseline scenarios (median = −43.2%, Wilcoxon's $P = 0.063$).

In the database, 24 cases report emissions from stored untreated and digested slurries. RCS for this operation unit (calculated by eq 3) are presented in Figure 5. These RCSs show a significant decrease in total GHG emissions (median = −81.9%, Wilcoxon's $P = 0.01$).

It is found that CO_2 and N_2O emissions are not usually reported for storage and have large interquartile ranges (CO_2 = 208.0% and N_2O = 61.2%). Consequently, nonsignificant changes in emissions between raw and digested slurry (Wilcoxon's Ps CO_2 = 0.584 and N_2O = 1.000) are obtained for those GHGs. Only one article[54] ($N = 5$) compares the CO_2 emissions from unprocessed and digested slurries. An explanation for this gap in the literature is that CO_2 from manure management systems is generally considered to be carbon neutral because it forms part of the atmospheric carbon cycle[67] (i.e., not the geological cycle related to combustion of fossil fuels). However, this meta-analysis includes the changes in emissions of CO_2 because these can potentially indicate the carbon-sink capacity of the digestate compared to the untreated slurry, as studied by Smith et al.[68]

For emissions of N_2O from storage of digestate and raw slurry, four papers[17,18,28,40] yield five cases (Figure 5). Scarce report of N_2O emissions from this operation unit is explained

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Environ. Sci. Technol. 2015, 49, 5211−5219

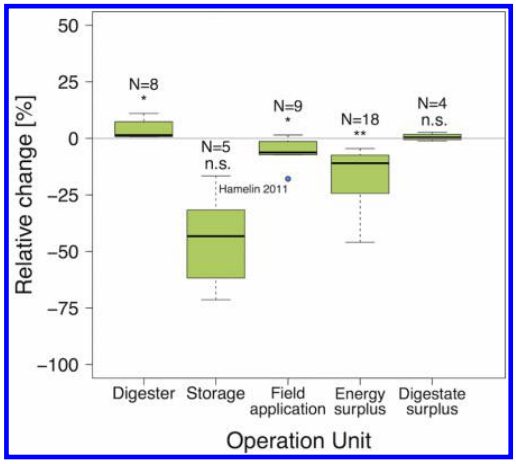

Figure 4. Box-plot for the RC of total emissions according to operation units with respect to baseline. Upper and lower sides of boxes: first and third quartile; line through the box: median; ○: outliers (>1.5 interquartile range); N = number of cases; positive values: emissions with AD are higher; negative values: emissions with AD are lower; n.s.: not significantly different from zero (Wilcoxon Signed Rank test $P > 0.05$); **: $P < 0.01$; *: $P < 0.05$; Z-values (respectively from left to right on the box plot): −0.566, −0.030, −0.013, 0.399, and −0.205.

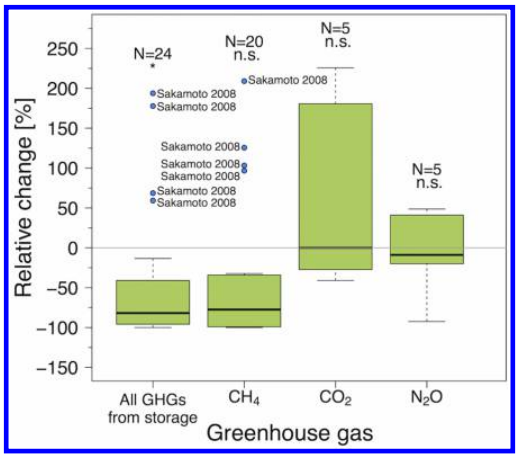

Figure 5. Box plots for the RCSs of GHG emissions from storage of digestate with respect to untreated slurry. Z-values: −0.465, −0.458, −0.538, and −0.045.

by low generation of this GHG in these anaerobic conditions.[28] This is because stored slurries contain neither nitrate nor nitrite which produce N_2O.[13] The AD process does not effect the concentration of these substances, and therefore, emissions from unprocessed slurry and digestate, as expected, are not significantly different.

