Nitrous Oxide and Methane Emissions from Storage and Land Application of Organic Fertilisers

With the Focus on Sewage Sludge

Agnes Willén
Faculty of Natural Resources and Agricultural Sciences
Department of Energy and Technology
Uppsala

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Cover: Full-scale storage of digested and dewatered sewage sludge at Hovgården waste disposal plant, Uppsala, Sweden.
(photo: Agnes Willén)

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Abstract

Organic fertiliser handling contributes to greenhouse gas emissions. Through storage and field experiments, this thesis examined strategies to reduce emissions of nitrous oxide (N_2O) and methane (CH_4) from storage and after land application of cattle slurry (CS) and sewage sludge (SS). Non-digested CS without a roof (1) and digested CS without (2) or with a roof (3) were stored during three months in summer and winter. Mesophilically digested SS without cover (1), with cover (2) or treated with ammonia (NH_3) and with cover (3), and thermophilically digested SS with cover (4), were stored during one year. CS treatments (1) and (3) were applied to soil in spring or in autumn. SS treatments (3) and (2) were applied in spring and autumn, respectively, and were either incorporated into the soil immediately or after four hours. A life cycle assessment was conducted to assess the impact on global warming potential, acidification potential, eutrophication potential and primary energy use of different management strategies for SS.

Digested CS had significantly higher CH_4 emissions than non-digested CS during summer storage. Using a roof in summer decreased CH_4 and increased N_2O emissions significantly, but these cancelled each other out on a global warming basis. Emissions of N_2O and CH_4 were small during winter storage and after land application. Treatment with NH_3 significantly reduced N_2O emissions from SS during storage and tended to lower CH_4 emissions. Thermophilically digested SS had more air-filled pores during storage and emitted significantly more N_2O than other treatments, but had the lowest CH_4 emissions. Emissions of N_2O after SS application to soil were low, but stimulated by wet soil and precipitation, while CH_4 emissions were negligible, with no differences between immediate and delayed incorporation. The LCA revealed that shorter storage time and covered storage could mitigate the environmental impact from SS management. NH_3 treatment generally reduced negative impacts on environment categories except for primary energy use, which was highest for this treatment. A combination of autumn and spring application was preferable to autumn-only application for most treatments through lowering total storage time.

Keywords: cattle slurry, greenhouse gas mitigation, methane, nitrous oxide, organic fertiliser, land application, sewage sludge, storage

Author's address: Agnes Willén, SLU, Department of Energy and Technology,
P.O. Box 7032, 750 07 Uppsala, Sweden
E-mail: Agnes.Willen@ slu.se

Dedication

Till Åke

Tänkt alla millioner år som inte du var född. Då fanns det människor som nu och hav och stenar, men inte samma människor som nu. Men samma hav och samma stenar.

Barbro Lindgren

If everything was perfect, you would never learn and you would never grow.

Beyoncé Knowles

Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Rodhe, L., Ascue, J., Willén, A., Vegerfors-Persson, B. & Nordberg, Å. (2015). Greenhouse gas emissions from storage and field application of anaerobically digested and non-digested cattle slurry. *Agriculture, Ecosystems & Environment*, vol. 199, pp. 358-368.

II Willén, A., Rodhe, L., Pell, M. & Jönsson, H. Nitrous oxide and methane emissions during storage of dewatered digested sewage sludge. Submitted.

III Willén, A., Jönsson, H., Pell, M. & Rodhe, L. (2016). Emissions of nitrous oxide, methane and ammonia after field application of digested and dewatered sewage sludge with or without addition of urea. *Waste and Biomass Valorization*, vol. 7 (2), pp. 281-292.

IV Willén, A., Junestedt, C., Rodhe, L., Pell, M. & Jönsson, H. Sewage sludge as fertiliser – environmental assessment of storage and land application options. Submitted.

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The contribution of Agnes Willén to the papers included in this thesis was as follows:

I Participated in the practical work and performed the data analyses.

II Planned the experimental work with the co-authors. Performed the practical work with some assistance. Performed the data analyses and wrote the paper with input from the co-authors.

III Planned the experimental work with the co-authors. Performed the practical work with some assistance. Performed the data analyses and wrote the paper with input from the co-authors.

IV Contributed data from Papers II and III and collected additional data from the literature. Set up the scenarios to be studied and performed the analysis with assistance from the co-authors. Planned and wrote the paper with some input from the co-authors.

Abbreviations

$(NH_2)_2CO$	urea
B_0	methane production potential
CH_4	methane
CO_2	carbon dioxide
CO_2eq	carbon dioxide equivalents
CS	cattle slurry
DM	dry matter
EF	emissions factor
EF_{CH4}	emissions factor for methane
EF_{N2O}	emissions factor for nitrous oxide
EPA	Environmental Protection Agency
GHG	greenhouse gas
GWP_{100}	global warming potential in a 100-year perspective
IPCC	Intergovernmental Panel on Climate Change
LCA	life cycle assessment
N	nitrogen
N_2O	nitrous oxide
NH_2OH	hydroxylamine
NH_3	ammonia
NH_4^+	ammonium
NO_2^-	nitrite
NO_3^-	nitrate
r	Pearson correlation coefficient
SS	sewage sludge
TAN	total ammoniacal nitrogen
VS	volatile solids

1 Introduction

1.1 Greenhouse gases and climate change

The mean global temperature (combined land and ocean surface) is rising and in 2012 was approximately 0.85 °C higher than at the end of the 19th century (IPCC 2013a). The reason for this change is that emitted greenhouse gases reinforce the atmosphere's greenhouse effect on the Earth's temperature. As the population increases in the world, so do emissions of greenhouse gases (van Beek *et al*. 2010). In accordance with the United Nations Framework Convention on Climate Change (UNFCCC), the concentration of greenhouse gases in the atmosphere must be stabilised at a level that would prevent dangerous anthropogenic interference with the climate system (UNFCCC 1992, 2015).

A recent global goal stipulates that efforts should be made to limit the global temperature rise to a maximum of 1.5 °C compared with the pre-industrial level (UNFCCC 2015). This goal is also included in the Swedish environmental objective "*Reduced climate impact"* to be met by 2050 (Swedish Environmental Protection Agency (EPA) 2016a). Within the Kyoto agreement, the European Union (EU) has committed to reducing greenhouse gas emissions by 20% of the level in 1990 by 2020 (EC 2016) and the Swedish parliament has committed to a vision of climate neutrality by 2050 (Swedish Government 2009).

Heat from the sun's radiation stays on the Earth thanks to the natural greenhouse gases in the atmosphere. Thus, the greenhouse effect is natural and necessary for life on Earth as we know it. Water vapour has the largest greenhouse effect in the Earth's atmosphere, but other greenhouse gases such as carbon dioxide (CO_2) are necessary to maintain the presence of water vapour in the atmosphere. Without these other gases, the temperature in the atmosphere would drop. This would reduce the atmospheric water vapour content and the temperature would thereby drop further and the Earth would freeze (IPCC 2013b).

The increase in anthropogenic emissions of greenhouse gases during the past 100 years has enhanced the natural greenhouse effect, which has led to higher mean global temperature and in turn has affected the climate and sea levels. Nitrous oxide (N_2O) is a powerful greenhouse gas with a global warming potential (GWP_{1000}) of N_2O, 298 times that of CO_2 (*i.e.* CO_2 equivalents or CO_2eq) in a 100-year perspective (IPCC 2013b). Methane (CH_4) has a GWP_{100} which is 34 times that of CO_2 (IPCC 2013b). The values for these potentials were recently revised; the old GWP_{100} factors for CH_4 and N_2O (IPCC 2007) are used in Papers I and IV, while the new values are used in Papers II and III.

1.2 Organic residue management

All over the world, in urban and rural areas, organic residues are produced in agriculture and in various industrial and household activities. Since many of the organic residues produced in agriculture, industries and households originate from crops produced on arable land, they are rich in plant nutrients and therefore should be recycled to arable land to keep a sustainable system. To further utilise this resource, the residues can be used before recycling to land for renewable energy production, to produce *e.g.* biogas. The European Waste Directive states an order of hierarchy on how waste should be managed; first, production of waste should be prevented; second, produced waste should be treated for reuse; third, waste should be recycled; fourth, other recovery options should be adopted, such as energy retrieval; and the last option is disposal (Parliament Directive 2008/98/EC, OJ L 312/10).

The amount of sewage sludge produced in wastewater treatment plants is minimised by applying dewatering processes such as centrifugation, drying beds, thermal drying and press systems (Tchobanoglous *et al*. 2003). Reuse and recycling alternatives for sewage sludge are *e.g.* use as fertiliser/soil conditioner or incineration followed by phosphorus recovery to be used as fertilizer. One constraint in recycling organic residues from human activities and industries as fertilisers is that they can contain human pathogenic microorganisms from infected individuals (WHO 2006). To reduce the pathogen content to acceptable levels, the residue needs to be sanitised before land application. At wastewater treatment plant the sewage sludge can be stabilised, *e.g.* processed by thermal or chemical treatment or to some extent also by long-term storage (Tchobanoglous *et al*. 2003; WHO 2006). Measures such as systematic information campaigns and disconnecting industries with hazardous wastewater can also be performed upstream.

Manure is produced by farm animals and sewage sludge is produced by humans and industries. The production rate of both these residue streams is more or less constant all year around. If the residues are to be used as fertiliser, they have to be stored for longer or shorter times prior to use, since fertilisation occurs only during a short period in the cropping season. Storage of organic fertilisers carries a risk of emissions of the greenhouse gases N_2O and CH_4 (Flodman 2002; Kebreab 2006; Majumder *et al.* 2014; Saggar *et al.* 2004; Webb *et al.* 2012). Land application of organic fertilisers also leads to emissions of greenhouse gases (Kebreab 2006; Saggar *et al.* 2004; Webb *et al.* 2012). Emissions of N_2O and CH_4 also represent a loss of organic carbon and plant-available nitrogen.

Emissions of greenhouse gases can be decreased by measures such as anaerobic digestion of the residues (Amon *et al.* 2006; Clemens *et al.* 2006; Petersen 1999) or storing them covered (Clemens *et al.* 2006; Hansen *et al.* 2006). Ammonia (NH_3) treatment prior to storage for sanitising purposes also has the potential to decrease greenhouse gas emissions, as it creates a toxic environment not only for pathogenic microorganisms but also for those microorganisms involved in production of N_2O and CH_4 (Schneider *et al.* 1996). Timing the application in relation to soil conditions and the needs of the crop (Rodhe *et al.* 2012; Scott *et al.* 2000) and incorporation of fertiliser into the soil (Thorman *et al.* 2007; Webb *et al.* 2004) are measures that could reduce greenhouse gas emissions from land application.

Land application of organic fertilisers leads not only to emissions of NH_3 (Bussink & Oenema 1998; Sommer & Hutchings 2001), but also loss of plant-available nitrogen, and also contributes to acidification and eutrophication on deposition. In addition, fine particulate matter containing NH_3 constitutes a health risk when inhaled (Goedkoop 2009).

When organic fertiliser is recycled to arable land, less chemical fertiliser needs to be used. This is beneficial for the environment, as the production process for chemical fertiliser requires energy and also emits greenhouse gases and CO_2 (Brentrup & Pallière 2014). In addition, supplementing the soil with organic matter improves its physical, chemical and biological properties (Loveland & Webb 2003). Addition of organic matter has been shown to improve the water-holding capacity and aggregate stability, enhance porosity and ease cultivation by lowering the penetration resistance for farm equipment and facilitating seedbed preparation (Loveland & Webb 2003).

Good management of wastewater and sewage sludge is important to reduce the environmental and sanitary hazards for the environment and humans.

2 Objectives and structure of the thesis

In order to reduce the anthropogenic contribution to the greenhouse effect, it is important to monitor activities within known sources of greenhouse gas emissions. By identifying the sources and quantifying their contribution, suitable mitigation measures can be suggested.

The overall goal of this thesis was to estimate the quantities of emissions of the greenhouse gases N_2O and CH_4 associated with management of organic fertilisers, with the focus on sewage sludge, and to formulate measures to reduce these emissions. Specific aims were to:

- Analyse the quantities of emissions and the emissions patterns of N_2O and CH_4 during storage and after land application of non-digested and digested cattle slurry and digested and dewatered sewage sludge (Papers I-III)
- Identify the effects of digestion, applying storage cover and treatment with NH_3 as measures to reduce N_2O and CH_4 emissions during storage of organic fertilisers (Papers I and II)
- Identify the effects of spreading strategies such as incorporation, timing and season of application on greenhouse gas emissions after land application of organic fertilisers (Papers I and III)
- Analyse the environmental impacts of different management strategies for storing sewage sludge and applying it to land as fertiliser (Paper IV).

The quantities of emissions and the mitigation potential of different treatment methods during handling of organic fertilisers were investigated in pilot-scale storage experiments and in field plot application experiments. As a final step, systems analysis of different sewage sludge handling chains was performed.

The structure of the Papers I-IV is summarised in Figure 1. In Paper I, emissions of N_2O and CH_4 from digested and non-digested cattle slurry were studied, both during subsequent storage and from soil after application to arable land in two different seasons. The emissions reduction potential of fitting a roof over the digested cattle slurry during storage was also evaluated, as were NH_3 emissions after land application in spring.

In Paper II, the effects of different storage strategies on emissions of N_2O and CH_4 from digested and dewatered sewage sludge were investigated. The treatments tested were mesophilic digestion and thermophilic digestion of the sludge prior to storage, NH_3 treatment of the sludge at the start of storage and coverage of the sludge during storage.

In Paper III, the effects of the strategies tested in Paper II were further investigated by quantifying the emissions of N_2O and CH_4 from arable land after application of digested and stored sewage sludge. Mesophilically digested and dewatered sewage sludge with and without NH_3 treatment was applied to arable land in spring and autumn, respectively. With application of NH_3-treated sludge, the loss of NH_3 was also measured.

In Paper IV, the environmental impact of different handling and land application systems for digested and dewatered sewage sludge were analysed using life cycle assessment. Beside climate impact, the study also included the impact categories eutrophication, acidification and primary energy use.

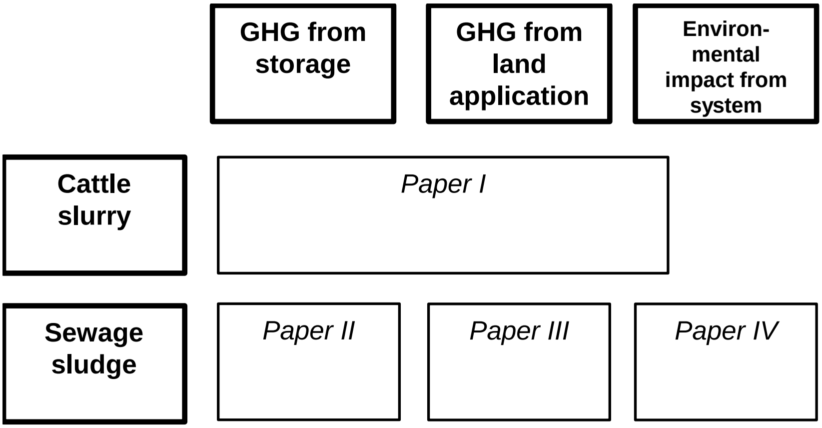

Figure 1. Structure of the work and the area covered by the four papers included in the thesis.

The hypotheses tested in this thesis were that emissions of greenhouse gases:

1. during storage of cattle slurry would be affected by covering the storage and by previous digestion,
2. during storage of sewage sludge would be reduced by covering the store or by the sanitisation measures thermophilic digestion and ammonia treatment, and
3. would be reduced by applying appropriate application strategies, such as timing and incorporation, for the type of organic fertiliser used.

