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Greenhouse Gases

Edited by Bernardo Llamas Moya and Juan Pous

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and **Juan Pous**

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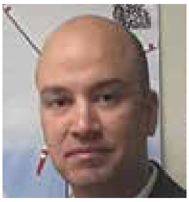
Meet the editors



Bernardo Llamas Moya is a Lecturer at UPM Technical University of Madrid. He has worked with the private sector in research and development projects and in the search for technologies to combat climate change. He has also collaborated on projects dealing with carbon dioxide capture for storage in deep geological formations and headed projects on carbon dioxide sequestration using microalgae systems and the production of bio-methane for the automobile sector. As well as his research and teaching on project management, he is also involved with INERGYCLEAN TECH, a new company which develops technologies to reduce carbon dioxide emissions in the energy sector.

Juan Pous was Director of Innovation at multinational infrastructures and services company Sacyr for 10 years, during which time he was responsible for quality, the environment, and R&D&I. His mission was to reduce the firm's carbon footprint, manage carbon dioxide emission quotas, reduce energy consumption among the company's multiple construction, industrial and services activities, and participate in drawing up the company's annual sustainability and CSR reports. Holds a Doctorate in Mining Engineering and is an Associate Lecturer at UPM Technical University of Madrid since 1996, where he has been a principal investigator on many projects, including three on improving energy efficiency, developing projects to calculate and certify carbon footprints, and developing models for carbon dioxide capture for storage in deep geological formations.

Contents

Preface

After the 2015 Paris Climate Conference (COP21), at which 195 participating countries agreed to take measures to reduce greenhouse gases, it was agreed to support measures to limit global warming to below 2°C.

According to forecasts by the Intergovernmental Panel on Climate Change, this measure may be possible if the level of carbon dioxide in the environment remains below 450 ppm. However, the concentration continues to increase and recent figures recorded at Mauna Loa (January 2016) showed CO_2 levels of 402 ppm.

Accordingly, it is now time to implement technological measures to reduce greenhouse gas emissions by industry - the use of fossil fuels has been clearly identified as the leading factor in greenhouse gas emissions, principally in the electric power and transport industries. In the former, where coal and natural gas are the main sources of primary energy, reducing CO_2 emissions obviously requires improving energy efficiency, using fuels with a lower carbon content, and CO_2 capture and storage. We must also, of course, remember the urgent need to make renewable energies the prime source of power generation, although they currently account for only a small percentage and the International Energy Agency forecasts that fossil fuels will continue to be used for some time.

The book opens by addressing how to change the model of the energy sector, as the primary issuer of greenhouse gasses (accounting for 60% of the total), focusing on the industrial sector. This change will necessarily involve redesigning business strategies. The same chapter also examines the overriding need for energy in order for societies to develop (developing countries).

The book then analyses recent advances in CO_2 capturing, another valid strategy to address the problem, transport (from site of emission to place of storage), and even storage in deep geological formations. Although, there are other scientific and technical currents that maintain which should be used for other industrial purposes (the molecule can be used for nutrition purposes and also massively in hydrocarbon exploitation techniques). Accordingly, we also discuss initiatives for its use in industry, including an innovative technology for its use in macrofouling remediation, carbon dioxide sequestration using microalgae systems and, lastly, to improve yields in greenhouse agriculture.

However, it is also necessary to reduce emissions of other greenhouse gasses, including methane, which has a radiative capacity 23-25 times higher than that of CO_2. This gas is emitted by the agro-industrial sector, the digestion of the organic part of solid urban waste, and other industrial sectors; the book examines the first of these sectors in depth. Considered diffuse emissions, reducing and quantifying them as methods to estimate overall greenhouse gas emissions in the agricultural and husbandry sub-sectors, is a challenge.

The book concludes with the measures to be taken to analyse greenhouse gas emissions; analysing their life cycle and calculating their carbon footprint, which are two most commonly accepted methods.

Accordingly, this book offers meaningful examples from the scientific world of how to mitigate and slow down climate change. Although other sectors remain outside the scope of this work, in the future we intend to publish further volumes discussing efforts made in other sectors to mitigate greenhouse gas emissions.

A few final words that we cannot afford to forget – the time is now! There is no excuse for each of us not to contribute in our own way to the fight against climate change. The sum of all our efforts is what will help us to roll back this pressing environmental problem.

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Chapter 1

The Changing Landscape of Energy Management in Manufacturing

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Additional information is available at the end of the chapter

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Abstract

The production and use of energy accounts for around 60% of global greenhouse gas (GHG) emissions, providing an intrinsic link between cause and effect. Considering that the manufacturing industry is responsible for roughly one-third of the global energy demand enforces the need to ensure that the manufacturing sector continually strives to reduce its reliance on energy and thus minimise GHG released into the atmosphere. Consequently, efficient management of energy consumption is of paramount importance for modern manufacturing businesses due to well-documented negative impacts regarding energy generation from fossil fuels and rapidly rising worldwide energy costs. This has resulted in a proliferation of research in this area which has considered improvements in energy consuming activities at the enterprise, facility, cell, machine and turret levels. However, there is now a need to go beyond incremental energy efficiency improvements and take more radical approaches to reduce energy consumption. It is argued that the largest energy reduction improvements can be achieved through better design of production systems or by adopting new business strategies that reduce the reliance of manufacturing businesses on resource consumption. This chapter initially provides a review of research in energy management (EM) at various manufacturing focus levels. The inappropriateness of current methods to cater for transformative and radical energy reduction approaches is discussed. In particular, limitations are found at the business strategy level since no technique exists to consider the input of these high level decisions on energy consumption. The main part of the chapter identifies areas of further opportunity in energy management research, and describes a method to facilitate further reductions in energy use and GHG production in manufacturing at the business strategy level.

Keywords: Energy management, Greenhouse gases, business strategy, manufacturing, sustainability

1. Introduction

There are two facts about the future of energy that we know: we will not be able to generate the same quantities from easily accessible fossil-based sources as we currently do, and in the short term this shortfall in energy supply will not be met by 'renewable' sources based on current projections of investment and development [1]. In addition, energy consumption is currently increasing (see Figure 1) and is expected to increase by 22% by 2020 compared to 2011 [2], due partly to increases in demand from China and India [3]. These factors will create what has been termed the 'energy gap' [4]: the difference between demand for energy and the ability to supply this demand, although it should be noted that demand is influenced by supply. The precise magnitude of this energy gap is difficult to predict but it will have a severe influence on the way energy is consumed in the foreseeable future.

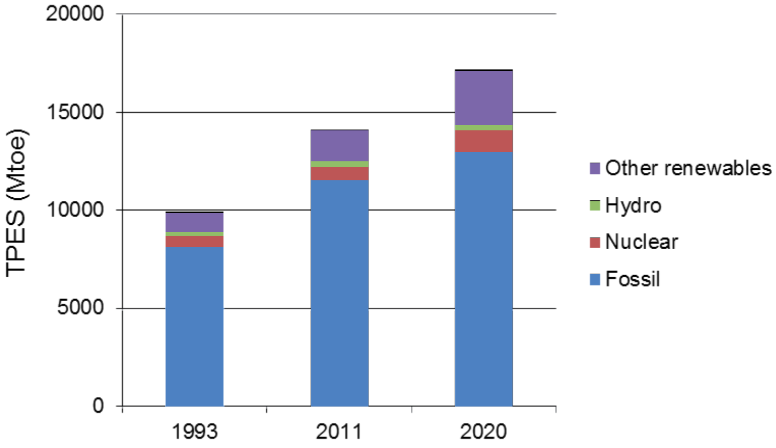

Figure 1. Total primary energy supply of resource by 1993, 2011 and 2020 (data from [2])

The management of energy consumption within the manufacturing sector is particularly important since it is one of the largest energy consuming sectors, directly and indirectly responsible for one-third of global energy use and carbon emissions [5]. This high level of manufacturing related energy consumption is particularly true in developed and developing countries [6]. Energy security is therefore vital for the future of the manufacturing industry and provides a significant incentive to reduce consumption levels. Other incentives also exist in the form of rising energy costs, national and international legislation and consumer demand for greener products. This need has not gone unnoticed and a wide range of approaches have been implemented by companies to reduce reliance on non-renewable (fossil-based) energy sources by improving management practices of energy consuming activities.

These EM techniques have been, in general, quite successful for specific applications but are limited in their scope and so can only ever have a predetermined impact on an enterprise's energy performance. Historically research and the resulting EM techniques have focused on current manufacturing operations and management practices and have therefore tackled problems that can be solved by existing industrial companies. However, modern manufacturing businesses are under ever-increasing pressures to deliver innovative solutions for highly complex tasks for adaptability, economic performance, maintainability, reliability, and scalability. The "Factory of the Future" [7] has to be adaptable not only to the needs of the market but also to the growing requirements for economic and ecological efficiency. Furthermore, such factories will have to take into consideration increased levels of social responsibility and, in particular, environmental sustainability. Based on these challenges, the need for development and validation of new industrial models and strategies is relevant for industrial transformation. These competitive sustainable manufacturing models and strategies will have to aim at achieving long-term economic sustainability through an increase in added value and improved production capability, responsiveness and quality as well as environmental sustainability through the decrease in the consumption of raw materials, water and energy.

The shape of manufacturing is therefore changing as life cycle approaches become more important for impact assessment and the use of ecological data to influence process planning becomes necessary to meet the environmental performance characteristics demanded by government, industry and consumers. In addition new business-strategies[1] are being explored [8–9], with a wide spectrum of product service systems, remanufacturing and product upgradeability, all likely standard models for the future of sustainable manufacturing industries.

This chapter, which identifies the existing trends in EM research for the manufacturing sector and develops new EM regimes that are important for continued advances in energy rationalisation, is divided into three main sections:

- A brief review and analysis of existing EM techniques for manufacturing with a short discussion on developing new EM techniques for evolving manufacturing approaches;
- A more detailed discussion regarding the need for the consideration of business strategies within EM for manufacturing, with the development of a procedure to facilitate this consideration; and finally,
- A case study to demonstrate the applicability of the developed EM procedure for the business strategy manufacturing level.

2. Review of Existing EM Techniques

Manufacturing enterprises and facilities can be highly complex, where monitoring energy consumption and associated GHG production can be cumbersome and expensive. Using a

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[1] In this work, business strategy defines the approach in which a manufacturer takes to fulfil the need or want of the customer. The manufacturer will supply a solution through either the provision of a product or service (which uses a product) and can, therefore, be a short-term or long-term interaction with the customer. Similarly, the business strategy also defines where and when and how often manufacturing processes are undertaken. In short, business strategy defines the model by which a company seeks to generate profit from its customers, but which is also linked to its suppliers and external governing bodies.

well-structured framework can help industrialists identify where to focus their efforts to achieve maximum energy savings. One structured approach to analysing a manufacturing system is to decompose the system hierarchically. A variation of the 'shop floor production model' as developed by the International Organisation for Standardization (ISO) can be used to categorise research conducted on various levels. The adapted model has five levels, ranging from a high level to a specific scope. The levels and the energy considerations for each are summarised as follows:

1. Enterprise level – supply chain of materials or components, network of production sites, inventory hubs, sales and distribution centres, R&D and the integration of various plants.
2. Facility level – building envelope, heating, ventilation and air-conditioning (HVAC), infrastructure of the facility and site energy generation.
3. Production/machine cell level – planning, production engineering and management, supply of material resources and maintenance.
4. Machine level – operation and control of equipment, lighting, cooling, work done on material and communication systems.
5. Turret or tool-chip level – actual transformation of material.

Further, Vijayaraghavan and Dornfeld [10] also suggested that at each level of analysis, there is a corresponding temporal scale of decision making that ranges from several days at the enterprise level to micro-seconds at the tool-chip level. The range of variation in the analysis and temporal scales along with the types of decisions that are made at each level is shown in Figure 2. It is considered by the authors that although the temporal timescales suggested by Vijayaraghavan and Dornfeld [10] are suitable for rapid, high-volume manufacturing processes (e.g., low-tech electronics), for products that are highly complex (e.g., jet engines) or for products that have very long product runs (e.g., cars), these decision timescales need to be extended. This is particularly the case when a decision is based on the use of sufficient historical data (which needs to be collected and interpreted). The current research considers temporal timescales between minutes (real-time) and years (strategic).

The following sections use the structure described above to briefly review some of the techniques for EM and minimisation published in recent academic literature. The review is not intended to be comprehensive (see [11] for a review with a wider scope) but is intended to show the shape of research in this field with respect to decision time scales for each manufacturing level. As will be shown, existing research (in EM) falls into the manufacturing level-timescale relationship described by Vijayaraghavan and Dornfeld [10]. This research is concerned with identifying the opportunities and needs for EM techniques that lie outside of this existing envelope. These new areas of energy consideration in manufacturing are shown in Figure 3.

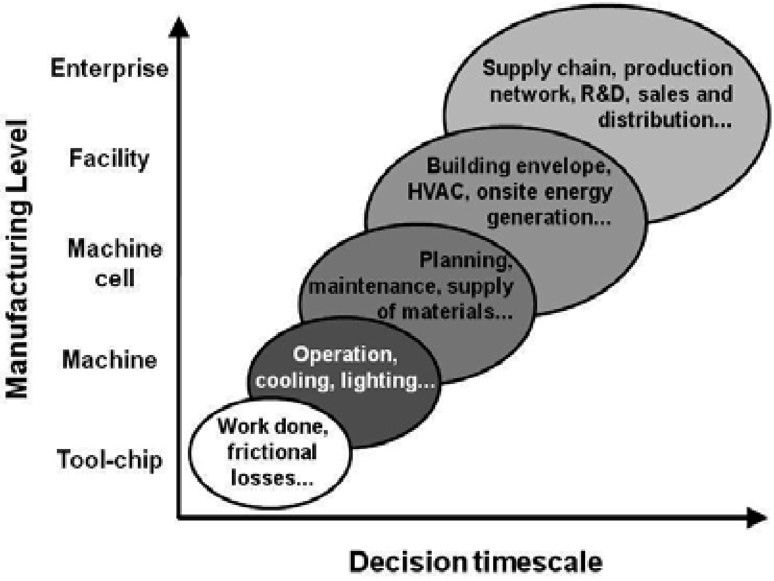

Figure 2. Energy considerations at different manufacturing levels. Adapted from [10].

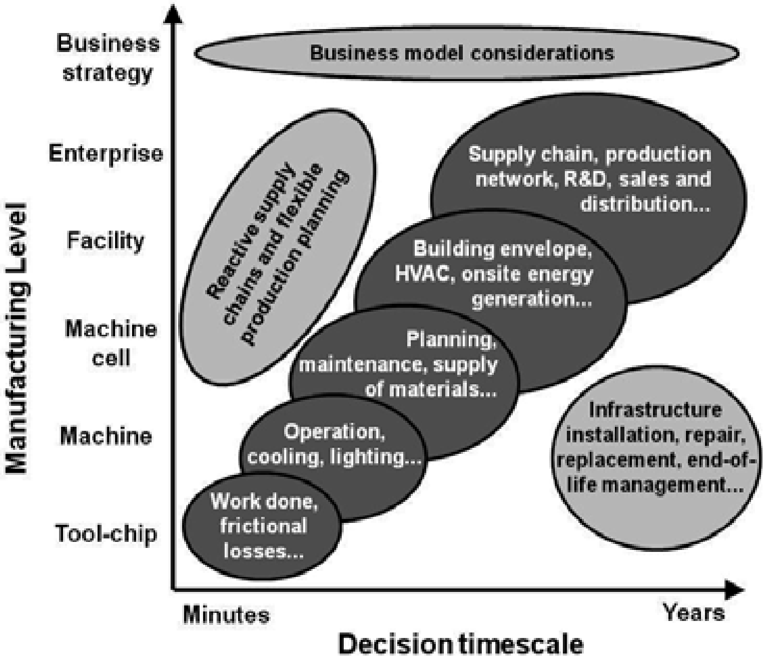

Figure 3. Energy considerations in manufacturing. Existing research predominantly in dark grey areas. New areas described in this research shown in light grey.

2.1. Energy Research on an Enterprise Level

Manufacturing enterprises extend beyond the walls of a factory that just produces goods; they encompass a range of activities from supply chain of materials or components to manufacturing processes and the logistics of the finished product. This involves a network of production sites, suppliers, inventory hubs as well as sales and distribution centres.

Various studies have reported techniques for EM at the enterprise level. Concentrating on logistics Kara and Manmek [12] found that the embodied energy of products could be reduced by selecting local suppliers and avoiding road transport for high quantities of raw materials over long distances. Their model focused on energy, materials and emissions, and waste with considerations for how each of these are used or produced within lengthy supply chains. Supplier location was shown to be a significant factor that can increase or reduce the embodied energy of the raw materials. A similar study [13] used Google Maps to carefully plan and optimise the embodied energy of transportation at the enterprise level. Both approaches require detailed data regarding transport modes and routes and, in the event of instigating changes, may require extensive replanning of multiple cross-linked supply chains. In addition, Kara et al. [14] detail a methodology for assessing the impact of global manufacturing on the embodied energy of products. They studied six different products manufactured from various raw materials in a global manufacturing network and found that product, material and key supply chain parameters played a crucial role.

Other research on the enterprise level has identified that energy improvements can be obtained by changing manufacturing models (e.g., Seliger et al. [15] showed that a phone that is remanufactured consumes less energy than a phone that has been sent to a land fill, over the production, use and end-of-life phases). This is because the remanufacturing pathway, despite requiring energy input into the reverse logistics, avoids repeating manufacturing steps with characteristically high energy consumption and environmental emissions.

The globalisation of businesses has led to long and multi-tiered supply chains, making the introduction of improvements across the entire enterprises complex and difficult. This has been reflected in the number of studies that have been carried out at the enterprise level with most publications focussing on case studies and observed trends rather than on new methodologies [11]. In general, the higher costs, coordination effort and complexity and communication difficulties of implementing sustainable supply chains has led companies to focus on internal activities that present far more achievable environmental (and financial) gains over shorter time periods.

2.2. Energy Research on a Facility Level

Research on the facility level primarily focuses on modelling and reducing the energy consumed by infrastructure and other high level services such as ventilation, lighting, heating and cooling. On-site energy generation is also taken into account.

A review of potential energy savings of a typical manufacturing facility has been performed [16] and focused on high-level redesign strategies. It was concerned with the potential energy saving that can be achieved through optimised building shape and form, improved building envelopes, improved efficiencies of individual energy using devices, alternative energy using systems in buildings, and through enlightened occupant behaviour and operation of building systems. In addition, a method for measuring plant-wide industrial energy savings that takes into account changing weather and production between the pre- and post-retrofit periods has been presented [17].

As a barrier to EM at the facility level, it has been highlighted there is a distinct lack of manufacturing energy performance indicators (EPIs), and this has led to difficulties of modelling 'plant level' energy consumption [18]. Benchmarking energy is essential for EM program development, yet it has been noted that most industries have not, or at least have not been able to, benchmark energy use across their plants. Combining the American Energy Star performance rating system with EPIs, it has been possible to quantify the average energy consumed for the manufacture of best practice vehicles [18]. On a more generic level, the development of energy performance benchmarks and building energy ratings for non-domestic buildings have been reported [19]. They outlined a methodology to develop energy benchmarks and rating systems starting from the very first step of data collection from the building stock.

Finally, on the facility level an economic comparison of three cogeneration steam systems for a wood pulping mill was carried out [20], finding that economic and environmental optimisation could not be achieved simultaneously.

2.3. Energy Research at the Machine Cell Level

At this level, research focuses on planning, production engineering and management, supply of material resources, transport waste material processing and maintenance. Energy flows are closely related to the running of these activities that may be affected by production plans, scheduling times and parameters.

Much of the research reported on the production level involves process planning and process routing for improved energy performance, although most research focuses on costs and cycle times. There is a lack of tools for optimising process flows based on sustainable development objectives (environmental), and those that have been proposed have few practical results [21]. In an attempt to bridge this gap, Tan et al. [21] combined manufacturing process planning and environmental impact assessments using a checklist analysis. They proposed an optimal decision making method for new components that include energy consumption as part of the sustainable development evaluation.

In addition, He et al. [22] have developed green manufacturing process planning and support systems where the raw materials, secondary materials and energy consumption, and other environmental impacts of process planning were optimised. This was supported with databases and model repositories. Integration of the optimisation of energy consumption of processes as part of the process selection algorithm in a process planning program is also possible as and has been demonstrated [23].

Information is critical on a production level: Chiotellis et al. [24], Müller and Löffler [25] and Herrmann et al. [26] have all proposed various information formats to aggregate energy values for decision making on a production level. These groups specifically noted a current lack of monitoring of energy flows within factories. In addition to the lack of monitoring systems, the amount of information required can be very complex and requires a robust framework to deal with information on all levels. They suggest that having online monitoring of the energy consumption within a factory not only provides greater energy transparency, but also provides a stream of useful information to be used for maintenance repair and overhaul. To facilitate this, they have introduced the concept of EnergyBlocks, which can help planners to evaluate the energy consumption profile of various alternatives and to deduce optimal system configuration. However, data volumes increase (almost exponentially) as you move down the manufacturing levels, and it is therefore important to set the correct resolution through appropriate hardware and software systems.

Muller and Loffler's [25] approach to the same problem provides guidance on energy-related decision making during the planning procedure, from the product definition to energy monitoring of the implemented plant. The availability of energy-related data in industry during the planning process is still very rare, and so the main challenge is the development of energy data standards for life cycle engineering (LCE) tools. They have suggested the development of energy performance ratios to influence more detailed standards and instruments such as the dynamic simulation of energy demands.

The correlation of energy usage with operations being performed in the manufacturing system through event stream processing techniques has been successfully implemented [10]. The framework temporally analyses the energy consumption and operational data of machine tools and other manufacturing equipment to enable decision making to improve the environmental performance of the machine tools.

2.4. Energy Research Associated with Production Machines and Equipment

Research associated with the machine level has been concentrated in two subcategories: the energy consumption of the machine for the 'work done' processes and the energy requirement of the machine for auxiliary processes (e.g., cooling and control).

Cooperative Effort on Modelling Process Emissions in Manufacturing (CO2PE!) is an international initiative [27] to cluster forces in different continents, involving machine builders as well as academics, to analyse existing and emerging manufacturing processes for their ecological impact in terms of direct and indirect emissions. Substantial research has been targeted to document, analyse and reduce process emissions for a wide range of available and emerging manufacturing processes [24, 28–31].

In the life cycle phases of product manufacturing, the focus of resource efficiency moves from the material applied per unit to resources used in the various production phases, for example, cooling lubricants, compressed air or hydraulic oil and on the energy requirements of the production processes [24]. Process relevant information is based on equipment energy consumption curves. Each curve is specific to a production equipment item and enables an accurate determination of the energy consumption of the item over the production time.

Similarly, Overcash et al. [32] produced an engineering rule-of-practice-based analysis of separate unit processes used in manufacturing. The information is collated in the form of a unit process life cycle inventory, which then helps to evaluate the manufactured products through the quantification of various parameters, including input materials, energy requirements, material losses and machine variables.

In the context of an integrated consideration of economic and ecological impact, energy profiles are an important basis for deriving optimisations to improve sustainability in manufacturing [33]. On the process level, these profiles permit the identification of substantial energy drivers in machines. In addition, the process-specific energy assessment has taken a step further to develop generalised 'equipment-level' energy models, using average energy intensities of different manufacturing processes to evaluate the efficiency of processing lines [34]. They concluded that modern processes enable smaller dimensions and scales to be produced with larger specific electrical energy requirements. They indicated that energy requirements depend on the production rate and are consequently not constant as assumed by Life Cycle Assessment software packages like Simapro or Umberto.

Dahmus and Gutowski [35] tracked energy flows when characterising the environmental impact of machining, making a distinction between the energy required for chip formation and operating the manufacturing equipment (Figure 4). In their studies, they showed that machine tools with increasing levels of automation reveal higher basic energy consumptions that result from the amount of additional integrated machine components.

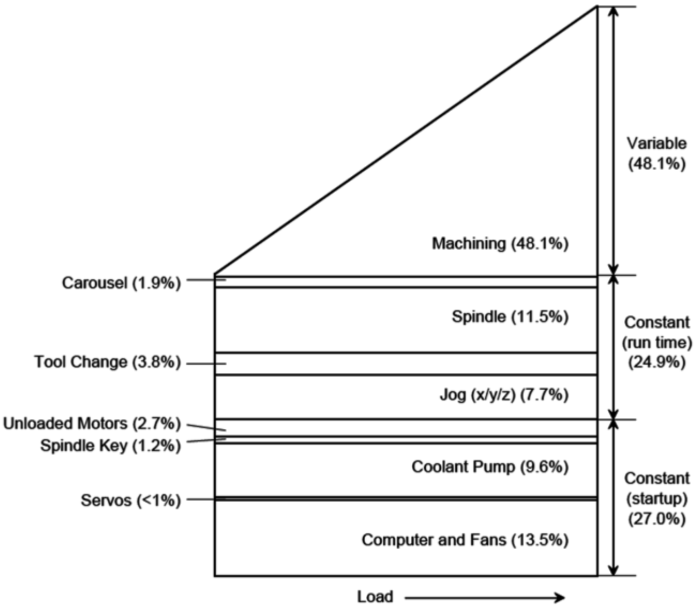

Figure 4. Machining energy use breakdown for a 1988 Cincinnati Milacron automated milling machine with a 6.0 kW spindle motor [35].

More specifically, a study on the energy consumption of cutting found that high speed cutting required less energy per unit manufactured compared to the conventional cutting speed [36]. They also found that the installation of kinetic energy recovery systems (KERS) can reduce average power consumption by up to 25% depending on workpiece geometry and machining time. As the energy efficiency of the system is highly part specific, a KERS should be custom defined. A framework has also been developed [37] for the recovery of waste heat energy from manufacturing processes.

Along the same theme, the improvement potential in two types of manufacturing equipment for discrete part production has been discussed [29]. Power requirements for activities in a machine tool was investigated and classified into productive and non-productive periods.

In contrast, however, Fleschutz et al. [38] conducted an energy simulation on 12 similar industrial robots within a workstation and found that the assigned operations strongly influenced the energy consumption of the respective robot. Even though the operating hours are the same for the robots, those that had more kinematic movements and little idle time resulted in energy consumptions that were double the other robots.

Process conditions and energy consumption are not normally static but depend directly on the specific conditions of the process and/or the production setting. The initiation of energy labels for production machines indicating the amount of electrical energy consumed for various production processes has been proposed [30]. Such information can be estimated by summarizing the electrical energy consumptions of single machine components (pumps and engines) or by using energy profiles to reveal the holistic energy absorption that is needed by machine tools.

There are, however, significant challenges in obtaining sufficient energy consumption data. It has been proposed that in the future, both the manufacturer of equipment and the operator should use consistent parameters to describe the energy performance of manufacturing systems and that equipment should have standardised metering ports [39].

2.5. Energy Research on the Turret Level (Theoretical Process Energy)

The lowest and most focused manufacturing level is the turret level, which represents the actual material transformation process itself. Energy assessment and management at this level involves knowledge of the interactions of the mechanical and chemical processes in order to establish theoretical energy consumption values of the process.

The research and application of improvement in energy efficiency at the turret level is highly process specific and therefore less appropriate to general application. As a reflection of this, less research has been published at this level. Most research is evaluative with little scope provided for developing models. Consequently, only a few examples reviewed here are used in further analysis in this chapter.

At this focus level, it has been shown that in machining, the ideal process energy is independent of operating parameters such as tool speed, feed and depth of cut [40]. Instead the machining energy is dependent on setup parameters, such as choice of cutting fluid, tool rake angle and part design parameters (material selection and the volume of material removed). Draganescu et al. [41] conducted experiments to model machine tool efficiency so that the specific consumed energy could be determined for establishing cutting parameters and the consumed energy necessary for removing a certain quantity of chips. Amongst many examples of theoretical mathematical modelling of machine processes, Draganescu et al. [41] and Kalpakjian and Schmid [42] have looked at the specific energy consumption for milling, and Ghosh et al. [43] have modelled the specific energy requirement of deep grinding.

Other studies of theoretical energy consumption of other manufacturing process can be found in [42] who give detailed explanations and descriptions of the energy required for cutting, forming and deformation. A detailed analysis on the specific cutting energy for bandsawing different work piece materials has been carried out [44]. The minimal energy required for turning and the optimal conditions for machining a product has been studied [45] and finally Kuzman and Peklenik [46] have done an energy evaluation of cold forming processes.

3. An Overview of the Current Scope of EM

There are clearly a large number of EM techniques that manufacturers can implement in order to reduce their energy consumption and their generation of GHGs. These techniques focus on many different aspects, and it can be confusing for manufacturers to decide which approaches are best for their particular setup. One way of categorising these different EM techniques is to define the temporal decision timescale. Within manufacturing, EM decisions can be made on one of four timescales: real-time (minutes-hours), operational (days-weeks), tactical (months) and strategic (years), with EM techniques at these levels being implemented by different groups of people who operate at different management levels.

Positioning the EM techniques reviewed in this chapter into a research map (Figure 5) that has manufacturing level and decision timescale as its axes reveals almost intuitive results. The more focused (lower manufacturing level) an EM technique, the shorter the timescale on which decisions can be made: adjusting machine setup parameters (turret level) can be done by one person in a few minutes, whereas reconfiguring a supply chain (enterprise level) will take a team of people months or even years. In the research map, this correlation seems linear, but since the x-axis is not continuous and the y-axis is not quantitatively scaled, a strict correlation is undefinable and inappropriate. Nonetheless, there are clear areas of the map that are not occupied by any of the reviewed EM techniques, and it is therefore suggested that there is a need for research to be undertaken to address these areas.

There are two areas of research in the current map (Figure 5) that would benefit from a growth research: lifecycle process system planning and eco-intelligent manufacturing and agile supply chains. A further area of research, not currently represented on the above map, is required to look at the impact on energy consumption of existing and future business strategies. These three research opportunities are discussed in the following sections, with EM at the business strategy level given a more in-depth consideration due to the importance of its potential for limiting GHG production (energy consumption) in order to meet a specific customer need.

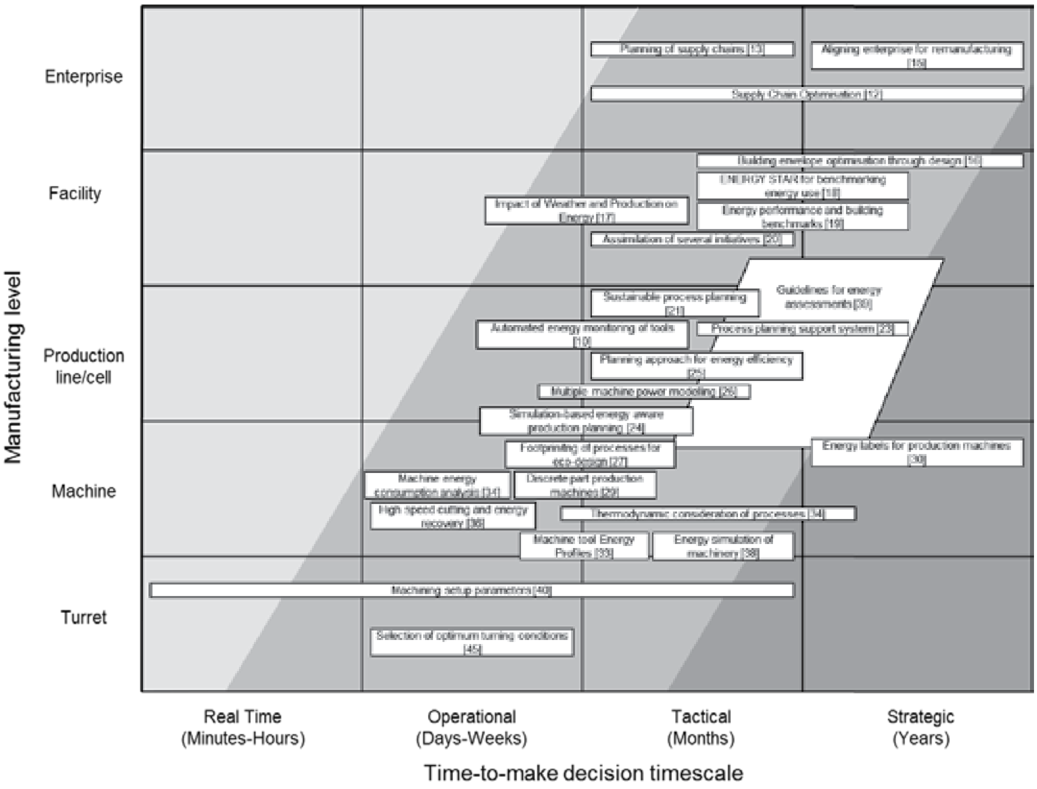

Figure 5. Research map showing the relation between manufacturing level and associated decision timescale. The mid-grey region is heavily populated, whereas EM techniques at for short-term facility and enterprise energy consumption and long-term process level energy consumption are largely undeveloped.

3.1. Lifecycle Process System Planning

Recently, as with products, manufacturers are beginning to take a life cycle view of not just their factories, but also the processes within the factories [47]. Primarily for economic reasons but also from an environmental point of view they are beginning to consider how best to ensure their machinery is maintainable and upgradeable, and what will happen to it at its end of life. Such a task can be highly complex since it is difficult to predict the requirement of future or long-term process capabilities, process utilisation levels and also production floor layouts. Life cycle process planning is, therefore, heavily dependent on a company's ability to roadmap the sector it operates in. However from an environmental perspective, it is highly important to be able to consider the resource intensity of processes throughout their lifetime. A host of life cycle process planning tools are therefore required to assist manufacturers in managing their long-term process requirements. For this, they require the development of an assessment framework and decision support tool to understand the life cycle impact of individual processes and process chains so that strategic decisions can be made about the purchase or upgrade of machinery to ensure minimal environmental and economic impact.

Such a suite of tools requires a consideration of energy consumption to ensure the processes are able to integrate with the long-term energy supply strategy of a particular facility. Life cycle process EM should consider flexible, reconfigurable process chains, peripheral energy requirements (cooling, transport systems, etc) and factory layout to ensure the most appropriate planning is carried out. EM tools developed in this area will need to provide manufacturers with clear strategies for the minimisation of process energy consumption over periods of many years. Such considerations will be key to the development of eco-efficient factories for sustainable industrial systems.

3.2. Eco-Intelligent Manufacturing and Agile Supply Chains

At the short end of the temporal decision timescale on the research map, there currently exists another area where no or very few EM techniques exist. In this region, which covers manufacturing levels between cell and enterprise, manufacturers are beginning to consider new short-term influences on their production and operations processes to improve economic and environmental performance. As part of a holistic approach, they require techniques to help them manage their energy consumption at this timescale.

At the production cell and factory levels, real-time consideration is required to be sensitive to energy availability, which may come from several sources (almost certainly involving traditional fossil-based energy) and which for any renewable component may vary in supply. In such circumstances, it is necessary to be able to rapidly influence production scheduling to ensure that energy intensive processes are carried out at periods of higher renewable energy availability to maximise the environmental benefit from this type of energy. Smart metering and smart energy grids are required to influence this eco-intelligent manufacturing. In fact, a new production planning regime, ‘environmental resource planning’, is required to not just take into account the immediate availability of energy supply mix, but a full range of eco-indicators, including emissions, water consumption, idle time of processes, and staff availability.

There is also a need for industry to be able to consider and manage energy at the enterprise level, but on the short real-time and operational timescales. Supply chains have historically been set up to optimise for time and cost to give manufacturers the best possible competitive advantage. However, this approach has led to disadvantages in fluctuating markets and increasingly, manufacturers are seeking to remain resilient by creating flexible reactive supply chains. The Triple-A Supply Chain described by Lee [48] promotes the need for agile supply chain arrangements that are able to respond to short-term changes in supply, allowing rapidly changing consumer demands or unforeseen disruptive events to be more easily worked around. The energy implications in an agile supply chain need to be managed even if it might not be a primary consideration. It is important for companies to be able to account for the resources that are required for their products from a life cycle approach, which includes being able to optimise the supply chain. Methods for systematically reacting to supply and demand problems are being developed [48] and incorporated into everyday business practices. EM techniques that are able to consider and influence these short-term reactive changes to supply chain operation will be essential for improving and maintaining environmental performance in the future manufacturing industry.

3.3. Energy Management at the Business Strategy Level

The preceding reviewed and hypothesised EM techniques for manufacturing are suitable for current make-sell business models that are optimised for economic benefit. Since profit is generated from the sale of products, successful manufacturing businesses have historically been those that produce and sell more than their competitors: a culture that has led to a disregard for resource consumption and pollution levels. This practice is now changing as businesses and consumers become more aware of, and active in achieving long-term sustainability. Manufacturers are investigating and implementing radical new strategies to remain commercially competitive whilst reducing resource consumption. It is therefore proposed here that new EM techniques will be required to support these new manufacturing business strategies.

The field of manufacturing has seen many improvements in sustainability performance over the last few decades. Strategies to reduce waste, lower emissions, improve energy efficiency, and so on have been implemented across the board but such activities have largely made improvements for individual processes only. In the long term, industrial sustainability will not be achieved simply by the development of new technologies or the utilisation of iterative improvements of current production processes. Accordingly, the appropriateness of existing business models are being challenged [49–51] for a future of industrial sustainability. The configuration of the industrial system will evolve dramatically, introducing new concepts such as cradle-to-cradle [52], slow manufacturing, local manufacturing [53], product service systems [9], and product compatibility and upgradeability [54].

An additional manufacturing level is required to consider implications of cost, energy and other resource consumption for these new business strategies [55]. Since for manufacturers the primary consideration in choosing a business strategy will always come down to cost and profit, it is unlikely that any manufacturing activities will be fully optimised for energy efficiency. However, by being able to understand how energy can be considered, measured and managed at this high level, significant energy improvements could still be made. Through the development of new EM techniques, it is important to be able to consider the life cycle manufacturing energy consumption of products as well as the life cycle energy consumption of manufacturing processes and facilities used to produce these products. Figure 6 shows an updated and simplified version of the EM technique research map, which includes the proposed business strategy manufacturing level. Preliminary guidelines for the consideration of energy consumption factors at this business strategy level are discussed by comparing two different business strategies for furniture.

Two distinct and simple business strategies for manufacturing household furniture may be described as the provision of either low-cost, short lifespan, or expensive, long lifespan products. The decision on which strategy to take is made at the conception stage of the business and may depend upon existing supply chain links, market opportunities or available workforce skill set for example. It is unlikely that such a strategic decision would ever be made

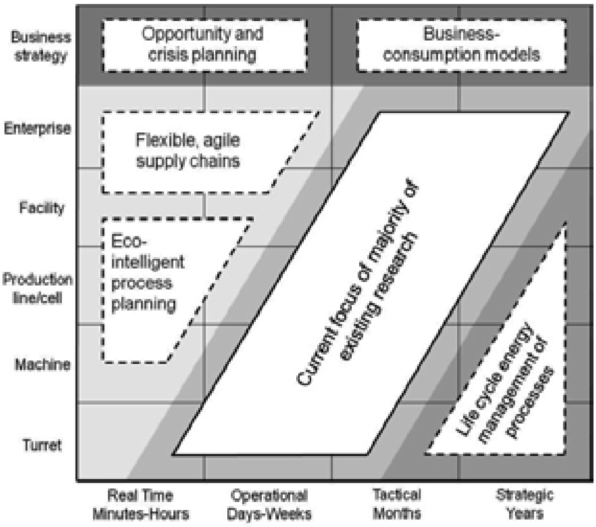

Figure 6. Manufacturing level-decision timescale map showing positioning of required focus for EM to contribute towards industrial sustainability.

purely on the merits of energy consumption levels, but the decision itself has a significant implication on energy use. Table 1 shows some differences between the individual approaches for the manufacture of the furniture. EM techniques are required to assess the different impacts of the two strategies to enable effective EM decisions to be made.

For the short life products, the manufacturer requires a rapid production throughput, and low cost, lightweight materials are likely to be used, which can be quickly manufactured. Because of the highly competitive low selling price of the short-life goods, profit margins are low and therefore there is an economic need to have high volumes of production ensuring that the market remains in constant need of new furniture. For this type of production, low manufacturing costs are essential and so rapid, highly efficient and centralised manufacture is of key importance, and therefore, the embedded energy [56] per product is likely to be relatively low.

Short-life furniture	Long-life furniture
· Energy efficient process	· High quality processes
· Rapid production	· Quality-driven production
· Automated production	· Semi-automated production
· High throughput	· Low throughput
· Low profit margins	· High profit margins

Table 1. A comparison of different manufacturing considerations for short- and long-life furniture.

Conversely, for long life products, materials and manufacturing processes are quality driven with less regard for cost, which will be easily recuperated by high profit margin sale prices. As the products are intended to last a long time, the manufacturer is keen on brand awareness and will ensure their products are of the highest quality. Slower, more energy intensive procedures are likely to be used with additional finishing, inspection and testing processes. Distributed manufacture from small facilities is likely to be preferred to be adaptable to regional market requirements. For this type of product, the embedded energy per unit is likely to be relatively high.

Since the object of manufacturing is to provide a functional unit for a particular market need, a key indicator is the length of time a product fulfils a need. The longer the life of the product with respect to energy consumed, the more energy efficient the manufacturing of the product. This energy per product year, E_{PY}, can be expressed in simple terms as E_{PY} = energy required for manufacture/product lifetime.

Applying this measure to the present example we can consider that the total energy consumption required for an item of furniture is the summation of embedded product energy, E_E, and amortised (i.e., per product) energy from the lifetime of the production processes (i.e., the energy required to produce, maintain and repair the process machinery), E_P, and the amortised energy from the facility, E_F, then the energy attributed to each year of the product's life can be expressed as $E_{PY}= (E_E+ E_P+ E_F)/L_P$, where L_P is the average anticipated product life in years. Note that if the producer has responsibility for the disposal of the product at its end of life, the energy requirement for this also needs to be considered in the above equation. Other considerations at this business strategy level might include the possibility of remanufacture (lowering future E_E), availability of renewable energy (lowering the impact of E_E), production at low energy demand periods and maintenance contracts.

The product lifetime is of utmost importance in the case where significantly different lifetimes of products are being considered. In this example of furniture, it is not unreasonable to assume an order of magnitude difference in lifespan. Assuming there is no significant difference between the production energy, the business strategy that manufactures longer life furniture will be preferable.

Regardless of which business strategy is used, the process of considering the energy consumption factors throughout the life cycle of the products can be used to influence the selection of manufacturing processes, facilities, facility operation times, and so on. Clearly, as with EM techniques at lower manufacturing levels, approaches at the business strategy level require availability of suitably reliable or indicative data, or appropriate assumptions. In addition because of the complexity of different business models, such high level EM may require significant input from techniques focussing at lower levels of EM (e.g., HVAC control to reduce E_E) to yield the best results.

There is a need for the development of new EM techniques at the business strategy level that assist manufacturers not only in deciding which production models are least energy intensive, but also in minimising energy consumption at the highest level with an integrated approach. Importantly, such EM techniques need data for the specific stages in a product's life cycle for which the manufacturer is responsible. By using energy per product year as the unit of measure, it is possible to compare between dissimilar manufacturing and business approaches.

The general approach suggested here is a three stage consideration of energy at the business strategy level. In the first stage, it is essential to set the boundaries and contributing factors for energy consumption. Boundaries will include everything that a manufacturer is responsible for or has direct control over during the entire product/s life time and could extend to the supply chain, providing sufficient information is available. Contributing factors should focus on high level energy consuming tasks such as embodied product energy, impact of energy sources, embodied life cycle energy of the factory infrastructure, post-life product responsibility and life span of manufactured product.

The second stage in the approach requires an understanding of the relationship between different energy considerations, assignment of appropriate variables and development of any relationships between factors. In most cases, it will be useful to evaluate the total energy consumption per product year for which the manufacturer is directly responsible (i.e., not during use cycle). It is not important to fully understand the details of each energy contributing factor, but it is important to understand how certain factors relate to one another. An example of this is described in Section 4.

The third and final stage is to identify the factor(s) that have the largest energy contribution and make improvements in these areas as appropriate.

Obviously, the current approach is generalised but is intended to give guidance for the development of future EM techniques for decisions at the business strategy level. Of key importance is sufficient understanding of the impact of business strategy on energy consumption and the specific actions that can be taken to reduce this reliance on energy.

4. A Case Study for EM Method at the Business Strategy Level

The life cycle approach for considering energy at the business strategy level can be applied to any product, provided that sufficient consideration is given to the contributing factors. The level of detail can be adjusted to allow for different levels of data availability or understanding, but it is important to assess the need for different energy consumption factors within the life cycle of the product.

It may be criticised that consideration of some factors are difficult at the business strategy planning stage. However, it is not necessarily essential to have firm data in order to be able to assess different strategies; sensible assumptions can be used to evaluate the energy implications of business strategies. The following example compares different business strategies for the manufacturing and provision of steel roofing material using energy data from [12]. Considerations for energy consumption should include manufacture of the sheeting, transport, maintenance or replacement and any energy consumption or benefit from end-of-life management. The data used for this case study is shown in Table 2.

Factor	Values
Steel sheet production[#]	178 MJ/m^2
Transport[#]	2 MJ/m^2
Replacement section manufacture	3.6 MJ/m^2 year
Maintenance of roof	3.6 MJ/m^2 year
End of life management[#]	-48 MJ/m^2

[#] Data from [12].

Table 2. Numerical values used for comparison between PSS and sale business strategies for steel roofing.

A manufacturer may evaluate the benefit with respect to energy consumption of supplying galvanised steel roof sheeting under a product service system (PSS) basis as opposed to the more common make-sell business model. Under a PSS, the building owner does not actually own the roofing material (ownership remains with the producer) but lease it on a fixed term basis (e.g., for the period of occupation of the building) with maintenance costs being covered by the producer. The 'user' simply pays for the use of the roofing. Setting the boundaries of the comparison between manufacturing processes carried out in-house by the manufacturer and the end-of-life management of the galvanised steel sheeting, Table 3 shows the different factors for consideration in this scenario.

Factor	Sale	PSS	Values/Assumptions
Steel sheet production (MJ/m^2)	$E_{x,prod}$	$E_{y,prod}$	$E_{x,prod}$=$E_{y,prod}$ = 178
Transport (MJ/m^2)	$E_{x,tran}$	$E_{y,tran}$	$E_{x,tran}$=$E_{y,tran}$ = 2
Replacement section manufacture (MJ/m^2 year)	$E_{x,rep}$	0	$E_{x,rep}$= $E_{x,prod}$/50 = 3.6
Maintenance of roof (MJ/m^2 year)	0	$E_{y,mnt}$	$E_{y,mn}$= $E_{y,prod}$/50 = 3.6
End-of-life management (MJ/m^2)*	0	$E_{y,eol}$	$E_{y,eol}$ = -48
Lifetime (years)	z	kz	z = 20 years

k, the ratio of the life of the PSS roofing to the life of the customer owned roofing.

*If the manufacturer instigates the recycling of the material, they can justify off-setting any energy benefit against their manufacturing energy consumption.

Table 3. Energy consumption factors considered for comparison between PSS and sale business strategies for steel roofing.

Using the factors from Table 3 in the equation $E_{PY}= (E_E+ E_P+ E_F)/L_P$, the energy per product year can be written for the sale and PSS business strategies, respectively, as $E_{x,py}=((E_{x,prod} + E_{x,tran})/z) + E_{x,rep}$ and $E_{y,py}=((E_{y,prod} + E_{y,tran} + E_{y,eol})/kz) + E_{y,mnt}$.

These two basic expressions can be used to determine the significant contributing factors of both the roofing sale and PSS strategies. Since from the above we can obtain the equality $((E_{x,prod} + E_{x,tran})/z) + E_{x,rep} = ((E_{y,prod} + E_{y,tran})/z) + E_{x,mnt}$, then we can obtain, $E_{y,py}= (E_{x,py}/k)+ (E_{y,eol}/kz)$.

Using the values from Table 3, and given that it can be shown that $E_{x,py} = 9.8$ MJ/yr/m^2, we find that, $E_{y,py}$=*(7.4/k).*

Thus it can be shown that if $k > 0.76$, then it will always be beneficial from a manufacturer's energy perspective to opt for the PSS strategy. In the PSS strategy, since the manufacturer generates income from each year the roofing material is in service, rather than from a one-off income generated through the sale of the steel sheeting, the value of k will likely be greater than 1. The incentive to prolong the life of the product by the manufacturer means that addition care may be taken in the maintenance of the roofing, at the expense of $E_{y,mnt}$.

Based on the given example, to make the sale strategy more competitive in terms of energy, manufactures could focus on methods of extending the life of the roofing (e.g., by additional coatings) or significantly reducing the embedded product energy (which will likely have a negative impact on life expectancy). As no actual energy is consumed at the business strategy level, energy improvements will ultimately come from the implementation of EM techniques at lower manufacturing levels.

In the given case study, it is possible to introduce additional terms into this comparison which may look at energy implications such as process machinery and infrastructure life cycle energy costs, warranty repair, supply chain PSS, for example, depending on the company's scope and business model.

Using the three stage approach proposed in this chapter it is possible to compare between different business strategies using limited data or assumptions. The output will give an indication as to the energy consumption factors that need to be considered in more detail to ensure the overall minimisation of energy use for manufacturing activities. However, significant work is required by academia and the manufacturing industrial sector to develop more focused EM techniques for the business strategy level.

5. Concluding Discussions

The need for EM and rationalisation within manufacturing has led to the development of a very large number of EM techniques. These techniques cover issues from machine–tool interaction to distribution logistics and supply chain management. A review of a cross-section of EM techniques has revealed a correlation between the manufacturing levels and decision timescale. As a consequence, there are areas of research that have not yet been addressed, such as the life cycle evaluation of production processes and the short-term management of energy supply and supply chain operations. This chapter asserts that there is a requirement for EM techniques to be developed in these currently uninhabited research spaces since manufacturers are continually searching for ways to reduce energy costs and improve environmental performance. Considerations for approaches to developing EM for life cycle impact of production processes include flexible, reconfigurable process chains, factory layouts and upgradability and maintainability. For eco-intelligent factories and reactive supply chains, energy supply security, production flexibility and supply chain agility will form the cornerstones of EM for manufacturers of the future.

In addition, as manufacturers consider more radical ways of reducing their environmental impact and maintaining market share in volatile consumer markets, new business strategies are being considered to generate income in ingenious ways. These new strategies are being developed with economic benefit as the primary focus, but it is also important for manufacturers to consider EM of these strategies to minimise the energy consumption of their activities in the long term. Therefore, building on the existing scope of EM techniques which have focussed on the manufacturing levels, this work suggests that new techniques need to be developed for an additional manufacturing level, namely business strategy, which is positioned above the enterprise level in the hierarchy. The business strategy level has been shown to be slightly different from the other manufacturing levels in that no energy is actually consumed at this level, but energy consumption for products and services are largely defined by decisions at this level. It is therefore reasoned that approaches to EM for business strategies should consider the energy expenditure that the manufacturer has direct control over for the life cycle of the product. This approach allows different business models to be evaluated using the same core framework, even if the strategies are markedly different.

A three stage high level procedure has been described for EM at the business strategy level, which consists of definition of scope and energy contributing factors, identification of interrelationships between energy factors and a comparison of potential strategies and finally a focus on the largest energy consuming factors using techniques from lower manufacturing levels. Of key importance at the business strategy level is that there is no requirement for detailed energy data that may be difficult to obtain at a planning stage. Instead, comparisons may be made between strategies based on a few well-grounded assumptions.

In summary, as manufacturing businesses become more energy aware and seek to remain competitive in highly transient and environmentally focused markets, new business strategies and increased production flexibilities are being explored. The manufacturing industry is evolving for the better, and new EM techniques will be essential in supporting this revolution.

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Chapter 2

The Choice between Economic Policies to Face Greenhouse Consequences

Donatella Porrini

Additional information is available at the end of the chapter

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Abstract

In the past few years, unstable and extreme weather patterns are increasingly occurring as phenomena of climate change, and the link to greenhouse gas (GHG) emissions is scientifically accepted. From an economic point of view, extreme weather patterns are causing major damage to health, property, and business.

In this chapter, following an economic analysis of law (EAL) approach, the issue of the comparison between the alternative environmental economic policies is analyzed starting from the consideration that the emissions of GHGs originate market failures: the environment appears as a "public good" that may not be appropriated and has no market price; the damage to the environment is a case of "externality," where it is fully or partly a social cost that is not internalized into the accounts of the parties causing it. In the EAL literature, an environmental policy instrument has been seen as it may play a role in correcting malfunction and subsequent inefficiencies.

In the first part of the chapter, we intend to revise the traditional analysis of the choice of environmental policies. The following part deals with the comparison between tax and tradable permit systems. Then the role that can be played by the insurance sector is considered. The different policy instruments are considered in the framework of climate as an economic global public good. And, finally, some conclusive remarks are presented in relation to the COP 21 conference in Paris in terms of the future policies against GHG effects.

Keywords: climate change, environmental policy choice, insurance, greenhouse gasses, COP 21

1. Introduction

Over the last centuries, climate change has been raised as a very important issue all over the world. The change in climate results from an increase in the earth's average atmospheric temperature, which is usually referred to as global warming. It may be due to both natural and human causes, especially greenhouse gas (GHG) emissions.

In response to increasing scientific evidence that human activities are contributing significantly to global climate change [1], decision makers are devoting considerable attention to public policies to reduce GHG emissions and thereby prevent or reduce such change.

The policies span a range of regulatory approaches. The main alternative is between command and control (CAC) and market-based (MB) instruments, and a relevant role can also be played by the insurance sector.

This chapter aims to describe the traditional theory on the choice of environmental policies following an economic analysis of law (EAL) approach (Section 2) to analyze the comparison between tax and tradable permit systems (Section 3), to outline the role of the insurance sector (Section 4), and to consider the different policy instruments in a context of economic global public goods. The final objective is to take into account the future COP 21 conference in Paris in terms of the choice of policy instruments against GHG effects.

2. The traditional issue of the choice of environmental policies

The problem of the choice of environmental policy instruments has been an issue since Pigou [2] analyzed the need for state intervention when private costs diverge from social costs and suggested that the solution would be to internalize the externalities through taxation.[1] Coase [4] criticized the proposed state intervention and affirmed that there is no reason to suppose that governmental regulation is called for simply because the problem is not very well handled by the market or the firm.

The ensuing debate has been conducted along these two opposite views: on the one hand, the supporters of the idea that the choice of policy instruments is to be applied as a public matter and the state, as policy designer, should select the optimal instruments and take responsibility for their imposition in the public interest, but, on the other, the supporters of MB instruments are trying to fight a battle against a sort of "anti-market" mentality based on a reluctance to apply MB instruments [5].

So the problem would be to compare the instruments that can be considered public oriented and those that can be considered market oriented, where the former is characterized by a public agency that defines a conduct rule and provides an enforcement system and the latter is characterized by instruments based on market mechanisms stimulating the conduct of the firm indirectly and by a private administration and enforcement system.

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[1] See the documents of the "Pigou club" [3].

Following an EAL approach, traditionally regulatory systems originate from the presence of market failure: in our specific case, the environment appears as a "public good" that may not be appropriated and has no market price; the damage to the environment is a case of "externality," in that it is fully or partly a social cost that is not internalized into the accounts of the parties causing it.[2] So the comparison of different instruments can consider how they may play a role in correcting malfunction and subsequent inefficiencies [7].

In this way, we can move from the theoretical definition of the efficiency of different instruments to their practical, and so direct, potential to achieve concrete objectives. In particular, the objectives that emerge as relevant in judging the practical efficiency of environmental policies are the following: first is the prevention in the sense of providing incentives for firms to improve safety standards, and second is the connection with technological change in the sense of encouraging firms to adopt lower risk technologies.

The first kind of environmental instrument is the so-called CAC that is characterized by a public agency that provides a definition of conduct rules and enforcement system. Thus, they could be defined as public-oriented instruments, which require the use of a particular technology or the observation of a performance standard, authorizing for the maximum amount that a source can emit.

CAC is divided into two phases as follows: "command", which sets a standard based on the maximum level of permissible emissions, and "control", which monitors and enforces the standard.

Regarding standards, they can be classified into two: ambient standards, which fix a minimum desired level of air or water quality or a maximum level of emissions that must be maintained, and emission standards, which fix a maximum level of permitted emissions that can be performance based, setting emission limits that each firm is allowed, or technology based, specifying the best technology to be used.[3]

As to the US experience with this kind of regulation, the activity of the Environmental Protection Agency (EPA) provides a clear example of regulation by an independent environmental authority. This agency performs its tasks through the setting of preventive standards, the enforcement of polluting emission thresholds, and the performance of inspections and, possibly, of actions brought to the federal courts. We cannot mention the European Community experience given that a standard setting system has not been established at a European level (but at national level) and that the European Environmental Agency (EEA) has only a very limited role.[4]

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[2] Economists consider environmental policies within the framework of the category of externalities, as evidenced by Cropper and Oates [6]: "The source of basic economic principles of environmental policy is to be found in the theory of externality."

[3] As Cropper and Oates [6] explain"…The determination of environmental policy is taken to be a two-step process: first, standards or targets for environmental quality are set, and, second, a regulatory system is designed and put in place to achieve these standards. This is often the environmental decision making proceeds. Under the Clean Air Act, for example, the first task of the EPA was to set standards in the form of maximum permissible concentration of the major air pollutants. The next step was to design a regulatory plan to attain these standards air quality."

The choice to develop a CAC regulatory system is based on the advantage of centralized agencies to assure a cost-effectiveness calculation on the base of the expected damage and of the marginal cost of different level of preventive care. The centralized structure presents the advantage to provide a continual oversight of problems and a broad array of regulatory tools.

Following the traditional EAL approach, well-defined standards generate the correct incentive for the firm to act with caution and make the best production and prevention decisions [8, 9].

CAC instruments use to be compared with MB instruments that are characterized by a private administration and enforcement system and stimulate indirectly the behavior of the firm. There are essentially two different types of those instruments: taxes that are fees imposed on emitters proportionate to the total amount of emissions released into the environment (they could be divided into emission charges, product charges, and user charges) and marketable (or tradable) permit systems that provide a fixed number of permits equal to the allowed total emissions, distributing them among polluting firms in a specific area.

The two types of MBI instruments can be seen in the following two different approaches: on one side, taxes follow a price approach because producers adjust the quantity, given a fixed price put on emissions; on the other side, a tradable permit system follows a quantity approach because the price is adjusted according to supply and demand, given a maximum quantity of emissions allowed.

3. Carbon tax versus tradable permit system

A carbon tax is a particular tax based on GHG emissions generated by burning fuels and biofuels, such as coal, oil, and natural gas. It has been introduced with the main goal to level the gap between carbon intensive (firms based on fossil fuels) and low carbon intensive (firms that adopt renewable energies) sectors. Due to the introduction of that form of taxation, the relative prices of goods and services will change; the emissions of intensive goods will be more expensive, whereas the emissions of less intensive goods will be lower. Thus, carbon tax provides a strong incentive for individuals and firms to adjust their conduct, resulting in a reduction of the emissions themselves. Hence, by reducing fuel emissions and adopting new technologies, both consumers and businesses can reduce the entire amount they pay in carbon tax.

A tradable permit system is defined as quantity-based environmental policy instrument. The regulatory authority stipulates the allowable total amount of emissions (cap) and the right to emit becomes a tradable commodity. Under a cap-and-trade system, prices are allowed to fluctuate according to market forces. Thus, the price of emissions is established indirectly. Permits could be allocated to firms through auction or free allocation.

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[4] The EEA was set up as a legally independent community body under council regulation (EEC) 1210/90. The EEA's core task is to provide decisionmakers with the information needed for making sound and effective policies to protect the environment and support sustainable development.

Similarly to other environmental taxes, carbon taxes are defined as priced-based policy instruments for the correlated effects to increase the price of certain goods and services, thereby decreasing the quantity demanded. On the other side, tradable permits are defined as quantity-based environmental policy instrument. Although both policy instruments are MB, their implementation is different: carbon taxes fix the marginal cost for carbon emissions and allow quantities emitted to adjust, whereas tradable permits fix the total amount of carbon emitted and allow price levels to change according to market forces.

Which is better? There is no simple yes or no answer, and the policies are not necessarily mutually exclusive. Several important advantages and drawbacks of the respective policies are outlined later.

A well-functioning emission trading system allows emission reductions to take place wherever abatement costs are lowest, regardless of international borders. As costs associated with climate change have no correlation with the origin of carbon emissions, the rationale for this policy approach is that an emission trading system allows to fix a certain environmental outcome and the companies are called to pay a market price for the rights to pollute. This is the reason why an emission trading system is suitable for international environmental agreements, such as the Kyoto Protocol, specifically for the characteristic that a defined emission reduction level can be easily agreed between states.

Emission trading is more appealing to private industry because, by decreasing emissions, firms can actually profit by selling their excess GHG allowances. Creating such a market for pollution could potentially drive emission reductions below targets.

A carbon tax would offer a broader scope for emission reductions [10]. A system of tradable permits entails significant transaction costs, which include search costs, such as fees paid to brokers or exchange institutions to find trading partners; negotiating costs; approval costs; and insurance costs. Conversely, taxes involve little transaction cost over all stages of their lifetime.

Carbon taxes are dynamic economic instruments that offer a continuum incentive to reduce emissions. In fact, technological and procedural improvements and their subsequent efficient diffusion lead to reductions in tax payment. In addition, trading systems are able to self-adjust because emission goals will be easier to meet; there will be a decrease in permits' demand and in their price but not as rapidly as taxes.

The implementation of an emission trading system is very complicated and requires technical steps, including treatment of sinks, monitoring, and enforcement. On the other hand, taxation is a very well-known instrument by policy makers, not very costly because it does not require monitoring and enforcement organization.

The revenue from carbon taxes can be used into the economy to reduce income taxes or levies on labor or capital investment. This may be part of a national or international reform of the taxation systems with the effects to shift the tax burden from "goods" like labor to "bads" like pollution.

In Table 1, we have summarized the main differences among CAC, carbon tax, and tradable permit system.

	Command and control	**Carbon tax**	**Tradable permit system**
Certainty over CO_2 price or cost?	No	Yes. The tax establishes a well-defined price	No. But price volatility can be limited by design features, such as a safety valve (price cap) or borrowing
Certainty over emissions?	No. Regulating the rate of emissions, the level uncertain leaves	No. Emissions vary with prevailing energy demand and fuel prices	Yes, in its traditional form. No, with the use of additional cost containment mechanisms
Efficiently encourages least-cost emission reductions?	No, but tradable standard is more efficient than non-tradable standard	Yes	Yes
Ability to raise revenue?	No	Yes. Results in maximum revenue generation compared with other options	Traditionally no
Incentives for R&D in clean technologies?	Yes and no. Standards encourage specific technologies but not Brod innovation	Yes. Stable CO_2 price is needed to induce innovation	Yes. However, uncertainty over permits' prices could weaken innovation incentives
Harm to competiveness?	Somewhat. Regulations increase the cost of manufacturing, but, unlike taxes of tradable permits, do not raise the price of fossil energy	Yes, though if other taxes are reduced through revenue recycling, competitiveness of the broader economy can be improved	Yes (as with a tax), but giving firms free allowances offsets potentially harmful effects on profitability
Practical or political obstacles to implementation?	Yes. Setting the level of standards is difficult	Yes. New taxes have been very unpopular	Yes. Identifying a reasonable allocation and target is difficult
New institutional requirements?	Minimal (unless tradable)	Minimal	Yes, but experience with existing trading programs suggests that markets arise quickly and relatively inexpensively

Source: Parry and Pizer [11].

Table 1. Command and control versus carbon tax versus tradable permit system

4. Insurance as an environmental policy instrument

A relevant role could be played by the insurance sector in the choice of political economic instruments for climate change.

As mentioned in Section 1, following the EAL approach, the emitters of GHGs externalize the true costs of their contribution to climate change, and this implies the need to recover these costs, which manifest through both the costs of impacts and the costs to prevent impacts. Because the insurance sector is the world's largest industry, the response of insurers to the broader climate change challenge will no doubt be the key to, at least partially, solve this internalization problem.

Generally, insurers can indirectly stimulate prevention behavior in their customers. In the case of climate change, they can play two primary roles through their insurance products. The first role is played in supplying and pricing traditional insurance coverage for damage deriving from climate change by the promotion of actions of businesses and individuals to align policy holders with climate-positive behaviors. The second is played in providing capital to new ventures and reducing the financial risk to investors by facilitate the creation of new markets and services that will help to solve the climate change problems.

In both the roles, insurance companies deal with the management of risk activities. In fact, climate change risk is managed by the insurers through the risks they accept from clients, given that climate change causes an increase in intensity and spreading the distribution of extreme weather events with resultant effects on property claims that could be catastrophic.[5]

Traditionally, insurance is the main mechanisms available to individuals and business to manage the financial consequences of risky events, such as natural hazards like windstorms and floods. Insurance companies used to work making each individual or business pay a premium to protect themselves against an uncertain loss. The premium is calculated by pooling risks across a large and diverse population considering the pool's expected losses.

In this way, the insurance industry provides a coverage for climate change consequences because climate experts predict changes in the intensity and the distribution of extreme weather events and of the resulting risk of catastrophic property claims.

But specifically, for what concerns the consequences of climate change, many problems arise to provide insurance coverage [13].

First, climate change is connected to global weather patterns that may increase the potential for losses so large. As more severe weather becomes more common and overall variability of conditions increases, there is a threat for the solvency of insurance companies.

Second, because uncertainties in assessing climate change's impacts are high and affect property, casualty, business interruption, and health; as a result, risk has significant ambiguous components and insurers are both likely to charge a significantly higher premium or avoid insuring the risk entirely.

Third, climate change–related risks may be correlated and create a skewed risk pool that could increase the probability of extremely large losses and also risks not well-distributed across existing insurers.

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[5] Insurance coverage can be also connected with the liability system. But, for what concerns the consequences of climate change, such as impacts of property damage from extreme weather events, the assignment of liability is a very complex topic. See Reference [12].

Finally, as a result of insurers' uncertainty aversion and need to protect against extremely large losses from single or related events, it is not clear that insurers will be willing to insure against some climate change–related risks at a price that policy holders are willing to pay.

Climate change will affect, and in some cases is already affecting, most major types of insurance products. Insurers will feel the impact of climate change on property and casualty insurance, where the insurer bears the risk of a loss suffered directly by the policy holder. These property and casualty claims include not only damage to insured property as a direct result of weather but also claims for business interruptions and other consequences of weather-induced events. Also, health and life insurers are going to face increasing costs.

Sometimes, insurance companies are involved in the systems of compensation fund that have been established in some countries. This is the case of special government disaster funds within the target to promote framework of contingency measures to cover the economic costs of natural disasters [14].

Other insurance products are the so-called "financial responsibility" products. This term includes the tools that require companies to demonstrate to have sufficient financial resources for eventual future environmental damage that may arise through their activities. In its common implementation, financial responsibility implies that a production activity is authorized only if companies can prove that they will be able to financially cover economic claims, for example, using surety bonds, cash accounts, deposit certificates, self-insurances, and corporate guarantees.

In the past few years, the insurance industry has developed financial products suitable for dealing with climate change-related risks in the direction to play a role far beyond simply compensating climate change's victims for their losses ex post. The activity of the insurance has become relevant as a political economic instruments within an ex ante strategy to financially manage large-scale catastrophes, as a complement of ex post instruments for the compensation of disaster losses.

Insurance industry is also developing alternative risk transfer products, given that conventional reinsurance arrangements may in future cover a smaller proportion of total losses, and there may be insufficient capital available to insurance markets to cover these losses [15].

A first kind of these insurance products are called "catastrophe bonds" and consist in securitizing environmental risks in bonds, which could be sold to high-yield investors. The catastrophe bonds are able to transfer risk to investors that receive coupons that are normally a reference rate plus an appropriate risk premium. By these products, insurance companies limit risk exposure transferring natural catastrophe risk into the capital markets. In this way, with the involvement of the financial markets, their global size offers enormous potential for insurers to diversify risks.

Weather derivatives are another kind of financial instrument used by companies to hedge against the risk of weather-related losses. Weather derivatives pay out on a specified trigger, for example, temperature over a specified period rather than proof of loss. The investor providing a weather derivative charges the buyer a premium for access to capital. If nothing happens, then the investor makes a profit.

With this kind of financial products, the insurance industry tries to reach two goals. First, there is the need for extra capital and to spread risks beyond the insurance sector. Particularly, cat bonds are used to spread insurance risk in the financial sector. The second goal is to improve the accuracy and the resolution of hazard data and the likely impacts on climate change with the involvement of financial market forecast ability.

The insurance industry can act to tackle the consequences of climate change by playing its part in climate change mitigation, through the promotion of ways to reduce GHG emissions. Insurers are also well placed to help society to adapt to the impacts of climate change, by promoting the effective limitation and management of risks from extreme weather-related hazards.

Individuals and companies that buy insurance products could be stimulated to address climate change-seeking mechanism to facilitate mitigation of GHG emissions and adaptation to the inevitable impacts of climate change [16]. In addition, the insurance companies themselves are motivated to take significant actions to mitigate GHG emissions and increase adaptive capacity to reduce overall uncertainty and other barriers to insurability and are also motivated to limit the insurers' potential exposure to catastrophic risks in excess of their capacity to avoid the potential for property and liability claims in excess.

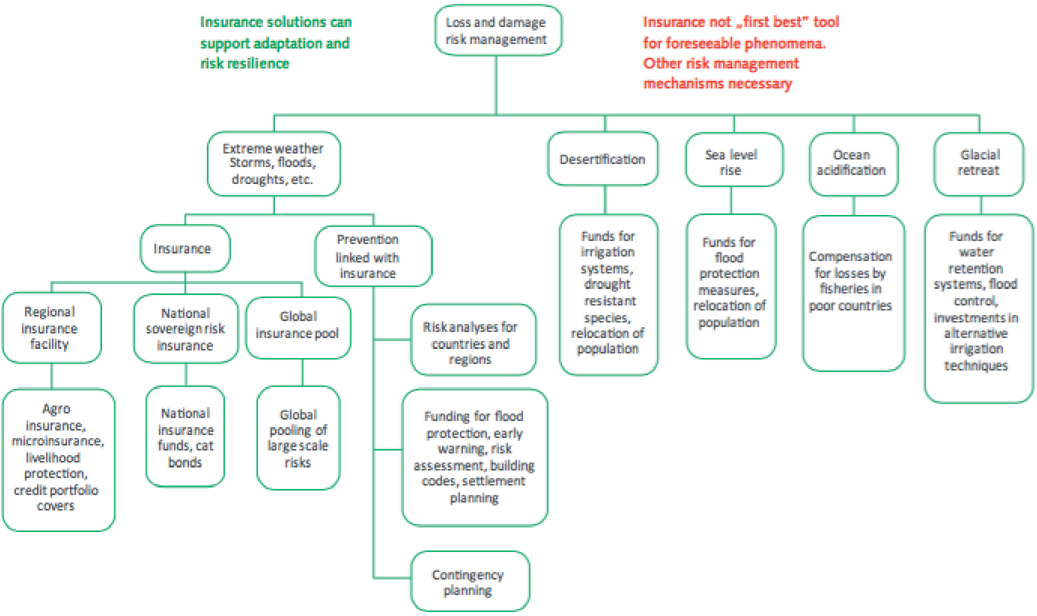
The insurance industry is also developing new products that would have the consequences to stimulate the adaptation to climate change. On the one hand, products help to create the conditions for active adaptation to build physically resilient communities; on the other hand, products provide capital and liquidity to help communities to cope with losses caused by climate change catastrophes.

Insurance products can be designed in a way for which simply their price reflects the level of climate change-related risk assumed by the insurer. These products, rewarding behavior that reduces risk of financial losses, encourage adaptive behavior. For example, insurance products that incorporate these features provide a premium discounts on property insurance for climate-resilient commercial or residential buildings.