The nonsignificant change in emissions of CH_4 (median = −77.5%, Wilcoxon's $P = 0.173$, Figure 5) is a highly unexpected result because 16 of 20 cases report mitigations. The reduction of this GHG is anticipated because, during AD, organic matter is degraded, resulting in a solid substrate with lower potential for CH_4 formation.[28,40] The nonsignificant change in emissions is related to the work of Sakamoto et al.[54] That article shows an increase in CH_4 emissions from stores by 96−209%. Their

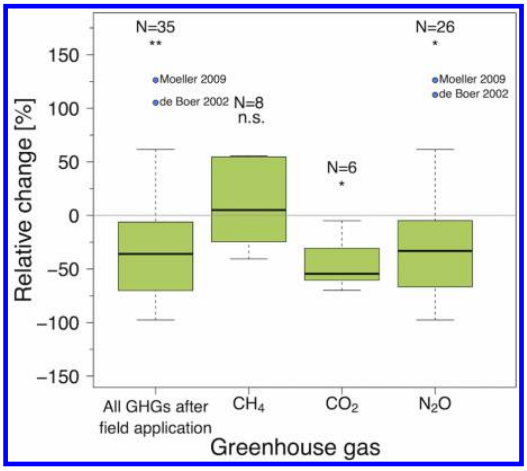

Figure 6. Box plots for the RCSs of GHG emissions from field application of digestate with respect to untreated slurry. Z-values: −0.168, −0.141, −0.362, and −0.146.

unusual results were obtained from a digestate removed directly from the bulk of an operating digester and not the outlet. This fact could explain an increase in the bacterial population and insufficient hydraulic retention time, which in turn could shift the methanogenic phase to the storage period. If these outliers are excluded, a significant mitigation in CH_4 emissions would be observed (median = −90.6%, Wilcoxon's $P = 4.78 \times 10^{-4}$). Accordingly, results of Clemens et al.[28] show that increasing the hydraulic retention times (from 26 to 56 days) results in reduction of CH_4 emissions from stored digestate with respect to untreated manure.

The articles that report emissions from storage of digestate mainly focus on CH_4. Consequently, a high correlation (Spearman's Rho = 0.99, $P = 4.93 \times 10^{-16}$) between RCSs (with respect to untreated slurry) of CH_4 and all GHGs for storage is obtained (N = 21; see SI−IV, Supporting Information), and these RCSs have similar medians and interquartile ranges (CH_4 = 65.0%; total GHGs from storage = 59.0%). In accordance to the Kernel density distribution for these RCSs, the best estimations for reduction of CH_4 and GHGs from storage are −78.5% and −76.0%, respectively.

Field Application of Slurry. Emissions from field application of untreated slurry and digestate together with standardized baseline scenarios are specified in five papers.[5,13,18,59,60] These articles yield 9 cases (see Figure 4) with an overall significant reduction of emissions (median = −6.3%, Wilcoxon's P = 0.020).

The RCSs for this operation unit is presented in Figure 6 and yields 35 cases. Results indicate that GHG emissions from digestate after field application are significantly less (median = −36.0%, Wilcoxon's $P = 2.61 \times 10^{-3}$) than from untreated slurry.

Five of the selected papers report emissions of CH_4 from field-applied slurries (N = 8). This GHG is the only to present nonsignificant differences between emissions of untreated manure and digestate (median = 5.0% and interquartile range = 79.3%). This is attributed to aerobic conditions after soil incorporation of slurries, that limit CH_4 formation for both materials.

Four papers[18,41,48,49] specify CO_2 emissions after field application (N = 6). Most of these articles study the effect of

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Environ. Sci. Technol. 2015, 49, 5211−5219

slurry treatment on carbon sequestration of soils.[41,48,49] In this respect, changes in emissions of CO_2 from this operation unit could be a new source of carbon credits. Results indicate that AD significantly reduces CO_2 emissions of slurry in this operation unit by −54.49% (Wilcoxon's $P = 0.031$). However, it should be noted that AD has been reported to reduce (by 15% according to Hamelin et al.[18]) the soil carbon pool, because the AD process removes easily biodegradable organic matter from the slurry.[49]