3 Background

3.1 Nutrients in agriculture

All plants require inorganic nutrients to grow. Macronutrients, *i.e.* nutrients that are needed in greater amounts, are *e.g.* phosphorus, nitrogen, potassium, calcium, magnesium and sulphur (IFA 2010). Micronutrients needed in only small (micro) amounts are boron, iron, manganese, copper, zinc *etc*. Not all elements in the latter group are essential to all crops (IFA 2010). Nutrients used by plants are partly recycled to the soil as animal manure or crop residues, and partly leave the farm as sold produce. The sold produce goes mainly to urban society, where it is consumed, and the nutrients end up in the sewage system and in water courses if not captured at wastewater treatment plants. The large proportion leaving farms means that the soil system is depleted of nutrients in the long run and hence a supply of nutrients from external sources is required. This is often achieved by the use of chemical fertilisers, but could to a large extent also be fulfilled by using animal manure and other organic fertilisers, such as treated food waste or sewage sludge. Most agricultural soils need addition of plant-available nutrient to be sufficiently fertile for economic production of food, feed and fibre (Dawson & Hilton 2011).

3.1.1 Phosphorus and nitrogen recycling

Phosphorus and reactive nitrogen (*i.e.* nitrogen that is biologically, photochemically or radiatively active) are lost from agricultural soils in many ways. The most significant losses are normally those leaving the system with the harvested crop, percolation and surface water and, for reactive nitrogen, also gaseous losses through denitrification. For sustainable production, the soil needs to be compensated for these losses, which is mainly done by adding chemical fertilisers from non-renewable resources. However, according to Steffen *et al*. (2015), the use of artificial nitrogen and phosphorus fertilisers needs to decrease by 50-60%, while at the same time more food needs to be produced due to a growing world population. This means that nutrient circulation efficiency must be improved. With this in mind, it is increasingly important to restrict the use of phosphorus and reactive nitrogen to essential uses and one obvious way is to increase the recycling rate of phosphorus and nitrogen from all sources possible, with two major sources being animal manure and sewage sludge.

Since sewage sludge is rich in phosphorus, the application rate of this product to soil is often restricted by its phosphorus content. According to Swedish regulations, on a soil with average or good content of phosphorus the fertilisation rate with sewage sludge should not exceed 110 kg phosphorus ha^{-1} during a five-year period (Swedish EPA 2002). Depending on the content of plant-available nitrogen and phosphorus in organic fertilisers, supplementation with chemical nitrogen, and sometimes also chemical phosphorus, may be needed to achieve a P:N ratio and level of availability that meet the needs of the crop.

3.2 Manure and sewage sludge production, management and use

3.2.1 Production

In 2015 the number of cattle in EU28 was 89,131,000 (Eurostat 2015). If the daily excretion of manure plus urine is assumed to be 50 kg wet weight per head of cattle and the moisture content of the excreta is assumed to be 87% (ASAE 2005), the yearly production of cattle excreta would be 211,000,000 Mg dry matter. The amount of sewage sludge produced in EU28 in 2012 was approximately 12,970,000 Mg dry matter (Eurostat 2012).

In 2013, the cattle population in Sweden was 1,428,000 head (Eurostat 2015). Using the same assumptions as for Europe, annual production of cattle excreta in Sweden was 9,282,000 Mg dry matter in 2015. The amount of nitrogen in Swedish manure in 2012 was approximately 130,000 Mg (Swedish EPA 2014a), whereof approximately 70% was produced by cattle. In 2012, the sewage sludge produced at 436 Swedish treatment plants amounted to 208,000 Mg dry matter (approx. 832,000 Mg wet weight assuming 25% dry matter) (Statistics Sweden 2014a). Its content of nitrogen was 9,000 Mg and of phosphorus 5,500 Mg.

3.2.2 Management and use in Sweden

Of the manure produced by cattle in Sweden, around 56% is managed as slurry and the remaining 44% as solid manure or pure urine (Statistics Sweden 2014b). The majority of the animal manure produced is used as fertiliser, meaning that 24,000 Mg cattle manure were applied to arable land in 2013, whereof 80% (by weight) were slurry and the remaining 20% were either solid manures or pure urine (Statistics Sweden 2014b). The content of phosphorus and nitrogen in cattle manure is approximately 8.6 and 41.2 g kg^{-1} dry matter, respectively, for slurry and 7.7 and 29.1 g kg^{-1} dry matter, respectively, for solid manures (Steineck *et al*. 1999). According to Statistics Sweden (2014b), 103,000 Mg nitrogen and 25,900 Mg phosphorus from manure were applied on agricultural land in the cropping season 2012/2013.

The sewage sludge produced in wastewater treatment plants in 2012 contained on average 26.4 g phosphorus kg^{-1} and 43.0 g nitrogen kg^{-1} dry matter of sludge. Of the total net production of sewage sludge, 23% was used as fertiliser on agricultural land in 2012, which was the largest single category of use (Eurostat 2012). The fraction recycled to arable land was somewhat lower than the 38% reported for the EU28 countries.

Sweden has long had a goal of closing the loop for urban food-related plant nutrients. For example, it has been specified that at least 60% of the phosphorus in wastewater should be recycled to productive land by 2015 (Swedish Government 2009). However, this goal has expired and a new goal of recycling 40% of the phosphorus and 10% of the nitrogen in sewage sludge to arable land has been proposed by the Swedish EPA, but not yet ratified by the government.

The management of sewage sludge as an organic fertiliser imposes environmental risks due to its content of heavy metals and the risk of losses of nutrients to recipient waters. Health risks due to the content of pathogens are also a concern. In Sweden, however, sewage sludge is gradually becoming cleaner due to awareness of the problem and systematic work to reduce its content of hazardous substances (Revaq 2014). Because of the risk of infection from pathogens at sewage sludge recycling, the Swedish EPA suggested in 2002 that sewage sludge should be sanitised before use on land and that storage for a year would meet the minimum requirement for sanitisation (class C) (Swedish EPA 2002). According to a new proposal from the Swedish EPA (2013), storage for a year is not enough for sanitisation of sewage sludge prior to use on arable land. Specific sanitisation measures are most likely required, such as thermophilic digestion (50-60 °C) or treatment with NH_3 (Swedish EPA 2013). However, as yet, no sanitisation requirement has been decided upon by the government.

Application of animal manure and sewage sludge to arable land within environmentally sensitive areas is restricted to the period between March and October. In March-July, application is not allowed on snow-covered, frozen or water-saturated soils. There are also restrictions on how and when land application of fertilisers can be carried out in August-October. The restrictions in autumn vary with region and level of area sensitivity.

In the growing season 2012/2013, 37 and 15 % of the total cropped area in Sweden received animal manure in autumn and spring, respectively (Statistics Sweden 2014b). It is more common to apply animal slurry in spring than in autumn. In 2013, approximately 77% of the animal slurry used was applied in spring and 23% in autumn (Statistics Sweden 2014b). However solid manure, which normally has a lower content of nitrogen and higher content of phosphorus than slurry, is normally spread in autumn. Sewage sludge is also most commonly applied to arable land in autumn, partly due to the risk of soil compaction in spring and partly because sewage sludge, just as solid manure, is considered a phosphorus fertiliser with relatively low mineral nitrogen concentration. In 2015, approximately 80% of the sewage sludge applied on arable land managed by one of the largest distributors of sewage sludge in Sweden was applied in autumn (July-October) (Wigh[1]).

3.3 Processes contributing to nitrous oxide and methane emissions

3.3.1 Nitrous oxide production

Nitrous oxide can be produced by different processes in agricultural systems and in wastewater treatment. When organic nitrogen is mineralised to release ammonium (NH_4^+), it can be emitted as NH_3. Part of the NH_3 can be nitrified to nitrate (NO_3^-), which in turn can be denitrified and emitted as nitrogen gas, N_2. Nitrous oxide can be produced in substantial amounts from both nitrification and denitrification (Figure 2).

Lithotrophic nitrification is an aerobic bacterial two-step process where NH_3 is first oxidised to nitrite (NO_2^-) by ammonia-oxidising bacteria via hydroxylamine (NH_2OH) and then the NO_2^- is further oxidised to NO_3^- by nitrite-oxidising bacteria (Figure 2). When oxygen (O_2) availability is limited, N_2O can be produced due to incomplete oxidation of NH_2OH (Robertson 1991). Nitrification is favoured by intermediate moisture content (Maag & Vinther 1996; Zaman & Chang 2004). It is temperature-dependent and is frequently shown to be inhibited at temperatures under 5 °C and to have its maximum around 30 °C (Shammas 1986; Zaman & Chang 2004). The pH affects the nitrification rate in that a decrease in pH from its optimum level (around pH 8-9) decreases the nitrification rate (Shammas 1986), but high pH also inhibits nitrifying activity (Kim *et al.* 2006).

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[1] Lisa Wigh. Ragn Sells. Personal communication 2016.

Denitrification is the anoxic process in which NO_3^- is reduced stepwise to N_2 via the intermediaries NO_2^-, NO and N_2O (Robertson 1991) (Figure 2). In wastewater treatment this process is normally accomplished by heterotrophic bacteria, but autotrophic bacteria can also show denitrifying activity (Tchobanoglous *et al.* 2003). Most denitrifiers are facultative and can use oxygen instead of nitrogen oxides as the terminal electron acceptor if present.

The availability of NO_3^-, oxygen and metabolisable carbon are factors that directly influence denitrification (Petersen & Andersen 1996). Increasing oxygen status and nitrate and nitrite deficiency (Firestone *et al.* 1978), as well as low pH (Liu *et al.* 2010), tend to shift the process towards release of more N_2O. Nitrous oxide can also be produced by nitrifier denitrification (Figure 2), where NO_2^- is reduced to N_2O under limited oxygen conditions (Kim *et al.* 2010).

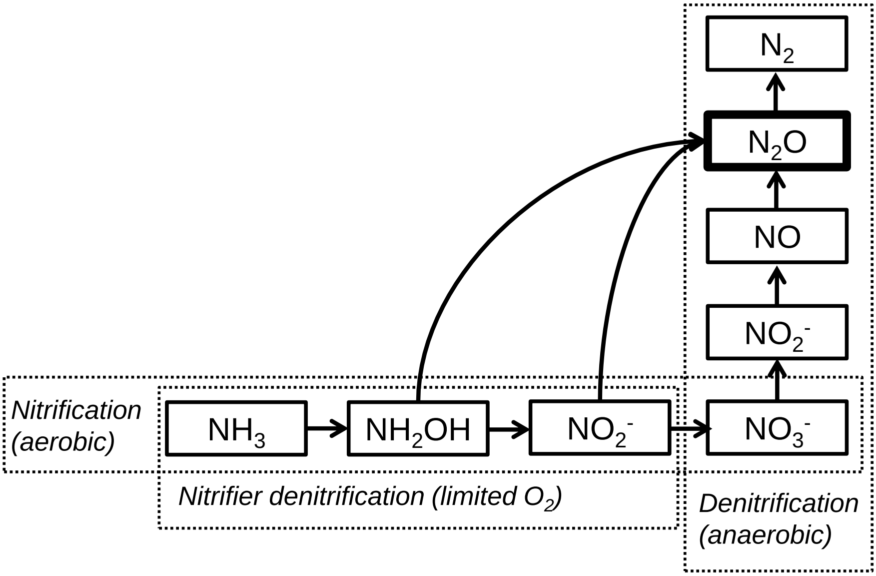

Figure 2. Production pathways of nitrous oxide (N_2O). Modified from Rapson & Dacres (2014) and Ermolaev (2015).

3.3.2 Methane production

Methane is produced in anaerobic environments by several groups of microorganisms in cooperation when organic matter is degraded. About 30% of the total global emissions of CH_4 originate from natural sources, whereof wetland soils are the main contributor (Le Mer & Roger 2001). About 70% of the CH_4 emissions are linked to anthropogenic activities (Le Mer & Roger 2001).

Substrates low in dry matter are greater sources of CH_4 due to their high moisture levels with low oxygen availability.

When organic matter is mineralised anaerobically, microorganisms first hydrolyse complex organic material (polymers) such as carbohydrates, proteins and fats to simple sugars, fatty acids, amino acids and peptides (Le Mer & Roger 2001) (Figure 3). These products are further fermented and anaerobically oxidised to produce acetate, CO_2 and hydrogen gas. In the last step, two groups of methanogenic archaea produce CH_4. Hydrogenotrophic methanogens reduce CO_2 to CH_4 using hydrogen as an energy source, while acetotrophic methanogens use acetate, formate or methanol as an energy and carbon source in production of CH_4 and CO_2 (Schnürer *et al*. 1994).

Methane can also be consumed in soils by microbial oxidation (Le Mer & Roger 2001). This can occur in the aerobic zones of submerged or water-saturated soils and in aerated soils, and is carried out by methanotrophic bacteria. Oxygen availability is the main factor limiting the activity of methanotrophs.

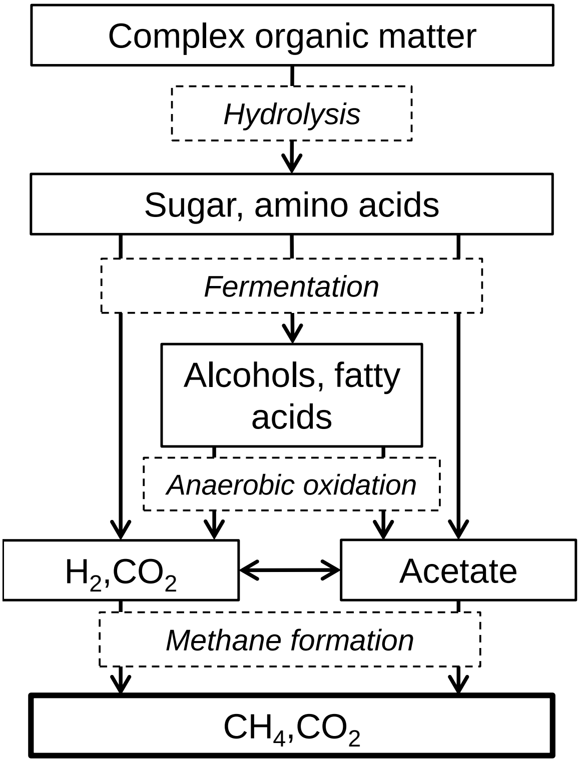

Figure 3. Schematic picture of the production of methane (CH_4). Modified from Jarvis & Schnürer (2009).

3.4 Greenhouse gases from agriculture, wastewater treatment and management of manure and sewage sludge

In 2004, the agricultural sector and the waste and wastewater sectors made up 14 and 3% of the global anthropogenic emissions of greenhouse gases, respectively (IPCC 2007) (Figure 4). The corresponding values for Sweden in 2011 were 13% and 3%, respectively (Swedish EPA 2014b). The largest contributors in the agricultural sector are CH_4 emissions from ruminants and N_2O emissions from soil processes. The largest contributor in the waste and wastewater sector is emissions from landfill (Swedish EPA 2014b). However, as a consequence of taxes and bans on sending certain organic materials to landfill, the CH_4 emissions from landfill in Sweden have declined steadily since 1990. Nitrous oxide may also be produced indirectly when emitted NH_3 is deposited and then nitrified or denitrified in aquatic and terrestrial ecosystems.

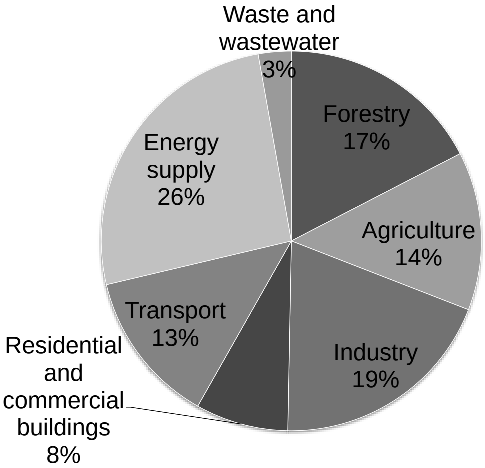

Figure 4. Global distribution of greenhouse gas emissions. Modified from IPCC (2007).