The recent tendency to supply coverage with differential premiums to customers depending on their level of protection from losses caused by weather-related disasters can be seen as a clear opportunity for insurers to reduce their own overall and maximum possible loss exposure while promoting communities overall resilience in the face of climate change's impacts. So, more often, policies include discounts for businesses or homeowners that have taken specific steps to ensure their buildings resistant to floods or other hazards. Moreover, insurance companies also condition their policies on compliance with laws such as building codes, thus playing a role in enforcing laws that promote climate change resilience.

The second kind of insurance products that stimulate adaptation is based on the availability of capital to cope with catastrophes. These are financial arrangements intended to bring needed capital that will reduce the risk that could derive from future climate-related hazards for those who are most likely to be in peril. These products can be defined as adaptation oriented because they help to build the capacity of nations, communities, and businesses to cope with climate change impacts.

Figure 1 shows the different roles that can be played by insurance sector as a form of environmental policy instruments.



Source: MCII [17].

Figure 1. The different roles of the insurance sector in the framework of climate change consequences

5. Policies choice in the case of climate change and the concept of "economic global public goods"

Dealing with the consequences of GHG emissions in terms of climate change implies a definition of "economic global public goods" that can be defined as goods with economic benefits that extend to all countries, people, and generations [18]. Following the EAL approach, they are special case of externalities with a global dimension.

Climate is clearly "global" in both causes and consequences; moreover, the emissions of GHG have effects on global warming independently of their location, and local climatic changes are completely linked with the world climate system.

In addition, global warming is characterized by other important features that imply some difficulties in the implementation of the instruments provided by the standard economic theory of policy choice. First, we cannot determine with certainty both the dimension and the timing of climate change and the costs of the abatement of emissions. Second, the effects of GHG concentration in the atmosphere on climate are intergenerational and persistent across time. Finally, it emerges a relevant equity issue among countries because industrialized countries have produced the majority of GHG emissions, but the effects of global warming will be much more severe on developing countries. In other words, the countries that have more responsibilities will face less consequence in the future and vice versa.

There are major governance issues involved in dealing with global public goods because global coordination is required [19]. With economic public goods, it is difficult to determine and reach agreement on efficient policies because they involve estimating and balancing costs and benefits where neither is easy to measure and both involve major distributional concerns. When dealing with economic public goods like global warming, it is necessary to reach through governments to the multitude of firms and consumers who make the vast number of decisions that affect the ultimate outcomes.

Because global warming is a global public good, the key environmental issue is global emissions, and the key economic issue is how to balance costs and benefits of global emission reductions. Climate change depends only on total GHG emissions and the time path of emissions not on the geographic location of emissions. Moreover, the impacts depend primarily on cumulative emissions that remain in the atmosphere not on the annual flow of emissions.

It is a global issue to decide what the distribution of emission reductions among countries should be and how the costs should be allocated, together with the need for differences among high- and low-income countries, high- and low-emitting countries, and high- and low-vulnerability countries.

Given the global nature of climate change, it is easy to understand the necessity of an action at international level, in order to efficiently implement the different policy instruments that we have analyzed earlier in this chapter.

First, the instruments based on tax mechanism need a method of coordinating policies among countries. In the international environment, it could assume the form of either an international tax or a harmonized domestic tax system. In the case of an international tax, the nations (and not the firms) pay the tax to an international agency, which receives and redistributes the tax revenues. On the other hand, in the case of harmonized domestic tax, the international community should negotiate an agreed level of a domestic emission tax, establishing adequate compensation for the losing countries from the gaining countries.[6]

Second, it is possible to establish an agreement that sets quantitative limits of emissions and allocates emission permits to firms (or States) but allows to trade among countries, in order to minimize abatement costs. The starting allocation of permits can be set through either an auction or a grandfather allocation. Under an auction, government (or the international community) sells the emission permits, whereas under the grandfather rule, the allocation of emission permits is based on historical records.

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[6] Nordhaus [20] hypothesizes the institution of an harmonized carbon tax (HCM), essentially equivalent to a "dynamic Pigouvian pollution tax for a global public good" and points out 10 different reasons to prefer it to a quantitative approach.

In the global-warming context, quantitative limits set targets on the time path of GHG emissions of different countries. Countries then can administer these limits in their own fashion, and the mechanism may allow transfer of emission allowances among countries, as is the case under the Kyoto Protocol.

The European Union Emissions Trading Scheme (EU-ETS) – the world's most extensive carbon pricing market – has now been in operation for 10 years. The EU-ETS was developed as a way of meeting the EU's GHG emission reduction targets in the most efficient and cost-effective manner. To do so, the EU-ETS sets a limit (a cap) on the total emissions; certain EU sectors (mostly heavy industry and aviation) are allowed to use during predefined trading periods. Permits are then distributed among polluters where one permit equals one ton of carbon dioxide equivalent. These permits can then be traded between market participants. As such, the total amount of pollution is set by an external authority, but market participants determine the permit allocation, thereby optimizing efficiency.

In addition, the involvement of the insurance sector as an efficient policy instruments needs a global approach.

Insurance sector can contribute to develop risk management strategy to minimize climate change consequences on an urgent basis to prevent further escalation of global warming. However, insurance needs to be a part of the overall policy of mitigation and adaptation that aims at reducing the severity of many impacts that could result from climate change if current adverse conditions prevail.

In order to organize their own operations to the new challenge, the insurance industry should include climate change risk in its internal governance procedures, in line with the existing financial corporate risk identification. To enable insurance companies to play a responsible role in tackling climate change consequences, they require a reliable, transparent, and international coordinated policy framework as well as long-term, appropriated GHG emission reduction goals coordinated at an international level.

6. Final remarks: COP 21 and the issue of the linkage of different national policies

In the COP 21 meeting in Paris at the end of the 2015, global climate policy has faced the tension between the efficiency benefits of uniform global policy and national and regional variation in tastes for differing policies. Although climate negotiations, going back to the framework convention, have had a coordinated global policy as their goal, it could be that we will head toward a less coordinated system of local, national, or regional policies.

In reality, as we have analyzed in the chapter, different countries are undertaking different policies ranging from CAC to MB approaches, such as carbon tax and tradable permit systems.

Variations in policies, although catering to local tastes and preferences, can lead to substantial inefficiencies, and the target will be to reach an optimal degree of policy homogenization.

There is a large literature on the importance of linking economic policies to face GHG consequences [21].

Some authors argue that the basic approach underlying emission reduction credit systems like the Kyoto Clean Development Mechanism (CDM) can be extended to create linkage opportunities in diverse emission control systems in ways that do not necessarily suffer from the shortfalls of the current CDM. Moreover, while emission reduction credit systems are designed to work with MB systems like tradable permits, they describe ways in which it can interact with tax systems as well as certain regulatory systems [22].

By clarifying the opportunities and challenges of insurance as an instrument for adaptation and outlining a practical way forward, it is hoped that this discussion contributes to the opportunities in adopting a comprehensive adaptation strategy that enables risk management and insurance through the funding of a global adaptation strategy [17].

In the near future, the challenge for COP 21 to reduce GHG emissions is to try to link heterogeneous climate policy instruments as a way to reach the solution of climate change issue in the long term.

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Chapter 3

Energy for Sustainable Development: The Energy–Poverty–Climate Nexus

Melanie L. Sattler

Additional information is available at the end of the chapter

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Abstract

Worldwide, 1.4 billion people lack access to electricity, and 2.7 billion people rely on traditional biomass for cooking. Most people living in energy poverty—without electricity access and/or using traditional biomass for cooking—are from rural areas of Sub-Saharan Africa, India, and other developing Asian countries (excluding China). At the same time, the poorest people are the most likely to suffer from the impacts of climate change.

Fortunately, innovative, sustainable energy technologies can allow developing countries to leapfrog to low-carbon renewable energy, while at the same time alleviating extreme poverty. Increasing energy access, alleviating rural poverty, and reducing greenhouse gas emissions can thus be complementary, their overlap defining an energy–poverty–climate nexus. Transitioning to more efficient low-carbon energy systems in rural areas can generate greater returns than similar efforts in industrialized areas.

Accordingly, this chapter provides an overview of: a) The linked problems facing developing countries of energy access, poverty, and climate change, and how these problems interact and compound each other. b) Potential renewable energy solutions, including off-grid solar, wind, clean biomass, micro-hydro, and hybrid systems. For each energy option, benefits and challenges will be discussed, along with examples of successful small-scale use in rural areas of developing countries.

Keywords: Sustainable energy, climate change, developing countries, renewable energy, energy–climate–poverty nexus

1. Introduction

Most of the world's people without access to electricity or clean energy are from rural areas of developing countries. At the same time, a person in a developing country is 79 times more likely to suffer from a climate-related disaster than a person in a developed country, according to the United Nations Development Programme [1].

Fortunately, for developing countries, increasing energy access, alleviating poverty, and addressing climate change can all be accomplished via sustainable energy. In fact, implementing renewable energy in rural areas can generate greater returns in terms of reduced greenhouse gas emissions than similar efforts in industrialized areas. Accordingly, this chapter will provide an overview of the current energy access problem in developing countries and potential innovative sustainable solutions. Off-grid renewable electricity options to be discussed include solar, wind, clean biomass, micro-hydro, and hybrid systems.

2. The Problems

The problems of energy access, poverty, and climate change are intertwined in the developing world. The poor often lack access to energy at all or have access only to inefficient and unhealthy forms of energy. Lack of energy makes it more difficult to address other aspects of poverty, such as lack of education or health care (imagine operating a school or hospital without access to electricity). As the poor gain access to energy, their contribution to climate change will increase, unless they leapfrog to renewable energy technologies. Unfortunately, the poor are the most vulnerable to many impacts of climate change, including increased food insecurity and amplified health risks. These interrelationships that constitute the energy–poverty–climate nexus problem are discussed in more detail below.

2.1. The Energy–Poverty Nexus

Worldwide, 1.4 billion people (20% of the world's population) currently lack access to electricity, and 2.7 billion people (40% of the world's population) rely on inefficient and unhealthy forms of biomass [2]. Air pollution levels indoors from 3-stone fires or inefficient stoves using biomass are many times higher than typical outdoor levels, even those in highly polluted cities. The World Health Organization (WHO) estimates that over 1.5 million die prematurely each year from household air pollution due to inefficient biomass combustion [2]. These deaths from cancer, respiratory infections, and lung diseases account for 4% of the global burden of disease—more deaths than those from malaria (1.2 million) or tuberculosis (1.6 million) [1]. Many of those who die are young children, who spend hours each day breathing in smoke from the cookstove [2].

Moreover, in regions where households rely heavily on unhealthy forms of biomass, women and children are typically responsible for fuel collection—a time-consuming and exhausting task. This strenuous work without sufficient recuperation can cause serious long-term physical damage for women. Heavy reliance on biomass can also cause land degradation, including deforestation, and local and regional air pollution [2].

As shown in Table 1, most of the people living in energy poverty—without electricity access and/or using traditional biomass for cooking—are from rural areas of developing countries, the majority in Sub-Saharan Africa, India, and other developing Asian countries (excluding China) [2]. At current growth rates, about half a billion "energy poor" will be added over the next 20 years [1].

Region	Number of people lacking access to electricity (millions)	Number of people relying on the traditional use of biomass for cooking (millions)
Africa	587	657
Sub-Saharan Africa	*585*	*653*
Developing Asia	799	1937
China	*8*	*423*
India	*404*	*855*
Other Asia	*387*	*659*
Latin America	31	85
Developing countries*	1438	2679
World**	**1441**	**2679**

*Includes Middle East countries.

**Includes Organisation for Economic Co-operation and Development (OECD) and transition economies.

Table 1. Number of people lacking access to electricity and relying on the traditional use of biomass for cooking, 2009 (million) [2]

Improving access to cost-effective, sustainable energy technologies is critical for addressing poverty in developing countries [1]. Although improving energy access is not one of the 8 globally agreed Millennium Development Goals (MDGs), it is a cross-cutting issue that directly impacts achievement of the goals [1]. More and better energy services are needed to end poverty, hunger, educational disparity between boys and girls, the marginalization of women, major disease and health service deficits, as well as environmental degradation [1, 2]. Without modern energy services, basic social goods such as health care and education are more costly in both real and human terms, and economic development is harder to perpetuate [1]. A clear correlation exists between energy and the Human Development Index (HDI) [3]. As the International Energy Agency and United Nations state, "Access to modern forms of energy is essential for the provision of clean water, sanitation and healthcare and provides great benefits to development through the provision of reliable and efficient lighting, heating, cooking, mechanical power, transport and telecommunication services" [2].

For the 1.4 billion people that lack access to electricity, they either live in locations too remote to be connected or cannot afford the fee to connect [4]. For locations that are off-grid, fossil fuels are often unaffordable due to the cost of delivery to remote locations [5].

2.2. The Energy–Climate Nexus

The climate change problem is largely a fossil fuel problem. According to the Intergovernmental Panel on Climate Change (IPCC) 2007 report, at least 57% of greenhouse gas emissions globally stem from burning of fossil fuels [6]. For carbon dioxide (CO_2), the most important anthropogenic greenhouse gas, 74% of emissions are due to combustion of fossil fuels [6]. When fossil fuels are burned for energy, the carbon stored in them, originally from biomass such as algae, is emitted almost entirely as CO_2. These fossil fuels include coal, oil, and natural gas, which are burned in electric power plants, automobiles, industrial facilities, and other sources.

2.3. The Poverty–Climate Nexus

The poorest people in the world are the most likely to suffer from impacts of climate change. According to the United Nations Development Programme (UNDP), a person in a developing country is 79 times more likely to suffer from a climate-related disaster than a person in a developed country [2]. The poor are especially vulnerable to the impacts of climate change, including reduced agricultural productivity and increased food insecurity; heightened water stress and insecurity; rising sea levels and increased exposure to climate disasters; loss of ecosystems and biodiversity; and amplified health risks [1]. According to the Human Development Report (HDR) 2007–2008, failure to address climate change will consign and trap the poorest 40% of the world's population, some 2.6 billion people, in downward spirals of deprivation [7]. Providing energy access will help poor areas adapt in the face of a changing climate [8].

Reductions in greenhouse gas emissions must include both developed and developing countries, including those with significant numbers of people living in poverty. According to the U.S. Environmental Protection Agency (EPA), greenhouse gas emissions from developing countries are expected to exceed those from developed countries in 2015 [9]. According to Casillas and Kammen [8], every dollar spent on the transition to more efficient low-carbon energy systems in rural areas has the potential to produce greater carbon mitigation returns than in more industrialized areas.

3. Potential Solutions

Since the problems of energy access, poverty, and climate change are interrelated in developing countries, solutions can be designed to solve all 3 problems simultaneously. Innovative sustainable energy technologies can allow developing countries to leapfrog to low-carbon renewable energy, while at the same time alleviating extreme poverty. Increasing energy access, alleviating poverty, and reducing greenhouse gas emissions can thus be complementary, their overlap defining an energy–poverty–climate nexus solution.

As mentioned above, according to the article published by Casillas and Kammen [8] recently in *Science*, transitioning to more efficient low-carbon energy systems in rural areas can generate greater returns than similar efforts in industrialized areas. Urban cities of developing countries may have access to electricity for lighting. Rural areas typically lack access altogether; hence, the need in these areas is the greatest [9]. Access to electricity in rural areas, even at modest consumption levels, can dramatically improve a community's quality of life. For example, electric lamps can allow children to study at night, and radios and cellular phones can greatly improve communication pathways [10]. This section will accordingly focus on renewable energy solutions for rural areas of developing countries.

Centralized electrification requires massive amounts of capital [10]. The dispersed nature of houses and low potential demand create little incentive for power companies to provide access to rural areas. In addition, extending the grid may be unrealistic due to transmission line costs or hard terrain [5]. Thus, in rural areas, off-grid and mini-grid solutions make the most sense. Such systems can consist of a single home or several small homes and businesses. The systems can be incremental and scalable and applied to many different conditions and environments [10]. Off-grid and mini-grid options for renewable electricity include solar, wind, clean biomass, and micro-hydro. These options for renewable power will be discussed in more detail below.

3.1. Solar Power

Solar energy is abundant in many locations in the developing world [5]. Many regard it as the most promising renewable source for developing countries [5, 11, 12]. The use of solar energy produces no on-site air pollutants [although pollutants are typically generated in the process of manufacturing photovoltaics (PV) cells].

Solar energy can be utilized in two ways: direct heat energy for various purposes (heating water, heating space) and direct current electricity generation using PV system. Electrical energy can be used immediately to pump water for irrigation or for refrigeration, lighting, or other purposes; alternatively, it can be stored in a rechargeable battery for later use [5]. This can help solve problems associated with its intermittency [12].

Individual houses can have their own PV system for lighting and small appliances, such as radio and mobile phone charging. A village can benefit from a larger PV system, with a micro-grid structure.

3.1.1. Solar Challenges

The primary barrier to widespread implementation of the solar PV technology is its cost, due to the high cost of the silicon base material and associated manufacturing processes [1]. In addition, production of solar cells currently requires sophisticated and expensive manufacturing facilities and highly trained personnel, which may not be available in developing countries. Nicole Kuepper, a Ph.D. student, won the Eureka Prize for Young Leaders in Environmental Issues and Climate Change for developing a simple, inexpensive way of producing solar cells in a pizza oven. The process uses a low-cost inkjet printing process, aluminum spray, and a low-temperature pizza oven, meaning that the solar cells can be made without high-tech environments or high-cost inputs [1].

Solar water heaters (SWHs) are relatively expensive to install ($500–$2100), although the initial investment can be recovered through future electricity savings [1]. For many families in rural areas, the purchase of a solar lighting set, even for lighting service only, is so hard that a systematic approach has to be designed, which enables them to pay only for the lighting service received instead of owning the whole hardware [5].

3.1.2. Solar Success Stories

Solar lanterns. Typically, solar-powered lanterns use solar energy to charge a battery that powers a solid-state light-emitting diode (LED), the most efficient lighting technology on the market. One solar lantern, the Mighty Light, costs around US$ 45 and lasts up to 30 years. It has replaced polluting dangerous kerosene lamps for thousands of households in Afghanistan, Guatemala, India, Pakistan, and Rwanda [1]. As of November 2010, around 9000 versions of a solar lantern called the "solar tuki" had been installed in Nepal [1].

Solar home systems. A solar home system is a PV system with capacity of 10–40 Wp (peak Watts). By 2007, Grameen Shakti had installed 100,000 solar home systems to power lights, motors, pumps, televisions, mobile phones, and computers in Bangladesh [1].

SELCO of India is an organization successfully installing solar home and business systems to provide electricity for lighting, SWHs, solar inverter systems (for use in communications and computing), and small business appliances. Since 1995, SELCO has been providing solar energy solutions to underserved households and businesses in India, based on the ideas that poor people can afford sustainable technologies, poor people can maintain sustainable technologies, and social ventures can be run as commercial entities [1].

Community solar systems. Community solar PV systems are commonly used for pumping water for drinking and irrigation. The solar panel may vary between 130 Wp and 40 kWp. The Promethean Power project promotes a version of community solar systems using concentrated solar thermal power rather than PV. The system, which can be manufactured locally, concentrates solar thermal energy to heat a fluid refrigerant. The solar thermal system is combined with a unique microscale generator adapted and scaled to suit the needs of underserved communities. The heated fluid expands through a rotary vane turbine (an automobile power-steering pump) to make mechanical energy that spins a generator (an automobile alternator). Massachusetts Institute of Technology (MIT) is installing the systems in Lesotho in Africa [1].

3.2. Wind Power

Like solar, the fuel source for wind power is free and unlimited. The use of wind turbines to generate electricity via a generator produces no on-site air pollution, although a small amount of emissions is produced during manufacture of the turbines. One life-cycle assessment found that off-grid wind turbines reduce greenhouse gas emissions by 93%, compared to off-grid diesel power generation systems [13]. An additional advantage is that wind turbines are simple mechanical systems that can be easily maintained and repaired [10].

3.2.1. Wind Challenges

One of the challenges associated with wind power is its intermittency. Researchers are developing solutions to this problem for off-grid wind systems. Short term, the electrical energy generated by the turbine can be stored in a battery [14]. Researchers have developed controllers that maximize capture of wind energy and avoid battery overcharge [15, 16]. Other researchers have proposed a hybrid energy storage system that can provide uninterrupted power, according to simulations. In the hybrid storage system, a battery is used for short-term energy storage, and a water electrolysis hydrogen system is used for long-term energy storage due to hydrogen's high mass energy density and very low leakage [17].

Another challenge is selecting an appropriate location for the turbine, due to the highly localized nature of wind. Low-cost anemometers may help alleviate this problem, but time must be spent to collect a sufficient amount of data [10]. Areas particularly suited to wind power because of their typical high wind velocities include coastlines, high ground, and mountain passes [12]. Wind power does not need water, so it is suitable for dry areas.

A third challenge is the need for a tower, so that the turbine is at least 10 m above the nearest obstacle. The tower itself could cost more than the wind turbine. Researchers are examining towers made from bamboo and other common and low-cost materials [10].

3.2.2. Wind Success Stories

The cost of commercially available wind turbines is several thousand US dollars per kilowatt, which is out of reach for most rural residents of developing countries [10]. Low-cost wind turbines with timber blades have been demonstrated successfully in Nepal [18]. Low-technology wind turbine generators, which can be made by people with limited technical skills, no advanced machining equipment, low capital cost, and limited exotic materials, have also been demonstrated [10]. The low-technology wind turbine was constructed in a joint effort by the IEEE Power & Energy Society Community Solutions Initiative and the Puget Sound Professional Chapter of Engineers Without Borders, USA.

3.3. Clean Biomass

Biomass sources in rural areas include human excrement, animal manure, and agricultural wastes. Biomass can be burned directly to produce heat energy or electricity via a microturbine, or it can be degraded by anaerobic microbes to produce biogas. Although burning biomass in inefficient cookstoves contributes to illness via indoor air pollution, as described above, biomass can be burned using clean technologies or used to generate clean-burning biogas. Biogas, typically 60–70% methane, can be used directly in natural gas-powered appliances or burned to generate electricity via a microturbine and generator [19]. It is expected that microturbines powered by biogas might eventually be competitive with diesel engines for village-scale power applications, with relatively low maintenance costs, high reliability, long lifetimes, and low capital costs [1]. Fuel cells might ultimately prove able to generate power at village scales from biogas, at very high efficiencies [1].

Anaerobic processes that produce methane from waste solve 2 problems at once: waste and energy. Anaerobic processes provide some of the simplest and most practical methods for minimizing public health hazards from human and animal wastes. Pathogens such as schistosome eggs, hookworm, flat/tape worm, dysentery *Bacillus*, poliovirus, *Salmonella*, and

Bacillus for paratyphoid are destroyed. A residence time of 14 days at >35°C in a small-scale system in a developing country can provide 99+% removal of pathogens, with the exception of roundworm [20, 21].

In addition, the solid residue from anaerobic waste treatment processes is a valuable fertilizer, which is stabilized and almost odorless. This fertilizer is especially a benefit in developing countries, due to its potential to boost crop yields.

3.3.1. Biomass Challenges

Ideally, energy should be produced from biomass that is not edible and that cannot be grown in places where edible crops could be grown, so that competition between uses of crops for energy and food does not become an issue. Producing energy from wastes avoids this issue.

Because of limits on the amount of land accordingly available for growing plants that can be used for energy, bioenergy cannot be viewed globally as the sole replacement or substitute for fossil fuels, but rather as one element in a broader portfolio of renewable energy sources [1]. In rural locations in developing countries without current access to electricity, however, biomass can provide a transformative local power source.

3.3.2. Biomass Success Stories

An improved biomass cookstove designed by Prakti Design Lab to meet the cooking requirements of rural households is around 40% percent more fuel efficient than traditional cookstoves and emits 70–80% less smoke [1].

In Senegal, proliferating invasive aquatic plants are being transformed into combustible pellets that can be used for cooking, replacing wood and charcoal. By impacting lake water quality, the plants' proliferation caused an increase in waterborne diseases. The plants are also created problems for fishermen, by jamming their nets, and farmers, by reducing access to water for livestock. Local fishermen and farmers will be recruited as plant removers, and 20 additional local workers will be hired and trained to manage the pellet production process. Based on capacity production of the compaction machine (4,000 kg/week) and a local price of US$ 0.28/kg, the pellets could generate income of about US$ 1,120/week for the local population [1].

3.4. Micro-Hydro

Micro-hydro systems use the natural flow of water to yield up to 100 kW output of electrical energy [22]. Simplicity, efficiency, longevity, reliability, and low maintenance costs make these systems attractive for rural development [23]. Like solar and wind, the fuel source for micro-hydro power is free, and the use of hydro-powered turbines to generate electricity produces no on-site air pollution.

Unlike large hydroelectric plants, micro-hydro systems do not require a dam and reservoir, which minimize their environmental damage. A portion of the river's flow is diverted to the micro-hydro intake. A settling tank may be used to allow silt to settle out of the water. A screen or bars screen out floating debris and fish. The water then flows through a channel, pipeline, or pressurized pipeline (penstock) to the powerhouse, which houses a turbine or waterwheel. The turbine turns a generator to produce electricity [22]. A variety of turbines may be used, including a Pelton wheel for high head, low-flow water supply, or a propeller-type turbine for low-head installations [24, 25].

3.4.1. Micro-Hydro Challenges

Micro-hydro systems obviously are limited to locations with a stream or river. The flow volume must be sufficient to supply local energy needs. In addition, a sufficient quantity of falling water must be available, which usually means that hilly or mountainous sites are best. A drop of water elevation of at least 2 ft is required or the system may not be feasible; the water does not “fall” enough distance to produce enough head [22, 24]. Another limitation is that the distance from the stream or river to the site in need of energy may be considerable [23].

The power produced may fluctuate depending on how much water is flowing in the stream or river and the velocity of flow [23]. Energy can be stored in batteries, so additional reserve energy available for time of low generation and/or high demand. However, because hydropower resources tend to be more seasonal than wind or solar resources, batteries may not be able to provide enough energy storage for summer or other seasons with severely limited water flow. Integrating the hydropower with a hybrid wind or solar system can help in areas where water flow is highly seasonal.

3.4.2. Micro-Hydro Success Stories

The main micro-hydro programs in developing countries are in mountainous regions, such as Nepal (around 2,000 installations, including both mechanical and electrical power generation) and other Himalayan countries [25]. In South America, micro-hydro programs are located in countries along the Andes, such as Peru and Bolivia. Smaller programs have been initiated in hilly areas of Sri Lanka, the Philippines, China, and elsewhere [25]. In a variety of locations, micro-hydro systems have been shown to increase employment opportunities in rural areas, which encourage young people to stay in the villages rather than drifting to the cities [25].

Maher et al. [26] describe the successful implementation of pico hydro (<5 kW) systems in two communities in Kenya. Costs for these systems were considerably less than comparable PV or auto battery systems. The systems were constructed locally using available materials and community labor.

3.5. Hybrid Systems

According to a report issued in 2010 by the International Energy Agency, UNDP, and United Nations Industrial Development Organization, combining solar, wind, biomass, and mini-hydro into an integrated/hybrid system supplying a mini-grid is probably the most promising approach to rural electrification [2]. A combination of technologies in an integrated system can promote reliability. A small backup generator may be operated on diesel, biogas, or biodiesel [5]. Hybrid village electrification systems have been implemented in various countries, including China, India, Ghana, South Africa, and Tanzania [1]. A number of studies have examined the feasibility of various kinds of hybrid off-grid systems: wind–diesel [14, 27], wind–solar [28, 30], wind–PV–diesel [31–33], hydro–PV–wind [34], wind–hydrogen [35], and solar–wind–biomass–hydro [36].

4. What Now? Next Steps

At the global level, a new development paradigm—a pro-poor global climate change agenda—should be embraced. National climate change adaptation and mitigation strategies should be directly linked with poverty reduction and sustainable development goals [1].

To ensure that every person in the world benefits from access to electricity and clean cooking facilities by 2030, the International Energy Agency, UNDP, and United Nations Industrial Development Organization estimate that investment of $36 billion per year will be required. To meet the more ambitious target of achieving universal access to modern energy services by 2030, an additional cumulative investment of $756 billion, or $36 billion per year, is needed. Although this sounds like a large number, it represents only 0.06% of average annual global gross domestic product (GDP) over the period. The resulting increase in primary energy demand and CO_2 emissions would be modest: in 2030, global electricity generation would be 2.9% higher, and CO_2 emissions would be only 0.8% higher [2]. Given that the up-front cost of new energy technologies is prohibitively expensive for poor communities, targeted financing and incentives are needed so that low-income communities, households, and entrepreneurs can invest in new energy technologies.

Students and young entrepreneurs in collaboration with nongovernmental organizations (NGOs) have done some of the most innovative work in new low-cost sustainable energy applications. Such partnerships should be promoted. The World Bank's Development Marketplace Grants, for example, provide global recognition and seed funding for creative ideas, technologies, and services that matter for development, so that they may grow and replicate.

5. Summary

The problems of energy access, poverty, and climate change are intertwined in the developing world. The poor often lack access to energy at all or have access only to inefficient and unhealthy forms of energy. As the poor gain access to energy, their contribution to climate change will increase, unless they leapfrog to renewable energy technologies. Unfortunately, the poor are the most vulnerable to many impacts of climate change, including increased food insecurity and amplified health risks. Access to energy can reduce their vulnerability to climate change impacts.

Fortunately, increasing energy access, alleviating rural poverty, and reducing greenhouse gas emissions can all be complementary, their overlap defining an energy–poverty–climate nexus.

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Solar, wind, biomass, and micro-hydro systems have all been used successfully in various locations to provide off-grid renewable power to rural areas. Each has advantages and drawbacks, depending on the particular location. Combining solar, wind, biomass, and mini-hydro into an integrated/hybrid system supplying a mini-grid is probably the most promising approach to rural electrification.

Providing universal access to modern energy services by 2030 would cost only 0.06% of average annual global GDP during the period. What else could be a more worthwhile investment?

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Native Forest and Climate Change — The Role of the Subtropical Forest, Potentials, and Threats

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Additional information is available at the end of the chapter

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Abstract

The subtropical rainforest of Argentina, called Yungas, has been subjected to rapid deforestation and degradation processes in recent years, especially in the lower district: "Pedemontana Jungle" (PJ; ≤900 m.a.s.l.). In Salta, in the north of the country, the rate of deforestation is around three times higher than the world average. The disappearance of PJ significantly limits the area of contact between Yungas and Chaco forest, which could have important consequences for natural and cultural biodiversity in the region (the largest number of aboriginal ethnic groups live here, most of which depend on native forest for their existence and identity). In addition, the loss and degradation of forests is the second largest sector of greenhouse gas (GHG) emissions to the atmosphere (about 18%), affecting the world climate. We present a synthesis of different studies developed in PJ forests, observing its role as reservoirs of carbon and discussing issues that could influence the total capacity of carbon sequestration of the same. This will contribute to build the reliable database on the sequestration potential, which will facilitate standardization of units, reduction of uncertainties, and contribution to a more efficient strategy to limit the GHG emission to the environment, providing some learning and useful recommendations.

Keywords: biomass, carbon sequestration, edge effect, fragmentation, native forest

1. Introduction

1.1. Deforestation, fragmentation, and climate change

According to recent studies, the forests covering about 30% of the earth's surface [1] contain 80% terrestrial biomass and provide habitat for about half of the world's known species of plants and animals [2]. Forests provide a wide range of ecological, economic, and social assets, as well as services such as climate regulation through the storage of carbon in complex physical, chemical, and biological processes [3–5]. Despite a wide recognition of the importance of native forests, recent data show that the loss of forest cover over the planet (deforestation) in 2000–2012 was 2.3 million km^2, while the gain (grown or planted) was 0.8 million km^2 [6]. Conversely, Keenan et al. reported a rate of 0.08% of forest loss in 2010–2015, while farmland continued expanding in 70% of the countries [1].

Native forests have been affected in terms of not only the total amount of existing surface (deforestation) but also the quality of the remaining fragments (degradation) [5, 7], therefore the biomass availability and its derived flow, which means a source of ecosystem goods and services, has been doubly modified. Several of them, such as soil protection, gas and climate regulation, water regulation, nutrient cycling, providing habitat and refuge, food production, raw materials and genetic resources, the provision of medicinal and ornamental resources, and others related to culture (recreation, aesthetics, and spirituality), are associated with biomass existence and generation [2, 4, 5]. Similarly, there are an increasing number of studies showing the interrelationship between the aboveground and subterranean processes, and particularly among the aboveground biomass (AGB) and soil, links that determine the abundance of species, coexistence, and succession [8, 9]. Therefore, any changes in the biomass, including degradation – although it is a hardly measureable phenomenon [10] – will affect soil characteristics, which, in turn, will modify reproduction patterns and survival of typical plants in the ecosystem in question and their associated fauna [2, 8, 9].

Deforestation and fragmentation of forests, have been an object of study of the scientific community for many years, but attention to these phenomena has begun to rise from the perspective of their contribution to global warming by greenhouse gas emissions [3, 10–15]. It is recognized that the change in land use (including forest degradation and deforestation) is the second sector of global importance in terms of GHG emissions (so-called LULUCF or land use, land use change and forestry) and is responsible for 20% of total emissions [16]; therefore, it is an important component of human impact on global climate.

Variations in the soil cover are one of the natural and anthropogenic forces that operate on different scales, influencing changes in regional and global climates [3, 13, 16]. Malhi et al. [13] document some interrelations in the Amazon forests, noting that they have a great influence on regional and global climates. They mention that the extraction of water from the soil, through the tree roots up to 10 m depth, and its return to the atmosphere ("perspiration service") is, perhaps, the most important regional ecosystem service. Therefore, the removal of trees through deforestation can become a driver for climate change and a positive feedback for externally forced climate change. In agreement with the other authors, forest loss also results in (i) decreased cloud cover and an increase in insulation; (ii) increase in the reflectance of the earth's surface, approximately offsetting the effect of clouds; (iii) changes in the aerosol loading of the atmosphere from a hyperclean "green ocean" atmosphere to a smoky and dusty continental atmosphere that can modify rainfall patterns; and (iv) changes in the surface roughness (and therefore the wind speed) and a large-scale convergence of atmospheric humidity, which generates precipitation [14, 15]. These large-scale interrelations repeat on lesser scales, although they have not been sufficiently studied.

Deforestation and fragmentation could increase the vulnerability of forests to climate change [2, 3, 17, 18], being two interlinked processes, since deforestation to open up new land for cultivation is concentrated in the periphery of existing forest fragments, reducing them in size and/or making them disappear. Both processes have been recognized as important drivers of biodiversity loss [2, 4, 5, 19–21].

1.2. Climate change in Argentina

In 2015, Argentina presented its Third National Communication (TNC) on Climate Change [22], with an updated GHG inventory as part of the fulfillment of their assumed commitments to the United Nations Framework Convention on Climate Change (UNFCCC). They inform that national emissions in 2012 imply a 0.88% participation in global emissions (429,437 Gg CO_{2eq}). The six sectors surveyed were as follows: (1) energy (43% of total emissions), (2) industrial processes (3.6%), (3) use of solvents and other products (0%), (4) agriculture and livestock (27.8 %), (5) land use change and forestry (LUCF) (21.1%), and (6) waste (6%). Within the LUCF sector – the third most important – the subsector of "forest and other land conversion" contributes 67% of emissions.

Of the total native forests, in 2002 (33 million ha), Yungas occupied 11.2% of the surface (3.7 million ha). A TNC report mentions that the loss of native forests in 2002–2010 was 3.5 million hectares (computed in "conversion of forests and other land") corresponding to the 8% loss of Yungas (280,300 ha), which caused a reduction of 7.5% of the total area. The rest of the removed area corresponded to the Chaco region, whose surface involved 70% of the total forests in the country (larger ecosystem) that year.

In effect, the Intergovernmental Panel on Climate Change (IPCC), in which more than 300 scientists from all over the world participate, warned that, in 2014, 4.3% of global deforestation occurred in Argentina [16]. At a local level, the Secretary of Environment for the Nation published, in the same year, the report "Monitoring of the area of native forest in Argentina," pointing out that between November 2007 (when the National Forest Act was enacted) and the end of 2013, 1.9 million hectares were removed – an average of 1 ha/2 min. Eighty percent of the deforestation is concentrated in four provinces: Santiago del Estero, Salta, Formosa, and Chaco [23].

At the same time, variations in local and regional climate had begun to be noticed in the country. The average annual temperature increased from 1960 to 2010 in almost all the northwest subregions (and Cuyo); in many areas (more than 0.5°C), the most notable changes were observed in spring. From 1950 to 2010, the annual average temperature, through the region was 0.6ºC and it reached 0.7°C in Salta and Jujuy [22]. At a national level, the average temperature increases from ½ to 1ºC. The possibility of increasingly intense heat waves has been forecast. In the northwest, an increase of 4–5º is projected by 2030, one of the highest on the planet. In the west and, notably, in the north of the country, there has been a shift toward the extension of dry winters. This could be generating problems with water availability for the populace, more favorable conditions for wildfires in forests and grasslands, as well as stress on livestock. This could bring implications on the biodiversity of the native forest remnants in

Yungas [22], and, at the same time, the disappearance of such remnants, which could provide feedback for those changes that are taking place at an atmospheric level.

Improving the understanding of biomass and carbon stocks in forests, therefore, provides valuable information for use land planning and designing comprehensive strategies in the context of global climate change. The purpose of this chapter is to present a synthesis of some of the different works developed in the subtropical forest of the Pedemontana Jungle, based on years of studies in the area. Studies were focused on the northern of the country, noting its role as carbon reservoirs and discussing factors that could influence the carbon sequestration total capacity of the same. The information presented here, without doubt, will contribute to the construction of a reliable database of this potential, which will facilitate standardization of units, reduction of uncertainties, and contribution to a more efficient strategy to limit GHG emissions, providing some learning and useful recommendations. Inasmuch as this ecosystem extends to Venezuela, the results obtained will provide a frame of reference for future studies on this ecological zone. This information is also necessary to improve the understanding of the distribution patterns of biomass and carbon at the global level and to describe patterns of land use. The results presented could guide in designing plans and management policies for these types of forests, at national and international levels.

2. Materials and methods

2.1. The Yungas ecosystem: Pedemontana Jungle

The phytogeographic Yungas province borders the Andes mountain range from Venezuela to Argentina [24]. The Argentine Yungas, which constitute a vital habitat for the fundamental role in the regulation of the water basins and protection against erosion, have been subjected to a long history of anthropogenic interventions, especially in low-lying areas, called the Pedemontana Jungles, which have a high agricultural potential [25].

The history of Pedemontana Jungle in the north of Argentina has been closely tied to the railway expansion, necessary for the transport of precious wood, tropical crops, and sugar. More recently, from the 1990s, soybeans won the major role, expanding rapidly in the foothills landscape and its transition to the Chaco plain. The deterioration from the advance of the agricultural frontier, coupled with logging, the commercial bird catching and poaching – among others – are causes for concern because of the almost 5 million hectares that cover the Argentine Yungas, the effectively protected area is only 5% of the total [21].

The Pedemontana Jungle, which stretches from 450 to 900 m.a.s.l. – other authors mention minor ranges [24] – and which represents 25% of the Yungas, has been considered as an ecosystem in danger of extinction, and its deforestation would eliminate 30% of the total Yungas biodiversity [25]. In this region, 120 species of mammals and 8 of the 10 species of neotropical cats are represented. Also, approximately 583 species of birds inhabit it, which represent 60% of the species in Argentina [26]. Likewise, in the Pedemontana Jungle of Argentina and Bolivia, they were identified 18 AICBA (Areas of Importance for the Conservation of the Birds of Argentina), noting that the AICBA including sectors of the Pedemontana Jungle, have a diversity of birds comparable to the cloud mountain forests (ecological zone of higher altitude than the PJ) and higher than the Chaco forests that surround them [27].

The physiography varies from submountain foothills to alluvial descents, presenting a hilly and wavy topography. The soils present in the study area are according to the taxonomic classification of FAO soils of the Phaeozem Haplic and Luvic type [28]. Soils of luvisol calcium were recorded only on the Coronel Moldes site.

The climograph and altitude for each of the studied sites are shown in Figure 1.

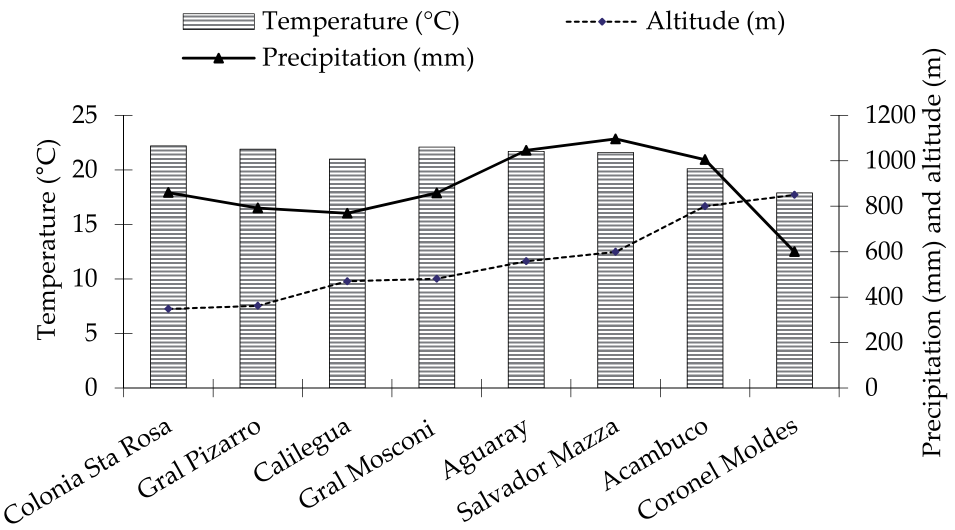

Figure 1. Annual average rainfall (mm), annual average temperature (°C), and altitude (m.a.s.l.) for different sites studied in the Pedemontana Jungle in northern Argentina (Salta and Jujuy provinces). Source: http://es.climate-data.org/location/145171/

2.2. Case studies

All the studies summarized in this chapter were carried out in the province of Salta, in northern Argentina, with the exception of case II, which was developed in the province of Jujuy. The province of Salta has an area of 155,500 km², occupying the sixth position at the national level, and with a value similar to the surface of Nepal, has a population of 1.2 million, making it the eighth most populous out of 23 at the national level.

Of the entire surface occupied by the Yungas ecosystem in the country, 61% of it extends through this province, making it essential to focus on studies in this particular region. Also, Salta has 23% of the total surface of the country's native forests, and deforestation in this province is triple the world average [29].

Some of the assumptions, which have been evaluated from various case studies (always focusing on the Pedemontana Jungle), are as follows (more detailed in Table 1):

i. The subtropical rainforests of the country have a greater capacity for carbon sequestration than subtropical dry forests at identical latitude.

ii. Carbon sequestration in forests disturbed by human activity is lower than in forests less seized by humans, releasing the difference of carbon into the atmosphere.

iii. The carbon stock, in legally protected forest sectors, is higher than in other sectors without protection located at identical latitude and under similar conditions.

iv. The potential for carbon sequestration in the Pedemontana Jungle is less if latitude increases.

v. The fragmentation of the Pedemontana Jungle generates microclimatic changes at the edges, which could affect carbon sequestration.

Case	I	II	III	IV	V
Legal protection	No	Yes	Yes and no	No	No
Site	Coronel Moldes	National Park Calilegua	Wildlife Reserve of Acambuco and Campo Pizarro	Aguaray and General Pizarro	Colonia Santa Rosa
Plot number	23 main plots (AGB_{10}) for each ecosystem; 23 plots of 50 m^2 (AGB_0); 23 plots of 5 m^2 (LUV); 46 plots of 1 m^2 (HUV and LI); 138 soil plots (SOC)	20 main plots (AGB_{10}); 20 plots of 50 m^2 (AGB_0); 40 plots of 1 m^2 (HUV and LI); 120 soil plots (SOC)	50 main plots (AGB_{10}); 50 plots of 50 m^2 (AGB_0); 250 soil plots (SOC)	50 main plots (AGB_{10}); 50 plots of 50 m^2 ($AGB0_0$); 250 soil plots (SOC) and 500 microclimatic instantaneous records (MIC)	78 main plots (AGB_{10}); 78 plots of 50 m^2; 468 soil plots (SOC); 156 microclimatic instantaneous records (MIC)
Carbon pool	AGB_0 AGB_{10} LI HUV LUV BGB SOC	AGB_0 AGB_{10} LI HUV BGB SOC	AGB_0 AGB_{10} BGB SOC	AGB_0 AGB_{10} BGB SOC MIC	AGB_0 AGB_{10} BGB SOC MIC

The acronyms AGB_{10}, AGB_0, HUV, LUV, LI, SOC, MIC are explained in the text.

Table 1. Methodological differences and similarities between the case studies.

2.3. Sampling design

The methodology used for each of the case studies presented in the next section shows some differences that are summarized in Table 1. In most cases, the data were collected following a random sampling design. Only in case V, the sampling was systematic.

The experimental design used was nested plots. Main plots had a total area of 100 m^2 and were rectangular plots. The criterion used to determine sample size for each stratum was an estimation of AGB of trees with a diameter at breast height (dbh) ≥ 10 cm during pre-sampling (90% probability and 20% mean standard error).

Carbon represents about 50% of the total oven-dried biomass present in forests [32]. Estimation of carbon pools in forests necessarily involves studying the different strata of biomass present in them. In the different studies, the following carbon pools and variables were measured:

a. Aboveground tree biomass: AGB refers to the total amount of aboveground living organic matter in trees and shrubs (≤ 1 cm dbh and ≥ 50 cm height) expressed as oven-dried tons. Total height (from ground level up to crown point) and dbh were measured in all trees with dbh ≥ 10 cm (called AGB_{10}) in 100 m^2 plots. When $1 \leq$ dbh ≤ 10 cm and height ≥ 50 cm (called AGB_0), trees were measured in 50 m^2 plots. In multiple-stemmed trees, only the longest stem was measured. If neither shoot was dominant, an average of similar shoots was calculated. The basal diameter was registered only when the stem was shorter than the dbh. Standing dead trees with dbh ≥ 1 cm and fallen trees with dbh ≥ 10 cm were measured in the same way as living trees. However, correction factors of 0.8 and 0.7, respectively, were applied to the biomass values obtained. For hollow or ill trees, a factor of 0.9 was applied.

b. Lignified understory vegetation (LUV): All shrubs shorter than 50 cm were collected in 5 m^2 plots within the corners of the main 100 m^2 plots.

c. Herbaceous understory vegetation (HUV): This fraction was removed in two 1 m^2 plots. These plots were located in opposite corners within the 100 m^2 plots used to measure AGB_{10}.

d. Litter (LI): Organic debris on the soil surface (including freshly fallen parts of plants, decomposing organic matter, and deadwood) with a diameter no greater than 10 cm were collected in the same plots used for HUV.

e. Belowground biomass (BGB) (tree roots): Due to the difficulties involved in the measurement of this fraction, it was estimated indirectly as a proportion of AGB_{10} for Chaco and Yungas.

f. Soil: Bulk density and percentage of organic carbon were determined in soil samples collected at a depth of 30 cm [30]. Vegetation and litter were removed from the soil surface prior to sampling. Bulk density was determined in two samples per plot using the cylinder method. Results from these samples were averaged. The percentage of organic carbon was measured following the method described in Walkley and Black. This measurement was performed on a composite sample built from four samples taken at identical distances within a linear transect along the longest axis of the 100 m^2 plots (dimensions of these plots were 5 m × 20 m).

Wet weight was recorded on site for LUV, HUV, and LI fractions. Dry weight was determined in the lab (registered after drying in an oven at 80°C until constant weight). The equation introduced by Cairns and coworkers [31], for tropical forest and lower latitudes than 25°, was used. The AGB fraction, also called as "biomass density" when expressed as tons of oven-dried weight per ha [32], is the main source of total biomass in a forest ecosystem. Its relevance as a GHG mitigation option is therefore crucial [11–13]. This fraction was thoroughly assessed using a nondestructive methodology: allometric equations (Table 2).

g. Solar radiation intensity (W/m^2): A LICOR 250 pyranometer was used with a silicon sensor with a resolution of 0.1 W/m^2. The measures of global radiation readings are precise to ±5%.

h. Air relative humidity (%): This was recorded using a psychrometer or hygrometric probe Vaisala HM 34. Reading is immediate and accuracy is ±2%. The sensor is the Humicap type. Measurements were taken at 1.5 m from ground level.

i. Air relative temperature (°C): This was registered with a Vaisala HM 34 probe, with temperatures ranging from −20 to +60°C. Measurements were taken at 1.5 m from ground level.

j. Soil temperature (°C): This was measured with a FLUKE 54 II digital thermometer with accuracy ranging from 0.05% + 0.3°C. Measurements were taken at 10 cm depth.

k. Soil humidity (%): This was estimated by two soil samples taken at 10 cm depth per plot.

Authors	Carbon pool	Equation	No.
Chave et al. (2005)	AGB_{10} and AGB_0	$AGB = \exp(-2.977 + \ln(S.D^2.H))$	(1)
Brown et al. (1989)	AGB_{10} and AGB_0	$AGB = \exp(-2.4090 + 0.9522 \ln(S.D^2.H.))$	(2)
Chave et al. (2005)	AGB_{10} and AGB_0	$AGB = 0.112(S.D^2.H.)^{0.916}$	(3)
Gehring et al. (2004)	AGB	$\text{Diameter (30 cm)} = 1.235 \times dap + 0.002 \times (dap)^2$ $AGB = \exp(-7.114 + 2.276{*}\ln(D_{30}))$	(4)
Cairns et al. (1997)	BGB	$BGB = \exp(-1.0587 + 0.8836 \times \ln(AGB))$	(5)
Macdicken, (1997)	SOC	$SOC = OC \times BD \times D$	(6)
Sevola (1975)	V	$V = -2.2910 + 0.0558 \times \log\ (D^2 \times H)$	(7)
Sevola (1975)	V	$V = -3.2794 - 0.0734 \times \log H^2 + 1.0580 \times \log(D^2 \times H)$	(8)
Sevola (1975)	V	$V = -2.4385 + 0.9560 \times \log(D^2 \times H) - 0.80350 \times \log(H / D)$	(9)
Chave et al. (2014)	AGB_{10} and AGB_0	$AGB = 0.0673 + (S.D^2.H)^{0.976}$	(10)

AGB = tree aboveground biomass (kg oven-dry); SB = stem biomass; S = wood density (oven-dried biomass per green volume, in t/m^3); D = diameter at breast height (1.3 m above ground, in cm); D30 = diameter at 30 cm above ground; H = total height (m); BGB = belowground biomass (t/ha); OC = concentration of organic carbon in the soil (%); BD = soil bulk density (g/cm^3) and D = depth of soil (cm); V = total tree volume, in dm^3, included stem, bark, and branches.

Table 2. Allometric equations used in this chapter.

The last five parameters called "microclimate factors" were measured in each preset distance, for each transect study, always at midday between 12 p.m. and 2 p.m. In the case of values per site, the different measurements taken were averaged per plot.

2.4. Estimation of biomass and carbon

Once field measurements were carried out, the data were computed clerically, carrying out the biomass estimate for each compartment, transforming it into carbon values (factor of 0.5 [32]) and achieving the sum of all the carbon pools. All equations used are shown in Table 2. Equation (1) was developed by Chave et al. [33] for "moist forest stand," while equation (3), by the same authors, was developed for "dry forest stands" (applied to the Chaco). Equation (10) was recently developed by these authors and was applied to the *Anadenatnhera colubrina* and *Cedrela angustifolia* species, for which no specific equations were found. Equation (4) was applied only in vines and required converting the dbh into diameters at 30 cm height, and then entering that value into the equation [34]. In the case of volumetric equations (7, 8, and 9) [35], the total biomass conversion was carried out by multiplying the total volume by the basic density of each species. Equation (7) was then applied to the *Calycophyllum multiflorum* species, equation (8) to *Phyllostylon rhamnoides*, and equation (9) to *Astronium urundeuva*, all equations being developed in the region.

The basic wood densities (dry) for different species were obtained from Ref. [36]. A basic density value obtained from the weighted average of the densities of each site's species was used for the species that for various reasons could not be identified. For estimation of SOC (soil organic carbon), equation (6) was used [30]. For data analysis, the nonparametric type test was chosen. We used the INFOSTAT® software, and a value of 0.05 was considered significant.

3. Results and discussion

3.1. Effect of temperature and humidity on the carbon stock: dry and humid subtropical forests at the same latitude

Contributors: Manrique, S.M. and Franco, J.

The subtropical moist forests of the country have a greater capacity of carbon sequestration than subtropical dry forests at identical latitude.

As was mentioned, the Chaco ecosystem is the largest surface area at the national level. It was interesting to compare facets of this ecosystem with the Yungas Pedemontana Jungle with regard to the potential for carbon sequestration at the same latitude. The work was carried out in the municipality of Coronel Moldes (25°16′00″ South latitude and 65°29′00″ West longitude), 60 km south of the capital of the province of Salta.

The province's climate is defined as subtropical mountainous with a dry season. However, the topography does allow the development of contrasting environments. Thus, the moist winds from the southeast enter the province and release their moisture from submountainous ranges that make up the sub-Andean hills in the north-central region of the country. This allows the spread of vegetation, which is a unique environment that runs along elevations in different altitudes, forming a north–south strip. The Chaco ecosystem develops on the plain that extends from the center of the country to the East, and in Salta two districts are exhibited: the semiarid Chaco and the mountain Chaco. Precipitation decreases as it moves eastward, shrinking from more than 650–700 mm per year in the Pedemontana Jungle ecosystem to values of less than 460 mm in the Chaco ecosystem. Temperatures also suffer a slight increase as it moves west away from the mountains, which have the moisture [37], marking isotherms in the range of tenths of degrees, as the distance between the mountains and the eastern point increases.

The starting points are corroborated in this study: the most humid ecosystem shows a carbon stock 43% larger than that stored in the driest ecosystem (Table 3). In the case of Yungas, the AGB fraction means almost 80% of the total biomass, although the greater fraction (AGB_{10}) alone implies 71%, leaving the AGB_0 a reduced participation. The BGB means more than 16% of total biomass, and the rest if divided between the LI (about 3%), the LUV (with almost 2%) and lastly, the negligible participation of HUV (0.1%). For the Chaco, the fraction AGB provides more than 71% of the total biomass, where the trees of larger diameters (AGB_{10}) mean 66% of this contribution. In this environment, the BGB takes on greater importance (with more than 21%), and is followed by – in the identical order shown in the Yungas environment – LI fraction (3.2%), LUV (2.6%), and HUV (0.6%) (Figure 2).

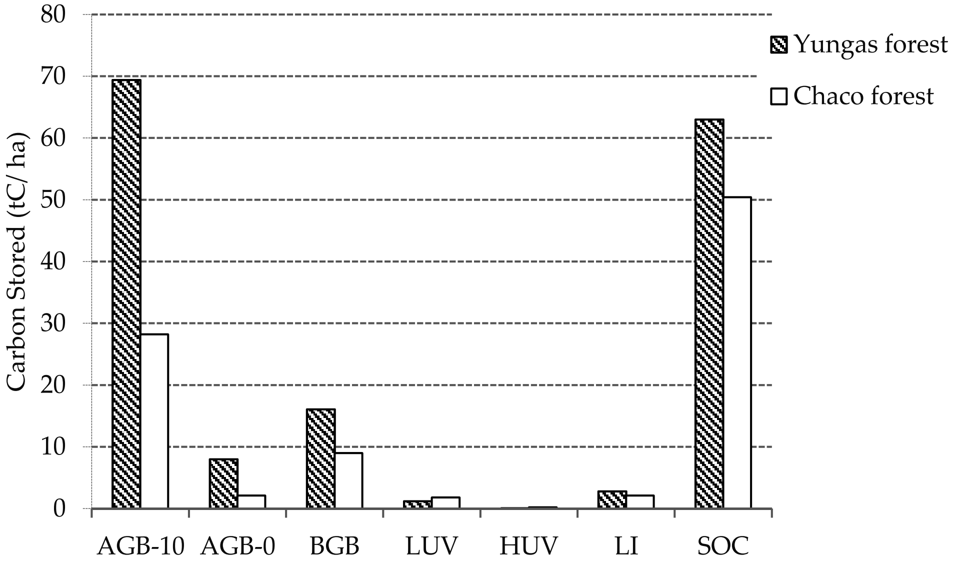

Figure 2. Carbon stock and contribution of each carbon pool studied. The acronyms AGB_{10}, AGB_0, BGB, HUV, LUV, LI and SOC are explained in the text.

Clearly, the AGB and SOC fractions are the two largest contributors in the two ecosystems. In Yungas, the AGB represents 48% of the total fixed carbon, while the SOC contributes 39%. In the case of the Chaco, 33% of the total carbon in the ecosystem is concentrated in AGB, while

54% remains captured in SOC. Soil is an important reservoir of carbon, becoming the most important fraction in dry environments. However, when we compare the absolute values of SOC in both environments, the soil shows a significant relationship with the vegetation found on the surface. In Yungas, it is 63 tC/ha, while in Chaco it is 50 tC/ha.

Sector	Average	Standard deviation
Yungas forest (Selva Pedemontana)	162	85
Chaco forest (Chaco Serrano)	92	42

Table 3. Carbon stock (tC/ha) in both ecosystems, Chaco and Yungas, in Coronel Moldes, Salta, Argentina.

Viglizzo and Jobbágy [21] point out that the carbon stocks in the biomass and in the organic fraction of the soil in Argentina vary from one ecoregion to another. The carbon stock in biomass is directly associated with the availability of vegetation biomass. In the tropical and subtropical regions of Argentina (e.g., Yungas), more than 50% of total carbon is found stored in the AGB fraction, which makes this element vulnerable and easily appropriable by humans. This relationship falls dramatically in areas dominated by grasslands/pastures (e.g., Chaco), and even more (without reaching 10%) in intensively cultivated ecosystems.

In Yungas, the average height was 11 m and average dbh was 17.6 cm, both higher than those for Chaco, although still lower than figures cited for pristine Yungas ecosystem [24, 25, 38]. Estimations made for tropical humid forests around the world range from 150 to 192 t/ha for closed, undisturbed forests and around 50 t/ha for open forests [39]. Certainly, different factors may be influencing these differences (rainfall, soil type and site features, topography, etc.) [32, 33, 39, 40]. Moreover, the structure of the forest in the Yungas area included in this study was clearly disturbed by humans and livestock. Numerous recent and decomposing stumps were found and there were unambiguous signs of wandering animals and persons. *Solanum riparium* was also abundant in this area, a species normally dispersed by wild animals or cattle. The appearance of typically Chaco species in sections of Yungas forest is probably a sign of human intervention in this region [24, 38].

Our results suggest that forest degradation is detectable not only in Yungas but also in Chaco. In environments similar to Chaco, discrepancies between these results (lower) and estimations made in similar environments in other forests of the world might be due to structural differences, altitude, latitude and humidity, gradients (24, 32, 33). However, in our case the level of degradation exerted by human activity in this environment might also be responsible for the discrepancies [20, 21, 41] (further details refer to [43]).

Economic activities such as agriculture and logging, which take place in these ecosystems, are arguably not respecting their carrying capacity. Local institutions do not seem to be capable of stopping, controlling, or regulating these activities. Whether entering into a market-based system like the one promoted by the Kyoto Protocol will be part of the solution to the problem of deforestation and conservation of local native forests remains to be seen. Decisions are highly political and many times the relevant decision makers are thousands of kilometers away. No decisions affecting the future of these forests should be taken until agreements on this issue are reached or until judiciary processes are properly finished. Competing claims on the ownership of the forestland, the products of the forests, and the provision of ecosystem services must be taken into consideration in a comprehensive forest management.

3.2. Effect of human influence on the carbon stock in forests

Contributors: Gallucci, G.B. and Manrique, S.M.

Carbon sequestration in forest disturbed by human activity is lower than in forests less seized by humans.

In case I, we identified that studied forest sectors clearly show human influence as a factor of degradation of the original structure of the same type. In this case study, it was interesting, particularly, to assess this difference and try to quantify it for samples of the same Pedemontana Jungle ecosystem, but this time as a protected area: Calilegua National Park (23°27′–23°45′ South latitude and 64°33′–64° 52′0″ West longitude). The park was created in 1979 to protect a representative sector of the Yungas and to protect the headwaters of the Calilegua streams, which are a part of the San Francisco River basin, and provide water to neighboring crops in the protected area. With an area of 76,320 ha, it is the largest national park in the Argentine Northwest. It is approximately 165 km from the city of Salta.

We studied two areas of the park (north and south sectors) separated by only 50 km but which have different accessibility to human influence. The north sector surrounding the town of Caimancito has been invaded by oil companies, which have conducted exploration activities in the area, and therefore have dissected the forest, leaving open "choppings" or paths of prospecting. This has led to the accessibility of nearby residents who have taken advantage of the forest and even have led their animals to graze there. In the south, on the other hand, exploration activities were not carried out and therefore, even if villagers could have accessed the site, on its more sheltered side (the other side of rivers that flow through the park), a better conservation has been maintained, which can be seen in the large, heavily wooded trees, and the high forest value that is still there. Surely, the presence of Park Rangers (Aguas Blancas section) in this sector has helped much in this protection.

Two sectors that maintain homogeneous topographic, edaphic, and climatic conditions were selected. Both sectors were compared through analysis of average annual rainfall records (56 years series) without finding statistically significant differences ($H = 0.01$, $p > 0.999$). Records of minima and maxima were also analyzed. The series of annual average temperatures were not statistically different ($H = 0.16$, $p = 0.686$). In the case of edaphic variables, existing cartographic studies allowed us to associate both sectors with the same series of soils. Organic matter samples taken in the area showed no significant differences ($H = 4.71$, $p=0.210$). It was assumed that both sectors had identical site conditions.

We evaluated the same carbon pools as in case I with the exception of LUV, which had no relevant participation in the previous case, and therefore it was not included in the pursuit of reducing the fieldwork effort and costs.

The obtained results allow us to advance with the basic assumption: the north sector, subject to anthropogenic influence, it showed a carbon stock 23% lower than the south sector, which had less accessibility and a better state of conservation (Table 4). These differences were statistically significant ($H = 11.20$, $p < 0.001$) only for the AGB stratum, but not for the other strata studied nor for the total carbon stock. Under similar conditions of climate, soil, geomorphology, altitude, and latitude, the human influence could explain these differences, as the AGB stratum is the easiest to appropriate by humans [10, 17, 19, 21]. The AGB make the largest contribution in both sectors to the carbon stock (53, 55%), followed by SOC (28–31%) and finally BGB (8–10%) depending on the sector analyzed (Figure 3).

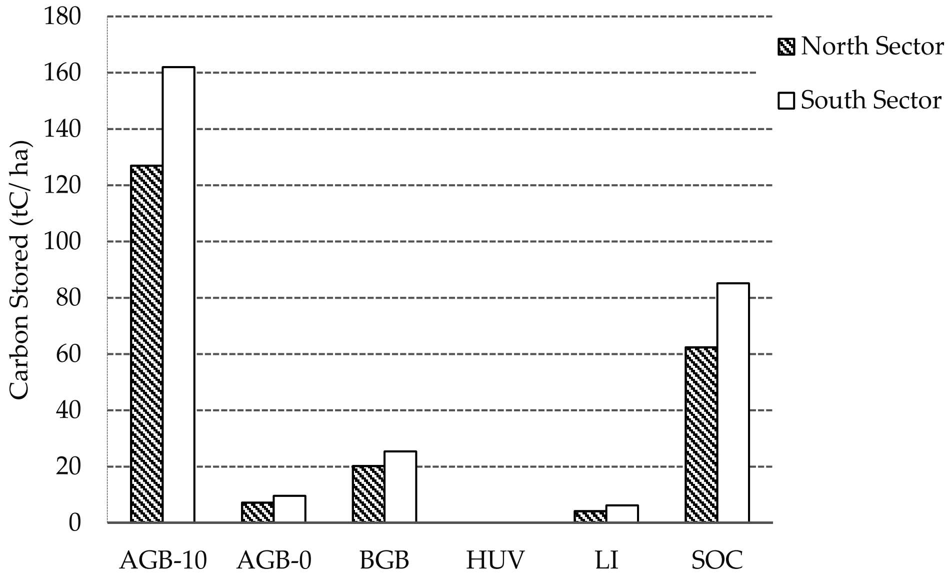

Figure 3. Carbon stock and contribution of each carbon pool studied. The acronyms AGB_{10}, AGB_0, BGB, HUV, LI and SOC are explained in the text.

Sector	Average	Standard deviation
Protected forest degraded (north sector)	221	116
Protected forest better preserved (south sector)	272	129

Table 4. Carbon stock (tC/ha) in both sectors, north and south, in Calilegua, Jujuy, Argentina.

Against the results, there is an urgent need to review the administration and safeguards for the Calilegua National Park, with a reinforcement of the Corps of Rangers in the area (currently with few people that must patrol the whole park). Other authors are agreed that the declaration to protect does not always mean adequate protection [43, 44]. The acquisition of more financial resources for the protected areas should be carried out in the light of a strict management plan and monitoring. Poaching, livestock grazing, and logging without authorization – with the thinning out of valuable wood species – must be eradicated from the core area, so that the Park can fulfill its role with the conservation of biodiversity, which has been included in the international statement "Yungas Biosphere Reserve."

3.3. Effect of legal protection on the ecosystem

Contributors: Manrique, S.M.; Vacaflor, P.; Fernández, M. and Franco, J.

The carbon stock in legally protected forest sectors is higher than in unprotected sectors located at the same latitude and under the same conditions.

In case II, two sectors of the legally protected Pedemontana Jungle were analyzed, which clearly show differences between them in their accessibility to human influence. It became interesting to continue in this line of study, exploring if the trend found in the former case could be due to a particular situation in the Calilegua National Park. In this case study, we sought to observe comparative sectors inside and outside legally protected regions located at the same latitude and altitude, and under the same conditions. We started to identify protected areas in the province which shelter samples from the Pedemontana Jungle. We finally worked in and out of the Provincial Reserve of Flora and Fauna of Acambuco (PRFFA) (22°12'38.5" South latitude and 63°56'23.1" West longitude) and in the National Reserve of Campo Pizarro (NRCP) (24°11'54.87 and 24°14'21.7" South latitude, and 64° 7'27.00" and 64° 9'23.79" West longitude). The creation of PRFFA dates back to 1979, and currently has an area of 32,000 ha. It is approximately 470 km from the city of Salta to PRFFA. In the case of NRCP, it was created in late 1995 with an area of 25,000 ha, and soon after a process of reversal and social conflict, the NRCP ended up with an area of 21,000 ha. It is approximately 280 km from Salta. In this study, efforts were concentrated in the carbon pools considered most significant in the prior cases, eliminating HUV and LI from the samples.

The results show that, on average, the carbon stock is similar in protected and nonprotected areas (Table 5). Having considered the average of all sectors included in the Reserves and the average of all the studied sectors not protected in them, no significant differences were found ($H = 0.85$, $p= 0.356$), by even analyzing just AGB separately ($H = 0.98$, $p = 0.322$). The initial assumption cannot be confirmed: no case shows that the legal protection has caused differences in the ecosystem it protects, neither favoring nor against. Yet we see different values if we consider the samples of the north sector and south sector separately, as will be discussed in the following section.

Sector	Average	Standard deviation
Protected forest	203	74
Unprotected forest	213	82

Table 5. Carbon stock (tC/ha) in both sectors, protected and unprotected forest, in Acambuco and Campo Pizarro, Salta, Argentina.

In terms of the importance of each of the studied carbon pools (Figure 4), the carbon fixed at the fraction of AGB returns to be larger than the fixed carbon in the soil (SOC).

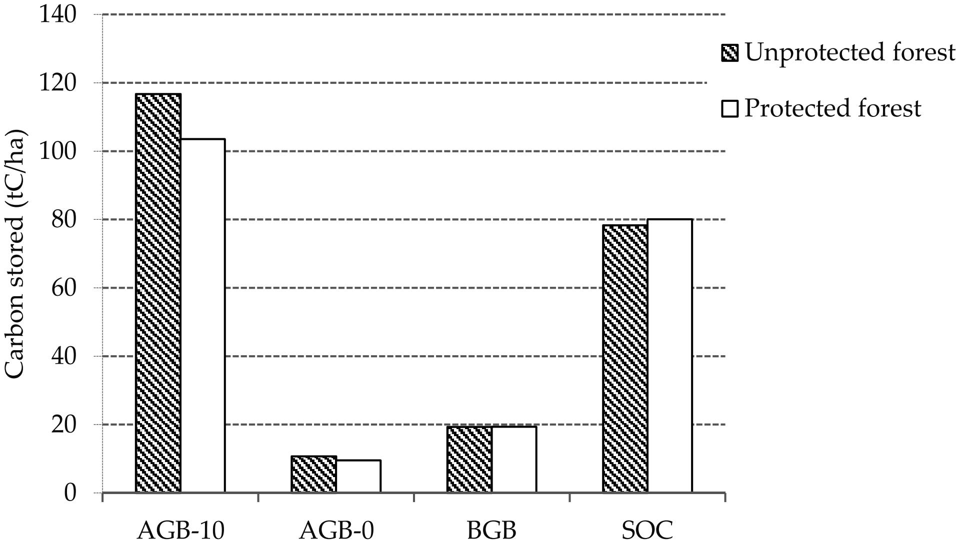

Figure 4. Carbon stock and contribution of each carbon pool studied. The acronyms AGB_{10}, AGB_0, BGB and SOC are explained in the text.

The inclusion of Pedemontana Jungle sectors within legal protection figures has not resulted in benefits in terms of their ability to sequester carbon in the different carbon pools. However, this consideration is not conclusive in the role of protected areas. Pedemontana Jungle sectors, within and without the protected areas, could be similar in their capacity to sequester carbon in two possible situations: (i) a good general ecosystem condition level, which still remains a certain continuity of ecosystem, and therefore, either inside or outside the Reserve, is of similar forest samples and show no particular features nor different structural configurations; (ii) a poor state of conservation, which has equally affected protected and nonprotected areas, imprinting similar features in the different sectors, by simultaneous intervention in the different forest sectors. A more in-depth study of other ecosystem variables would perhaps lean toward one alternative or another. However, the different log of measured carbon stock in case II in Calilegua National Park, or the degradation features in the two types of ecosystems (Yungas and Chaco), which were observed in case I, clearly indicates that the forests have not received the attention they should have over the years.

Therefore, these thoughts should be a trigger to continue with deeper and more comprehensive evaluation and to draw attention to the need to review and update control schemes and monitoring of native forests – mainly protected areas. The global community has recognized the importance of forests for biodiversity, and has prioritized the preservation of forest biodiversity and ecosystem functions through multiple multilateral agreements and processes. For example, the Aichi Biodiversity Targets established by the Convention on Biological

Diversity (CBD) in its strategic plan include halving the rate of loss of natural habitats including forests (target 5) and conserving 17% of terrestrial areas through effectively and equitably managed, ecologically representative, and well-connected systems of protected areas (target 11). Currently, designating protected areas is one of the primary strategies for conserving biodiversity. Different authors have discussed the increase in protected areas over the past century; however, they find that many key biodiversity areas are not adequately covered by protected area status [44].

The always-protected system areas will be limited to preserve all the original diversity, but even so, it is imperative that these areas exist and continue to expand with scientific criteria.

3.4. Effect of latitude and altitude on the carbon stock

Contributors: Manrique, S.M.; Vacaflor, P. and Fernández, M.

The potential of carbon sequestration in the Pedemontana Jungle is less if the latitude increases.

In case III, the average carbon stock in protected and unprotected areas was approximately similar, although with different values from cases I to II. This led to the analysis of the position within the ecosystem of the studied sites. In case I, with 162 tC/ha, the forest is at 25°16 and 65°29. In case II, with 221–272 tC/ha, the forest is approximately between 23°27 and 64°33. Analyzing other sectors located at different latitudes could confirm the trend of higher values of biomass and the north sector of the Pedemontana Jungle (e.g., Calilegua showing a value 100% greater than the Coronel Moldes value) and values that decrease toward the south. It was interesting, therefore, to explore case III results separately, taking as a northern sector, the plots carried out near Aguaray (22°12 and 63°56) and, as a southern sector, those carried out near General Pizarro (24°11 and 64°7).