The mechanisms that produce N_2O are highly sensitive to oxygen availability, soil moisture content, and organic carbon in the slurry.[43,45,48] These variable conditions result in the large interquartile range obtained (61.8%; see Figure 6) for the RCSs of N_2O emissions. It is found that the median RCS of N_2O emissions results in a significant decrease by −33.1% (Wilcoxon's $P = 0.02$). This emission mitigation can be mainly attributed to denitrification processes, which have been reported to be the dominant mechanism in N_2O formation.[48,53,69] Denitrification occurs in anoxic conditions created when: (i) high water content in the soil restricts oxygen transport,[70] and (ii) carbon in the organic substrate reacts with the available oxygen.[45] AD can reduce these denitrifying processes with respect to untreated manure because it lowers the organic carbon content. Consequently, less carbon promotes aerobic conditions or is available for the metabolism of denitrifying bacteria. For these reasons, the carbon content in soils plays a key role in denitrification. This mechanism could explain the outlier of de Boer et al.[58] (see Figure 6), in which high amount of carbon is locally available after digestate application, thus increasing denitrification and N_2O emissions, with respect to the untreated manure.

To a less extent, N_2O is also liberated as an intermediate of nitrification.[28,41] Nitrification reactions convert ammonium (NH_4^+) in the manure or digestate into NO_3^-. The NO_3^- can then take part in denitrification reactions.[28,41] Because AD reduces the organic material, the NH_4 proportion increases and consequently nitrification activity is enhanced. This is the explanation of Moeller et al.[43] for their unusual results (second outlier in the N_2O distribution of Figure 6). The authors report an increase in emissions after AD because digestate has higher NH_4^+ content than raw slurry and, additionally, the water content of the soil is below the field capacity.

N_2O is the GHG most reported for this operation unit; thus, the RCSs of total GHG emissions after field application exhibit a strong correlation with the RCSs of this GHG (Spearman's Rho = 0.96, $P = 1.67 \times 10^{-6}$, linear relation $R^2 = 0.97$). Results from the Kernel distribution indicate that the best estimate for RCSs of N_2O and total GHGs from field applied slurries is −38.6% and −35.9%, respectively.

Energy Surplus for Export. The estimation of fossil fuel offsets and their associated negative emissions depend on the energy sources used in baseline scenarios (e.g., embodied carbon of national grids). Therefore, to enable comparison between cases, it is assumed that surplus energy in the AD scenarios is exported to replace electricity from natural gas (see Methodology Section), as approached by other authors,[71,72] having negative emissions (offsets).

In the database, eight[5,12,13,18,44,50,59,60] papers ($N = 18$) report the offset of emissions due to replacement of fossil fuels by biogas and also comply with the baseline scenario definition. Although, no outliers are present (see Figure 4) in this RC distribution, the large IQR (16.9%) shows that there is not agreement over the quantification of fossil fuel offset in the literature, even if the same fuel is assumed. This can be explained by the differences in AD yields assumed or measured in the different AD systems and operation conditions. In fact, the lowest offset of fossil fuel (−4.51%) is obtained from the work of De Vries et al.,[5] which assumes the lowest methane yield in this RC distribution (25 m^3_{CH4}/kg_{VS}).

Overall, the RCs of this operation unit indicates that the offset of fossil fuels significantly reduces the emissions with respect to the baseline scenarios (median = −11.0% and Wilcox's $P = 7.63 \times 10^{-6}$).

Digestate Surplus for Export. The offset of mineral fertilizers by digestate is considered as an operation unit in seven papers.[5,13,16,18,44,46,50] However, only four[5,13,18,50] also report the emissions of the complete baseline scenarios. An interesting observation is that all of these articles also include the offset of fossil fuels from energy replacement.