The management of all types of organic fertilisers causes emissions of greenhouse gases. Of the greenhouse gases emitted from agriculture in Sweden, 10% originates from manure management (Swedish EPA 2014a). The dominant greenhouse gas from storage of manure is CH_4 and the dominant greenhouse gas from land application is N_2O.

Many of the treatment processes in wastewater treatment plants involve emissions of N_2O and CH_4 (Czepiel *et al.* 1993, 1995; Daelman *et al.* 2012; Kampschreur *et al.* 2009). It has been shown that both N_2O and CH_4 can be emitted from the grit tanks, aeration tanks and sludge storage tanks at treatment plants (Czepiel *et al.* 1993, 1995). Daelman *et al.* (2012) identified the buffer tank for digested sludge and the storage tank for dewatered sludge as the main sources of CH_4, while Kampschreur *et al.* (2009) identified the activated sludge units as the main contributor of N_2O.

3.4.1 Storage

Storage of manure (Kebreab 2006; Saggar *et al.* 2004; Webb *et al.* 2012) and sewage sludge (Flodman 2002; Majumder *et al.* 2014) leads to emissions of N_2O and CH_4. Management of animal manures contributes around 1.3% of anthropogenic emissions of greenhouse gases in Sweden (Swedish EPA 2014b). This can be compared with the annual emissions of N_2O and CH_4 from sewage sludge storage which, according to Flodman (2002), could comprise around 5% and 0.1% of the total Swedish anthropogenic emissions of N_2O and CH_4, respectively, if all the sewage sludge in Sweden were stored for one year.

Nitrous oxide emissions from stored organic fertilisers are reported to be positively related to temperature (Jungbluth *et al.* 2001; Majumder *et al.* 2014). Emissions of N_2O can also be increased by rainfall events, as nitrate from nitrification in the upper layers of the fertiliser can percolate down the profile with the water to reach deeper anaerobic zones and there become denitrified (Börjesson & Svensson 1997). Nitrous oxide emissions from storage of slurry are mainly released from slurry with a surface crust (Rodhe *et al.* 2012; Sommer *et al.* 2000). The porous surface crust contains sites with and without oxygen, especially when the crust dries. Hence, NH_3 may be nitrified in aerobic zones and NO_3^- denitrified in adjacent anaerobic zones, both processes producing N_2O in their pathways (Sommer *et al.* 2000).

The CH_4 emissions during storage of organic fertilisers are positively correlated with temperature, since a higher temperature increases microbial activity (Clemens *et al.* 2006; Hansen *et al.* 2006; Massé *et al.* 2008; Sommer *et al.* 2007), as shown by observed higher emissions in warmer seasons compared with colder (Clemens *et al.* 2006; Husted 1994; Rodhe *et al.* 2009, 2012). Stored digested sewage sludge, even though possessing some aerated zones, will always be dominated by anaerobic environments. Therefore stored sewage sludge can host many methanogens from the preceding digestion process, leading to an obvious risk of CH_4 emissions during storage.

3.4.2 Land application

The bacteria performing nitrification and denitrification are common inhabitants of the soil ecosystem (Stenberg *et al.* 1998). Hence, N_2O is produced naturally by the soil, but production and emissions increase when fertilisers are applied (Clemens *et al.* 1997; IPCC 2006). The amount of N_2O produced and emitted depends on parameters such as soil texture (Syväsalo *et al.* 2004), soil water content (Davidson 1993; Perälä *et al.* 2006; Pitombo *et al.*

2015; Velthof & Mosquera 2011), temperature (Scott *et al.* 2000) and the properties of the fertiliser applied (Clemens *et al.* 1997). The presence of a crop can reduce the amount of N_2O emitted (Jarecki *et al.* 2009; Parkin *et al.* 2006). More N_2O can potentially be produced if the soil contains both aerobic and anaerobic sites in close proximity (Senbayram *et al.* 2009). The NO_3^- formed by nitrification can then diffuse to the anaerobic sites to be denitrified (Nielsen *et al.* 1996).

Since CH_4 production requires anaerobic conditions, formation of CH_4 in aerated soils is low (Le Mer & Roger 2001; Smith *et al.* 2003) and waterlogging of the soil is normally required for CH_4 emissions. Aerated soils can act as a sink of CH_4 (Le Mer & Roger 2001), *i.e.* negative emissions caused by methane oxidisers residing in aerobic zones.

3.5 Ammonia emissions from organic fertiliser management

In Sweden, agriculture is the largest contributor to NH_3 emissions, accounting for over 80% of total emissions (Swedish EPA 2016b). The corresponding value for all of Europe in 2013 was 93% (Eurostat 2013). Emissions of NH_3 represent loss of plant-available nitrogen and also contribute to acidification and eutrophication by subsequent deposition. After being emitted, NH_3 is either deposited with particles or dissolved in precipitation (Denmead *et al.* 2008).

In biological processes, NH_3 and NH_4^+ (collectively called total ammoniacal nitrogen) are produced by mineralisation of organic nitrogen, such as that contained in proteins and urea. Ammonia and NH_4^+ ions exist in equilibrium, meaning that if more total ammoniacal nitrogen is in the form of NH_4^+, less is in the form of NH_3 and *vice versa* (Brady & Weil 2008). Increased pH and increased temperature are factors that can shift this equilibrium towards more NH_3. In aqueous solution, NH_3 acts as a weak base, acquiring hydrogen ions from H_2O to yield NH_4^+ ions and hydroxide ions. In contrast, the NH_4^+ ion acts as a weak acid in aqueous solution because it dissociates to form hydrogen ions and NH_3.

Most NH_3 losses from organic fertilisers occur from the surface of ammoniacal solutions of the fertiliser (slurries or solids) (Sommer & Hutchings 2001). Ammonia emission is a surface phenomenon, in that the NH_3 is transferred to the ambient air from the air layer in direct contact with the ammoniacal solution by diffusion, convection and other transport (Sommer & Hutchings 2001). The flux depends on the difference between the concentration of NH_3 in the surface layer and in the air close to this surface, while emissions of NH_3 occur when the surface layer concentration is higher than the air concentration.

The amount of NH_3 emitted from storage is determined by factors such as pH, nitrogen concentration, temperature, wind speed and management strategies such as covering (Bussink & Oenema 1998). Emissions from cattle slurry have been reported to represent 0-20% of the total nitrogen content (Bussink & Oenema 1998), while emissions from solid organic fertiliser storage may be 0.3-34% of the total nitrogen content at the start of storage (Hansen *et al*. 2006).

Depending on the origin of the material and the storage method used, organic fertiliser contains differing concentrations of NH_4^+, which on application to soil can be volatised to NH_3. The amount of NH_3 emitted from land-applied fertiliser is determined by factors such as air temperature, fertiliser pH, wind speed, concentration of NH_3 at the fertiliser surface, dry matter content of the fertiliser, soil type, soil infiltration, area of manure exposed and time of exposure (Sommer & Hutchings 2001).

3.6 Measures to reduce greenhouse gas and ammonia emissions from organic fertiliser management

3.6.1 Digestion

In 2014, 783,000 Mg animal manure (wet weight) were digested in Sweden, whereof one-third was digested as the sole substrate in 35 on-farm digestion plants and the rest was co-digested in 20 large-scale plants (Swedish Energy Agency 2015). The on-farm digestion plants produced approx. 269,000 Mg digested manure. In the same year, 5,717,000 Mg sewage sludge (wet weight before dewatering) were digested in Sweden, producing 674,000 Mg digested and dewatered sewage sludge (Swedish Energy Agency 2015). Sewage sludge is digested at large wastewater treatment plants. In Sweden, the dominant digestion process for treating manure and sewage sludge is digestion at 35 °C (mesophilic digestion), with a hydraulic retention time in the digester of 15-30 days. However, digestion can also be conducted at other temperatures, *e.g.* 50-60 °C (thermophilic digestion) or 5-20 °C (psychrophilic digestion). Different bacterial communities dominate at different temperatures (Gallert & Winter 1997).

In anaerobic digestion, part of the carbon is transformed to CH_4 and CO_2 (Gerardi 2003). The amounts and proportions of CH_4 and CO_2 formed depend on *e.g.* the degradability of the substrate and its retention time in the digester. In Swedish wastewater treatment plants, anaerobic digestion has long been applied to stabilise dewatered sewage sludge. Digestion of manure and sewage sludge can benefit the environment, in that the CH_4 produced can replace fossil fuels (Swedish EPA 2014a). However, the emissions of greenhouse gases from the digestion plant itself and from management of the digested substrate also need to be accounted for. The changes in properties of the substrate subjected to the digestion process, along with increased storage temperatures, can stimulate emissions of greenhouse gases and of NH_3.

Lower N_2O emissions have been reported from storage of digested manure compared with non-digested (Petersen 1999), while Clemens *et al.* (2006) observed no differences. Nitrifying bacteria in general are sensitive to high temperatures (Grunditz & Dalhammar 2001; Jiang & Bakken 1999), implying that thermophilic digestion should reduce these bacteria and potentially also the amount of N_2O emitted.

The methanogens are dependent on easily degradable carbon and the higher the degree of degradation in the digester, the less easily degradable carbon will be available for the methanogens in subsequent storage of the digested substrate. In line with this, Amon *et al.* (2006) and Clemens *et al.* (2006) reported higher emissions of CH_4 from stored non-digested than digested manure. The methanogens in the digested substrate are adapted to the temperature of the reactor and therefore cooling the digested substrate is important for decreasing the emissions during subsequent storage.

Digestion of manure and sewage sludge can benefit crop production, since the process makes nitrogen more available for plants as organic nitrogen is mineralised to NH_4^+. However, the increase in pH during digestion opens the way for increased NH_3 emissions during storage and after land application (Pain *et al.* 1990). In line with this, Sommer *et al.* (2006) and Clemens *et al.* (2006) showed that digested manure emitted more NH_3 than non-digested manure after land application. In contrast, Rubæk *et al.* (1996) and Hansen *et al.* (2004) measured lower NH_3 emissions from application of digested manure compared with non-digested, probably due to better infiltration of the digested fertiliser into the soil, since it had a lower dry matter content than the non-digested fertiliser.

3.6.2 Ammonia sanitisation

Ammonia has a sanitising effect in that the NH_3 molecule can diffuse across cell membranes. When this occurs, the pH is raised inside the cell, which affects the ion balance, giving a toxic effect (Schneider *et al.* 1996). A benefit of sanitisation with NH_3 is that the NH_3 is not consumed during treatment and thus the fertiliser value is increased, provided that NH_3 is not lost to the atmosphere (Nordin *et al.* 2009). If the sanitised material is covered in an efficient manner, the NH_3 emissions can be reduced (Chadwick 2005; Sagoo *et al.* 2007). The sanitising effect can thus be expected to continue during the storage period and pathogenic microorganisms will be prevented from re-growing.

Ammonia treatment may be achieved by addition of urea [$(NH_2)_2CO$]. When applied to a substrate that contains high concentrations of the bacterial enzyme urease, such as sewage sludge or manure, urea is rapidly mineralised to CO_2 and NH_3 (Equation 1).

$$(NH_2)_2CO + H_2O \xRightarrow{urease} CO_2 + 2NH_3 \qquad (equation\ 1)$$

Nitrifying bacteria (Anthonisen *et al.* 1967) and methanogens (Hansen *et al.* 1998) are both sensitive to high NH_3 concentrations and thus NH_3 treatment should reduce their activity and consequently production of N_2O and CH_4. However, high pH not only leads to a higher proportion of total NH_4^+ being protolysed to NH_3, increasing the sanitation effect, but also increases the risk of NH_3 being emitted to the atmosphere (Brady & Weil 2008). Thus it increases the requirement for an efficient cover.

3.6.3 Covered storage

Covering stored organic fertiliser may be an effective way of reducing NH_3 emissions. Chadwick (2005) showed a 90% reduction from cattle manure heaps on combining covered storage with compaction of the fertiliser. Sagoo *et al.* (2007) also demonstrated a 90% lowering of NH_3 emissions from poultry manure by using a cover.

Studies show contradictory results regarding whether storage with a cover or roof emits less or more greenhouse gases than storage without. A cover/roof that protects the fertiliser from sun and wind may reduce N_2O emissions, since it prevents the fertiliser from drying (Hansen *et al.* 2006). Methane emissions could be reduced by a roof (Clemens *et al.* 2006), while a cover that reduces oxygen availability may cause higher emissions of CH_4 (Chadwick 2005), but has also been shown to reduce CH_4 emissions (Chadwick 2005; Hansen *et al.* 2006 Rodhe *et al.* 2009), perhaps as a consequence of lowered temperatures (Chadwick 2005).

3.6.4 Incorporation of organic fertiliser at land application

Fertilisers rich in easily available nitrogen in the form of NH_4^+ increase the risk of NH_3 emissions. Emissions of NH_3 after land application of organic fertilisers are effectively reduced by restricting the exchange with the surrounding air, which may be achieved by incorporating or injecting the fertiliser into the soil (Rodhe *et al.* 2006; Thomsen *et al.* 2010; Wulf *et al.* 2002). Injection or incorporation of the fertiliser immediately after surface application can dramatically reduce the cumulative NH_3 emissions, since up to 50% of emissions occur during the first hours after application (Misselbrook *et al.* 2002). Some fertilisers, such as urea (chemical fertiliser), are required by

Swedish law to be incorporated within four hours after application to reduce the NH_3 losses, while others (*e.g.* animal manure) must be incorporated within four or 12 hours in some periods of the year or if *e.g.* the soil has not been sown with a crop (Swedish Board of Agriculture 2012).

Incorporation or injection of organic fertilisers into soil has previously been shown in several studies to increase N_2O emissions (Rodhe *et al.* 2006; Thomsen *et al.* 2010; Thorman *et al.* 2007; Velthof & Mosquera 2011; Weslien *et al.* 1998; Wulf *et al.* 2002). This is often explained by the formation of anaerobic zones in close proximity to aerobic environments, promoting simultaneous nitrification and denitrification. However, other researchers report the opposite, *i.e.* that incorporation or injection reduces emissions of N_2O (Thorman *et al.* 2007; Webb *et al.* 2004), while yet other studies have found no differences in emissions between incorporated/injected fertiliser and surface application (Clemens *et al.* 1997; Sommer *et al.* 1996).

3.6.5 Timing of application of organic fertiliser

Since soil water content (Davidson 1993; Perälä *et al.* 2006; Pitombo *et al.* 2015; Velthof & Mosquera 2011) and temperature (Scott *et al.* 2000) greatly influence emissions of N_2O after land application of organic fertilisers, application in different seasons may lead to different emissions rates. High soil moisture content, which is more prevalent in autumn, leads to higher emissions of N_2O after application of organic fertiliser (Pitombo *et al.* 2015), while a combination of warm soil surface (10-25 °C) and precipitation (Scott *et al.* 2000) or warm soil and high soil moisture (Rodhe *et al.* 2012) has been shown to stimulate N_2O fluxes.

Ammonia emissions are also temperature-dependent, in that more NH_3 is emitted at higher temperatures (Sommer & Hutchings 2001). Solar radiation *per se* also increases NH_3 emissions by increasing the turbulence in the atmosphere and thereby the transport of NH_3 and by driving evaporation of water, which increases the concentration of total ammoniacal nitrogen.

3.7 Life cycle assessment

Life cycle assessment (LCA) can be used for assessing the possible environmental impacts of a product or a service. The methodology is standardised in ISO 14040:2006 and 14044:2006. According to ISO 14040 (ISO 2006a), LCA is defined as the “compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle” (ISO 2006a).

Life cycle assessment can be used for identifying hotspots in the life cycle where the impact on the environment can be improved, for decision making, to select suitable environmental indicators, for comparing products or services and for marketing purposes (*e.g.* environmental declaration of a product) (ISO 2006a). The ISO standards 14040 and 14044 detail the requirements for conducting an LCA (ISO 2006a, 2006b).