Sector	RI (W/m^2)	RH (%)	RT (°C)	SM (%)	ST (°C)
North sector	0.065 a	43.55 a	26.94 a	9.9 a	22.09 a
	(0.02–0.44)	(21.7–86.7)	(16.6–36.55)	(3.15–17.25)	(20.15–25)
South sector	0.065 a	36.9 a	31.66 b	7.24 ab	24.2 b
	(0.02–0.13)	(16.35–55)	(25.4–37.8)	(2.3–14.4)	(22.85–30.8)

RI = radiation intensity; RH = relative humidity; RT = relative temperature; SH = soil moisture; ST = soil temperature. Mean and range for each variable. Means followed by different letters (a, b) within the same column indicate statistically significant differences ($P < 0.05$).

Table 6. Average climatic conditions.

The loss of species diversity and conditions of humidity and altitude from north to south, along the gradient in which the Pedemontana Jungle extends within Argentina, has been previously documented [27, 40]. Therefore, it was interesting to know in this case if this trend was also clearly reflected in the carbon stocks of the studied sectors of the Pedemontana Jungle. If the previous studies, the participation of the HUV and LUV strata was between 0.01% and 0.02% and the LI carbon pool was between 1.5% and 3%. Therefore, in this study efforts were concentrated in the strata of AGB, BGB, and SOC. The chosen sectors show the average weather conditions (for the same season, day, and year), which differ significantly in air relative temperature (RT), moisture and soil temperature (SM and ST, respectively) (see Table 6).

Studies of carbon stock results show that the two sectors are clearly separated in terms of their potential. The northern sector has the largest records of total carbon with an average of 242 tC/ha, while the southern sector registers an average 28% lower (Table 7) with statistically significant differences ($H = 12.38$; $p < 0.01$). These values can be associated with different microclimates, possibly generated by a latitude effect, whose influence on climatic variables can be seen in Table 6. In all cases, the differences are in favor of a cooler, more humid climate in the northern sector and warmer and drier in the southern. Although the number of analyzed sectors in a latitudinal gradient in the Pedemontana Jungle (narrow strip of north–south direction), are not representative of the whole distribution, the data can be interpreted in light of the existing scientific studies in the area [25, 27, 40].

Once again, the two carbon pools that make a greater contribution to the total ecosystem carbon stock are AGB and SOC, being greater in the case of the northern sector, meaning 52% and 34% of the total carbon stock, respectively (Figure 5). This implies that more than 86% of total carbon is concentrated in these two fractions. In the southern sector, the participation of these carbon pools is 47% and 38% for AGB and SOC, respectively, but with greater involvement of the SOC carbon pool in this case.

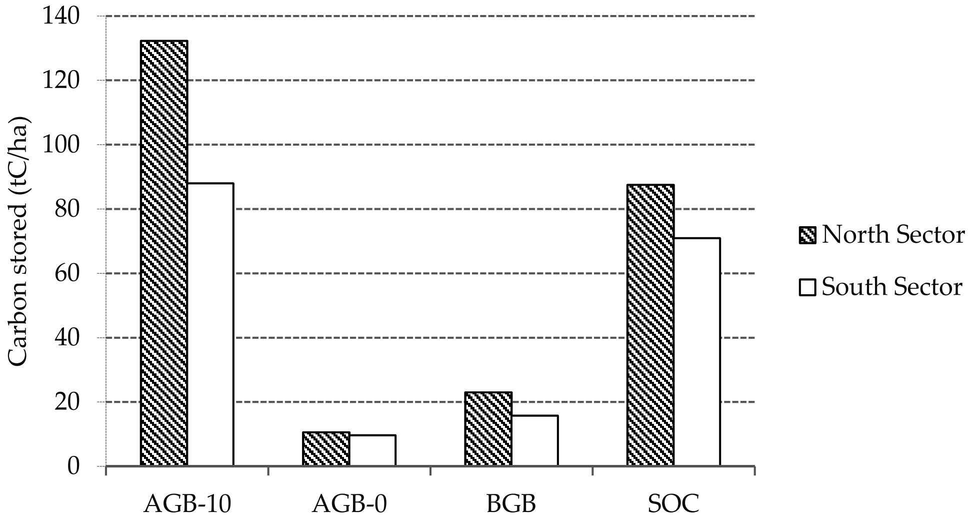

Figure 5. Carbon stock and contribution of each carbon pool studied. The acronyms AGB_{10}, AGB_0, BGB, and SOC are explained in the text.

Sector	Average	Standard deviation
Forest in the north (22° latitude)	242	96
Forest in the south (24° latitude)	174	68

Table 7. Carbon stock (tC/ha) in both sectors, north and south, in Salta, Argentina.

However, always considering the altitude of the Pedemontana Jungle, as the latitude increases, the altitude decreases in general terms. It has been recognized that the floral changes are influenced by complex interactions of weather and edaphic variables in Yungas altitude ranges [24, 25, 40]. Beyond the fact that the associated variables of increasing altitude (which in this study varies between 22° S and 24° S) and/or altitude (which varies between 500 and 700 m.a.s.l. in the southern sector and between 700 and 900 m.a.s.l. in the north) would more or less determine overt changes at the level of species and ecosystems, such variations exist without doubt, and they are defining two sectors of the same forest in terms of carbon sequestration potential.

These observations indicate that it is essential to preserve sectors of different latitudes and altitudes in the Pedemontana Jungle, since there are intrinsic factors that are defining differential features in the biomass and carbon stock, as well as, in every ecosystem functions associated with these particular conditions [40]. Other authors have already pointed out that the recommendation in all cases is to maintain connectivity of Yungas in distribution, safeguarding different sectors of the Pedemontana Jungle, varying in latitude and altitude [27].

Human influence, not analyzed in this study, will, no doubt, imprint differential features over time if their presence is not restricted, since we have observed signs of livestock and logging in the different studied areas. In the southern sector, where the Pedemontana Jungle has been deeply fragmented and immersed in an array of crops, it is considered that there might be a microclimatic influence on the fragments by the existence of rough edges [7, 18]. This aspect will be dealt with in the following section.

3.5. Effect of fragmentation on the carbon stock

Contributors: Manrique, S.M.

Fragmentation of the Pedemontana Jungle generates microclimate changes at its edge, which could affect the sequestration of the carbon stock.

The fragmentation of forests, reducing surface and insulation, exposes organisms, which remain in the fragment, to conditions differing from their ecosystem, which is primarily manifested in the contact between two different environments, which has been defined as "edge effect" [18], and that impact toward the forest interior.

Microclimatic changes caused as a consequence of contrasting conditions between the remnant forest and the adjacent field, subjected to different uses (cultivation, planting, and pastures), would seem to be the most immediate and apparent fragmentation changes [7]. Several authors have recognized that, at the edge of the fragments is an environmental gradient toward the interior: generally brightness, evapotranspiration, temperature, and wind speed decrease, while soil moisture and humidity increase toward the interior of the fragment. Biological changes could then arise as a result of these changes in the microclimate of the fragment edges [7, 18].

This study sought to analyze and quantify the possible microclimatic changes generated in the fragment edges of the Pedemontana Jungle, also observing the distribution of five representative tree species (by their frequency [24]). The studied species were as follows: (i) *Calycophyllum multiflorum Griseb, Castelo*, (ii) *Phyllostylon rhamnoides J.Poiss., Taub*, (iii)*Astronium urundeuva Engl.*, (iv) *Anadenanthera colubrina Vell., Brenan,* and (v) *Cedrela angustifolia DC*. It was estimated that the typical species, "climax" or more conservative ones of the population (e.g., those that have higher demands for their germination or growth requirements and with low tolerance for humidity fluctuations), could be more easily eliminated like those selected for this study. These species, which have a high degree of integration, complexity, and efficient energy use, are recognized as more susceptible to edge changes [18]. Therefore, in fragmented environments, the survival advantage is given to those pioneer species with a maximum tolerance for a wide range of environmental conditions.

Five forest sectors in the Colonia Santa Rosa municipality were worked (23°20′00 south latitude and 64º 30′15″ west longitude): four, clearly turned into fragments, and one continuous (not fragmented) taken as a standard for comparison. The fragments were of distinct sizes: two large (sites 1 and 2 between 160 and 180 ha) and two small (3 and 4 between 3 and 5 ha). The distance from the city of Salta is 250 km.

The results of microclimatic records (taken from the edge toward the inside of the fragments, except in the site 5 as it was not considered the same edge but worked in an inside sector, looking for original ecosystem conditions) suggest that (Figure 6):

- High radiation intensity (RI) values are recorded at the edge (around 800 W/cm^2 on average) and almost constant values under cover (forest interior), which mean, almost, only up to 2% of that value. The differences were statistically significant ($H = 16.19$; $p < 0.01$).
- Soil moisture (SM) in the interior is twice that of the edge (with maximum values of up to 16%) showing significant differences ($H = 29.20$; $p < 0.001$).
- Air relative humidity (RH) increases toward the interior, reaching values up to 7 times higher than those at the edge (up to 53% relative humidity (RH)). The differences are significant ($H = 5.41$; $p = 0.048$).
- Soil temperature (ST) is one of the most stable variables, although differences can be detected: considering 100% at the edge (18°C on average) is reduced to 25% in the interior. The differences are not statistically significant ($H= 5.94$; $p = 0.311$).
- Air relative temperature (RT) decreases by 12% in the interior, showing nonsignificant values ($H = 5.69$; $p = 0.337$).

Changes are not manifested with identical magnitude in all cases. The smaller fragments tend to register values higher or lower for the measured variables (results not shown).

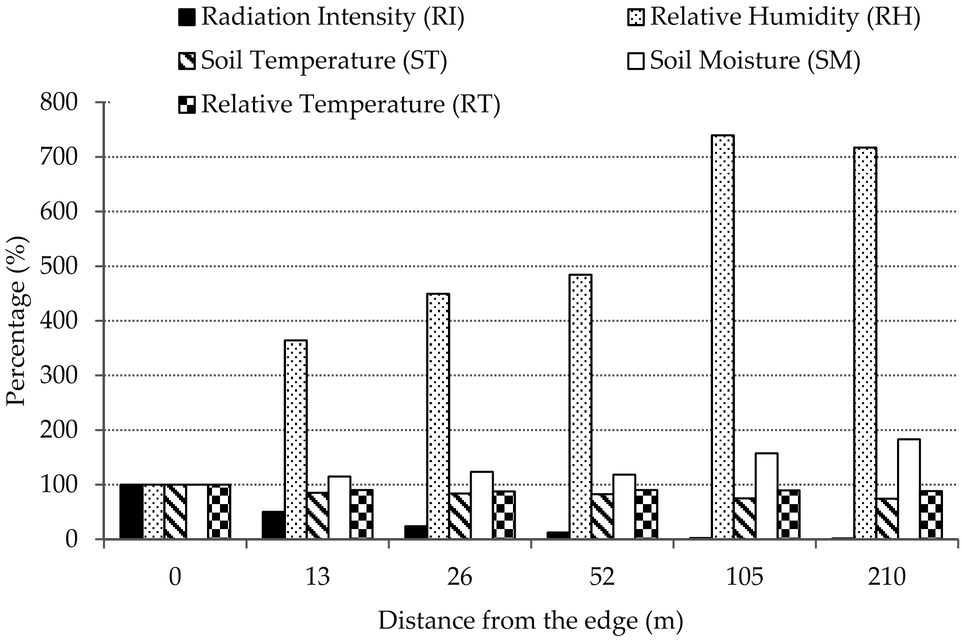

Figure 6. Microclimatic variables studied in fragments from edge to inside. Values are expressed in relative terms as a percentage of value at the edge (considered as 100%). The units are the following: RI= W/cm^2; ST= °C; RT=°C; RH= %; SM= %.

Microclimatic variables are interrelated. Thus, for example, the RH and the RT are inverse and strongly related; the RI and RT relate directly and the RH and RI in reverse. This means that the intensity of radiation reaching the edge of the plot is influencing the relative temperature directly (higher radiation and higher relative temperatures) and inversely with relative humidity (greater radiation and lower relative humidity). In addition, the relative humidity and temperature inversely influence themselves (where there are higher values of relative temperature, there are lower values of relative humidity).

In the AGB case, the relative participation of each species to the biomass stock varies according to site between 9% and 22 % for *C. multiflorum*, 5% and 79% for *P. rhamnoides*, 0% and 15% for *A. urundeuva*, 11% and 48% for *A. colubrina,* and between 0% and 23% for *C. angustifolia*. In general, the best-represented species is *P. rhamnoides*, followed by *A. colubrine*, and *C. multiflorum*. The fraction of ≤10 cm dbh ("sprout") contributes to their maximum values up to 6% of total AGB per site. AGB decreases significantly ($H = 53.66$; $p < 0.001$) from site 5 (179 ± 36 t/ha) to site 1 (116.4 ± 32.2 t/ha), site 2 (106 ± 44.6 t/ha), site 4 (16 ± 6.7 t/ha), and lastly site 3 (10.37 ± 4.1 t/ha). The studied species represent approximately 86–90% of the total in the case of the forest (according to plot). In the fragments, the five studied species not only have lower AGB but also have proliferated heliophyllum species, typical of open environments, and species composition has changes (results not shown). It cannot be concluded that carbon sequestration in vegetation is less because of the microclimatic edge effect. Although there are clear differences in the AGB$_{10}$, the correlation of different distance values does not give significant values

($r = 0.03$; $p = 0.804$), nor in the AGB_0 ($r = 0.20$; $p = 0.134$). The AGB of key species differs among fragments, but it cannot be said that a whole biomass has declined, since other shrubs and herbaceous species have proliferated. Larger studies are necessary to evaluate this aspect in depth.

Carbon sequestration in SOC, estimated up to 10 cm depth, increases from 19.3 ± 5 tC/ha in the site 3 (small forest fragment) to 23.4 ± 5 tC/ha in the site 4 (small forest fragment), 28.8 ± 7.5 tC/ha in the site 1 (large forest fragment), 28.9 ± 12.2 tC/ha in the site 2 (large forest fragment), and 34.8 ± 8.8 tC/ha in the forest or site 5 (Figure 7).

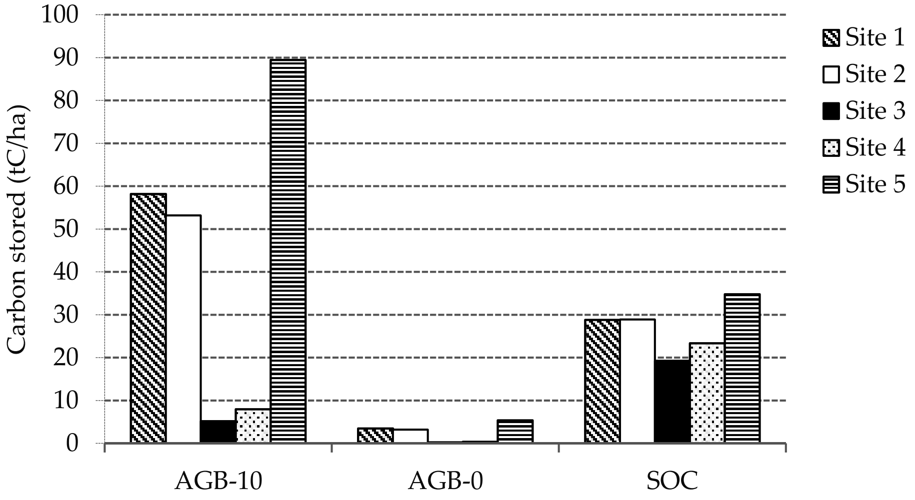

Figure 7. Carbon stock and contribution of each carbon pool studied (AGB includes only five species studied). The acronyms AGB_{10}, AGB_0 and SOC are explained in the text.

It can be assumed that the influence of these changes will affect, in the middle or long term, the composition and facilitate the establishment the different species, according to their requirements. Mainly, the dominant tree species (climax) could result in changes in its germination and survival, promoting the success of pioneers species implantation, and altering the original composition and structure of the forest [18].

4. Main remarks

The studies presented in this chapter offer insight into the varied potential of the Pedemontana Jungle for sequestration of atmospheric carbon, and how this potential can be influenced by human intervention in processes of deforestation, degradation, and fragmentation.

The carbon stock estimated for the Pedemontana Jungle ranges from 162 tC/ha (in Coronel Moldes) to 272 tC/ha (in Calilegua). In all cases, greater carbon storage occurs in the AGB fraction (from 47% to 55% of the total), where AGB_0 fraction provides between 6 and 10% of the total stock. Soil (SOC) constitutes the second most important carbon pool. Its contributions range from 28% to 39% according to the site.

The Pedemontana Jungle sequesters 43% more carbon than the Chaco forest at the same latitude. Moreover, the potential of carbon sequestration in the Pedemontana Jungle increases as the latitude decreases, sequestrating 28% more carbon at 22° than 24° south latitude.

Carbon sequestration in the Pedemontana Jungle sectors least affected by humans (degradation) is 23% higher than in more degraded areas. There are no advantages for sites that are legally protected (i.e., carbon sequestration is approximately similar). Forest degradation practices such as unsustainable timber production, overharvesting of fuel wood, extensive cattle ranching, and fires at the edge of forest fragments are less easily observed than deforestation, but they can contribute substantially to emissions. Forest degradation can also be a precursor to deforestation. These multiple changes in land use and forest area need to be monitored at the national level.

The Pedemontana Jungle sectors that have been left isolated are subject to edge effect, with changes clearly visible in microclimatic variables. The AGB in fragments is notably reduced for the main five tree species studied, but the species composition has also changed.

The potential impact of climate change on forest remnants is still unpredictable and depends on each one's resilience, on the remnant's adaptive capacity to climate change, and the magnitude and intensity of the phenomenon manifested in each area. At the same time, deforestation, degradation, and fragmentation of the Pedemontana Jungle could be affecting its ecological and social integrity, and the ability to provide ecosystem services of supply and regulation in the long term, and therefore its ability to respond to the global climate change impact.

Human management has taken over the ecosystem services that sustain the most important production systems from an economic standpoint. For example, irrigation water for cattle pastures and soil for agriculture. In many forests, such as the Pedemontana Jungle, other ecosystem services, for example, cultural or climatic regulation, are subordinated to these major objectives. The consequences of this imbalance in handling are shown negatively in the middle and long term, whereas in the short term, it cannot be seen most of the time. Vulnerable ecosystems are thus generated from the biophysical and social point of view, with a reduced capacity to respond to additional disturbances such as global climate change.

Forests require immediate support, with long-term policies independent of the ideologies, and management plans developed on technical bases, which are based on compliance with Article 41 of the National Constitution, "*All citizens enjoy the right to a healthy and balanced environment, suitable for human development and for productive activities that meet present needs without compromising those of future generations; and have the duty to preserve it...*" Land use plans should prioritize the conservation of ecosystems of high ecological value, such as the Pedemontana Jungle or Chaco, moreover, in a province where the natural biodiversity is accompanied by cultural biodiversity (with nine aboriginal ethnic groups), and where the forests are the principal sustainers of life.

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Greenhouse Gas Emissions – Carbon Capture, Storage and Utilisation

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Additional information is available at the end of the chapter

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Abstract

According to the recent information, CO_2 concentration in the atmosphere reached 402 ppm at the beginning of 2016. On the other hand, fossil fuels remain as the major source to produce energy. The International Energy Agency estimate that those fuels will remain as the most used source during coming decades.

Carbon capture and storage technology is the most promising technology to significantly decrease CO_2 emissions. Nevertheless, it may be possible to use CO_2 as a raw material for other industrial uses. In this chapter, authors explain both ways to decrease CO_2 emissions.

Keywords: CCS technology, CO_2 capture technologies, CO_2 storage, CO_2 uses, macrofouling

1. Introduction

The Fifth Assessment Report from the Intergovernmental Panel on Climate Change states that human influence on the climate system is clear [1]. The CO_2 concentration in the atmosphere is continuously growing. The latest value is 402.52 ppm (January 2016, Mauna Loa Observatory), which is 2 pmm higher than the value registered in January 2015 [1].

Carbon capture and storage (CCS) is a way of 'decarbonising' fossil fuel power generation. It involves capturing carbon dioxide (CO_2) emitted from high-producing sources, transporting it and storing it in secure geological formations deep underground, to mitigate the effect of greenhouse emissions on climate change [2].

The transported CO_2 can also be reused in processes such as enhanced oil recovery (EOR) or in the chemical industry, a process sometimes known as carbon capture and utilisation (CCU). CCS can be applied to fossil fuel power plants (coal and gas-fired power stations) and to industrial CO_2-emitting sources such as oil refineries or cement, chemical and steel plants. Rather than being a single technology, CCS is a suite of technologies and processes. While some of these have been operated successfully for decades, progress in applying large-scale CCS to power generation globally has been slow (Figure 1).

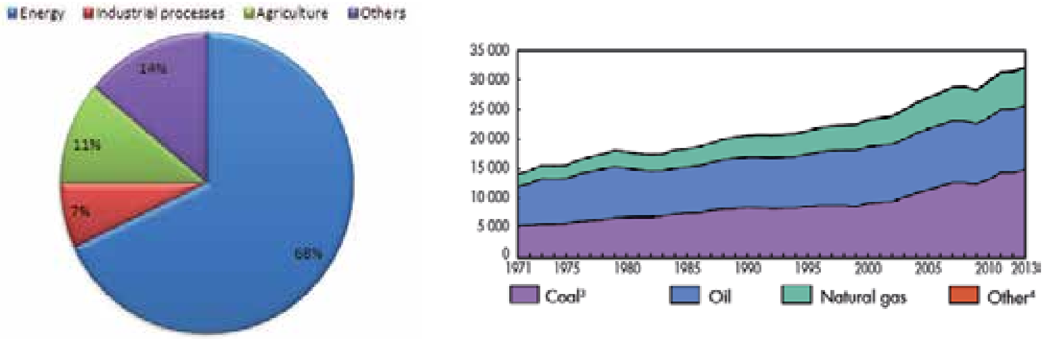

Figure 1. Shares of global anthropogenic greenhouse gas emissions (GHG) and world CO_2 emissions from fuel combustion by fuel (Mt of CO_2) [3, 4].

Carbon capture and storage (CCS) is likely to be a crucial part of the least-cost path to decarbonisation. It can provide a back-up role for variable renewables and help to manage swings in demand. CCS also has a crucial role in decarbonising heavy industry where there are limited options, and in the longer term would help to maximise the emission reduction obtained from scarce supplies of sustainable bioenergy as well as opening up other decarbonisation pathways.

The European Commission has also emphasised that ‘CCS may be the only option available to reduce direct emission from industrial processes at the large scale needed in the longer term’.

In this chapter, authors review the carbon capture, storage technology (including the CO_2 transport through pipeline), and CO_2 utilisation technologies.

2. CO_2 capture

This process consists of the separation of CO_2 from flue gas produced during the combustion of fossil fuels and can be applied to large flue gas stationary sources as thermal power stations and industrial processes.

Current CO_2 capture technology (first generation) is adapted from gas separation processes already in industrial use. There are several technologies and strategies to capture CO_2 from stationary sources: pre-combustion, post-combustion and oxy-fuel (Figure 2).

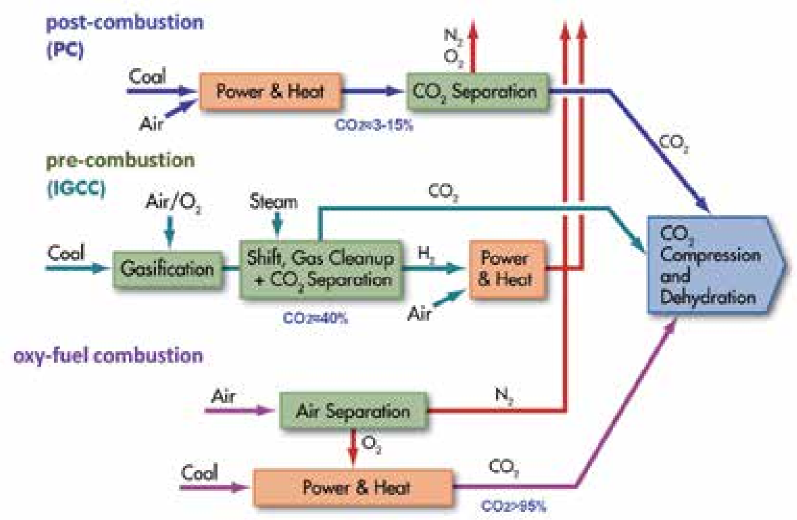

Figure 2. Summary of CO_2 capture technologies (adapted from IPCC) [2].

3. First generation of capture technologies

3.1. Post-combustion capture

Post-combustion capture follows the conventional application of a specific purification unit applied for a particular pollutant removal (CO_2 in this case). Figure 3 illustrates a typical block diagram of the post-combustion process that offers a great feasibility and versatility in terms of operating conditions and process integration.

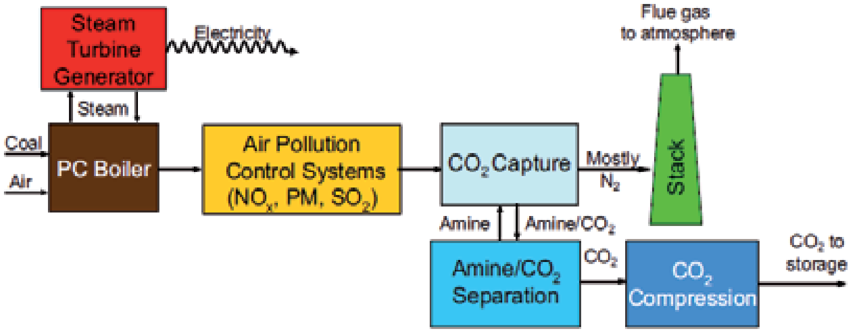

Figure 3. Simplified scheme of a fossil-fuel power plant using a post-combustion capture unit [5].

CO_2 concentration in the flue gas from a combustion process varies from 4 to14% in natural gas and coal-power plants, while other industries such as cement, iron and steel and petrochemical produce flue gas ranging between 14 and 33%. The key drawbacks hindering the large-scale implementation of this technology lies in the large volume of gas that should be treated and the low CO_2 concentration of the flue together with high energy requirements, mainly related to CO_2 desorption process. The presence of large amounts of dust, O_2, SOx, NOx and trace pollutants such as Hg and the relatively high temperature of the flue gas, typically between 120 and 180°C, are also design challenges that have significant impact on the capture costs.

The technologies currently available for post-combustion capture are classified into five main groups: absorption, adsorption, cryogenics, membranes and biological separation. The most mature and closest to market technology and so, the representative of first generation of post-combustion options, is capture absorption from amines.

3.2. Chemical absorption from amines

Post-combustion capture using chemical absorption by aqueous alkaline amine solutions has been used for CO_2 and H_2S removal from gas-treating plants for decades [6]. Amines react rapidly, selectively and reversibly with CO_2 and can be applied at low CO_2 partial pressure conditions. Amines are volatile, cheap and safe in handling. They show several disadvantages as they are also corrosive and require the use of resistant materials. Furthermore, amines form stable salts in the presence of O_2, SO_X and other impurities such as particles, HCl, HF and organic and inorganic Hg trace compounds that extremely constrain the content of those compounds in the treated gas.

The most widely used amine is monoethanolamine (MEA), which is considered as a benchmark solvent because of its high cyclic capacity, significant absorption-stripping kinetic rates at low CO_2 concentration and high solubility in water. Some other amine-based solvents such as diethanolamine (DEA), triethanolamine (TEA), diglycolamine (DGA), N-methyldiethanolamine (MDEA), piperazine (PZ), 2-amino-2-methyl-1-propanol (AMP) and N-(2-aminoethyl)piperazine (AEP) have also traditionally been utilised.

A typical chemical absorption scheme is shown in Figure 4. A low CO_2 concentrated flue gas is introduced in the absorber in crosscurrent with lean solvent from the stripper at 50–55°C and ambient pressure. CO_2 reacts with amines in the absorber according to the overall reaction:

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \tag{1}$$

As CO_2 is absorbed, rich amine from the absorber bottom is fed into a cross-exchanger with lean amine before it is introduced into the stripper. The stripping temperature varies between 120 and 150°C, and the operating pressure reaches up to 5 bar. A water saturated CO_2 stream is released from the top and is subsequently ready for transport and storage, while lean amine leaving the stripper is pumped back into the absorber.

The high energy penalty related to amines regeneration (a high-intensive energy process because of the stripper operating conditions and solvent used) and solvent degradation are the issues most hindering a large deployment of this technology.

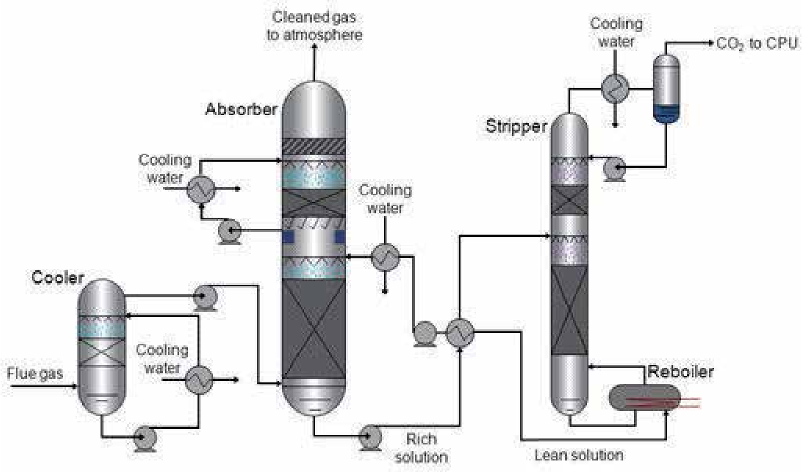

Figure 4. Diagram of a conventional CO_2 capture process using amine-based chemical absorption.

3.3. Pre-combustion capture

In pre-combustion CO_2 capture, CO_2 separation occurs prior to fuel combustion and power generation (Figure 5). The fuel reacts at high temperature and pressure with either oxygen or/ and steam under sub-stoichiometric conditions, and thereby a gas stream primarily composed of CO and H_2 is obtained. This CO/H_2 gas mixture is commonly known as *synthesis gas* or **syngas**.

In general, steam is utilised in case fuel is solid, namely gasification, whereas sub-stoichiometric oxygen is used with liquid and gaseous fuels. Both reactions occur at elevated temperature (1,400°C) and pressure (3–7 Mpa), as seen in Equations 2 and 3.

Steam reforming:

$$C_xH_y + xH_2O \leftrightarrow xCO + \left(x + \frac{y}{2}\right)H_2; \Delta H_r > 0 \tag{2}$$

Partial oxidation:

$$C_xH_y + xO_2 \leftrightarrow xCO + \left(\frac{y}{2}\right)H_2; \Delta H_r < 0 \tag{3}$$

Steam reforming needs a secondary fuel to provide the energy supply necessary for the reaction that occurs and a catalysts to improve the kinetic of this process. In Equation (3), the primary fuel is partially oxidised by a limited amount of oxygen. Partial oxidation produces less H_2 per fuel unit than stream reforming, but the kinetic reaction is faster, it requires smaller reactors and neither catalyst nor energy supply from a secondary fuel.

Once particulate matter is removed, the syngas passes through a two stages catalytic reactor, where CO reacts with steam to produce CO_2 and further yield H_2: *water-gas-shift (WGS) reaction*.

WGS reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2; \Delta H_r = -41\,kJ/mol \tag{4}$$

The syngas resulted is mainly composed of CO_2, ranging from 15 to 40%v/v, and H_2 at elevated pressure from which CO_2 can be easily separated by a physical absorption mechanism and then CO_2 can be easily released by simply dropping pressure.

Before the syngas from WGS reactor is separated into its primary components, the sulphur compounds, mainly in COS and H_2S form, are removed to avoid its emission to the atmosphere. Sulphur is then recovered in either as solid in a Claus plant or as sulphuric acid.

The sulphur-free syngas has a high CO_2 concentration and an elevated pressure (2–7 MPa), thus making physical absorption highly recommended for CO_2 separation, although adsorption process such as pressure swing adsorption (PSA) is also utilised.

The remaining nearly pure H_2 stream could be burned in a combined cycle power plant to generate electricity, but H_2 turbines require further development. Power fuel cells and transportation fuels are alternative options for using H_2 in the future, currently under development.

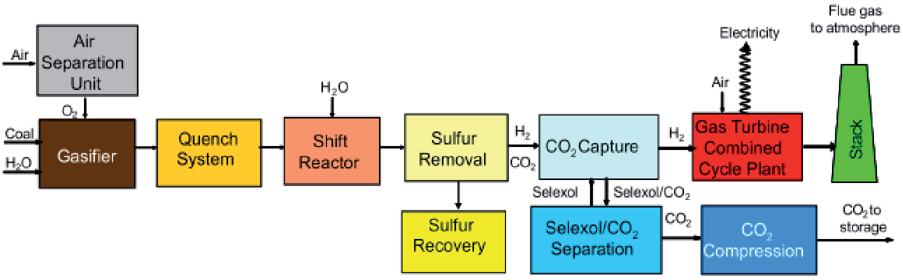

Figure 5. Simplified scheme of an integrated gasification combined cycle (IGCC) coupled with a pre-combustion CO_2 capture and storage unit using a physical absorption process [5].

3.4. Oxy-combustion capture

Oxy-combustion or oxy-fuel capture is considered as one of the most promising CCS technologies that would be economically competitive in fossil-fuel power plants and industrial facilities. It has been developed for both new designs and retrofitting of existing plants, although it is best adapted to newly designed power plants. A basic process flow diagram is given in Figure 6. Oxy-combustion technology is based on the use of high purity O_2 as oxidiser in an O_2/CO_2 mixture instead of air during the combustion process. It has been first proposed

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for coal boilers and gas turbines but can be applied to any type of fossil fuel utilised for thermal power production. As burning with O_2 at high concentration can produce high flame temperatures in the boiler, part of the exhaust gas from the boiler, mainly CO_2 and water vapour (FGR flue gas recirculation stream), is recycled to control temperatures to levels compatible with available boiler materials. The flue gas obtained from this system consists mainly of CO_2 and H_2O and are accompanied by minor quantities of N_2, SOx, NOx, Ar and Hg. Water can be easily removed by condensation, producing a highly CO_2 concentrated flue gas. The CO_2 content varies from 70 to 95%v/v, depending on the process configuration, air in-leakages, fuel characteristics and the purity of O_2.

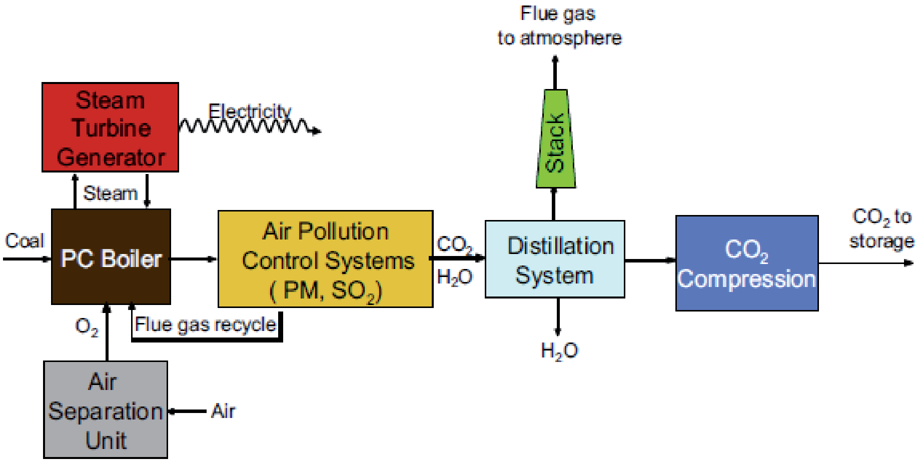

Figure 6. A simplified scheme of a fossil-fuel power plant based on the oxy-combustion concept [5].

Oxy-combustion requires large amounts of high purity (95–99%) O_2 for power production. A typical 500 MWe fossil-fuel power plant would need 9,000–10,000 t/d to operate under oxy-combustion conditions [7]. Currently, cryogenic distillation is the only available technology that can supply those amounts of O_2. An air separation unit (ASU) can provide around 4,500–7,000 t/d of oxygen, while other alternative technologies such as vacuum pressure swing adsorption (VPSA) units and membranes can only produce one order of magnitude below ASU production.

The ASU would consume up to 60% of the total electricity required for carbon capture and reduces the overall efficiency of the power plant by about 7–9%, reaching up to 15% in some cases. Furthermore, the availability and rapid response of the ASU to load changes have been noted as crucial challenges for the global oxy-combustion plant operation and feasibility. New technologies for O_2 production as ion transport membranes (ITM) or VPSA have shown promising results related to energy consumption, but the large amounts of O_2 required in power plant operation avoid currently its commercial deployment.

The CO_2 stream obtained from oxy-fuel combustion shows high levels of water vapour, sulphur compounds, N_2, O_2 and impurities such as mercury in the flue gas. NOx emission is low when compared with air combustion.

The CO_2 gas quality has significant impact on the capture cost by this technology, and uncertainties on the future regulatory requirements of CO_2 quality for its transport and storage has influence on the process configuration of the oxy-combustion plant, gas cleaning unit performance, overall CO_2 recovery capacity and on the energy requirements for CO_2 compression and purification.

4. Emerging technologies for CO_2 capture

The most promising emerging technologies applied to carbon capture are discussed in this section to complete the overview of the CO_2 capture technologies currently under research.

4.1. Chemical looping combustion

Chemical looping combustion (CLC) is a promising technology for fuel combustion, which can be beneficial in carbon capture applications. It is based on the use of an oxygen carrier, typically a metal oxide, to supply the O_2 needed for the fuel combustion process, producing a highly CO_2 concentrated exhaust gas. Iron, nickel, cobalt, copper, manganese and cadmium are commonly used as oxygen carriers in CLC.

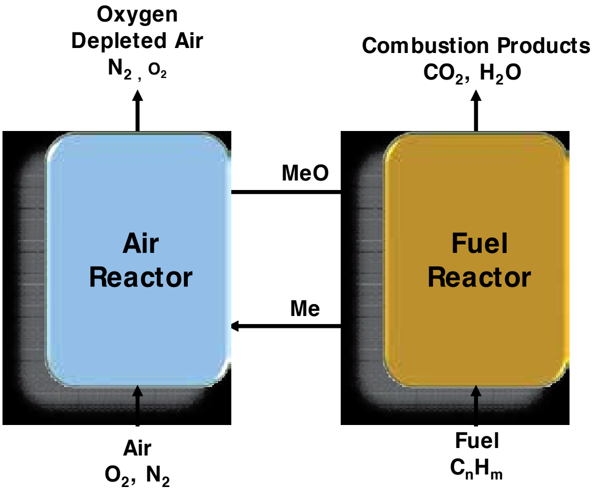

Figure 7. A simplified scheme of a chemical looping for oxy-combustion.

CLC consists of two fluidised bed reactors, namely reducer and oxidiser. In the reducer reactor, fuel is fed along with the metal oxide containing oxygen, which is transferred from the metal oxide to the reactor as the combustion occurs (Figure 7). A flue gas containing over 99%v/v of CO_2 can be obtained by a simply condensation stage because of the fact that the exhaust gas at the reducer outlet is primarily formed by CO_2 and water vapour. This stream is then sent to further compression and permanent storage.

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Reducer:

$$\left(2n+m\right)M_yO_x+C_nH_{2m}\leftrightarrow\left(2n+m\right)M_yO_{x-1}+mO+nCO_2. \tag{5}$$

Oxidiser:

$$M_yO_{x-1}+\frac{1}{2}O_2\leftrightarrow M_yO_x+N_2+O_2\left(excess\right). \tag{6}$$

4.2. Hydrate-based separation

This separation approach is based on the hydrate formation from high pressure water in contact with the flue gas containing CO_2. Hydrates are crystalline under suitable low temperature and high pressure conditions. A pure CO_2 stream is then obtained as CO_2 is released from the hydrates, achieving up to 99% of CO_2 recovery.

4.3. Calcium looping

Calcium looping is based on the reversible reaction between CaO and CO_2 to form calcium carbonate.

Calcium looping consists of two fluidised bed reactors, namely carbonator and calciner. In the carbonator, primary fuel is burned and CaO reacts with the CO_2 formed from the fuel combustion following the reaction seen in Equation (7). Carbonator temperature is within 650–700°C, depending on the system pressure.

Carbonator:

$$CaO\left(s\right)+CO_2\left(g\right)\leftrightarrow CaCO_3\left(s\right). \tag{7}$$

Calciner:

$$CaCO_3\left(s\right)\leftrightarrow CaO\left(s\right)+CO_2\left(g\right). \tag{8}$$

$CaCO_3$ is then heated by secondary fuel combustion in the calciner. CaO is regenerated and CO_2 is released for storage according to the reaction in Equation (8). The calciner temperature can reach 900°C, depending on the CO_2 partial pressure.

This technology shows benefits for carbon capture. Limestone is cheap and widely available, and there is a potential for process integration, which can lead to low energy penalties, i.e., heat released from carbonisation can be utilised in a steam cycle or the heat used in the calciner reactor can be recovered in the carbonation process.

4.4. Partial oxy-combustion

The energy consumption required for solvent regeneration and high purity oxygen production is the major drawback of post-combustion and oxy-combustion technologies. A new hybrid concept has been proposed to reduce the energy requirements associated with CO_2 capture step combining a partial oxy-fuel combustion (using oxygen-enriched air instead of high purity oxygen as oxidiser) and a CO_2 separation process treating a flue gas with a higher CO_2 concentration than in conventional air combustion (Figure 8).

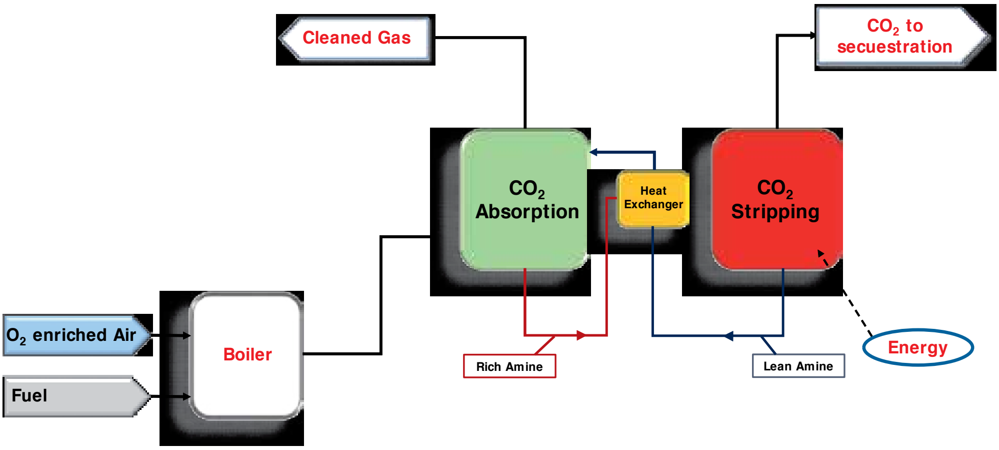

Figure 8. A simplified scheme of a partial oxy-combustion plant.

The combination of a less-constrained ASU for oxygen production and a carbon capture process using membranes instead of amine solvents can conduce to a minimal energy requirement associated with an oxygen purity ranging between 0.5 and 0.6 molar fraction.

4.5. Biological CO_2 capture

Biological CO_2 capture from a gas mixture is based on natural reactions of CO_2 with living organism, mainly enzymes, generally proteins and (micro)algae. Enzymes catalyse CO_2 chemical reaction and enhance CO_2 absorption rate in water. Enzymes can be also immobilised at the gas-liquid interface to promote CO_2 dissolution from the bulk gas. In this sense, carbonic anhydrase enzyme supported in a hollow fibre with liquid membrane has been reported as a potential method applied to CO_2 capture, achieving up to 90% CO_2 capture associated with low energy requirements in the regeneration process at laboratory-scale experiments. Carbonic anhydrase promotes carbonic acid formation from dissolved CO_2 and enhances CO_2 absorption from gas phase using and extremely low CO_2/enzyme ratio. CO_2 separation using enzymes must incorporate a tailored regeneration process to produce a high concentrated CO_2 exhaust stream. Membrane boundary, fouling, long-term operation and pore wetting are identified as the most relevant technical issues to be addressed before the scale-up of this CO_2 capture approach.

The use of algae is also considered a promising CO_2 capture option among natural occurring reactions. Algae consume CO_2 through photosynthesis mechanism. The use of algae in CO_2 capture would avoid subsequent CO_2 compression and storage stages, but there are some key issues that must be addressed for its large-scale deployment. In fact, algae require excessive amount of water and large gas-liquid interface surfaces that drastically limit their application in carbon capture. Algae are also highly susceptive to changes in operating conditions and to the presence of impurities such as vanadium and nickel.

4.6. Ionic liquid absorption

Significant progress has been made in the application of ionic liquids (ILs) as alternative solvents to CO_2 capture because of their unique properties such as very low vapour pressure, a broad range of liquid temperatures, excellent thermal and chemical stabilities and selective dissolution of certain organic and inorganic materials. ILs are liquid organic salts at ambient conditions with a cationic part and an anionic part.

ILs have the potential to overcome many of the problems of associated with current CO_2 capture techniques. ILs are particularly applicable in absorption of CO_2 while effectively avoiding the loss of sequestering agents. Other advantage of ILs is that they can be combined into polymeric forms, increasing the CO_2 sorption capacity compared with other ILs and conventional solvents and greatly facilitates the separation and ease of operation.

5. CO_2 transport

Currently there are more than 6,500 km of CO_2 pipelines worldwide. Most of them deliver CO_2 to EOR operations in the United States, but there is also a growing number under development for CO_2 storage projects

The relative development of the infrastructure to transport CO_2 is still in its early stages. This is reflected by the low number of existing infrastructures developed to transport CO_2 from stationary sources into geological structures. Table 1 provides an overview of the current developments for CO_2 transportation globally. All of these examples have been developed in relation to the EOR technique, where the CO_2 source is found mainly in natural reserves. In Europe, only a few projects are in operation, but there are plans to deploy an extended CO_2 pipeline network along Europe to optimise CO_2 storage structures.

These examples may be used to study CO_2 conditions; in addition, many CO_2 pipeline projects are based on well-known designs and materials commonly used in natural gas pipeline specifications. The most profitable way to transport CO_2 is in its dense phase [9].

To avoid two phases, it has been suggested that the most efficient way to transport CO_2 is as its supercritical phase [8, 9], which occurs at a pressure higher than 7.38 MPa and a temperature of more than 31.1 °C. To maintain these conditions, this type of transportation may require the use of booster stations in the pipeline layout to maintain the required pressure and temperature.

Pipeline	Location	Length (Km)	Diameter (inches)	Estimated maximum (10^6t/year)
Cortez	US	808	30	23.6
Sheep Mountain	US	656	NA	11.0
Bravo	US	351	20	7.0
Dakota Gasification/Weyburn	US/Canada	328	14	2.6
Choctaw	US	294	20	7.0
Bairoil	US	258	NA	23.0
Central Basin	US	230	16	4.3
Canyon Reef Carriers	US	224	16	4.3
Comanche Creek	US	193	6	1.3
Centerline	US	182	16	4.3
Delta	US	174	24	11.4
Snohvit	Norway	153	NA	0.7
Borger	US	138	4	1.0
Coffeyville	US	112	8	1.6
OCAP	The Netherlands	97	NA	0.4
Beaver Creek	US	85	NA	NA
Anton Irish	US	64	8	1.6
El Mar	US	56	6	1.3
Chaparral	US	37	6	1.3
Doliarhide	US	37	8	1.6
Lacq	France	27	NA	0.1
Adair	US	24	4	1.0
Cordona Lake	US	11	6	1.3

Table 1. Current CO_2 pipelines. The first long distance CO_2 pipeline was in the 1970s. Main utilisation of the natural & anthropogenic CO_2 is EOR activities [8].

Material selection should be compatible with all states of the CO_2 stream. They should be defined to prevent corrosion and maximum material stress. In addition, eligible materials need to be qualified for the potential low temperature conditions that may occur during a pipeline depressurisation situation.

The design of a pipeline should meet the requirements set by appropriate regulations and standards. CO_2 pipelines shall be designed according to applicable regulatory requirements. The Recommended Practice for Design and Operation of CO_2 refers to the following pipeline standards: ISO 13623:2009, DNV-OS F101:2012 and ASME B31.4 or ASME B31.8.

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Usually CO_2 pipelines are designed using existing national standards for gas and liquid transportation pipes, while additional CO_2 specific design issues are taken into consideration by the pipeline construction/operation companies to guarantee the reliable and safe operation of a given pipeline.

The use of carbon steels (e.g., with API X-60 and X-65) for the transportation of CO_2 streams has been ongoing for more than 30 years, as required in EOR projects. During the 2002–2008 period, 18 incidents were reported with no fatalities and/or injuries.

	Range
Length (km)	1.09–808
External diameter (mm)	152–921
Wall thickness (mm)	5.2–27
Capacity design (Mt/y)	0.06–28
Pressure min (bar)	3–151
Pressure max (bar)	21–200
Compressor capacity (MW)	0.2–68

Table 2. Summary of the current parameters considered in the CO_2 transport phase.

The cost of pipeline transportation will be determined by the pipeline route, in which physical and social geography will be crucial conditions.

The three major cost elements for pipelines are (1) construction costs (e.g., materials, labour, booster station, if needed, and others), (2) operation and maintenance costs (e.g., monitorisation, maintenance, energy costs) and (3) other costs (design, insurance, fees, and right-of-way).

6. CO_2 storage

At present, there are three possible geological structures that may be considered for CO_2 storage: depleted hydrocarbon and production, deep saline aquifers, and coal seams.

6.1. Depleted hydrocarbon fields

The CO_2 can be stored in supercritical conditions, rising by buoyancy and can be physically held in a structural or stratigraphic trap, the same way as the natural accumulation of hydrocarbons occurs. The advantage of the capacity of containment system has been demonstrated by the retention of oil for millions of years. If the site is in production, it is used to increase the recovery of oil or gas (EOR recovery – enhanced oil, gas-enhanced recovery – EGR). These operations, EOR/EGR, provide an economic benefit that can offset the costs of the capture, transport and storage of CO_2.

6.2. Deep saline aquifers

They are the best options for storing large volumes of CO_2 because of its size and found more than 800 meters below the surface. The supercritical CO_2 is 30–40% less dense than typical saline water from these formations, which means that the CO_2 naturally rise by buoyancy through the reservoir until it is caught or becomes longer solution term. They require an impermeable cap rock to ceiling (shales or layers of evaporites) and a porous and permeable rock store (sandstone or limestone) that promotes the injection, migration and trapping.

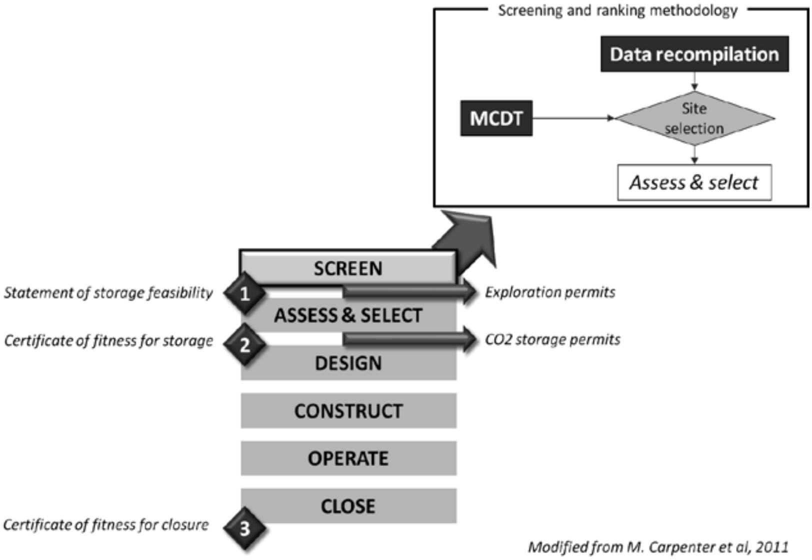
6.3. Coal seams

CO2 in gaseous form is injected into the coalbed, 300 to 600 metre depth, and adsorbed on the matrix pores, releasing the existing CH_4 in the same (two molecules of CO_2 adsorbed by each CH_4 molecule that travels). This has led to the possibility of storing CO_2 in coal seams, while CH_4 recovered is valued. This technique is called 'enhanced coalbed methane production' (ECBM).

Coal properties (range, degree and permeability) determine the suitability of the site, either for storage or storage with only CH_4 recovery.

6.4. Site selection and exploration

Figure 9 represents a proposed work flow for any CO_2 storage project. It is possible to determine three mayor phases: pre-injection, injection and post-injection phases.



Modified from M. Carpenter et al, 2011

Figure 9. Work flow proposed for basin screening (Definition phase) [10].

In general, most of the areas that could be suitable for storing CO_2 are not well explored geologically. For this reason, pre-injection phase is crucial to decrease the inherent risk in subsurface exploration.

Screen phase could be differentiated by the data recompilation task and the multicriteria decision tool. It is integrated as a preliminary phase, and it is connected with a second phase called *characterisation phase,* which corresponds to site maturation and testing.

Those criteria should comprise both technique and socio-economic criteria, and they should answer several questions such as where, how much quantity, and which conditions. All of these criteria and questions will contribute to solve and select the most suitable emplacement for storing CO_2 [10].

There are different examples and analogues that can be useful for the definition of criteria. Analogues can be natural (releases and resources) and industrial.

Assess or characterisation task is related to three major ways to explore the sub-surface: outcrops, geophysics and wells.

To decrease the inherent risk of exploration, it is necessary to consider all of the three sub-phases:

- Outcrops exploration provides samples of seal and storage formation, to evaluate some properties such as hydrogeology and geomechanical properties (permeability, porosity, etc.)
- Geophysics survey will provide and describe geological structures, and in some cases hydrogeology parameter (i.e., total dissolved solid, TDS).
- Few techniques may be used if the structure should be 1,000 m deep: seismic reflection is the most important technology (Figure 10), but other technologies such as magneto-telluric or gravimetric may provide relevant information regarding to the geological structure and resistivity of the original fluid.

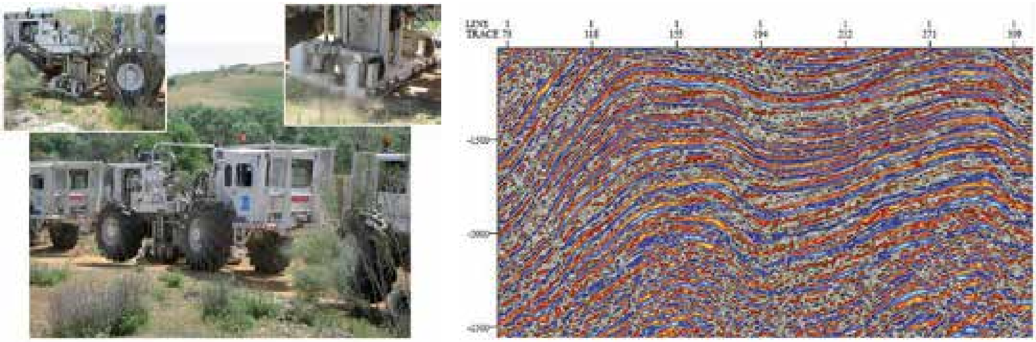


Figure 10. Seismic survey based on vibroseis. Example of a seismic profile.

- Wells will provide real information of the storage and caprock formation in sub-surface conditions. Test will provide information about geomechanical, hydrogeological properties and it may be possible to test interaction between the rock and CO_2.

7. Monitoring techniques

Considering the injection phase, control of the behaviour of injected CO_2 is one of the most important tasks. For instance, the control and monitoring strategy must:

- Demonstrate that the injected CO_2 is stored in the selected reservoir and therefore must be a guarantee that the company responsible for fulfilling its commitment to reducing emissions.
- Check that no intrusion occurs in other exploitable aquifers and water resources.
- Check for surface environmental effects occur, and therefore, you must provide the affected population security and peace on the operations of injection.

The monitoring strategy should not be limited to the operational and post-operational periods but has an important role during the pre-operational stage by conducting the baseline of the injection site [11]. This baseline defines the set of physical, geochemical and biological processes operating in the storage area before any activity injection. The baseline is critical because especially in the early stages of injection, the changes are not evident, both in depth and on the surface, and comparison with the undisturbed condition is needed. The development of the baseline may have added value; for example, building trust and showing the population from the beginning that the project is under control and that any anomaly is detected. Numerous methods have been proposed for monitoring CO_2 in geological repositories. Of these, one can clearly distinguish two types: (a) to detect the evolution of CO_2 injected into deep and (b) for leakage from storage. In the first type, these methods are generally based on geophysical techniques, while in the second type, the range of methods is broader, including geochemical, physical and biological techniques. Therefore, the final selection of the monitoring strategy should take into account the following aspects [12, 13]:

- Efficiency in detecting small changes in behaviour warehouse
- Implementation in large tracts of land
- Reasonable economic cost

Compliance with these requirements will be conditioned by the type of store and its area of influence. Clearly, monitoring techniques will be very different in stores on-shore and off-shore, and within a storage type, geological, hydrological and even ecological characteristics will favour the implementation of a methodology or other.

The monitoring deployment is based on the following aspects: (a) characterisation of the area, (b) establishing a base line CO_2, (c) establishment of potential areas of migration and release of CO_2 (and other gases) and (d) validation and development of techniques for monitoring CO_2.

Emission	Leakage	Description/Comments	Phases of the CO_2 Storage
Leak paths through wells and boreholes	Operating or abandoned wells	It is important to identify all abandoned at the site (or close to it) wells These wells can become the main roads of leakage	· Characterisation · Injection · Post-injection
	Blowouts (uncontrolled emissions from injection wells)	May cause leakage of high flows in short periods of time. It is considered that it is unlikely incidents if safety standards are met during drilling	· Injection
	Future removal of reservoirs of CO_2 can be a problem in the reservoirs of coal deposits	Can be a problem in the reservoirs of coal deposits	· Post-injection
Leak paths and natural migrations through faults and fractures	Through faults and fractures	May origin leak high flows Proper site characterisation can reduce the risk of leakage	· Characterisation · Injection · Post-injection
	By dissolving CO_2 in a fluid and subsequent transport natural circulation of fluid	Proper site characterisation (evaluation of hydrogeology) can reduce the risk of leakside of gas	· Characterisation · Injection · Post-injection
	Through the pore system in low permeability rocks when the capillary inlet pressure is exceeded or if the CO_2 has been in solution	Proper site characterisation can reduce the risk of leaks An exhaustive control of the injection pressure is needed	· Characterisation · Injection
	By a stroke if the reservoir	Proper site characterisation overflows can reduce the risk of leakage	· Injection · Post-injection
Another type of leak	Methane release could occur as a result of the displacement of CH_4 by CO_2	It happens in depleted oil and gas	· Characterisation · Injection · Post-injection

Table 3. Possible types of leakage of CO_2 in a geological storage [13, 14, 15].

8. CO_2 uses

8.1. Current uses of CO_2

Nowadays different applications are known that can be used for demonstrating that CO_2 is a useful, versatile and safe product. Figure 11 illustrates most of the current and potential uses of CO_2.

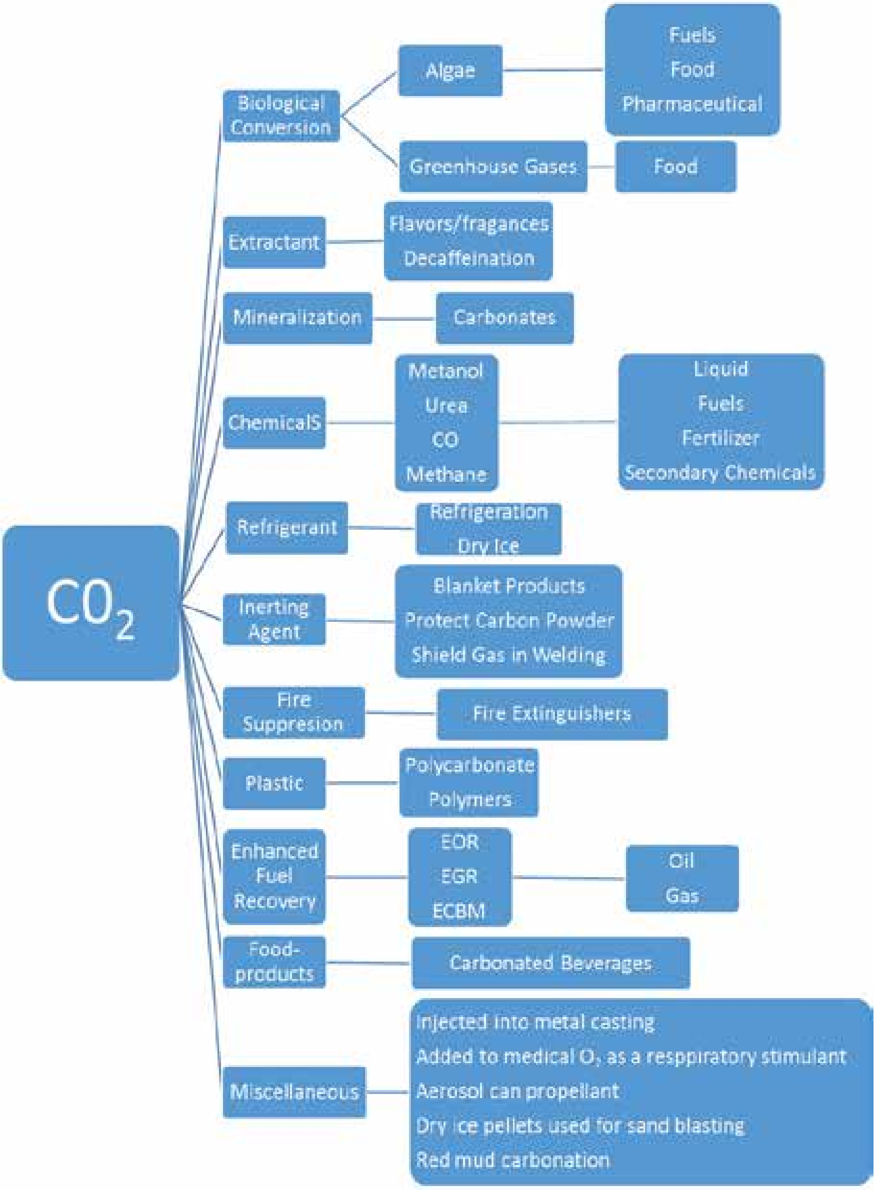


Figure 11. CO_2 uses. Different pathways for utilisation CO_2.

There are many classifications that can be made about the use or valuation of large-scale CO_2 and including the three categories proposed by Vega [16] for type of uses, which also is used by the PTE-CO2, 2013 (Technology Platform Spanish CO_2). To wit:

1. Direct or technology use: use of CO_2 with different technologies and market applications such as use for oil recovery, for dry cleaning, waste carbonation, food, water treatment or extraction with supercritical CO_2 compounds, including others.
2. Improved biological use: CO_2 fixation in biomass by growing microalgae and carbonic fertigation.
3. Chemical use: artificial photosynthesis and chemical conversion to high added value products and fuels.

8.2. Direct use of CO_2

8.2.1. Enhanced oil recovery (CO_2-EOR)

As much as two-thirds of conventional crude oil discovered in U.S. fields remain unproduced, left behind because of the physics of fluid flow. In addition, hydrocarbons in unconventional rocks or that have unconventional characteristics (such as oil in fractured shales, kerogen in oil shale or bitumen in tar sands) constitute an enormous potential domestic supply of energy.

Carbon dioxide is used in oil wells for oil extraction and to maintain pressure within a formation.

There are many methods for EOR and each has differences that make it more useful based on specific reservoir challenges and other parameters. Choosing the right method by screening the reservoir and fluid properties can ultimately reduce risk by eliminating inefficiencies.

CO_2 EOR is an 'EOR' technology that injects CO_2 into an underground geologic zone (oil/hydrocarbon containing 'reservoir') that contains hydrocarbons for the purpose of producing the oil. The CO_2 is produced along with the oil and then recovered and re-injected to recover more oil.

When the maximum amount of oil is recovered from the reservoir, the CO_2 is then 'sequestered' in the underground geologic zone that formerly contained the oil and the well is shut-in, permanently sequestering the CO_2.

CO_2 injection is a technology successfully used from more than 50 years. The first patent for CO_2-EOR appeared in 1952 and in 1964 began field trials. In the first commercial project of CO_2-EOR in Texas, in 1972 (SACROC project), CO_2 was supplied from a gas plant, where the CO_2 was eliminated in the production of ammonia At present the CO_2 is sent from geological formations (natural) from Bravo Dome in Colorado, and Mc Elmo Dome in New Mexico.

Nowadays, two techniques are largely used for CO_2-EOR:

- **Miscible water-alternating-gas (WAG) process.** Injection alternates between gas (usually natural gas or CO_2) and water; the miscible gas and oil form one phase. The WAG cycles improve sweep efficiency by increasing viscosity of the combined flood front (Figure 12).

- **Cyclic gas injection.** Most gas-injection EOR projects today use CO_2 as the injected gas. When CO_2 is pumped into an oil well, it is partially dissolved into the oil, rendering it less

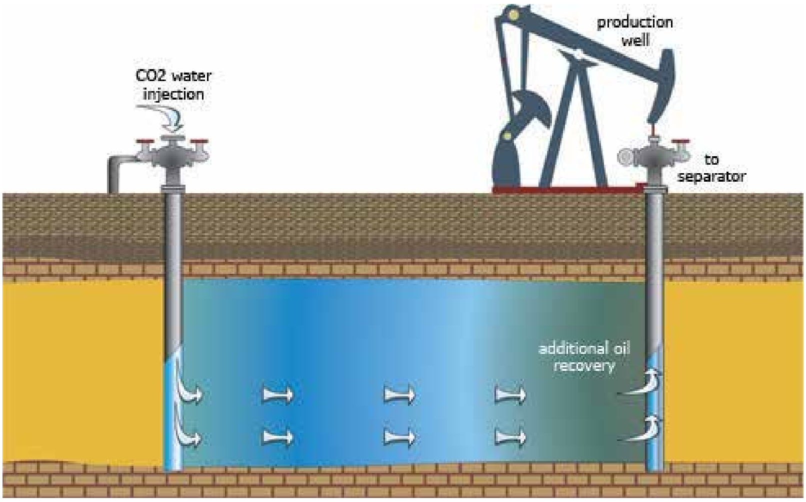


Figure 12. CO_2-EOR operation diagram. CO_2 injection into reservoir to 'flood'. Diagram courtesy of Dakota Gasification Company.

viscous, allowing the oil to be extracted more easily from the bedrock. The CO_2 used to increase oil recovery can be naturally occurring, or an effective means of sequestering an industrial by-product. In this case, carbon dioxide, under pressure, is injected between oil wells to freeing the stranded oil. CO_2 is a superior agent in recovering stranded oil as the CO_2 naturally reduces the surface tension that traps the liquid oil to in the oil reservoir. When the oil is recovered from the production well, CO_2 is also produced, but is easily separated from the crude oil because the CO_2 reverts back to its gaseous state when the pressure is removed.

8.2.2. Fire suppression

Some fire extinguishers use CO_2 because it is denser than air. Carbon dioxide can blanket a fire, because of its heaviness. It prevents oxygen from getting to the fire and as a result, the burning material is deprived of the oxygen it needs to continue burning.

8.2.3. Supercritical CO_2 uses

When CO_2 is at suitable temperature and pressure above the critical point (Figure 13), it is called supercritical CO_2.

This state emphasises its capacity to dissolve chemicals and natural substances of similar way as do different organic solvents such as hexane, acetone or dichloromethane. Therefore, the first applications focused on **the extraction of natural substances** as an alternative to using organic solvents. Thus, **removal of caffeine** (coffee or tea) with supercritical CO_2 is the most mature application at industrial level and is also used in the **extraction of hops or cocoa fat.**

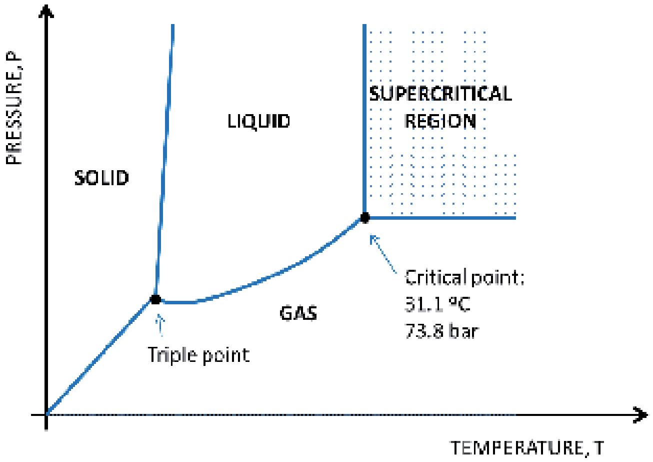


Figure 13. CO_2 phases diagram.

The dry cleaning with CO_2 is one of the most popular applications of supercritical fluids in the textile sector. This method is characterised by removing stains from the fabrics and garments where no harmful organic solvents for the average ambient, such as perchlorethylene (PER), common in conventional dry cleaning processes are used and without causing discoloration or shrinkage and without leaving odour.

One of the main advantages of supercritical CO_2 is that its solubility can easily be controlled suitably adjusting the pressure and temperature, allowing **fractionate mixtures** where all components are soluble.

Supercritical CO_2 extraction coupled with a fractional separation technique is used by producers of **flavours and fragrances** to separate and purify volatile flavour and fragrance concentrates. Like any solvent, supercritical CO_2, it allows processing chemicals by precipitation or recrystallisation, obtaining particles of controlled size and shape, without excessive fines without thermal stresses and controlling the shape of a polymorphic substance.

It is, therefore, a cutting-edge technology with great potential, because it is a new way to obtain natural products; it allows the adaptation of new high quality products with appropriate value to consumer habits; enables the development of new non-polluting processes and initiate the development of a tertiary sector led to the new technology.

8.2.4. Food and beverages

Liquid or solid CO_2 is used for quick freezing, surface freezing, chilling and refrigeration in the transport of foods. In cryogenic tunnel and spiral freezers, high pressure liquid CO_2 is injected through nozzles that convert it to a mixture of CO_2 gas and dry ice 'snow' that covers the surface of the food product. As it sublimates (goes directly from solid to gas states), refrigeration is transferred to the product.

Carbon dioxide gas is used to carbonate soft drinks, beers and wine and to prevent fungal and bacterial growth. CO_2 has an inhibitory effect on bacterial growth, especially those that cause discoloration and odours.

CO_2 has an inhibitory effect on bacterial growth, especially those that cause discoloration and odours (Figure 14).

Figure 14. CO_2 applications in food.

It is used as an inert 'blanket', as a product-dispensing propellant and an extraction agent. It can also be used to displace air during canning.

Cold sterilisation can be carried out with a mixture of 90% carbon dioxide and 10% ethylene oxide, the carbon dioxide has a stabilising effect on the ethylene oxide and reduces the risk of explosion.

8.2.5. Water treatment

Carbon dioxide can change the pH of water because of its slightly dissolution in water to form carbonic acid, H_2CO_3 (a weak acid), according to Equation 9:

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{9}$$

Carbonic acid reacts slightly and reversibly in water to form a hydronium cation H_3O^+, and the bicarbonate ion HCO_3^-, according to Equation 10:

$$H_2CO_3 + H_2O \rightarrow HCO_3^- + H_3O^+ \tag{10}$$

This chemical behaviour explains why water, which normally has a neutral pH of 7 has an acidic pH of approximately 5.5 when it has been exposed to air.

At the moment, CO_2 technology is widely introduced in treatments such as sewage water, industrial water or drinking water remineralisation.

