Main environmental considerations of slurry acidification

Report from WP5, Activity 2

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Preface

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Introduction

Livestock farming has a strong impact on the environment, especially the management of animal manure. Increasing animal production will lead to an increase in the amount of manure. This can be perceived as both a positive and negative development. On the positive side, manure contains essential nutrients that are crucial for crop growth and can, therefore, be seen as a valuable fertiliser. Compared to using only mineral fertiliser, soil quality might be maintained or improved by the use of manure. This is due to the presence of organic matter in manure. On the other hand, natural resources are needed to handle and transport manure, and emissions to the environment occur during manure storage and field application. The main environmental problem associated with animal slurry management are pollution by ammonia emissions and leakage of nitrate compounds to water. Other important environmental impacts include greenhouse gases, such as methane and nitrous dioxide, as well as odour.

Most importantly, fertilised soils and livestock are significant sources of nitrogen pollution, both through leakage to water and atmospheric emissions from livestock housing, during storage, and from field-applied manure. Livestock manure produced large emissions of ammonia (NH_3), nitrous oxide (N_2O) and methane (CH_4). Emissions of NH_3 are largely responsible for the acidification and eutrophication of nitrogen-limited ecosystems (Sutton *et al*., 2008). Emissions of N_2O and CH_4 contribute considerably to the radiative forcing of the atmosphere. Enteric fermentation and animal manure together account for 80% to the global CH_4 emissions from agriculture and about 35–40% of the global anthropogenic CH_4 emissions (Steinfeld *et al*., 2006). In 2014, the livestock sector contributed a share of 53% methane, 21% nitrous oxide, and 75% ammonia to total agricultural emissions in the European Union (EU-28) (UNECE, 2016; UNFCCC, 2016).

One way to minimize ammonia emissions from the animal slurry is to decrease slurry pH by the addition of acids or other substances. This solution has been used in Denmark by farmers since 2010, and its efficiency with regard to the minimization of NH_3 emissions has been documented in multiple studies. However, the impact of such treatment on other gaseous emissions during storage is not as clear, since several studies have reported different scenarios. Lowering the pH will impact multiple chemical and microbial processes in the slurry, changing the composition of the acidified liquid manure. As a consequence, slurry acidification might influence the emissions of other gases, such as nitrous oxide or methane, and, after soil application, the fertilizer value of the acidified slurry, as well as the associated nitrogen, phosphorous or carbon dynamics, which might differ from patterns already known for non-acidified slurry (Wenzel and Petersen, 2009). Similarly, the impact of the soil application of acidified slurry on plant production and diffuse pollution has been considered in several studies.

The aim of this literature review report is to give a general understanding of the environmental effects of slurry acidification. This report will be the main output since target groups, such as farmers, advisors and authorities at various levels, will utilise the results when assessing the environmental impact of their livestock operations. This report will also be an intermediary output since it will be used in the overall economic and environmental analysis.

1. Emissions related to slurry management

Among the many sources associated with emissions from the livestock sector, emissions from manure management are prominent. Emissions from manure management include emissions from animal housing, during the handling and storage of manure, grazing, and the application of manure as fertilizer to soils. Manure management alone accounts for 31% of GHGs and almost all of the NH_3 emissions from livestock in the EU-28 (UNECE, 2016; UNFCCC, 2016). The main emissions and their impact on the environment are shortly discussed in the following section.

It is important to note that emissions of NH_3, CH_4 and N_2O might occur simultaneously from multiple sources of manure management systems. Animal excreta in housing and manure storage systems, as well as from land following manure application, are the main sources of NH_3 and N_2O. Enteric fermentation in ruminants is the dominant source of CH_4 emissions. Manure storages are also a significant source of CH_4 (Sommer et al., 2004). Most agricultural soils are a sink for CH_4 and a source of N_2O, depending on drainage, soil properties, fertilization practices, and climatic conditions (Oenema et al., 2001).