An LCA consists of four phases; (1) goal and scope definition, (2) inventory analysis, (3) impact assessment and (4) interpretation. The work is iterative, meaning that as new information is gained during the process, the content in any of the phases may be changed (ISO 2006a). In the goal and scope definition phase (1), the goal of the study, system boundaries and the functional unit are decided. The functional unit is a reference unit to which the data in the LCA are related. The inventory analysis (2) is the phase where all input data are gathered, while in the impact assessment phase (3) these data are divided into impact categories such as global warming or eutrophication. In the last phase (4), the results are interpreted and potential hotspots are identified (ISO 2006a).

Life cycle assessments are commonly used to compare end use alternatives for wastes and manure. For example, Sandars *et al.* (2003) used LCA to compare treatments and application techniques for pig manure. Their results showed that different application techniques were beneficial for different impact categories (*e.g.* splash plate application was beneficial in terms of nitrate leaching, but the worst option in terms of acidification, eutrophication and GWP_{100}). Wu *et al.* (2013) compared GWP_{100} from land application and incineration of cattle manure and showed that incineration was the better option in this case. However, no impact categories other than GWP_{100} were included.

Previous LCA studies have shown the importance of including both storage and land application when assessing the management of sewage sludge production and its use in terms of GWP_{100}, potential acidification and potential eutrophication (Dalemo *et al.* 1998; Johansson *et al.* 2008). Similar results have been reported for digested food waste (Chiew *et al.* 2015). However, storage and land application are not always included in LCAs of sewage sludge management.

Using organic residues such as sewage sludge as fertilisers means that less chemical fertiliser needs to be produced, which can affect the results of an LCA substantially, depending on the system boundaries used. Lundin *et al.* (2000) found that including avoided production of chemical fertilisers had a great impact on the total results of their LCA on wastewater treatment and sewage sludge management, while Tillman *et al.* (1998) found the opposite.

4 Methodology

4.1 Storage experiments (Papers I and II)

Paper I describes a two-part storage experiment on cattle slurry, which was stored during summer (91 days) or winter (105 days), while Paper II describes a one-year storage experiment with sewage sludge.

4.1.1 Experimental set-up

Two pilot plants were constructed to determine emissions of N_2O and CH_4 from cattle slurry and sewage sludge during storage (Figures 5a and b). The cattle slurry experiment consisted of three treatments and the sewage sludge experiment of four treatments, with all treatments performed in triplicate (Table 1). The substrate entering the digester consisted of 95% cattle slurry and 5% solid cattle manure with some feed residues. The sewage sludges used were collected from two wastewater treatment plants and were mixtures of sewage sludge from primary (mechanical), secondary (biological) and tertiary (P precipitation) treatment steps. Both the cattle slurry and the sewage sludge were transported to the experimental facility without intermediate storage.

The digestion processes applied for some of the treatments in the studies and the properties of the organic fertilisers are described in Paper I and Paper II, respectively. Both storage experiments were set up as randomised complete block designs with three replicates (blocks) per treatment.

The pilot plants for cattle slurry and sewage sludge consisted of nine 3 m^3 (Paper I) and 12 4 m^3 (Paper II) cylindrical containers, respectively. The containers for the cattle slurry experiment were half-buried in the ground, while the containers in the sewage sludge experiment stood on an asphalt surface but were surrounded up to their fill level by mesophilically digested and dewatered sewage sludge. Both constructions were designed to mimic the thermal conditions in full-scale storage.

A roof made of polyvinyl chloride sheeting placed on flat steel net was used for one of the treatments in the cattle slurry experiment. It was inserted 0.05 m above the slurry surface and was thus not air-tight. A tarpaulin sheet placed directly on the surface of the sewage sludge was used to cover three of the treatments in the sewage sludge experiment.

The ammonia-treated sewage sludge was prepared by mixing urea into mesophilically digested and dewatered sewage sludge just before filling the containers.

Table 1. *Treatments studied for determination of emissions of N_2O and CH_4 from cattle slurry and dewatered sewage sludge during storage*

Experiment (Paper)	Treatments
Cattle slurry (Paper I)	Non-digested, stored without roof
	Digested, stored without roof
	Digested, stored with roof
Sewage sludge (Papers II and IV)	Mesophilically digested, stored without cover
	Mesophilically digested, stored with cover
	Mesophilically digested, ammonia treated, stored with cover
	Thermophilically digested, stored with cover

4.1.2 Greenhouse gas measurements

Emissions of N_2O and CH_4 from the storage containers in the two experiments were measured using a closed chamber technique by placing an air-tight lid above the surface (Figures 5b and d), creating a closed headspace above the organic fertiliser from which gas samples were collected with a 50 mL syringe at 0, 15 and 30 minutes after closure, as described by Rodhe *et al.* (2009).

4.1.3 Additional samplings and measurements

At the start and end of the experiments, composite material samples were collected from each type of slurry (Paper I) and each sludge container (Paper II) for physical and chemical characterisation. For the sewage sludge experiment, samples were also collected from the bottom and top layers of each container at the end of the storage period. Temperature was recorded continuously in the fertilisers throughout the experiments, at 0.1 m and 0.2 m below the surface in the cattle slurry experiments and at the bottom of the stored mass in the sewage sludge experiments. Weather data were collected from nearby weather stations for both experiments and, in addition, ambient air temperature was measured at the site for the sewage sludge storage experiment.

a
Photo: Lena Rodhe

b
Photo: Lena Rodhe

c
Photo: Dick Gillberg

d
Photo: Dick Gillberg

Figure 5. a) Pilot-scale cattle slurry storage facility, b) greenhouse gas (GHG) sampling of stored cattle slurry, c) pilot-scale sewage sludge storage facility and d) GHG sampling of stored sewage sludge. During gas sampling, air-tight lids were placed above the fertiliser surface and gas was collected manually using a syringe at 0, 15 and 30 min after deployment in the cattle slurry experiment and at 0, 30 and 60 min in the sewage sludge experiment.

4.2 Land application experiments (Papers I and III)

4.2.1 Experimental set-up

Two experiments were set up to determine emissions of N_2O and CH_4 from arable land treated with cattle slurry and sewage sludge. Both sets of experiments consisted of two sub-experiments with one application in spring and one in autumn. In spring, NH_3 emissions were also measured.

The cattle slurry used was taken from the cattle slurry storage experiment and the sewage sludge applied in autumn was taken from the sewage sludge storage experiment. The urea-treated sewage sludge used in spring was taken from another experiment (Nordin *et al*. 2015) using sludge from the same wastewater treatment plant as the mesophilically digested sewage sludge used for autumn application and in the storage experiment (Paper II). This sludge had been treated similarly to the urea-treated sewage sludge in the storage experiment, *i.e*. with the same amount of urea and stored under cover.

The two experiments were designed as a plot set-up. The size of the individual plots in the cattle slurry experiment was 2 m x 12 m. The plots in the sewage sludge experiments were 6 m x 12 m for the sewage sludge treatments and 3 m x 12 m for the unfertilised control. However, in autumn, sewage sludge was applied only on three sub-plots of 1.5 m x 1.5 m set out randomly in each plot, because the soil was too wet to carry heavy machinery.

The cattle slurry and sewage sludge land application experiments were set up in similar way, with all plots in the spring and autumn application sub-experiments included in the same experimental area. The plots were set out in a randomised block design with three blocks (Papers I and III). Both experiments had unfertilised control plots. The cattle slurry experiment consisted of two treatments that were applied in both spring and autumn sub-experiments and the sewage sludge experiment included two incorporation timings in both sub-experiments (Table 2). Winter wheat and spring barley were sown in autumn and spring, respectively, in the cattle slurry experiments. Spring barley was sown in spring in the sewage sludge experiment, but no crop was sown in autumn as the soil was too wet.

Table 2. *Treatments studied for determination of emissions of N_2O, CH_4 and, in spring, also NH_3 after land application of cattle slurry or sewage sludge*

Experiment (Paper)	Treatments	Time
Cattle slurry (Paper I)	Control, no fertiliser	Spring/autumn
	Non-digested, 4 h delayed incorporation	Spring
	Digested, 4 h delayed incorporation	Spring
	Non-digested, immediate incorporation	Autumn
	Digested, immediate incorporation	Autumn
Sewage sludge (Paper III)	Control, no fertiliser	Spring/autumn
	Digested, ammonia-treated, immediate incorporation	Spring
	Digested, ammonia-treated, 4 h delayed incorporation	Spring
	Digested, immediate incorporation	Autumn
	Digested, 4 h delayed incorporation	Autumn

4.2.2 Greenhouse gas measurements from land-applied organic fertiliser

In the two field experiments, emissions of N_2O and CH_4 were measured using closed static chambers (Livingston & Hutchinson 1995) (Figures 6a and b). In each experimental plot, three steel frames equipped with a channel-shaped water seal were pushed 0.05 m into the soil. At the time of measuring, the channels were filled with water and an air-tight chamber was placed on the frame, so that the air above the soil was enclosed in the chamber. Gas was sampled 0 and 1 h after closing the chamber, using a syringe. On the first sampling day, after sealing, samples were taken at 0, 0.5 and 1 h from one chamber in each treatment of the cattle slurry experiment and at 0, 0.5, 1, 1.5 and 2 h from one chamber in the sewage sludge experiment, to verify linearity.

a
Photo: Lena Rodhe

b
Photo: Lena Rodhe

Figure 6. a) Sampling frames pushed into the soil and b) greenhouse gas measurement in the field using closed chambers placed on the frames.

4.2.3 Additional samplings and measurements

Prior to the two experiments, the upper soil layer (0-0.2 m) was sampled for analysis of soil properties (Papers I and III). Additional soil samples were collected at two depths (0-0.05 and 0.05-0.10 m) using steel cylinders to determine soil bulk density and moisture content. The fertilisers were also sampled for characterisation. Soil temperature and moisture at 0.02-0.05 m depth were recorded continuously during the experiment and temperature was also measured inside and outside one of the closed chambers during all gas samplings. Weather data were collected from nearby weather stations for both experiments.

4.2.4 Ammonia measurements from land-applied organic fertiliser

At spring application in the cattle slurry and sewage sludge experiments, NH_3 emissions were measured with a dynamic chamber technique immediately after application of the organic fertilisers (Svensson 1994). In one control plot and in all treatment plots, two chambers were installed per plot, each equipped with a holder for samplers for determination of the equilibrium concentration of NH_3 and a holder for a sampler for analysis of ambient air. The samplers placed in the holders were passive diffusion samplers, one for concentration measurements and two for measuring laminar boundaries. Appropriate exposure times for the diffusion samplers used were determined by measuring the instantaneous concentration of NH_3 in the chambers with a hand-held instrument (Kitagawa precision gas detector, Komyo Rikagku Kogyo KK, Tokyo, Japan). The NH_3 emissions between the measurement periods were calculated from interpolated values of the NH_3 concentrations adjusted for the prevailing weather conditions during the interval, according to Malgeryd (1998).

4.3 Gas analyses and calculations (Papers I-III)

The gas samples collected from the static chambers were analysed for N_2O and CH_4 using a gas chromatograph equipped as described in Papers I-III. The gas emissions at each measuring time were calculated by linear regression from the increase in concentration over time in the closed chamber. By averaging the flux between two adjacent sampling occasions and integrating over this period, cumulative emissions of N_2O and CH_4 were estimated for the experimental period.

4.4 Choice of sampling method

Several methods for measurement of emissions of greenhouse gases exist, but not all of them are applicable for measurements on storage and in fields. Two main categories of methods that could be considered suitable are micrometeorological methods and chamber methods.

Micrometeorological methods can cover large areas and do not alter the conditions of the area measured (Hu *et al.* 2014). However such methods are very expensive and often complex to handle. In addition, some assumptions need to be made in most cases (Brown *et al.* 2002; Hu *et al.* 2014; Ro *et al.* 2013). The fact that micrometeorological methods are not applicable for small areas makes them difficult to use in close proximity to other sources of the gas of interest, such as experimental fields or pilot plants with several treatments, as in the experiments conducted in Papers I-III. Thus chamber techniques were more applicable for the experiments included in this thesis and are presented in detail below.

4.4.1 Chamber methods

Chamber methods can be grouped according to two fundamentally different principles, called non-steady state and steady state chambers or non-through flow and through flow chambers or, in the terminology used in this thesis, closed and open chambers.

Chambers can range in size from a few litres to as large as a whole barn used as a chamber (open system) (McGinn 2006). Chambers can be either automatic or manual, the first being opened and closed through *e.g.* a pneumatic system and the latter opened and closed by an operator. A manual chamber is thus much cheaper in terms of capital investment, but more labour-intensive (Rapson & Dacres 2014).

In the closed chamber method, the increase in gas concentration over a certain time inside the chamber is measured. The time for gas accumulation is normally restricted to short periods, in order to reduce the effect of the emitted gas on the fluxes from the emitting surface (McGinn 2006). For the same reason, the chamber should be vented, *e.g.* by removing the chamber, between measurements. A closed chamber can be equipped with a pressure vent or kept entirely closed, with the former enabling atmospheric pressure changes inside the enclosed volume (Livingston & Hutchinson 1995). Closed chambers can be installed permanently at one site or moved to extend the number of sampling sites (Hu *et al.* 2014). Concentration changes over time can be followed by continuous or repeated sampling.

Open chambers are designed for a constant flow of air through the chamber and the difference in gas concentration between the air entering and leaving the chamber is measured (Livingston & Hutchinson 1995). The flow rate through the chamber is measured and open chambers can be either passive or dynamic. The flow through the passive chambers is created naturally by climate and topography, while the dynamic chamber is equipped with a fan to create an airflow (Hu *et al.* 2014).

On comparing open and closed chambers for N_2O measurements at the same site, Ambus *et al.* (1993) found that the average N_2O flux determined by the open chambers was 1.8-fold the average from the closed chambers. They concluded, however, that the N_2O flux was determined with sufficient precision by both methods, since the difference between the methods was insignificant compared with the spatial variability found with the open chambers.

4.4.2 Methods for measuring ammonia emissions

Both chamber methods and micrometeorological methods, as presented above, can be used to determine NH_3 emissions, but tracer methods are also frequently employed (Harper 2005).

In the tracer method, an inert tracer gas (such as sulphur hexafluoride) or an isotope (such as ^{15}N) is released in known amounts and the ratio between the tracer and the gas of interest in the collected gas sample is analysed (Hu *et al.*

2014). However, this method is not suitable for soils and feedlots, since it is almost impossible to adequately simulate the release of the gas of interest in these contexts. The technique is more commonly applied for estimating emissions from animal houses and enteric CH_4 emissions from animals (Hu *et al.* 2014).

It is preferable to use techniques that do not disturb the sample area and microclimate (Harper 2005). However, chamber methods are still often used because they are cheaper and simple and suitable for small field plots, and may have a lower sensitivity requirement for measuring gas concentrations.

4.4.3 Method choice in Papers I-III

Chamber equipment is suitable for scientific studies because it allows for treatment replication (Parkin *et al.* 2012) and is useful for comparisons between treatments (Rochette & Eriksen-Hamel 2008). Small chambers have the advantage that measurements can easily be replicated and many treatments and small areas compared. Chambers are also low-cost compared with other methods and often also simple in construction and operation (Hu *et al.* 2014).

However, there are drawbacks with chamber methods, *e.g.* the chamber creates an artificial, constrained environment in which increasing gas concentrations may create saturated conditions, affecting the gas production rate (Parkin *et al.* 2012). Deployment of a chamber may also alter the soil and headspace temperature (Rochette & Eriksen-Hamel 2008).

The closed chamber method used for measuring N_2O and CH_4 in the experiments included in this thesis was chosen because of its simplicity of use and the low cost. This method has been used successfully in previous studies by some of the co-authors of Papers I-III (*e.g.* Rodhe *et al.* 2006, 2009, 2012).