The increased requirements of drinking water in large cities becomes necessary to use sources of very soft water and because of its low salinity and pH are very aggressive and can bring on corrosion phenomena in the pipes of the pipeline, with the appearance of colour and turbidity

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when these pipes are made of iron, and by undermining these ones made with cement fibre by dissolving the calcium carbonate ($CaCO_3$), because of excessive aggressive CO_2.

The introduction of carbon dioxide in the pipes regulates a state of equilibrium between dissolved bicarbonates, calcium carbonate inlaid and the CO_2 added.

Therefore, for the treatment of soft or aggressive waters, the use of CO_2 in combination with lime or calcium hydroxide is advisable to increase water hardness. This process is called **remineralisation** and is meaningful in water treatment plants, because soft water is indigestible.

The use of CO_2 in wastewater neutralisation, Figure 15, offers great advantages in the operation and the environment by preventing other chemicals:

- Better working conditions. Eliminate the risk of burns, toxic fumes and other injuries from handling mineral acids
- Safe neutralisation. Avoiding risk of over-acidification with strong acids
- Low initial investment. Simple equipment, insurance and small dimensions
- Automated process. Automation avoids the handling of corrosive acids in the plant, pH control is automatic
- Economy

Figure 15. Dosing system for sewage.

8.2.6. Carbonate mineralisation

The alkaline waste management presents significant problems, mainly because of its volume and its geochemical properties that do not allow disposing in conventional landfills. Therefore, the accelerated carbonation of this waste is another technological uses of CO_2.

Carbonate mineralisation refers to the conversion of CO_2 to solid inorganic carbonates. Naturally occurring alkaline and alkaline-earth oxides react chemically with CO_2 to produce minerals, such as calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$). These minerals are highly stable and can be used in construction or disposed of without concern that the CO_2 they contain will release into the atmosphere. One problem is that these reactions tend to be slow, and unless the reactions are carried out in situ, there is a large volume of rocks to move. Carbonates can also be used as filler materials in paper and plastic products.

8.2.7. Biological utilisation

Green plants convert carbon dioxide and water into food compounds, such as glucose and oxygen. This process is called photosynthesis (Equation 11).

$$CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2 \tag{11}$$

The reaction of photosynthesis is as follows: Biological applications are based primarily on the use of CO_2 as food for plant growth. In a similar way as the plants take advantage of sunlight and CO_2 for biomass, or other products, 'imitating' nature, improving its results. Therefore, this technology is also known as biomimetic transformation.

There are two main ways in the biological utilisation process: greenhouses carbonic fertilisation and growth of microalgae.

8.2.7.1. Greenhouses carbonic fertilisation

CO_2 is found naturally in the atmosphere and, therefore, in the **greenhouse** environment. It is essential for plant growth, since it represents the carbon source for organic compounds they need, in short, for compounds that constitute their biomass (leaves, stems, fruits, etc.).

CO_2 is not the only factor involved in photosynthesis, so that for its use, other factors must be at levels that do not limit the process. Light, temperature, amount of available nutrients and the relative humidity are other environmental factors affecting photosynthetic activity.

During photosynthesis, plants capture light energy and CO_2 through the leaves, and water and nutrients through the roots. Thanks to these elements and chlorophyll leaves, plants get synthesise sugars and various organic compounds required for their development. Photosynthesis is responsible for plant growth. Therefore, favouring photosynthesis we managed to promote the development of the plants and agriculture in our case.

Yields of plant products grown in **greenhouses** can increase by 20% by enriching the air inside the greenhouse with carbon dioxide. The target level for enrichment is typically a carbon dioxide concentration of 800 ppm – or about two-and-a-half times the level present in the atmosphere (Figure 16).

In the CENIT SOST-CO_2 project that includes the entire life cycle of CO_2, researching technology uses as chemical and biological uses, the following results were confirmed, among others [18]:

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Figure 16. Carbon fertilisation in hydroponics culture greenhouses.

- Rating combustion gases from combined cycle plants to use in vegetable crops in greenhouses, in applications in irrigation pipes to prevent clogging and to balance the pH in nutrient solutions.
- With regard to the quality of gas from CCGT, it can be recommended for direct use in greenhouses or other agricultural uses.
- The carbonic fertilisation allows early crop production along with a greater amount of product with better quality.

8.2.7.2. Growth of microalgae

Microalgae are photosynthetic microorganisms that can grow in diverse areas mainly in water media where the forced culture can be carried out in diverse type of reactors in concordance with its design and operation. The advantage of this process is that microalgae are a microorganism with a high production rate (some species are able to duplicate their biomass in 24 hours), and therefore with increased demand for CO_2 conventional terrestrial plants.

The investigation of microalgae culture for different purposes began in the middle of last century, when the United States launched the 'Aquatic Species Program'. At that time, the research focused on the possibility of obtaining biofuels from microalgae: mainly methane and hydrogen, but after the oil crisis in the 1970s the biodiesel was also considered.

Biofixation of CO_2 by microalgae, especially as an option for the utilisation of flue gases from power plants, has been the subject of extensive investigations in the United States, Japan and Europe (IEA-GHG Biofixation Network). However, none of the related projects have demonstrated the feasibility of the concept at a pre-industrial level. What is more, CO_2 fixation efficiency is quite low because of the photobioreactors used in those pilot plants (raceway or open-ponds) (Figure 17).

The current production of microalgae is mainly focused around a few species, such as *Spirulina*, *Chlorella*, *Dunaliella* or *Haematococcus* for nutritional purposes (for humans) and animal feed (especially aquaculture). Other sectors, such as cosmetics, effluent treatment and bioenergy, have shown interest, incorporating these or other species of microalgae and cyanobacteria into commercial products. Currently, 95% of the production of microalgae is based on open systems

Figure 17. Microalgae culture in open system (raceway) and close photobioreactor (Almeria University and Palmerillas Research Center).

(raceways or circular open ponds). These systems have a low rate of CO_2 fixation and it is estimated to be around 20–50% of the injected gas is effectively set by microalgae [17].

8.2.8. Use of CO_2 in chemicals

Carbon dioxide gas is used to make urea (used as a fertiliser and in automobile systems and medicine), methanol, inorganic and organic carbonates, polyurethanes and sodium salicylate. Carbon dioxide is combined with epoxides to create plastics and polymers.

Corn-to-ethanol plants have been the most rapidly growing source of feed gas for CO_2 recovery.

8.2.8.1. Artificial photosynthesis

Because CO_2 is a practically inert molecule, artificial photosynthesis of CO_2 involves the use of large amounts of energy so it must use a clean source of energy (such as solar radiation).Therefore, the use of catalytic agent to facilitate the process allowing even take place at ambient temperature and pressure is necessary. In this case, it is also called as photocatalysis or photoreduction.

In photocatalysis two processes occur: CO_2 reduction and oxidation of other compounds. Early works on the photocatalytic reduction of CO_2 in aqueous solution were published between 1978 and 1979 ([19, 20]), and later numerous investigators have studied the mechanism and efficiency of the process using different catalysts (oxides of titanium, zinc and cadmium, cadmium sulphide, silicon carbide), and reducing (water, amines, alcohols) and R light sources (lamps xenon, mercury, halogen). Thus, it has been shown that by using specific semiconductors and reducing agents, can be obtained a great variety of products (methane, methanol, formaldehyde, formic acid, ethanol, ethane, etc.).

Along with thermodynamics, catalysis is one of the core technologies for an economically interesting use of CO_2 as feedstock in chemical processes. This is one of the areas most

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sophisticated and complex of modern chemical research. It is one of the major challenges for the scientific and technological developments related to the fields of energy and catalysis, as was highlighted in the report to officiate Sciences US Department basic Energy: more than 85% of all products are produced using chemical catalysis [21].

Photocatalysis involve the production of reactions because of the incidence of light on a semiconductor material. Unlike metals, these materials have a forbidden energy band, which extends from the top of the so-called valence band to the bottom of the conduction band (Figure 18).

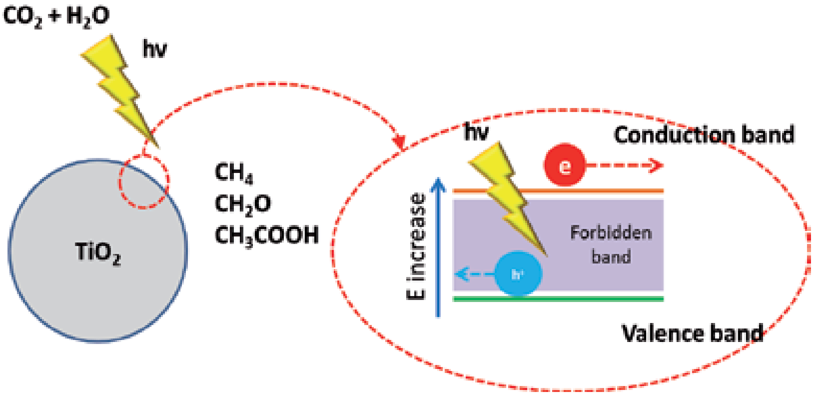


Figure 18. Diagram of behaviour of a semiconductor, TiO_2, in light presence and participation in the photocatalytic CO_2 reduction organic products.

The main disadvantage in these cases remains in the low process efficiency.

In general, the process of photocatalytic reduction of CO_2 requires a milder conditions and lower energy consumption than chemical reduction [22].

8.3. Chemical conversion

Large quantities are used as a raw material in the chemical process industry, especially for urea across CO_2 reaction with NH_3 and later dehydration of the formed carbamate. Urea is the product most used as agricultural fertiliser. It is used in feed for ruminants, as carbon cellulose explosives stabiliser in the manufacture of resins and also for thermosetting plastic products, among others.

Methanol production, where CO is added as additive, is very a well-known reaction. The production is carried out in two steps. The first step is to convert the feedstock natural gas into a synthesis gas stream consisting of CO, CO_2, H_2O and hydrogen. This is usually accomplished by the catalytic reforming of feed gas and steam. The second step is the catalytic synthesis of methanol from the synthesis gas. If an external source of CO_2 is available, the excess hydrogen can be consumed and converted to additional methanol.

CO_2 is also used, to make inorganic and organic carbonates, carboxylic acids, polyurethanes and sodium salicylate. Carbon dioxide is combined with epoxides to create plastics and polymers (Figure 19).

Figure 19. Different products made with CO_2 derivatives.

9. New ways for CO_2 uses

In general, the area of CO_2 utilisation for carbon storage is relatively new and less well known compared to other storage approaches, such as geologic storage. Thus, more exploratory technological investigations are needed to discover new applications and new reactions.

Many challenges exist for achieving successful CO_2 utilisation, including the development of technologies capable of economically fixing CO_2 in stable products for indirect storage.

Significant innovation and technical progress are being made across a number of utilisation technologies. The **electrochemical reduction** could be really attractive because it is an excellent way for renewable energy storage.

9.1. Power to gas technology (P2G)

In the 3rd Carbon Dioxide Utilisation Summit, October 2014 in Bremen, Germany, ETOGAS GmbH presented its turn-Key plan and technology Power-to-Gas for SNG through electrolysis processes [18].

This technology uses CO_2 as a feed gas for the production of carbon products with Etogas methanation plant (Figure 20), which are reactor systems for conversion of H_2 and CO_2 to methane (synthetic natural gas). The produced gas is DVGW- and DIN-compliant synthetic natural gas and can be used directly, e.g., as a fuel for a CNG vehicle.

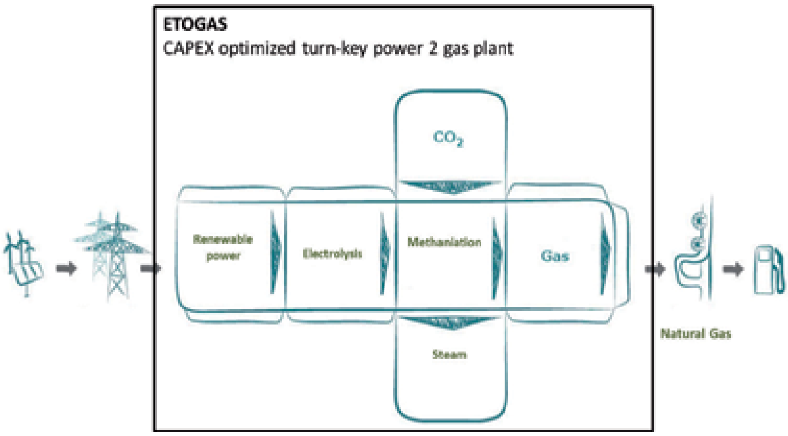


Figure 20. SNG schematic process. Source: ETOGAS Project.

9.2. Electrochemical CO_2 utilisation

According to DNV GL, electrochemical CO_2 utilisation presents some advantages as follows:

Production de-coupled from the sun (flexibility in renewable energy source); land use is minimised and no limitation with respect to geography; no competition with food (corn, sugar); flexibility in end fuel – ethanol, butanol or diesel (depending on the organism used); flexibility in electrochemical process (matching to supply/demand of renewable energy); and significant net reduction in CO_2 emission (Figure 21).

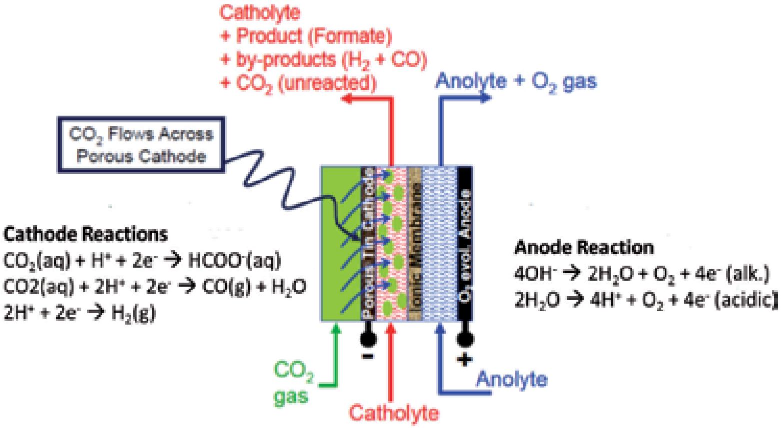
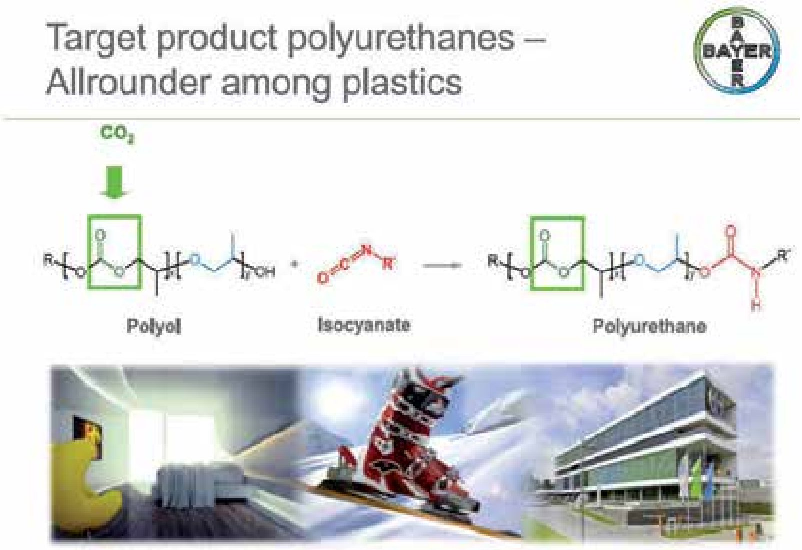


Figure 21. Electrochemical production of formic acid (HCOOH) and CO. Source: third Carbon Dioxide Utilisation Summit. DNV GL.

9.3. Polymers production

Bayer MaterialScience (Germany) in the Project "Dream Production" combines part of waste streams of coal-fired power plants, CO_2, with the production of polymers. The target is the design and development of a technical process able to produce CO_2-based polyether polycarbonate polyols on a large scale. The first step was to convert the CO_2 in new polyols, and these polyols showed similar properties such as products already on the market and can be processed in conventional plans as well (Figure 22).



Target product polyurethanes – Allrounder among plastics

Figure 22. Target product polyurethanes – All rounder among plastics. Source: 3rd Carbon Dioxide Utilisation Summit. Courtesy: Bayer.

The CO_2 thus acts as a substitute for the petroleum production of plastics. Polyurethanes are used to produce a wide range of everyday applications. When they are used for the insulation of buildings, the polyurethane saves about 80% more energy than it consumes during production. Light weight polymers are used in the automotive industry, upholstered furniture and mattress manufacturing.

9.4. Macrofouling control in industrial facilities

In the past years, several projects have been focused in the **direct use of flue gases** from Combined Cycle Power Plants for developing different applications. In this way, the project CENIT SOST-CO2 has demonstrated the use of flue gases from CCPP in a direct way to control the pH in the cooling water systems with refrigeration tower and Iberdrola has developed an application for power plants.

Another application for the future will be "CO_2 for Zebra Mussel Control". A project developed by Iberdrola and the University of Salamanca shows that carbonic acidification just in the moment when the larva of zebra mussel are in the adequate phase (pediveliger) causes a much greater lethality than inorganic acids because of the synergistic effect of the lethal hypercapnia by physiological changes in cell metabolism of the larvae. (*CDTI Project: Seguimiento de la incidencia del mejillón cebra (Dreissena polymorpha) en el Ciclo Combinado de Castejón 2009-2011. Iberdrola – Universidad de Salamanca).*

The project LIFE13 ENV/ES/000426. CO2FORMARE [23], "Use of CO_2 as a substitute of chlorine-based chemicals used in O&M Industrial processes for macrofouling remediation", led by Iberdrola Generación, seeks to demonstrate the viability of using CO_2 from combustion gases to control macrofouling *(fouling caused by larger organisms, such as oysters, mussels, clams and barnacles*) in a thermal power plant (Castellon CCPP), cooled by sea water. First estimates indicate that a 400 MW CCPP (Figure 23) may be necessary to use up to 50,000 t CO_2 yr^{-1}, [23].

CO2FORMARE Project

IBERDROLA

Development in Castellon Combined Cycle Power Plant

Generación Térmica SETTE-Química

Figure 23. Castellon Power Plant. Courtesy: Iberdrola.

10. Others

The Carbon Storage Program of the NETL (National Energy Technology Laboratory) of US Department of Energy supports four main CO2 utilisation research areas: **cement**, **polycarbonate plastic, mineralisation** and **enhanced hydrocarbon recovery.** Several projects on active CO_2 utilisation focused in these areas receive Department of Energy (DOE) funds that aim to obtain the goals for the Carbon Storage Program.

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Review of Recent Developments in CO_2 Capture Using Solid Materials: Metal Organic Frameworks (MOFs)

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Additional information is available at the end of the chapter

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Abstract

In this report, the adsorption of CO_2 on metal organic frameworks (MOFs) is comprehensively reviewed. In Section 1, the problems caused by greenhouse gas emissions are addressed, and different technologies used in CO_2 capture are briefly introduced. The aim of this chapter is to provide a comprehensive overview of CO_2 adsorption on solid materials with special focus on an emerging class of materials called metal organic frameworks owing to their unique characteristics comprising extraordinary surface areas, high porosity, and the readiness for systematic tailoring of their porous structure. Recent literature on CO_2 capture using MOFs is reviewed, and the assessment of CO_2 uptake, selectivity, and heat of adsorption of different MOFs is summarized, particularly the performance at low pressures which is relevant to post-combustion capture applications. Different strategies employed to improve the performance of MOFs are summarized along with major challenges facing the application of MOFs in CO_2 capture. The last part of this chapter is dedicated to current trends and issues, and new technologies needed to be addressed before MOFs can be used in commercial scales.

Keywords: CO_2 capture, solid sorbent, MOFs, ZIFs

1. Introduction

1.1. Environmental problem and CO_2 emissions

The increasing level of CO_2 emission is considered one of the major environmental challenges that our planet is facing today. The concentration of greenhouse gases in the atmosphere reached a new record in 2013, with CO_2 at 396 ppm which represents 142% of the concentration of the pre-industrial era [1]. Findings of a recent global atmosphere watch reported in a greenhouse gas bulletin [1] revealed that CO_2 concentration has increased between 2012 and 2013, more than any other year since 1984, which was attributed to the reduced uptake by the earth's biosphere. This alarming level of CO_2 shows the urgency for taking immediate actions to prevent serious repercussions of climate change. On December 2015, at the Paris Climate Conference (COP21), 195 countries adopted a historical and the first legally binding global climate agreement to keep the increase in global average temperature to well below 2°C above pre-industrial levels. The discovery of new fossil fuel reserves, combined with rising energy demand, led to an increase in the number and capacities of power plants worldwide. This situation is expected to extend into the future due to various factors such as industrial development and economic growth, especially in developing nations, which in turn is expected to further contribute to increasing levels of greenhouse gas emissions in years to come. According to a recent report by the Energy Information Administration, energy consumption is projected to rise by 56% between 2010 and 2040. Fossil fuels will continue to supply about 80% of the world energy through 2040. Industrial energy consumption represents the greatest share of emissions and is projected to consume more than 50% of the energy delivered in 2040. According to currently implemented regulations regarding fossil fuels, CO_2 emissions from power plants is projected to increase by 46% compared to emission level in 2010 [2].

Among several approaches that could be used to overcome the greenhouse gas effect is the utilization of clean energy alternatives which could be the ultimate solution to the climate change problem in terms of reducing CO_2 emissions. However, these green technologies still require significant modifications to the current energy framework. The great challenges facing these green technologies lie in the difficulty for implementation at industrial scale, which makes it economically infeasible when compared to fossil fuel-based power plants. This implies that unless green energy alternatives and energy infrastructure for the commercialization and the implementation of these new technologies are attained, the pursuit of new CO_2 emission reduction technologies will continue to be the most practical method to address greenhouse gas effects until the advancement in clean energy technologies reaches commercial stages.

There are three different strategies to reduce emissions of CO_2 from fossil fuel-based power plants. These include post-combustion capture in which CO_2 is separated from the combustion flue gas stream that is mainly composed of nitrogen and some other minor components such as water vapor and oxygen. The separation process in this scheme is a downstream unit which allows for an easy retrofit of a post-combustion capture unit to an existing power plant. However, the limitations of this technique include a low CO_2 partial pressure, relatively high flue gas temperature and large quantities of CO_2 in the flue gas stream [3, 4]. In the pre-combustion capture scenario, the fossil fuel is treated under certain temperature and pressure to gasify the fuel and produce hydrogen. This method offers streams with high CO_2 partial pressure and thus easy separation by utilizing variety of solvents; however, it requires significant modifications to the power generation plant. The last scenario is called the oxy-fuel capture in which the fuel is burned under a pure oxygen environment which requires the separation of oxygen/nitrogen from an air stream. The process produces pure CO_2 and water vapor which can be easily recovered through a simple condensation unit. Each separation scenario requires a different capture technology, and therefore the properties, characteristics, and operation of the separation process are also entirely different among the three strategies. The most advanced process for implementation in the field is post-combustion. We will therefore, in this chapter, focus on the post-combustion separation applications.

1.2. Existing technologies for CO_2 capture

In order to locate metal organic frameworks (MOFs) on the map of the technologies used for CO_2 capture applications, we will briefly describe the major technologies that have been employed and discuss their advantages and limitations. Figure 1 shows the different technologies used for CO_2 capture, whereas MOFs are used under the category of membranes and adsorbents.

The most widely investigated technology for CO_2 capture from flue gas is absorption using aqueous amine solutions such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA), as well as blends of different amines [5–7]. Amine scrubbers are considered a well-developed technology and is available in commercial scale for post-combustion capture applications [8]. The major limitations of this technology include the high energy required for solvent regeneration, stability of the amine system at the regeneration conditions, and the negative influence of impurities present in the flue gas that might significantly affect the stability and performance of the solvent [9, 10].

Under the category of absorption technology and in order to overcome the limitations of amine-based technologies, aqueous ammonia as a solvent for CO_2 separation has also been widely used to benefit from the low heat of absorption of ammonia-based solvents as compared to amine systems. Besides, the ammonia can also absorb other impurities existing in the gas stream such as NO and SO_x. The major drawback of ammonia-based solvents lies in the need to cool the flue gas prior to introducing it to the absorption column to prevent ammonia losses to the gas stream. This adds a huge energy requirement considering the large volume of flue gas stream that typically needs to be treated [11]. The chilled ammonia process faces similar issues in addition to fouling of the heat exchanger by ammonium bicarbonate deposition from saturated solutions [4].

Great efforts have been made to find new and efficient materials for absorptive CO_2 separation. Ionic liquids (ILs) are liquid salts composed of cations and anions, have been proposed as promising solvents to replace the existing amine-based solvents. ILs possess several remarkable properties that make their application in CO_2 separation one of the hottest research topics in the last few years [12–14]. These properties include low volatility, high CO_2 solubility, good thermal stability, and the possibility of systematically tuning the structure toward certain properties [15–17]. Several review papers reporting experimental data related to CO_2 solubility, selectivity, effect of ILs structure on performance, and the stability of ILs are available [12, 18]. Recent developments on the application of the amine-modified ILs, known as task-specific ILs (TSILs), are also widely discussed in the literature [19, 20], including both physical and chemical interactions with CO_2. Unfortunately, many ILs and TSILs suffer from a common problem of high viscosity after CO_2 absorption. Even though some recent reports mentioned the availability of ILs with low viscosities, it is still evident that much work has to be done to overcome this limitation. Finding cheap routes for the synthesis of these materials is one of the greatest challenges facing researchers working in this area [21]. In this chapter, a great portion will be dedicated to the incorporation of ILs into the pores of MOFs to improve their CO_2 capture capabilities.

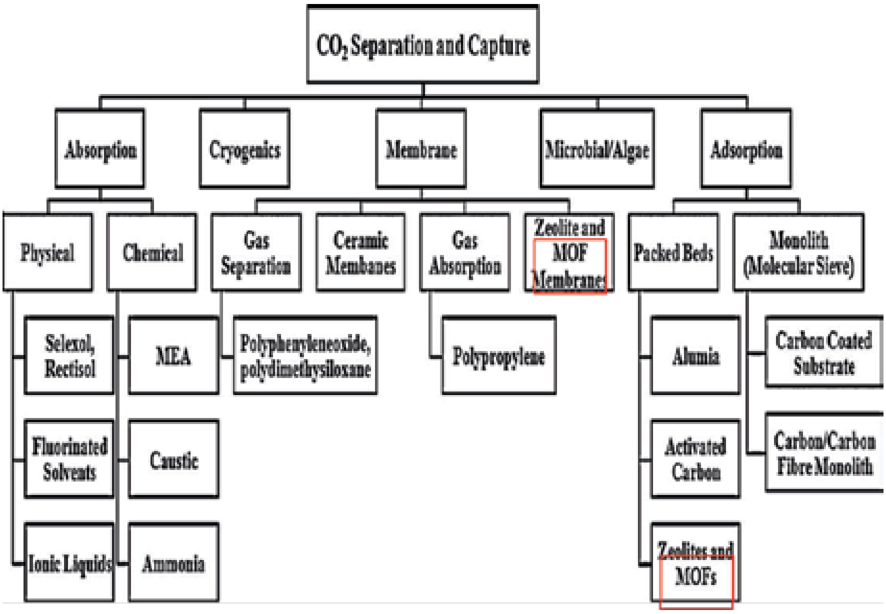


Figure 1. Different technologies used for CO_2 capture [22].

2. CO_2 capture using solid sorbents

2.1. Criteria for the evaluation of solid sorbents

In order to evaluate solid materials for their performance in CO_2 separation from flue gases, some important performance criteria must be met. These include:

- **Adsorption capacity**: it is a key criteria in evaluating solid sorbent performance. It provides information on the amount of CO_2 that could be adsorbed by a given solid material. It can be represented in terms of gravimetric uptake which is the amount of CO_2 adsorbed per unit mass sorbent (gram CO_2/gram sorbent, or cm^3 CO_2/gram sorbent). The volumetric uptake is another measure for capacity, and it reports the CO_2 uptake per volume of sorbent material (gram CO_2/cm^3 sorbent, or cm^3 CO_2/cm^3 sorbent). This criterion is of great importance because it represents the amount of sorbent needed for a particular duty and therefore the size of the adsorption bed. It is also considered a crucial factor in determining the energy requirement during the regeneration step.

- **Selectivity for CO_2**: it represents the CO_2 uptake ratio to the adsorption of any other gas (typically nitrogen for post-combustion capture, and methane for natural gas). It is an essential evaluation criterion, and affects the purity of the adsorbed gas, which will significantly influence the sequestration of CO_2. The simplest method to estimate the selectivity factor is to use single-component adsorption isotherms of CO_2 and nitrogen.

- **Enthalpy of adsorption:** it represents another critical parameter in the evaluation of the performance of solid sorbents. It is a measure of the energy required to regenerate the solid sorbent, and it therefore significantly influences the cost of the regeneration process. It represents the affinity of the material toward CO_2 and measures the strength of the adsorbate–adsorbent interaction.

- **Physical, thermal, and chemical stability:** in order to reduce operating costs, solid sorbents must demonstrate stability under flue gas conditions, adsorption operation conditions, and during the multi-cycle adsorption–regeneration process. In particular, stability in the presence of water vapor is essential for the sustainable performance of the solid sorbent. In addition to thermal properties of the solid sorbent, heat capacity and thermal conductivity are also important in heat transfer operations.

- **Adsorption/desorption kinetics:** the time of the adsorption–regeneration cycle greatly depends on the kinetics of the CO_2 adsorption–desorption profile, which is measured in breakthrough experiments. Sorbents that adsorb and desorb CO_2 in a shorter time are preferred as these reduce the cycle time as well as the amount of sorbent required, and ultimately the cost of CO_2 separation.

- **Cost of the sorbent material:** it is an important factor in the selection of the sorbent material. Materials that exhibit excellent adsorption attributes, and are readily available at low cost, are considered the main targets for researchers working in the field of CO_2 capture. Besides, the environmental impact of synthesizing these materials is considered one of the greatest challenges to overcome.

In the following sections, we describe the main solid sorbents used for CO_2 capture, their applications, major attributes, and limitations.

2.2. Zeolites

Zeolites are porous crystalline aluminosilicate materials available naturally, but can also be prepared synthetically. The zeolite framework is composed of tetrahedral T atoms where T could be Si or Al, connected by oxygen atoms to form rings of different pore structures and sizes. The pore size of the zeolite framework varies between 5 and 12 Å [23]. They are widely used as catalysts in the refining industry [24, 25], fine chemicals synthesis [26, 27], and in gas separation applications [28, 29]. Zeolites are considered promising candidates in CO_2 capture application as has been widely reported in the literature [30–32]. CO_2 can be adsorbed on zeolites through different mechanisms, such as molecular sieving effect based on the difference in size [33, 34]. Separation can also take place based on polarization interactions between the gas molecule and the electric field on the charged cations in the zeolite framework [33]. Accordingly, CO_2 removal with zeolites can be controlled by changing the pore size, polarity, and the nature of the extra framework cation. Among the different zeolites investigated for CO_2 capture applications, zeolite 13X is the most widely studied sorbent, and is considered the benchmark technology for solid sorbents [35, 36]. Research on the use of zeolites as sorbents for CO_2 capture can be categorized into different areas depending on the approach and the techniques adopted to address the improvement in capture performance. These categories comprise tuning the pore size, designing zeolites with controlled polarities, investigating novel zeolites, optimizing the cation exchange, and most recently incorporating amine moieties and other chemical functions into the zeolite frameworks. Ocean et al. [37] have studied the selectivity to adsorb CO_2 by controlling the pore size of an NaKA zeolite through the synthesis of nanosized NaKA zeolites. Overall, the adsorption kinetics on the nanosized crystals was fast enough for CO_2 capture applications; however, the formation of a thin layer on the nanosized NaKA zeolite, due to intergrowth on the surface, did not considerably improve the adsorption kinetics. In contrast, Goj et al. [38] performed atomistic simulations for silicalite, ITQ-3, and ITQ-7, and reported a positive effect on CO_2 uptake and selectivity by tuning the pore apertures. Sravanthi et al. [39] provided a novel approach to control the pore size and volume by utilizing pore expansion agents and obtained average pore size around 30 nm. The application of the pore-expanded MCM-41 in CO_2 separation resulted in the uptake of about 1.2 mmol/g.

Several studies have been conducted to control zeolite affinity toward CO_2, which can be realized by tuning the polarity of the zeolite through alteration of the Si/Al ratio and the nature of the cation. Remy et al. [33] studied the selective separation of CO_2 on low-silica KFI zeolite (Si/Al = 1.67) by employing ion exchange with Na, Li, and K. Li-exchanged KFI has shown the highest CO_2 uptake which was attributed to the large pore volume as compared to Na and K cations. In comparison with high-silica KFI sample (Si/Al = 3.57–3.67), Li–KFI had the highest capacity at low pressure due to the strong electrostatic field. The overlap between pore size and polarity effects is also strongly observed for amine-supported zeolites, which have gained considerable attention in the last few years [40–45]. For instance, Ahmad et al. [46] have impregnated melamine into β-zeolite and obtained dynamic CO_2 uptake of 3.7 mmol/g at atmospheric pressure and temperature of 25 °C. The major challenge facing amine-modified zeolites is the tradeoff between the increased affinity toward CO_2 (strong interaction with the sorbent) and the reduction in pore volume, and consequently the uptake, especially, at low pressures. Factors such as amines loading, distribution, and the nature of the cation can play a vital role to avoid the blockage of the porous structures with the bulky amine moieties [42, 47]. Kim et al. [48] have performed a rigorous investigation through the simulation of thousands of zeolites to evaluate the adsorption properties of these materials and identify the optimum structures for improved CO_2 separation attributes. This study provides a systematic approach to rank and select appropriate zeolites for the required capture objectives. However, important factors such as stability under humid environment, adsorbent and process cost, and the availability of zeolite structures were not taken into consideration.

The hydrophilic nature of most zeolite structures is considered a major drawback of zeolites especially for post-combustion CO_2 applications [49, 50]. Water competes with CO_2 on the available sorption sites and might influence the zeolite structure and framework [51]. As explained earlier, the presence of the exposed cation sites increases CO_2 uptake. In a recent study by Serena et al. [52], the relationship between the water content of the zeolite and the density of the cations was investigated, and a linear relationship was found to describe the decrease of the cation population with increasing water content. This observation highlights the detrimental effect of the presence of water vapor on the adsorption of CO_2 on zeolites.

2.3. Carbon-based CO_2 capture

Carbon-based adsorbents have been used for CO_2 separation in different forms including activated carbons (ACs), carbon nanotubes (CNTs), and graphenes. Activated carbons have an amorphous porous structure with high surface areas that are readily available for CO_2 uptake. They have been widely investigated as sorbents for CO_2 removal due to their low cost and the availability of raw materials [53–55]. However, there are no active sites to bond with the adsorbed CO_2 as cations in zeolite sorbents. This weak interaction results in lower enthalpy and therefore lower energy requirement for regeneration. On the contrary, ACs have very low CO_2 uptake at low pressures due to the absence of the electric field on the surface. Kacem et al. [56] performed a comparison between the performance of ACs and zeolite for CO_2/N_2 and CO_2/CH_4 separation based on their capacity, regeneration capacity, and reusability. It was concluded that at higher pressures (above 4 bars), the CO_2 uptake for ACs was much higher than zeolites. Also, the recovered CO_2 after the regeneration of ACs had higher purity than in the case of zeolites. When compared to zeolites, ACs maintain their adsorption stability even in the presence of water vapor which does not cause any framework failure [57].

In order to enhance the adsorption capacity on ACs, several studies have been conducted in order to improve the affinity toward CO_2 by introducing amine-based functional groups [58–61]. In a recent study, Maria et al. [62] described a systematic surface modification of microporous ACs through a stepwise chemical treatment. They were successful in grafting amine and amide functional groups on the surface of ACs with only 20% loss of surface area. Gibson et al. [63] studied the polyamine-impregnated porous carbons and achieved 12 times higher CO_2 capacity than bare porous carbon. Chitosan and triethylenetetramine have been successfully impregnated onto the surface of ACs and have shown 60 and 90% increased CO_2 uptake at 298 K and 40 bars. In addition to amine functional groups, ammonia-modified ACs, at atmospheric pressure and a temperature range from (303 to 333) K, have been studied [64]. Authors report that an enthalpy of 70.5 kJ/mol was obtained compared to 25.5 kJ/mol for the pristine ACs, suggesting the possibility of chemisorption. Another report has also supported the improved adsorption capacity and selectivity by employing NH_3 at high temperature and has considerably improved CO_2 uptake from 2.9 mmol/g for the bare AC to 3.22 mmol/g for the modified one at 303 K and 1 bar.

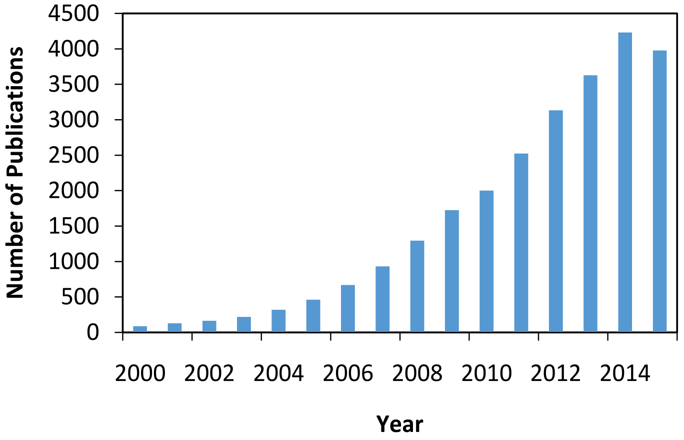
Several studies have been dedicated to the application of amine-modified carbon nano tubes (CNTs) as solid sorbents for CO_2 separation [65–69]. Industrial grade CNTs have been functionalized with tetraethylenepentamine (TEPA) by Liu et al. [65], and the effects of amine loadings on the CO_2 uptake, heat of adsorption, and adsorbent regenerability were investigated. TEPA-impregnated CNTs have shown an enhanced capacity of 3.09 mmol/g at 343 K. Similar studies were also reported using different amines such as (3-aminopropyl)triethoxysilane (APTES) [70], polyethyleneimine (PEI) [67], and other amines (primary, secondary, tertiary, diamines, and tri-amines) [71].

Graphene is a planar sheet of carbon atoms extended in two dimensions, and was discovered in 2004 [72]. Graphite-based capture was recently introduced (after 2011) as a promising candidate for CO_2 capture applications, and research is growing rapidly in this area [73–77]. A recent review by Najafabadi is available on the current status and research trends of using graphene and its derivatives as solid sorbents for CO_2 capture [78]. Research in this area involves grafting various functional groups on graphene such as N-doped graphene composites (surface area = 1336 m^2/g), as reported by Kemp et al. [79], which showed a reversible CO_2 capacity of 2.7 mmol/g at 298 K and 1 atm as well as enhanced stability for repeated adsorption cycles. Borane-modified graphene was also reported by Oh et al. [80], obtaining a CO_2 uptake of 1.82 mmol/g at 298 K and 1 atm. Some novel hybrid materials have also been introduced to obtain better improvements in the adsorption properties, including mesoporous graphene oxide (GO)-ZnO nanocomposite [81], mesoporous TiO_2/graphene oxide nanocomposites [82], Mg–Al layered double hydroxide (LDH), graphene oxide [83], MOF-5 and aminated graphite oxide (AGO) [84], UiO-66/graphene oxide composites [85], and MIL-53(Al) and its hybrid composite with graphene nanoplates (GNP) [86].

2.4. Metal organic frameworks

A more recent class of porous materials was manufactured and named metal organic frameworks. They represent one of the promising adsorbents and have gained significant attention during recent years for gas separation applications [87, 88]. MOFs are composed of metal ions or clusters (nodes) bridged by organic ligands (connecters) to form various structures and networks. MOFs are well recognized for their extraordinary surface areas, ultrahigh porosity, and most importantly the flexibility to tune the porous structure as well as the surface functionality due to the presence of organic ligands that can easily be chemically modified [89, 90]. One main advantage of MOFs over other solid materials is the possibility to tailor the pore size and functionality by rational selection of the organic ligand, functional group, metal ion, and activation method.

Several review papers are available in the literature for gas separation using MOFs [91–96]; however, great progress has been achieved during the past four years (2012 onward). In order to address the limitations of MOFs and investigate new structures, novel functional groups, in addition to hybrid systems and technologies, more studies are needed to explore the mechanisms involved and to improve the uptake capacity in a humid environment. For these reasons, considerable effort has been observed during the past decade to address gas separation and adsorption using MOFs. Figure 2 shows the number of publications on CO_2 capture and separation using MOFs during the past 15 years, which reflects the growing interest of MOFs as efficient solid sorbents.



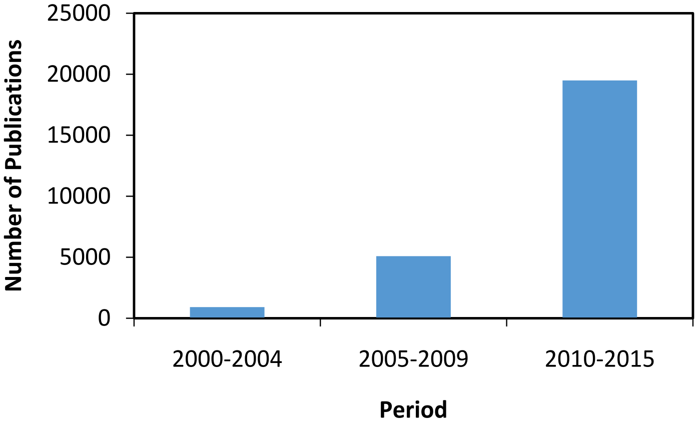


Figure 2. Number of publications on CO_2 capture using MOFs (based on Web of Science database)

3. Adsorption of CO_2 on metal organic frameworks

CO_2 capture performance of different MOFs will be comprehensively reviewed in terms of their capacity, selectivity, heat of reaction, and major challenges facing researchers, and some ideas to approach these challenges will also be provided. The next section is dedicated to review the most recent studies of CO_2 capture and separation on MOFs, and we will mainly target the works published in the last four years.

3.1. Evaluation of MOFs in CO_2 Capture

As introduced earlier, capacity, selectivity, and heat of adsorption are considered the main criteria for the evaluation of MOFs for CO_2 separation. CO_2 uptake is a proportional function of pressure in the gas phase, where the low pressure corresponds to post-combustion applications. The gravimetric uptake of CO_2 is indicative of the ability of MOFs to adsorb CO_2 and, therefore, we have reported CO_2 uptake along with MOF surface area, and other properties for MOFs published after 2012 which could be added to the published reviews that have listed these data in a table format. Table 1 represents the properties of MOFs at high-pressure applications, while Table 2 presents the low-pressure data.

	Surface Area (m^2/g)							
Common name	BET	Langmuir	Capacity (wt%)	Pressure (bar)	Temp. (K)	Selectivity	Qst (kJ/mol)	Ref.
UiO(bpdc)	2646	2965	72.5	20	303			[97]
ZJU-32	3831		49	40	300			[98]
UPG-1	410	514	11.9	9.8	298	24	24	[99]
$Cu_3(H_2L^2)(bipy)_2.11H_2O$			6.4	8.5	298			[100]
$Cu_3(H_2L^2)(etbipy)_2.24H_2O$			4.7	9.6	298			[100]
NU-111	4932		61.8	30	298		**23**	[101]
HTS-MIL-101	3482		52.8	40	298			[102]
DGC-MIL-101	4198		59.8	40	298			[102]
UTSA-62a	2190		43.7	55	298		16	[103]
ZIF-7	312	355	20.9	10	298		33	[104]
{Ag3[Ag5(l3-3,5-Ph2tz)6](NO3)2}n			12.3	10	298	10.5	19.1	[105]
{Ag3[Ag5(l3-3,5-tBu2tz)6](BF4)2}n			5.4	10	298	14	15	[105]
Basolite® C 300	1706.42		41.9	224.99	318		18	[106]
Basolite® F300	1716.46		24.1	224.99	318		19	[106]
Basolite® A100	1524.8		26.9	224.99	318		9	[106]
IRMOF-8	1599	1801	7.8	1	298		21.1	[107]
IRMOF-8-NO2	832	926	3.8	1	298		35.4	[107]
MIL-101(Cr)	2549		24.2	30	303			[108]
HKUST-1	1326		26.3	30	303			[108]
DMOF	1980		38.1	20	298	12[a]	20	[109]
DMOF-DM1/2	1500		27.5	20	298			[109]
DMOF-Br	1320		24.3	20	298			[109]
DMOF-NO2	1310		32	20	298			[109]

	Surface Area (m^2/g)							
Common name	BET	Langmuir	Capacity (wt%)	Pressure (bar)	Temp. (K)	Selectivity	Qst (kJ/mol)	Ref.
DMOF-TM1/2	1210		23.9	20	298			[109]
DMOF-TF	1210		16.2	20	298	9^a	18	[109]
DMOF-Cl2	1180		26.4	20	298	17	21	[109]
DMOF-OH	1130		24.8	20	298			[109]
DMOF-DM	1120		25.4	20	298	23^a	23	[109]
DMOF-TM	1050		23.6	20	298	28^a	29	[109]
DMOF-A	760		17.1	20	298			[109]

^{a} IAST selectivity

Table 1. Adsorption capacities at high pressure

	Surface Area (m^2/g)							
Common name	BET	Langmuir	Capacity (wt%)	Pressure (bar)	Temp. (K)	Selectivity	Qst (kJ/mol)	Ref.
rht-MOF-pyr	2100		12.7	1	298		28	[110]
rht-MOF-1	2100		11	1	298		29	[110]
JLU-Liu22	1487		15.6	1	298		30	[111]
SIFSIX-3-Zn			8.9	1	298			[112]
SIFSIX-3-Cu			9.6	1	298			[112]
SIFSIX-3-Co	223		10	1	298		47	[112]
SIFSIX-3-Ni	368		10.3	1	298		51	[112]
$\{[H_2N(CH_3)_2]_4[Zn_9O_2(BTC)_6(H_2O)_3].3DMA\}c_n$	844	1132	10.9	0.91	298		29	[113]
$\{[NH_2(CH_3)_2, Cd(BTC)].DMA\}_n$	406	539	6.4	0.91	298	30	34.7	[113]
Ni-DOBDC	798		18.2	1	298			[114]
Py-Ni-DOBDC	409		12	1	298			[114]
UiO(bpdc)	2646	2965	8	1	303			[97]
ZJU-32	3831		4.8	1	300			[98]
Cu-TDPAH	1762		18.4	1	298	200^a	33.8	[115]
Zn/Ni-ZIF-8-1000		750	9.9	1	298	30^a	61.2	[116]
ZIF-8-1000			9.6	1	298	23.5^a	49.7	[116]

	Surface Area (m^2/g)							
Common name	BET	Langmuir	Capacity (wt%)	Pressure (bar)	Temp. (K)	Selectivity	Qst (kJ/mol)	Ref.
Zn(5-mtz)(2-eim).(guest) [ZTIF-1]	1430	1981	8.2	1	295	81	22.5	[117]
Zn(5-mtz)(2-pim).(guest) [ZTIF-2]	1287	1461	3.8	1	295		20	[117]
UTSA-49	710.5	1046.6	13.6	1	298	95.8		[118]
ZJNU-40	2209		16.4	1.01	296		18.4	[119]
UPG-1	410	514	2.1	1	298	24	24	[99]
InOF-8			6.9	1	295	45.2		[120]
$Cu_3(H_2L^1)(bipy)_2.9H_2O$			2.5	1	195			[100]
$Cu_3(H_2L^2)(bipy)_2.11H_2O$			2.3	1	298			[100]
$Cu_3(H_2L^2)(etbipy)_2.24H_2O$			0.5	1	298			[100]
UiO-66(Zr100)	1390	1644	6.2	1	298		26	[121]
UiO-66(Ti32)	1418	1703	6.4	1	298		28	[121]
UiO-66(Ti44)	1749	2088	7.2	1	298		34	[121]
UiO-66(Ti56)	1844	2200	8.8	1	298		37	[121]
NU-111	4932		4.8	1	298		23	[101]
JLU-Liu1	145	221	5.9	1	298		47.7	[122]
HTS-MIL-101	3482		12.3	1	298			[102]
DGC-MIL-101	4164		14.5	1	298			[102]
UNLPF-1			13.9	1	273			[123]
UTSA-62a	2190		8.1	1	298		16	[103]
[Zn2(BME-bdc)x(DB-bdc)2_xdabco]n			21.7	0.91	195			[124]
Zn-DABCO	1870	1902	7.2	1	298		22.4	[125]
Ni-DABCO	2120	2219	8.1	1	298		25.8	[125]
Cu-DABCO	1616	1678	6.2	1	298		22.4	[125]
Co-DABCO	2022	2095	4.1	1	298		29.8	[125]
ZnAcBPDC	920		11.7	0.9	293			[126]
ZnBuBPDC	850		7.6	0.89	293			[126]
Mg/DOBDC	1415.1		25	1	298		47	[127]
Co/DOBDC	1089.3		21.6	1	298		37	[127]

	Surface Area (m^2/g)							
Common name	BET	Langmuir	Capacity (wt%)	Pressure (bar)	Temp. (K)	Selectivity	Qst (kJ/mol)	Ref.
Ni/DOBDC	1017.5		20.5	1	298		42	[127]
MIL-100(Cr)	1528.7		9.5	1	298			[127]
ZIF-7	312	355	9.1	1	298			[104]
{Ag3[Ag5(l3-3,5-Ph2tz)6](NO3)2}n			1.6	1	298	10.5	19.1	[105]
{Ag3[Ag5(l3-3,5-tBu2tz)6](BF4)2}n			1.6	1	298	14	15	[105]
CuBTTri	1700		10.8	1	293			[128]
pip-CuBTTri	380		7.1	1	293	130[a]	96.5	[128]
Basolite® C 300	1706.42		9.4	0.95	318		18	[106]
Basolite® F300	1716.46		2.4	0.95	318		19	[106]
Basolite® A100	1524.8		4.4	0.95	318		9	[106]
IRMOF-8	1599	1801	51.2	30	298		21.1	[107]
IRMOF-8-NO2	832	926	31.3	30	298		35.4	[107]
CPM-5	2187		8.8	1	298	16.1	36.1	[129]
Ni-MOF-74	1252	1841	19.4	1	298			[130]
Mg-MOF-74	1416	2085	30.1	1	298			[130]
MIL-101(Cr)	2549		6.8	1	303			[108]
HKUST-1	1326		13.2	1	303			[108]
[Cu(tba)2]n			7.3	1	293	25[a]	36.0	[131]
IRMOF-74-III-CH3	2640		10	1	298			[132]
IRMOF-74-III -NH2	2720		10.4	1	298			[132]
IRMOF-74-III-CH2NHBoc	2170		7	1	298			[132]
IRMOF-74-III-CH2NMeBoc	2220		6.6	1	298			[132]
IRMOF-74-III-CH2NH2	2310		10.8	1	298			[132]
IRMOF-74-III-CH2NHMe	2250		9.6	1	298			[132]
DMOF	1980			1	298	12[a]	20	[109]
DMOF-DM1/2	1500		8.1	1	298			[109]
DMOF-Br	1320		6.4	1	298			[109]

	Surface Area (m^2/g)							
Common name	BET	Langmuir	Capacity (wt%)	Pressure (bar)	Temp. (K)	Selectivity	Qst (kJ/mol)	Ref.
DMOF-NO2	1310		9.9	1	298			[109]
DMOF-TM1/2	1210		8.1	1	298			[109]
DMOF-TF	1210		3.3	1	298	9[a]	18	[109]
DMOF-Cl2	1180		8.8	1	298	17[a]	21	[109]
DMOF-OH	1130		9.6	1	298			[109]
DMOF-DM	1120			1	298	23[a]	23	[109]
DMOF-TM	1050		13.3	1	298	28[a]	29	[109]
DMOF-A	760		10.6	1	298			[109]
CPM-33a	966	1257	12.6	1	298		22.5	[133]
CPM-33b	808	1119	19.9	1	298		25	[133]
Ni3OH(NH2bdc)3tpt	805	1115	14.8	1	298		21.5	[133]
Ni3OH(1,4-ndc)3tpt	222	310	4.6	1	298		25.3	[133]
Ni3OH(2,6-ndc)3tpt	1002	1392	7.9	1	298		24.7	[133]
Ni3OH(bpdc)3tpt	724	1009	5.5	1	298		18.7	[133]
ZIF-7-S	150		3.7	1	303			[134]
ZIF-7-D	25		9	1	303			[134]
ZIF-7-R	5		8.7	1	303		34	[134]
HKUST-1		2203	12.8	1	313			[135]
Fe-MIL-100		2990	6.6	1	313			[135]
Zn(pyrz)2(SiF6)			10.8	1	313			[135]
Mg2(dobpdc)		1940	23.8	1	313			[135]
Ni2(dobpdc)		1593	21.2	1	313			[135]
mmen-Mg2(dobpdc)			15.8	1	313			[135]
mmen-Ni2(dobpdc)			7.3	1	313			[135]
mmen-CuBTTri			11.3	1	313			[135]

[a] IAST selectivity

Table 2. Adsorption capacities at low pressure

3.2. Strategies to Improve the CO_2 Capture Performance on MOFs

Several strategies have been adopted to improve the performance of MOFs in CO_2 capture applications. The ability to precisely tune the MOF structures has led to versatile approaches that can be utilized to enhance CO_2 uptake, selectivity, and the affinity toward CO_2. These methods could be classified into effects of open metal sites, pre-synthetic modifications of the organic ligand, and post-synthetic functionalization schemes.

3.2.1. Open Metal Sites

Open metal sites in MOFs are formed by the removal of a solvent molecule coordinated to the metal nodes by applying vacuum and/or heat after the synthesis of framework in a process called “activation.” The presence of open metal sites on the MOF framework has a great impact on the selectivity toward CO_2 as well as on the binding energy between the adsorbed CO_2 molecules and the surface of MOF sorbents. These coordinately open metal centers act as binding sites where CO_2 molecules can attach and bind to the pore surface by the induction of dipole–quadrupole interactions. Allison et al. [136] have developed a systematic procedure to precisely understand the interactions between the CO_2 molecule and the force field generated by the open metal sites in MOF-74. The developed method allows for accurate estimation of adsorption isotherms using computational approach which enables the evaluation of different hypothetical open metal sites. These observations confirm previous findings of Kong et al. on understanding CO_2 dynamics in MOFs with open metal centers [137]. Among the MOF family, HKUST-1, M-MIL-100, M-MIL-101, and M-MOF-74 are the most widely studied frameworks with open metal sites (M represents the metal site). However, to precisely investigate the influence of the open metal sites, we need to isolate the effects of the nature of organic ligands, the synthesis route, and functional groups present in the framework. It was observed that utilizing light metal sites provides higher surface areas, and therefore improve CO_2 uptake at low pressures for MOF-74 [138]. Several studies have reported the effects of metal centers using computational approach as reported for M-MOF-74 [138–140] where noble metals such as Rh, Pd, Os, Ir, and Pt are considered promising candidates for CO_2 capture (see Figure 3).

Casey et al. [141] studied the isostructural series of HKUST-1 for various metal centers (Mo, Ni, Zn, Fe, Cu, and Cr) to get insights into the adsorption mechanism and the force field created by different metal types. It was found that the presence of divalent metals such as Mg^{2+} significantly increased CO_2 binding strength and resulted in higher selectivity toward CO_2. In addition to the nature of the metal nodes, it was found that the activation method plays a vital role in determining CO_2 uptake and affinity toward CO_2 which was in agreement with Llewellyn et al. [142] for MIL-100 and MIL-101, where various activation methods resulted in different CO_2 loadings and heat of adsorption.

In a recent study, Cabelo and coworkers [143] investigated the interaction between CO_2 and the unsaturated Cr(III), V(III), and Sc(III) metal sites in MIL-100 framework using variable temperature infrared spectroscopy. The enthalpy of adsorption for Cr(III), V(III), and Sc(III) were amounted to be (−63, −54, and −48) kJ/mol, respectively, which are considered among the highest values for CO_2 adsorption on MOFs with open metal centers to date. The synthesis and characterization of an M-DABCO series (M = Ni, Co, Cu, Zn) were described by Sumboon et al. [125] to systematically evaluate the effect of the metal identity on surface area, pore volume, and CO_2 uptake. It was concluded that Ni-DABCO has shown the highest pore volume and specific surface area due to the high charge density present at the metal center. Comparison

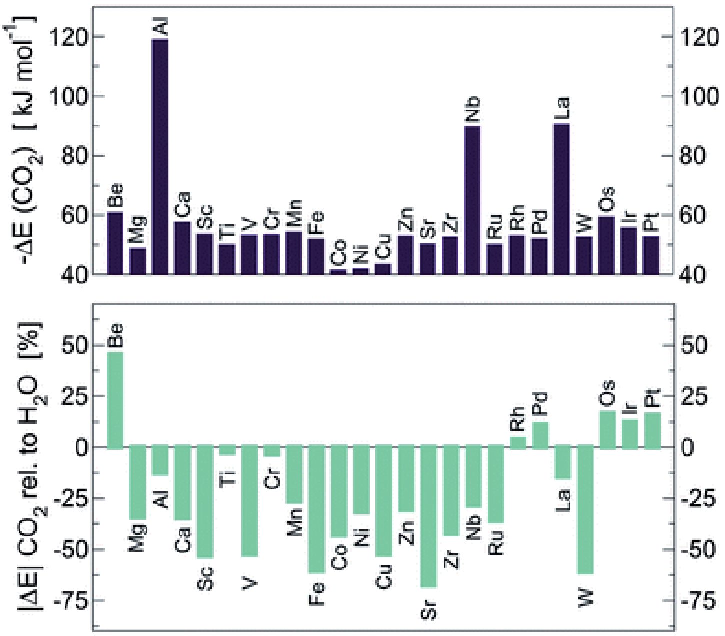


Figure 3. Top: ΔE for CO_2 adsorption (in kJ/mol) in M-MOF-74. Bottom: Magnitude of the adsorption energy of CO_2 relative to H_2O. A positive value in this plot means that CO_2 binds more strongly than H_2O (Adapted from [139]).

of the M-DABCO with activated carbons and MIL-100(Cr) revealed that the unsaturated cations possess exceptional CO_2 uptake of 180 cm^3/g at 1 bar and 298 K [as compared to 30 cm^3/g for ACs and 60 cm^3/g for MIL-100(Cr),144].

3.2.2. Pre-synthetic Modifications of MOFs

Organic ligands are the linkers that connect the metal nodes together and therefore determine the framework structure, pore volume, pore window, and surface area which are very crucial characteristics in CO_2 separation process. Ligand functionalization is considered to be a powerful tool to improve the adsorption of CO_2 on MOFs due to the wide range of functional groups and the ease of modifying the organic ligand through strong covalent interactions. In a recent computational work by Torrissi et al., the impacts of various functional groups attached to the ligand part were investigated by density functional theory (DFT) [145]. The incorporation of amine functional moieties to the organic ligands has witnessed much attention in recent years, due to the proven positive effect of the presence of open nitrogen sites on the MOF frameworks [146]. Keceli et al. [147] studied four biphenyl ligands modified with amide groups of different chain lengths. Varying the length of the alkylamide group has shown a great impact on the porosity, surface area, and CO_2 capacity. It was also evident that the activation procedure has great influence on the surface area of the resulting material which is attributed to the different mechanisms of solvent removal from the MOF framework. Three amino-functionalized MOFs have been prepared from 2-aminoterephthalate (ABDC) and three different metals (Mg, Co, and Sr). Despite a low surface area (63, 71, and 2.5 for Mg, Co, and Sr, respectively) and a relatively low CO_2 uptake (1.4 mmol/g at 1 bar and 298 K), the prepared MOFs had exceptional selectivity toward CO_2 (396 was recorded for Mg-ABDC) and exhibited high heat of adsorption [148]. Shimizu and coworkers [149] used 3-amino-1,2,4-triazole ligands to design a 3D structure MOF with 782 m^2/g surface area and 0.19 cm^3/g pore volume that is capable to achieve CO_2 uptake of 4.35 mmol/g at 1.2 bar and 273 K. Moreover, the as-synthesized MOF has shown enthalpy of adsorption of 40.8 kJ/mol at zero coverage which was comparable to the commercial zeolite NaX (48.2 kJ/mol). In a similar study, Xiong et al. [118] used triazole ligands to prepare a new framework called UTSA-49 by incorporating nitrogen atoms and methyl functional groups on 5-methyl-1H-tetrazole ligands which recorded 13.6 wt% CO_2 uptake at 1 bar and 298 K and 27 kJ/mol enthalpy (Figure 4). These observations were in agreement with work reported by Gao et al. for the influence of triazolate linkers [150]. It is essential to understand the synergistic effect between the multiple functional groups on the pore surface and their size exclusion effects which are considered potential approaches to optimize the performance of functionalized MOFs. Table 3 summarizes CO_2 capture properties of MOFs modified with different amino functional groups.

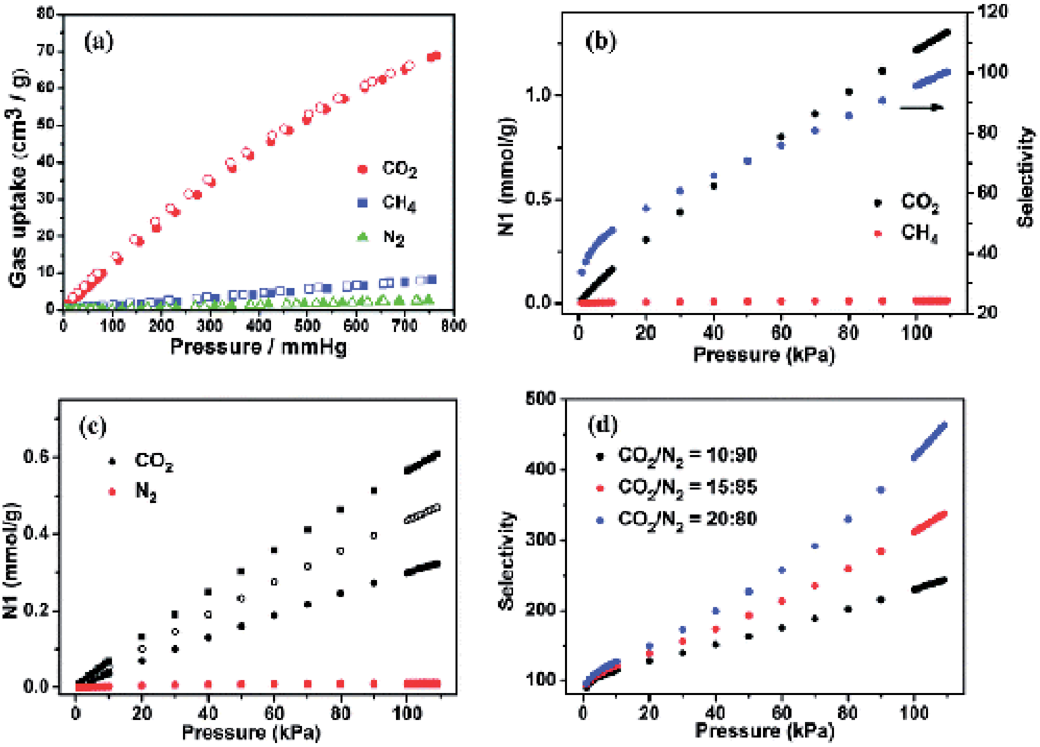


Figure 4. (a) Adsorption (solid) and desorption (open) isotherms of carbon dioxide (red circles), methane (blue squares), and nitrogen (green triangles) on UTSA-49a at 298 K. (b) Mixture adsorption isotherms and adsorption selectivity predicted by IAST of UTSA-49a for CO_2 (50%) and CH_4 (50%) at 298 K. (c) Mixture adsorption isotherms predicted by IAST of UTSA-49a for CO_2 and N_2 (10:90, 15:85, and 20:80) at 298 K. (d) Mixture selectivity predicted by IAST of UTSA-49a for CO_2 and N_2 (10:90, 15:85, and 20:80) at 298 K. Adapted from [118].

MOF name	Type of functional group	CO_2 uptake (wt. %)	Enthalpy of adsorption (kJ/mol)	Pressure	Temperature	Surface area (m^2/g)	Ref.
ZIF-10	IM	20.9	14.9	0.9	298	-	[151]
ZIF-68	(bIM)(nIM)	41.3	33.3	0.9	298	1220	[151]
ZIF-69	(cbIM)(nIM)	38.1	25.9	0.9	298	1070	[151]
ZIF-71	dcIM	18.0	19.4	0.9	298	-	[151]
$Cu_2(\mathbf{L})(H_2O)_2$	Pyrazol	32	-	1	195	844.5	[152]
$[Zn_2(\mathbf{L})]$	Pyrazol	37.4	-	1	195	1075.4	[152]
$[Cd_2(\mathbf{L})]$	Pyrazol	24.6	-	1	195	571.7	[152]
$[Co_2(\mathbf{L})(H_2O)_6]$	Pyrazol	31.6	-	1	195	734.6	[152]
Zn4(bpta)2-1	Bipyridine pillar ligands	8.2	34.82	1.2	298	413	[153]
Zn4(bpta)2-1	Bipyridine pillar ligands	3.1	27.69	1.2	298	51	[153]
Cu2L (DMA)4	Acrylamide	22.2	35	1	296	1433	[154]
Zn(ad)(ain)	2-Aminoisonicotinate and adeninate	9.2	40	1	298	399	[155]
bio-MOF-11	Adenine	22.2	33.1	1	273	1148	[156]
bio-MOF-12	Adenine	16.2	38.4	1	273	-	[156]
bio-MOF-13	Adenine	10.4	40.5	1	273	-	[156]
bio-MOF-14	Adenine	8	-	1	273	17	[156]
$Cu(tba)_2$	Triazol	7.3	36	1	293	-	[131]

Table 3. CO_2 uptake for MOFs modified with amine containing ligands

Apart from amine groups, there are other functional moieties that are proven to be effective in enhancing the performance of MOFs in CO_2 capture. Phosphonate and sulfonate organic ligands have gained tremendous attention recently due to their significant improvements in MOF stability toward water [157]. Several studies are reported based on the use of phosphonate and sulfonate ligands, for instance, the selective CO_2/N_2 separation over nitrogen-containing phosphonate MOFs was studied by Marco et al. [100], and the synthesis, stability, porosity of the phosphonate MOFs [158], and their major applications were reported for water stability studies [159–161]. The shielding effect exhibited by phosphonate groups were responsible for the improved stability under humid conditions up to 90% relative humidity at 353 K as observed for CALF-30 [161]. The enhanced water stability of these MOFs was attributed to the kinetic blocking effect which makes the framework completely hydrophobic [159].

MOFs containing nitrogen-donor building blocks were also widely investigated, particularly adenine group which was extensively used due to framework robustness, richness in nitrogen sites, and framework diversity [162]. Song et al. [163] reported the preparation of three new adenine-based MOFs by controlling the adenine coordination with Cd metal sites. This study has provided insight into the controlled synthesis of MOFs by controlling the structure building units (SBU) which can be utilized to extend the idea to include multiple building units within the same framework. Similar studies are also available based on adenine groups as building units, where the effect of the adenine functionalization on framework topology, porosity, and adsorption behavior was investigated [164]. The use of Zn-adeninate SBU led to the discovery of highly porous Bio-MOF-11 to 14 series [165] and Bio-MOF-100 [166] with exceptional surface area (4300 m^2/g) and very large pore volume (4.3cm^3/g); however, the framework stability of these materials still needs to be addressed as the material tends to lose its porosity under harsh activation environment. This issue has been tackled by Zhang et al. [167] to prepare more stable adenine-based PCN-530 structure. Lin et al. have observed high density of open nitrogen-donor sites on 1,3,5-tris(2H-tetrazol-5-yl)benzene (H3BTT) which was responsible for the enhanced CO_2 capacity [146] through the improvement of the framework porosity and the utilization of nitrogen sites readily available to adsorb CO_2. However, the richness of nitrogen atoms in the framework does not necessarily favor CO_2 adsorption, as reported by Gao et al. [110] for the case of tetrazolate-based rth-MOF that has more exposed nitrogen sites as compared to pyrazolate-based rht-MOF and yet was showing less CO_2 uptake attributed to the strong electric field observed on the pyrazolate-based rht-MOF.

Other ligand modifications are also reported in literature by deploying several types of functional groups such as hydroxyl groups (OH) on Zn(BDC) [168], $(CH_3)_2$, (OH), and (COOH) on MIL-53(Al) [145], NO_2 on IRMOF-8 [107] as well as alkyl and nitro groups grafted on DUT-5 [169]. Based on the contribution by Yaghi's group [170], several studies were dedicated to understand the effects of ligand extension on the pore size, surface area, and the sorption behavior of MOFs [98, 109, 133, 171–173]. Recently, zeolite-like MOFs denoted as ZTIFs have attracted great interest due to their unique characteristics for tuning the structure toward various applications [174, 175]. New frameworks (ZTIF-1 and ZTIF-2) were recently reported based on the incorporation of tetrazolates into Zn-Imidazolate structures [176], with similar structures. UTSA-49 was also reported by Chen and coworkers for the selective separation of CO_2/N_2 mixture [117].

Lately, the idea of mixed ligand approach for the synthesis of MOFs with tunable properties has gained much attention which allows for incorporating several functionalities within each ligand to target certain properties such as improving the stability and the capacity for CO_2 simultaneously [177]. For instance, the water stability issue was tackled by Marco and coworkers [178] by utilizing two heterocyclic N-donor-mixed phosphonate-based organic ligands. The designed MOF has shown great water stability and achieved CO_2 uptake of 77 cm^3/g at low pressure and 195 K. By deploying the mixed-ligand approach, Liu et al. [179] have successfully prepared Co-based MOFs containing both benzenetricarboxylic- and triazole-based ligands by using a solvo-thermal synthesis technique. The synthesized MOFs displayed CO_2 uptake of up to 15.2 wt. % at 1 bar and 295 K as well as remarkable selectivity toward nitrogen. A detailed investigation of mixed ligand approach in the design of MOFs is available in literature [180, 181]; however, further work is still needed to optimize the synthesis conditions and correlate the observed performance to the appropriate constituents on the organic ligands. Recent work by Yaghi et al. provided tools to quantitatively map different functional groups incorporated into the same MOF structure [182].

3.2.3. Post-synthetic Functionalization of MOFs

As mentioned previously, tuning the affinity of the framework functionalities toward CO_2 is crucial for improving adsorptive capacities. The aim is to decorate the pore surface in order to have high adsorption selectivity and capacity and yet minimize the regeneration energy. In addition to the pre-synthetic modification of the organic linker, post-synthetic functionalization of MOFs (PSM) is considered a viable route to insert functionalities into the MOF structure after the formation of the basic framework. This approach can overcome the limitations observed in pre-synthetic functionalization, for instance precise control of the synthesis conditions is needed to preserve the functional groups during the solvo-thermal synthesis conditions. Note that some functional groups are not stable under synthesis conditions which require a narrow range of conditions to prepare the MOFs. Others, however, cannot be introduced to the synthesis mixture due to solubility issues, hindrance effects, and they might participate in the crystallization process and yield unwanted materials. Besides, inserting functional groups on the metal sites prior to the synthesis of the framework might intervene in the formation of the building units which can result in the deterioration of the crystal structure [183–185]. PSM is therefore considered an attractive pathway to tailor the properties of MOFs toward better CO_2 capture performance.