1.1. Ammonia

Approximately 40% of the global anthropogenic NH_3 and N_2O emissions are associated with manures from livestock production (Bouwman et al., 1997, Galloway et al., 2004; Oenema et al., 2005; Dalgaard et al. 2014). Ammonia is emitted from all stages of slurry management: up to 20% of total N is emitted from livestock buildings, up to 28% of total N is emitted during outdoor storage. After field application with a boom with trailing hoses, up to 20% of ammoniacal N (NH_4-N) is emitted (Nyord et al., 2013); when band spread on short-cut grassland, almost all NH_4-N could be lost as NH_3 (Rodhe & Etana, 2005). As NH_3 is volatilized to the air more NH_4-N is transferred to NH_3. The fertiliser value of slurry is very much reduced by the NH_3 volatilisation (McCrory and Hobbs, 2001).

Ammonia emissions contribute to terrestrial and aquatic nutrient imbalances, eutrophication and acidification (Bouwman et al., 1997; McCrory and Hobbs, 2001, Sutton et al., 2008). Even at extremely low concentrations, aquatic life will be harmed by ammonia (e.g., algal blooms and hypoxia) (Richardson, 1997; Paerl et al., 2002). In terrestrial ecosystems, this leads to a loss of plant species and habitat diversity (Smith et al., 1999; Carfrae et al., 2004). In the atmosphere, a significant fraction of fine particulate matter is composed of ammonium nitrate and ammonium sulfate. Locations with elevated concentrations of fine particulate aerosols have been statistically associated with increased pulmonary and cardiac disorders (Pope, 2000). Other potential consequences include vegetation or ecosystem changes due to higher concentrations of N; N saturation of forest soils; and soil acidification through nitrification and leaching.

Examples of techniques that can reduce NH_3 volatilisation are acidifying additives, cooling of slurry, air-tight covers during storage and urease inhibitors (McCrory and Hobbs, 2001; Petersen and Sommer, 2011).

1.2. Greenhouse gases

In addition to ammonia, livestock manure contributes considerably to global emissions of greenhouse gases (GHG), especially methane (CH_4) and nitrous oxide (N_2O). Emissions of N_2O and CH_4 contribute considerably to the radiative forcing of the atmosphere, as the global warming potentials (GWP_{100}) for N_2O and CH_4 are, respectively, 298- and 25-times higher than that of CO_2 per kg (IPCC, 2007). Livestock contribute between 8% and 11% of the total global greenhouse gas emissions (O'Mara, 2011). Approximately 40% of the global anthropogenic NH_3 and N_2O emissions are associated with manures from livestock production (Galloway et al., 2004; Oenema et al., 2005). Enteric fermentation and animal manure together contribute some 80% to the global CH_4 emissions from agriculture and about 35–40%

to the global anthropogenic CH_4 emissions (Steinfeld et al., 2006). An increasing number of countries are implementing regulations that restrict emissions of nitrous oxide (N_2O) and methane (CH_4) from livestock production. However, it is important to look at the complete production and manure handling chain, as emissions from downstream processes might be influenced by mitigation measurements earlier in the chain (Chadwick et al., 2011).

1.2.1. Nitrous oxides

N_2O emissions contribute to climate change, and it is also the most important chemical species leading to stratospheric ozone depletion (Ravishankara et al. 2009). Nitric oxide (NO), on the other hand, contributes to the formation of ozone in the troposphere and is a vital precursor to acid rain (Williams et al. 1992).

Both N_2O and NO are mainly produced by nitrification and denitrification processes in soils (Firestone and Davidson 1989). N_2O is mostly formed in complex environments with low oxygen contents and at the interface between aerobic and anaerobic conditions (Russow et al., 2009). Manure management is responsible for 30–50% of N_2O emissions from livestock production (O'Mara, 2011), while the emissions vary widely between manure management systems (Oenema et al., 2005). During slurry storage, N_2O emissions depend on storage conditions and temperature (Petersen et al., 2013). Indirect N_2O emissions might occur after other losses of reactive nitrogen, such as NH_3 emissions and NO_3^- leaching and runoff from manure.