Other chamber types could be an alternative to the closed, manual chambers used in Papers I-III. For example, an automatic chamber would be less labour-intensive (Rapson & Dacres 2014) and thus allow more chambers to be used at the same time or measurements to be made more frequently. However, the equipment is often costly. There is also the option of using open chambers. A drawback with such chambers is that they require sufficient time to reach steady state (Livingston & Hutchinson 1995) and therefore it could be more suitable to use non-steady-state (closed) chambers if multiple samples are to be collected on the same measuring occasion, in order to reduce the total sampling time.

Gas concentrations in closed chambers normally initially increase linearly (Anger *et al.* 2003; Yamulki & Jarvis 1999), although some studies have shown that linear regression is not always the best method for calculating gas concentrations in a closed chamber (*e.g.* Parkin *et al.* 2012). However, if linearity is tested and proven to be acceptable in the first measurement, later measurements can be performed with fewer headspace samples (Chadwick *et al*. 2014; Conen & Smith 2000), especially when, as in the field experiments included in this thesis, large numbers of chambers are used to improve plot-level flux estimates (Rochette *et al*. 2015).

The chamber method used for measuring NH_3 emissions in the experiments included in this thesis was chosen because of its simplicity of use and low cost (Papers I and III). This method has previously been used successfully by some of the co-authors of Papers I-III (*e.g*. Rodhe *et al*. 2006).

4.4.4 Methodological issues

The main practical issue with the pilot-scale methodology of the storage experiment for sewage sludge (Paper II) was that the cylinders prevented precipitation water from running away as it would from a full-scale storage facility where the fertiliser is stacked in heaps. A wet vacuum cleaner was used to remove the water from the covered treatments, but precipitation still flowed over the edges of the cover at times, causing water-logging of the sludge surface during the second half of the storage period, except for the thermophilically digested sludge. This issue meant that the difference between the covered and non-covered treatments was not as pronounced as intended and that the resemblance with a full-scale storage was somewhat reduced.

Plastic sheeting was placed under each cylinder and reaching around 0.2 m up the sides, so no liquid exchange between container content and surrounding sewage sludge was possible, meaning that no water could exit. Furthermore, the edges of the cylinders could have prevented wind from drying the surface of the uncovered treatment. It can be speculated the above constraints created an environment dissimilar to full-scale storage, which might have reduced the differences between covered and non-covered treatments.

On land application, the NH_3-treated sludge (Paper III) turned out to be sticky and consequently could not be as evenly distributed over the soil surface as intended (58% coefficient of variation for six replicates). This possibly influenced the results, but was compensated for to some extent by applying three chambers per sub-plot.

During gas analysis of CH_4 in the sewage sludge storage experiment (Paper II), the highest concentrations exceeded the detection limit of the instrument (cutting off the peaks) and could hence not be fully detected. This was dealt with by presenting the emissions calculated from the cut-off peaks as minimum values.

4.5 Analysis of potential methane production (Papers I and II)

Empirically measured methane production potential was determined by placing the fertilisers in gas-tight flasks together with inoculate and water and placing the flasks on a shaking table at 37 °C until production of CH_4 had almost ceased in all flasks (after 100 and 105 days for the cattle slurry and sewage sludge experiments, respectively). During the experimental period, the gas pressure was measured for calculation of gas volume and, in addition, gas samples were collected for determination of CH_4 concentration. Additional measurements were made on flasks with only inoculum. The total amount of CH_4 on each sampling occasion was calculated based on the concentration of CH_4 and pressure, with CH_4 amount in the inoculum flasks subtracted. Methane production potential was expressed as normal-mL CH_4 g^{-1} volatile solids (VS), where normal-mL is the volume at 0 °C and 1 atmosphere pressure.

4.6 Statistical analysis (Papers I-III)

All statistical analyses were performed using Statistical Analysis Software (SAS, ver. 9.4, SAS Institute Inc., Cary, NC, USA). One-way ANOVA with blocks followed by pair-wise comparisons with t-test (PROC GLM) were used for analysis of differences in means. Pearson correlation coefficient (r) was used for correlation analyses (*e.g.* between emissions and temperature) (Papers II and III). Interactions between treatment and time for the gas fluxes of N_2O and CH_4 were analysed with a mixed linear model (PROC MIXED) (Paper I).

4.7 Life cycle assessment (Paper IV)

4.7.1 Goal and scope

The goal of the LCA was to assess the environmental impact of different strategies for sewage sludge storage and land application. The storage treatments studied were: (1) digested sewage sludge stored without cover, (2) digested sewage sludge stored with cover, and (3) digested NH_3-treated sewage sludge stored with cover. Land application alternatives assessed were: (1) all sludge applied in autumn, (2) all sludge applied in spring, and (3) sludge applied in both autumn (80% of the sewage sludge) and spring (20% of the sewage sludge). The functional unit used was the amount of digested sewage sludge considered to replace 1 kg of chemical phosphorus fertiliser, since sewage sludge is primarily considered a phosphorus fertiliser. It was assumed that 60% of the total phosphorus content in the sewage sludge replaced chemical phosphorus (Foley *et al.* 2009). The system included effects of transport of sewage sludge to the storage facility, emissions of N_2O, CH_4 and NH_3 during storage and land application, tractor use for land application, production of cover and urea, and avoided production and transport of chemical fertilisers. Impact categories included were GWP_{100} (including direct emissions of N_2O and CH_4 and indirect N_2O emissions via NH_3), potential acidification, potential eutrophication and primary fossil energy use.

4.7.2 Inventory analysis

Data on greenhouse gas emissions from stored sewage sludge are scarce and were mainly derived from Paper II, complemented with data from Flodman (2002) and, for NH_3 emissions, from Karlsson & Rodhe (2002). Data on greenhouse gas and NH_3 emissions from land application were derived from IPCC (2006) and Karlsson & Rodhe (2002), respectively. For data on energy use and greenhouse gas emissions for chemical nutrient production, Brentrup & Pallière (2014) and data on transportation were retrieved from Ecoinvent 3.1 (Ecoinvent Centre 2015).

4.7.3 Impact assessment

Input data were gathered using the life cycle inventory software GaBi (ver. 6.0, 2016, Thinkstep, Leinfelden-Echterdingen, Germany) and Microsoft Excel was used for further calculations. The assessment method used was CML 2001 (Centre of Environmental Science of Leiden University (CML) 2001).

4.7.4 Interpretation

Microsoft Excel was used for visualisation and additional calculations in the interpretation of data. An additional analysis was also conducted to check the sensitivity of the results to changes in some of the input variables.

5 Results and discussion

5.1 Storage of cattle slurry and sewage sludge

5.1.1 Greenhouse gas emissions

Emissions of N_2O from stored cattle slurry were low in terms of losses related to the initial nitrogen content and were even negligible in five of the six storage cases studied (Table 3). The NH_3-treated mesophilically digested sewage sludge emitted almost no N_2O, the mesophilically digested sewage sludge stored with and without cover emitted some N_2O and the thermophilically digested sewage sludge emitted substantial amounts.

Methane emissions in terms of losses related to the initial content of carbon were larger from digested cattle slurry than from untreated slurry (Table 3). The CH_4 measurements on sewage sludge during storage indicated higher emissions from mesophilically digested sewage sludge stored with and without cover than from NH_3-treated mesophilically digested sewage sludge and thermophilically digested sewage sludge. It should be noted, however, that the reported data are minimum values due to the previously mentioned analytical issues.

Production of N_2O and CH_4 during storage of organic fertilisers involves a complex set of chemical, physical and biological parameters and emissions are therefore difficult to predict. Major parameters influencing the magnitude of emissions are temperature, the content of active microbes and easily available carbon and nitrogen, moisture content and oxygen status and porosity of the fertiliser (Webb *et al.* 2012), which will be discussed in further detail below. The physical and chemical properties of the cattle manure and the sewage sludge are presented in Table 4.

Table 3. *Emission factors for nitrous oxide (N_2O) and methane (CH_4) emissions from stored cattle slurry (Paper I) and sewage sludge (Paper II)*

Fertiliser type	Treatment	N_2O emissions (% of initial Tot-N)			CH_4 emissions (% of initial Tot-C)		
		Summer (91 days)	Winter (105 days)	Whole year	Summer (91 days)	Winter (105 days)	Whole year
Cattle slurry	Stored without roof	0.0	0.0		0.3	0.0	
	Digested, stored without roof	0.0	0.0		1.6	0.0	
	Digested, stored with roof	0.2	0.0		1.6	0.0	
Sewage sludge	Mesophilically digested			0.3			>1.1
	Mesophilically digested, stored with cover			0.2			>1.3
	Mesophilically digested, ammonia-treated, stored with cover			0.0			>0.4
	Thermophilically digested, stored with cover			1.3			>0.2

Table 4. *Physical and chemical properties of cattle slurry and sewage sludge at the start of storage experiments (Papers I and II). Content of:* DM *= dry matter,* VS *= volatile solids, Tot-N = total nitrogen, tan = total ammoniacal nitrogen, Tot-C = total carbon*

Fertiliser type	Treatment	DM	VS	pH	Tot-N	TAN	Tot-C
		(%)	(% of DM)		(kg Mg^{-1} DM)		
Cattle slurry	Non-digested, stored without roof, summer	7.9	84	7.2	40.5	15.8	450
	Digested, stored without roof, summer	5.0	76	7.7	56.0	19.0	262
	Digested, stored with roof, summer	5.0	76	7.7	56.0	19.0	262
	Non-digested, stored without roof, winter	3.3	76	7.4	57.6	12.7	190
	Digested, stored without roof, winter	4.1	72	7.9	73.2	24.1	215
	Digested, stored with roof, winter	4.1	72	7.9	73.2	24.1	215
Sewage sludge	Mesophilically digested, stored without roof	29.5	60.9	7.8	11.8	3.0	102
	Mesophilically digested, stored with cover	29.2	61.6	7.6	11.7	2.7	102
	Mesophilically digested, ammonia treated, stored with cover	29.1	61.6	8.6	16.8	6.6	100
	Thermophilically digested, stored with cover	29.5	51.4	7.7	8.1	2.6	82

5.1.2 Temperature

The results from both the cattle slurry and sewage sludge storage studies clearly indicated seasonal variations in emissions patterns of N_2O and CH_4.

The emissions of N_2O in the cattle slurry experiment were much higher in the warm summer than in the cold winter, when almost no emissions were observed. In the sewage sludge experiment, the emissions of N_2O were first quite high during autumn when storage began and then declined during winter, after which they increased in spring for the thermophilically digested sewage sludge. The emissions did not increase in spring for the treatments with mesophilically digested sludge, presumably due to the water layer covering these cylinders during the second half of the storage period, which reduced oxygen diffusion. Previous studies have shown positive relationships between N_2O emissions and temperature (Jungbluth *et al.* 2001; Majumder *et al.* 2014).

The CH_4 emissions were much lower in winter than in summer in the cattle slurry experiment (Table 3). This indicates that microbial activity was greatly retarded by the prevailing low temperatures in winter (Tables 3 and 5). The emissions pattern for sewage sludge was similar to that for cattle slurry, especially for the mesophilically digested sludge with and without cover, with higher emissions during summer and lower during winter. This pattern was less pronounced for the thermophilically digested sludge and the mesophilically digested sludge treated with NH_3, both showing overall lower emissions of CH_4 (Papers I and II). These results demonstrate that the amounts of CH_4 emitted during storage of organic fertilisers can be substantially reduced by lowering the temperature. Previous studies on CH_4 emissions from storage of animal manures have shown similar seasonal changes in CH_4 emissions, with increasing emissions with higher temperatures (Clemens *et al.* 2006; Husted 1994; Rodhe *et al.* 2009, 2012).

The CH_4 emissions, expressed per kg VS, for stored non-digested cattle slurry were 80% lower in the cold winter compared with the warm summer (Paper I). The corresponding value for digested slurry stored with or without a roof was almost 100%. It is important to bear in mind that the cattle slurry stored in the summer and in the winter in the experiments in Paper I was not the same slurry, and hence factors other than temperature could have affected the emissions. An algorithm used by Sommer *et al.* (2004) predicted a 31% reduction in emissions of CH_4 on cooling non-digested pig slurry to 10 °C from an initial 15 °C during storage in winter and 20 °C in the summer. With combined digestion and cooling, the reduction in both gases were estimated to be 59%. The mean temperature in the cattle slurry experiment (Paper I) was 14.2 °C in summer and 2.9 °C in winter, *i.e.* a similar temperature difference as that reported in Sommer *et al.* (2004). However, overall the temperatures were higher in the study by Sommer *et al.* (2004), meaning potentially higher emissions even at the lower temperature. Clemens *et al.* (2006) showed close to 100% decrease in CH_4 emissions when digested cattle slurry was stored at 4 °C instead of 11 °C.

The average temperature in the sewage sludge experiment, covering the corresponding summer period as that in the cattle slurry experiment, was 13-15 °C in the different treatments. The temperature in the sewage sludge experiment in the winter corresponding to that in the cattle slurry experiment was 5-6 °C. There was a decrease in CH_4 emissions due to low winter temperatures also in the sewage sludge storage experiment, but the size of this decrease could not be well defined due to the problems in quantifying high emissions.

To explore the effect of cooling on N_2O and CH_4 emissions from sewage sludge, the average N_2O flux for a winter period corresponding to the length of the winter period in the cattle slurry storage experiment (15 December-30 March) was extrapolated to cover a full year. This calculation indicated a reduction in total emissions of N_2O for the year ranging from 81% to almost 100% for all sludge treatments except the NH_3-treated sludge, compared with the actual emissions measured during the year with both warm and cold temperatures. In the latter treatment, emissions of N_2O were increased by cooling the sludge, but were still much lower than in any other treatment. Emissions of CH_4 according to the same calculation method were reduced by 44-90%. This demonstrates the potential mitigating effect of lower temperature during storage of organic fertilisers.

5.1.3 Digestion prior to storage

Emissions of CH_4 were higher from digested cattle slurry than from non-digested cattle slurry during summer storage (Table 3). This could not be explained by mean temperature differences, since those were very small (Table 5). Contrasting results, but not statistically significant, were indicated for the winter period, showing lower emissions of CH_4 from digested cattle slurry than from non-digested. This demonstrates the complexity of emissions, which is further emphasised by the fact that some previous studies report lower CH_4 emissions from digested manure (Amon *et al.* 2006; Clemens *et al.* 2006).

Emissions of CH_4 were during storage lower from the sewage sludge digested at thermophilic temperature than from the sewage sludge digested at mesophilic temperature (Table 3). The difference between the process temperature in the digester and that in subsequent storage was much larger for sewage sludge digested thermophilically (53 °C) than for sludge digested mesophilically (37.5 °C) (for storage temperatures, see Table 5). Thus during storage, the methanogens in the thermophilically digested sewage sludge were farther away from the temperature in the digester and therefore possibly relatively less active than the methanogens in the mesophilically digested sewage sludge. It could be speculated that such a difference could partly explain the difference in CH_4 emissions between the two treatments. However, the somewhat different substrates fed into the digesters could to some extent also explain the differences in CH_4 emissions.

A range of factors related to operation of anaerobic digesters affect the composition of the digested substrate, including retention time and temperature (Gallert & Winter 1997). The cattle slurry studied here was digested at the same temperature as the mesophilically digested sewage sludge (38 and 37.5 °C, respectively) while the digestion temperature in the thermophilic sludge digestion was 53 °C. The hydraulic retention time was 30 days for the cattle slurry, while it was 15 and 15-17 days for the mesophilically and thermophilically digested sewage sludge, respectively. The degree of degradation of sewage sludge in the reactor was 28% of dry matter for the mesophilic temperature and 33% for the thermophilic temperature. The amount of CH_4 produced during digestion was not measured in the experiments, but for cattle slurry and sewage sludge is reported to be 120-490 and 240-490 m^3 CH_4 Mg^{-1} dry matter, respectively (Linné *et al*. 2008).