In order to make use of high amine affinity toward CO_2, several amine moieties were selected for the modification of various solid sorbents [186–189] including MOFs [190, 191]. Ethylene diamine (en) is considered the most commonly used type of amine for PSM of MOFs for CO_2 capture application. In 2014, Lee et al. [192] reported grafting the diamine into the expanded MOF-74 or Mg(dopbdc) structure at amine loadings of 16.7 wt. % at room temperature which exhibited very high CO_2 uptake of 13.7 wt% at 0.15 bar higher than the 12.1 wt. % capacity reported by McDonald et al. for N,N'-dimethylethylenediamine (mmen) grafted on Mg(dopbdc) [173]. The isosteric heat of adsorption was recorded to be 49 to 51 kJ/mol indicating chemisorption of CO_2 molecules which was further confirmed by the formation of carbamic acid probed by the in situ Fourier transform infrared spectroscopy (FTIR) experiments. The en grafted Mg(dopbdc) was further evaluated for the multicycle adsorption, and it has only lost 3% of its CO_2 uptake after five cycles. Moreover, en-Mg(dopbdc) has also shown stable structure and capacity after exposure to different moisture contents, and therefore this material has a potential for large-scale CO_2 capture (see Figure 5). NH_2, CH_2NH_2, CH_2NHMe along with other functional groups were recently grafted on IRMOF-74, and it was found that IRMOF-74-III-CH_2NH_2 displayed CO_2 capacity of 3.2 mmol/g at 1 bar [132]. The sodalite-type structure Cu-BTTri was also grafted by en functional group [193] which showed chemisorption interaction with the adsorbed CO_2 molecule as can be observed from the high isosteric heat of adsorption (90 kJ/mol). However, the en-Cu-BTTri has only shown improved capacity at low pressure while the unmodified MOF shows higher uptakes at high pressure which is attributed to the significant reduction in Brunauer–Emmett–Teller (BET) surface area from 1770 to 345 m^2/g due to the pore blocking effect of the en group. In an attempt to address this issue, McDonald at al. functionalized mmen group on Cu-BTTri and preserved a BET surface area of 870 m^2/g with 96 kJ/mol isosteric heat of adsorption, nitrogen selectivity of 327, and CO_2 uptake of 9.5 wt.% under 0.15 bar CO_2/0.75 bar N_2 mixture at 25 °C. The negative impact of alkylamine functional groups on reducing the surface area was evident, and one approach to overcome this issue is to introduce ligand extension prior to the introduction of the amine group so as to increase the MOF porosity and avoid the pore-blocking problem during PSMs [132]. Also, a deep insight into the mechanism of CO_2 adsorption on alkylamine-grafted MOFs is crucial to further understand the interactions for improved structural design and amine loadings [194]. Other amine functionalities such as piperazine were also grafted into Cu-BTTri [128] and exhibited 2.5 times higher CO_2 uptake as compared to bare Cu-BTTri, while the heat of adsorption confirms the chemisorption interactions. The area reduction was also evident as it was reduced from 1700 m^2/g to 380 m^2/g (similar to ethylendiamin, (en)- Cu-BTTri [195]). Pyridine was also grafted on Ni-DOBDC to improve the water stability and increase the hydrophobicity of the material [196]. Experimental observations supported by simulations results confirmed the enhanced water stability for the Pyridine-Ni-DOBDC samples while maintaining the CO_2 uptake at atmospheric conditions and low pressures. It was also concluded that the amine moiety was grafted on the unsaturated metal sites of the framework, which makes this approach desirable for amine functionalization. From a combined experimental and simulation study, it was found that pyridine modification of an MOF can reduce H_2O adsorption while retaining considerable CO_2 capacity at conditions of interest for flue gas separation. This indicates that post-synthesis modification of MOFs by coordinating hydrophobic ligands to unsaturated metal sites may be a powerful method to generate new sorbents for gas separation under humid conditions. Amine functionalization to target the water stability of MOFs will be further discussed in the next section.

It is evident from the previous discussion that amine impregnation into MOFs always sacrifices the surface area of the final product. Therefore, the choice of the amine that can improve the affinity toward CO_2 and attain high surface area simultaneously is a trade-off issue. MIL-101 materials were reported to have the highest pore volume and surface area among MOFs to date (BET = 3125 m^2/g and 1.63 cm^3/g). Hence they allow the incorporation of amines with longer alkyl chains such as polyethyleneimine while at the same time maintaining relatively high surface area (1112.6 m^2/g after 75 wt% amine loading). PEI-loaded MIL-101 prepared by Lin et al. [197] exhibited remarkably high CO_2 uptake of 4.2 mmol/g at 0.15 bar and 298 K with exceptional CO_2/N_2 selectivity of 770 at 25 °C.

Optimization of amine loadings and distribution within the MOF structure is a detrimental factor for the impact of these functionalities on the performance in CO_2 capture process. Precise control of the different factors during the grafting process is crucial to append these groups exactly on the unsaturated metal centers, while avoid blocking the pores and hindering access to the interior volume. Improving the PSM methods is considered one of the means to achieve the ideal grafting and amine distribution [191].

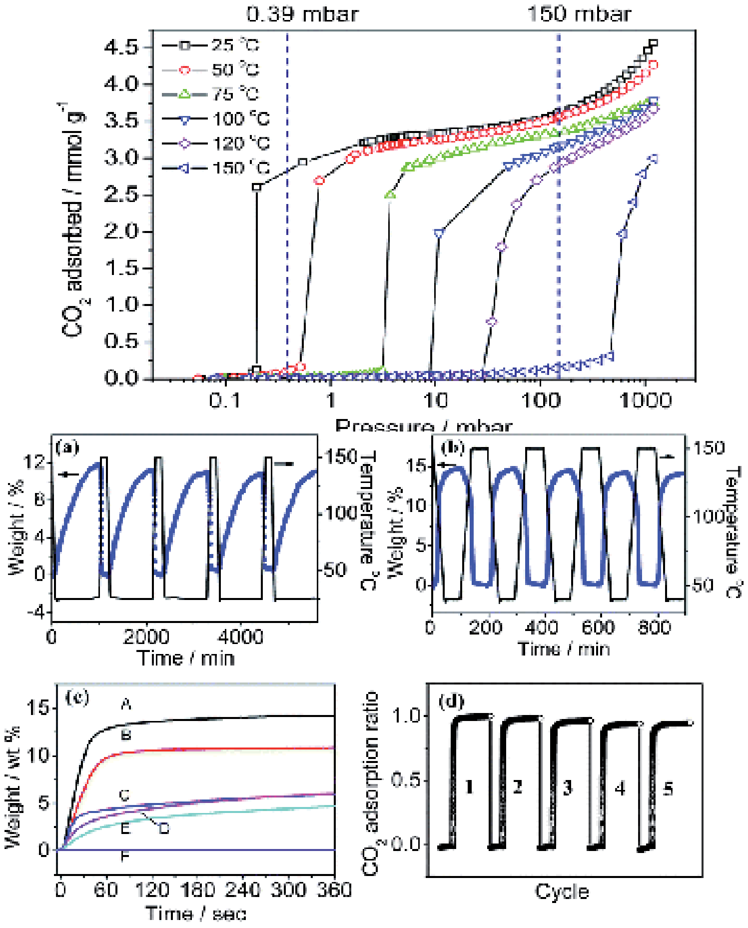


Figure 5. Top: Adsorption isotherms of CO_2 for 1-en at the indicated temperatures. Bottom: Adsorption–desorption cycling of CO_2 for 1-en showing reversible uptake from (a) simulated air (0.39 mbar CO_2 and 21% O_2 balanced with N_2) and from (b) simulated flue gas (0.15 bar CO_2 balanced with N_2). (c) time-dependent CO_2 adsorption for porous materials (A = 1-en, B = mmen-Mg_2(dobpdc), C = 1, D = Mg-MOF-74, E = Zeolite 13X, F = MOF-5). (d) CO_2 adsorption ratio of 1-en in flue gas (after 6 min exposure to 100% RH at 21 °C) to 1-en in flue gas (Adapted from [192]).

4. Recent Advances and Current Trends

4.1. Hybrid Systems Based on MOFs

For more efficient utilization of MOFs sorbents, several hybrid systems based on MOFs with other solid sorbents have been investigated in the literature. The objective of having hybrid materials is to utilize the synergism between the two sorbents and therefore ultimately improve the overall performance in CO_2 separation. Moreover, sorbents such as activated carbons, graphenes, and CNTs provide the added feature of high surface area and easily functionalized sites which contribute to the tuning of the final properties of the composite material. CNTs represent one of the effective candidates that can improve the properties of MOFs for gas adsorption applications. Zhu et al. [198] incorporated HKUST-1 in the interspace of CNTs. The designed composite exhibited superior selectivity and a CO_2 saturation capacity of 7.83 mmol/g at 298 K, which was attributed to the high porosity and surface area. In a similar study, multiwall CNTs, well dispersed in MIL-101 (Cr), were successfully prepared and maintained the same framework and crystal structure as MIL-101. An increase of 60% in CO_2 uptake was observed for the MWCNT-MIL-101 composite which was attributed to the increased porosity as a result of incorporating CNTs [199], as was confirmed by similar work on MWCNT-MIL-53(Cu) composite [200].

Graphene oxide composites with different MOFs are extensively reported in the literature such as HKUST-1 [201], MOF-5 [202], and Cu-BTC [203]. Graphite oxide (GO) is considered a stabilizing agent for MOFs under humid environment, and it has shown remarkable CO_2 capacity of 3.3 mmol/g and great stability under simulated flue gas conditions for GO/Cu-BTC composite [203]. The synthesis of Cu-based MOFs composite with aminated graphite oxides (GO) was carried out and fully characterized by Zhao et al. [204]. The composite exhibited 50% enhanced porosity as compared to the parent MOF and displayed unique structure and pore sizes effective for size exclusion separation of CO_2 from the flue gas. Silica aerogel (SA) was also investigated as a promising candidate for hybrid systems with ZIF-8 [205]. The detailed characterizations of the SA/ZIF-8 confirmed the presence of the two phases in the composite after sol–gel synthesis procedure with different ZIF-8 loadings and mild BET surface area [205].

Several composite materials have been reported for various applications; however, utilizing these hybrid systems in CO_2 adsorption might be a promising route for improving the CO_2 capture process. Ahmed et al. [206] published a review of information related to the synthesis and adsorption applications of MOF composite materials.

4.2. Ionic Liquids/MOF Composites

Ionic liquids as solvents for the absorption separation of CO_2 from flue gas are discussed in Section 1.2 in order to overcome the limitations related to the poor dynamics of CO_2 separation in ILs due to their high viscosity. MOFs can act as an ideal support material for the incorporation of ILs into their porous structure while preserving their unique properties. The concept of immobilization of ILs into solid sorbents has been reported for various applications. For instance, ILs immobilization on mesoporous silica was reported for the catalytic esterification reaction [207], ILs addition into polymer gels for ionic conductivity applications [208], ILs/Zeolite composites [209], in addition to several review papers available on this topic indicating the widespread use of this new approach over the past years [210, 211]. Computational investigation of the theoretical possibility of incorporating ILs into MOFs was studied by Jiang's group for (BMIM)PF6 IL supported on IRMOF-1 for CO_2 capture applications [212]. The confinement effects of the narrow pore on the ILs and the ionic interactions between $[BMIM]^+$ favor the open pore while the anion, $[PF6]^-$, was attached to the open metal sites, was observed in a simulation study. It was ascertained that CO_2 was favorably attached to the $[PF6]^-$ anions sites. The study demonstrated that IL/MOF composites are a potential candidate for CO_2 adsorption and have displayed significantly high CO_2/N_2 selectivity. To the best of our knowledge, the first report on an experimental attempt to immobilize ILs into MOF structures was published by Liu et al. [213] for the insertion of Bronsted acidic ILs (BAIL) into the pores of MIL-101 using post-synthetic approach with triethylene diamine (TEDA) or imidazole (IMIZ) as a solvent assisting during the functionalization process. Nitrogen adsorption isotherms of bare MIL-101, TEDA-BAIL/MIL-101, and all (IMIZ-BAIL/MIL-101) samples showed type-I isotherm indicating the microporous nature of the composite. BET surface area was 1873 m^2/g for the bare MIL-101 which was slightly decreased to 1728 m^2/g and 1148 m^2/g for IMIZ-BAIL/MIL-101 and TEDA-BAIL/MIL-101, respectively. Following this leading report, Jhung's group [214] successfully grafted up to 50 wt.% acidic chloroaluminate IL on MIL-101 which reduced the BET surface area of the bare MIL-101 by around 60%. The incorporation of ILs with basic nature which is favorable for CO_2 adsorption was for the first time reported by Kitagawa et al. [215]. A detailed characterization and investigation of the phase behavior of the immobilized 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylamide) denoted as EMI-TFSA ILs into ZIF-8 was presented in this study. A reduction of 29% in pore volume was measured in N_2 adsorption isotherm experiments and computational calculations. The EMI-TFSA/ZIF-8 composite has shown distinctive ion conductivity at low temperature as reported in a second paper by the same group [216]. The prospect of IL/MOF composite for gas separation is still under computational investigation with no reported experimental studies of CO_2 adsorption on these composites. Recently, Vincent-Luna et al. [15] investigated the effects of adding room temperature ILs (RTILs) into the pores of Cu-BTC structures. The adsorption of CO_2, N_2, CH_4, and their mixtures were studied by utilizing various RTILs having the same cation 1-ethyl-3-methylimidazolium $[EMIM]^+$ and different anions such as bis[(trifluoromethyl)-sulfonyl]imide $[Tf2N]^-$, thiocyanate $[SCN]^-$, nitrate $[NO3]^-$, tetrafluoroborate $[BF4]^-$, and hexafluorophosphate $[PF6]^-$. The RTIL/Cu-BTC composite has shown enhanced CO_2 uptakes at low pressures with high CO_2/N_2 selectivity due to the polarization driving force rendering these materials as a promising system for post-combustion CO_2 capture. Another application of IL/MOF composite as a precursor for the preparation of nitrogen and boron–nitrogen (N- and BN-)-decorated porous carbons was recently reported by Aijaz et al. [217] as a novel synthesis strategy.

4.3. Ab/Adsorption in Ionic Liquids/MOF Slurry System

Another approach to utilize the combined synergistic advantages of MOF and IL composites is through a novel hybrid adsorption–absorption technology. This novel technology can provide an efficient approach to utilize the high capacity, selectivity, and low heat of adsorption of the solid sorbents along with the advantages of having a continuous flow process that allows for better heat integration and separation rates in contrast to the conventional batch process used in adsorption-only process. Mass transfer enhancement due to the dispersion of fine solids in liquid solvents was studied and insight into the mechanism and the analysis of different mass transfer resistances were described by Zhang and coworkers [218] which was in agreement with previous findings [219–221]. As far as enhancement of CO_2 capture in slurry systems is concerned, a study dealing with AC particles dispersed in K_2CO_3 aqueous solution was reported by Sumin et al. [222] to investigate the influence of the hydrodynamics on the mass transfer improvements. In a similar work by Rosu et al. [223], AC particles were also

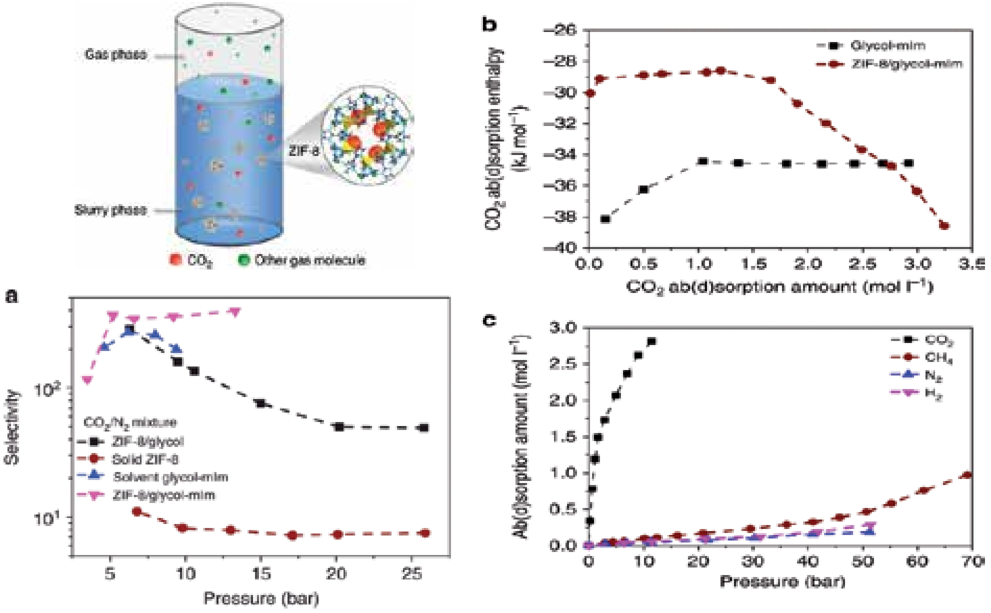


Figure 6. Top left: schematic of the slurry system. (a) Comparison of selectivity toward N_2. (b) ab/adsorption enthalpy. (c) CO_2 uptake at 303.15 K (Adapted from [225]).

found to improve the absorptive CO_2 capture process. The unique characteristics of MOFs in CO_2 adsorption and their recent applications in aqueous solution environment [224] have opened the door toward the possibility of immersing MOF particles in various physical and chemical solvents for CO_2 separation application. This novel unit operation process can overcome the limitations reported for conventional adsorption on MOFs such as high pressure drop and the necessity for formulating the powders into different shapes and sizes which affects their structural stability and reduces the active surface area. Liu et al. [225] reported, for the first time, the preparation of ZIF-8/glycol and ZIF-8/glycol/2-methylimidazole slurries (Figure 6). CO_2 uptake of 1.25 mmol/L was recorded for the slurry system with CO_2/N_2 selectivity of 394 at 1 bar, and most importantly a very low enthalpy of 29 kJ/mol. In a similar work by Lei et al. [226], ILs [EMIM, TF2N] and [OMIM, PF6] were used to prepare slurry systems with ZIF-8 and ZIF-7. CO_2 adsorption in the slurry system has shown a promising performance with isosteric heat of adsorption less than 26 kJ/mol. Following these two studies, the solubility of CO_2 in physical solvents such as methanol mixed with ZIF-8 was also investigated [227]. The study revealed that ZIF-8 can significantly improve the low pressure-CO_2 uptake in physical solvents and can dramatically reduce the solvent losses by evaporation to the gas phase at the top of the absorber. Increasing ZIF-8 loadings has shown further enhancement of the CO_2 capacity, as observed previously [225]; however, it is worth noting that a high solid loading in the slurry system was not recommended from process engineering point of view as it might cause some problems during the pumping of the slurry mixture and increases the solid losses in the multicycle separation process [225].

For future studies on MOF-based slurry systems, there is basic selection of criteria that needs to be satisfied by both MOF and the liquid solution. The selection of the MOF possessing the appropriate pore size for the preparation of the slurry system is very important to guarantee that the size of the liquid is large enough and does not occupy the pores which leaves no space for CO_2 to adsorb. Moreover, the structural stability of the MOF in the aqueous solution is essential so that it does not lose its porous framework nor its surface area. The selection of the liquid candidate is crucial, as it should not provide any extra mass transfer resistance for CO_2 molecules. Further, experimental and computational investigations are still required to understand the separation mechanism in slurry mixtures and to have insight into the different types of interactions between the gas, liquid, and solid materials.

5. Challenges and Outlook

In conclusion, MOFs are considered the largest growing research area in CO_2 capture, with great achievements and developments. Due to their versatile structures and possibilities for various functionalization approaches, the door is still open for further improvements and advancements of their performance under real flue gas conditions, and in large-scale applications. Although we have reported MOFs with distinguished properties and exceptional CO_2 capacity, selectivity, and stability, there are still some concerns that need to be addressed before reaching commercial scale level. The lack of information about the performance of MOFs under real gas mixture conditions is one of the key issues to understand the actual working uptakes and identify any possible limitations. Further experimental testing of MOFs using, for example, a gas mixture containing all the impurities that might be present in an actual flue gas is needed high-throughput technique. Computational gas mixture studies can provide essential information in this regard; however, experimental investigation is still considered the most reliable approach. MOF stabilities in humid conditions, high temperature, and harsh mechanical stress situations must be given much attention. Several studies were performed to target MOF stability, and great achievements were recorded in this field [228, 229], as reviewed in references [160, 230]. Finally, in the following section, we focus on water stability studies as it is one of the main drawbacks of MOFs.

5.1. Water Stability of MOFs

Water stability is a major challenge that has to be overcome before metal organic framework can be used in removing carbon dioxide from flue gas. The core structure of MOF reacts with water vapor content in the flue gas leading to severe distortion of the structure and even failure. As a consequence, the physical structure of MOF is changed, e.g., reduction of porosity and surface area, etc. that decreases the capacity and selectivity for CO_2. Complete dehydration of flue gas increases the cost of separation. It is therefore essential for MOFs to exhibit stability in the presence of water up to certain extent [91].

Metal–ligand coordination bond, which is the most significant part of MOF, is hydrolyzed with water, resulting in the displacement of ligand bond; and as a consequence, the whole structure usually collapses [91]. The stability of MOF in the presence of water depends on the strength of metal ligand bond. pK_a values of the ligand atom can be considered as the strength of this metal- ligand bond. Since the hydrolysis reaction between MOF and water molecule is governed by Gibbs free energy and activation energy of the reactant and product molecules, thermodynamics and kinetics factors have great influence on the water stability of MOF [160]. Insight into the molecular structure, more specifically the metal–ligand strength, the weakest part of MOF, and thermodynamics as well as kinetics study of hydrolysis reaction are very important to improve water stability. Several strategies based on these two important aspects have been taken into consideration.

Jasuja et al. [231] performed a study on the effects of functionalization of the organic ligand in a series of isostructural MOFs in the Zn(BDC-X)-(DABCO)0.5 family on water stability. In this experiment, they cyclically stabilized an unstable parent structure in humid conditions through the incorporation of tetramethyl-BDC ligand. The results of molecular simulation disclosed that the kinetic stability is improved due to the carboxylate oxygen in the DMOF-TM2 structure which acted as a shield to prevent hydrogen-bonding interactions and subsequent structural transformations. Hence, electrophilic zinc atoms in this structure became inaccessible to the nucleophilic oxygen atoms in water, resulting in prevention of the hydrolysis reactions for the displacement ligand. They also performed another study to evaluate the effect of strength of metal–ligand coordination bond and catenation in the framework on water stability [232]. According to their results, the non-interpenetrated MOFs constructed from a pillar ligand of higher pK_a exhibited higher stability; however, interpenetrated MOFs constructed from a pillar ligand of lower pK_a values exhibited less stability. The interpenetration in MOF with incorporation of ligands of relatively high basicity exhibited good water stability. By considering the results of previous experiment, they synthesized cobalt-, nickel-, copper-, and zinc-based, new pillared MOFs of similar topologies which exhibited good water stability [233]. The grafted methyl group on the benzene dicarboxlate (BDC) ligand introduced steric factors around the metal centers; consequently, water stability of MOF drastically improved. The basicity of BTTB-based MOFs synthesized with bipyridyl pillar ligands had lower basicity than DABCO; however, they exhibited better stability in the presence of humid condition.

Bae et al. [114] performed a study to modify Ni-DOBDC with pyridine molecules. The study showed that pyridine molecule made the normally hydrophilic internal surface more hydrophobic; as a result, water absorption was reduced, while substantial CO_2 capture capacity was retained to a certain level. Fracaroli et al. [132] improved the interior of IRMOF-74-III by covalently functionalizing it with a primary amine, and used a MOF, IRMOF-74-IIICH2NH2, for the selective capture of CO_2 in 65% relative humidity.

Zhang et al. [234] performed a study to modify the surface of the MOF hydrophilic to hydrophobic to improve water stability. They demonstrated a new strategy to modify hydrophobic polydimethysiloxane (PDMS) on the surface to significantly enhance their water resistance by a facile vapor deposition technique. In this study, they successfully coated three vulnerable MOFs according to the water stability (MOF-5, HKUST-1, and ZnBT), while the porosity, crystalline characteristics, and surface area were unchanged.

All these studies demonstrated that water stability of MOFs can be improved by incorporating specific factors (e.g., metal–ligand strength, thermodynamic and kinetic factors, etc.) which govern the structural stability of the framework.

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Carbon Dioxide Geological Storage (CGS) – Current Status and Opportunities

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Abstract

Carbon dioxide sequestration has gained a great deal of global interest because of the needs and applications of mitigation strategy in many areas of human endeavors including capture and reduction of CO_2 emission into atmosphere, oil and gas enhanced production, and CO_2 geological storage. In recent years, many developed countries as well as some developing ones have extensively investigated all aspects of the carbon dioxide geological storage (CGS) process such as the potential of storage sites, understanding the behavior of CO_2, and its interaction with various formations comprising trapping mechanisms, flow pattern, and interactions with formation rocks and so on. This review presents a summary of recent research efforts on storage capacity estimation techniques in most prominent storage options (depleted oil and gas reservoir, saline aquifers and coal beds), modeling and simulation means followed by monitoring and verification approaches. An evaluation of the more interesting techniques which are gaining attention in each part is discussed.

Keywords: carbon dioxide, geological storage, CGS

1. Introduction

Carbon dioxide (CO_2) is one of the most emitted greenhouse gases (GHG) which causes heat trapping of the earth and contributes to the global climate change. This global issue led to the public concern and has become a serious problem in the developed and developing countries [1]. Accordingly, the increase of GHG in the atmosphere has led to a rise in the average global temperatures with a warming forecast of 1.8–4.0°C [2]. Recent surveys conducted, see [2–5], show that the CO_2 concentrations has risen from pre-industrial levels of 280 parts per million (ppm) to present levels of ~380 ppm in the atmosphere and this increase in CO_2concentration depends on world's expanding use of fossil fuels. Further studies, according to the CO_2

emissions from fossil fuel power plants, represent the amount of emissions around 23 Gton-CO_2 per year and 26% of the total emissions approximately[1, 2, 6]. Reports from on-road transportation emissions also indicate the high contribution of CO_2 in atmosphere especially in urban areas. It contributes around 10% of the total global and 20% of the European atmospheric CO_2 emissions [7]. Based on the Intergovernmental panel on Climate Change (IPCC) report in 2005, 72% of the anthropogenic greenhouse effect is due to the CO_2 emission and it is considered as the most important GHG contributor [1]. The Kyoto Protocol in 1997 also recommends that the nations minimize their CO_2 emissions up to 95% of 1990 levels by 2012. In this regard, the mitigation options of the CO_2 have been defined in many national and international scales and the scientists have been looking and developing for the techniques which reduce the CO_2 emissions [8–11]. The options include reduction in using carbon-intensive fuels and improving energy efficiency in order to decrease the CO_2 emissions into the atmosphere or carbon sequestration.

CO_2 sequestration is the process of injecting CO_2 into sub-surface to reduce the emissions of anthropogenic CO_2. According to the IPCC 2005, the storage options are classified into three groups: (1) ocean storage, (2) mineralization, and (3) geological storage. Ocean storage consists of injecting the CO_2 into deep oceans and immobilizing it by dissolving or forming a plume which is heavier than water under the ocean. The ocean is the largest storage option of CO_2 and can contain 40000 Gton of carbon in contrast to the 750 Gton in the atmosphere. The ocean storage has not yet been considered as a pilot scale since it is still in the research phase and may also have dire consequences in marine life in case of leakage during and after the storage. [1, 12]. Mineralization process provides an opportunity to store the CO_2 for a long period of time without any special concern about the permanent mitigation quality. It includes the CO_2 conversion to a solid inorganic carbonates which is stable for a long time. The only considerable problem in this process is related to the high cost of implementation [13]. The CO_2 geological storage (CGS) is considered as the main process for CO_2 sequestration in the developed world [14–16]. The candidate CO_2 storage facilities consist of deep saline aquifer and unmineable coal deposits, as well as depleted and mature oil and gas reservoirs which can contain 2200 Gton of carbon dioxide [17]. Based on an estimation reported by the European technology platform for zero emission fossil fuel power (ZEP), the contribution of each option for the storage potential of CO_2 is shown in Figure1. [18]

As for CGS's regulation in Europe in 2009, the European Union approved that seven million tons of CO_2 could be stored by 2020 and up to 160 million tons by 2030, assuming a 20% reduction in GHG emissions by 2020 [19]. Over the past decade, many developed countries have extensively investigated the potential of CO_2 storage sites as well as understanding the behavior of CO_2 and its interaction with different reservoir formations as a prerequisite to increase the effectiveness and integrity of the CGS projects. These comprise advanced scientific knowledge about CO_2 behavior such as trapping mechanisms (physical and chemical), flow patterns, and interactions with formation rocks that can be achieved by improved techniques such as flow simulation, reservoir modeling, reservoir monitoring, and verification [20].

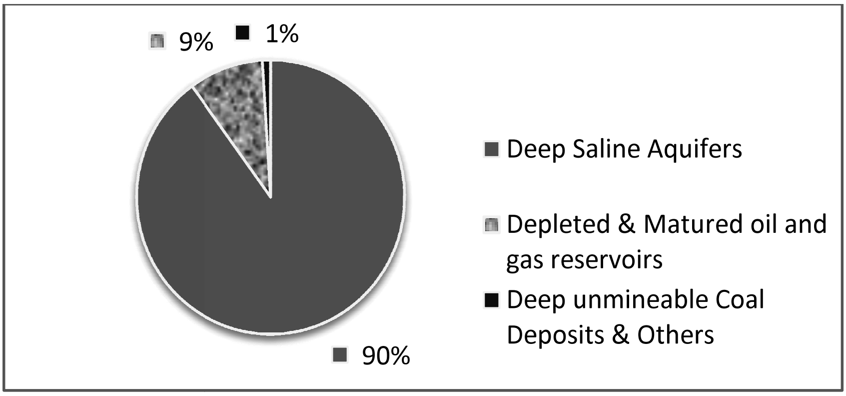

Figure 1. The contribution of most important CGS techniques in the world's CGS projects.

2. CGS: Storage Capacity

In recent years, there have been a number of surveys related to the storage capacity estimation methods in CGS fields [21]. The first groups of estimation assessments were simple with no technical component similar to the estimations held in Europe by Holloway and van der Straaten, in 1995, while the other recent ones have taken into account the complexities and more sophisticated methods of estimating the CO_2 storage capacity [22–28]. One should keep in mind that the capacity estimation in any different scale (global, reservoir, basin, or region) and time frame is a difficult process due to our lack of knowledge about subsurface in most areas of the world and also the uncertainties and inaccessibility of the available data [29]. However, there is a wide variety of estimation techniques proposed by different authors (CSLF, IPCC, and Bradshaw et al.) which mainly rely on a simple algorithm depending on various storage mechanism [26, 28, 30].

In 1979 and 1988, the concept of resource pyramids was developed by Masters and McCabe for the first time and was later proposed to demonstrate the accumulation and quality of the CO_2 storage potentials in the form of three pyramids as an important factor for capacity estimation, including (1) high level, (2) techno-economic, and (3) trap-type and effectiveness pyramid [31, 32]. This concept consists of the main aspects of CO_2 storage such as different time scales and assessment scales, various assessment types, and different geological storage options [29]. For instance, as it has been demonstrated in Figure2, the techno-economic resource pyramid calculates the storage capacity in mass instead of the volume and includes the maximum upper limit of capacity estimate with various time and assessment scales. On the other hands, it reveals three levels of theoretical, realistic and viable estimates in which the theoretical portion includes the entire pyramid whereas the realistic and viable parts have covered the top two portions and only the top portion of pyramid respectively [28, 30].

In an investigation which was performed by Kopp et al. in 2009, to estimate the effective storage capacity, some models were proposed by authors, including(1) CSLF model (proposed by Bachu et al. in 2007 in which the effective storage volume is calculated by reducing the capacity

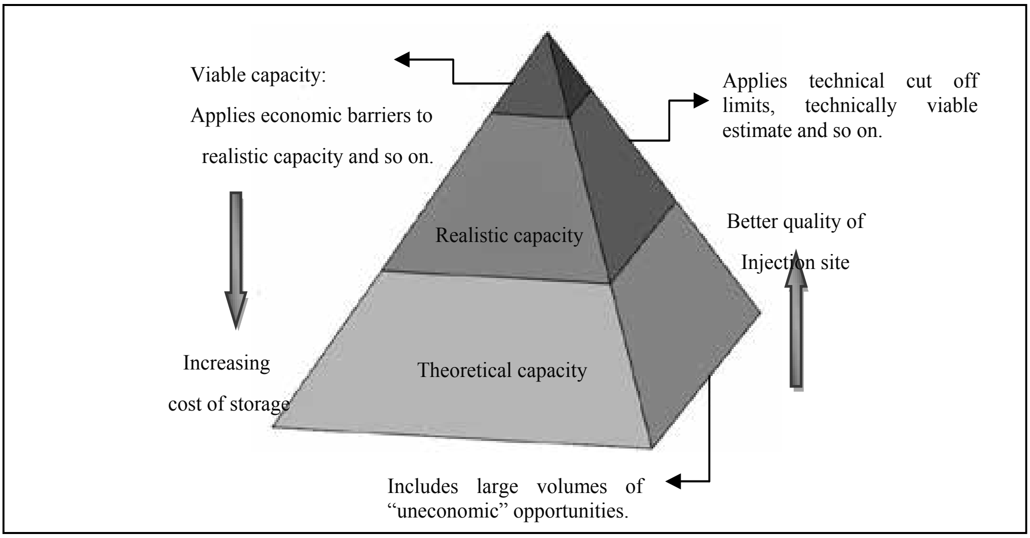

Figure 2. Techno-Economic Resource Pyramid for capacity estimation in CO_2 geological storage.

coefficient from theoretical capacity), (2) Doughty model (proposed by Doughty et al. in 2001 which estimated the effective capacity as a volume fraction for CO_2 storage), and (3) Kopp model (based on Doughty model while the pores containing dissolved CO_2 is much larger than those containing free gas [33]).

According to CO_2 storage capacity estimation surveyed by Bachu et al., based on a summary of carbon sequestration leadership forum (CSLF), different timeframes and field scales are accounted considering various trapping mechanisms (physical and chemical mechanisms) [26]. Bachu et al. have demonstrated the approaches based on different geological potential with generally assessing the opportunity of other storage options like man-made underground cavity and the basalts such as Deccan Plateau in India; however, they need more investigations.

2.1. Estimation techniques in depleted oil and gas reservoir

DOE (2006), 'Methodology for development of carbon sequestration capacity estimates' and CSLF (2007), 'Estimation of CO_2 storage capacity in geological media – phase II' are the major investigations regarding the storage capacity estimation approaches in geological formations. The CSLF (2007) employs a techno-economic resource pyramid in the capacity estimation process for depleted oil and gas reservoir based on McCabe (1998), while the DOE (2006) utilizes volumetric equations and Monte Carlo approach to estimate the uncertainty and capacity storage by incorporating various trapping mechanisms in depleted oil and gas reservoirs [31]. Another integration of DOE and CSLF with simple version of SPE (Society of Petroleum Engineering) petroleum resource management system is proposed and called CO2CRC storage capacity classification [34, 35]. They have reported that on account of greater amount of data in term of oil and gas fields, the estimation process is the easiest among the geological formations. It should be noted that the other methods which are employed in saline aquifers can be used here for CO_2 storage volume estimation: 'volumetric-based estimation' and 'production-based estimation' [35, 36].

Bachu et al., provided a good overview of storage capacity estimates in oil and gas reservoirs to compare the other geological formation such as coal beds and saline aquifers [26]. Based on Bachu et al., the capacity estimation in oil and gas reservoirs is more convenient than other geological formations, and these geological formations are discrete in contrast to the continuous coal beds and saline aquifers [26]. Estimation of the CO_2 storage capacity is also difficult for a number of reasons: In estimation process, some assumption would be made, such as volume occupied by hydrocarbons is available for CO_2 after production for pressure-depleted reservoirs with no hydrodynamic contacts. On the other hand, formation water influx as the consequence of pressure decline and water trapping can be inversed due to the CO_2 injection and increase in the pore spaces which may cause some pores to be unavailable for CO_2 storage. Thus, the original reservoir pressure has the maximum limitation for CO_2 injection into the depleted reservoirs [37]. According to the volume of original oil and gas at surface conditions, theoretical mass storage capacity can be accounted through an equation proposed by Bachu et al.[26]. They also provided an extrapolation to account the theoretical storage capacity in another correlation. In some cases, the actual volume availability to CO_2 storage can be reduced and would be stated by capacity coefficient (equation expressed by Doughty and Press, 2004) [38]. But based on Bachu and Shaw, in 2005, enough data are not available for assessing these coefficients, and estimations are mostly carried out by numerical simulations [9, 38]. One of the specific issues in CO_2 storage in depleted reservoirs is CO_2 flood-enhanced oil recovery. Because of some reasons, the capacity estimation in this case is already an effective estimation. The promising storage sites for CO_2 enhanced recovery can be performed at regional and basin scales such that this criterion decreases the effective capacity to practical storage capacity [39–41].

2.2. Estimation techniques in saline aquifers

As it has been illustrated in recent studies, deep saline aquifers are the most favorable storage option in comparison to the depleted reservoirs and coal beds [1, 27, 28, 39]. In contrast, the numbers of projects which have been conducted by the industries are not considerable due to some reasons, including availability of anthropogenic CO_2 and the related data, site assessment difficulties, poor injectivities, and high cost of monitoring [42]. According to the DOE, a volumetric equation is proposed to CO_2 storage estimation in saline aquifers, while each type of trapping mechanisms is also needed for calculation of the basin-scale assessments [35]. In CSLF methodology for deep saline aquifers, storage estimations based on structural and stratigraphic trapping mechanisms are similar to depleted oil and gas reservoirs, whereas the mass of CO_2 related to the effective storage volume would be more difficult to calculate. Moreover, the storage estimation based on solubility trapping at the basin and regional scales can be calculated by the relation proposed by Bachu and Adams [36, 41].

Bachu et al. proposed a theoretical approach to CO_2 storage estimation considering each type of trapping mechanism in deep saline aquifers [26]. They introduced a simple time-independent volumetric equation used for depleted oil and gas reservoirs in which the traps have been saturated by water rather than being occupied with hydrocarbons. Similar to equation mentioned above, a relation related to the CO_2 mass storage limitation also has developed here for basin- and regional-scale assessments, which can be utilized for theoretical and effective capacity estimations. For residual gas trapping method, the storage volume can be calculated with a time-dependent equation proposed by the authors with regard to the concept of actual CO_2 saturation at flow reversal by Juanes et al. [43]. The solubility mechanism is a time-dependent, continuous, and slow process which can be performed effectively after finishing the injection process. If this trapping system occurs in thick and high permeable aquifers, a convection cell can be constituted and the dissolution process will be improved, while in the case of thin aquifers, this mechanism is less efficient [44, 45]. Capacity storage at the basin and regional scale can be assessed through an equation proposed by Bachu and Adams whereas at the local and site scale, numerical simulation is required for precise estimation of the storage capacity [41]. Estimation through mineral trapping cannot be applied at the regional and basin scales due to the lack of available data and the complex intrinsic of mineral trapping and the chemical and physical related mechanisms. The only remaining approach is numerical simulation which is suitable for site and local scale during a long period of time. According to recent research, mineral trapping mechanism can be compared to the solubility mechanisms with regard to the long time period required here [46, 47]. Hydrodynamic trapping mechanism consists of all the mentioned features of the mechanism and it needs various time scales for acting. This process cannot be evaluated at regional and basin scale estimations due to the different acting time scales through various trapping mechanisms. Hence, it should be considered in a specific point of time and the numerical simulation applied to estimate the storage capacity at local and site scales [26, 48].

De Silva and Ranjith conducted a complete investigation related to the CO_2 estimation methods on saline aquifers and assessed different aspects of the estimation process such as operating time frame, resource circles (pyramids), and trapping mechanisms and factors affecting the storage capacity [50]. The proposed equations in each trapping system are based on the relations recommended by Bachuet al. [26]. The evaluated parameters which can affect the storage capacity consist of *in-situ* pressure, injectivity, temperature, permeability, and compressibility. According to De Silva and Ranjith, eight methods have been introduced to estimate theoretical and effective capacity of CO_2 storages (volumetric method, compressibility method, flow simulation, flow mathematical models, dimensional analysis, analytical investigation, Japanese methodology, and Chinese methodology), while to calculate the practical and matched capacities, the local conditions need to be considered [26, 49, 50]. In a quick and simple volumetric method, the porosity, area, thickness, and storage efficiency of the storage reservoirs are important in capacity estimation according to an equation mentioned by DOE and Ehlig-Economides and Economides [see 51, 52], while van der Meer and Yavuz have proposed another equation to measure the CO_2 mass [53]. To calculate the volume of CO_2 per volume of the aquifers, Eccles et al. have introduced another relation including measuring the effective capacity storage at a special depth [54]. The more comprehensive equation to calculate the storage capacity by compressibility method was shown by

Zhou et al. [55]. The most effective method to assess the capacity is the flow simulation which includes volumetric formulas and more reservoir parameters rather than other methods [56]. Mass balance and constitutive relations are accounted in mathematical models to capacity assessment and dimensional analysis consists of fractional flow formulation with dimensionless assessment and analytical approaches [33]. From the formulations demonstrated by Okwen and Stewart for analytical investigation, it can be deduced that the CO_2 buoyancy and injection rate have affected the storage capacity [57]. Zheng et al. have indicated the equations employed in Japanese and Chinese methodology and have noted that some parameters in Japanese relation can be compared to the CSLF and DOE techniques [58].

2.3. Estimation techniques in coal beds

According to the IPCC 2005, the coal bed storage process is currently in the demonstration phase. MacDonald of Alberta Energy reported the storage in coal bed in 1991 for the first time [59]. One of the most prominent factors to guarantee the successful economic CO_2 storage process is the permeability of coal and it should be more than 1 mD (miliDarcy) [60]. The main problem in CO_2 storage in coal bed process is the limitation of available data about location and capacity of promising sites [30, 26, 28]. It should be noted that the main trapping mechanism in storage process regarding the coal beds is adsorption, and it is necessary to assess the rank, grade, and type of the coal in order to achieve more information about adsorption capacity of the coals [35].

The CSLF and DOE proposed models such as volumetric equation to estimate the coal capacity through substituting the intrinsic methane by injected CO_2 process. Bachu et al. have reported the relation demonstrating the initial gas in place after coal adsorption process proposed by van Bergen et al. and White et al. [59, 61, 62]. One should keep in mind is that since the adsorption is one of the main parts of the storage process, adsorbed gas capacity estimation is also important to investigate [63]. Langmuir equation is a simple and efficient relation for single-layer adsorption capacity estimation in low-pressure conditions [64–66]. In case of high pressure and high temperature, other methods are more suitable such as Bi Langmuir, extended Langmuir, Sips, Langmuir-Freundlich, Toth, UNILAN, two-dimensional EOS, LRC (loading ratio correlation), Dubinin-Radushkevich (D-R) and Dubinin-Astakhov (D-A) [59, 67–73]. A modified Langmuir and Toth correlation was expressed by Himeno et al. and Bae and Bhatia, which includes the substitution of pressure by fugacity high dense phase conditions [74, 75]. Another mathematical power equation proposed by Saghafi et al. can be used to estimate the adsorption capacity [66].

Storage capacity estimation for the stored gas content can be performed through the equation suggested by White, van Bergen et al., CSLF, and Vangkilde et al. [61, 76, 77]. Palarski and Lutynski expressed another relation to estimate the CO_2 storage components in coal seams [78]. To estimate the large-scale storage capacity of 45 important coal basins during Enhanced Coal Bed Methane Recovery (ECBM) in China, Li et al. used an equation which can be modified to a simpler form without considering the different coal bed basins [63, 79].

3. CGS: Modeling and Simulation

To study the behavior of CO_2 during and after the CGS process, numerical modeling is considered as the only effective tool prior to the experimental and field demonstrations instead of analytical and semi-analytical solutions on account of some limitations and simplifications [80–83]. In the past few years, various numerical modeling and reservoir simulations approaches have been documented in the literature at the pilot and commercial scales which are using common numerical methods such as finite difference, finite element, and finite volume methods. One of the most efficient means for reservoir modeling is TOUGH2 simulator developed by Pruess et al. and used successfully in Rio Vista reservoir. In this study, an extension of EOS7R and EWASG modules have been developed to simulate the gas and water flow called EOS7C [84-88]. Omambia and Li carried out a CO_2 numerical modeling in a deep saline aquifer (Wangchang basin, China) using a fluid/property module of TOUGH2 called ECO2N which is adapted from EWASG module [89]. This module was evaluated in a separate study for the CGS process in saline aquifers by Pruess and Spycher [86, 90]. TOUGHREACT, a non-isothermal reactive geochemical transport code, was utilized to simulate the CO_2 disposal in deep aquifers by Xu et al., which was performed by merging the reactive chemistry term into the TOUGH2 framework [91–95]. An efficiency evaluation of CGS was performed in Frio brine pilot project using the TOUGH2 simulator to identify the uncertainties related to nature of the earth by Hovorka et al. [96]. In a previous study at the University of Stuttgart, the MUFTE-UG simulator has been evaluated for CO_2 sequestration in various fields of application such as simulation, CO2SINK, and CO2TRAP [97, 98]. At the Ketzin CO_2 storage site, the ECLIPSE 100/300 and MUFTE-UG codes were employed to perform a history matching [99]. Pawar et al. have investigated a preliminary study to model and simulate the CGS in a depleted oil reservoir by ECLIPSE 100 [100]. Another 2/3 dimensional simulation survey with consideration of reactive flow and transport in deep saline aquifers has been performed by Kumar et al. with GEM simulator (computer modeling groups) [101]. ECLIPSE and DuMux simulators are also taken into consideration to understand the thermal effect during CO_2 injection and movement in the porous medium.

According to the CGS simulation methods, there have been some comparative investigations between the various simulators, such as reported by David et al. and Jiang [102]. David et al. have compared six simulators for numerical simulation of CGS in coal beds: (1) GEM, (2) ECLIPSE, (3) COMET2, (4) SIMED II, (5) GCOMP, and (6) METSIM 2. Additional features are needed to be taken into consideration based on Law et al., such as coal matrix swelling, diffusion of mixed gas, non-isothermal effect, water movement, and so on [103]. According to the recent survey by David et al. GEM and SIMED II are suitable to consider multi-component liquids while ECLIPSE and COMET 2 can handle only two component fluids [103, 104]. In 2011, Jiang demonstrated an overview of the various simulator applications and their numerical features including TOUGHREACT, MUFTE, GEM, ECLIPSE, DuMux, COORES, FEHM, ROCKFLOW, SUTRA, and other types of simulators. Numerical methods and physical models play an important role in the simulators outcomes. Selecting the best simulator among those presented above is highly based on the desired application. For example, the ELSA simulator can be applied efficiently in semi-analytical estimation of fluid distributions; ROCKFLOW is suitable in the case of multi-phase flow and solute transport modeling; GEM is an aqueous geochemistry tool while for the low-temperature situation PHREEQC is more applicable; and for the multi-component, three phase, and 3D fluid flow simulation with consideration of reservoir heterogeneities, COORES would be a robust means [85, 102, 104, 105]. Zhang et al. had a quick look on different types of simulators mentioned earlier and have suggested a new parallel multi-phase fluid flow simulator for CGS in saline aquifers called TOUGH+CO_2 which has been developed on the basis of a modified TOUGH2 family of cods, TOUGH+ and TOUGH2-MP including all the ECO2N features capabilities [83]. This brand new simulator has proved to be a successful and robust means, which has been used in a number of large-scale simulation projects [106–113].

Another group of surveys has focused on the direct modeling of some effective transport phenomena which are essential for predicting parameters that have an important role in underground gas sequestration process such as diffusivity and convection. Azin et al., in 2013, have conducted study regarding correct measurement of diffusivity coefficient [114]. The modeling was based on a method proposed by Sheika et al. to analyze pressure decline data and the impact of pressure and temperature on the measurement of diffusivity coefficient [114]. GholamiY., et al., in 2015, have also investigated the measurement of CO_2 diffusivity in synthetic and saline aquifer solutions at reservoir conditions with emphasis on the role of ion interactions [114–117]. A non-iterative thermodynamic predictive model has investigated by Azin et al. to calculate the effect of gas solubility [118–120]. The effects of convective dissolution and diffusivity mixing have also been surveyed with finite-element method by GholamiY., et al. They have used Streamline Upwind Petrov-Galerkin (SUPG) method and crosswind artificial diffusion and found that the dissolution is controlled by convective dissolution in bulk water [115, 121]. Another numerical simulation was done by Azin et al. to predict the onset of instability in CO_2 underground injection [114]. It was found that depending on Rayleigh number, there is a wave number at which instability occurs earlier and grows faster [114].

4. CGS: Monitoring and Verification

Precise monitoring and verification is required to have an appropriate risk management strategy for the CGS projects [1]. The monitoring and verification process should be commenced from site selection and characterization followed by atmospheric and remote sensing, near and deep surface methods, as well as well bore-monitoring techniques. Different types of monitoring tools are introduced and used in recent literature: acoustic velocity structure imaging by seismic, density distribution imaging by gravity, electrical resistivity structure imaging, and fluid content imaging of potential reservoir rocks by the electromagnetic methods [20, 122]. After injecting the CO_2 into the sequestration sites, electromagnetic and gravitation sensors are employed for seismic surveys of storage integrity such as CO_2 flow and transportation quality in porous media and behavior of cap rock in contact to the CO_2. The leakage measurement in atmospheric level can be done by open path, flux tower, and InSAR systems (satellite-based infrared and interferometric synthetic aperture radar) [20].

Otway Basin Pilot project in Australia is the first CGS project in which monitoring techniques were used [122]. In 2010, the CSEM have considered landing base imaging and passive magnetotelluric in deep crustal scales surveys by Sreitch and colleagues [124]. According to the surveys performed by Arts et al. and Chadwick et al., the 4D gravity and seismic techniques have been successfully accomplished in Sleipner site [125–127]. The 4D vertical seismic profiling (VSP) has been commonly used to quantitative monitoring of the CO_2 plume with tracer injection, well logging, micro-seismic and pressure–temperature measurements which is applied successfully at Frio and Nagaoka project [128–144]. In Frio Brine and Otway Pilot projects, tracer monitoring has been employed to assess the CO_2 breakthrough [145, 146]. The Eddy covariance and hyperspectral imaging in a shallow subsurface site are important computational issues that were examined to monitor the CO_2 leakage in Montana [147, 148]. Another successful surface monitoring technique tested at In Salah project was InSAR which was incorporated into other monitoring techniques such as seismic, gravity, and electromagnetic [149–153]. At Ketzin sequestration site, the monitoring methods included cross-hole resistivity, seismic, and microbiology with temperature and pressure profiling [154-160].

5. Conclusions

In summary, the methods of theoretical and effective capacity estimation of CO_2 storage comprise volumetric and compressibility methods, flow mathematical and simulation models, dimensional analysis, analytical investigation and Japanese/Chinese methodology.

The CSLF model employs a techno-economic resource pyramid in the capacity estimation process for depleted oil and gas reservoir, while the DOE model utilizes volumetric equations and Monte Carlo approach by incorporating various trapping mechanisms. According to the CO2CRC, storage capacity classification in terms of oil and gas fields is the easiest among the other geological options due to the greater amount of data. A volumetric equation has been proposed to CO_2 storage estimation in the most favorable storage option (saline aquifers) while each type of trapping mechanism is also needed for calculation of the basin-scale assessments. The CSLF methodology has been considered for deep saline aquifers as well as depleted oil and gas reservoir based on structural and stratigraphic trapping mechanisms. Estimation through mineral trapping cannot be applied at the regional and basin scales due to lack of data availability. The only remaining approach, numerical simulation, is suitable for site and local scale for a long period of time. Despite the application of the hydrodynamic trapping mechanism in various time scales, it cannot be evaluated at regional- and basin-scale estimation. To calculate the storage capacity based on compressibility concept, a more comprehensive equation has been addressed recently including flow simulation employing volumetric formulas and more reservoir parameters.

In coal bed capacity estimation, the Langmuir equation provides a simple and efficient relation for single layer low-pressure conditions. In the case of high pressure and high temperature, Bi Langmuir, extended Langmuir, Sips, Langmuir-Freundlich, Toth, UNILAN, two-dimensional

EOS, LRC (loading ratio correlation), Dubinin–Radushkevich (D-R), and Dubinin-Astakhov (D-A) are more suitable.

One of the most efficient means for reservoir modeling is the TOUGH2 simulator developed in Rio Vista reservoir and an extension of EOS7R and EWASG modules also has been proposed to simulate the gas and water flow called EOS7C. A fluid/property module of TOUGH2 called ECO_2N has been utilized for CO_2 modeling in saline aquifers. TOUGHREACT, a non-isothermal reactive geochemical transport code, was utilized to simulate the CO_2 disposal in deep aquifers by entering the reactive chemistry term into the TOUGH2 framework. MUFTE-UG simulator has been evaluated for CO_2 sequestration in various fields of application such as simulation, CO_2SINK, and CO_2TRAP. Another survey with consideration of reactive flow and transport in deep saline aquifers has been performed using the GEM simulator. ECLIPSE and DuMux simulators are also taken into consideration in a study to understand the thermal effect during CO_2 injection and movement in the porous medium.

Six simulators including GEM, ECLIPSE, COMET2, SIMED II, GCOMP, and METSIM2 have been compared for CGS in coalbeds. GEM and SIMED II simulators are suitable for multi-component liquids while ECLIPSE and COMET2 can handle only two component fluids. Other comparison studies including TOUGHREACT, MUFTE, GEM, ECLIPSE, DuMux, COORES, FEHM, ROCKFLOW, SUTRA, and other types of simulators have been carried out throughout the world. Selecting the best simulator among those presented is highly based on the desired application. The ELSA simulator can be applied efficiently in semi-analytical estimation of fluid distributions. ROCKFLOW is suitable in the case of multi-phase flow and solute transport modeling. GEM is an aqueous geochemistry tool, while for the low temperature situation PHREEQC is more applicable. For multi-component, three phase, and 3D fluid flow simulation with consideration of reservoir heterogeneities, COORES would be a robust means. The new parallel multi-phase fluid flow simulator for CGS in saline aquifers called TOUGH+CO_2 has been developed on the basis of a modified TOUGH2 family of cods, TOUGH+ and TOUGH2-MP including all the ECO_2N feature capabilities and has proved to be a successful and robust means in a number of large scale simulation projects.

The CSEM have considered landing base imaging and passive magnetotelluric in deep crustal scale surveys in 2007. The 4D gravity and seismic methods have performed well in the Sleipner project. The 4D vertical seismic profiling (VSP) has been commonly used for quantitative monitoring of the CO_2 plume with tracer injection, well logging, and micro-seismic and pressure-temperature measurements with successful application at Frio and Nagaoka. In Frio Brine and Otway Pilot projects, tracer monitoring has been employed to assess the CO_2 breakthrough. The Eddy covariance and hyperspectral imaging in a shallow subsurface site are important computational issues that were examined to monitor the CO_2 leakage in Montana. Another successful surface monitoring technique tested at In Salah project was InSAR which incorporated to other monitoring techniques such as seismic, gravity, and electromagnetic. At Ketzin sequestration site, the monitoring methods included cross-hole resistivity, seismic, and microbiology with temperature and pressure profiling.

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Chapter 8

Methane Emissions from Rice Production in the United States — A Review of Controlling Factors and Summary of Research

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Additional information is available at the end of the chapter

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Abstract

Flooded rice (*Oryza sativa* L.) cultivation has been identified as one of the leading global agricultural sources of anthropogenic methane (CH_4) emissions. Furthermore, it has been estimated that global rice production is responsible for 11% of total anthropogenic CH_4 emissions. Considering that CH_4 has a global warming potential that is approximately 25 times more potent, on a mass basis, than carbon dioxide (CO_2) and rice production is globally extensive and concentrated in several mid-southern and southern states and California, the purpose of this review is two-fold: (i) discuss the factors known to control CH_4 production in the soil and transport to the atmosphere from rice cultivation and (ii) summarize the historic and recent research conducted on CH_4 emissions from rice production in the temperate United States. Though some knowledge has been gained, there is much more that still needs to be learned and understood regarding CH_4 emissions from rice production in the United States, its contribution to climate change, and potential mitigation strategies. Extending the current knowledge base surrounding CH_4 emissions from rice cultivation will help regulatory bodies, such as the Environmental Protection Agency, refine greenhouse gas emissions factors to combat the potential negative effects of climate change.

Keywords: Methane, emissions, rice production, agriculture, soil texture

1. Introduction

Methane (CH_4) is a known and potent greenhouse gas that is produced by anaerobic *Archaea* under anoxic conditions. Agricultural activities have been recognized as contributing an estimated 50% to global anthropogenic CH_4 emissions [1], while an estimated 31% of anthropogenic CH_4 emissions have been attributed to agricultural activities in the United States (US)

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[2]. Due to the anaerobic conditions that form in saturated soils, which is a prerequisite for CH_4 production, flooded rice (*Oryza sativa* L.) cultivation has been specifically identified as one of the leading global agricultural sources of anthropogenic CH_4 emissions, accounting for approximately 22% of the total global agriculturally related CH_4 emissions [3]. Furthermore, it has been estimated that global rice production is responsible for 11% of total anthropogenic CH_4 emissions [1,3].

While numerous factors have been determined to impact CH_4 emissions from rice cultivation, due to a general lack of field data, the United States Environmental Protection Agency (USEPA) currently uses a single emissions factor for all non-California-grown, primary rice crops [4]. Therefore, the purpose of this review is two-fold: (i) discuss the factors known to control CH_4 production in the soil and transport to the atmosphere from rice cultivation and (ii) summarize the historic and recent research conducted on CH_4 emissions from rice production in the temperate United States.

2. The greenhouse effect

The greenhouse effect is a mechanism by which certain gases such as carbon dioxide (CO_2), CH_4, nitrous oxide (N_2O), and water (H_2O) vapor absorb and release infrared radiation, interfering with the ability of solar radiation to leave Earth's atmosphere. The absorption of thermal radiation by H_2O and CO_2 was discovered through laboratory experiments in 1859 [5]. However, other gases including CH_4 and N_2O were not recognized as greenhouse gases until the 1970s [6].

Global warming potential (GWP) is a metric that allows the warming impact of various greenhouse gases to be quantitatively compared on the same scale. The assignment of GWP values to gases requires knowledge of the contribution to global warming of gas emissions over time based on the amount of radiation per mass that the gas can absorb and emit as well as the atmospheric lifetime of the gas. Global warming potentials are assigned relative to that of CO_2, thus the 100-yr GWP of CO_2, CH_4, and N_2O are 1, 25, and 298, respectively [7]. For example, 1 kg of CH_4 released to the atmosphere is equivalent to 25 kg of CO_2 being released. Global warming potentials allow greenhouse gas emissions to be reported as CO_2 equivalents in order to compare warming effects of various gases on a single scale.

The current climate change problem is not a result of the greenhouse effect itself, but rather from an increasing greenhouse effect resulting from anthropogenic activities that have increased atmospheric concentrations of greenhouse gases. Prior to 1750, the atmospheric CO_2 mixing ratio was about 280 parts per million (ppm) [8]. Since the beginning of the industrial era, atmospheric CO_2 has risen drastically to 379 ppm in 2005 [7] and 395 ppm as of April 2013 [9]. Between 1750 and 2005, atmospheric CH_4 increased from about 700 parts per billion (ppb) to 1,774 ppb [7]. Nitrous oxide was more variable ranging from 180 to 260 ppb prior to 1750, but has similarly increased to a mixing ratio of 319 ppb in 2005 [7]. While atmospheric N_2O and CO_2 concentrations have increased steadily over the past several decades, the growth rate (i.e., concentration increase) of atmospheric CH_4 seems to be declining. The growth rate of atmospheric CH_4 has decreased from highs of about 1% per year in the 1970s and 1980s to nearly zero between 1999 and 2005. However, the decreasing growth rate is poorly understood [7].

3. Greenhouse gas emissions

Globally, CO_2 accounted for about 76% of greenhouse gas emissions in 2004, with around 75% of CO_2 emissions resulting from fossil fuel use and much of the remainder from deforestation and biomass decomposition [10]. Methane and N_2O accounted for 14 and 8%, respectively, of the estimated global greenhouse gas emissions in 2004. Major CH_4 sources include agricultural activities, waste management, and energy use, while N_2O emissions are primarily a result of agricultural activities, such as fertilizer use and soil management [10]. In the US in 2013, an estimated 82% of the total greenhouse gas emissions were CO_2, 10% were CH_4, and 5% were N_2O [2]. Major sources of greenhouse gas emissions are generally the same in the US as the global sources mentioned above. The major global sectors responsible for greenhouse gas emissions are energy supply (26%), industry (19%), forestry (17%), agriculture (14%), and transportation (13%) [10]. In comparison, the major US sectors responsible for greenhouse gas emissions are energy supply (31%), transportation (27%), industry (21%), commercial and residential (12%), and agriculture (9%) [2].

Although agricultural activities do not dominate total greenhouse gas emissions, agriculture contributes an estimated 50 and 60% of global anthropogenic emissions of CH_4 and N_2O, respectively [1]. Agriculture in the US is responsible for an estimated 36% of anthropogenic CH_4 emissions and 79% of anthropogenic N_2O emissions [2]. Enteric fermentation, rice cultivation, and manure management contribute an estimated 64, 22, and 8%, respectively, to global anthropogenic agricultural CH_4 emissions, while agricultural N_2O emissions are dominated by agricultural soil management (80%) [3]. In comparison, enteric fermentation, rice cultivation, and manure management contribute to 70, 4, and 26% of US anthropogenic agricultural CH_4 emissions [2]. Although rice cultivation makes up a small portion of CH_4 emissions in the US, globally rice cultivation accounts for approximately 11% of total anthropogenic CH_4 emissions.

Methane emissions from US rice cultivation were estimated to be 8.3 Tg CO_2 equivalents in 2013, a reduction from 9.3 Tg CO_2 equivalents in 2012 due to a decline in rice production area [2]. Arkansas was responsible for 36% of the estimated CH_4 emissions from rice cultivation, although Arkansas accounted for 43% of the total US rice production in 2013. Louisiana was the next leading contributor to CH_4 emissions accounting for 27% of 2013 emissions, while harvesting 16% of 2013 production [2,11]. Louisiana and Texas CH_4 emissions are large relative to their production areas due to extensive ratoon cropping in 2013, which occurred on an estimated 38 and 68%, respectively, of the production area in those states [2]. A ratoon crop is a second crop that is managed and produced after the first or primary crop is harvested. California, Mississippi, and Missouri, none of which reported any ratoon cropping, contributed 14, 3.6, and 4.5%, respectively, to the estimated 2013 CH_4 emissions from US rice cultivation [2].

The USEPA periodically publishes CH_4 emissions factors based on research data. Separate emission factors of 178 kg CH_4-C ha^{-1} $season^{-1}$ and 585 kg CH_4-C ha^{-1} $season^{-1}$ were used in the inventory estimates for non-California-grown, primary rice cropping and ratooned cropping areas, respectively, as is consistent with the Intergovernmental Panel on Climate Change [3], which recommends calculating separate emissions factors for as many different factors and cultural practices as is possible. Emissions factors for California rice production are 200 and 100 kg CH_4-C ha^{-1} $season^{-1}$ for winter-flooded and non-winter-flooded rice, respectively [2]. While it is known that factors such as water management, soil properties, rice cultivar, fertilizer management, and residue management have strong impacts on CH_4 emissions from rice cultivation, data available from US studies limit the further disaggregation of these factors [2]. The non-California-grown, primary crop emissions factor is based on US studies with emissions ranging from 46 to 375 kg CH_4-C ha^{-1} $season^{-1}$ [13–20] and the ratoon crop factor is based on studies conducted in Louisiana with emissions ranging from 361 to 1118 kg CH_4-C ha^{-1} $season^{-1}$ [21,22]. The California-specific emissions factors include studies with emissions ranging from 47 to 166 kg CH_4-C ha^{-1} $season^{-1}$ for the non-winter-flooded and from 98 to 277 kg CH_4-C ha^{-1} $season^{-1}$ for the winter-flooded rice [23,24].

4. Rice production

Rice is a semi-aquatic, cereal grain that makes up about 21% of total global grain production [25]. The importance of rice is further exemplified by the fact that rice is a staple food crop for about half of the global population, with direct human consumption accounting for 85% of rice production compared to 72% of wheat (*Triticum aestivum* L.) and 19% of maize (*Zea mays* L.) production [26,27]. In Southeast Asia, 60% of human food intake is provided by rice as well as 35% of food intake in both East Asia and South Asia [26]. Rice has the ability to support more people per unit of land area than wheat or maize because rice produces, on an average yield basis, more food energy and protein per hectare than wheat or maize [28]. Therefore, any potential negative environmental consequences associated with rice production have to be taken seriously.

4.1. Rice production extent

Common rice (*Oryza sativa*) is commercially produced in 112 countries worldwide, spanning latitudes from 53°N along the Amur River at the China–Russia border to 35°S in central Argentina [26]. In 2012, more than 158 million ha globally were planted to rice, with average yields of 4.4 Mg ha^{-1} for a total global production of 470 Tg of rice. Comparatively, nearly 216 million ha were planted in wheat in 2012, with average yields of 3.0 Mg ha^{-1} for a total of 656 Tg of global wheat production. More than 174 million ha were planted in maize in 2012, with an average yield of 4.9 Mg ha^{-1} and a total global production of 857 Tg of maize [25]. Global rice production peaked in 1994 at 534 Tg of rice, with Asia being responsible for 90% of that production [29]. The majority of global rice production occurs in east, south, and southeast Asia, which together accounted for 90% of global production in 2012. Substantial production also occurs in South America (Brazil and Peru), Sub-Saharan Africa (Nigeria and Madagascar), Europe (Italy and Spain), Egypt, and the US [25].

China and India currently dominate global rice production accounting for 30 and 22%, respectively, of the total global production in 2012. The third-, fourth-, and fifth-ranked global producers in 2012 were Indonesia (8%), Bangladesh (7%), and Vietnam (6%). The remaining top 10 producers, in order, were Thailand, the Philippines, Burma, Brazil, and Japan, followed by the eleventh-ranked US, which accounted for 1.3% of global production [25]. The US, however, plays a larger role in global exports contributing 9% of 2012 global exports and ranking fifth after Thailand (21%), India (20%), Vietnam (20%), and Pakistan (10%). Global exports in 2012 were estimated to be 8% of total production, while the US exported 55% of 2012 production [30]. Global rice yields in 2012 were estimated to be 4.4 Mg ha^{-1} compared to 8.3 Mg ha^{-1} in the US, which was second only to Egypt (8.8 Mg ha^{-1}) among the major rice-growing countries. The two top rice-producing countries, China and India, had estimated yields of 6.7 and 3.6 Mg ha^{-1}, respectively [25].

Nearly 1.1 million ha of rice were planted in the US in 2012, yielding an average of 8.3 Mg ha^{-1} for a total production of 9.0 Tg of rice prior to milling, compared to 23 million ha planted with an average yield of 3.1 Mg ha^{-1} for a total of 62 Tg of wheat production, and over 39 million ha of planted maize with average yields of 7.7 Mg ha^{-1} for a total production of 274 Tg [11]. The four major regions that produce rice in the US are the Arkansas Grand Prairie, the Mississippi Delta, which is made up of portions of Arkansas, Missouri, Mississippi, and Louisiana, the Gulf Coast (Texas and southwest Louisiana), and California's Sacramento Valley. Most US states produce primarily long-grain cultivars, while much of the medium-grain rice and nearly all of the short-grain rice is produced in California [11]. Although Oklahoma and Florida are often included as rice-producing states, the six previously mentioned states have made up essentially all of US production in recent years [11]. Arkansas is the leading state in both area of cultivation and total production, contributing 48% of total US rice production in 2012, followed by 23% of production by California and 13% of production by Louisiana [11]. Arkansas rice production takes place in the eastern portion of the state with the top five rice-producing counties in 2012 being Poinsett, Lawrence, Arkansas, Greene, and Cross, which made up 35% of the state's production area [31].

4.2. Global rice production practices

Rice production practices vary globally based on economic, cultural, and climatic factors, each of which show temporal and spatial variability throughout the rice-growing countries. A simple classification or characterization of rice production systems is nearly impossible on a global scale due to the variability of factors that influence production. Classifications of rice production techniques are commonly based upon flood presence (e.g., upland or lowland), water source (e.g., irrigated or rainfed), and stand establishment technique (e.g., transplanting, direct-seeding, or water-seeding) with many combinations and variations of these techniques occurring throughout the globe [32]. In one of the most recent classification attempts, Chang [33] classified global rice production into five major agroecosystems: (i) irrigated wetland, which made up 53% of global rice production area and had the greatest yield potential at 3 to

5 Mg ha^{-1}, (ii) rainfed wetland, making up 26% of global area and yielding 2 to 4 Mg ha^{-1}, (iii) flood-prone or tidal swamps, which made up an insignificant area, (iv) deep water (1–5 m), making up 8% of global area, and (v) dryland, which made up an estimated 13% of global production area with average yield potentials of 1 to 1.5 Mg ha^{-1}.

While a small portion of rice is produced under upland conditions, the majority of rice production requires substantial quantities of water in order to maintain a flood on the semi-aquatic crop. In much of the tropical rice-growing area, particularly south and southeast Asia, rainfed rice is the main production system, where most of the production comes from wet-season harvests and the cropping season is determined by rainfall patterns [32]. In temperate production areas, rice production must coincide with suitable temperatures for the crop which, coupled with inadequate rainfall, requires that temperate rice be almost entirely irrigated in order to maintain a flood for the duration of the growing season [32]. The utilization of irrigation in temperate areas allows greater control of environmental factors, which ultimately tends to increase yields, while rainfed systems may suffer from droughts and floods that may substantially damage crops and reduce yields [32].

Direct-seeding and transplanting are common establishment techniques in both irrigated- and rainfed-wetland systems, while direct-seeding is the major practice in dryland and deep-water agroecosystems [33]. While transplanting does occur in irrigated- and direct seeding occurs in rainfed-wetland systems, it is more common for irrigated systems to utilize direct-seeding and for rainfed systems to use transplanting techniques [32]. Transplanting systems involve raising seedlings in a nursery seedbed area at the beginning of the season and transplanting into puddled paddy soils early in the vegetative growth stage. Transplanting is the major establishment system for rainfed rice in tropical Asia, with the majority of production in northeast India, Bangladesh, and Thailand relying upon transplanting techniques [32]. Direct-seeding by grain-drilling or broadcasting pre-germinated seeds onto puddled soil is practiced in parts of India, Sri Lanka, Bangladesh, and the Philippines, while drill-seeding into dry soil is the most common practice in the US and other mechanized regions such as Australia [32]. Rice seed may be broadcast onto dry or moist soil by airplane followed by harrowing to cover seeds, but this establishment method requires more seed and stand establishment is often poorer than with drill-seeding [32]. Water-seeding is an establishment technique that originated and is practiced in parts of Asia, where pre-germinated seeds are broadcasted from an airplane into already flooded paddies or fields [32]. The rice-production system, and associated specific production practices, can significantly affect CH_4 production and emissions.

4.3. Rice production practices in the US

Rice production under mechanized US systems requires high temperatures, nearly level land, plentiful water, and soils that inhibit percolation of floodwater, so production is limited to Arkansas, Louisiana, Mississippi, Missouri, Texas, California, and Florida [34]. All US rice is produced using high-input, mechanized production practices, but practices vary somewhat from region to region based on differences in climate, soils, weed proliferation, and other factors that influence production. Essentially, all US rice is irrigated and sources of irrigation water include shallow or deep groundwater, runoff reservoirs, rivers, bayous, and lakes [34].

It is estimated that between 1000 and 2500 m^3 ha^{-1} of water are required to produce a rice crop in the southern US and generally less than one third of that requirement is met by rainfall [35]. Levees, which separate fields into bays, or paddies, and control flood depth (i.e., by use of gates or spills), are commonly constructed on contours that were surveyed on 3 to 6 cm vertical intervals. This creates winding, contour-shaped levees in fields that are not precision-leveled, whereas precision leveling to a uniform grade of 0.2% or less allows the construction of uniformly spaced, straight levees and may reduce the number of levees required [34].