The RCs of these cases (for this operation unit) are presented in Figure 4. The median (+0.4%) presents a nonsignificant increase with respect to the baseline standardized emissions (Wilcox's $P = 0.789$). The value is positive due to higher offsets of inorganic fertilizers in the baseline scenarios by utilizing untreated manure. After AD, the volume of the slurry decreases as a result of carbon extraction. Therefore, it is expected that more mineral fertilizers are needed to compensate for less-available biosolid in the AD scenario. The low IQR of 2.3% shows agreement between the cases available. However, the nonsignificant result is an indicator that more research on the quantification of offsets of mineral fertilizers by digestate and untreated manure, together with baseline scenarios emissions, is needed.

Implications of Results. The RCs obtained in this meta-analysis can be utilized for estimating the emissions from different activities of AD scenarios when the baseline emissions are known (e.g., calculated by IPCC methodologies). The negative emissions from biogas replacing fossil fuels are the mitigations most compared against baseline scenarios in the literature. In contrast, it is found that negative emissions from replacing inorganic fertilizer by digestate are scarcely reported with emissions from reference scenarios. For storage and field application of slurries, extensive research on changes in CH_4 and N_2O emissions, respectively, is found. Most work on these operation units has compared specific emissions from untreated and digested slurries, rather than utilizing a baseline scenario. The only operation unit shown to significantly increase emissions from dairy farms is the digester due to leaks. However, empirical work was not found to measure these fugitive emissions and compare them against emissions from baseline scenarios. It is expected that this quantification of the effects of AD on GHG emissions from different operation units can meaningfully contribute in determining more accurate carbon footprints of dairy farms, for example, within life-cycle assessments and clean development mechanism projects.

Although different feedstocks are out of the scope of this work, the systematic review of the literature suggests that there is sufficient research work to extend the database and meta-analysis to codigestion of manure with other agricultural, municipal, and/or agro-industrial wastes.[73] Codigestion could increase the methane yields in the AD process because organic cosubstrates would contribute carbonaceous species for CH_4 formation. Thus, codigestion would improve the energy output and increase the environmental benefits of AD.

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Environ. Sci. Technol. 2015, 49, 5211−5219

■ ASSOCIATED CONTENT

Supporting Information

Examples of relative changes calculations; qualitative variables in the database; overall RCs of specific GHGs; kernel density distribution for RCSs. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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Appendix B

Example calculation of relative changes

This Appendix shows examples of the calculations undertaken to estimate the relative changes of cases found in Part I of the developed database [266]. The original functional units (from articles selected and input to the database) are presented to illustrate the non-dimensionalisation process.

There are two relative changes utilised in this work: i) those that are estimated by the changes in emissions related to baseline scenarios and that are applied for each operation unit ($RC_{GHG,Op}$) and; ii) those that are calculated for the changes in emissions from the slurries ($RCS_{Slurry,Op}$), using emissions from untreated manure for the baseline scenario and digestate for the AD scenario. The latter *RCS* is only applied for the operation units "storage" and "field-application of slurries.

Relative changes of operation units ($RC_{GHG,Op}$)

Equation 5.1 is utilised to estimate the $RC_{GHG,Op}$. The subscripts "GHG" refer to total GHGs or a specific emission (CO_2, CH_4 or N_2O) and "Op" is the operation unit, which emits the GHGs. By using standardised baseline scenarios as the reference (i.e. denominator of Equation 5.1) the comparison of changes in emissions among operation units is possible.

AD of slurry

Emissions from this operation unit correspond to leaks from the digester, thus, only are present in the AD Scenarios. This example uses the values reported by Hamelin et al. [133] (Figure S2 of that work and case N.68 of the database [266]), the $RC_{GHG,D}$ is estimated as:

$$RC_{GHG,Digester}\,[\%] = \frac{(7-0)\,[kg_{CO2e}\cdot ton_{slurry}^{-1}]}{352\,[kg_{CO2e}\cdot ton_{slurry}^{-1}]} \times 100 = +1.98\,[\%]$$