Degradation is typically more efficient at thermophilic temperatures compared with mesophilic (Vindis *et al*. 2009). Thus for thermophilic digestion a higher degree of degradation will normally be achieved with the same retention time, as was the case for the digested sludge in this thesis. Both the thermophilically digested and mesophilically digested sewage sludge were produced from mixed primary, secondary and tertiary sewage sludge. Thus, both the higher digestion temperature and the higher degree of degradation for the thermophilically digested sludge mean that it probably had a lower content of easily degradable organics.

Table 5. *Mean temperatures in the fertiliser and ambient air during storage of cattle slurry (Paper I) and sewage sludge (Paper II)*

Fertiliser type	Treatment	Summer* (˚C)	Winter** (˚C)	Whole year (˚C)
Cattle slurry	Stored without roof	14.2	2.9	
	Digested, stored without roof	14.8	4.9	
	Digested, stored with roof	14.8	4.9	
	Ambient air	18.1	6.9	
Sewage sludge	Mesophilically digested, stored without cover	12.8	5.1	11.5
	Mesophilically digested, stored with cover	13.0	5.6	11.8
	Mesophilically digested, ammonia-treated, stored with cover	13.3	4.7	11.1
	Thermophilically digested, stored with cover	14.9	6.5	13.7
	Ambient air	15.9	-0.2	7.5

*26 May to 25 August

**15 December to 30 March

5.1.4 Ammonia treatment

The NH_3 treatment demonstrated the most distinct and consistent results of the four sewage sludge storage treatments tested (Paper II). Total emissions of both N_2O and CH_4 related to the initial content of nitrogen and carbon, respectively, were negligible in the sludge treated with NH_3 (Table 3). Addition of urea has been proven to achieve sanitisation of faeces (Vinnerås 2007) and high concentrations of NH_3 inhibit general microbial activity, *e.g.* as in anaerobic digestion (Chen *et al.* 2008). There are several mechanisms proposed for NH_3 inhibition, such as a change in the intercellular pH or inhibition of specific enzyme reactions (Chen *et al.* 2008). In Paper II, the pH in the NH_3-treated sludge was higher than in the other treatments (Table 4). High pH increases the concentration of NH_3, which inhibits nitrifying activity, especially at high levels of total ammoniacal nitrogen (Kim *et al.* 2006). Thus, it is likely that the high concentrations of NH_3 in the NH_3-treated sludge inhibited the activity of both ammonia-oxidising bacteria and nitrite-oxidising bacteria, and thereby prevented nitrification and subsequent N_2O emissions (Kim *et al.* 2006).

Among the anaerobic microorganisms in the digestion process, methanogens are especially sensitive to high NH_3 concentrations and are therefore likely to be inhibited by high concentrations of NH_3 (Chen *et al.* 2008). Both NH_4^+ and NH_3 can directly or indirectly cause inhibition of anaerobic digestion systems, but NH_3 is suggested to be the main cause of inhibition (Yenigün & Demirel 2013, Chen *et al.* 2008).

Emissions of NH_3 were not measured in any of the storage experiments and calculated mass balances from the sewage sludge experiment (Table 4 in Paper II) did not give any hints on the nitrogen loss as NH_3. However, since the cover was not fully air-tight, some emissions could be expected to have taken place. Emissions of NH_3 from uncovered solid manure has been reported to range from 0.3 to 34 % of the total nitrogen content at the start of storage (Hansen *et al.* 2006). Based on literature reviews, Karlsson & Rodhe (2002) suggest a Swedish national emissions factor for NH_3 of 1% of total nitrogen for liquid manure storage with roof (there is no national factor for covered stored solid manure), which would amount to 0.17 kg NH_3 Mg^{-1} dry matter for the NH_3-treated sewage sludge.

5.1.5 Covered storage

The roof above the digested cattle slurry storage significantly increased the emissions of N_2O in the summer (Paper I and Table 3). The roof prevented precipitation and a surface crust was formed. When the surface crust dried, nitrification, and thereby the production of N_2O, was enabled. Production of N_2O with a drying surface crust has previously been shown by Sommer *et al.* (2000). In contrast to the roof over the cattle slurry, there was a tendency (not statistically significant) for the cover to reduce N_2O emissions in the sewage sludge experiment.

When solid organic fertiliser (*e.g.* sewage sludge or farmyard manure) stored without a cover dries out, it gradually becomes more aerobic, a process starting at the surface and then moving inwards. This can stimulate nitrification and hence production and emissions of N_2O. Since there was a water layer on top of both the covered and non-covered mesophilically digested sewage sludge during the second part of the storage period in Paper II, the non-covered sewage sludge did not dry. The water layer most likely reduced gas exchange in both treatments and thus also possibly reduced the differences regarding N_2O emissions between the treatments.

The CH_4 emissions as a percentage of initial carbon content were decreased by using a roof on the cattle slurry storage facility (Paper I), while the cover applied directly on the sewage sludge surface slightly increased CH_4 emissions (Paper II). This shows the importance of distinguishing between different types of cover for organic fertiliser storage. A roof installed above the surface prevents precipitation from entering the storage and also slows down drying of the fertiliser surface. A cover applied directly to the surface serves the same purpose as a roof, but also prevents gas exchange. Thus, a roof at a distance above the surface, as for the cattle slurry, does not give the same oxygen-depleting effect as a cover placed on the surface, as for the sewage sludge.

The cover prevented precipitation and thereby to some extent permitted drying of the surface, possibly promoting CH_4 oxidation (Petersen *et al.* 2005). Covering also effectively reduces NH_3 emissions, meaning that high concentrations of NH_3 and NH_4^+ can be retained in the fertiliser, inhibiting production of CH_4 (Chen *et al.* 2008). It could be speculated that NH_3, although not measured here, could explain the significantly lower CH_4 emissions in summer per unit mass of initial volatile solids from the cattle slurry treatment with a roof (Table 3 in Paper I), since there were no temperature differences or other factor that could explain the differences. A cover directly on the surface of the fertiliser, as in the sewage sludge experiment, creates anaerobic conditions favourable for CH_4 production, hence the increase in CH_4 release from covered sewage sludge compared with non-covered (Paper II). However, Rodhe *et al.* (2012) reported lower CH_4 emissions from non-digested pig slurry stored covered with plastic sheeting than when stored without sheeting. This result could not be explained by any of the parameters measured. Other studies have attributed observed lower emissions from covered manure heaps with prevailing anaerobic conditions to lower temperature (Hansen *et al.* 2006). However, no differences in temperature were observed between either digested cattle slurry stored with or without a roof (Paper I and Table 5) or digested sewage sludge stored with or without a cover (Paper II and Table 5).

5.1.6 Fertiliser texture

The thermophilically digested sewage sludge, which originated from Sunne municipality, had almost twice as high calculated free air space (18%) as the mesophilically digested sewage sludge (10%), which originated from Uppsala municipality (Paper II). Free air space was calculated according to Haug (1993) and is also commonly known as air-filled pore space.

The N_2O emissions were higher from the thermophilically digested sludge than from the other sludges or from the cattle slurry (Table 3). It was visually apparent that the thermophilically digested sewage sludge consisted of larger lumps than the mesophilically digested sludge. The difference in free air space and structure implies increased oxygen diffusion (Haug 1993) down the sludge profile in the thermophilically digested sewage sludge. This most likely enabled more nitrification, and thus more N_2O production from this process, compared with the mesophilically digested sewage sludges, which were water-logged, sealing the top of the experimental cylinders. Promotion of N_2O production by increased oxygen supply in the sludge profile has previously been shown by Börjesson & Svensson (1997).

The decrease in NH_4-N and increase in NO_3^--N + NO_2^--N concentrations in the thermophilically digested sewage sludge during the storage period indicated nitrification to be the likely source of N_2O (Table 2 in Paper II). The presence of nitrification was also indicated by a pH drop in the top layer (Table 3 in Paper II). Assays of the potential ammonium oxidation rate, the first step in nitrification, in the sewage sludge used in Papers II and III showed a much higher rate in the thermophilically digested sewage sludge after one year of storage than in the other treatments (Jöngren 2006). Furthermore, potential ammonium oxidation rate was especially high in the samples from the top layer of the cylinders.

The large free air space in the thermophilically digested sewage sludge meant that precipitation entering the storage facility due to overflow of the side walls of the cover could percolate down the sewage sludge profile in this container, after having dissolved some nitrate in the surface layers. On reaching the deeper anaerobic layers the nitrate was probably denitrified, with some additional N_2O production. Nitrous oxide produced via denitrification was indicated by a decrease in total nitrogen and an increase in pH (Table 2 and Table 3 in Paper II).

The low emissions of N_2O from the NH_3-treated sludge, besides being caused by inhibited microbial activity as discussed above, could also partly be explained by its poor structure. During wastewater treatment, polymers are added to thicken the sewage sludge. The urea addition and NH_3 treatment seemed to negate the structurally improving effect imparted by the polymer and caused the sludge to become very sticky. This collapse of the structure slowed down air diffusion in the material and hence nitrification and associated N_2O emissions were reduced.

The moisture content of 92-97% in the cattle slurry at the start of the storage experiment meant that it contained essentially no air (Paper I). At such high moisture contents, large amounts of CH_4 could be expected to be produced due to limited oxygen availability (Le Mer & Roger 2001). Higher emissions of CH_4 were seen from the mesophilically digested sewage sludge stored with and without a cover than from the thermophilically digested sewage sludge. The larger free air space in the thermophilically digested sewage sludge compared with the mesophilically digested sludge also implies reduced CH_4 emissions as a consequence of a more aerobic environment, which was proven by the much higher nitrification of ammonia (Paper II).

It is important to bear in mind that the sewage sludges digested at different treatment plants, though dominated by human excreta and treated by the activated sludge technique, were not identical, as they originated from different municipalities with different industrial profiles and processed with some differences in technique. Therefore the differences in structure discussed above could be due to differences in sludge composition rather than just to different digestion temperatures.

5.1.7 Methane production potential

The methane production potential at the start and the end of the storage period was lower for the thermophilically digested sewage sludge than for the sludge in the other treatments (Table 6). This demonstrates that digestion at higher temperature, without changing the retention time, results in a higher degradation rate than digestion at lower temperature. In line with this, the CH_4 emissions in the storage experiment with thermophilic sludge were lower than from the other treatments. Similarly, the cattle slurry during winter storage showed higher methane production potential and CH_4 emissions from the non-digested cattle slurry than from the digested slurry. However, in the summer experiment with cattle slurry, higher methane production potential and lower CH_4 emissions were found for non-digested cattle slurry than for digested slurry. In studying greenhouse gas emissions from storage facilities at biogas plants fed with energy crops and animal manure, Liebetrau *et al.* (2013) also found that the potential CH_4 production of the slurry and the actual CH_4 emissions from storage did not always correlate. In determination of the maximum CH_4-producing capacity of a substrate, such as the methane production potential assay, the conditions for CH_4 production are optimised, *e.g.* by controlling the temperature and adding an inoculum to boost the digestion. In contrast, the conditions in a storage facility are often less favourable and more exposed to environmental changes. Thus, any prediction of CH_4 emissions from methane production potential values should be made with both a good understanding of limiting parameters and with great caution.

Table 6. *Methane production potential (B_0) of cattle slurry (start of storage) and digested sewage sludge (start and end of storage) (Papers I and II)*

Fertiliser type	Time	B_0 (normal-mL CH_4 g^{-1} VS)
Cattle slurry	Start summer	270
	Start winter	239
Digested cattle slurry	Start summer	121
	Start winter	121
Mesophilically digested sewage sludge stored without cover	Start	204
	End	100
Mesophilically digested sewage sludge stored with cover	Start	204
	End	88
Thermophilically digested sewage sludge stored with cover	Start	92
	End	67

5.2 Land application of cattle slurry and sewage sludge

5.2.1 Greenhouse gas emissions

Following application to land, there was a trend for lower emissions of N_2O, in terms of per cent of both applied nitrogen and total ammoniacal nitrogen, from cattle slurry (Paper I) than from sewage sludge (Paper III) when comparing corresponding spring applications and corresponding autumn applications (Table 7). In both studies (45-72 days long; Table 7), the emissions factor for nitrous oxide (EF_{N2O}) was lower than the suggested IPCC factor for mineral and organic fertilisers of 1% (IPCC 2006). This was expected, since the IPCC value gives the total sum of emissions from all nitrogen applied over a year, which is much longer than the periods measured in the experiments reported in this thesis.

The emissions of CH_4 in both land application experiments (Papers I and III) were negative, negligible or low (Table 7). This in line with findings in previous studies on application of organic fertiliser to aerated arable soil (Amon *et al.* 2006; Le Mer & Roger 2001; Pitombo *et al.* 2015; Rodhe *et al.* 2006; Smith *et al.* 2003).

Table 7. *Emission factors for nitrous oxide (N_2O) and methane (CH_4) following application to soil of cattle slurry and sewage sludge in spring or in autumn and, for sewage sludge, with immediate or delayed incorporation (Papers I and III). Tot-N = total nitrogen,* TAN *= total ammoniacal nitrogen, Tot-C = total carbon*

Fertiliser type	Time and incorporation timing	N_2O % of Tot-N	N_2O % of TAN	CH_4 % of Tot-C	Measuring Period, days
Non-digested cattle slurry	Spring 4 h delayed incorporation	0.20	0.31	0.025	72
Digested cattle slurry	Spring 4 h delayed incorporation	0.10	0.18	-0.008	72
Non-digested cattle slurry	Autumn Immediate incorporation	0.59	1.32	-0.005	50
Digested cattle slurry	Autumn Immediate incorporation	0.44	0.82	0.000	50
Ammonia treated digested sewage sludge	Spring Immediate incorporation	0.32	0.74	-0.003	67
	Spring 4 h delayed incorporation	0.20	0.46	-0.003	67
Digested sewage sludge	Autumn Immediate incorporation	0.71	2.38	0.001	45
	Autumn 4 h delayed incorporation	0.34	1.16	0.001	45

5.2.2 Timing of application

The low soil temperatures in spring and autumn in both the cattle slurry and sewage sludge application experiments and the dry soils in spring are conditions that can explain the rather low emissions of N_2O (Table 7), expressed as percentage of applied total nitrogen, compared with the default IPCC emissions factor of 1% (IPCC 2006). Emissions of N_2O have previously been shown to be lower from applying organic fertilisers to soil during cold periods compared with warmer periods (Rodhe *et al.* 2012; Smith *et al.* 2003) and from drier soils compared with wetter soils (Scott *et al.* 2000; Smith *et al.* 2003). Compared with other studies conducted in Northern Europe, the calculated EF_{N2O} in Papers I and III was in the same range or only slightly lower. For example, Weslien *et al.* (1998) reported an EF $_{2O}$ range of 0.29-0.45% in spring (45 days measuring period) and 0.76-0.95% in autumn (78 days) from pig slurry applied to sandy loam with different techniques. Perälä *et al.* (2006) reported an EF_{N2O} of 0.7% (5 months) from pig slurry injected into a Vertic Cambisol.

For sewage sludge application, there was a statistically significant positive correlation between soil moisture (characterised by wet soil) and N_2O emissions in the autumn. Similarly, Perälä *et al*. (2006) found higher N_2O emissions during periods of wetter soil and Velthof & Mosquera (2001) showed higher emissions of N_2O during years with wetter soils compared with a year with dry soils. However, even if the soil moisture has an impact on N_2O emissions, the positive correlation is not necessarily valid for all moisture contents, because N_2O emissions are often highest in intermediate soil moisture ranges where both nitrification and denitrification can occur (Davidson 1993).