The two stand establishment techniques utilized in the US are dry-seeding and water-seeding. Dry-seeding techniques, particularly drill-seeding, are predominant in most of the US, while water-seeding techniques are used extensively in California and to a small degree in southwest Louisiana and other regions as a weed control method [34]. A continuously flooded, water-seeding technique is used in California, where pre-germinated seeds are broadcast by airplane into flooded fields and the seedlings grow through a standing flood, while a pinpoint-flood, water-seeding technique is used in Louisiana, where seeds are broadcast into a flooded field that is drained within a few days and then permanently flooded after drying for 3 to 5 days [34,36]. In dry-seeded systems, seed is most often drilled into a well-pulverized, firm, and weed-free seedbed in 15- to 25-cm rows to a depth of 2.5 cm or less. When rice is following a high-residue crop, such as rice, maize, or wheat, it is necessary to till the land in the fall or early spring so that decomposition of the residue does not immobilize nutrients after the subsequent rice crop is planted, whereas rice following soybean (*Glycine max* L.), a crop that produces relatively little residue, may not require as much preparation because crop residues are not as abundant or as persistent compared to that of rice or maize [34,37].

Water management at and shortly after planting varies across US systems, but a permanent flood is established in all systems usually by the four- to five-leaf vegetative growth stage/beginning tillering (V4-5) [38]. Flush irrigation is used as necessary to promote germination and seedling growth in dry-seeded rice systems prior to establishment of a permanent flood, which typically occurs three to four weeks after emergence (i.e., the V4 to V5 growth stage). Drainage during the season is typically avoided except if a nutrient deficiency, such as zinc, is detected, to aerate the soil in order to treat or prevent disorders, such as straighthead and hydrogen sulfide toxicity, or to apply pesticides. Fields are drained prior to harvest in order to dry the soil enough for operation of harvest equipment [34]. Fields are flooded again within five to seven days after primary-crop harvest in ratoon cropping systems, which are common in southwest Louisiana, Texas, and Florida, and the flood is again maintained until harvest of the ratoon crop [34].

Crop rotations are important in rice, especially where weedy/red rice is problematic and difficult to control during rice cropping seasons. In order to suppress weedy rice, nearly all rice in Louisiana is grown either in a 1:1 rotation with soybean or a 1:1:1 rotation where crawfish (*Procambarus clarkia*) are double-cropped following rice, with soybean produced the following season [34]. In 2012, greater than 70% of Arkansas rice was produced in rotation with soybean, with most of the remaining production in a rice–rice rotation [39]. In California, approximately 70% of rice is produced in a rice–fallow or rice–rice rotation [40].

4.4. Arkansas rice production practices

Arkansas is the leading rice-producing state, accounting for 40 to 50% of total annual production in the US [11]. Rice production in Arkansas began in 1902 when 0.4 ha were planted in Lonoke County. Production increased over time until 1955 when government quotas limited production to 202,350 ha. The limitation was lifted in 1974 and production increased again, peaking in 1981 at 623,240 ha, again in 1999 with 667,755 harvested hectares, and finally in 2010 with 724,413 ha [31]. In 2012, 518,016 ha rice were harvested in Arkansas [11]. Rice production in Arkansas is highly mechanized with a heavy dependence upon synthetic fertilizers, chemical pest control, and machinery. Planting of rice in Arkansas generally begins the last week of March and extends into early June with floods typically being established by the end of May or early June. Harvesting operations usually begin in mid-August and peak in early- to mid-September [31].

Arkansas rice is produced on a wide variety of soils ranging from sandy to clay soils with the differing textural classes generally requiring different management, especially with regards to tillage practices and nutrient management [39, 41]. Production on sands and sandy loams is minor and has been decreasing from 3.1 and 5.2% of Arkansas area, respectively, in 2007 to 0.7 and 3.7%, respectively, in 2012. Arkansas production on clay and clay-loam soils, however, has increased from under 40 to 48% between 2007 and 2009 but declined to 43% in 2012. Production on silt-loam soils has remained fairly steady at 52% in 2007 and 53% in 2012 [39,42].

Dry-seeding techniques have always dominated in Arkansas. Water-seeding has varied between 2 and 8% of the production area between 2007 and 2012, with an estimated 5% of the 2012 Arkansas rice area being water-seeded [39,42]. Approximately 80% of 2012 Arkansas rice area was drill-seeded, compared to approximately 20% being broadcast-seeded [39]. Conventional tillage accounted for over half of Arkansas planted-rice area, while stale-seedbed (i.e., tillage and floating, or leveling the field, in the fall or winter) and no-tillage accounted for 35 and 10% of the planted-rice area, respectively, in 2012 [39]. Stale-seedbed and no-tillage are oftentimes utilized on clay soils where conventional tillage produces a cloddy seedbed with poor seed-to-soil contact [41].

While pinpoint, water-seeding techniques do occur in Arkansas, over 90% of the Arkansas rice production area utilizes a delayed-flood system, where the permanent flood is not established until the four- to five-leaf growth stage, which generally occurs approximately three to four weeks after emergence [39]. Fields are drained two to three weeks prior to harvest and most fields remain unflooded until the subsequent rice crop is produced, while nearly 20% of Arkansas rice area is winter-flooded [34,39]. Over 75% of Arkansas rice is irrigated by groundwater with 10 and 13% of the rice area utilizing water stored in reservoirs and from streams/rivers, respectively [39].

The two methods of nitrogen (N) fertilization in Arkansas are (i) the standard two-way split system, where 65 to 75% of the total N is applied pre-flood with the remainder applied at mid-season in one or two applications between beginning internode elongation and half-inch internode elongation [i.e., reproductive stage 0 (R0) to 1 (R1)], and (ii) the single optimum pre-flood system, where a single N application is made immediately prior to flooding. Nitrogen fertilizer rate recommendations have previously been based only on cultivar, soil texture, and previous crop. Implementation of the new N-Soil Test for Rice (N-STaR) enables recommendations to be adapted to the soil's ability to supply N to the rice crop on a field-by-field basis, reducing the likelihood of over- and under-fertilization of N [43]. Ammonium-N sources, such as urea and ammonium sulfate, are used in order to prevent N loss through denitrification that occurs with nitrate-containing fertilizers. Phosphorus and potassium are incorporated prior to planting as recommended by routine soil tests [43]. Organic amendments are uncommon, although poultry litter is utilized to a small degree, especially in precision-leveled fields.

5. Flooded soils

The saturated soils that occur during wetland, or lowland, rice cultivation give rise to a set of physical, chemical, and biological properties that are quite different from upland soils. Rice is the only major row crop produced under flooded-soil conditions and the absence of air-filled pores along with reduced soil–atmosphere interactions result in an almost entirely different set of processes than those occurring in upland cropping systems.

5.1. Physical characteristics of flooded soils

The major physical difference between saturated and unsaturated soils involves the availability and rates of movement for gases and solutes. Under aerated conditions, the soil atmosphere contains essentially the same gases as the atmosphere although the proportions of oxygen (O_2) and CO_2 differ from the atmosphere due to soil respiration [44]. Carbon dioxide diffuses into the atmosphere from the soil due to production during respiration and O_2 diffuses into the soil as it is consumed during respiration. The saturation and ponding of flooded soils greatly reduce gas transport between the soil and atmosphere compared to aerated soils and plant-mediated transport of gases by diffusion is often the main exchange mechanism between the soil and atmosphere in saturated or flooded systems [45]. As a flooded soil dries, gases trapped in the soil may escape due to increases in diffusion and convective flow rates that occur as water escapes soil pores.

While solute movement by diffusion may be greater in saturated soils due to an increase in water-filled pore space, diffusion of gases through water is roughly three to four orders of magnitude slower than diffusion of gases through air [46,47]. Both diffusive and convective flow of gases and solutes are related to pore connectivity and tortuosity, so it is expected that movement of gases and solutes are slower in fine-textured soils, such as clays and clay loams, than in coarser-textured soils, such as silt loams and sands, which generally have larger, more connected pores [47]. Convective flow of gases in saturated soils can occur as dissolved gases move with moving soil water, which is dependent largely upon soil texture and structure, and as ebullition, which is where gases escape as bubbles through ponded water [47]. Generally, diffusion dominates gas transport in fine-textured soils, such as clay loams and clays, and diffusion rates typically decrease as particle size decreases, which is due to differences in size, orientation, and shape of soil pore spaces [45,48]. Soil texture also affects the amount of time it takes for a soil to become saturated with infiltration rates in clayey soils estimated to be 1 to 5 mm hr^{-1} compared to 10 to 20 mm hr^{-1} in soils such as silt loams [47]. The amount of time a soil takes to become saturated has an effect on chemical and biological processes that develop as the system becomes anaerobic.

5.2. Soil redox potential

Isolation of flooded soils from the atmosphere and depletion of soil O_2 induces biological and chemical reactions that create anaerobic and reducing conditions rather than the aerobic and oxidized conditions that generally occur in upland soils. Organic matter decomposition slows under anaerobic conditions, but as organic matter is oxidized, transformations such as denitrification and manganese (Mn) and iron (Fe) reduction occur as well as production of gases such as hydrogen sulfide (H_2S) and CH_4. Soil reduction/oxidation (redox) reactions are coupled half-reactions where the oxidation of organic matter, which provides electrons, is coupled with the reduction of elements or compounds that act as electron acceptors [49]. Oxygen is the major electron acceptor under aerobic conditions, but as O_2 is depleted, the sequence of electron acceptors shifts to NO_3^-, MnO_2, $Fe(OH)_3$, SO_4^{2-}, and CO_2, which are theoretically reduced in that order based on thermodynamic favorability [44,50]. The reduced forms of the previously mentioned terminal electron acceptors are H_2O, N_2, Mn^{2+}, Fe^{2+}, H_2S, and CH_4, respectively. Soil redox reactions in a controlled laboratory environment may follow the theoretical sequence, but environmental conditions in the field result in spatial variability of oxidizable organic compounds, electron acceptors, and microorganisms that cause substantial overlap of the terminal electron acceptor sequence [44,49].

Soil redox potential (Eh) is a measure of the electrical potential status of a system that results from the tendency of substances in the system to donate or acquire electrons [51]. Soil redox potential is measured in millivolts (mV) using a platinum electrode along with a mercury chloride (HgCl) or silver chloride (AgCl) reference electrode, both connected to a voltmeter [49]. Combination platinum electrodes are also available that can continuously monitor soil Eh when connected to a logger box. When using AgCl electrodes, a correction factor of approximately +200 mV is added to field-measured voltages in order to adjust measurements to the standard hydrogen electrode [52]. In well-aerated soils, soil Eh may be as great as +700 mV, but Eh values near –300 mV may be observed in saturated organic-matter-rich soils [51]. As a system shifts from aerobic to anaerobic and soil redox potential declines, atmospheric O_2 is reduced first at +380 to +320 mV, followed by NO_3^- (+280 to +220 mV), MnO_2 (+220 to +180 mV), $Fe(OH)_3$ (+110 to +80 mV), SO_4^{2-} (–140 to –170 mV), and CO_2 (–200 to –280 mV), based on measurements by Patrick and Jugsujinda [53].

6. Methane emissions from rice

Methane emissions from any ecosystem, particularly a rice agroecosystem (Figure 1), are governed by the magnitude and balance of microbial CH_4 production (methanogenesis) and oxidation (methanotrophy), which occur by separate microbial communities. The two groups of microorganisms are adapted to different environmental conditions, and, as a result, are affected differently based on the structure and conditions of an ecosystem, which results in variability of CH_4 production and oxidation potentials across time and space [54]. With low CH_4 production rates or long diffusion pathways, it seems that the majority of the CH_4 produced is oxidized. Conversely, in cases where CH_4 production rates are high or diffusion paths are short, less CH_4 is oxidized and a greater portion reaches the atmosphere [54] (Figure 1).

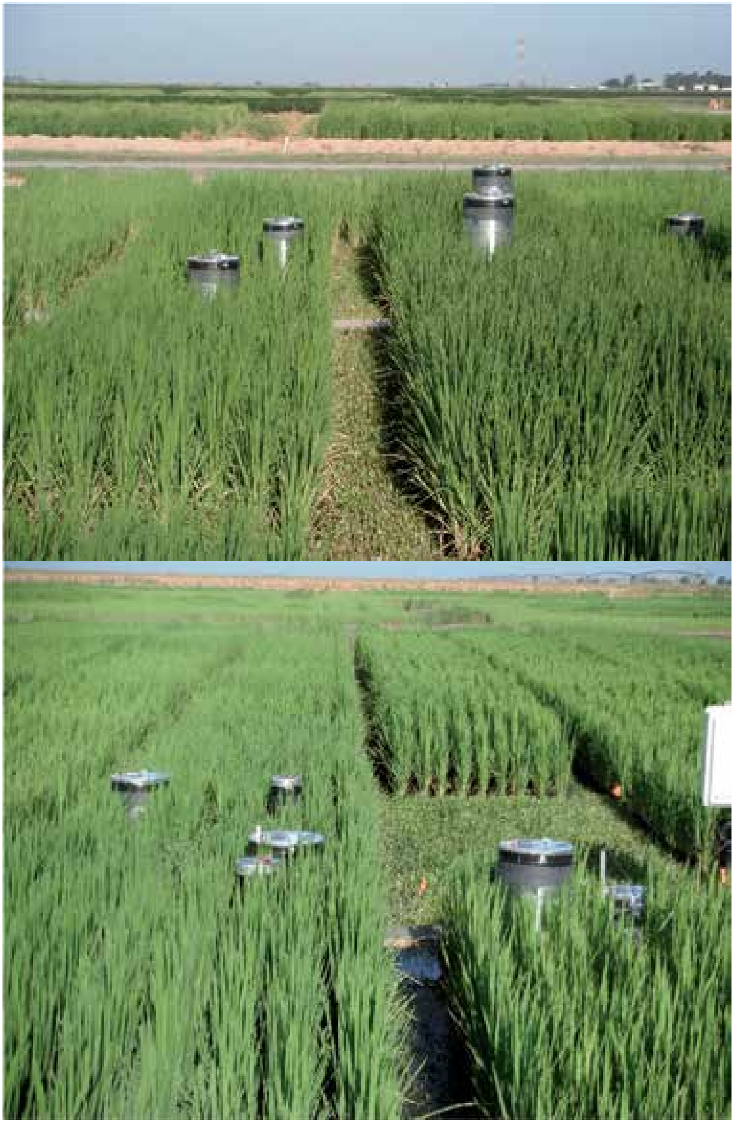

Figure 1. Chamber-based measurements of methane emissions from small plots at the Rice Research and Extension Center near Stuttgart, AR (top), and at the Northeast Research and Extension Center at Keiser, AR (bottom). Photographs taken by K. Brye.

6.1. Methane production and oxidation

Methane production occurs toward the end of a complex anaerobic decomposition process in which soil organic matter (SOM) is degraded to acetate, hydrogen gas (H_2), and CO_2 by a community of various fermenting microorganisms, which are mostly bacteria. Methanogenic *Archaea* are then able to split acetate into CH_4 and CO_2 (i.e., acetoclastic methanogenesis) or utilize H_2 and CO_2 to produce CH_4 (i.e., hydrogenotrophic methanogenesis) [55,56]. Methanogens encompass a large group of strictly anaerobic, obligate *Archaea*, which is currently composed of three classes, six orders, 12 families, and 35 genera [56]. Rice Cluster I is a specific group of methanogens identified by Grosskopf et al. [57] that contains enzymes in order to detoxify highly reactive O_2 species, allowing the methanogens to survive in aerated soils or oxygenated rhizospheres, and occurs preferentially in environments that undergo transient aerobic conditions, such as in rice fields [55,58]. Rice Cluster I has been detected in almost all rice field soils tested [59,60] and occurs in great abundance in rice soils and on rice roots, representing up to 50% of total methanogens in rice fields [61]. Rice Cluster I has been identified as occupying a niche on rice roots by producing CH_4 from photosynthates released as root exudates [55,62]. Recent research has confirmed that methanogens are ubiquitous in aerobic soils and have the ability to produce CH_4 as soon as anoxic conditions form and substrate is available [56]. Conrad [63] reported that methanogens isolated from the soil of rice fields were not killed but only inhibited by high redox potentials or O_2 exposure, allowing them to survive drainage and maintain their population size throughout the year in a state of low activity.

Most methanogens are mesophiles and neutrophiles, with optimal growth occurring between 30 and 40°C and between a pH of 6 and 8 [54]. Methanogens are highly sensitive to variations in temperature and pH and CH_4 production is greatly reduced when soil temperatures are low or in acidic or alkaline soils [56]. Within the optimal temperature range, which is generally the case during the rice growing season, temperature has a positive effect on methanogenesis, causing an increase in CH_4 production as temperature increases [54,56].

Methane oxidation is achieved by a group of aerobic *Proteobacteria* known as methanotrophs, which only utilize CH_4 or methanol as a source of C and energy and are currently classified into two phyla, three orders, four families, 21 genera, and 56 species [56]. One group, known as low-affinity methanotrophs, is capable of oxidizing high CH_4 concentrations (>100 ppm) and exists at oxic–anoxic interfaces, where the methanotrophs consume CH_4 produced in anoxic environments [56]. Another group, known as high-affinity methanotrophs, exists in upland soils and possesses the ability to oxidize CH_4 at low atmospheric levels (<2 ppm) [64]. Unlike methanogenesis, methanotrophy is not impacted greatly by temperature, although CH_4 oxidation is decreased below 10°C and above 40°C, or pH, as similar CH_4 oxidation has been observed in soils with pH values ranging from 3.5 to 8 [56]. Due to the differing effect of temperature on methanogenesis and methanotrophy, CH_4 production increases as soil temperatures increase, while CH_4 oxidation changes little, resulting in a general increase in CH_4 emissions as soil temperature increases throughout the rice growing season. This effect has been confirmed in a laboratory incubation of anaerobic soils at various temperatures between 5 and 25°C [65].

6.2. Substrate for methane production

Available SOM stimulates CH_4 production due to enhanced fermentative production of acetate and H_2/CO_2 and, in principle, CH_4 production could be expected to be proportional to organic C inputs, but the reduction of nitrate (NO_3^-), iron (Fe), manganese (Mn), and sulfate (SO_4^{2-}) all precede methanogenesis and reduce the amount of available C for CH_4 production [54]. Methane production may be stimulated by root exudates [66–68] or the application of animal manures [69], green manures [70–73], or rice straw [67,70,73–75], while the application of composted organic C sources does not greatly increase CH_4 production [73,75,76]. This indicates that the amount of available organic C (OC) is more important in determining CH_4 production than total OC (TOC), as composted residue contains lower amounts of degradable C, on a mass basis, compared to fresh residues [77]. Yagi and Minami [73] and Wang et al. [78] confirmed a positive correlation between CH_4 production and readily mineralizable C, while studies have indicated no clear relationship between soil TOC and CH_4 production [68,79–81]. Research conducted by Denier van der Gon and Neue [76] determined that increasing fresh OM inputs would result in increases in CH_4 production up to a point where another factor becomes limiting; however, fresh green manure inputs up to 20 Mg ha^{-1} still indicated OC limitations. In most rice production situations, organic residue inputs are below 20 Mg ha^{-1} and will generally exhibit an increase in CH_4 emissions as organic inputs increase.

Using ^{13}C-labeled rice straw incorporated at 6 Mg ha^{-1}, Watanabe et al. [82] determined that 42% of season-long CH_4 emissions originated from rice straw C, 37 to 40% from the rice plant, and 18 to 21% from SOM. The contribution of SOM to CH_4 production was fairly consistent over the growing season, while the contribution from rice straw decreased from nearly 90% at 14 days after transplanting to only 11 to 16% during heading and grain fill. In contrast, the contribution of living rice plants to CH_4 production increased over time and amounted to 65 to 70% during heading and grain fill [82]. Chidthaisong and Watanabe [83] also observed that the contribution of rice straw to CH_4 production was greatest at 20 to 40 days after flooding, while plant-derived C became increasingly more influential as the season progressed. The link between root exudates and CH_4 production has been observed directly by Aulakh et al. [84], who showed a positive correlation between TOC in root exudates and CH_4 production. Several others have observed an inverse relationship between grain yield and CH_4 production [19,85], indicating that lower grain yields are accompanied by greater CH_4 production as a result of greater root exudation, which was confirmed by Aulakh et al. [66]. Using ^{13}C-labeled CO_2, it was observed that photosynthates were a major source of CH_4 and accounted for 4 to 52% of CH_4 under field conditions [86,87].

6.3. Duration and timing of methane production

Methane production occurs for some period of time following a period of prolonged saturated conditions and continues until the C substrate becomes limiting or environmental conditions limit methanogenesis (i.e., the soil becomes too cold, hot, or aerated). In flooded soils, the rate of reduction processes is determined by the composition and texture of a soil as well as the content of inorganic electron acceptors [i.e., NO_3^-, MnO_2, $Fe(OH)_3$, SO_4^{2-}] and available C, so the amount of time between flooding a soil and the onset of methanogenesis can vary from several days to several weeks [88]. From the onset of methanogenesis, CH_4 emissions from rice systems generally increase over time as the soil becomes more reduced and usually shows one or more of three general peak flux trends. Early season peak fluxes are generally attributed to decomposition of freshly incorporated residues and generally occur within 20 to 40 days after flooding [83,89] and late-season peaks are thought to result from decomposition following senescence of rice roots [90,91]. The other time period of peak fluxes generally occurs near the time of 50% heading (i.e., approximately the time of anthesis) and has been linked to the sink-source relationship of photosynthates in the plant when CH_4 fluxes have been observed to increase during vegetative growth as root exudates increase and decrease following heading as fixed-C is translocated to developing grain. This plant-related peak has been observed in several studies [15–17,80,92–94,95] and similar seasonal trends have been observed in root growth [96–98], root exudation rates [66], and anaerobic root respiration rates [99].

6.4. Transport mechanisms

The three mechanisms by which CH_4 is transported from a ponded soil to the atmosphere are diffusion through the floodwater, ebullition, and plant-mediated diffusion. Diffusion of CH_4 through overlying floodwater is minor as diffusion of gases is approximately 10,000 times slower through water than through air [46]. Ebullition, bubbles forming and forcing their way to the surface, may be a significant transport mechanism early in the season, especially with high OM inputs, soil disturbances, and in coarse-textured soils, but generally plays only a small role in CH_4 transport, which diminishes as plants mature and plant-mediated transport (PMT) increases [76,100]. The majority of CH_4 emissions from a rice system occur through the rice plants via aerenchyma cells, where studies have indicated that about 90% of season-long emissions are released through the rice plants, compared to 8 to 9% released by ebullition and 1 to 2% by diffusion through the floodwater [100–104].

Based on experiments using artificial atmospheres of various gas compositions, Denier van der Gon and van Breemen [105] determined that PMT is driven by molecular diffusion and not affected by transpiration or stomatal opening. Others have observed a decreasing CH_4 concentration gradient from the soil to the rice root aerenchyma, shoot aerenchyma, and atmosphere, indicative of a diffusive transport pathway from the soil to the atmosphere through the plant [104,106]. Other studies have also confirmed that CH_4 transport is not related to transpiration and is unaffected by cutting plants just above the water surface [103,104,107]. However, Hosono and Nouchi [108] determined that PMT was reduced linearly as roots were cut and increased with root growth up to heading, indicating that the surface area of roots in contact with soil solution is important in determining PMT. Several studies have determined that the most restrictive zone of CH_4 transport through the rice plant is the root–shoot transition zone where dense intercalary meristem cells restrict movement from the root aerenchyma to the shoot aerenchyma [101,105,106,109,110].

It has been postulated that CH_4 in the gaseous form or dissolved in water enters into root aerenchyma, which forms by degeneration of cortical cells between the exodermis and the vascular bundle, where the dissolved CH_4 is gasified and moves by diffusion from the root aerenchyma through the restrictive transition zone into the aerenchyma of the culm and then to the atmosphere [104,107,109]. It has been determined that CH_4 is released from the rice plant mainly through the lower leaf sheaths. Examining the cultivar 'Koshihikari' with a scanning electron microscope, Nouchi et al. [104] and Nouchi and Mariko [107] observed CH_4 release from 4-μm diameter, hook-shaped micropores arranged regularly approximately 80 μm apart on the abaxial epidermis of leaf sheaths as well as from the connections of leaf sheaths to the culm at nodes. Butterbach-Bahl et al. [106] also determined that CH_4 is primarily released through the lower leaf sheaths, however, micropores were not observed in the cultivars 'Roma' or 'Lido'. More research is required to determine differences in CH_4 release from various cultivars. It has been determined that rice cultivars have differences in CH_4 transport capacity, likely in relation to differences in aerenchyma morphology and the root–shoot transition zone [101] and that CH_4 transport capacity increases as soil temperature increases [108]. Research indicates that PMT is the dominant mechanism of CH_4 release from rice soils and that the rate of transport can be influenced by cultivar or environmental conditions.

7. Factors affecting methane emissions from rice

Through numerous research efforts since the 1980s, several factors have been determined to affect CH_4 emissions from rice cultivation. Due to the complex balance of methanogenesis and methanotrophy that determines how much CH_4 escapes the rice system to the atmosphere along with the large variety of cultural and environmental conditions around the globe, there is large variability in the impact of different factors across time and space. There are a few soil, environmental, and plant factors, however, that seem to have somewhat consistent impacts on CH_4 emissions from rice.

7.1. Soil factors affecting methane emissions from rice

Various studies have observed inconsistent results of N fertilizer application on CH_4 emissions including an increase in emissions with added N [85,90,111,112], a decrease in emissions with added N [113,114], or no impact of added N on CH_4 emissions [15,75,115]. Banger et al. [116] conducted a meta-analysis and determined that CH_4 emissions were significantly greater from N-fertilized rice in 98 out of 155 data pairs, indicating that the increase in plant growth and C fixation resulting from N-fertilization generally increases CH_4 emissions. Wang et al. [78] postulated that the effect of urea on CH_4 emissions may be impacted by pH, where it was observed that urea may cause a decrease in emissions in alkaline soils as urea hydrolysis increases soil pH, limiting the neutrophilic methanogens. In acidic soils, however, the increase in pH from urea hydrolysis shifts the soil pH toward neutral and enhances methanogenesis. Research has consistently indicated that ammonium sulfate reduces CH_4 emissions relative to urea application [70,113,116], likely due to the impact of soil acidification and sulfate reduction decreasing the available C substrate for methanogenesis. Similarly, other studies have determined that oxidized Fe [80,117–120] or NO_3^- [120] amendments have the ability to reduce CH_4 emissions. In addition, Lu et al. [121] observed a 19 to 33% reduction in CH_4 emissions with the application of P due to enhanced root growth and root exudation that was measured in the P-deficient treatment.

Multiple studies have indicated no significant correlations between CH_4 emissions and any static soil properties [68,81] or between CH_4 emissions and total soil C [79,80], while readily mineralizable C has been shown to be positively correlated with CH_4 emissions [75,78]. Particle-size distribution is one soil property that has been regularly related to CH_4 emissions as emissions have been positively correlated with soil sand content [78,80,118,119,122] and inversely correlated with soil clay content [71,78,118,119,122,123]. Studies have observed an increase in CH_4 entrapment resulting from increasing clay contents [71,78], and Sass and Fisher [91] attributed the reduction in CH_4 emissions from clay soils to the entrapment and slow movement of CH_4 that allows more CH_4 to be oxidized in aerated zones surrounding roots and at the soil surface. In a laboratory incubation study, Wang et al. [78] observed varying degrees of CH_4 entrapment, even among soils with similar sand and clay contents, where the greatest entrapment (98%) was measured from a Sharkey clay (very-fine, smectitic, thermic Chromic Epiaquerts) soil compared to 81 and 68% entrapment from a Beaumont clay (fine, smectitic, hyperthermic Chromic Dystraquerts) and a Sacramento clay (very-fine, smectitic, thermic Cumulic Vertic Endoaquolls), respectively. This research indicates that clayey soils have the capability of restricting movement of CH_4 to the atmosphere and that other factors, such as clay minerology and soil chemical properties, may impact emissions more than simply the total amount of clay.

7.2. Environmental factors affecting methane emissions from rice

Two major environmental factors that impact CH_4 emissions from rice are temperature and soil saturation status. Numerous studies have observed increases in CH_4 fluxes in relation to increasing soil temperatures [100,108,124]. A study conducted in Japan observed a 1.6-fold increase in emissions from one year to another under the same management and location resulting from an increase in average air temperature from 24.6 to 26.9°C [119]. Methanotrophic activity changes only slightly between 10 and 40°C, while temperature has a strong influence on methanogenesis [56], which leads to a decrease in the proportion of CH_4 oxidized and an increase in emissions as soil temperature increases. Van Winden et al. [65], for example, reported 98% CH_4 oxidation at 5°C compared to 50% oxidation at 25°C.

Soil saturation status has a profound influence on CH_4 emissions through the impact of saturation on soil redox processes, such as methanogenesis. Methane emissions have been observed from soils at an Eh as great as –100 mV [125], while emissions increase as Eh decreases. The amount of time required after saturation to reach low redox potentials conducive to methanogenesis varies based on soil textural and chemical properties [119], but generally occurs within several days or weeks after flooding. Studies have indicated that a single mid-season drainage can reduce CH_4 emissions by as much as 65% [68,70,75,95,113,126], however, the potential for greenhouse gas mitigation is reduced or negated due to an increase in N_2O emissions resulting from the drainage [70,113,126,127]. Further research is needed in order to more adequately understand the balance between CH_4 and N_2O emissions under various water management regimes as well as the impact that N management has on emissions when fields are drained.

7.3. Plant factors affecting methane emissions from rice

Due to the strong impact of rice plants on CH_4 transport and CH_4 production from root exudates and residue, there are several plant factors that significantly impact emissions from rice cultivation. A strong relationship between plant growth and CH_4 emissions has been observed in many studies [16,17,80,92–95], particularly in temperate regions, where much of the previous crop's residue decomposes during the winter. Studies have indicated that CH_4 emissions are up to 20 times greater from soil planted with rice than from unvegetated soil [67,107,123], indicating the large influence of rice plants on emissions.

One of the major plant factors impacting CH_4 emissions from rice is whether or not a ratoon crop is grown. This impact is reflected in the USEPA's emissions factors, which are 178 kg CH_4-C ha^{-1} for non-California primary rice crops and an additional 585 kg CH_4-C ha^{-1} when a ratoon crop is produced [2], based on ratoon crops studied in Louisiana [21,22]. The large increase in emissions from ratoon crops is likely a result of large quantities of residue inputs from the harvest of the primary crop in addition to well-developed root systems that further increase the available C for methanogenesis. Lindau et al. [22] observed a significant positive correlation between rice straw additions from a primary crop and resulting emissions from the following ratoon crop.

Another plant factor that has a substantial impact on CH_4 emissions is biomass accumulation. Huang et al. [128] determined that CH_4 fluxes measured during the growing season were positively correlated to aboveground and belowground dry matter on the dates of flux measurements. Additional studies have observed positive correlations between season-long CH_4 emissions and aboveground [16,72,102,128] and belowground dry matter [129]. These studies have indicated a strong relationship between plant growth and CH_4 emissions, which may result from an increase in available substrate as root exudates have been correlated to biomass [66].

Cultivar selection has also been shown to be an important plant factor influencing CH_4 emissions from rice. While the mechanisms for cultivar differences in CH_4 emissions have not been extensively studied, it appears that differences likely arise from variability in CH_4 transport capacity, biomass or dry matter production, root exudation, and microbial community dynamics among cultivars. Butterbach-Bahl et al. [101], for example, attributed a 24 to 31% difference in emissions between two pure-line cultivars to differences in CH_4 transport capacities, as no differences were observed between CH_4 production or oxidation. Aulakh et al. [84] observed a positive correlation between TOC from root exudates and CH_4 production potential, indicating the potential for cultivar differences in emissions based on variable root exudation rates. Previous studies have reported reduced emissions from semi-dwarf relative to standard-stature cultivars [22,91,130]. The difference in CH_4 emissions between semi-dwarf and standard-stature cultivars observed in these studies may be a result of the positive correlation between dry matter and C exudation rates from roots [84] or between aboveground dry matter and CH_4 emissions [16,72,102,128]. While a reduction in emissions from semi-dwarf cultivars is oftentimes linked to reduced dry matter accumulation, Rogers et al. [93] observed a reduction in aboveground dry matter that was not accompanied by a reduction in emissions. Furthermore, Sigren et al. [130] measured greater emissions accompanied by greater soil

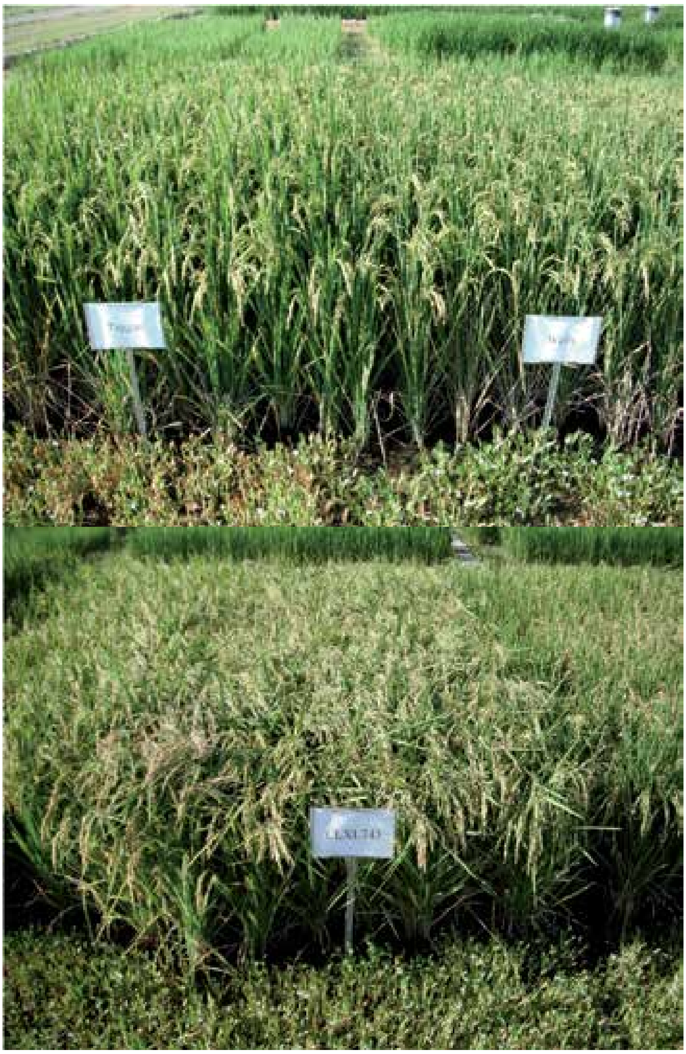

Figure 2. Methane emissions from standard-stature, conventional rice varieties, such as “Taggart” (top left) and “Wells” (top right), and hybrids varieties, such as “CLXL745” (bottom) have recently been studied in the field at the Rice Research and Extension Center near Stuttgart, AR. Photographs taken by K. Brye.

acetate concentrations from a standard stature (‘Mars’) relative to a semi-dwarf cultivar (‘Lemont’), while aboveground dry matter was similar between the two cultivars. Huang et al. [128] indicated that, while biomass may explain differences in emissions within one cultivar, the intervarietal differences in biomass are small in comparison to differences in emissions, indicating that another factor besides aboveground dry matter impacts intervarietal differences in CH_4 emissions.

Cultivar differences, however, extend beyond the impact of biomass production on emissions. Ma et al. [131] observed a 67% increase in CH_4 oxidation from a hybrid cultivar accompanied by a reduction in emissions and soil CH_4 concentration relative to pure-line cultivars. Additional studies have also identified 25 to 37% reductions in fluxes from hybrid relative to pure-line cultivars [93,132,133] (Figure 2). This indicates that greater methanotrophic activity in the rhizosphere of hybrid cultivars may reduce CH_4 fluxes by oxidizing a greater proportion of the produced CH_4. It is clear that cultivar selection has the potential for mitigation of CH_4 from rice cultivation. However, due to the lack of understanding the mechanisms for differences in emissions, it appears that direct CH_4 flux measurements from various cultivars are necessary in determining emissions differences until further research clarifies the understanding for cultivar differences in CH_4 emissions (Figure 2).

8. Conclusions

Though some knowledge has been gained, there is much more that still needs to be learned and understood regarding CH_4 emissions from rice production in the US, its contribution to climate change, and potential mitigation strategies. Additional field research needs to be conducted to better assess the magnitudes and relative contributions the various known factors have on CH_4 production and emission from soils used for rice production.

It is possible that a single CH_4 emissions factor for application to all non-California-grown, primary-crop rice in the US is too general. Consequently, the single CH_4 emissions factor may be a severe overestimation for some rice-producing areas, while being an underestimation for other areas. Only after additional data have been generated can regulatory agencies, such as the USEPA, further refine greenhouse gas emissions factors to reflect the large variety of soils and agronomic cultural practices throughout the temperate US and combat the potential negative effects of climate change.

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Chapter 9

Greenhouse Gases Production from Some Crops Growing Under Greenhouse Conditions

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Additional information is available at the end of the chapter

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Abstract

Greenhouse gases, such as carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4), play an important role in global climate change. For example, CO_2 production occurs as a result of the seasonal cycles of the biotic processes of photosynthesis and respiration, as well as through anthropogenic activities and abiotic processes such as the burning of fossil fuels. Many activities, such as Agribusiness (the production of crops and animals for food) create greenhouse gases. Our research group has studied several soil treatments such as wastewater, wastewater sludge, vermicomposting, and urea among others, in order to study the effects of soil treatments on the production of greenhouse gases (CO_2, N_2O, and CH_4) in several cultivars, but mainly in maize, sunflower and the common bean. The principal aim of this chapter is to show how these greenhouse gases are affected by the type of treatment, the properties of the soil, and the cultivar in question. We also look at which processes are involved in the production of CO_2, N_2O, and CH_4 from cultivated soil. We present a review of several experiments carried out under *in vitro* or greenhouse conditions.

Keywords: Greenhouse gases production, wastewater sludge, fertilizers, treatments

1. Introduction

Global food demand is increasing rapidly, while the associated potential negative environmental impacts are also growing. Land clearance, the intensive use of existing croplands, inadequate agricultural management systems, and soil pollution could all contribute to an increase in the production of greenhouse gases (GHG). Understanding the future environmental impacts of global crop production, while at the same time achieving greater yields with lower impacts, requires quantitative assessments of future crop demand and an understanding of how different production practices affect yields and environmental variables [1].

It is well known that crop management systems, the quality of the soil and the weathering conditions are just some of the factors used in order to assess production of GHG. Therefore, an understanding of the future environmental impacts of crop production is essential in order to achieve greater crop yields without decreasing the quality of the environment and social welfare. Additionally, Tilman [2] reported that the recent intensification of agriculture, coupled with the prospect of even further intensification in the future, will have major detrimental impacts on the world's ecosystems.

Agriculture is rightly recognized as a source of GHG production, with concomitant opportunities for its mitigation. In fact, agricultural soils can constitute either a net source or sink of the three principal GHG [3]. Soil management practices can influence GHG flux by changing at least one of the following soil properties and its associated management: 1) The soil climate (temperature and water content); 2) The physicochemical environment of the soil; 3) The soil's microorganisms (diversity and abundance); 4) The amount and chemical composition of organic or mineral fertilizers applied to the soil; and 5) Pesticides might have a strong effect on the soil microbiota (type and amount). Even a minimal change in one or more of the properties described above could control the rate and extent of GHG production and also affect the aeration and diffusion of these gases.

The objective of this chapter is to discuss how the soil production rate of GHG is affected by treatment type, soil properties, and cultivar. This review will also discuss which processes are involved in the production of CO_2, N_2O, and CH_4 when crops are grown under *in vitro* or greenhouse conditions, and will discuss how these processes work.

2. The Atmosphere, Global Climate Change and Greenhouse Gases

The atmosphere of the Earth has evolved and changed over time and had reached a point of equilibrium. However, anthropogenic activities arising from the Industrial Revolution and subsequent development have changed Earth's atmospheric conditions. Since the industrial era began, a new phenomenon has been observed — that of global climate change (GCC). Many different sources are involved in the production of gases, with concern centering on the production of GHG in particular, as these gases are the ones implicated in the increasing rate of global warming on Earth. The main gases involved in this warming are methane (CH_4), nitrous oxide (N_2O), and carbon dioxide (CO_2). Additional and important GHGs include water vapour, which has an effect on global climate change that can be used as a baseline with which to compare the remaining GHG. The production of these gases arises as a result of anthropogenic activities, mainly the combustion of fossil fuels (CO_2), extensive livestock and cattle farming (CH_4), and agriculture (N_2O) through denitrification or nitrification processes, and occasionally CO_2 depending on the type of fertilization employed.

As we can see, global climate change is a phenomenon caused by GHG that are emitted into the atmosphere. However, the main problem is not the emission of these gases, because these gases have actually been present in the Earth's atmosphere for thousands of years and they are the products of natural processes such as volcanic eruptions, plant and animal respiration and the microbial decomposition of organic matter. The contribution of human activity has resulted in the production of large amounts of these gases and their increased concentration in the atmosphere results in global warming. The most obvious effects of global warming are the continuous increase of global temperature and the changes in atmospheric conditions. All the elements of the environment are interrelated, and as a consequence, changes in one of them lead to changes in others. Sometimes these changes are small and imperceptible, while others can be very obvious. The rate of these changes is very important because if they are too rapid, then the ability of organisms to adapt to the new conditions might not be sufficient to ensure their survival as the natural process of adaptation takes thousands and thousands of years as a part of the evolutionary processes of life on Earth. The effects of these phenomena are the extinction of species and other serious negative effects on both the agriculture and fishing industries that are important economic activities the world over.

It is important to mention that the likely impacts of global warming could be different in different types of ecosystems because of the difference in climatic conditions in those ecosystems, but the effects on the abundance and distribution of biodiversity will be constant. All of these facts suggest that the natural conditions of the planet are being seriously affected by global climate change, global warming and GHG production, so we have a serious and worldwide environmental problem to address. However, there are many strategies, such as the use of alternative sources of energy, which could be implemented around the world to mitigate the damage being caused to the planet and to promote environmental awareness with favorable results in the future.

3. Experiments under *in vitro* conditions

We are interested in understanding which soil processes are involved in GHG production, and how they work, in several treatments or fertilizers. The production of CO_2, N_2O, and CH_4 when crops were grown under *in vitro* or greenhouse conditions was studied. These experiments were carried out using different types of soil (nitrogen depleted and/or alkaline-saline) and several crops were studied.

One of the experiments was conducted in order to investigate the evolution of nitrogen and its loss as a part of the nitrogen cycle. Different fertilizers or treatments were tested. These were ammonium sulphate [$(NH_4)_2SO_4$, 200 mg NH_4^+ kg^{-1}], wastewater sludge (200 mg NH_4^+ kg^{-1}), sterile wastewater sludge (200 mg NH_4^+ kg^{-1}) and a control (distilled H_2O). All of the treatments were added with KNO_3 at 100 mg N kg^{-1}, in two different soils (one agricultural and N depleted soil, and the second a saline-alkaline and N depleted soil) at 40% of water holding capacity (WHC) under *in vitro* conditions for 56 days. The variables were CO_2, N_2O, NH_4^+-N, NO_2^--N, and NO_3^--N, and were measured and assessed [4]. The soils used were specifics, i.e. the first soil was an agricultural soil which had mainly been cultivated with maize (> 25 years), low fertilization (< 50 kg N ha^{-1}) and was both C and N depleted (6.5 g organic C kg^{-1}, 0.2 g total N

Kjeldahl kg^{-1}, pH 7.8, electrolytic conductivity (EC) 1.0 dS m^{-1}, and the textural soil classification was loamy sand) from Otumba, in the State of Mexico (Mexico) (19° 42′ N, 98° 49′ W). The second soil was classified as an uncultivated soil (some grasses and small trees could be found) as a result of its former lake bed origin. It was found to be N depleted and alkaline-saline, pH 10.3, EC 12.4 dS m^{-1}, 49 g organic C kg^{-1}, and 0.6 total N Kjeldahl kg^{-1}, from Texcoco, State of Mexico (Mexico) (19° 30′ N, 98° 53′ W). The results showed that production of CO_2 from the Otumba soil was not affected by the addition of NH_4^+ or NO_3^-, i.e. both fertilizers produced a similar amount of CO_2, approximately 350 mg CO_2-C kg^{-1} dry soil. The sterilized sewage sludge increased the production of CO_2, > 1,000 mg CO_2-C kg^{-1} dry soil, i.e. over twice the production compared with that of the controls (soils treated with ammonium or nitrate). When wastewater sludge was added, the CO_2 production was ~ 3,100 mg CO_2-C kg^{-1} dry soil, a value twice that of sterilized sludge and eight times that of the controls. In the Texcoco soil, a similar contour was found in the CO_2-C dynamics. The control treatments present > 350 mg CO_2-C kg^{-1} dry soil. The soil treated with sterilized sludge showed a concentration of CO_2 that was > 1,100 mg CO_2-C kg^{-1} dry soil (2.1 times that of the controls) while the treatment with sewage sludge was ~ 2,100 mg CO_2-C kg^{-1} dry soil (over five times that of the controls). Different soils showed similar contours in C dynamics, and these results revealed that CO_2 production was not particularly different and that the processes involved were rather similar in the different soils investigated. Wastewater sludge is characterized by large amounts of organic matter (organic C) and it's suppose got a large amounts of organic matter easily decomposable. So, the sludge is easily and rapidly mineralized in both soils [4]. When sewage sludge was sterilized, the microbiota were destroyed and this might have affected the properties of the organic matter in the sludge [4]. It could be that the organic matter was more readily accessible for the soil microorganisms, so that the production of CO_2 should be higher in soils with sterilized sludge, but the results revealed that this is not necessarily true. The results also showed that the soil microorganisms and the sludge microorganisms could be exerting a synergistic action on the degradation of organic matter because the degradative action of the microorganisms of the soil or the sludge alone cannot improve the degradation of organic matter in the treated soil or in the sludge [4].

The ammonium dynamics showed that the initial concentrations of N were reduced after the first 3 days, and after that, a release of the mineral occurred from day 3 up to day 14. Later still, the concentration of ammonium decreased by up to < 14 mg N kg^{-1} dry soil for all the treatments in both the Otumba and Texcoco soils, and the ammonium concentration decreased by up to < 2 mg N kg^{-1} dry soil for all treatments, except for the soil treated with sterilized sludge, < 31 mg N kg^{-1} dry soil. The contour of the ammonium dynamics was similar in both the Otumba and Texcoco soils. Many abiotic and biotic processes might affect the concentration of NH_4^+ in soil, such as NH_4^+ fixation in the soil matrix, volatilisation of NH_3, and immobilization or oxidation of NH_4^+. Some soil processes were occurring at too low a level to be detectable, such as NH_4^+ fixation and the volatilisation of NH_3. The nitrate dynamics were similar in both soils. The concentration of NO_3^- was ~120 mg N kg^{-1} dry soil in the control treatment in both soils. The ammonium concentration was similar in both soils, > 200 mg N kg^{-1} dry soil, treatments with sludge reached > 255 mg N kg^{-1} dry soil and > 300 mg N kg^{-1} dry soil in the Texcoco and Otumba soils respectively, and soils treated with sterilized sludge increased the concentration to > 300 mg N kg^{-1} dry soil in the Texcoco soil, while in the Otumba soil it was > 325 mg N kg^{-1} dry soil. These results suggest that soil fertilized with wastewater sludge showed an increased NO_3^- concentration with a hypothetic mineralisation of ~ 60% at day 56 [4].

The production of N_2O was measured in both soils for seven days under C_2H_2 (10% v/v) conditions. The control treatment showed a N_2O production of < 0.02 mg N kg^{-1} with or without C_2H_2 in the Otumba soil. N_2O production increased when ammonium was added to the Otumba soil, 0.04 mg N kg^{-1}, but the addition of C_2H_2 reduced it to 0.01 mg N kg^{-1}. When the sterilized and non-sterilized sludge were added to the Otumba soil, N_2O production increased to 1 mg N kg^{-1} dry soil without C_2H_2 and 0.49 mg N kg^{-1} dry soil with C_2H_2. In the Texcoco soil, the control treatment was below 0.005 mg N kg^{-1} dry soil, but when C_2H_2 was added an increase to 0.09 mg N kg^{-1} dry soil was observed. Soil treated with ammonium increased the production of N_2O (0.04 mg N kg^{-1}), but under C_2H_2 conditions the concentration was low at 0.01 mg N kg^{-1} dry soil when compared with the control treatment. Soils treated with sterilized and non-sterilized sludge increased the production of N_2O (2.1 mg N kg^{-1} and 0.75 mg N kg^{-1}) compared with the control treatment, however, the addition of C_2H_2 increased the N_2O concentration of soil treated with sludge (2.1 mg N kg^{-1} dry soil) compared with soil treated with sterilized sludge (1.8 mg N kg^{-1}). It could be argued that the addition of easily decomposable organic matter into the soil will induce the denitrification process, where NO_3^- is reduced to N_2O and N_2 as final products. There are factors that could be important in controlling the production of N_2O in denitrification, such as oxygen, pH and the ratio of nitrate / available carbon [5]. There are additional parallel factors for NO that are less well understood [5]. It was evident that in a soil treatment of wastewater sludge or sterilized sludge, the N loss was increased. The microorganisms from the soil and the sludge were found to be working together in order to degrade the organic matter in the sludge. In addition, it could be suggested that more denitrifiers may be present in the Texcoco soil than in the Otumba soil, and a decrease of 50 mg NO_3^--N was counted at day 56, and the N_2O concentration was approximately double (plus 1 mg N_2O kg^{-1} dry soil) that of the Otumba soil on the day 7 [4]. When NO_3^- (an e^- acceptor) is present in excess compared to organic C (an e^- donor), the denitrifiers could be said to be "spendthrift" with respect to NO_3^- and in general produce N_2O as the major product. When the same NO_3^- is limited, the denitrifiers use it to its maximum potential as an e^- acceptor and reduce it all to N_2 (dinitrogen) [5]. Schimel and Holland (2005) explain that while the major producer of NO is nitrification, N_2O can also be produced in large quantities by nitrification or denitrification due to the fact that it is less reactive and can outflow from soils — even wet soils.

In our study, the microorganisms in the soil and sludge acted together synergistically in the reduction process, i.e. N_2O to N_2, the denitrification process, and in the Texcoco soil under C_2H_2 conditions, but the main contribution was from the soil microorganisms under the same conditions. In particular, the production of N_2 was almost 50% of the total gas evolved. When sterilized sludge was applied to the Texcoco soil, minimal N_2 was produced (~0.2 mg N_2O-N kg^{-1}). Furthermore, untreated soil showed an increase in N_2O when C_2H_2 was added (~0.07 mg N_2O-N kg^{-1}) and the N_2 produced was approximately 75% of the total gas evolved, under the conditions established. In the Otumba soil, the N_2O was produced by nitrification process (at

40% WHC), and showed in the soil treated with ammonium, sludge and sterilized sludge at 0.04, 1.0, and 1.0 mg N_2O-N kg^{-1} respectively, when compared with untreated soil. N_2O production was low when C_2H_2 was added to the Otumba soil, and no N_2 was produced under these conditions. It can be established that when organic matter with a high N content is added to soil, it significantly increases N_2O production compared to untreated soil or soil fertilized with ammonium [$(NH_4)_2SO_4$] in both soils (an ordinary soil and an alkaline-saline soil). The major source of production of N_2O was found in all treated soils to be as a result of the nitrification process, and the production of N_2 was not recorded in the Otumba soil in this experiment. In the Texcoco soil, the major source of production of N_2O was as a result of the denitrification process by microorganisms in the soil, and the production of N_2 was approximately 50% of the total gas evolved (1.1 mg N_2O-N kg^{-1}).

4. Experiments under greenhouse conditions

4.1. First experiment under greenhouse conditions

Subsequent studies were established in order to better understand plant growth and the production of GHG (CO_2 and N_2O) when a regular *Bacillus subtilis* strain was inoculated on the surface of the sunflower (*Helianthus annuus* L.) cultivar seeds under greenhouse conditions. The *B. subtilis* strain was characterized as PGPR, i.e. showing antagonistic activity against *Fusarium oxysporum* and *Rhizoctonia solani* AG1, phosphate solubilizing activity, 1-aminocyclopropane-1-carboxilate deaminase, and indole-3-acetic acid production. The strain was found as regular PGPR, for more details see [6].

The soil was collected from Alcholoya (Acatlán, in the State of Hidalgo, Mexico). This soil is an agricultural soil with a pH of 6.5, electrolytic conductivity (EC) 0.7 dS m^{-1}, 846 g kg^{-1}, organic C content was 11.1 g C kg^{-1} soil, and total N content 1.0 g N kg^{-1} soil. The soil was sampled from three different plots (400 m^2), ~ 800 kg was obtained and each plot was pooled separately and passed through a 5 mm sieve. Thirty-six sub-samples of 6.5 kg of soil from each plot were placed in cylindrical pots (Ø = 16 cm, 50 cm) with 7 cm of gravel in the bottom. Four treatments were applied, with nine pots for each of the three soil sites sampled ($n = 27$). The first treatment was unfertilized and uncultivated soil (used as the CONTROL treatment), the second treatment was unfertilized soil cultivated with sunflowers (SUNFLOWER treatment), the third treatment was soil cultivated with sunflowers and fertilized with 0.5 g urea (75 kg N ha^{-1}, UREA treatment), and the fourth treatment was soil cultivated with sunflowers (seeds were dressed with *B. subtilis*) and fertilized with 0.5 g urea (BS treatment). All treatments were irrigated with tap water, with an additional input of 19 kg mineral-N ha^{-1} as NO_2^--N and NO_3^--N. In addition, twelve days after the emergence of the plantlets, they were fertilized with another 0.5 g of urea (the UREA and BS treatments), giving a total amount of 150 kg N ha^{-1}; and three weeks after sowing the plantlets were drenched with 4 mL of a bacterial suspension (at the same concentration as described above) adjacent to the plantlet roots at a depth of 3 cm. From the beginning of the experiments and approximately every two days for the following 30 days, the pots were closed air-tight and their atmosphere was analysed for CO_2 and N_2O at times of 0, 3, 15 and 30 mins. The experiment was repeated twice [6].

The daily CO_2 production rate for some treatments was large at the beginning of the experiments (data not shown). The daily CO_2 production rate showed a drop, remaining < 5 mg C kg^{-1} day^{-1} on day 2 and after that it remained at < 8 mg C kg^{-1} day^{-1} for all treatments up to end of the experiments. The mean CO_2 production rate was not significantly different between treatments. The daily N_2O production rate remained ≤ 0.75 μg N kg^{-1} day^{-1} for the SUNFLOWER and CONTROL treatments. Meanwhile, in the BS and UREA treatments, the daily N_2O production rate remained ≤ 2.1 μg N kg^{-1} day^{-1} with a maximum score of production in the first 14 days. The mean of the N_2O production rate of BS treatment was significantly high when compared with the SUNFLOWER and CONTROL treatments. Cultivating soil with sunflowers (SUNFLOWER treatment) did not affect the production of CO_2 compared with the CONTROL treatment (uncultivated soil). It is well known that cultivated soil frequently increases the production of CO_2, possibly due to the activities of the microorganisms degrading the easily decomposable organic matter such as the dying roots and root exudates in the rhizosphere, thereby increasing the production of CO_2 from the soil. Soils cultivated with sunflowers and fertilized with urea did not affect the production of CO_2. Applying urea to soil commonly has no effect on the production of CO_2 from soils. However, the production of CO_2 might be stimulated when urea is applied to N depleted soil as reported in Phillips and Podrebarac (2009), where the CO_2 production was tripled when 112 kg urea-N kg^{-1} was applied to an arable soil. Increases in CO_2 production with several doses of urea-N application indicate that agronomic-scale N inputs might stimulate microbial carbon cycling in arable soils [7]. The inoculation of *B. subtilis* on sunflower roots in soils fertilized with urea did not show any effect on the production of CO_2 compared with the UREA treatment. The application of UREA to the soil resulted in more than a doubling of the mean N_2O production rate when compared with the CONTROL treatment. The production of N_2O and NO in the soil is the result of factors such as ion concentrations and soil conditions under chemical disequilibrium, i.e. the oxidative process of NH_4^+ to NO_3^- under aerobic conditions, nitrification, and a reductive process of NO_3^- to N_2 under anaerobic conditions, and denitrification or the nitrifier denitrification [5, 8, 9]. According to the IPCC, N_2O is the main gas produced and released to the atmosphere by soil microorganisms [9]. So, when urea is applied into the soil, hydrolysis of the urea is immediately started, releasing NH_4^+ into the soil, which is rapidly transformed to NO_3^- with the simultaneous production of N_2O by the same process. A high concentration of NO_3^- in soil favours the production of N_2O due to the presence of anaerobic micro-sites in highly compacted soil.

A principal component analysis (PCA) was undertaken to investigate several plant biometric parameters and soil properties in the production of N_2O and CO_2. The analysis was carried out to include all variables. The PCA revealed that BS treatment has an effect on the shoots of plants, i.e. the shoot length, dry weight of shoot, and the fresh weight of shoot. UREA treatment has an effect on roots, i.e. the dry weight of roots, length of roots, and fresh weight of roots, and a minimal effect on seed weight. Otherwise, the soil properties PCA showed that both the BS and UREA treatments had an effect on NO_3^- and EC at depths of 0-15 cm and 15-30 cm. The

BS treatment also has effect on the production of N_2O and the UREA treatment has an effect on NH_4^+ at a depth 0-15 cm and a slight effect on CO_2 production. These results were found to correspond with a production rate of N_2O that was ≤ 2.1 μg N kg^{-1} day^{-1} with a maximum production in the first 14 days of more than that in the UREA treatment (< 1.5 μg N kg^{-1} day^{-1}). Additionally, the PCA showed that *B. subtilis*, as a regular strain, had a marked effect on the production of N_2O but not on CO_2 production. This strain might be involved in nitrifier denitrification (or aerobic nitrification-denitrification) as was reported by Kim et al. [10] and Yang et al. [11]. Both research groups demonstrated that the *Bacillus* genus is involved in nitrification and denitrification, namely *B. subtilis*, *B. cereus* and *B. licheniformis*, where *B. subtilis* is involved in the nitrification process and *B. licheniformis* is involved in denitrification or aerobic denitrification [10]. Yang et al. reported that the strain of *Bacillus subtilis* A1 is an aerobic heterotrophic nitrifying–denitrifying bacterium, which is able to convert NH_4^+ to N_2 under fully aerobic conditions, while growing either autotrophically or heterotrophically [11]. In our experiment, the environmental condition of the soil was aerobic throughout the experiment, so it could be hypothesized that the *B. subtilis* strain could be involved in the nitrification process or the nitrifier denitrification process (or aerobic denitrification).

4.2. Second experiment under greenhouse conditions

The second experiment was carried out using wastewater sludge as an organic fertilizer. It tested the effect of the sludge or urea on sunflower growth, and the effect of some soil properties on the production of CO_2 and N_2O. The plant characteristics were also evaluated. Wastewater sludge or sewage sludge is generated during wastewater treatment and is an unavoidable by-product. However, the sludge can be seen as an invaluable by-product when it is applied to the soil as stabilized sludge. Also, this waste management is the most economical form of disposal employed to reduce the large amount of sewage sludge. In addition, wastewater sludge is organic matter rich in minerals and is an outstanding source of C and N, *inter alia*. Applying sludge to the soil offers the opportunity of recycling nutrients for use by plants, while at the same time returning C as organic matter to the soil in order to improve agriculture processes.

This experiment was carried out in the same way as the previous experiment (described above). The wastewater sludge was collected from the Reciclagua treatment plant, S.A. de C.V., where wastewater from various industries (including the food industry) and households is treated. The properties of the sewage sludge were pH 8.1, EC 7.9 dS m^{-1}, water content 847 g kg^{-1}, organic C content 288 g kg^{-1}, total N content 41.8 g kg^{-1}, NH_4^+ 13 g N kg^{-1}, NO_2^- 8.3 mg N kg^{-1}, and NO_3^- 122 mg N kg^{-1}. For more details of these, see [12]. Four treatments were established in cylindrical pots, comprising nine soil samples from three sampled plots ($n = 27$). The treatments were: i) unfertilized and unsown soil (CONTROL treatment), ii) unfertilized soil cultivated with sunflowers (SUNFLOWER treatment), iii) cultivated soil fertilized with 0.5 g urea (0.5 g urea × 2 applications, equivalent to 150 kg N ha^{-1}, UREA treatment), and iv) soil cultivated and fertilized with 30 g sludge (SLUDGE treatment). The sludge was added so as to be equivalent to 150 kg N ha^{-1}, assuming that sludge mineralisation was 40% mineral N during the crop cycle. Tap water supplied a total amount of 19 kg mineral-N ha^{-1} through irrigation in all treatments and throughout the experiment. In order to measure the production of gases, the pots were closed airtight approximately every two days for the first 30 days, and their atmospheres were analysed for CO_2 and N_2O at sequential times of 0, 3, 15 and 30 mins. The experiment was replicated twice [12].

The results showed that the CONTROL, SUNFLOWER and UREA treatments were not significantly different with respect to the production rate of CO_2 (1.59, 2.03 and 2.6 mg C kg^{-1} day^{-1}, respectively) (Table 1). The CO_2 production rate of sunflowers cultivated in soil fertilized with sewage sludge (SLUDGE treatment) was 2.96 mg C kg^{-1} day^{-1} and was significantly different compared with the CONTROL treatment. In other words, soil cultivated and fertilized with sewage sludge was equivalent to both the soil cultivated and fertilized with urea, and the unfertilized soil. It should be taken in account that several factors affect CO_2 production in the soil, such as rhizosphere respiration and soil microbial respiration, soil moisture, soil temperature, substrate quantity and quality, vegetation type, and land use and management regimes [13].

Treatment	CO_2 mg C kg^{-1} day^{-1}	N_2O μg N kg^{-1} day^{-1}
CONTROL	1.59 B	0.18 B
SUNFLOWER	2.03 AB	0.27 B
UREA	2.60 AB	0.66 B
SLUDGE	2.96 A	2.50 A
Least significant difference	1.14	0.74
Standard error of estimate ($P < 0.05$)	0.41	0.26

Values with the same letter show no significant difference between treatments ($P < 0.05$).

Table 1. The production rates of CO_2 and N_2O from soil cultivated with *H. annuus* under greenhouse conditions.

On the other hand, the rate of production N_2O was significantly different in cultivated soil fertilized with sludge, 2.5 μg N kg^{-1} day^{-1} compared with the remaining treatments, 0.7, 0.3, and 0.2 μg N kg^{-1} day^{-1} for the UREA, SUNFLOWER, and CONTROL treatments respectively. As previously discussed, wastewater sludge is an organic matter which is rich in easily decomposable material. In addition, it has been demonstrated that microorganisms from the sludge plus those from the soil work together synergistically to accelerate the decomposition of organic matter [6]. The high levels of microbial activity stimulated by the addition of material with high C and N contents could increase the production of both CO_2 and N_2O. According to Kool et al. [9], the loss of N in our experiment might primarily be as a result of the nitrifier nitrification process (from ammonium oxidation) followed by the nitrifier denitrification process. As a result, the wastewater sludge had a NH_4^+ concentration of 13 g N kg^{-1}, an amount of ammonium which might not be oxidized to N_2O so rapidly. The chemical composition of organic or mineral fertilizers — or even residues applied to the soil — is an important factor in regulating the magnitude of N_2O production.

A PCA was performed on all relevant properties of the soil. The first principal component explained about 22% of the observed variation, while the second accounted for 17% of the observed variation. On the related scatter plot, the UREA treatment lies in upper right quadrant and the SLUDGE treatment is in the upper left quadrant. The SUNFLOWER and CONTROL treatments were found in lower left and right quadrants respectively (Figure 1).

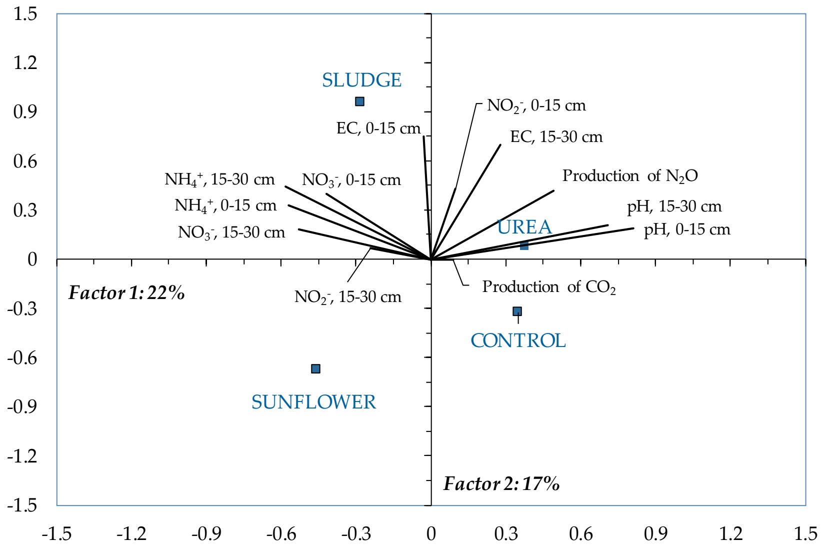

Figure 1. Results of a principal component analysis (PCA) performed on soil properties under greenhouse conditions ($n = 27$).

The UREA treatment seems to have an effect on the pH of soil at both depths (0–15 and 15–30 cm) and also affects the production of CO_2 and N_2O. The PCA also revealed that the SLUDGE treatment affected EC at a depth of 0–15 cm and had a slight effect on both ammonium and nitrate concentrations at both depths.

4.3. Third experiment under greenhouse conditions

In this study, the effect of urea, wastewater sludge and vermicomposting on the production of CO_2 and N_2O was investigated. The Otumba soil (State of Mexico, Mexico), which was characterized as a sandy loam with pH 7.6, EC 1.15 dS m^{-1}, and an organic C content of 7.2 g C kg^{-1}, was used in this study. Wastewater sludge was again collected from Reciclagua S.A. de C.V. (as described above). The vermicompost was prepared with wastewater sludge from Reciclagua and *Eisenia fetida*. The vermicompost was obtained from a mixture of sludge (1,800 g) and manure (800 g) with 70% water content, and was added to 40 individuals of *E. fetida* with the mixture being conditioned over three months. The properties of the vermicompost were pH 7.9, EC 11 dS m^{-1}, organic C content 163 g kg^{-1}, and a total N content of 2 g kg^{-1}. As well, the vermicompost presented < 3 CFU g^{-1} *Salmonella* sp., no *Shigella* sp., and no helminth ova.

Forty-five sub-samples of 3.25 kg soil were prepared, i.e. three soil samples, three replicates, and five treatments were established. The treatments were: i) soil fertilized with 0.07 g urea kg^{-1}, (UREA treatment), ii) soil fertilized with 21.2 g sewage sludge kg^{-1} (H-SLUDGE treatment), iii) soil fertilized with 12.8 g sewage sludge kg^{-1} (L-SLUDGE treatment), iv) soil fertilized with 81.5 g vermicompost kg^{-1} (VERMI treatment), and v) unfertilized soil (CONTROL treatment). The amount of urea was 80 kg N ha^{-1} for the UREA, H-SLUDGE, and VERMI treatments, while the L-SLUDGE treatment was 48 kg N ha^{-1}. The production of CO_2 and N_2O was analysed every two days at 0, 3, 15 and 30 mins, until day 97. The cultivar of common bean used was Negro-8025 (from Universidad Autónoma Chapingo, Texcoco, State of Mexico). Tap water was used for irrigation at a rate of 500 mL every seven days. The experiments were triplicated and ran for 117 days in total.

A large amount of CO_2 was recorded at the end the experiment (from day 45 until day 82). The UREA treatment had no significant effect on CO_2 production when compared with the CONTROL treatment (0.043 mg C kg^{-1} dry soil). Wastewater sludge was found to increase the mean production of CO_2 in the soil at 0.064 mg C kg^{-1} compared with the untreated soil, and the VERMI treatment showed the largest mean CO_2 production at 0.1 mg C kg^{-1}. Urea had no significant effect on CO_2 production when compared with the CONTROL treatment. Occasionally, urea might stimulate the production of CO_2 in N depleted soils. Wastewater sludge increased CO_2 production through the mineralization of organic C and the increasing of microbial activity in the rhizosphere. Similarly, vermicomposting stimulated plant growth and increased root exudates and microbial activity in the rhizosphere. The high levels of CO_2 produced towards the end of the experiments could be related to rapid root growth and the beginning of root decomposition. For example, common bean plants at 49 days after sowing (flowering and nodule senescence begins) showed a decrease in the number of nodules, and their nodule cell walls slowly became thinner and degraded [14] thereby improving the environment for the growth of microorganisms and increasing the production of CO_2 towards the end of the experiments.

The mean production of N_2O was -0.004 μg N kg^{-1} in the CONTROL treatment. Soil fertilized with urea increased the mean production of N_2O to 0.015 μg N kg^{-1}. Wastewater sludge increased the mean production to 0.11 μg N kg^{-1} and 0.58 μg N kg^{-1} in the L-SLUDGE and H-SLUDGE treatments respectively, and the vermicompost mean was 0.32 μg N kg^{-1} dry soil. N_2O production in order of effect size of treatment was: wastewater sludge (H-SLUDGE) > vermicomposting > wastewater sludge (L-SLUDGE) > urea > unfertilized soil. Nitrifier nitrification and nitrifier denitrification were presumably the processes that contributed the most to the production of N_2O under aerobic conditions.

4.4. Fourth experiment under greenhouse conditions

Juárez-Rodríguez et al. applied the sludge derived from anaerobically digested cow manure in the production of biogas (methane-air), to maize (*Zea mays* L.) cultivated in a nutrient-low, alkaline-saline soil with EC 9.4 dS m^{-1} and pH of 9.3. The results showed that the CO_2

production increased 3.5-fold in the soil cultivated with maize and sludge, and increased 3.1-fold after the sludge was added to the soil. The production of CO_2 from soil cultivated with maize showed a 1.6-fold increase compared with the uncultivated and unfertilized soil, 1.5 mg C kg^{-1} day^{-1}. N_2O production was -0.0004 μg N kg^{-1} soil day^{-1} in unfertilized soil, and in soil cultivated with maize was 0.3 μg N kg^{-1} day^{-1}. Soil treated with sludge increased the production of N_2O up to 4.6 μg N kg^{-1} soil day^{-1}. Nevertheless, it was found that cultivated soil produced 2.4 μg N kg^{-1} soil day^{-1}, reducing N_2O production. It was also found that applying the anaerobically digested cow manure stimulated the growth of maize cultivated in an alkaline and saline soil, and the production of CO_2 and N_2O was increased.

4.5. Fifth experiment under greenhouse conditions

In this study, the main aim was to investigate how maize fertilized with wastewater at 120 kg N ha^{-1} affected crop growth, soil properties and the production of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) compared with plants fertilized with urea [16].

The soil was collected from the Mezquital Valley, located near Pachuca in the State of Hidalgo (Mexico). The irrigation water used was slightly alkaline with a pH of 8.4. The experiment was carried out under greenhouse conditions. Soil collected from three sub sites was placed into cylindrical pots. Five treatments were established in order to study the effect of wastewater and urea on the cultivation of maize (*Zea mays* L.). The treatments were: a) SMWW, maize plant plus wastewater; b) SMUREA, maize plant plus urea as fertilizer; c) SUREA, uncultivated soil and urea as fertilizer; d) SWW, uncultivated soil plus wastewater; and e) SCONTROL treatment, soil plus tap water. Soils from the SMWW and SWW treatments were irrigated with 1000 mL of wastewater every 7 days from the first day onwards, making a total of 13 times overall. This means that a total amount of mineral N equivalent to 120 kg N ha^{-1} was added to each maize plant, i.e. the recommended amount of N fertilizer for maize.