where 7 $kg_{CO2e}\cdot ton_{slurry}^{-1}$ corresponds to all GHGs emitted from the digester and 0 $kg_{CO2e}\cdot ton_{slurry}^{-1}$ is explicitly shown in this example to illustrate that there are no emissions from this operation unit in the baseline scenario. The value for baseline total emissions is 352 $kg_{CO2e}\cdot ton_{slurry}^{-1}$, which corresponds to the addition of emissions from storage (146 $kg_{CO2e}\cdot ton_{slurry}^{-1}$) and field application (205 $kg_{CO2e}\cdot ton_{slurry}^{-1}$) of untreated slurry, and fossil fuel consumption for dairy activities (1.03 $kg_{CO2e}\cdot ton_{slurry}^{-1}$). It should be noted that for the latter, the authors report the consumption of 5.59 $kWh_{El}\cdot ton_{slurry}^{-1}$, to which an EF of 0.1836 $kg_{CO2e}\cdot kWh^{-1}$ (electricity from natural gas), is applied.

Storage of slurry

For the "Storage" operation unit, this example considers the values provided in Table 6 of the work from De Vries et al. [136] (case N. 17 of Part I of the database [266]). From the reference, the total emissions from slurry storage ($GHG_{AD,Storage}$ and $GHG_{B,Storage}$) is extracted and the relative change is calculated as:

$$RC_{GHG,Storage}\,[\%] = \frac{(20.3-87)\,[kg_{CO2e}\cdot ton_{slurry}^{-1}]}{108.0\,[kg_{CO2e}\cdot ton_{slurry}^{-1}]} \times 100 = -61.8\,[\%]$$

where the denominator is calculated as the addition of emissions from storage (87.0 $kg_{CO2e}\cdot ton_{slurry}^{-1}$), field application (19.0 $kg_{CO2e}\cdot ton_{slurry}^{-1}$) and fossil fuel consumption (2.0 $kg_{CO2e}\cdot ton_{slurry}^{-1}$) in the baseline scenario.

Field application of slurry

Work from Michel et al. [131] presents emissions according to farm activity in Table 7

Table B.1: Summary from Scenario 1 (baseline) and Scenario 2 (AD scenario) of Battini et al.[142] used for this operation unit.

	Unit	Quantity
Milk production	$ton_{FPCM} \cdot yr^{-1}$[a]	1799.9[b]
Natural gas consumption (baseline)	$MJ \cdot yr^{-1}$	221,112[c]
Electricity consumption (baseline)	$MJ \cdot yr^{-1}$	293,897[c]
Emissions from field-application (baseline)	$kg_{CO2e} \cdot kg_{FPCM}^{-1}$	0.13[d]
Emissions from storage (baseline)	$kg_{CO2e} \cdot kg_{FPCM}^{-1}$	0.37[d]
Electrical energy production (AD-scenario)	$MWh \cdot yr^{-1}$	329.77[e]
Power consumption for digester	% of electricity produced	11.9[f]
Power consumption of CHP	% of electricity produced	3[f]

[a]FPCM: Fat and Protein Corrected Milk. Location of the values in the reference[142] are given in: [b]Table 1, [c]Table 4, [d]Figure 2b,[e]Page 201, [f]Table 5.

(case N. 19 in Part I of the database [266]). For this operation unit the emissions related to plant production (i.e. use of slurries on soils) were considered. The calculation for the relative change is:

$$RC_{GHG,Field}\,[\%] = \frac{(487.4-440.3)\,[kg_{CO2e} \cdot ha^{-1} \cdot yr^{-1}]}{3{,}204.7\,[kg_{CO2e} \cdot ha^{-1} \cdot yr^{-1}]} \times 100 = +1.47\,[\%]$$

where the denominator corresponds to the difference between emissions from emissions of digested and untreated slurry after soil-incorporation. The value for standardised baseline emissions (denominator) is determined as the sum of emissions from storage (2,393.6 $kg_{CO2e} \cdot ha^{-1} \cdot yr^{-1}$) and field application (440.3 $kg_{CO2e} \cdot ha^{-1} \cdot yr^{-1}$) of untreated slurry, and fossil fuel consumption for dairy activities (370.8 $kg_{CO2e} \cdot ha^{-1} \cdot yr^{-1}$).

Energy surplus for export

For this operation unit, energy balances are carried out to estimate the energy surplus available for export. This example considers the work from Battini et al. [142] (Tables 1, 4 and 5 of that work or case N. 82 in the database [266]). The relevant data of the reference is summarised in Table AB.1.