One month after spring application of sewage sludge, a N_2O peak was observed and was most likely induced by precipitation (Figure 1 in Paper III). Despite rainfall events during the latter part of the measuring periods in both seasons of the cattle slurry application experiment and in the spring in the sewage sludge application experiment, no further emissions peaks were observed. Similarly, Sänger *et al*. (2010) showed in a laboratory incubation experiment with soil amended with biogas slurry and composted cattle manure that after a first peak of N_2O emissions, further water addition simulating heavy rainfall did not induce any significant emissions. This indicated that most mineralised nitrogen in the fertiliser had already been consumed by nitrification and denitrification early after the onset of the first rainfall and that the increase in soil moisture then inhibited further nitrification of potentially remaining or newly produced NH_3 (Bateman & Baggs 2005; Philatie *et al*. 2004).

In the cattle slurry experiment, a crop was sown in both seasons (Paper I), whereas in the sewage sludge experiment a crop was sown in spring but not in autumn (Paper III). As crops take up nitrogen as they grow, potentially less nitrogen will be available for production of N_2O if a crop is present compared than when there is no growing crop (Jarecki *et al*. 2009; Parkin *et al*. 2006). Similarly, Wagner-Riddle & Thurtell (1998) showed that emissions of N_2O were reduced during the winter season when an overwintering crop was sown compared with bare soil.

The low soil temperatures prevailing in both seasons and especially in the autumn in both land application experiments (Table 8) can be one reason for the low CH_4 production (Le Mer & Roger 2001).

Table 8. *Environmental and soil parameters at the time of application (moisture content and dry bulk density) of cattle slurry and sewage sludge or during the whole experiment (mean soil temperature and total precipitation)*

Fertiliser type	Time	Length of experiment	Mean soil temperature during measurement	Total precipitation during measurement	Mean moisture content at application		Mean dry bulk density at application	
Soil depth			0.02-0.05 m		0-0.05 m	0.05-0.10 m	0-0.05 m	0.05-0.10 m
		days	°C	Mm	% of dry soil		Mg m^{-3}	
Cattle slurry	Spring	72	17.4	92	10.7	17.7	1.28	1.34
	Autumn	50	3.0	74	15.6	21.7	1.20	1.32
Sewage sludge	Spring	67	14.5	171	17.5	24.6	1.29	1.41
	Autumn	45	3.4	66	31.1	29.2	0.79*	1.26

* Low due to incorporated crop residues

5.2.3 Digestion prior to land application

The emissions of N_2O after land application tended to be lower from cattle slurry that had been digested compared with untreated slurry (Table 7 and Paper I). This could be a result of higher input of organic carbon from the non-digested slurry compared with the digested (at autumn application both total carbon and volatile solids were higher in the non-digested slurry than in the digested), since more carbon was most likely degraded during the digestion process, which could drive denitrification (Petersen & Andersen 1996; Starr & Gillham 1993). Similarly, Bertora *et al.* (2008) reported lower N_2O emissions after land application of digested pig slurry compared with non-digested. Comparable results were also indicated when spreading non-digested and digested mixtures of cattle and pig slurry (Petersen 1999). In contrast, no effect of digestion on N_2O emissions after land application of cattle slurry was seen by Clemens *et al.* (2006) and Thomsen *et al.* (2010). The latter findings could be due to the higher NH_4^+ input from the digested slurry levelling out the effect of higher input of carbon from the non-digested slurry if the residue is applied based on weight or volume, and not on mineral nitrogen (Clemens *et al.* 2006). The varying results point out the complex interactions between fertiliser characteristics such as pH, organic content, nitrogen content and soil characteristics such as pH, texture and moisture. However, there are other possible benefits connected with digestion, since the mineralisation of organic nitrogen to NH_4^+ during the process makes nitrogen more accessible to the plants and thus decreases the need for mineral fertiliser (Möller & Stinner 2009).

5.2.4 Incorporation of organic fertiliser at application

There was a tendency for higher cumulative N_2O emissions when the sewage sludge was incorporated immediately after application than when it was incorporated after 4 hours (Paper III). Similarly, Webb *et al.* (2004) observed higher cumulative N_2O emissions after land application of solid pig manure (dry matter 25.5%) incorporated immediately compared with a 4-hour delay in incorporation. The lower N_2O emissions for the delayed incorporation could partly be explained by higher losses of NH_3 during the 4-hour waiting time before incorporation of the sewage sludge (Paper III). Webb *et al.* (2004) observed lower NH_3 emissions from their soil when pig manure was incorporated immediately after application compared with a 4-hour delay. However, the differences in N_2O emissions between incorporation times in Paper III were not statistically significant, as also found by Webb *et al.* (2004) on repeating their experiment one year later.

5.2.5 Fertiliser characteristics

A lumpy structure, such as that of digested and dewatered sewage sludge, permits formation of anaerobic microsites with the potential for coupled nitrification and denitrification, leading to N_2O formation (Nielsen *et al.* 1996; Senbayram *et al.* 2009). This can partly explain the somewhat higher N_2O emissions observed from the drier and lumpier sewage sludge than from cattle slurry, related to the content of both initial nitrogen and total ammoniacal nitrogen, when comparing corresponding spring and autumn application. However, other factors such as soil properties, application rates and years of application also differed between the experiments, and are also likely to have affected the N_2O emission rates.

The N_2O fluxes from both cattle slurry and sewage sludge peaked at about 10 days after application (Papers I and III). Since some of the nitrogen in organic fertilisers needs to be mineralised before nitrification can take place, this delayed N_2O peak was most likely due to nitrification followed by denitrification (Velthof *et al.* 2003). The delayed peak could also be a matter lag time for adaptation for the microbes. If the peaks had occurred earlier, they would more likely be a result of denitrification of NO_3^- already present in the soil stimulated by the addition of easily available organic substrates, as proposed by Chadwick *et al.* (2000) and Velthof *et al.* (2003). The physical and chemical properties of the cattle manure and the sewage sludge are presented in Table 9.

A second peak was observed after spring application of both cattle slurry (Paper I) and sewage sludge (Paper III). Both peaks were preceded by rainfall and it is likely that they were a consequence of denitrification after previous nitrification of mineralised nitrogen from the fertiliser (Velthof *et al.* 2003).

Addition of NH_3 via urea to sewage sludge before storage is primarily a sanitisation measure, but Paper II showed that it can also be used as a measure to reduce emissions of greenhouse gases. A positive side-effect of urea addition to sewage sludge is the resulting increase in mineral nitrogen, which should increase its value as a fertiliser. The total ammoniacal nitrogen in the sewage sludge was increased from 30 to 44% of total nitrogen by the urea treatment. This is a similar fraction to that in the non-digested cattle slurry applied in the autumn and only somewhat lower than that in the digested cattle slurry also applied in the autumn (55%).

All N_2O emissions factors for fertiliser application in spring, which ranged from 0.10 to 0.32% of added nitrogen and 0.18 to 0.74% of added total ammoniacal nitrogen, were lower than in the wetter autumn, ranging from 0.34 to 0.71% of added nitrogen and 0.82 to 2.38% of added total ammoniacal nitrogen, regardless of fertiliser type (Table 7). This correlation between high moisture and high N_2O emissions has been reported previously (Senbayram *et al.* 2009) and can be explained by factors driving the denitrification process (redox potential, NO_3^- and carbon availability and oxygen diffusion) depending on water availability and free pore space.

The different treatments of the sewage sludge altered its physical properties, although this was not evident from the data presented. The addition of urea made the sewage sludge sticky and the resulting non-homogeneous material was difficult to spread, resulting in uneven distribution of nitrogen.

The very small amount of CH_4 emitted in spring after land application of sewage sludge was released soon after application (Paper III). The sticky texture of the NH_3-treated sludge applied in spring could possibly explain the early emissions of CH_4 compared with sewage sludge application in autumn. The non-homogeneous texture of the NH_3-treated sludge might have created anaerobic microsites in the soil, allowing CH_4 to be produced, while the sewage sludge without NH_3 treatment was better broken down and finely scattered by the incorporation process.

Table 9. *Physical and chemical properties of cattle slurry and sewage sludge at application to land (Papers I and III) Content of:* DM *= dry matter,* VS *= volatile solids, Tot-N = total nitrogen,* TAN *= total ammoniacal nitrogen, Tot-C = total carbon*

Fertiliser type	Time	DM	VS	pH	Tot-N	TAN	Tot-C
		%	% of DM		kg Mg^{-1} DM		
Non-digested cattle slurry	Spring	2.4	74	7.5	70.8	45.8	417
Digested cattle slurry	Spring	3.8	74	7.9	71.1	44.7	421
Non-digested cattle slurry	Autumn	5.7	81	6.8	43.9	19.8	453
Digested cattle slurry	Autumn	3.7	74	7.6	54.1	29.2	402
Ammonia-treated digested sewage sludge	Spring	26.9	59	8.6	67.1	29.2	319
Digested sewage sludge	Autumn	24.6	58	8.2	51.5	15.3	306

5.2.6 Ammonia emissions

The NH_3 emissions in the sewage sludge experiment were measured during 24 h after application. However, no statistically significant difference between immediate incorporation and the 4-hour delay in incorporation could be seen. There was a tendency for lower NH_3 emissions during the 24 h measuring period from the direct incorporation treatment. During the 24 h period, 55-65% of NH_3 losses occurred during the first 3 h after application for both treatments, *i.e.* before incorporation in the delayed incorporation treatment. It could be speculated that if the measurements had continued for a longer time, the difference would have been even more pronounced. Incorporation is frequently suggested as an effective method for reducing NH_3 emissions after land application of organic fertilisers and is mandatory in many regions in Sweden (Swedish Board of Agriculture 2012).

The emissions of N_2O tended to be higher from the immediately incorporated treatment than from the treatment with delayed incorporation, indicating more NH_4-N left in the sewage sludge that could be nitrified in the immediately incorporated treatment, partly due to higher emissions of NH_3 from the delayed incorporation compared with the immediate.

From the above, there appears to be a goal conflict between mitigation strategies for NH_3 and N_2O emissions, although quite small in this specific case. This shows the complexity and goal conflicts involved in managing fertilisers in such a way that the impact on the environment is minimised, while at the same time the crop production rate is maximised. A similar goal conflict has been reported in studies comparing different application techniques for animal manure (Rodhe *et al.* 2006; Thomsen *et al.* 2010; Wulf *et al.* 2002). In all three of those studies, a reduction in NH_3 emissions was achieved by injecting the slurry into the soil compared with surface application or shallow injection. However, from an environmental perspective this reduction was in conflict with the observed increase in N_2O emissions at injection and the increased energy requirement for application. On the other hand, the decreased odour and decreased loss of plant-available nitrogen compared with surface application are frequently used arguments for injecting or incorporating organic fertiliser as soon as possible after application.

5.3 Sewage sludge life cycle assessment

In addition to the experimental work, an LCA focusing on the environmental impacts of storing and land application of sewage sludge was conducted.

In the handling chain of sewage sludge consisting of storage, transport, land application and avoided production of chemical fertiliser, storage was found to dominate the overall GWP_{100} effect from the system (Paper IV). This finding stresses the importance of including storage in systems analyses of organic fertiliser management, as previously highlighted by *e.g.* Chiew *et al.* (2015), Johansson *et al.* (2008) and Spångberg *et al.* (2014).

Covering the sewage sludge during storage was beneficial for all impact categories, irrespective of application timing (Table 10). Ammonia treatment of the sewage sludge was also beneficial in terms of GWP_{100} and tended to be favourable in terms of potential eutrophication, and for autumn and combined autumn and spring application also for potential acidification, compared with no NH_3 treatment. Potential acidification was slightly higher for NH_3-treated sewage sludge compared with non-treated at spring application. In terms of energy consumption, however, NH_3 treatment of the sludge was the worst scenario at all application timings, due to the energy-demanding process for the production of urea (Table 10).

Lowering the GWP_{100} from storage by covering the sludge or treating it with NH_3 means that more nitrogen will remain in the sludge. This will yield a larger fertilising effect when applied to soil, but also a higher risk of N_2O and NH_3 emissions in the field. This was clearly shown by the large contribution from land application to acidification potential from covered and from NH_3-treated sewage sludge, for which NH_3 emissions played a key role (Paper IV).

This thesis highlights the importance of considering more than a single category of environmental effects when dealing with such complex systems as the management of organic fertilisers. For example, it is clear from Paper IV that from a GWP_{100} point of view NH_3-treated sewage sludge has advantages over non-treated, but it is much less favourable in terms of energy use due to the large energy use in the production of urea.

The choice of system boundaries in LCA has a crucial impact on the final results. This is clearly shown when comparing the results in Paper IV with those in similar studies on sewage sludge management applying other system boundaries. Tillman *et al.* (1998) did not consider a system expansion including avoided chemical fertiliser to have a large impact on the system. This is in contrast to findings in Paper IV (see Figures 2 and 5 in that paper) and is most likely a result of the wider system boundary applied by Tillman *et al.* (1998), which also included the preceding wastewater treatment process.

If there is a requirement for sanitising sewage sludge before applying it to land, then an additional operation, such as pasteurisation or thermophilic digestion, with guaranteed retention time would be required for the treatments other than the NH_3-treated sludge. These additional operations would require energy and other resources and would most likely have large effects on the overall energy use. Therefore, the choice of system boundaries is also important for correctly evaluating the energy use in the treatment process of the sludge.

As described in section 3.2.2, in Sweden sewage sludge is most commonly applied in the period late summer to autumn. The LCA suggested that the autumn application scenario is preferable to spring application for all sewage sludge storage treatments. There are two main reasons for this. First, since spring application is only possible for a short period of time (one month was assumed in the LCA), the storage time is longer than for other application timings (Paper IV). Since storage has such a large effect on emissions of greenhouse gases, the longer storage period explains spring application being the less favourable alternative in terms of GWP_{100}. Second, in the LCA the emissions of NH_3 were assumed to be larger in spring than in autumn, which gives rise to higher acidification and eutrophication potential in spring and also primary energy use due to the larger need of chemical nitrogen.

The land application studies (Papers I and III) suggested that drier soil in spring and summer leads to somewhat lower emissions of N_2O after land application of organic fertilisers, compared with autumn application when the soil contains more moisture. Pradel *et al.* (2013) also concluded in a model of sewage sludge application to land that the soil and prevailing weather conditions have a large influence on N_2O emissions. This was not considered in the LCA in Paper IV, but if it had been the GWP_{100} from land application would probably have been somewhat lower in spring or somewhat higher in autumn.

Furthermore, when accounting for NO_3^- leaching, which often occurs from soils with low clay content and when crops do not take up nitrogen fast enough, spring application was preferable to autumn application in terms of eutrophication potential. Leaching of nitrogen also means that more chemical nitrogen needs to be produced, which makes spring application preferable in terms of primary energy use too.

5.3.1 Carbon sequestration in soil

The application of organic fertilisers adds organic matter to the soil, which leads to increases in carbon stocks and long-term carbon sequestration (Wang *et al.* 2015), and thus less CO_2 in the atmosphere and lower global warming potential. When including carbon sequestration in the LCA (7% of the carbon applied; Chiew *et al.* 2015; Spångberg *et al.* 2014), the GWP_{100} for the total system of sewage sludge management (storage, transport and land application) was reduced by 14-56% from the different treatments and land application times, compared with the scenarios without carbon sequestration. The lowest GWP_{100} reduction (14-16%) was seen for sewage sludge stored without cover and the highest for sewage sludge stored with cover (49-52% reduction) and for ammonia-treated sewage sludge stored with cover (53-56% reduction).