The concentration of NH_4^+ was larger in the soil treated with urea and wastewater than in the untreated soil, as the urea was hydrolysed and the wastewater contained high concentrations of NH_4^+. The addition of wastewater to the soil doubled the production of CO_2 and approximately 0.2 g C was produced from the soil due to the decomposition of the wastewater after 70 days. In other words, 34% wastewater C was mineralized. However, urea may only occasionally stimulate CO_2 production when a soil is N depleted. Plants take CO_2 from the atmosphere, but mineralization of root exudates increases the production of CO_2. The production of CO_2 increased towards the end of the period of maize growth. This indicated that the phenological stage of the plants affected CO_2 production. The growth of maize plants was similar under the SMWW (wastewater) and the SMUREA (urea) treatments, even when the release of nutrients was delayed by mineralisation from the organic matter in the wastewater. When wastewater was applied to the soil, the mean production rate of CO_2 increased significantly at 2.4-fold, 1.7 μg C kg^{-1} h^{-1}, compared with the SCONTROL treatment at 0.7 μg C kg^{-1} h^{-1} (Table 2). Meanwhile, cultivating maize increased CO_2 production 3.2-fold, 5.6 μg C kg^{-1} h^{-1}. The SWW, SMWW or SUREA treatments did not show a significant difference in the production of N_2O compared with the SCONTROL (1.5×10^{-3} μg N kg^{-1} h^{-1}). The addition of urea did not affect the CH_4 oxidation rate (0.1×10^{-3} μg C kg^{-1} h^{-1}), nor did the SMUREA treatment (cultivated soil fertilized with urea), but the addition of wastewater to the soil significantly increased CH_4 production to 128.4×10^{-3} μg C kg^{-1} h^{-1}. Soil irrigated with wastewater increased the global warming potential (GWP) up to 2.5-fold compared with the SUREA treatment (soil plus urea), whereas cultivated soil increased the GWP 1.4-fold. Crops irrigated with wastewater might limit the use of N fertilizer and water from aquifers. Nevertheless, the amount of fertilizer applied must be limited due to nitrate (NO_3^-) leaching and the production of CO_2, N_2O and CH_4 – that they could be produced in significant amounts –, and at the same time the salt content of the soil will accumulate, limiting the growth of the crop.

Soils can be either a net sink or a net source of CH_4, depending on several factors such as the moisture level, N level, and the nature of the ecosystem in question. Methane is used up by methanotrophic microorganisms, which are ubiquitous in several soils, and is produced by methanogenic microorganisms in the soil under anaerobic conditions. Agricultural systems are not normally large sources or sinks of CH_4. Only under certain conditions are they sources of CH_4 — after application of manure or other organic materials, or moderate to high levels of irrigation. Our results showed that soil irrigated with wastewater — with or without maize — increased CH_4 production significantly (SMWW and SWW treatments) particularly after irrigation, due to temporary anaerobic conditions.

Treatment	**CO_2 (μg C kg^{-1} h^{-1})**	**N_2O (μg C kg^{-1} h^{-1})**	**CH_4 (μg C kg^{-1} h^{-1})**	**GWP [a] (g C kg^{-1} soil)**
SMWW	5.6 A[b]	2.8×10^{-3} A	163.6×10^{-3} A	1.97
SMUREA	4.95 A	4.5×10^{-3} A	8.4×10^{-3} C	1.44
SUREA	0.9 C	3.3×10^{-3} A	0.1×10^{-3} C	0.36
SWW	1.7 B	2.5×10^{-3} A	128.4×10^{-3} B	0.90
SCONTROL	0.7 C	1.5×10^{-3} A	1.5×10^{-3} C	0.26

[a] The global warming potential (GWP) of the gases produced was calculated considering CO_2 production equivalent to 310 for N_2O, 21 for CH_4 and 1 for CO_2 (IPCC, 2007) over a 90-day period, minus the C that was stored in the roots per kg soil.

[b] Values with the same letter show no significant difference between treatments ($P < 0.05$).

Table 2. Production of greenhouse gases, CO_2, CH_4 (μg C kg^{-1} soil h^{-1}), and N_2O (μg N kg^{-1} soil h^{-1}) from five treatments: a) soil + plant + wastewater (SMWW), b) soil + plant + urea (SMUREA), c) soil + urea (SUREA), d) soil + wastewater (SWW), and e) soil + water (SCONTROL).

Fertilizing maize with urea or wastewater had a similar effect on plant growth, so wastewater might be useable as a crop fertilizer. The treatments with urea or wastewater had no effect on the pH of soil in this experiment due to the fact that the soil is a vertisol, characterized by a clay type 2:1, with a large capacity for the exchange of protons and consequently, a high buffering capacity. The addition of wastewater increased the production of both CO_2 and CH_4 compared with the soil treated with urea, but did not increase the production of N_2O. The irrigation of crops with wastewater might in the long term be a far more environmentally friendly approach to that of using water from aquifers that take long periods of time to fill, as long as the amount of wastewater applied is restricted to the amount required by the cultivated crop due to possible substantial losses of mineral N through several process such as the production of CO_2, CH_4 and N_2O, and the fact that soil salinization could increase rapidly.

5. Conclusions

The organic fertilizers or treatments (vermicompost, wastewater sludge, anaerobically digested cow manure, and wastewater) might increase the production of greenhouse gases, as do several abiotic and biotic factors involved in microbial activity within the soil. Sludge as a soil fertilizer offers the opportunity for the recycling of plants nutrients and the recovery of C as organic matter and its use in soil to improve agriculture. The high levels of microbial activity stimulated by the addition of this high C and N content material could increase both CO_2 and N_2O production. It should be taken in account that several factors are involved in the production of gases in the soil such as rhizosphere respiration, vegetation type, and soil microbial respiration, as well as abiotic factors such as soil moisture, soil temperature, substrate quantity and quality, and land use and management regimes.

Environmental and economic implications must be considered in order to make well-informed decisions on the management of soil treatments, i.e. how many, how often and what kind of organic fertilizer should be used in order to improve crop production and simultaneously limit soil deterioration and greenhouse gases production.

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Chapter 10

Mitigating Greenhouse Gas Emissions from Winter Production of Agricultural Greenhouses

Lilong Chai, Chengwei Ma, Baoju Wang, Mingchi Liu and Zhanhui Wu

Additional information is available at the end of the chapter

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Abstract

Consuming conventional fossil fuel, such as coal, natural gas, and oil, to heat agricultural greenhouses has contributed to the climate change and air pollutions regionally and globally, so the clean energy sources have been increasingly applied to replace fossil energies in heating agricultural greenhouses, especially in urban area. To assess the environment performance (e.g., greenhouse gas (GHG) emissions) of the ground source heat pump system (GSHPs) for heating agricultural greenhouses in urban area, a GSHPs using the shallow geothermal energy (SGE) in groundwater was applied to heat a Chinese solar greenhouse (G1) and a multispan greenhouse (G2) in Beijing (latitude 39°40′ N), the capital city of China. Emission rates of the GSHPs for heating the G1 and G2 were quantified to be 0.257–0.879 g CO_2 eq. m^{-2} day^{-1}. The total GHG emissions from heating greenhouses in Beijing with the GSHPs were quantified as 1.7–2.9 Gt CO_2 eq. $year^{-1}$ based on the electricity from the coal-fired power plant (CFPP) and the gas-fired power plant (GFPP). Among different stages of the SGE flow, the SGE promotion contributed most GHG emissions (66%) in total due to the higher consumption of electricity in compressors. The total GHG emissions from greenhouses heating with the coal-fired heating system (CFHs) and gas-fired heating system (GFHs) were quantified as 2.3–5.2 Gt CO_2 eq. $year^{-1}$ in Beijing. Heating the G1 and G2 with the GSHPs powered by the electricity from the CFPP, the equivalent CO_2 emissions were 43% and 44% lower than directly burning coal with the CFHs but were 46% and 44% higher than the GFHs that burn natural gas. However, when using the GFPP-generated electricity to run the GSHPs, the equivalent CO_2 emissions would be 84% and 47% lower than the CFHs and the GFHs, respectively.

Keywords: urban agriculture, greenhouse heating, greenhouse gases, fossil energy, shallow geothermal energy

1. Introduction

Agricultural buildings, such as horticultural greenhouse, usually require additional heating during winter and cold days in high latitude regions of the Northern Hemisphere [1, 2]. In northern China and many European countries, coal-fired heating system (CFHs) and the natural gas-fired heating system (GFHs) are dominant heating methods in greenhouses [3, 4]. However, conventional fossil fuels, such as coal, natural gas, and oil, which are nonrenewable and are the major greenhouse gas (GHG) contributors, may lead to the global climate change, air pollution, and energy crisis [5-7].

Renewable and clean energy, such as solar, geothermal, and shallow geothermal energy (SGE), has been increasingly applied to replace fossil energy systems in heating agricultural buildings (especially in urban area) across the world [8-11]. The SGE is mainly the stored solar energy in groundwater and soil layers less than 200 m deep from the earth soil surface [12, 13]. It can be used as heat source or sink for air conditioning in residential, industrial, and agricultural buildings with the ground source heat pump system (GSHPs), also known as geothermal heat pumps (GHPs) [4, 14].

The GSHPs has been applied to heat agricultural greenhouse in many countries [15-18]. The GSHPs could be considered with zero GHG emissions if the electricity was the only energy source that could be consumed by the system. However, producing electricity in coal-fired power plant (CFPP) or gas-fired power plant (GFPP) would emit a large quantity of GHG (e.g., CO_2). Besides, the refrigerant (e.g., R22 and R134a) used by the heat pump unit has been reported with the high risk of leaking in the year-round operation [19]. Therefore, assessing GHG emissions of the GSHPs should consider both direct and indirect sources.

In northern China (the area with altitude higher than 30° in the Northern Hemisphere) [20], there was mainly two kinds of horticultural greenhouses: the Chinese solar greenhouse (denoted as G1), which may or may not require assisted heating depending on the building design and the plants be cultivated, and the multispan greenhouses (denoted as G2), which require 100% assisted heating systems (primarily in the form of coal burning or gas burning) during winter time [21, 22]. The Chinese solar greenhouse, characterized with east-west orientation, transparent camber south roof, and solid north roof and east and west walls, usually has higher heat-preserving capacity than multispan greenhouse and requires less heating [23, 24]. However, the healthy growth of thermophilic vegetables, such as cucumber and tomato, and most flowers in Chinese solar greenhouse still requires assisted heating especially during cold winter nights or consecutive days of snowing or cloudy [3].

By the end of 2007, about 19,300 ha of greenhouses and tunnels had been constructed and used in Beijing, the capital city of China [25, 26], primarily for producing vegetables, flowers, and fruits. About 6000 ha Chinese solar greenhouses (the structure similar to G1) and 1000 ha multispan greenhouses (the structure similar to G2) may require assisted heating in winter with the systems of the CFHs and GFHs [27]. Therefore, quantifying the heating rate and GHG emission rate for the primary types of agricultural greenhouses with different heating systems and energy sources is important for developing the national or regional GHG emissions inventory of the greenhouse heating and mitigation strategies.

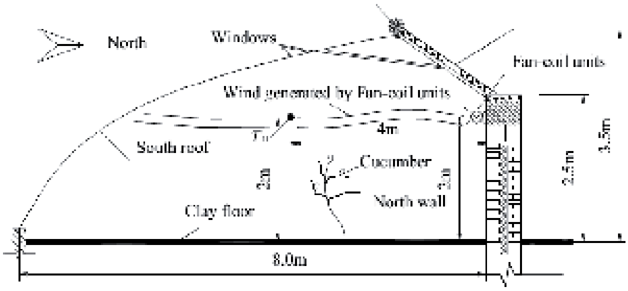
The objectives of this chapter are to (1) address the environmental concern on agricultural production over winter; (2) quantify the heating loads and the GHG emission rates for the two primary agricultural greenhouses (the G1-Chinese solar greenhouse and the G2-multispan greenhouses) in northern China; (3) assess the annual GHG emissions inventory of the greenhouse heating with different energy sources in Beijing, the capital city of the China; and (4) identify the difference between the shallow geothermal energy and the conventional fossil energy systems in GHG emissions of agricultural greenhouses heating.

2. Materials and Methods

2.1. Selected/tested greenhouses and the GSHPs

A Chinese solar greenhouse (G1, Figure 1 and Table 1) and a multispan greenhouse (G2, Figure 2 and Table 1), two important types of greenhouse in Northern China, were equipped with the groundwater-type GSHPs (Figure 3 and Table 2) in Beijing (latitude 39°40′N) and tested for developing heating rate and GHG emission rate. Performances of GHSPs were compared to CFHs and GFHs. In addition, different electricity generation methods (e.g., coal and gas power plant) were considered for assessing the GHG emissions of the GSHPs.

(a) Cucumbers in the G1



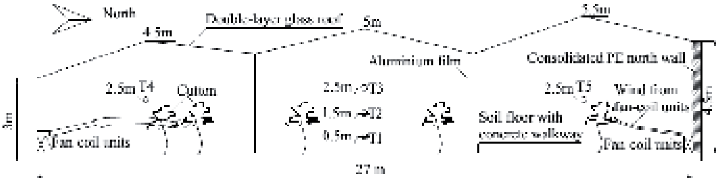
(b) The profile of the G1

Figure 1. The Chinese solar greenhouse (G1)

Section	Construction and coverage material	Surface area, m^2
Chinese solar greenhouse (G1)		
(1) North wall	240 mm clay brick+100 mm polystyrene heat preservation layer+240 mm clay brick	150
(2) East and west end walls	240 mm clay brick+100 mm polystyrene heat preservation foam board+240 mm clay brick	36
(3) South roof	0.15 mm single layer transparent polyethylene (south roof was covered with 10 mm needled felt heat blanket at winter nights)	510
(4) North roof	50 mm steel plate+100 polystyrene heat preservation layer+50 mm steel plate	108
(5) Floor	Bare soil (clay)	480
Multispan greenhouses (G2)		
(1) North wall	5 mm coated steel sheet+100 mm polystyrene heat preservation layer+5 mm coated steel sheet	126
(2) East and west wall	20 mm double-layer glass	110
(3) South wall	20 mm double-layer glass	98
(4) North roof	20 mm double-layer glass	108
(5) Floor	Bare soil for planting with concrete walkway (floor area was covered with aluminum film at horizontal height of 3.5 m at winter nights)	756

Table 1. Characteristics of the testing greenhouses.

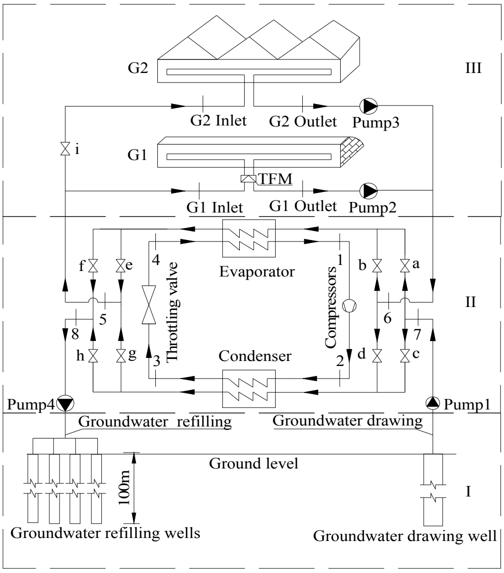
(a) Cottons in the G2



(b) The profile of the G2

Figure 2. The multispan greenhouse.

(a) The heat pump and water circulating system



(b) Diagram of the GSHPs greenhouse heating system

Figure 3. The groundwater type of GSHPs. (I is the stage of SGE extraction, II is the stage of SGE promotion, and III is the stage of greenhouse heating. **a**–**i** are valves installed in different water pipes. Pump 1 is groundwater drawing pump; pumps 2 and 3 are circulating water pumps; and pump 4 represent the groundwater backfilling pump. TFM is the thermal flow meter installed position. 1–8 represent the thermodynamic points in each section of GSHPs [18].

The GSHPs started to heat greenhouses on October 15, 2007 and ended on February 4, 2008. Cucumbers and strawberries were grown in G1 and cotton was grown in G2 during heating tests. The fan coil units in two greenhouses were controlled by the T-type thermocouple controllers automatically. For G1, the indoor air temperature was controlled in the range of 18°C–20°C, and for G2, the indoor air temperature was controlled in the range of 18°C–22°C, considering the poor thermal stability caused by the larger volume in G2.

Elements	**Performance parameters**
(1) Compressor	Manufacturer: four Danfoss hermetic scroll compressor; rated power of electric motor driving: 16.08×4 kW; refrigerant: 58 kg R22. Rate of refrigeration capacity: 380 kW; rate of heating capacity: 450 kW.
(2) Condenser	Horizontal shell–tube model
(3) Evaporator	Dry evaporator model
(4) Throttle	Copper capillary tube
(5) Fan-coil	In G1: FP-136; rated input power: 56 W; number: 6. In G2: 42VM006; rated input power: 87 W; number: 45
(6) Pumps	Flux: 33.2 m^3 h^{-1}; rated input power: 11 kW; number: 4
(7) Control system	PLC touching screen controller

Table 2. Characteristics of the GSHPs.

2.2. Power inputs and heating rate quantification

The heat provided by the GSHPs for heating greenhouses was quantified with the thermal flow meter (TFM) (Model DN35 and DN100, Beijing Jingyuan Liquid Apparatus Company, Beijing, China). A weather station (Qingsheng Electronic Science and Technology Co. Ltd., Handan, China) installed in the agriculture station was used to monitor outdoor environmental factors. Total electricity consumption of the GSHPs was recorded with watt-hour meter (Shanghai Huaxia Ammeters Manufactory, Shanghai, China).

2.3. Quantifying the GHG emissions

There are six kinds of gases (Table 3) highlighted as the GHG in Intergovernmental Panel on Climate Change (IPCC 2006) [5]. For the greenhouse heating with the CFHs and GFHs, carbon dioxide (CO_2) is the only GHG to be considered. But for the GSHPs greenhouse heating, most electricity consumed (in Beijing area) was generated in the CFPP or the GFPP, and the process of the power generation could emit large amount of CO_2 [25]. Besides, it has been reported that the leaking fraction of the refrigerant (i.e., R22(HFC-22) in this study) used in the GSHPs is around 0.02 kg^{-1} (2%) per year [19]. The R22 was not listed as one of the six primary GHG in the IPCC (2006), but it was reported with 1.28 times of the global warming potential (GWP) of the R134a (HFC-134a) [28]. Therefore, the GWP of R22 was estimated to be 4902, 1830, and 557 based on 20a, 100a, and 500a, respectively, based on the relationship of the GWP with the R134a.

The GHG emissions from heating G1 and G2 with the GSHPs can be quantified with Eq. 1.

$$\mathrm{EM}_{\mathrm{GSHPs-Gi-j}} = M_{\mathrm{GSHPs-G}i-j} * f_{j-\mathrm{co}_2} + \frac{HE_{\mathrm{GSHPs,G}i}}{HE_{\mathrm{GSHPs,G}}} M_{\mathrm{R22,Gi}} * f_{\mathrm{R22-leak}} * f_{\mathrm{R22-co}_2} \tag{1}$$

where $\mathrm{HE}_{\mathrm{GSHPs,G}}$, total energy provided by the GSHPs for heating G1 and G2 during whole winter (monitored with TFM), MJ; $\mathrm{HE}_{\mathrm{GSHPs,G}i}$, total energy provided by the GSHPs for heating

GHG	20a	100a	500a
CO_2	1	1	1
CH_4	72	25	7.6
N_2O	289	298	153
HFCs(HFC-134a)	3830	1430	435
PFCs (PFC-116)	8630	22,800	32,600
SF6	16,300	22,800	32,600

Note: Data were cited from IPCC 2006[5], expressed in CO_2 eq.

Table 3. GWP of different greenhouse gases

the greenhouse of type *i* (G1 or G2) during whole winter (monitored with TFM), MJ; $\mathrm{EM}_{\mathrm{GSHPs}-\mathrm{G}i-j}$, equivalent CO_2 emissions from the GSHPs for heating greenhouse *i* (G1 or G2) be driven by electricity generated in power plant *j* (CFPP or GFPP), kg CO_2 eq.; $M_{\mathrm{GSHPS}\text{-}\mathrm{G}i-j}$, the coal or natural gas consumed in power plant *j* (CFPP or GFPP) for generating the electricity that the GSHPs had used for heating greenhouse *i* (G1 or G2), kg C or kg CH_4; $M_{\mathrm{R22,G}i}$, the amount of the refrigerant R22 in the GSHPs be allotted for heating greenhouse *i* (G1 or G2), kg; $f_{j-}\ \mathrm{co}_{2\,2}$, the CO_2 emissions coefficient of fossil energy (coal or natural gas) in power plant *j* (CFPP or GFPP), kg CO_2 eq. $(\mathrm{kg\ C})^{-1}$ or kg CO_2 eq. $(\mathrm{kg\ CH_4})^{-1}$; $f_{\mathrm{R22-}}\ \mathrm{co}_{2}$, the equivalent CO_2 emissions coefficient of R22, kg CO_2 eq. kg^{-1} R22; and $f_{\mathrm{R22-leak}}$, the leaking fraction of total R22, %.

The carbon (C) or natural gas (assumed to be 100% as CH_4 in calculating CO_2 emissions) consumed to produce the electricity consumed by the GSHPs was estimated for the CFPP and GFPP based on Eq. 2.

$$M_{\mathrm{GSHPs}-\mathrm{G}i-j}=\frac{3600\ \mathrm{ELE}_{\mathrm{GSHPs,G}i}}{\mathrm{CV}_j} \tag{2}$$

where $\mathrm{ELE}_{\mathrm{GSHPs,G}i}$, total electricity consumed by the GSHPs in heating greenhouse *i* (G1 or G2) during winter production, kWh; and CV_j, conversion factor between heat and electricity in CFPP or GFPP, 0.27 was used for CFPP, and 0.42 was applied to GFPP in this study [29].

The GHG emissions from the GSHPs were compared with two primary greenhouse heating systems used in northern China: the CFHs and the CFHs. The equivalent quantity of CO_2 emissions from the GSHPs, CFHs, and GFHs was quantified based on the same heat energy provided by the GSHPs during whole winter for the G1 and G2 (Eqs. 3–6). In northern China, the heating efficiencies of CFHs and GFHs were considered as 0.6 and 0.8, respectively [27, 29].

$$M_{\mathrm{carbon}-\mathrm{G}i}=\frac{\mathrm{HE}_{\mathrm{GSHPs,G}i}}{F_{\mathrm{carbon-heat}} * f_{C-\mathrm{HE}}} \tag{3}$$

$$M_{\text{Gas-G}i} = \frac{HE_{\text{GSHPs,G}i}}{F_{\text{gas-heat}*f_{\text{G-HE}}}} \tag{4}$$

$$\text{EM}_{\text{CFHs,G}i} = M_{\text{Carbon-G}i} * f_{\text{C-co}_2} \tag{5}$$

$$\text{EM}_{\text{GFHs,G}i} = M_{\text{Gas-G}i} * f_{\text{G-co}_2} \tag{6}$$

where EM_{CFHs}, CO_2 emissions from greenhouse CFHs, kg CO_2; EM_{GFHs}, CO_2 emissions from greenhouse GFHs, kg CO_2; $f_{\text{C-CO2}}$, CO_2 emissions coefficient of the CFHs, kg CO_2 (kg C)$^{-1}$; $f_{\text{G-co2}}$, CO_2 emissions coefficient of the natural GFHs, kg CO_2 (kg CH_4)$^{-1}$; $f_{\text{C-HE}}$, the heating efficiency of the CFHs, dimensionless; $f_{\text{G-HE}}$, the heating efficiency of the GFHs, dimensionless; $F_{\text{carbon-heat}}$, specific calorific value of burning per kg carbon, MJ (kg C)$^{-1}$; $F_{\text{carbon-heat}}$, specific calorific value of burning per kg natural gas, MJ (kg CH_4)$^{-1}$; $M_{\text{carbon-G}i}$, the carbon consumed in heating greenhouse *i* (G1 or G2) during whole winter, kg C; $M_{\text{gas-G}i}$, the natural gas consumed in heating greenhouse *i* (G1 or G2) during whole winter, kg CH_4; and $M_{\text{R22-G}i}$, the R22 used in the GSHPs be attributed to greenhouse *i* (G1 or G2) based on the proportion of heat energy received by G1 and G2, kg.

Under the normal temperature and atmospheric pressure (288 K and 1 atm), burning a kilogram of the standard coal (C) and natural gas (CH_4) in oxygen (O_2) completely has potential to emit 3.67 and 2.75 kg CO_2, respectively, with Eqs. 7 and 8 [30]. Meanwhile, the $F_{\text{carbon-heat}}$ and $F_{\text{gas-heat}}$ were quantified as 29.3 and 52.6 MJ for burning each kilogram of the C and CH_4, respectively.

$$1\,\text{kg C} + 2.67\,\text{kg O}_2 \rightarrow 3.67\,\text{kg CO}_2 + 29.3\,\text{MJ energy} \tag{7}$$

$$1\text{ kg CH}_4 + 4\text{ kg O}_2 \rightarrow 2.75\text{ kg CO}_2 + 2.25\text{ kg H}_2\text{O} + 52.6\text{ MJ energy} \tag{8}$$

Total GHG emissions from greenhouses heating in Beijing can be estimated based on the total area of greenhouses (similar to G1 or G2) and heat rate per square greenhouse floor (Eqs. 9–11):

$$\text{EMG}_{\text{Beijing,GSHPs,}j} = \frac{A_{\text{G1, Beijing}} \times f_{\text{G1,heating}}\text{EM}_{\text{GSHPs,G1-elej}}}{480} + \frac{\text{A}_{\text{G2, Beijing}} \times f_{\text{G2,heating}}\text{EM}_{\text{GSHPs,G2-elej}}}{756} \tag{9}$$

$$\text{EMG}_{\text{Beijing,Carbon}} = \frac{A_{\text{G1, Beijing}} \times f_{\text{G2,heating}}\text{EM}_{\text{CFHs,G1}}}{480} + \frac{\text{A}_{\text{G2, Beijing}} \times f_{\text{G2,heating}}\,\text{EM}_{\text{CFHs,G2}}}{756} \tag{10}$$

$$\mathrm{EMG}_{\mathrm{Beijing,gas}} = \frac{A_{\mathrm{G1,\ Beijing}} \times f_{\mathrm{G2,heating}}\mathrm{EM}_{\mathrm{GFHs,G1}}}{480} + \frac{\mathrm{A}_{\mathrm{G2,\ Beijing}} \times f_{\mathrm{G2,heating}}\mathrm{EM}_{\mathrm{GFHs,G2}}}{756} \tag{11}$$

Where, $\mathrm{EMG}_{\mathrm{Beijing,GSHPs},\,j}$, equivalent CO_2 emissions from the GSHPs heating for greenhouses similar to G1 and G2 be driven electricity generated in the power plant *j* (CFPP or GFPP), kg CO_2 eq. in Beijing; $\mathrm{EMG}_{\mathrm{Beijing,carbon}}$, equivalent CO_2 emissions from the CFHs heating for greenhouses similar to G1 and G2 in Beijing, kg CO_2 eq; and $\mathrm{EMG}_{\mathrm{Beijing,gas}}$, equivalent CO_2 emissions from the GFHs heating for greenhouses similar to G1 and G2 in Beijing, kg CO_2 eq.

3. Results and Discussion

3.1. Emissions from the GSHPs

Total heat energy provided by the GSHPs for G1 and G2 were 149270.4 and 640659.1 MJ during 2007–2008 winter at the electricity consumptions of 10826.1 and 44372.2 kWh, respectively. The electricity consumed by the GSHPs usually came from the power plants of CFPP and GFPP in northern China. Therefore, the difference between the CFPP and GFPP in producing GHG at different stages of the SGE in the GSHPs was compared (Table 4).

	SGE extraction	**SGE promotion**	**SGE heating**	**Inventory**
Electricity from CFPP				
G1 electricity consumption, kWh	2440.6	7135.5	1250.3	10826.4
G1 standard coal consumption, kg C	1095.5	3202.7	561.2	4859.4
G1 GHG emissions, kg CO_2 eq.	4020.3	11754.0	2059.5	17833.8
G2 electricity consumption, kWh	10003.0	29245.0	5124.2	44372.2
G2 standard coal consumption, kg C	4489.8	13126.4	2300.0	19916.2
G2 GHG emission, kg CO_2 eq.	16477.4	48174.0	8440.9	73092.3
Electricity from GFPP				
G1 electricity consumption, kWh	2440.6	7135.5	1250.3	10826.4
G1 natural gas consumption, kg CH_4	397.7	1162.8	203.7	1764.2
G1 GHG emissions, kg CO_2 eq.	1093.7	3197.6	560.3	4851.6
G2 electricity consumption, kWh	10003.0	29245.0	5124.2	44372.2
G2 natural gas consumption, kg CH_4	1630.0	4765.6	835.0	7230.7
G2 GHG emission, kg CO_2 eq.	4482.6	13105.4	2296.3	19884.3

Note: (1) G1=480m^2, heated with GSHPs for 146 days; G2=756 m^2, heated with GSHPs for 111 days. (2) In calculating the CO_2 emissions, the CH_4 was assumed to be 100% chemical component of the natural gas.

Table 4. GHG emission from G1 and G2 heating with GSHPs.

In producing the amount of the electricity consumed by the GSHPs for G1 and G2, about 4.9 and 20 t of coal (C) were consumed in CFPP. If use the GFPP produced electricity, the total natural gas burned could be 1.8 and 7.2 t (CH_4). During 2007–2008 winter heating, the GWP of the GHG emissions from G1 and G2 (Figure 4) was estimated to be 18.3 and 74.9 t CO_2 eq. with the CFPP and 5.3 and 21.7 t CO_2 eq. with the GFPP, respectively, over a 20-year time horizon. The GWP of 100a was 1.5%–1.6% lower than 20a for G1 and 5.3%–5.4 % lower than 20a for G2 due to the reduced GWP on R22. Similar to HCFC-22, R22 has shorter atmospheric lifetime [5]. Generally, the CO_2 eq. contributed by the leak of R22 accounted for 2.4% and 8.4% in the scenarios of CFPP and GFPP, respectively.

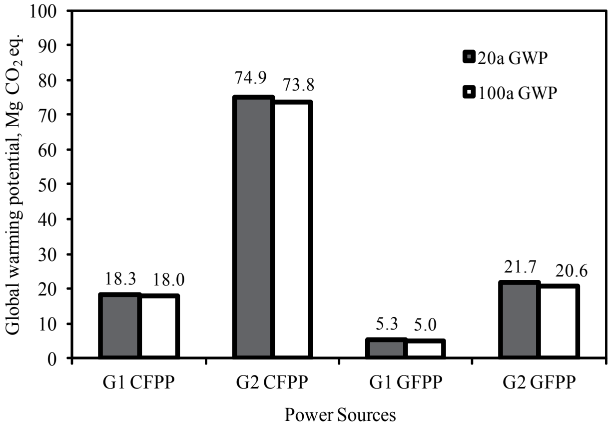


Figure 4. GWP of the GHG emissions derived from the GHSPs heating in G1 and G2.

Among different stages of the SGE flow, most GHG emissions (66%) happened at the stage of SGE promotion due to the higher consumption of electricity in compressors. Therefore, improving the efficiency of the compressors has the potential to reduce the GHG emissions from the GHSPs heating.

3.2. Greenhouse gas emissions from fossil energy systems

Providing G1 and G2 with the same quantity of heat that the GSHPs has provided (i.e., 149270.4 and 640659.1 MJ) requires the CFHs to consume 8.49 and 36.40 t of standard coal and the GFHs to consume 3.55 mg (4964 m^3 at 288 K and 1 atm) and 15.22 t (21,304 m^3 at 288 K and 1 atm) of natural gas (CH_4), respectively. Accordingly, the GHG emissions from heating G1 and G2 (Figure 5) were estimated to be 32.7 and 133.7 t CO_2 eq. for the CFHs system and 9.8 and 41.8 t CO_2 eq. for the GFHs system.

3.3. Standardized GHG emissions from greenhouse heating

The unit electricity consuming rate of the GSHPs was 0.15 and 0.53 kWh m^{-2} d^{-1} for heating G1 and G2 and which can be standardized as 1500 and 5300 kWh ha^{-1} d^{-1} in Beijing during

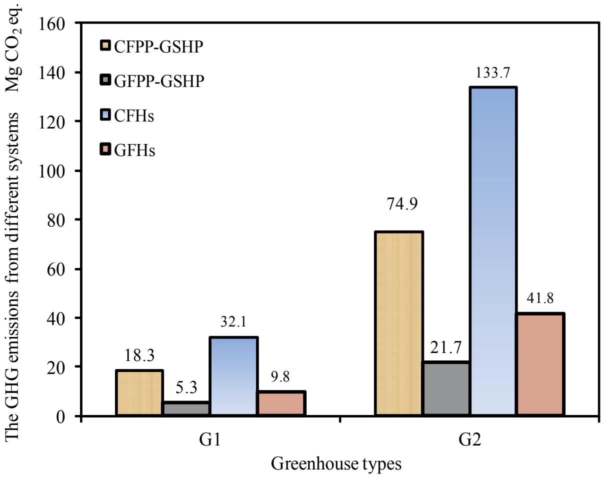
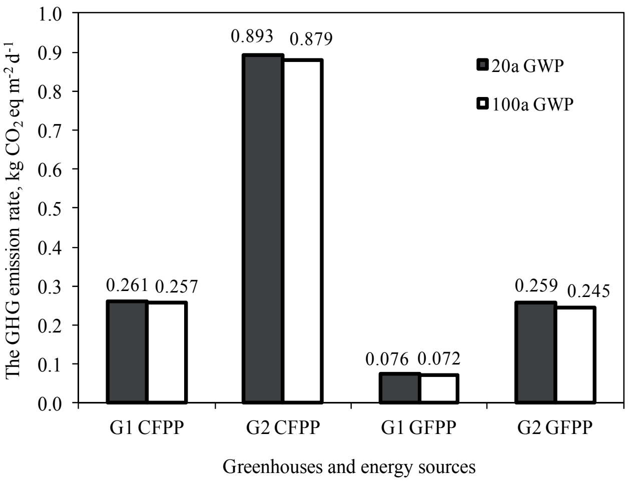


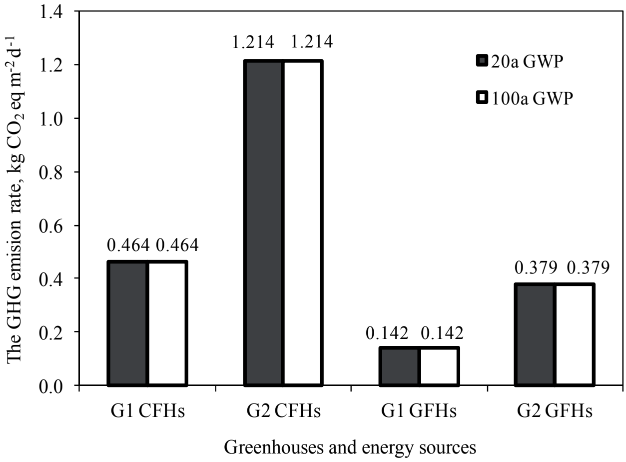
Figure 5. The GHG emissions from the GHSPs and the fossil energy systems.

2007–2008 winter. The 20a and 100a GWPs of the GHG emissions from the GSHPs heating for G1 and G2 (Figure 6a) were 0.076–0.893 and 0.072–0.879 g CO_2 eq. m^{-2} $d^{-1,}$ respectively. The GHG emission rate of G2 is 3.42 times of G1 because Chinese solar greenhouse has better heat-preserving capacity than multispan greenhouses.

Regarding to the CFHs and GFHs, the standardized GWPs of the GHG emissions (Figure 6b) were 0.142–1.214 CO_2 eq. m^{-2} day^{-1}, and there were no difference between 20a and 100a because the GWP of the CO_2 will not change with the time.



(a) The shallow geothermal energy



(b) The fossil energy

Figure 6. Standardized GHG emissions (GWP) for different greenhouse types and energy sources.

3.4. Emissions inventory in Beijing, China

According to the areas of the G1 and G2 in Beijing that require assisted heating (6000 ha Chinese solar greenhouses-G1 and 1000 ha multispan greenhouses-G2), the total GHG emissions from greenhouses heating with the CFHs or GFHs were quantified as 5238 or 2294 Mt CO_2 eq. in Beijing, and there is no difference between 20a and 100a GWP (Figure 7).

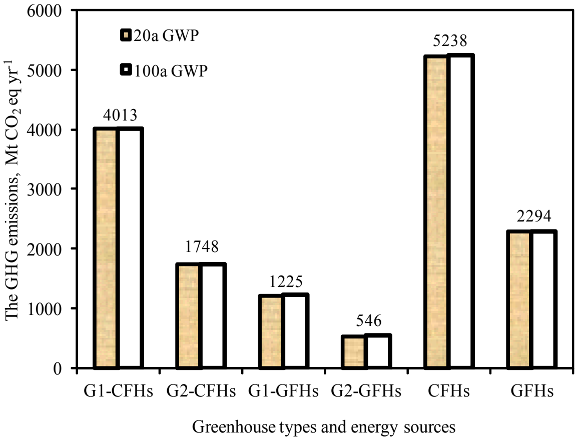


Figure 7. Total GHG emissions from heating greenhouses with fossil energies in Beijing.(G1-CFHs, heating all the G1-type greenhouses in Beijing with CFHs; G2-CFHs, heating all the G2-type greenhouses in Beijing with CFHs; G1-GFHs, heating all the G1-type greenhouses in Beijing with GFHs; G2-GFHs, heating all the G2-type greenhouses in Beijing with GFHs).

The total GHG emissions from heating greenhouses in Beijing with the GSHPs were quantified as 1658 and 2909 Mt CO_2 eq., based on 20a GWP or 1619 and 2839 Mt CO_2 eq. based on 100a GWP (Figure 8). The GHG emissions from heating G1-type greenhouses are higher than heating G2-type of greenhouses due to the large area of the G1 built and used in Beijing during 2007–2008 winter.

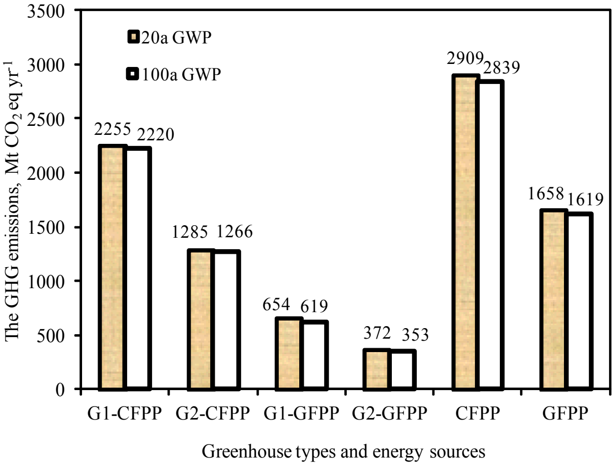


Figure 8. Total GHG emissions from heating greenhouses with the GSHPs in Beijing (G1-CFPP, heating all the G1-type greenhouses in Beijing with the GSHPs be powered with the electricity generated in CFHs; G2-CFPP, heating all the G2-type greenhouses in Beijing with the GSHPs be powered with the electricity generated in CFHs; G1-GFPP, heating all the G1-type greenhouses in Beijing with the GSHPs be powered with the electricity generated in GFHs; G2-GFPP, heating all the G2-type greenhouses in Beijing with the GSHPs be powered with the electricity generated in GFHs).

Applying the GSHPs to heat G1 and G2 with the electricity from the CFPP, the equivalent CO_2 emissions were 43% and 44% lower than directly burning coal with the CFHs but were 46.4% and 44.2% higher than the GFHs that burning natural gas. However, when using the GFPP generated electricity to run the GSHPs, the equivalent CO_2 emissions would be 83.5% and 83.8% lower than directly burning coal with the CFHs and were 45.9% and 48.1% lower than the GFHs that burning natural gas.

3.5. Uncertainty evaluation

It was assumed that all the solar greenhouse and multispan greenhouses with the same heating rate of G1 and G2 in this study, which would lead to errors due to the varying structures and materials in different greenhouses. For the solar greenhouses with improved wall materials and structures, the heat loss and heating rate would be lower [31]. Besides, heat-preserving technologies, such as multilayer aluminum foil heat reflecting materials, would have lower heat loss and heating rate than G2 in this study [3].

The shallow geothermal heat used in the GSHPs came from the groundwater (14°C), which has different GHG emissions from the borehole or U-tube-based HPs [19, 32]. Besides, the leaking factor of R22 was assumed to be 2% per year based on European studies, which may be changing with the change of the pump unit and maintenance of the system.

The GHG emissions calculated in this study are based on the real heating quantity required by G1 and G2 during winter heating, and the cycle of the SGE from extraction, enhance, and greenhouse heating was considered, the analysis can be considered as a partial life cycle assessment (LCA). However, a full LCA analysis could be applied to account the GHG emissions from greenhouse constructing with different materials, the transportation of the coal or natural gas for the location of the greenhouses, and the plants cultivated in the greenhouses [33-35].

In this study, we assumed that all the G1-type Chinese solar greenhouses would need additional heating in calculating the GHG emissions. However, novel structures and materials were applied for building Chinese solar greenhouses in Beijing in recent years [36], which improved the heat-preserving capacity of the greenhouse so that heating was not required in winter time. Therefore, the GHG emissions from heating Chinese solar greenhouse could be lower than the amount calculated in this study.

4. Summary

The unit electricity consuming rate of the GSHPs were 0.15 and 0.53 kWh m^{-2} d^{-1} for heating the Chinese solar greenhouse (G1) and multispan greenhouse (G2) or expressed as 1500 and 5300 kWh ha^{-1} d^{-1} in Beijing. The 20a and 100a GWPs of the GHG emissions from the GSHPs heating for G1 and G2 were 0.076–0.893 and 0.072–0.879 g CO_2 eq. m^{-2} $d^{-1,}$ respectively.

The total GHG emissions from heating greenhouses in Beijing with the GSHPs were quantified as 1658–2909 Mt CO_2 eq. Among different stages of the SGE flow, most GHG emissions (66%) happened at the stage of SGE promotion due to the higher consumption of electricity in compressors.

The total GHG emissions from greenhouses heating with the CFHs or GFHs were quantified as 5238 and 2294 Mt CO_2 eq. in Beijing, respectively. Applying the GSHPs to heat G1 and G2 with the electricity from the CFPP, the equivalent CO_2 emissions were 43% and 44% lower than directly burning coal with the CFHs but were 46.4% and 44.2% higher than the GFHs that burning natural gas. However, when using the GFPP-generated electricity to run the GSHPs, the equivalent CO_2 emissions would be 83.5% and 83.8% lower than directly burning coal with the CFHs and were 45.9% and 48.1% lower than the GFHs that burning natural gas.

The glass-covered G2 consumed more heating energy than G1 during the heating period. This demonstrated that the Chinese solar greenhouse design had better heat preservation than the glass greenhouse. Besides, novel structures and materials applied for building Chinese solar greenhouses in Beijing could further reduce the GHG emissions from heating.

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Chapter 11

Livestock as Sources of Greenhouse Gases and Its Significance to Climate Change

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Additional information is available at the end of the chapter

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Abstract

This chapter outlines the role of livestock in the production of greenhouse gases (GHGs) that contributes to climate change. Livestock contribute both directly and indirectly to climate change through the emissions of GHGs such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). As animal production systems are vulnerable to climate change and are large contributors to potential global warming, it is vital to understand in detail enteric CH_4 emission and manure management in different livestock species. Methane emissions from livestock are estimated to be approximately 2.2 billion tonnes of CO_2 equivalents, accounting for about 80% of agricultural CH_4 and 35% of the total anthropogenic CH_4 emissions. Furthermore, the global livestock sector contributes about 75% of the agricultural N_2O emissions. Other sources of GHG emission from livestock and related activities are fossil fuels used for associated farm activities, N_2O emissions from fertilizer use, CH_4 release from the breakdown of fertilizers and from animal manure, and land-use changes for feed production. There are several techniques available to quantify CH_4 emission, and simulation models offer a scope to predict accurately the GHG emission from a livestock enterprise as a whole. Quantifying GHG emission from livestock may pave the way for understanding the role of livestock to climate change and this will help in designing appropriate mitigation strategies to reduce livestock-related GHGs.

Keywords: climate change, enteric methane, GHG, livestock, manure management, modeling

1. Introduction

The Intergovernmental Panel on Climate Change (IPCC), convened by the United Nations, has reported evidence that human activities over the past 50 years have influenced the global climate through the production of GHG [1]. Increasing concentrations of GHGs in the atmosphere have contributed to an increase in the Earth's atmospheric temperature, an occurrence known as global warming [2]. Indeed, average global temperatures have risen considerably, and the IPCC [1] predicts increases of 1.8–3.9ºC (3.2–7.1ºF) by 2100. With business as usual, Earth's temperature may rise by 1.4–5.8ºC by the end of this century, and the scientific community warns of more abrupt climatic change in the future [3].

The livestock sector accounts for 40% of the world's agriculture gross domestic product (GDP). It employs 1.3 billion people and creates livelihoods for one billion of the world's population living in poverty [2]. As animal production systems are vulnerable to climate change and are large contributors to potential global warming through methane (CH_4) and nitrous oxide (N_2O) production, it is vital to understand in detail enteric CH_4 emission and manure management in different livestock species [4]. Before targeting GHG reduction strategies from enteric fermentation and manure management, it is important to understand the mechanisms of enteric CH_4 emission in livestock, the factors influencing such emission. In addition, an understanding of the available prediction models and estimation methodology for quantification of GHGs is essential. A thorough understanding of these will in turn pave way for formulation of effective mitigation strategies for minimizing enteric CH_4 emission in livestock [5].

This chapter will focus on four main areas: (i) livestock's role as a source of GHGs, and the contribution that this makes to climate change; (ii) enteric CH_4 emission and manure management related to CH_4 and N_2O as primary sources of GHGs related to livestock activities; (iii) the methodologies used to quantify enteric emission; and (iv) modeling of GHGs in livestock farms as important step towards finding solution for livestock-related climate change.

2. Livestock and climate change from global food security perspectives

FAO estimated that 1526 million cattle and buffaloes and 1777 million small ruminants are being maintained globally. The population of cattle and buffaloes and small ruminants is expected to be 2.6 and 2.7 billion, respectively, by the year 2050. Furthermore, livestock are an integral element of agriculture that supports the livelihood of more than 1 billion people across the globe. This sector satisfies more than 13% of the caloric and 28% of the protein requirements of people worldwide. The global demand for milk, meat, and eggs is expected to increase by 30%, 60%, and 80%, respectively, by the year 2050 in comparison to the 1990 demand. This increased requirement will be fulfilled either by increasing the livestock numbers or through intensifying the productivity of existing stock.

Climate change is seen as a major threat to the survival of many species, ecosystems, and the sustainability of livestock production systems in many parts of the world [6]. The growing human population will almost doubled the global requirement for livestock products by 2050. It is during the same period adverse changes in the climate are also expected. Recent industrial developments have curtailed the land used for agricultural activities, considerably threatening food security in both developed and developing countries. Hence, livestock production has a key role to play in bringing food security to these countries. We need high-quality research in animal science to meet the increasing demand for livestock products in the changing climate scenario [7].

3. Livestock as source of greenhouse gas (GHGs)

Livestock contributes both directly and indirectly to climate change through the emissions of GHGs such as CO_2, CH_4, and N_2O [8]. Globally, the sector contributes 18% (7.1 billion tonnes CO_2 equivalent) of global GHG emissions. Although it accounts for only 9% of global CO_2, it generates 65% of human-related N_2O and 35% of CH_4, which has 310 times and 23 times the global warming potential (GWP) of CO_2, respectively [9] (Fig. 1).

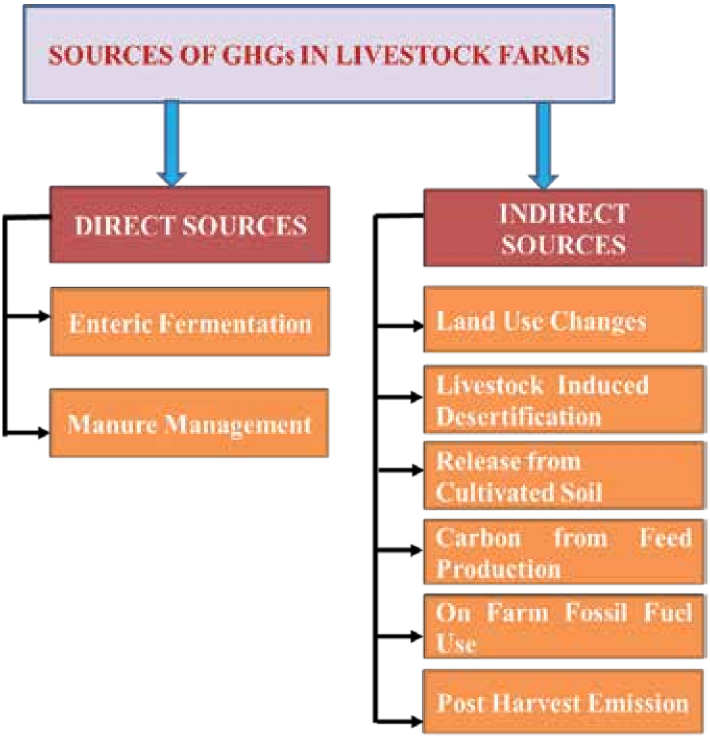

Figure 1. Different sources of GHGs from livestock sector.

There are two sources of GHG emissions from livestock: (a) enteric fermentation where specific microbes residing in the rumen produce CH_4 as a by-product during digestion and (b) anaerobic fermentation of livestock manure producing CH_4 and denitrification and denitrification of manure producing N_2O. Methane production appears to be a major issue and largely arises from natural anaerobic ecosystems, and fermentative digestion in ruminant animal [10]. Much of the global GHG emissions currently arise from enteric fermentation and manure from grazing animals. The development of management strategies to mitigate CH_4 emissions from ruminant livestock is possible and desirable. Carbon dioxide (CO_2) are also produced in livestock farms and are primarily associated with fossil fuel burning during operation of farm machineries in the process of fertilizer production, processing and transportation of refrigerated products, deforestation, desertification, and release of carbon from cultivated soils. Enhanced utilization of dietary "C" will improve energy utilization and feed efficiency hence animal productivity, decrease overall CH_4 emissions, and thereby reduce the contribution of ruminant livestock to the global CH_4 inventory.

Ruminant animals, such as cattle, sheep, buffaloes, and goats, are unique due to their special digestive systems, which can convert plant materials that are indigestible by humans into nutritious food. In addition to food, these animals also produce hides and fibers that are utilized by humans. This same helpful digestive system, however, produces CH_4, a potent GHG that can contribute to global climate change. Livestock production systems can also emit other GHGs such as N_2O and CO_2. The most important GHGs are CO_2, CH_4, and N_2O, all of which have increased in the last 150 years and have different global warming potential. According to Sejian et al. [11], the warming potential of CO_2, CH_4, and N_2O are 1, 25, and 310, respectively. Taking into account the entire livestock commodity chain – from land use and feed production, to livestock farming and waste management, to product processing and transportation – about 18% of total anthropogenic GHG emissions can be attributed to the livestock sector [2].

Livestock production is the largest global source of CH_4 and N_2O – two particularly potent GHGs [12, 13]. The principal sources of N_2O are manure and fertilizers used in the production of feed. The biggest source of CH_4 is from enteric fermentation. The rising demand for livestock products therefore translates into rising emissions of CH_4 and N_2O. According to one study, if current dietary trends (increasing global consumption of animal products) were to continue, emissions of CH_4 and N_2O would more than double by 2055 from 1995 levels [14].

3.1. Enteric methane emission

Worldwide livestock emits around 7.1 Gt CO_2-eq GHGs per year, which accounts for 15% of the human induced GHGs emissions. Additionally, 5.7 Gt CO_2-eq GHGs is also emitted from the ruminant supply chain wherein cattle, buffaloes, and small ruminant production contribute 81%, 11%, and 8%, respectively. Methane emissions from livestock have two sources, one from enteric fermentation and another from excrement. Enteric fermentation in ruminants annually contributes ~90 Tg CH_4 to the atmospheric pool, while ~25 Tg comes from the excrement. Apart from the role of enteric CH_4 in global warming, its emission from the animal system lead to a loss of biological energy (6–12% of intake), which otherwise would have been utilized by the host animal for various productive functions. Reducing the loss of energy in the form of enteric CH_4 is crucial, especially in developing countries like India where feed and fodder availability is already in short supply.

3.1.1. *Indian livestock and enteric methane emission*

India has approximately 512 million livestock (19th Livestock census, Government of India). Of the total livestock population, about 60% are cattle and buffaloes, which comparatively emit more enteric CH_4 than any other livestock species. Emissions of enteric CH_4 can be elevated when these species are fed fibrous feeds. Estimations of enteric CH_4 emissions from Indian livestock have been calculated using different approaches (Table 1). There is a lack of consistency in the published data; some have reported very high emissions from Indian livestock while others have reported much lower emissions [15]. This large variation in predicted enteric CH_4 emission from Indian livestock is attributed to the different approaches used for the calculation of emissions. The average of the published data is in the range of 9–10 Tg per year, which appears to be a realistic value. Methane emissions from excrement in India are low because the disposal system (generally stored as heap in the open environment) does not support the favorable anaerobic conditions required by methanogens. However, in the developed world where excrement is mainly stored in lagoons, manure is a major source of CH_4 emissions.

Source	**Base year**	**Emission (Tg/yr)**	**Approach**
Ahuja [16]	1985	10.40	Default CH_4 emission factors
ALGAS[a] [17]	1990	18.48	IPCC methodology
Singh [18]	1992	9.02	*In vitro* gas production and dry matter digestibility coefficients
Garg and Shukla [15]	-	7.25	-
EPA[b] [19]	-	10.04	-
Swamy and Bhattacharya [20]	1994	9.0	Methane emission factors
Jha et al. [21]	1994	8.97	IPCC tier II
Chhabra et al. [22]	2003	10.65	GIS approach
Singh et al. [23]	2003	9.10	*In vitro* gas production, feeding practices in different agro-ecological regions
Patra [24]	2010	14.3	IPCC tier 1

[a] Asia Least-Cost Greenhouse Gas Abatement Strategy.

[b] United States Environmental Protection Agency.

Table 1. Estimates of enteric methane emission from Indian livestock

Based on the IPCC default emission factors, Kamra [25] determined the enteric CH_4 emission from Indian livestock. Buffalo, yak, and mithun contribute a maximum of 55 kg CH_4/head/yr; however, sheep and goat contribute only 5 kg/head/yr. The enteric CH_4 emission from crossbred cattle is much higher than the indigenous cattle (46 vs 25 kg/head/yr). Both cattle and buffaloes aggregately emit more than 90% of the total enteric CH_4 from livestock, while sheep and goat together contribute around 7.70% (Fig. 2). Pig production is the next major emitter contributing 0.57% of the total enteric CH_4 emission from livestock in India. The contribution from other livestock species is negligible.

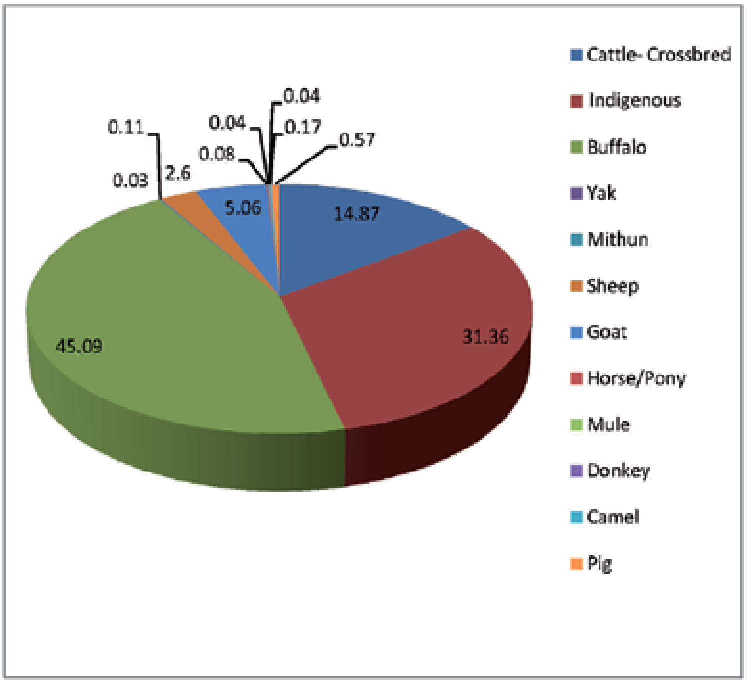

Figure 2. % Species wise enteric methane emission (modified from Kamra [25]).

3.1.2. *Why rumen methanogenesis is an obligation*

The rumen is the harbor for diverse anaerobic microbe populations that accomplish different functions from degradation of complex carbohydrates to the removal of fermentation metabolites in a syntrophic way [26]. H_2, which is produced in large volumes during enteric fermentation, needs to be removed from the anaerobic vat in order to maintain favorable rumen conditions for both the rumen microbes and host animal. Under normal rumen functioning, metabolic H_2 is used for the reduction of CO_2 to CH_4, which in turn is eructated into the atmosphere via the mouth and nostrils. The microbes of the so-called *archaea* or methanogens are the CH_4 producing machinery inside the rumen. The majority of the rumen methanogens are hydrogenotrophic, which utilize H_2 as a substrate for methanogenesis.

Rumen methanogenesis is a necessary but energy-wasteful process as it corresponds to a significant loss of biological dietary energy (6–12% of intake) in the form of CH_4.

Among the various end products of rumen fermentation, H_2 is a central metabolite where its partial pressure in the rumen determines the extent of methanogenesis and the possible extent of oxidation of feedstuffs [27]. H_2 in the rumen is generally referred as *currency of fermentation* [27]. The removal of H_2 from the rumen is a prerequisite for the continuation of rumen fermentation. However, the methanogens constitute only a small fraction of the rumen microbial community, but they are very crucial in H_2 utilization [28]. Apart from the methanogenesis, other hydrogenotrophic pathways (reductive acetogenesis, sulfate and nitrate reduction) are also present in the rumen, but the extent of H_2 utilization through these pathways is not clear. In order to keep the rumen functional and the animal alive, rumen methanogenesis is the primary and thermodynamically efficient way of metabolic H_2 disposal from the rumen, and that is why it is generally regarded as a necessary but wasteful process.

3.1.3. Enteric methane estimation methodology

Several methods are available for measuring enteric CH_4 production, and the selection of the most appropriate method is based on several factors such as cost, level of accuracy, and experimental design [29, 30].

3.1.3.1. Individual animal techniques

By far, the most suitable method to quantify individual ruminant animal CH_4 measurement is by using respiration chamber, or calorimetry. The respiration chamber models include whole animal chambers, head boxes, or ventilated hoods and face masks. These methods have been effectively used to collect information pertaining to CH_4 emissions in livestock. The predominant use of calorimeters has been in energy balance experiments where CH_4 has been estimated as a part of the procedures followed. Although there are various designs available, open-circuit calorimeter has been the one widely used. There are various designs of calorimeters, but the most common one is the open-circuit calorimeter, in which outside air is circulated around the animal's head, mouth, and nose and expired air is collected for further analysis.

3.1.3.2. Tracer gas techniques

Methane emission from ruminants can be estimated by using the ERUCT technique (Emissions from Ruminants Using a Calibrated Tracer). The tracer can either be isotopic or nonisotopic. Isotopic tracer techniques generally require simple experimental designs and relatively straightforward calculations [31]. Isotopic methods involve the use of (3H-)CH_4 or (14C-)CH_4 and ruminally cannulated animals.

3.1.3.3. Sulphur hexafluoride (SF_6) technique

Nonisotopic tracer techniques are also available for measurement of CH_4 production. Johnson et al. [32] described a technique using SF_6, an inert gas tracer. This method has been widely used in sheep and cattle. Methane emission rates are calculated based on the equation $QCH_4 = QSF_6 \times [CH_4] / [SF_6]$, where QCH_4 is the emission rate of CH_4 in g/day, QSF_6 is the known release rate (g/day) of SF_6 from the permeation tube, and $[CH_4]$ and $[SF_6]$ are the measured concentrations in the canister.

3.1.3.4. In vitro gas production technique (IVGPT)

Various aspects of in vitro gas production test have been reviewed by Getachew et al. [33], and these authors reported that gas measurement were centered on investigations of rumen microbial activities using manometric measurements and concluded that these methods do not have wide acceptability in routine feed evaluation since there was no provision for the mechanical stirring of the sample during incubation. Another *in vitro* automated pressure transducer method for gas production measurement was developed by Wilkins [34], and the method was validated by Blummel and Orskov [35] and Makkar et al. [36]. There are several other gas-measuring techniques such as (i) Hohenheim gas method or Menke's method [37]; (ii) liquid displacement system [38]; (iii) manometric method [39]; (iv) pressure transducer systems: manual [40], computerized [41], and combination of pressure transducer and gas release system [42].

3.2. Livestock manure as an important source of GHGs

In addition to enteric CH_4 production, livestock manure contributes directly and indirectly to GHG gas production via CH_4, N_2O, and CO_2 production. Manure from livestock includes both dung and urine. Manure management plays a key role in amount of CH_4 and N_2O produced and liberated into the environment. The amount of CH_4 produced in solid-state manure management contribute less when compared to liquid state. However, dry anaerobic management system provides suitable environment for N_2O production. The liquid/slurry manure systems provide favorable environments for the growth of the microbes, which in turn enhances the CH_4 gas production. Various factors that affect CH_4 and N_2O production include the amount of manure, the VFA present, the type of feed, the management systems, and the ambient temperature. In addition, the duration of the storage of waste also influences N_2O production,

3.2.1. Methane emission from manure management

Anaerobic digestion processes occur in manure with the help of microbial consortia to produce CH_4 and CO_2 and consists of four phases: (i) hydrolysis of complex organic particulate matter into simpler low molecular weight compounds; (ii) acidogenesis of simpler low molecular weight organic compounds to organic acids and alcohol; (iii) acetogenesis of organic acids and alcohols to H_2, CO_2, acetic acid, and acetate; and (iv) methanogenesis involves the consumption of acids or hydrogen to produce CH_4 and CO_2. The aforementioned four phases are done by four different groups of bacterial consortia, namely, hydrolytic bacteria, acidogenic bacteria, acetogenic bacteria, and methanogenic bacteria, respectively [43]. CH_4 is also emitted from the collection yard, but it is a minor source. The greatest amount of CH_4 is emitted during storage especially in slurry, the reason being the prevalence of complete anaerobic environment. Solid manure also acts as a source of CH_4 emission. CH_4 is emitted immediately after manure application to the field; however, once the O_2 diffuses into manure, it inhibits CH_4 production [44].

3.2.1.1. Factors affecting methane production from manure

There are several factors that affect the CH_4 production from manure, which includes temperature, organic matter present, microbe load, pH, moisture, and type of feed. However, CH_4 emitted from manure depends primarily on (i) the management system such as solid disposal system, liquid disposal systems, e.g., ponds, lagoons, and tanks, which can emit up to 80% of manure-based CH_4 emissions, while solid manure emits little or no CH_4. (ii) Environmental conditions are also important. The higher the temperature and moisture, the more CH_4 produced. (iii) CH_4 emissions also depend on the quantity of the manure produced, which depends on the number of animals housed, the amount of feed the consumed, and the digestibility of the feed. (iv) Manure characteristics depend on the animal type, feed quality, and rumen microbes present in the rumen and digestive tracks. Manure handled in liquid form tends to release more amount of CH_4 when compared to solid or manures thrown into the pasture, which do not decompose anaerobically. High temperatures with neutral pH and high moisture content enhance CH_4 production [45].

3.2.2. Nitrous oxide emission from manure management

Nitrous oxide is produced from manure by nitrification, denitrification, leaching, volatilization, and runoff. Nitrification and denitrification are direct emissions. N_2O is 16 times more potent than CH_4 and 310 times more potent than CO_2 over a 100-year period [46]. N_2O acts as a source of NO in the stratosphere, which indirectly causes depletion of ozone (O_3), increasing UV radiation reaching the Earth's surface [47]. An increase in animal stocking rates and intensive gazing results in the deposition of huge amounts of N via animal excreta (urine + dung); farm management practices that enhance soil organic N mineralization also lead to N_2O production [1, 48, 49].

3.2.2.1. Mechanism of nitrous oxide production

The emission of N_2O from manure occurs directly by both nitrification and denitrification of nitrogen contained in the manure. This emission mainly depends on the N and C content of the manure during various types storage and treatment. The nitrification process strictly needs oxygen, while subsequent denitrification is an anaerobic process.

Manure from livestock mixes with the soil or in the tank, lagoons, etc., where the microbes break down organic N to inorganic NH_4+ through mineralization. In this step, the organic N becomes available for plants and microorganisms. Microorganisms (*Nitrosomonas* genus) can take up NH_4+ and oxidize it to nitrite (NO_2-). In the next step, *Nitrobacter* and *Nitrococcus* oxidize NO_2- to nitrate (NO_3-) by nitrification. This process of oxidation of NH_4+ to NO_3- is known as nitrification, which is also done by other genera like *Nitrosococus and Nitrosospira* and subgenera *Nitrosobolus* and *Nitrosovibrio* [50, 51].

Studies show that N_2O was emitted from animal houses at the rate of 4–5 mg N m^{-2} d^{-1}, with straw as bedding material, whereas when no bedding material was used, little or no N_2O was emitted from slurry-based cattle or pig building as complete anaerobic condition would have maintained [52]. Deep litter system with fattening pigs showed much higher emission compared to slurry based pig houses, while mechanical mixing still further increased N_2O emission [53]. In cattle collection yards, there had been very less or no N_2O emission as the anaerobic condition prevents conversion of NH_4+ to NO_3-.

Stored solid manures acts as a source of N_2O production/consumption and emission. Covering heaped manure shows reduction in NH_3 emissions but has no effect on N_2O emission, while other studies showed that both were reduced. The addition of chopped straw reduced N_2O emission by 32% from the small scale of cattle manure. [54]. Slurry or liquid manure with no cover showed negligible N_2O release, while slurry with straw cover might act as a source of emission [55]. N_2O emission occurs following manure application to soil [56]. Various factors that affect N_2O release from soil include (i) type of manure, (ii) soil type, (iii) manure composition, (iv) measurement period, (v) timing of manure application, (vi) amount of manure applied, and (vii) method of application.

3.3. Other sources of GHGs from livestock farm

If all parts of the livestock production lifecycle are included, livestock are estimated to account for 18% of global anthropogenic emissions [57]. According to Gill and coworkers [57], apart from enteric fermentation and manure management, the other sources of GHG emission from livestock and related activities are fossil fuels used during feed and fertilizer production and transport of processed animal products.

4. Models for forecasting the greenhouse gas emission in livestock farms

Agricultural production is recognized as a significant contributor to GHG production. Intensive dairy production, in particular, contributes to significant quantities of CH_4 and several forms of nitrogen (N), which can contribute to N_2O production. Over the past 10 years, research studies have attempted to address various sources of GHG emissions within the dairy production system. These sources have included housing [58], manure removal, storage, and treatment systems [59]. Others have compared GHG emissions from conventional farming practices to those employed in organic production. Many of these studies have looked at one section of the production chain in isolation. However, dairy production is a complex system involving inputs such as feed and fertilizer, animals with inherent physiological structures for fermentation of feedstuffs, and the production of manure, storage systems, cropping systems, and export of meat and milk.

It is very easy to understand that attempting to design and conduct research trials to ascertain the effect of one or multiple changes on production, economics, and GHG emissions from a dairy production system would be expensive and time consuming. Therefore, the use of whole farm models, with short-term studies for validation, is an attractive alternative. The integrated farm system model (IFSM) apart from evaluating alternate agronomic feeding, manure storage, and disposal strategies, also accounts for fossil fuel used in farming activities. In real sense, these models do not predict production of GHG but assist in generating some basic information required to predict GHG based on published data.

The development of whole-farm approaches for the mitigation of GHG emissions has been taken up recently by several research groups. A common feature of whole farm models is the ability to calculate CH_4 and N_2O emissions from all farm activities. Furthermore, the models vary considerably on many other aspects. General characteristics of whole farm models include model type, CH_4 and N_2O emissions, CO_2 emissions, C sequestration, NH_3 and NO_3 emissions, P cycling, pre chain emissions, animal welfare, economics, biodiversity, product quality, soil quality, and landscape aesthetics [60]. Whole farm model (WFM) uses pasture growth and cow metabolism for predicting CH_4 emissions in dairy farms. Also included in the WFM is climate and management information. However, recent reports also suggests that WFMs may incorrectly estimate CH_4 emission levels as they do not take into account the DMI and diet composition while predicting the enteric CH_4 emission. This low prediction efficiency of WFMs may lead to substantial error in GHG inventories [10, 11].

The integrated farm system model (IFSM) is a simulation model that integrates the major biological and physical processes of a crop, beef, or dairy farm and evaluating the overall impact of management strategies used to reduce CH_4 emissions [61, 62]. The IFSM is a process-based whole farm simulation including major components for soil processes, crop growth, tillage, planting and harvest operations, feed storage, feeding, herd production, manure storage, and economics [63]. IFSM predicts the effect of management scenarios on farm performance, profitability, and environmental pollutants such as nitrate leaching, ammonia volatilization, and phosphorus runoff loss. The dairy greenhouse gas model (DairyGHG) is a type of IFSM that was developed to provide an easy to use software tool for estimating GHG emissions and the carbon footprint of dairy production systems [64]. Recently, FAO developed a global livestock environmental assessment model (GLEAM), which reported that livestock-related activities contributed around 7.1 gigatonnes CO_2-eq per annum, indicating the prominent contribution of livestock to climate change [65].

A whole-farm approach is a powerful tool for the development of cost-effective GHG mitigation option. The modeling technology can be used to assess the technical, environmental, and financial implications of alternative farm management strategies, under changing external conditions. Whole farm models (WFMs) can reveal relevant interactions between farm components and is useful for integrated scenario development and evaluation. Further, the whole-farm approach ensures that the potential negative trade-offs are taken into account and that positive synergies are identified. In addition, the whole farm models are also used to explore future farm strategies, and since it is operated on farming level, it also provides opportunity for farmers to learn and understand the underlying processes on their own farm. Hence, the whole-farm approach is also helpful in communicating the mitigation option to the farmers, and this could be more beneficial if the models additionally evaluate costs and benefits associating with farming activities.

5. Conclusion

Livestock undoubtedly need to be a priority focus of attention as the global community seeks to address the challenge of climate change. Livestock contribute directly as well as indirectly to global GHG pool. The two primary sources of GHG from livestock are enteric fermentation and manure management. There are several techniques available to quantify CH_4 emission, and the application of appropriate technique depends on objectives of the study. Further, simulation models offer a great scope to predict accurately the GHG emission in farm as a whole. This information will be very valuable in understanding the role of livestock to climate change in depth, and this understanding will help in designing suitable mitigation strategies to reduce livestock-related GHGs.