The emissions of the baseline scenario were estimated assuming all energy requirements are fulfil with electricity from natural gas with an EF of 0.1836 $kg_{CO2e} \cdot kWh^{-1}$. Therefore, the calculation of GHG emission from fossil fuel (FF) consumption in the baseline scenario is:

$$GHG_{B,FF}[kg_{CO2e}kg_{FPCM}^{-1}] = \frac{(221{,}112+293{,}897)\left[MJ \cdot yr^{-1}\right] \cdot \frac{1}{3.6}\left[kWh \cdot MJ^{-1}\right] \cdot 0.1836\left[kg_{CO2e} \cdot kWh^{-1}\right]}{1{,}799.9\left[ton_{FPCM} yr^{-1}\right] \cdot 1{,}000\left[kg_{FPCM} ton_{FPCM}^{-1}\right]}$$

$$GHG_{B,FF}[kg_{CO2e} \cdot kg_{FPCM}^{-1}] = 0.02\,[kg_{CO2e} \cdot kg_{FPCM}^{-1}]$$

where the subscript "B" refer to baseline and "FF" to the emissions from fossil fuels used in dairy activities. The emissions of this operation unit are added to the emissions from storage and field-applied untreated slurries (values in Table AB.1), resulting in 0.52 $[kg_{CO2e} \cdot kg_{FPCM}^{-1}]$ for the complete baseline scenario.

In the AD scenario, only electricity is reported to be available for export. This surplus electricity (E_s) is calculated as follows:

$$E_s[kWh \cdot yr^{-1}] = 329.77 \left[MWh \cdot yr^{-1}\right] \cdot 1{,}000 \left[kWh \cdot MWh^{-1}\right] \cdot (1 - 0.119 - 0.03)$$

$$-(293{,}897) \left[MJ \cdot yr^{-1}\right] \cdot \tfrac{1}{3.6} \left[kWh \cdot MJ^{-1}\right]$$

$$E_s[kWh \cdot yr^{-1}] = 198{,}996\,[kWh \cdot yr^{-1}]$$

where the values 0.119 and 0.03 correspond to the fraction of electric energy used for the AD system (see Table AB.1). Similar calculations for surplus energy have been made for 13 cases in the database [131, 133, 134, 140, 142, 144]. It is assumed in this work that the surplus energy offsets the use of electricity from natural gas with an EF of 0.1836 $kg_{CO2} \cdot kWh^{-1}$, hence emissions avoided by this operation unit are:

$$GHG_{AD,FF}[kg_{CO2e} kg_{FPCM}^{-1}] = \frac{(-198{,}996)\left[kWh \cdot yr^{-1}\right] \cdot 0.1836 \left[kg_{CO2e} kWh^{-1}\right]}{1{,}799.9 \left[ton_{FPCM} yr^{-1}\right] \cdot 1{,}000 \left[kg_{FPCM} ton_{FPCM}^{-1}\right]}$$

$$GHG_{AD,FF}[kg_{CO2e} \cdot kg_{FPCM}^{-1}] = -0.02\,[kg_{CO2e} \cdot kg_{FPCM}^{-1}]$$

Using Equation 2 and the values calculated above, the relative change of this case for this operation unit is as follows:

$$RC_{GHG,FF}\,[\%] = \frac{(-0.02 - 0.02)\,[kg_{CO2e} \cdot kg_{FPCM}^{-1}]}{0.52\,[kg_{CO2e} \cdot kg_{FPCM}^{-1}]} \times 100 = -7.69\,[\%]$$