Table 10. *Treatment and application scenarios for the environmental impact categories: global warming potential (*GWP_{100}*), potential acidification, potential eutrophication and energy use (Paper IV). The scenarios consist of three spreading regime: application in autumn, application in spring, or application both in autumn and spring. Application of digested sewage sludge stored without cover applied in autumn is defined as reference. The basic scenario is compared with spring or spring and autumn application of digested sewage sludge stored with cover and digested sewage sludge treated with ammonia and stored with cover. Better (+) and worse (-) grades are given for alternatives that were 20% higher or lower than the basic scenario.*

Impact category	Digested sewage sludge stored without cover			Digested sewage sludge stored with cover			Digested sewage sludge treated with ammonia and stored with cover		
	Autumn application	Spring application	Spring and autumn application	Autumn application	Spring application	Spring and autumn application	Autumn application	Spring application	Spring and autumn application
GWP_{100}	Reference	0	0	+	+	+	+	+	+
Potential acidification		0	0	+	+	+	0	0	0
Potential eutrophication		0	0	+	+	+	0	0	0
Energy use		-	0	+	+	+	-	-	-

The inclusion of carbon sequestration reduced the GWP_{100} for all treatments and for the land application subsystem even to negative values (Paper IV), *i.e.* it gave a net cooling effect on the climate. In a shorter perspective, the effect would be even greater. If 7% of carbon were sequestered in the soil over a 100-year perspective, then assuming that the mineralisation of organics follows a first-order equation, roughly 59% would be sequestered over 20 years. The CO_2eq in a 20-year perspective (factor of 289 for N_2O and 72 for CH_4; IPCC 2007) are different from those in a 100-year perspective (factor of 298 for N_2O and 25 for CH_4 (IPCC 2007)), but the net effect on the climate of land application of sewage sludge was even better in a 20-year perspective than in a 100-year perspective. This means that using sewage sludge as a fertiliser actually decreased global warming over a 100-year perspective and even more over a 20-year perspective.

5.3.2 Global warming potential calculated from data in Papers I-III

The GWP_{100} was also calculated from the data on cattle slurry management in Paper I and from the data on sewage sludge management in Papers II and III. For cattle slurry management, emissions of N_2O, CH_4 and indirect N_2O from emitted NH_3 from storage during three summer and three winter months and after land application were recalculated to CO_2eq m^{-3} and summed as described in Paper I (Figure 7). The GWP_{100} for sewage sludge management data from Paper II-III was calculated in the same way with the exception that the sewage sludge experiment covered a full year of storage and thus for simplicity, half the storage period was considered to have summer-like conditions and half winter-like conditions when calculating NH_3 emissions during storage. Ammonia emissions after land application in autumn were not measured and instead the Swedish standard values of 10% and 15% NH_3 loss of added total ammoniacal nitrogen at immediate and 4 hours delayed incorporation, respectively, were used (Karlsson & Rodhe 2002). Carbon dioxide emissions and indirect N_2O emissions from nitrogen leaching were not included in any of the calculations.

For all treatments included in the cattle slurry study (Paper I) and for mesophilically digested sewage sludge stored with a cover (Paper II), storage was the main contributing factor to GWP_{100} (Figure 7), as also shown in the LCA study (Paper IV). For the urea-treated mesophilically digested sewage sludge, however (Paper II), land application contributed more than storage (Figure 7). During storage, CH_4 contributed more than N_2O for both cattle slurry and sewage sludge in all treatments except for the thermophilically digested sewage sludge, where N_2O dominated. Nitrous oxide dominated after land application for both fertiliser types and in all treatments.

The mitigation potential tested in Papers I-III of this thesis seemed to be highest for NH_3 treatment, followed by thermophilic digestion of sewage sludge. However, the mitigation effect of NH_3 treatment was only seen during storage, since GWP_{100} after land application of NH_3-treated sewage sludge was quite high. For the thermophilically digested treatment, it is not fully clear if the higher digestion temperature was the reducing factor or if the reduction was related to the more porous structure of the sludge.

Season of land application had an impact, in that GWP_{100} induced by emitted gases was lower in spring than in autumn for both cattle slurry and sewage sludge. The addition of NH_3 to the sewage sludge increased the risk of higher GWP_{100} after land application compared with sludge without NH_3 treatment. However, the lower emissions of NH_3 from spring application and immediate incorporation of sewage sludge with NH_3 addition, compared with autumn application and immediate incorporation of sewage sludge without NH_3 addition, further indicate that spring application involves lower GWP_{100} than autumn application.

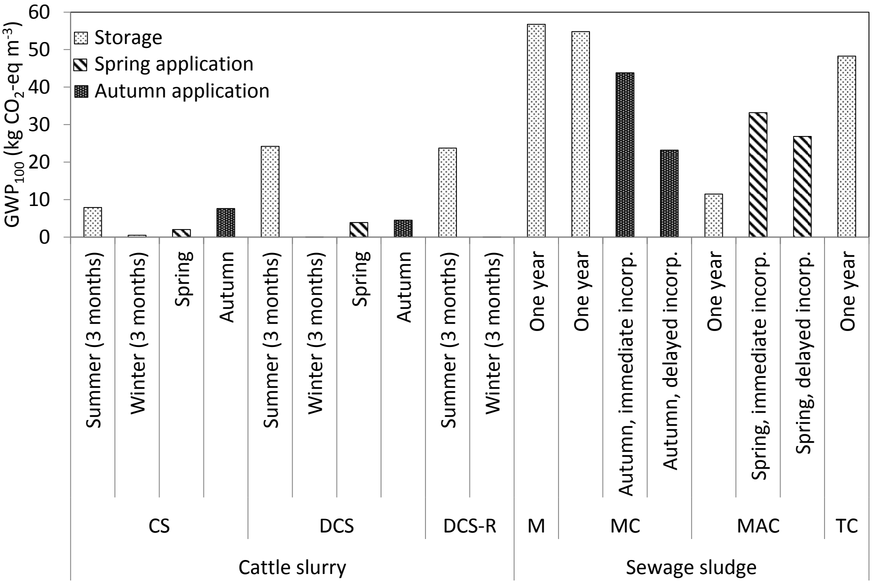

Figure 7. Global warming potential (GWP_{100}) in terms of CO_2eq from storage during three months in summer and winter and land application in spring and autumn of cattle slurry (Paper I) and one-year storage and application in spring and autumn of sewage sludge (Papers II and III). Cattle slurry stored without roof (CS), digested cattle slurry stored without roof (DCS), digested cattle slurry stored with roof (DCS-R), mesophilically digested sewage sludge stored without cover (M), mesophilically digested sewage sludge stored with cover (MC), mesophilically digested sewage sludge with ammonia addition stored with cover (MAC) and thermophilically digested sewage sludge stored with cover (TC).

The GWP_{100} per m^3 was in most cases much higher for sewage sludge management than for cattle slurry, both during storage and after land application (Figure 7). One reason for this, other than the different properties of the substrates, as regards storage was the differing duration of storage, which was 3 months for cattle slurry and one year for sewage sludge. However, when calculating GWP_{100} per content of Tot-N and Tot-C (data not shown) the GWP_{100} was higher from the digested cattle slurry than from all the sewage sludge treatments and the GWP_{100} from non-digested cattle slurry was higher than from all the mesophilically digested sewage sludge treatments.

The GWP_{100} for sewage sludge management estimated in the LCA study (Paper IV) was different from that calculated from actual emissions data in Papers II and III. For mesophilically digested sewage sludge stored with cover, this was due to EF_{N2O} derived from the study in Paper III being 0.34% of total nitrogen applied, while in the LCA it was set to 1%. Furthermore, the storage time for the sewage sludge applied in the autumn in Paper III was one year, compared with nine months assumed in the LCA study (Paper IV). Besides, the GWP_{100} was for the LCA calculated on the amount digested sewage sludge considered to replace 1 kg of chemical phosphorus fertiliser, while it for Papers I-III was based on cubic meters of fertiliser.

5.4 Other mitigation options for organic fertiliser management

5.4.1 Acidification

In contrast to ammonia treatment, which increases the pH of the sludge, there is also an option to lower the pH instead, by adding *e.g.* sulphuric acid or hydrochloric acid, to reduce the emissions of both NH_3 and CH_4 (Petersen *et al.* 2012, Ottosen *et al.* 2009). Methane emissions from stored cattle slurry in the study by Petersen *et al.* (2012) were reduced by up to 87% on addition of hydrochloric acid to reach pH 5.5. Methanogens and sulphate-reducing bacteria compete for the same energy molecules, such as acetate, hydrogen, propionate or butyrate. Hence, CH_4 emissions can potentially be reduced by sulphuric acid addition (Chen *et al.* 2008). Ottosen *et al.* (2009) attributed the reduction in CH_4 emissions to the drop in pH following acidification increasing the concentration of free protonised short-chain volatile fatty acids that are inhibitory for several microbial activities. The reduction in pH also reduces the concentration of free NH_3, and hence reduces NH_3 losses (Ottosen *et al.* 2009).

Acidification of organic fertilisers adds costs to the farmer, both directly for acid purchase and equipment needed, and indirectly as the need for liming to reduce the risk of soil acidification from spreading will increase. The cost has been estimated to 10% of the total production cost with 75 livestock units, with a decline to 1% with 500 livestock units (Petersen *et al.* 2012). However the effective reduction in NH_3 emissions that has been reported repeatedly (*e.g.* Petersen *et al.* 2012; Kai *et al.* 2008) means a residue with more nitrogen remaining and, hence, a product with higher fertiliser value. Thus savings could be made by lowering the need for chemical fertilisers. In addition, energy and emissions are saved when less chemical fertiliser is produced.

5.4.2 Gas collection from storage

Methane is, as previously mentioned, the main greenhouse gas emitted during storage of organic fertilisers under conditions with low oxygen availability. Instead of finding ways of reducing the CH_4 emissions from storage, it could be possible to take advantage of the CH_4 produced. This could be achieved by applying a gas-tight cover on the storage facility and collecting the emitted gas (Lund Hansen *et al*. 2006). The amount of CH_4 collected from a storage tank with digested municipal waste was estimated to 3% of the CH_4 that could be produced from this substrate in a biogas reactor (Lund Hansen *et al*. 2006). In that calculation, a degradation rate of the feedstock in the biogas reactor of 80% was assumed. If the degradation rate in the reactor were lower, significantly more CH_4 could potentially be collected from storage (Lund Hansen *et al*. 2006). However, making the storage tank gas-tight would increase its cost, especially as it would contain an explosive gas.

5.4.3 Cooled storage

The results (Papers I and II) clearly demonstrated the greenhouse gas reduction potential of storage in cool temperatures compared with warm. This has also been shown previously by Clemens *et al*. (2006) and Sommer *et al*. (2004), and is discussed in section 5.1.2. Cooling of storage can be implemented in different ways. In a Dutch study, it was demonstrated that passive cooling, by moving an indoor storage facility with a mean temperature of 17 °C to an outdoor environment yielding an average annual temperature of 10.2 °C, resulted in a decrease in CH_4 emissions of about 66% (Hilhorst *et al*. 2002). Sommer *et al*. (2004) showed that active cooling can be achieved by implementing a heat exchanger in an animal house and using the excess heat from the animal manure for heating the animal houses. This is feasible in temperate regions where animal houses have a need for heating and would reduce the need for fossil fuel for heating. Active cooling can also be performed using groundwater. It has been shown that 10 °C groundwater was able to cool the surface of pig slurry to 14 °C, which reduced the emissions of CH_4 and NH_3 by 30-50% (Hilhorst *et al*. 2002).

5.4.4 Incineration

Incineration is a thermal process where the organic matter is destroyed (Houillon & Jolliet 2005). The process requires dehydration and flue gas treatment. The fly ash, *i.e.* the residues from flue gas treatment of the incineration process, is sent to an ultimate waste storage centre. In 2010, 27% of the sewage sludge produced in Europe was incinerated (Horizon 2020 2015). Most of the incineration in Europe occurs in the southern countries and in Germany.

Arguments for incinerations are that with this management option, the recycling of heavy metals and other hazardous substances is avoided. The process also enables destruction of pathogens and organic matter and produces energy. Besides, transportation costs are strongly reduced, since the residue quantity (fly ash and residues from flue gas treatment) is very small (Houillon & Jolliet 2005).

With incineration, no organic matter can be recycled and the recycling of nutrients is limited. There is also a risk that if sewage sludge is incinerated, the incentives for improvements in the upstream management of wastewater are reduced, since the sludge does not need to be very clean if it is not recycled to land.

Phosphorus may be recovered from incineration by different methods. One method is to use the fly ash as it is, but this means that heavy metals in the fly ash are recycled to land (Zhang *et al.* 2002). To avoid this, the ash can *e.g.* be mixed with magnesium chloride or calcium chloride and compacted to pellets that are heated to 1000 °C, during which a great deal of the metals react with the chloride compound and evaporate, but the phosphorus remains in the pellets (Linderholm *et al.* 2012). Phosphorus can also be recovered as calcium phosphate by dissolving phosphate ions in liquid sodium hydroxide and crystallising the phosphate ions using hydrated lime (Nakakubo *et al.* 2012).

6 Conclusions and future research

6.1 Conclusions

- The emissions factor for nitrous oxide as a percentage of initial total nitrogen content (EF_{N2O}) was close to zero for all cattle slurry treatments during both summer and winter storage, except for digested cattle slurry stored under roof during summer, when it was 0.2%. The corresponding EF_{N2O} for one year of storage of digested and dewatered sewage sludge ranged from zero to 1.3%.
- The emissions factor for methane as a percentage of initial total carbon content (EF_{CH4}) during summer storage of cattle slurry ranged from 0.3 to 1.6%, and was zero during winter. The corresponding EF_{CH4} for one year of storage of digested and dewatered sewage sludge ranged from 0.2 to 1.3% (minimum values).
- The EF_{N2O} after land application of cattle slurry ranged from 0.20 to 0.59%. The corresponding EF_{N2O} for sewage sludge ranged from 0.20 to 0.71%.
- The emissions of methane after land application of both cattle slurry and sewage sludge were negligible.
- There was great potential for achieving a reduction in both nitrous oxide and methane emissions from storage by lowering the temperature.
- Digestion of cattle slurry increased emissions of methane during summer storage compared with the non-digested cattle slurry. Emission of nitrous oxide also increased during summer storage of digested cattle slurry stored under roof, compared with the other treatments.
- Covering the storage facility strongly reduced ammonia emissions and potentially also greenhouse gas emissions.
- Ammonia treatment of sewage sludge eliminated the emissions of nitrous oxide and reduced the emissions of methane.

- Appropriate timing of application, with favourable weather and soil conditions, lowered the risk of formation of nitrous oxide and application to dry and cool soils was preferable.
- Immediate incorporation of sewage sludge did not prove advantageous compared with delayed incorporation in terms of nitrous oxide emissions.
- There seems to be more to gain from implementing mitigation measures during storage than after land application, since more nitrous oxide and methane are emitted during storage than after land application.
- Life cycle assessment demonstrated the importance of applying wider perspectives, since measures to mitigate greenhouse gases could have diverse effects on a connected system, *e.g.* the sanitisation ammonia treatment of sewage sludge decreased emissions of both nitrous oxide and methane and increased nitrogen availability to plants, but increased primary fossil energy use.
- Replacing chemical phosphorus and nitrogen with sewage sludge has great potential in reducing the impact on global warming potential and primary energy use.
- Management systems for organic fertilisers should preferably be designed to minimise storage, especially during warm periods. Land application should, when possible, be limited to periods when the soil is dry and the temperature low.

6.2 Future research

Further investigations of greenhouse gas emissions from full-scale or large-scale sewage sludge storage are needed to get more detailed data on emissions patterns and magnitudes. It would also be valuable to include emissions of carbon dioxide and to evaluate the potential difference between sewage sludge of different structure and storage at different temperatures.

More research is needed on how much chemical phosphorus and nitrogen can actually be replaced by sewage sludge. The degradability of carbon from organic fertilisers should also be evaluated, since the global warming potential is reduced as long as the carbon is stored in the soil.

Additional long term studies on emissions of nitrous oxide, methane and ammonia after land application of organic fertilisers are needed to retrieve more reliable emissions factors.

The applicability and cost of different greenhouse gas mitigation options (*e.g.* cover, ammonia treatment or cooled storages) need to be further investigated to find practically and economically viable solutions.

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