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Chapter 12

Life Cycle Assessment Method – Tool for Evaluation of Greenhouse Gases Emissions from Agriculture and Food Processing

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Abstract

The chapter focuses on the use of the Life Cycle Assessment method to monitor the emission load of foods from different systems of farming production. The products of the conventional and organic farming production intended for public catering are compared within the SUKI and UMBESA international projects. Conventional farming is mainly characterized by high inputs of mineral fertilizers, chemical pesticides, the use of hormones and stimulants in animal husbandry. It is a system based on the highest possible yields without respecting the natural principles of nature. Conversely, organic farming is a system of production established by the legislation that respects fundamental natural cycles, such as crop rotation, ensures welfare of animals, prohibits the use of fertilizers, pesticides, and other substances of synthetic origin. However, lower yields are a big disadvantage. In the Czech Republic, only about one tenth of the agricultural fund is currently used for organic farming. Arable land constitutes only about 10% of the total area of agricultural land, other areas are mainly grasslands and orchards. The work primarily aims to answer to the question whether the selection of foods may contribute to decrease in greenhouse gas emissions, which is a part of the objectives of many policies. Besides the comparison of agricultural production, processed and unprocessed foods, local and imported foods and fresh and stored foods were compared as well. The Life Cycle Assessment (LCA), which is used to assess environmental impacts of products and services throughout their entire life cycle, was used to quantify the emission load. This method may be briefly characterized as a gathering of all inputs and outputs that take place during the production in the interaction with the environment. These inputs and outputs then also determine the impact on the environment. The LCA consists of four successive and iterative phases: This concerns the definition of objectives and scope, inventory analysis, impact assessment and interpretation of the results. The LCA was originally developed for the assessment of impacts of especially industrial products. Certain methodological problems and deficiency, which bring a level of uncertainty of the results, have been caused by its adaptation to agricultural product assessment, but this method is

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still recommended for comprehensive assessment of environmental impacts of agricultural production and the comparison of different agricultural products. In this study, a Cradle-to-Gate assessment was performed, which means that the impacts of products (in this case the emission formation) were evaluated only to the delivery of foods to public facilities, further treatment and waste management was not assessed. About 20 most frequently used foods for school catering facilities were compared. The results of the project confirm the general assumption about the less emission load of unprocessed, fresh and local products. It may not clearly state that products from organic farming produce less emissions when comparing agricultural systems. It always depends on the particular crop. The absence of synthetic substances such as fertilizers and pesticides reduces the emission load of organic farming, on the other hand, a higher number of mechanical operations and especially the lower income clearly increase the emission burden, therefore, in several cases, lower emission loads of crops were achieved using the conventional farming system. However, less emission may be achieved within the organic farming system. Among 11 evaluated agricultural products, 8 organic products and only 3 conventional ones go better. The situation is different regarding the following phases of food production, processing and transport. The transport phase significantly worsens the environmental profile of organic foods, because transport distances are too far due to insufficient processing capacity and underdeveloped market networks, and often exceed the emission savings from the agricultural phase. On the contrary, conventional foods are carried within relatively short distances, therefore the final emission load of conventional foods is in many cases fewer than the load of organic foods. This fact is also confirmed by the result of the study, because among 22 evaluated foods, organic food goes better in 11 cases and conventional food in 11 cases as well.

Keywords: LCA, conventional farming, organic farming, greenhouse gases, food

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1. Introduction

Currently, agriculture is one of the largest anthropogenic activities with global impact. The area of agroecosystem that covers about one third of the landmass [1] is directly related to the need of humans to survive and it follows the population growth to a large extent. With the growing population curve, the pressure on natural habitats and their conversion to agricultural land and intensification of farming on existing agricultural land also increases. Since the population growth continues very rapidly and also the consumption of meat, respectively animal products, and the energy consumption in agriculture increase, we cannot expect that in the foreseeable future, a spontaneous reversion of the trend of increasing environmental load will come [2].

The environmental load increase impacts the soil, water, biodiversity and, last but not least, the atmosphere. Climate changes and anthropogenic contribution to them have become a frequently discussed issue in recent years. It is not clear yet to what extent these changes are natural and to what extent they are influenced by human activities. Many questions have not been answered yet and the discussion on whether the climate change is determined by natural evolution or negative consequences of human activity is still held [3]. Just the anthropogenic share of changes, especially in terms of GHG (Greenhouse gases) emission production, may be regulated while this activity is one of the priorities of sustainability.

Climate changes have a significant impact on agricultural systems in the world and can be a crucial factor in ensuring sustainable food production. [4] states that, within the European Union, the largest polluters are energetics, which releases 27.8% of anthropogenic greenhouse gas emissions, transport with 19.5% and industry with 12.7%. Agriculture is with 9.2% in fourth place. Current agricultural trends tending to sustainability should establish more environmentally friendly ways while maintaining the ability of the population food assurance. In order to take steps in this direction, it is necessary to understand agricultural impacts and be able to quantify them. In the case of greenhouse gases, the accurate quantification is quite difficult. However, there are some methods that can help to implement it. One of the methodological tools is the Life Cycle Assessment - LCA. It can be used to quantify GHG emissions, respectively emission saving options. It is a transparent scientific tool [5] which evaluates the environmental impact on the basis of inputs and outputs within the production system [6]. Additionally, LCA analysis currently offers (as one of the few tools) a comprehensive approach to assess the environmental effects [7]. A very valuable tool is LCA analysis thanks to its ability to incorporate and compare different farming systems, their individual processes and products and most of their environmental impacts [8].

Considering the choice of farming system, respectively changes within particular farming systems, as a tool for mitigation, we need to quantify their total impact first and to find the most problematic areas in terms of emissions that can provide space for an effective change. The choice of farming system could be one of the ways to reduce the anthropogenic share of GHG emissions while organic farming seems to be one of the ways. In the last decade, organic farming has become an important element in the environmental friendliness policy and the policy of quality of food in Europe because, inter alia, it reduces the use of synthetic fertilizers and other chemicals such as pesticides [9]. However, mitigation can be achieved also within conventional and integrated farming systems and within food production in general. Reduction of emissions and environmental load in general is a necessary way to long-term sustainability within current population conditions.

2. Literature search

2.1. Climate change and agriculture activities

Anthropogenic activities have a very strong impact also on the environment. With increasing population curve, globalization, technological progress and higher consumer demands, also environmental pressure and environmental impacts grow. There are many impacts from impacts on water, soil, biodiversity to the impacts on the air. Just the anthropogenic air pollution and its relation to climate changes is a big current issue.

Agriculture is ranked among the five major anthropogenic activities contributing most to the production of greenhouse gases. Global GHG emissions from agriculture reach values from 5,1 to 6,1 billions tons of CO_2 equivalent [10]. [11] sets out the share of emissions of greenhouse gases (CO_2, N_2O and CH_4) from particular fields of human activities, while his findings indicate that agriculture in 2000 contributed to the anthropogenic emissions with 13.5%. More than one third of agricultural emissions are field emissions (especially N_2O), methane (CH_4) makes up about one third. Also [12] states that agriculture contributes to the worldwide emission production with the share of 10-12%, while until 2030, we can expect an increase of even half these values [13]. Agriculture is a significant emission producer in the EU also according to [14]. The total share of GHG emissions from agriculture within the EU-27 was 10.1% in 2011 [15]. We can find similar values also in the paper by [16] who states that this share within the EU-15 was 10.2% in 2009. In the Czech Republic, the share of agricultural emissions in total greenhouse gas emissions is calculated at 6.42% [17].

According to [18], 29% of emissions produced within the EU is related to the food production. However, these emissions arising within food production are related not only to the field cycle but also to the production of fertilizers and agrochemicals, processing or all process transport. [18] sets the share of food production to anthropogenic emissions to 22-31% while the most significant proportion (15%) is related to transport.

[19] also stated the high dependence of agriculture on non-renewable materials and to a great extent, the resulting increased GHG emissions production. Agriculture produces emissions in many ways. For example, CO_2 is released during the consumption of fossil fuels or within reduction of organic matter content in the soil. N_20 is released as a result of fertilizer application, CH_4 from the digestive tract of some livestock species. We can conclude that the amount and composition of our diet reflect the specific features of particular technological processes in agriculture and thus the different GHG emission production. Therefore, the change in the way of nutrition in industrialized countries can be extremely important to ensure sustainable development (admittedly conditional on the stabilization of anthropogenic GHG emissions) [20].

2.2. Farming systems

Production systems have their own characteristics and can be categorized into groups e.g. according to density and the resulting impact on the environment. Conventional farming systems are commonly widespread, alternatively, there are integrated and organic farming systems.

2.2.1. Conventional farming

Conventional farming is the most common way of farming in agriculturally advanced countries. Its main objective is to maximize production. Other farming aspects are secondary. Conventional farming is implemented in various intensity degrees. Environmentally friendly processes beyond the ordinary laws are not enforced and monitored. Still, conventional farmers can implement these processes and farm in accordance with environmental protection. However, the European Union introduces a number of rules and legislative provisions for conventional farming leading to limiting inputs in order to protect the environment. On the contrary, in its extremely intensive forms, the conventional farming often leads to excessive environmental damage. The precision farming is a technologically advanced form of conventional farming that reduces environmental load to some extend through more efficient and optimized inputs.

2.2.2. *Integrated farming*

Integrated farming is a kind of an intermediate step between conventional and organic farming systems, originally based on integrated plant protection and extended to other agrotechnical processes. Its objective is the sustainability of farming system and it is largely focused on procedures friendly to the environment. However, unlike organic farming, it is not strictly limited by legislation and it is possible, if necessary, to apply procedures that are forbidden within organic farming (e.g. the use of some agrochemicals).

2.2.3. *Organic farming*

Organic farming is a special kind of farming that cares about the environment and its particular components through restrictions or bans on the use of substances and procedures that burden the environment or increase the risk of contamination of the food chain. Within livestock breeding, it ensures their behavioural and physiological needs in accordance with the requirements of specific legislation. It becomes an environmentally friendly alternative to other farming systems [21]. The main goals of organic farming include:

- Maintenance and improvement of soil fertility.
- Genetic resources protection and biodiversity maintenance.
- Preservation of landscape features and their harmonization.
- Water management, keeping water in landscape and the protection of surface and groundwater against contamination.
- Efficient use of energy, focusing on renewable resources.
- The pursuit for maximum nutrients recirculation and a prevention of the entry of extraneous substance into agroecosystem.
- Production of quality food and raw materials.
- Optimization of life for all organisms, including humans.

Organic farming systems create more potential to reduce greenhouse gas emissions than conventional. The biggest difference is due to the absence of chemical fertilizers. The Farming Systems Trial at Rodale Institute, an American long-term research comparing organic and conventional agriculture, states that the introduction of organic farming nationwide in the USA would manage to reduce CO_2 emissions by up to a quarter due to increased carbon sequestration in soils [22]. The disadvantage of organic farming is less production per the area unit that increases the unit emission load. [23] states that yields of organic farms are on average 17% lower than within conventional farming systems. The impact of organic system on the mitigation is usually measured per the area unit in order to enhance the objectivity. However, it is important to convert it also to the production unit.

2.3. A Life Cycle Assessment

The aim of the assessment of the effects of agricultural products on the environment is to evaluate their impact on environment sustainability [24], especially in terms of food consumption patterns [25]. As stated by [26], the system sustainability can be evaluated on the basis of inputs and outputs and their conversion to CO_2e. [27] states that the measurement of GHG emissions suffers from certain inaccuracy. The reason for this error is that emissions in agriculture are influenced by complex biological processes with a wide range of variables.

There are some suitable methods to assess environmental impacts of agricultural activities [28] such as Life Cycle Assessment (LCA), Ecological Footprint or Emergy Analysis. [29]. The LCA method may be briefly characterized as an assessment of all inputs, outputs and possible impacts on the environment during the entire life cycle [30]. LCA analysis is a tool that enables to assess environmental impacts within the product life cycle. Social or economic aspects may be included as well, however, the calculation of their impacts has only just begun [31] and the main focus is on the environmental component which evaluates, according to [32], the environmental impact of a product based on the assessment of the material and energy flows, that the monitored system shares with its surrounding space (environment).

[33] states that the LCA is an appropriate instrument because it enables to express the relationships between the food production, transport and production of CO_2.

With the LCA analysis, the impact categories - the impact on climate, water pollution and air pollution - are mostly evaluated. Whereas, impacts such as biodiversity or pesticide toxicity are seldom evaluated because of methodological problems [34]. The LCA study consists of four basic stages: Definition of objectives and the scope, Inventory, Impact assessment and Interpretation [32].

2.3.1. Goal and Scope definition

In the first stage of the LCA analysis, it is necessary to define the objective and the scope of the paper before the actual start [35]. The study goal and scope definition determine the next procedure character and the circumstances in which the study outputs are valid [32]. [36] requires to establish a study goal and scope while the study scope means to determine the product system, the functional unit and system boundaries, to determine allocation rules, the assessment methodology, hypothesis and limits and data quality.

In the objectives of the study, there must be clearly specified who it is addressed to, the reasons for the study and the intended use of the results [36]. This increases the transparency of the study and the comprehensibility of the context of the results since different recipients emphasise different aspects.

The study scope results form goals and is determined by financial resources of the ordering authority and the available time of the processor [5]. The study scope describes the most important methodological choices, hypothesis and limits [35] that are described below.

2.3.1.1. Function and functional unit

To compare products (systems), it is necessary to define also the functional unit. The functional unit is described as a quantified performance of a product system which serves as a reference unit in a study of life cycle assessment [36]. It is an essential element which all study results are related to. It must be chosen so as to be easily expressible and measurable. The functional unit is the starting point for searching for alternative ways how to fulfil the function with a lower negative impact on the environment [5]. [37] states that the determination of functional units is as a crucial step especially when comparing systems with different levels of production per hectare such as conventional and organic farming system. [38] sees fit to set the production unit instead of the area unit as a functional unit. On the contrary, [9] recommends to involve both functional units into calculations and perform the calculations for both the unit area and the unit of production. This is confirmed also by [39] who states that LCA analysis outputs are usually set per the production unit. Some authors, such as [40], state that LCA outputs should by calculated in relation to the area unit allowing the better expression of environmental load carrying capacity. With the LCA analysis, we cannot perform both calculation methods and use the production unit as well as the area unit as a functional unit [2].

2.3.1.2. System boundaries

Each product system consists of a variable number of processes involved in the product life cycle. However, the product under consideration is often related to other processes that may no longer be important for the LCA study. The system boundary serves to the separation of essential and non-essential processes of the product life cycle. Since the choice of system boundaries significantly affects LCA study outcomes and in addition, its intensity and complexity, system boundaries should always be well considered and clearly defined. The choice of system boundaries is carried out with regard to the studied processes, studied environmental impacts and selected complexity of the study. Not-including any life cycle stages, processes or data must be logically reasoned and clearly explained [32].

Determination of system boundaries is always a very important step, especially in the area of food production and agriculture, where the clearly identifiable technological processes and systems meet the natural processes and procedures influenced by a number of factors [41]. The system boundary defines which unit processes will be included in the monitored system [36]. The system boundary definition virtually defines which life-cycle stages will be analysed (in the case the whole life cycle was not included) or what unit processes and elementary flows will or will not be considered. The system boundaries can be restricted to the processes within the farm [42], or can extend into other phases from pre-farming processes, through transport and storage, to the end user, respectively consumption. [43] states that although it would be desirable to include the entire product cycle, most studies of food production omit some phases, usually trade and other related sections. Their impact is mostly negligible in relation to e.g. the agricultural phase [44]. When comparing conventional and organic farming systems, we can also omit the calculation of load from buildings and infrastructure because there are only small differences between farming systems while slightly more noticeable difference is apparent within animal production [45].

System boundaries determine not only which processes will be incorporated into the product scheme, but also define the geographic and temporal scope of the study to determine its purview. Defining the geographical scope (local, regional, national, continental or global) or determination of the exact study location is important for the environmental aspects of various material and energy flows because their impacts may be different in different geographical conditions. E.g. due to different ways of development of power in each country, the environmental impact of power development and hence of energy consuming processes is different. Using unsuitable system boundaries or oversight of important factors such as the place and method of energy development can lead to false results.

2.3.1.3. Allocation principles

During the life cycle assessment, the study authors are very often confronted with the fact that the product system has at its end more than one output. In these cases, we use the allocation. Allocation means the assignment of the share of total environmental burden to particular outputs [32]. The Standard recommends to avoid the allocation whenever possible, e.g. by extending systems or sub-division processes [36].

In the case we cannot avoid the allocation using the above mentioned methods, the Standard proposes to use the allocation based on the physical principle such as weight or energy content of final products.

2.3.1.4. Data quality

The quality of data entering the LCA study is to be determined in view of temporal, spatial, technological, data sources (it must be determined whether primary data required or secondary data can be used), their accuracy etc. It concerns the determination of all requirements for the input data [5].

2.3.2. Life Cycle Inventory

The inventory tasks is to collect environmentally important information about relevant processes involved in the product system. Inventory collects information about unit processes at first and subsequently, an inventory of inputs and outputs of the system and its surroundings is carried out. The goal is the identification and quantification of all elementary flows associated with product system. Inventory analysis is the nature of the technical implementation of LCA studies. It is an essential part of a study, has high demands for data availability, practical experience in modelling product systems and, in the case of using database tools, it is necessary to master them perfectly and to understand their function [46]. The inventory phase principle is data collection that is used to quantify values of the elementary flows. This phase represents a major practical part of the LCA study, time consuming and with demands for data availability and author's experience with modelling product system studies [47].

2.3.3. Life Cycle Inventory Assessment

The inventory results should be presented in clear form, how much and what substances from the environment enter the system and how much get out. These results serve for subsequent life cycle impact assessment [48]. The aim of the life cycle impact assessment is to measurably compare the environmental impacts of product systems and to compare their severity with new quantifiable variables identified as impact category. The impact categories are areas of specific environmental problems such as global warming, climate changes, acidification, eutrophication, ecotoxicity and others. Already in the phase of definition of the LCA study scope, it is necessary to describe what impact category will be applied and which of their environmental mechanisms will serve as a basis for impact assessment [46].

2.3.4. Interpretation

The outcome of the LCA study is a large amount of different values from the inventory as well as from the life cycle assessment. An important task for the study author is to sort the data and their appropriate and understandable interpretation [32]. The need for proper interpretation is also stated by [49] who states that on the basis of LCA outcomes, there are often taking steps with significant economic, environmental and other impacts, while there is the risk that incorrect and misleading interpretation of outputs can lead to a deepening of existing or creating new problems. Since the form of presentation of data often affects their meaning, the life cycle interpretation has become an integral part of LCA studies and gained some rules. On the general, interpretation of LCA consists of structuring data with regard to the most important processes or process groups and the most important substances, performing sensitivity analyses and evaluation of the uncertainties of the study, discussion of the data meaningfulness in relation to the study completeness and the input data quality, and the final summary and formulation of realistic recommendations.

3. Goal of the study

The main objective of the Czech - Austrian SUKI (Sustainable Kitchen) project was to assess the total amount of GHG emissions produced by public catering facilities.

These emissions originate both within energy consumption for the kitchen operation (ie. lighting, heating, ventilation, cooling, operating kitchen appliances, cooking process), but mainly in the food production, processing and transport to catering facilities. While direct energy consumption in the kitchen can be determined relatively easily, emissions from food production are unexplored areas in the Czech Republic. The project set the target to answer following questions using the emission quantification:

- What is the influence of the production method (conventional, organic) on the GHG emission production?
- What is the influence of the place of the food origin (region / outside the region) on the GHG emission production?

- What is the influence of the food processing method (raw, processed, fresh, frozen) on the GHG emission production?

By answering these questions, we can deduce the possibilities and limits of greenhouse gas emission savings without compromising the food quality which is also subject to the actual selection of foods, meals and a preparation process. The aim is to promote catering facilities on the path to sustainable production and at the same time to the food nutritional quality improvement. Through targeted food selection, they can take a step towards sustainable development and a healthy diet, contribute indirectly to the global reduction of greenhouse gas emissions while promoting regional organic farming.

4. Methodological procedure

In the first project stage, it is necessary to identify the most widely used ingredients heading for school catering facilities. For this purpose, we used annual lists of purchased raw materials from partner catering facilities that were processed by tabulating and from them, all the ingredients that made up at least 80% of the raw materials used kitchens during the year were selected. These lists also provide a good comparison between Czech and Austrian cuisines.

The second step and the focus of this chapter was to evaluate the emission load of individual foods from the list of most common foods. There was used the simplified Life Cycle Assessment method in which only the Climate change Impact category was assessed. Detailed description of the LCA methodology is shown in the literature review, the following text describes practical method implementation.Food emission load evaluation using the LCA method

4.1. Goal and Scope definition

On the basis of evaluation of consumption of involved catering facilities, 11 most commonly used products were selected. When work them into other raw materials, we can expand the list to final 22 products that heading for school kitchens. For each product, a comparative study focused on the comparison of organic and conventional versions, imports and regional variants was elaborated, if possible, the also a comparison of the fresh and stored product was made, as well as a comparison of different stages of processing. The results should serve as an answer to the question whether the selection of the food contributes to reducing greenhouse gas emissions. The target group are the chiefs of kitchens, school principals, cooks, diners, farmers, suppliers, as well as actors at the regional and national political level.

Evaluated systems were modelled with the cradle to gate principle, thus the product system of particular foods was terminated at the point of entry into the school canteen. The following presentation of food and related activities, as well as waste management of the product and its packaging materials were not included in the LCA. One kg of the final food was selected as a functional unit. In the case the allocation was necessary, the weight-economic allocation was used.

4.2. Life Cycle Inventory

At this stage, it was necessary to collect the relevant data relating to the entire product system. The product system was divided into sub-processes: agriculture, processing and trade. For agriculture, inputs relating to the consumption of seeds, fertilizers, pesticides and fuel within agricultural operations for crop production, feed consumption, energy and fuel within the livestock sector were surveyed. Emissions from nitrogen fertilizer application within crop production calculated according to the methodology [50] and emissions from manure management in the livestock production, calculated according to the methodology [51], were integrated into agriculture. A general framework for crop and livestock products is shown in Figure 1 and Figure 2.

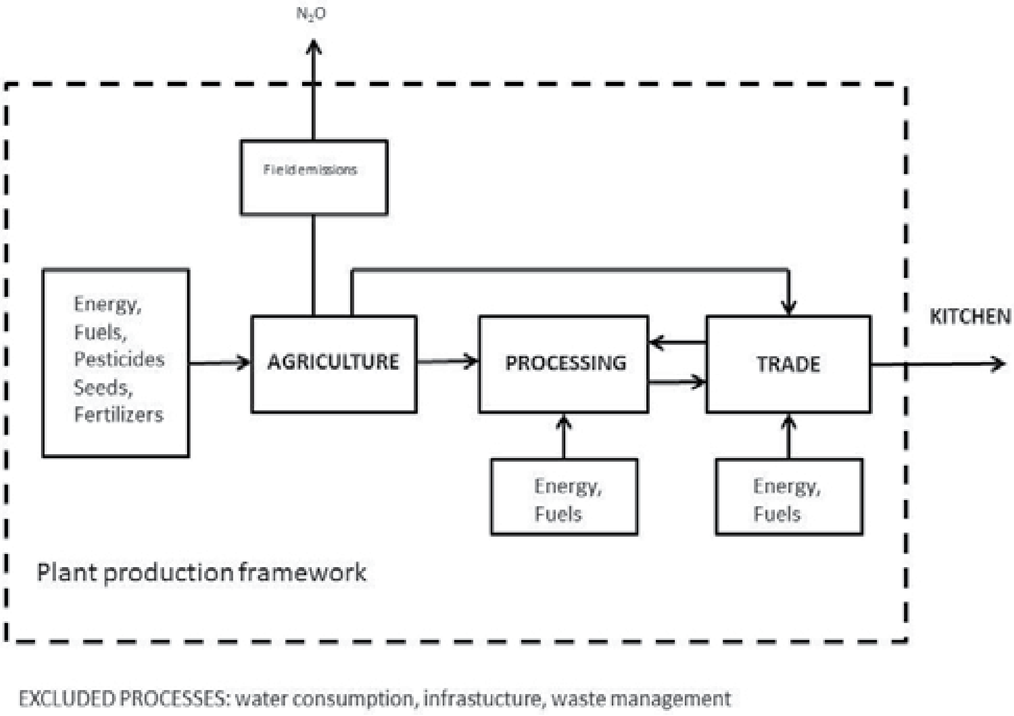

Figure 1. Framework of plant food product LCA

For processing, the data on energy consumption were collected, within the trade, it was travel distance, information on cargo and storage time of various foods. All data was obtained primarily from farmers, processors and traders, absent sufficient data, it was supplemented by data from available databases, especially the Ecoinvent database.

From a geographical point of view, regarding the data quality, the data corresponds primarily to the Czech Republic, secondarily to Central Europe. In terms of time, data corresponding to the term 2000 - 2012 were obtained, from a technological point of view, data corresponds to the widely used average technologies.

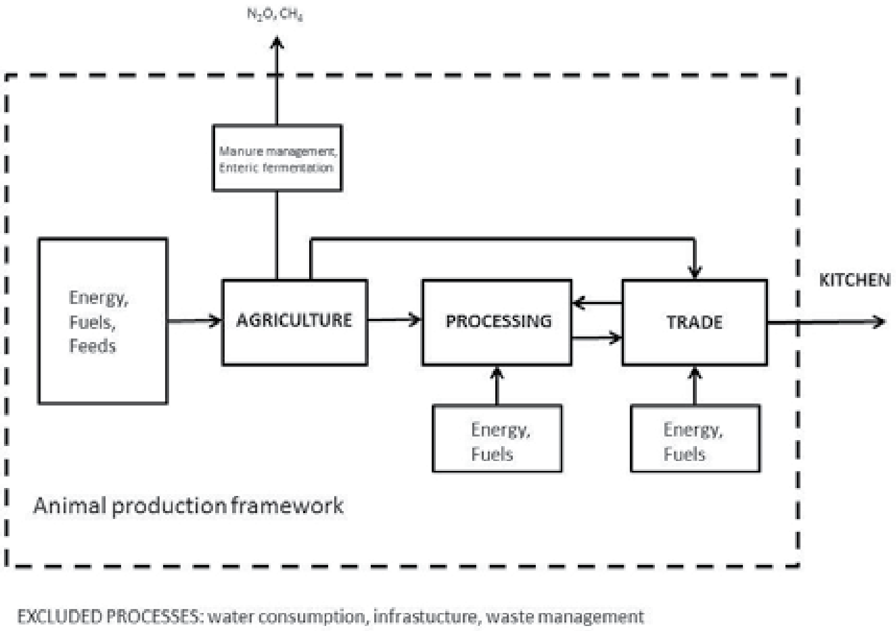

Figure 2. Framework of animal food product LCA

4.3. Life cycle inventory assessment

The results were calculated using the SIMA Pro software. To obtain the necessary results, the Recipe Midpoint (H) Europe method has been chosen as a characterization model. Results come from the climate change impact category and they are expressed in kg of a carbon dioxide equivalent (CO_2e).

4.4. Interpretation

Result interpretation and discussion is given below.

5. Results

Based on the analysis of the annual consumption of foods of participating catering facilities, there were 22 of the final products which constitute the largest food consumption selected.

5.1. Emission load in food production

5.1.1. Agricultural phase

A basic emission load resulting from agriculture involves the calculation of greenhouse gases in the field phase. In the context of comparing the formation of greenhouse gas emissions in the cultivation of selected crops and breeding of selected species within conventional and organic farming systems, the total greenhouse gas emissions with twelve agricultural products were observed. This total amount sum was divided into subgroups within crop production: agricultural engineering, fertilizers, pesticides, seed and field emission, and in the context of animal production to: feed consumption, manure management, and in the case of cattle on enteric fermentation.

In the case of crop production, the conventional farming system differs from the organic one in the total CO_2e emissions production as well as in the production within subgroups. Although the production of GHG emissions differs within particular subgroups, in total with most studied crops, the production of CO_2e is lower in the organic farming system. In the primary agricultural study, [52] monitored a set of crops including wheat, rye, potatoes, onions, carrots, tomatoes and cabbage, while the higher greenhouse gas emissions expressed as CO2e within the conventional farming system in the Czech Republic were found with all investigated crops except onions. The greatest differences were found with carrots and cabbage where the ecological variants produced almost 60% lower emissions than the conventional variant. The extension study [53] complements the study with the comparison of emission load of organic and conventional apples and rice, where the results showed almost the same burden for rice and in the case of apples, 33% lower emissions within organic farming. Another extension study [54] comparing garlic proves again 40% lower emissions when grown in the organic farming system. In conclusion, it can be summarized that in the context of plant production, eight of ten evaluated products were better as an organic variant, one raw material showed the same emissions in both variants and only one crop was better in the conventional variant. Results and emission savings are summarized in the Table 1.

Group	Product	Organic*	Conventional*	save BIO
corn products	wheat	0,4218	0,4606	8%
	rye	0,2972	0,5364	45%
	rice	0,6197	0,6266	1%
vegetables products	potatoes	0,1256	0,1446	13%
	cabbage	0,0329	0,0774	58%
	carrot	0,0411	0,0987	58%
	tomato	0,0671	0,0871	23%
	onion	0,0997	0,0828	**-20%**
	garlic	0,2480	0,4306	42%
fruit products	apple	0,0568	0,0848	33%

*in kg CO_2e/kg of products

Table 1. Emission of GHGs from the plant production (agriculture phase only)

Comparative studies show positive and negative factors of organic farming which are mainly lower yields and specific agronomic rules. It coincides e.g. with findings by [55]. The organic farming is more agricultural operations intensive as compared with the conventional one. For most crops, emissions from production of one kg are higher due to more intensive agricultural technology (especially mechanical protection against pathogens), while the difference is even increased by generally lower yields in organic farming. Emission load within the agrotechnical phase in the organic farming system is increased also by some operations related to pre-seeding soil preparation. The possibility of reducing GHG emissions by changes in agricultural technology is highlighted e.g. by [56] who identifies the main potential for reduction within tillage.

The fundamental difference between the conventional and organic farming system in terms of GHG emissions is obvious within fertilization. While organic farming uses organic fertilizers (especially manure or slurry), the use of synthetic fertilizers within the conventional farming system increases significantly the share of emissions. This is stated also by [57] who gives synthetic fertilizer decrease as one of the main tools for reducing CO_2e emissions. From an economic perspective, the nitrogen in organic farms is financially much more demanding than industrially produced nitrogen. This is a powerful incentive to try to prevent losses and learn how to use recycling technology [58]. Timing and management of nitrogen application are crucial. Soil mineralization processes should deliver components to plants when the plants are most in need [10]. In conventional farming, GHG emissions are increased also due to the use of pesticides. In organic farming, this load is completely eliminated, respectively, transferred to the agrotechnical phase in the form of mechanical plant protection. However in total, it is a relatively low proportion of total emissions. [59] can see here another opportunity to save emissions.

Within plant production, in organic farming, there is space for reducing greenhouse gas emissions per the production unit and an increase in income, while maintaining the current input structure.

To compare the emission load of livestock products, several studies were carried out again. Initial work [61] compared load from conventional and organic cattle breeding without milk production. One kilogram of organic beef produced twice higher emissions than one kilogram of conventional meat. Another study [53] compared pork. Organic pork was again worse than conventional meat in terms of emissions. On the contrary, when comparing variants of milk, organic milk was a little emission-less burdensome than conventional milk. The latest from animal studies compared the production of eggs [62], where organic eggs produce almost 40% lower emissions than conventional eggs. Results and emission savings are summarized in the Table 2.

The higher emission load in organic farming systems is mainly due to technology of rearing and fattening when in the organic farming system, young ones are fed with breast milk while in conventional breeding, they are fed with feed. Production of breast milk causes significantly more emissions then production of crops for feed mixtures. Additionally, within conventional breeding, the emission load is divided among several products (meat, milk).

Product	Organic*	Conventional*	save BIO
milk	1,336	1,420	6%
egg	0.219	0.383	43%
beef	24,10	11,45	**-110%**
pork	6,643	5,143	**-29%**
*in kg CO_2e/kg of products(in egg study in kg CO_2e/egg)			

Table 2. Emission of GHGs from the animal production (agriculture phase only)

5.1.2. Manufacturing phase

Environmentally friendly farming systems that utilize anti-erosion measures, advanced methods of nitrogen management and other measures, have the potential to sequester carbon and reduce greenhouse gas emissions [63]. This creates a positive environmental potential which may however be discarded in the following, or vice versa agricultural stage preceding, parts of the food production process which could result in a significant increase in CO_2e emissions. [64] states that within cereal production, the production of fertilizers in the pre-farming cycle makes up 35% of total emissions, while the farm stage only 27%.

Importance of pre-farming and post-farming stage can be documented by the example of potato, where [65] states the production of 0.145 kg of CO_2e in the conventional and 0.126 kg of CO_2e in organic farming system per one kilogram of potatoes. However, if we take into account also other phases (especially the processing and transport), the load resulting from potato products in relation to potatoes grows significantly. For one kilogram of peeled potatoes in the Czech Republic, it is 0.262 kg of CO_2e in conventional 0.247 kg of CO_2e in organic farming systems. However, for the manufacture of chips, it is already 2.072 kg of CO_2e in conventional and 2.271 kg of CO_2 in organic farming systems per one kilogram of finished product. And in the case of mashed potatoes, even in conventional production, it is 3.201 kg of CO_2e and in organic production 3.192 kg of CO_2e. These findings suggest that the differences between the production systems are relatively small if we compare it to the difference in CO_2e emissions between processed and unprocessed products. Another important factor is also common transport distances. Their importance is higher with the processed products that are in their life cycle more transported (besides transporting raw materials, there is still transport of semi-finished products between processing units). The transport distance is also affected by the density of processing networks and infrastructure. The results of the finished material (see Table 3) in our study [53] showed that eleven of the 22 evaluated products have better results as a conventional variety and eleven products have better result as a organic variety. This indicates a lack of potential of a manufacturing and sale network for organic products.

Group	Product	Organic*	Conventional*	save BIO
corn products	wheat	0,4593	0,4699	2%
	rye	0,3336	0,5495	39%
	wheat flour	0,6463	0,5861	**-10%**
	rye flour	0,5080	0,6737	25%
	roll	0,8100	0,7766	**-4%**
	bread	1,0431	1,0632	2%
	pasta	0,7336	0,7020	**-5%**
	rice	0,6197	0,6266	1%
vegetables products	potatoes	0,1931	0,1867	**-3%**
	peeled potatoes	0,2475	0,2624	6%
	puree	3,1918	3,2009	**0%**
	pommes	2,2714	2,0718	**-10%**
	cabbage	0,0851	0,1151	26%
	carrot	0,1158	0,1517	24%
	tomato	0,1748	0,1802	3%
	onion	0,1749	0,1285	**-36%**
	peeled onion	0,2428	0,1789	**-36%**
fruit products	apple	0,1273	0,1189	**-7%**
milk products	milk	1,4870	1,5603	5%
	yoghurt	1,7390	1,8123	4%
meat products	beef	24,5313	11,6510	**-111%**
	pork	6,7452	5,3083	**-27%**

*in kg CO_2e/kg of products

Table 3. Emission of GHGs from the final products

Besides transport distances, also the way of transportation has the influence. E.g. [63] states that significant energy savings could be achieved by rail preference which can reduce power consumption by up to half while emissions of greenhouse gases are reduced comparably. These factors, together with the production technology may, in some cases, eliminate emissions savings resulting from environmentally friendly management system. The principle of regionality which reduces unnecessary transport processes is thus superior to the principles of organic farming, since its failure may to reduce or completely eliminate the environmental potential, respectively, the emission savings resulting from organic farming,. Reducing the environmental potential can be demonstrated e.g. by the example of the production of bread in conventional and organic farming systems in the Czech Republic. Thanks to the low-volume technologies in production of bread in organic processing capacities, produced greenhouse gas emissions are much higher, so the positive effect of previous organic cultivating of wheat and flour production is eliminated [66]. Post-farming life cycle stages of agricultural products are very significant in terms of GHG emission production because within them, the emission savings generally made by organic farming in relation to conventional farming can be devalued. Assuming that the growing agricultural systems with arable land and permanent crops and grazing systems worldwide can sequester up to 200 kg C ha-1 year-1, the global carbon sequestration can reach 2.4 billion tons of CO_2e year -1. This minimum idea of conversion to organic farming would be able to lose 40% of global agricultural GHG emissions [10]. Environmentally friendly and organic farming systems are such an important tool for reducing greenhouse gas emissions.

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Carbon Footprint as a Tool to Limit Greenhouse Gas Emissions

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Additional information is available at the end of the chapter

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Abstract

The Carbon Footprint is the amount of greenhouse gases (GHG) produced during the life cycle of a product, a process, or a service (expressed in equivalent tons of carbon dioxide per functional unit of analyzed product/process/service). The patterns of fossil fuel combustion, carbon capture and sequestration, and conventional and unconventional fossil fuel production, but also the emissions linked with consumer behavior, can be analyzed considering their carbon footprint. In this chapter the carbon footprint tool is introduced, linking it to fossil energy systems and renewable energy systems, as well as the main products on the market, to provide information on which technology should be promoted to reduce GHG emissions.

Keywords: Carbon Footprint, ISO 14067, GHG, Life Cycle Assessment

1. Introduction

Carbon footprint, as an indicator of the impact of the emissions of GHG of products and services, is interesting for enterprises, consumers, and politicians [1]. Investors control the carbon footprint of their products as it is an indicator of their investment risk. Purchasing managers are interested in the carbon footprint of the goods that they are dealing with, and the market is beginning to offer consumers carbon-labeled products. These are the reasons for the popularity of product carbon footprint. It is defined as the mass of cumulated CO_2 emissions that can be measured through a supply chain or through the life cycle of a product [2]. The average per capita carbon footprint of continents and of the most important nations is reported in Table 1 (data are expressed in equivalent tons of carbon dioxide per capita per year). Also the contribution of different sectors is reported (expressed in percentage).

	Country footprint [tCO2e/p]	Construction (%)	Shelter (%)	Food (%)	Clothing (%)	Manufactured products (%)	Mobility (%)	Service (%)	Trade (%)
Europe	13	9	21	16	3	12	21	17	6
USA	29	7	25	8	3	12	21	16	8
Canada	20	8	18	8	2	9	30	18	6
South America	5	6	8	36	3	8	22	13	5
Russian Federation	10	9	40	15	1	3	16	17	1
Asia	7	11	14	24	4	11	19	16	4
Africa	2	6	13	40	2	6	10	22	3
Australia and New Zealand	16	8	18	18	3	9	19	16	13

Table 1. Carbon footprint of continents and most important nations [3]

Carbon footprint is most appropriately calculated using life-cycle assessment or input-output analysis [3,4]. In this sense it is based on the ISO 14040 [4] and ISO 14043 [5] norms, on life cycle assessment (LCA). Specific norms for carbon footprint of enterprises and products are ISO 14064 (part 1,2, and 3) [6-8], ISO 14067 [9], and PAS 2500 [10]. Carbon footprint calculation process is shown in Figure 1.

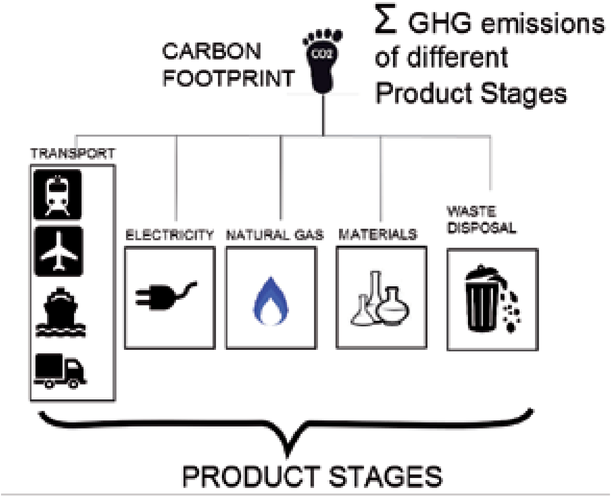

Figure 1. Carbon footprint calculation

Main emissions due to the most important processes are added through the whole life cycle. Carbon footprint of a purchased good or service can be calculated using Equation 1 [11].

$$PCF=S1+S2+S3+S4+OE \tag{1}$$

Where:

- S1 is the sum across purchased goods and services;
- S2 is the sum of emissions due to material inputs;
- S3 is the sum of emissions due to transport of material inputs;
- S4 is the sum of emissions due to waste outputs;
- OE stands for other emissions emitted in provision of the good or service.

In order to calculate carbon footprint, it is very important to consider the boundaries of the process: which emissions should be considered in calculation of the footprint? This problem can be solved by considering three definitions: Scope 1, Scope 2, and Scope 3.

Scope 1 indicates direct emissions, for example, on-site emissions; Scope 2 indicates emissions embodied in the purchased energy; and Scope 3 indicates all the emissions not covered under Scope 2, such as those associated with transport of goods and waste disposal [12].

Another important aspect is the functional unit, which is defined as a measure of the function of the studied system, and it provides a reference to which the inputs and outputs can be related. This enables the comparison of two essential different systems.

2. Carbon footprint of renewable energy systems

2.1. Carbon footprint of transport fuels

The carbon footprint of transport fuels has been analyzed in several studies starting from 1990. One of the most important is the study realized by Sheehan et al. [13] at National Renewable Energy Laboratory of the United States.This is an LCA study that includes the impact of CO_2 emissions. Most important operations belonging to the petroleum diesel product system include crude oil extraction, its transport to an oil refinery, crude oil refining to diesel fuel, its transportation to the user, and its use in a bus engine.

In addition to energy and environmental outputs in each step, energy and environmental inputs from raw materials use are also included. Generally, life cycle flows include all raw materials used for extraction. Likewise, life cycle flows from intermediate energy sources such as electricity, back to the extraction of coal, oil, natural gas, limestone, and other primary resources should be included.

Life cycle presents a typical allocation case because the refining process is a multiple product process and the other sub-products obtained during diesel production are shown in Figure 2, together with the definition of the most important processes involved in the refining step.

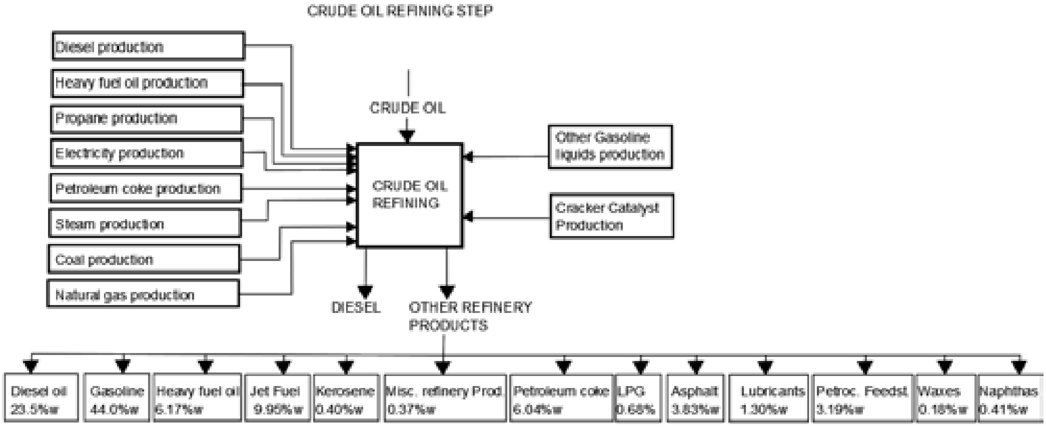

Figure 2. Crude oil refining step [13]

The final results show that diesel production and use account for a total emission of CO_2 of 633 gCO_2eq/bhp-h. The processes that contribute most to the release of CO_2 emissions are refining (which is responsible for 10% of the emissions) and petroleum combustion in the engine (which is responsible for 87% of the emissions).

2.2. Carbon footprint of electricity generation through fossil fuels

The electricity supply sector is responsible for over 7,700 million tonnes of CO_2 emissions annually (2,100 Mt C/yr); being 37.5% of total CO_2 emissions [14]. The annual carbon emissions, associated with electricity generation, is projected to surpass the 4,000 Mt C level by 2020 [15]. Past and projected electricity production from fossil fuels is shown in Table 2 and also CO_2 emissions per kWh.

	1995	2000	2010	2020
Coal	4,949	5,758	7,795	10,296
Natural Gas	1,932	2,664	5,063	8,243
Oil	1,315	1,422	1,663	1,941
Average GHG emissions (g CO_2/kWh)	158	157	151	147

Table 2. Past and projected global production from the electricity generating sector (TWh/yr) and average CO_2 emissions per kWh [14]

The efficiencies of modern thermal power stations using the steam cycle can exceed 40% based on lower heating value, although the average efficiency of the installed stock worldwide is closer to 30%. Recently, efficiencies of 48.5% have been reported and, with further development, by 2020, they could reach 55% at costs only slightly higher than current technology.

Physical carbon sequestration is more useful with the emissions of large point sources of CO_2 such as power plants. It can be captured either before combustion, in an IGCC or in a reforming process (transforming steam to methane), or after combustion from the flue gas stream using amine solvents, for example. The volume percentage of CO_2 in exhaust flue gases is between 4% (for gas turbines) and 14% (for a pulverized coal-fired plant), which means that large volumes of gas have to be treated using efficient solvents, and this will result in high-energy consumption because of solvent regeneration. These techniques will achieve an efficiency of 80–90% in carbon capture. Other carbon capture techniques include cryogenics, membranes, and adsorption. After the CO_2 has been captured, it is pressurized, typically up to 100 bar, before transportation to storage areas. CO_2 capture and compression imply a decrease on the thermal efficiency of a power plant, which has been estimated to be equal to 8–13%. The cost of CO_2 capture in power plants comprises between \$30 and 50/t CO_2 of emissions; while the cost of CO_2 transportation is influenced by the distance and the capacity of the pipeline and ranges between \$1 and 3/t CO_2 per 100 km. The cost of underground storage, which excludes the costs due to compression and transport, is estimated to range between \$1 and 2/t CO_2 stored. With the development of new technologies, for example the development of new solvents and system components, the costs of carbon capture and storage would decrease.

2.3. Carbon footprint of residential heating systems based on fossil fuels

Glaeser and Kahn [16] evaluated the emissions released by American households for heating purposes. The two primary heating sources for households are fuel oil and natural gas. On the one hand in the United States, the use of fuel oil is pretty rare, with the exception of the Northeast, and it is used as a source of home heating in few metropolitan areas; on the other hand, natural gas is the most common home heating source; and in some areas electricity is also used. Natural gas consumption is driven primarily by climate.

For fuel oil and natural gas, there are conversion factors that enable to move from energy use to CO_2 emissions. In the case of fuel oil, the factor is 22.38 lb of CO_2 per gallon.

It can be considered that about 20,000 kWh/yr are required to heat a typical house in developed countries. If hard coal, oil, natural gas, and LPG are used, the annual total CO_2 emissions are 8,280 kg CO_2/yr, 6,280 kgCO_2/yr, 4,540 kg CO_2/yr, and 5,180 kg CO_2/yr, respectively [17]. These data agree with those reported by Johnson [18], which are shown in Figure 3.

2.4. Life cycle carbon footprint of shale gas

Recent advances in drilling and fracking technologies have made the access to huge deposits of natural gas in shale deposits technically and economically feasible. These are located across the United States and elsewhere [19,20], and thus shale gas production has grown about 48% per year from 2006 to 2010 in the United States. This fact will influence the American and the world energy outlooks for the near future, together with the variation in the oil price [21]. The

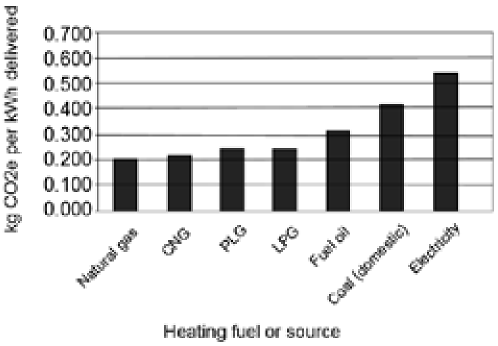

Figure 3. Carbon footprint of different heating fuels [18]

growth of the shale gas industry has brought important benefits, such as significant job growth, decoupling gas and oil prices, providing an alternative to the more polluting use of oil in transportation and of coal in power generation [22,23]. The carbon footprint of shale gas can be calculated evaluating or measuring the direct CO_2 emissions from its final use and evaluating indirect CO_2 emissions produced from fossil fuels used to extract, develop, and transport it. Also methane fugitive emissions and emissions from venting have to be considered. Literature studies have shown that the indirect CO_2 emissions throughout shale oil life cycle are relatively small than that of the direct combustion of the fuel. In fact indirect emissions range between 1 and 1.5 g CO_2/MJ−1 [24], whereas direct emissions range between 13-15 g CO_2/MJ [25,26]. Indirect emissions from shale gas are comparable with those due to conventional gas production [26].

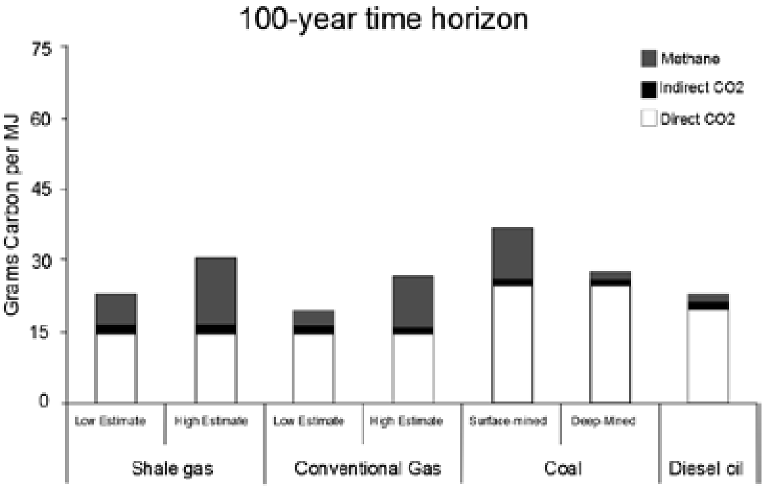

Figure 4. Comparison of GHG emissions from shale gas and conventional natural gas with low and high estimates of fugitive methane emissions, surface-mined coal, deep-mined coal, and diesel oil; time horizon equal to 100 years [27]

From the most important studies available in literature, it can be inferred that both carbon footprints of shale gas and of conventional gas are dominated by direct CO_2 emissions and fugitive methane emissions. In Figure 4 direct emissions of CO_2 during combustion of shale gas, conventional gas, coal, and diesel oil are represented with white bars, whereas indirect emissions occurring during the development and the use of the energy sources are represented in black bars, and fugitive emissions of methane are represented with grey bars. All the emissions have been normalized to the quantity of energy released during combustion.

3. Carbon footprint of renewable energy systems

3.1. Carbon footprint of transport biofuels (biodiesel, bioethanol, biomethane)

The GHG emissions released during biodiesel life cycle are about 40–65% of those released during conventional diesel life cycle. For bioethanol technologies, the GHG emissions are deeply influenced by the technology. Emissions of the whole life cycle of bioethanol produced from corn can be about 80–90% of those of competitor fossil fuels. For bioethanol produced from sugar cane, a reduction of 75-80% in fossil fuels emissions can be achieved. Important factors that influence the final results are the amounts and type of fossil fuels used in the life cycle as energy carriers to produce, transport, and process the feedstock. Also non-CO_2 emissions, generated during the cultivation phase, such as N_2O, have to be considered. Besides, the efficiency in the conversion process is important too, together with the degree to which biomass is used to provide the energy required by the process, and feedstock yields during the cultivation phase. The mass and energy balances are also influenced by the capacity of the bioenergy plant and the scale of the project. In the case of large-scale projects, there will be important land use changes that can influence carbon stocks in the soil. Table 3 shows GHG emissions per kilometer travelled.

Transportation Fuel	**GHG Emissions (gCO_2-eq./km)**
Bioethanol from sugar cane	50-75
Bioethanol from other crops (corn, sugar beet, wheat)	100-195
Biogas	25-100
Biodiesel (rapeseed, soy, sunflower)	80-140
Fischer Tropsch diesel from biomass	15-55
Bioethanol from lignocellulose	25-50
Gasoline	210-220
Diesel	185-220
Natural gas	155-185

Table 3. GHG emissions per kilometer travelled using renewable fuels and fossil fuels [28]

3.2. Carbon footprint of electricity generation through renewable energy

The carbon footprint of electricity generation through RES (Renewable Energy Systems) are described in this section. Hydro-electricity is described first, and then wind power, followed by bioenergy systems and solar energy.

Hydro-electricity is the most developed renewable resource worldwide, even if it has to face social and environmental barriers [29]. In fact societal preferences are difficult to predict, while hydro-sites are often difficult to reach, which results in high transmission and capital investment costs. These are difficult to be accepted by private power companies. The global economic hydropower potential ranges between 7000 and 9000 TWh per year. Particularly rural communities without electricity appear to be convenient for small (<10 MWe), mini- (<1 MWe), and micro- (<100 kWe) scale hydro schemes. They have low environmental impacts, and generation costs are around 6–12 c/kWh. Emissions of GHG linked with hydro-electricity operation are due to flooding of land upstream of a dam that can imply a loss of biological carbon stocks and can produce methane emissions due to vegetation decomposition.

Wind power is a technology that has been developed recently. It has an intermittent flow and produces about 4% of total global electricity. In 2013 the production capacity reached 282,000 MWe, which implies a huge development, respect from year 2000 [30]. Denmark is producing about 40% of its total electricity consumption from wind power, and it's one of the main exporters of wind turbine technology. Many wind turbines will be sited off-shore. On the one hand in this way future demand can be met, the advantage is to increase the rated output to more than 3 MWe, to decrease costs linked with operation and maintenance, to have more reliable plants; on the other hand the cost of investment for wind turbines is decreasing, while the installed capacity increases. So wind power is becoming competitive with other sources of energy in highly windy areas. The costs of electricity generation in this case range between 3 and 5 c/kWh. The investment costs will fall from $1000 to $635/kWe and operating costs will decrease to about 0.01 c/kWh - 0.005 c/kWh [31].

Bioenergy can be produced from agricultural and forestry residues, animal effluents, the organic fraction of municipal solid wastes, and dedicated energy crops. Since biomass is widely spread in the territory, it is an interesting source of energy for rural and mountain areas. The challenge is to optimize the production of biomass, collection and logistics, optimize its conversion to energy and delivery to the end user, to provide a service that is economically competitive with that obtainable using other fossil fuels. Residual biomasses, such as bagasse, rice husks, straw, olive husk, bark, and sawdust often have a corresponding cost for disposal. Therefore, biomass-to-energy conversion, in the case of residues, can have good economic performance, especially in rural areas, where there is abundance of them. Denmark produces about 40% of the electricity it consumes through cogeneration plants, using wood waste and straw. Also biogas is produced from animal breeding effluents. Energy crops are less promising in the short term due to their higher production costs in terms of $/GJ of available energy. Also the competition for land use with food crops is becoming an issue. Biomass as a fuel is more reactive than coal if it is used in gasification process, which promotes the use of biomass in IGCC systems, that are approaching to commercial realization. Besides if coupled with carbon capture, biomass integrated gasification combined cycle can be a carbon-negative technology, because CO_2 is absorbed during biomass cultivation and production, and it is not released in the IGCC plant, due to carbon capture. On the one hand, capital investment for a biomass gasification–combined cycle plant, working with an high pressure reactor, is decreasing from \$2000/kWe to \$1100/kWe by 2020; on the other hand operating costs (fuel supply included) will decline from 3.98 to 3.12 c/kWh [31]. Actually operation costs for a traditional plat working with boiler plus steam turbine are about 5.50 c/kWh.

The cost of solar photovoltaic (PV) is slowly decreasing from \$5,000/kWe to \$4,000/kWe installed. The increase in the installed capacity corresponds to an increase in scale-up of manufacturing plants and the use of mass production techniques that are the main reasons for costs reduction. Also operating costs are quite high, being about 20–40 c/kWh. Promising new applications for solar PV are represented by grid connected buildings and by large installations (up to 1 MWe), which are pushing innovation in inverters and net metering systems. Other important markets for photovoltaic power systems are off-grid applications for rural areas, especially in developing countries where there is a need for electrification projects. The worldwide installed PV capacity is estimated to be about 178 GWe in 2014, while it will reach about 400 GWe in 2020. Conversion efficiencies of silicon cells are continuously improving. The efficiency of commercial monocrystalline modules is about 13–17%, whereas the efficiency of multicrystalline module is about 12–14%. Literature studies show that a single factory of 400 MWe capacity (obtainable with 5 million panels) can reduce production costs of 75%, due to economies of scale [32]. Neij [33] calculated that a \$100 billion investment in manufacturing capacity would be needed in order to reach an acceptable generating level of 5 c/kWh (excluding back-up supply or storage costs). Capital costs for concentrated solar will fall from \$4000/kWe to \$2500/kWe by 2030 (Table 4) [34].

Technology	**PF + fgd, NO_x, etc.**	**IGCC and super-critical**	**CCGT**	**PF + fgd + CO_2 capture**	**CCGT +CO_2 capture**	**Nuclear**	**Hydro**	**Wind Turbines**	**Biomass IGCC**	**PV and Solar thermal**
Energy source	Coal	Coal	Gas	Coal	Gas	Uranium	Water	Wind	Biofuel	Solar
Emissions (gC/kWh)	229	190-198	103-122	40	17	0	0	0	0	0
Reduction potential to 2020 (MtC/yr)	Baseline	55	103	5-50	N.A.	191	37	128	77	20
Cost of C reduction (\$/t C avoided)	Baseline	-10-40	0-156	159	71-165	-38-135	-31-127	-82-135	-92-117	175-1400

PF, pulverised fuel; fgd, flue gas desulphurization; IGCC, integrated gasification combined cycle

Table 4. Cost estimates of alternative mitigation technologies in the power generation sector compared to baseline pulverized coal-fired power plant and natural gas Combined Cycle with Gas Turbine (CCGT) power stations and the potential reductions in CO_2 emissions to 2020 [14]

3.3. Carbon footprint of residential heating systems based on renewable energy

Heat production and hot water supply to buildings are essential and important worldwide. The problem is how to produce them in a sustainable way, replacing fossil fuels. Today, it is intensively being discussed how to do so in the best way in future energy systems in which the combustion of fossil fuel should be reduced or completely avoided. One way could be through the promotion of low energy buildings in which the consumption of energy can be reduced or even removed (through the use for example of solar thermal heating systems). Another way could be the one to use excess heat produced from the industrial sector, waste incineration, power stations based on large-scale exploitation of geothermal energy, solar thermal energy, and heat pumps powered by excess wind energy. In these cases, a district heating network becomes essential. Table 5 shows the comparison of GHG emissions for different household.

Heat Source	GHG Emissions (gCO_2-eq./MJ)
Biomass (i.e., wood chips, pellets)	520
Geothermal	15
Solar thermal	1030
Coal	110150
Oil	90120
Natural gas	7085
Electricity from natural gas (space heating)	180210
Electricity from oil (space heating)	265295
Electricity from coal (space heating)	290320

Table 5. GHG emissions per unit output in the heating sector (taken from [28])

The development of district heating systems is linked with the development of other systems such as combined heat and power systems, which generate waste heat, together with power. These increase the fuel use efficiency [35]. Also heat pumps should be introduced in residential heating systems [18]. In some countries like Norway, district heating system's GHG emissions have been compared with those of individual heating systems and it has been found that the first have lower CO_2 emissions.

4. Carbon footprint of products

4.1. Carbon footprint in the food industry

Food industry sector is one of the major contributors to climate change [36]. In Sweden, it has been estimated that about 25% of GHG emissions from the private sector are due to the consumption of food [37]. In the European Union, food industry contribution to GHG emissions is estimated to be about 31% [36,38]. GHG emissions in the transport sector are mainly due to CO_2; while in agriculture most emitted GHG are methane (CH_4) and nitrous oxide (N_2O). The CO_2 emitted from land use change represents also an important source of emissions of the food production system. Starting from the publication of the Fourth Assessment Report of the IPCC in 2007 [39], the calculation of food carbon footprint has become more and more popular. Food carbon footprint is calculated by companies also for marketing purposes [40-42]. Also research efforts in the calculation of carbon footprint of food and in the estimate of its uncertainty have increased in recent years [43-46] (see Figure 5). Challenges in calculating the carbon footprint of food products can be linked with the functional unit, system boundaries and allocation, land use change, carbon sequestration in soils, uncertainties, and variation.

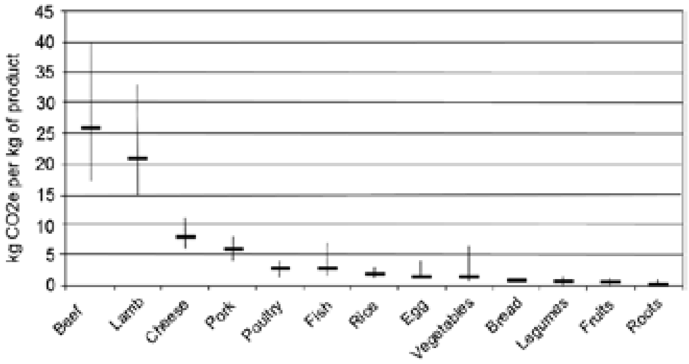

Figure 5. Carbon footprint of different types of food products at retail. Average values estimated to be representative for food products sold on the Swedish market. Error bars show ranges of values found in the literature. Emissions from land use change and carbon stock changes in soils are not included [47]

Besides marketing purposes, carbon footprint is calculated in the food sector also with the aim at reducing its value, producing more sustainable food. The main ways to reduce the product carbon footprint of food are as follows: by reducing emissions of CO_2 due to energy use in agriculture (for example improving energy efficiency and using renewable energy sources) and reducing CH_4 emissions from enteric fermentation and N_2O emissions from fertilizer nitrification in soil. CH_4 emissions can be reduced to some extent by altering the diet fed to ruminants [48], but the risk of pollution swapping is great [49,50]. N_2O emissions from soils can be reduced by optimizing nitrogen use and promoting N_2O inhibitors.

Another way to reduce GHG emissions in the food sector is changing the consumption patterns [51-54]; for example, switching from diets based on meat to diets in which proteins are also supplied by vegetables.

Being on-farm emissions (from cultivation and animals breeding) the most important source of GHG in food life cycle, numerous studies have tried to reduce them. Ahlgren [55] has used LCA to evaluate the use of biofuels in tractors and the substitution of mineral nitrogen fertilizers. This implied that 3–6% of a farm's available land was needed to produce the required biomass (to produce biofuels and fertilizer).

Another issue is represented by dairy production and the carbon footprint of milk [56,50]. An important area of research is the production of animal feed for the different diets used in livestock production [57-58].

4.2. Carbon footprint in the textile industry

Many enterprises in the textile and clothing industry are involved in product carbon footprint calculation. They range from fiber manufacturers (e.g., Lenzing, Advansa, Dupont) to producers of flooring material (e.g., InterfaceFlor, Desso, Heugaveld), to fashion brands (united in the Sustainable Apparel Coalition), to other organizations (European Commission and the Dutch branch organization Modint). They are using LCA to calculate the environmental impacts of textile-related products. Also educational textile and fashion institutes (e.g., the Amsterdam Fashion Institute) are promoting life cycle thinking, picking up the signals from companies and other organizations. A literature survey [59] shows that Collins and Aumônier [60] compiled a LCI (Life Cycle Inventory) on textile products upon references dating from 1978 to 1999. Another research executed by Kalliala and Talvenmaa [61] reports, for example, spinning energy, which is derived from a study out of 1997. In-depth investigation on weaving led to the research of Koç and Çinçik [62]. In the recent work of Shen [63], non-renewable energy use for the production processes of different fabrics is given, based upon a report from 1997 [64].

Walser et al. [65] have published a LCA study using inventory data for polyester (PET) textile production. The authors also noticed that the data in the Ecoinvent database [66] on cotton and bast fibers do not specify the yarn size, which has an important influence on energy use.

Figure 6 presents the carbon footprint of cotton textiles and of synthetic textiles. In the case of cotton, different yarn thickness are taken into account. They are expressed on decitex (abbreviated dtex). In the case of synthetic textiles, only yarn thickness of 70 dtex is taken into account.

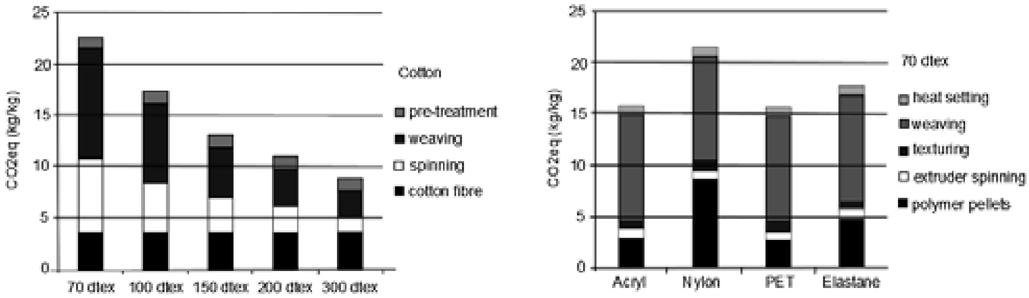

Figure 6. Carbon footprint of cotton textiles with yarn thickness comprised between 70 and 300 dtex (left) and synthetic textiles - acryl, nylon, PET, elastane-, with yarn thickness of 70 dtex (right) [59]

4.3. Carbon footprint in the cement industry

The cement industry is one of the sectors that contributes most to climate change, accounting for roughly 5% of the total CO_2 emissions worldwide [67]. Therefore reducing these emissions is a primary goal in order to comply with the objectives laid down in the Kyoto protocol to combat climate change. Currently, the cement industry, belonging to the WBSCD (World Business Council for Sustainable Development), has launched the Cement Sustainable Initiative program to meet the challenges of sustainable development. The carbon footprint is the most promising tool to evaluate the impact of carbon emissions of different products and can be an indicator to be used for eco-labeling. Several efforts have been made to develop it [68]. The study of Cagiao et al. [69] is based on the MC3 approach, also called organization-product-based-life-cycle assessment (OP-LCA). Given its top-down approach, this methodology first allows the organization's footprint to be calculated and then distributing it among the products that it manufactures. Some of the advantages are as follows:

- **a.** It is a single methodology to be used both for organizations and products.
- **b.** It uses all the financial accounts as input data.
- **c.** The information flows automatically through the value chain.
- **d.** The scope is always the same for all the analyses.
- **e.** It is simple and easy-to-understand and adaptable.
- **f.** Both the carbon footprint and the ecological footprint of the organization can be obtained [70-72].

The study of Cagiao et al. [69] was carried out with three potential scenarios in mind: case A pertaining to a conventional integral plant; case B which refers to a grinding plant; and case C, an integral plant which has been subject to the best available technical improvements. All the plants have the same productivity of 1,000,000 t/year. A summary of main results is proposed in Table 6.

Process	Emissions	Case
Carbon footprint of cement industry	1,003,555.2 tCO_2/year	Case A
	907,384.2 tCO2/year	Case B
	790,278.3 tCO2/year	Case C
Carbon footprint of one ton of cement	1.00 tCO2/tcement	Case A
	0.91 tCO2/tcement	Case B
	0.79 tCO2/tcement	Case C
Main parts of the carbon footprint produced	Direct emissions (75.33%) and wastes (17.98%)	Case A
	Materials (75.07%) and services (14.60%)	Case B
	Direct emissions (77.06%) and wastes (15.18%)	Case C
Reduction of total footprint by using BATs	213,276.9 tCO2/year (21.25% of initial carbon footprint)	

Table 6. Carbon footprint of cement production [69]

5. Product Carbon Footprint (PCF) case study

Fantozzi et al. [73] presents the study of the carbon footprint of a typical food product in Central Italy: truffle sauce. This is a mixture of vegetable oil and truffle in proportions of 33% and 67% respectively and minor components and spices (garlic, salt, pepper, etc.). Both truffles and olives are cultivated and harvested in a farm in Umbria (Italy). Olives are crushed in a mill that is situated few kilometers from the farm. Once it has been produced, the extra virgin oil, together with the truffle, is transported to another facility to produce bottled truffle sauce. The carbon footprint calculation is based on ISO 14076 technical standard. Product Category Rules (PCR) have been developed (see Table 7).

Stage	Rule	Description
Scope and functional unit	Scope	Calculate PCF of truffle sauce (expressed in kgCO_2eq/kg product)
	System boundary	Cultivation, transformation, packaging, and waste disposal are taken into account, while consumption is neglected
	Allocation	Allocation based on system expansion has to be preferred to allocation based on mass and economic value
Product definition	Truffle sauce	Truffle sauce is a mixture of vegetable oil and truffle in proportions of 33% and 67% respectively and minor components and spices (garlic, salt, pepper, etc.) that were not considered in the analysis
	LC stages	Cultivation; Milling; Truffle production; Transport; Sauce production
PCF calculation	Software	Simapro software was used to design process tree, and calculate PCF, based on the impact method GWP 100 years. Cut-off on processes impact is set to 1% to ease results view
	Data uncertainty	Data uncertainty was measured based on used instruments precision and on the uncertainty of Simapro datasets
Results communication	Label	A carbon footprint label was designed for the package

Table 7. Product Category Rules of truffle sauce [73]

The cut-off threshold on life cycle processes is about 1%. This decision is due to the need to simplify the process tree diagram. All the calculations are referred to the growing season 2011/2012.

The boundaries of the system analyzed are shown in Figure 7. Truffle sauce life cycle has been divided in the following product stages:

- cultivation;
- truffle production;
- truffle sauce production;
- packaging.

This is a clear example of a cradle-to-grave study, so GHG fluxes comprise also disposal of the packaging. The consumption phase is not considered in the study. The functional unit is 1 kg of truffle sauce.

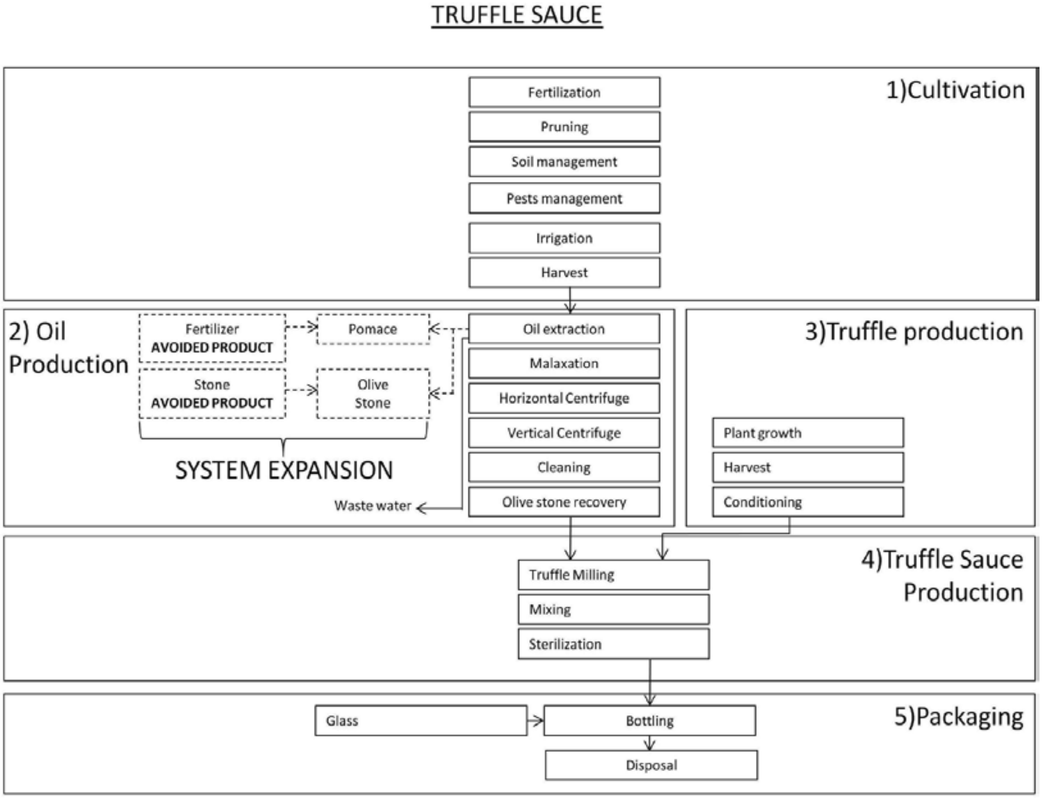

Figure 7. System boundaries [73]

Results of the analysis are proposed in Table 8. Cultivation gives an important contribution to the final impact of truffle sauce, while truffle production has a reduced impact, because it is a very extensive production. Olive trees cultivation uses fertilizers, diesel fuel for field operations, electricity for the olives harvest, herbicides and pesticides.

Life Cycle Stage	Contribution (kg CO_2eq/kg product)
1) Cultivation	0.94
2) Milling	0.28
3) Truffle production	0.09
4) Sauce production	0.06
5) Packaging production & disposal	0.77
6) Transport	0.03
7) Avoided emissionsAvoided fuel - Avoided fertilizer	0.18 0.02
Total	1.93

Table 8. Carbon footprint of truffle sauce [73]

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