Digestate surplus for export

In Table 1 of Zhang et al.[140] (case N. 51 of the database[266]), 101 $GJ \cdot yr^{-1}$ (28.1 $kWh \cdot yr^{-1}$) are reported to be offset in soil amendment (replacement of inorganic fertilisers by digestate). Assuming that the energy reported came from the combustion of natural gas with EF of 0.1836 $kg_{CO2} \cdot kWh^{-1}$, the relative change is calculated as:

$$RC_{GHG,Digestate}\,[\%] = \frac{(-28.1*0.1836-0)\,[Mg_{CO2e} \cdot yr^{-1}]}{446.95\,[Mg_{CO2e} \cdot yr^{-1}]} \times 100$$

$$RC_{GHG,Digestate}\,[\%] = \frac{(-5.15-0)\,[Mg_{CO2e} \cdot yr^{-1}]}{446.95\,[Mg_{CO2e} \cdot yr^{-1}]} \times 100 = -1.15\,[\%]$$

where the negative symbol indicates that offset of emissions occur due to replacing mineral fertiliser by digestate. No offsets are reported for the baseline of this operation unit (i.e. use of untreated slurry as fertiliser), therefore, $GHG_{B,Digestate}$ is zero. However, for other cases, untreated manure is utilised in the baseline scenarios, thus, these relative changes can differ in sign (+/-).

Relative change in emissions from slurry ($RCS_{GHG,Op}$)

To estimate the $RCS_{GHG,Op}$, Equation 5.2 is used. These calculations are applied to cases in the database that compare emissions from untreated and digested cattle manure. These emissions are associated particularly with the storage and field application of slurries. Therefore, one example of each of these operation units is given below.

Storage of slurry

This example shows the case reported by Amon et al.[121] for CH_4 emitted from storage of raw and digested manure. This corresponds to case N. 16 of the database [266]. The functional units have been standardised from Table 4 of Amon et al.[121], from "$kg_{CH4} \cdot m^{-3}_{slurry}$" to $[kg_{CO2e} \cdot m^{-3}_{slurry}]$, utilising GWP_{CH4} of 25. Thereafter, the $RCS_{CH4,Storage}$ is calculated as:

$$RCS_{CH4,Storage}\,[\%] = \frac{(33{,}565-101{,}142)\,[g_{CO2e} \cdot m^{-3}_{slurry}]}{101{,}142\,[g_{CO2e} \cdot m^{-3}_{slurry}]} \times 100 = -66.8\,[\%]$$

where 33,565 $kg_{CO2e} \cdot m^{-3}_{slurry}$ of CH_4 emissions are emitted from storage of digestate and 101,142 $kg_{CO2e} \cdot m^{-3}_{slurry}$ from untreated manure. The result implies that 66.8% of the CH_4 emitted from raw slurry is eliminated when replaced by digestate.

Field application of slurry

The following example considers the N_2O emissions from field-applied slurries reported by Clemens and Huschka[117] (case N.40 in the database [266]). In Figure 2 of the cited article (case with 54% water filled pore space), the authors present the emissions of N_2O. These have been converted to corresponding emissions of carbon dioxide, utilising GWP_{N2O} of 298. The $RCS_{N2O,Field}$ is calculated as follows:

$$RCS_{N2O,Field}\,[\%] = \frac{(697.3-5{,}504.1)\,[mg_{CO2e}\cdot m_{soil}^{-2}]}{5{,}504.1\,[mg_{CO2e}\cdot m_{soil}^{-2}]} \times 100 = -87.3\%$$

where 697.3 $mg_{CO2e}\cdot m_{soil}^{-2}$ of N_2O emissions are emitted from storage of digestate and 5,504.1 $mg_{CO2e}\cdot m_{soil}^{-2}$ from storage of untreated manure. Therefore, in this case, 87.3% of N_2O emissions are reduced from field-applied slurries when cattle manure undergoes AD.

Appendix C

Example of answered questionnaire

This Appendix presents a sample questionnaire utilised in Chapter 6, to collect information from the case study farms. In particular, the following is a translation of the questionnaire responded by the Guatemalan farm A (i.e. originally in Spanish). This questionnaire is publicly available online [1].

Contact information

Name of the farm: Santa Teresa-La Laguna

Address: XXX[2]- La Libertad, Petén.

Representative: F.B. (Administrator)

E-mail and phone number: XXX-XXX

Farm production

Which are the main products of the farm? (choose one to three)

✓Milk

✓Meat

Fruit and/or vegetables

Maize or similar.

Other (please specify):

[1]Spanish questionnaire at http://goo.gl/forms/u1BwBOs1bs. It should be noted that for the English case study, the questionnaire was carried out in person.

[2]Information is kept confidential, as agreed with farm representative.

What is the annual production of those specified above?

[For milk,] *"55,000 litres per year. The market was small, but it is now growing and we are considering to increase this production. For meat, there are 260 steers (1,000 pounds [per head] on average and 26/28 months of age. 100 female cattle and 100 oxen."*

What is the livestock and what is its feed?

"The livestock for milking is aproximately 600 heads, with 520 annual births. The male are feed and kept for meat production and the female are partially sold. The rest is for replacing our own herd. The farm was established 17 years ago approximately, transforming wetlands in grasslands. There was grass planted (Brizanta, Estrella, German grass and Humidicola). The livestock has had 100% grass as diet. The density of animals is 1.54 head per hectare."

On average, how many cows are milked in a year?

"There are approximately 30 cattle milked per month, each one is milked for 9 months. Therefore, 60 different cows are milked in a year."

How are cows milked in the farm?

"They are manually milked."

Is the dairy cattle food produced in the farm?

✓Yes

No

Partially

Other (please specify):

Is there information available on the composition of the cattle manure?

Yes

✓No

Other (please specify):

If yes to the previous question, what composition information is available? (choose from the following):

[Not applicable]

Basic composition (carbon, hydrogen, oxygen and/or nitrogen).

Volatile solids.

Chemical and/or biological oxygen demand.

Organic composition (proteins, carbohydrates, lipids, fibre).

Biochemical methane potential.

Other (please specify):

How much of the cattle manure is collected per year, month and/or day?

"None. Cattle are on grasslands all day, except when milking. The manure from milking stalls is returned to grasslands."

If there is a manure management in place, please describe it.

[Not applicable]

Energy consumption in the farm

Does the farm have access to grid electricity? (choose one from the following)

Yes

✓No

✓Other (please specify): *"This year* [2014] *light* [refering to electricity grid] *will arrive."*

How much electricity did you consume last year?

"*0*" [zero].

What is this grid electricity used for? (choose from the following)

[Not applicable]

Lights

Electrodomestic appliances

Milk production process.

Refrigeration of milk.

Pumps for manure management.

Other (please specify)...

Does the farm have access to gas grid? (choose one from the following)

Yes

✓No

Other (please specify):

How much grid gas did the farm consume last year?

"*0*" [zero].

What is the grid gas used for? (choose from the following)

[Not applicable]

Cooking.

Space heating.

Milk production process.

Other (please specify):

Does the farm consume other fossil fuels?

✓Yes

No

How much of other fossil fuels are consumed annually [do not consider transport]?

"1,400 litres of diesel and 2,200 litres of petrol for water pumps and electricity generation. More fuels are consumed for for the farm's pick-up service (i.e. staff and material transport)."

Anaerobic digestion for the farm

Do you know what anaerobic digestion is? Choose from 1 to 10, where 1 is "No, I have never heard about this" and 10 is "Yes, I know exactly what this is about".

1 2 3 4 ✓5

6 7 8 9 10

Have you considered anaerobic digestion to process livestock manure in the farm? (Choose one from the following):

Yes, AD is implemented.

Yes, it will be implemented.

✓Yes, but there is human resources missing to implement it.

Yes, but the initial inversion is too expensive.

Yes, but I do not have access to information to continue its consideration.

No

Other (please specify):

Is the a community near the farm which you could sell electricity and/or gas?

✓Yes

No

✓Other (please specify): Electricity.

Could you sell fertiliser to the community near the farm?

✓Yes

No

Other (please specify):

Carbon footprint of the farm

Do you know what the carbon footprint of the farm is?

✓No

Yes, an environmental agency assessed it.

Yes, a government representative assessed it.

Yes, we assessed it.

Other (please specify):

Are you interested in decreasing the carbon footprint of the farm?

Yes

No

✓Depends on the cost.

Other (please specify):

Are you familiar with the Clean Development Mechanism of the Kyoto Protocol?

Yes

✓No

Other (please specify):