1.2.2. Methane

Methane emissions from livestock management are mainly caused by enteric fermentation by ruminants, followed by liquid manure (slurry) management. When manure is stored or treated as a liquid in a lagoon, pond or tank, it tends to decompose anaerobically and produce a significant quantity of CH_4. Methane is produced under strictly anaerobic conditions, with a slurry pH between 6 and 8 and at temperatures above 15°C (Sommer et al., 2013). The principal factors affecting methane emission from livestock manure are the amount of manure that is produced and the portion of the manure that decomposes anaerobically.

1.2.3. Carbon dioxide

The carbon (C) sources for carbon dioxide (CO_2) emissions are categorised into two groups: biogenic C and fossil C. The IPCC (2006) does not document CO_2 emissions from manure management, as these are derived from short-cycled C that is captured by photosynthesis by crops and returned to the atmosphere as respired CO_2. Fossil CO_2 is derived from the degradation of non-renewable natural resources. With respect to manure management, this could be resources used for electricity production, diesel for machinery, the use of limestone and changes in the soil C pool. Decisions about whether an emission is biogenic or fossil is not always straightforward. An artificial boundary needs to be applied that defines the difference between short-cycled and long-term pools of C. Carbon dioxide emissions from changes in the soil C pool are on the boundary between being fossil or biogenic, depending on the timeframe for analysis. Soil C pools change due to the addition of organic matter (OM) from living plants and trees (which could also be in the form of manure) and withdrawal in the form of CO_2 by degradation of this OM. However, certain pathways and pools contain C that is stored long-term (e.g., mineralised soil C). The added C that is still present in the soil at the end of the analysed timeframe can be perceived to be non-biogenic or fossil C. The longer the time frame for analysis, the more of the added C will be degraded and returned to the atmosphere as CO_2.

1.3. Nitrate

Nutrient losses to aquatic environments mainly occur by runoff and leaching through the soil profile. Growth in marine water is often limited by N. When nitrate (NO_3^-) enters these waterbodies; it can lead to algal bloom and eutrophication. Groundwater quality can also be affected by nitrate leaching, and this can be especially problematic when the water is used as drinking water. Leaching and runoff of NO_3^- depend on a variety of factors, such as soil type, precipitation, groundwater level, N application levels, the share of organic N in the slurry, and time of application. Runoff mainly occurs in the first couple of days after manure application during heavy rainfall, while N leaching can occur many years after application due to the mineralisation of organic N (Sørensen and Jensen, 2013).

1.4. Phosphorus

Another nutrient that might be lost by surface runoff or leaching through the soil profile is phosphorus (P). Growth in freshwater is often limited by P, and P entrance to these waterbodies can lead to eutrophication. In addition, phosphorus is a non-renewable resource for which there is no substitute (Scherer and Pfister, 2015).

In general, phosphorus is strongly bound in the soil, but under certain circumstances, leaching and surface runoff can occur. These circumstances are manure application to soil types with preferential flows, direct exposure of manure P to running water after application and repeated application of manure to the same area over many years, which can increase the risk of long-term P leaching (Sørensen and Jensen, 2013).

1.5. Hydrogen sulfide

Hydrogen sulfide has been reported as a main toxic substance associated with swine operations. Acute exposure to such gases emanating from animal manure can cause severe health impairment to farm operators (Donham et al.,1982). The concentration of H_2S above stored swine slurry is usually below 1 ppm (Ni et al., 2010). However, when the slurry is agitated (e.g., during emptying of slurry pits), this induces a short-term peak of very high H_2S concentrations (Blanes-Vidal et al., 2009b).

1.6. Odour

Odorous emissions are a key concern in intensive livestock production. Odorous emissions are associated with the whole slurry management chain, including animal housing, slurry storage and field application. Ammonia, sulphuric compounds, phenolic compounds, indoles and organic acids are examples of odorous compounds (Sommer and Feilberg, 2013). There are two approaches to measuring odour: analytical techniques that measure concentrations of individual compounds and sensory techniques that use threshold olfactometry (Blanes-Vidal et al., 2009a,b). In their review of odour control in swine production, Liu et al. (2014) highlight the need for further research on technologies for odour control during manure handling and treatment. The technologies analysed in their study are solid-liquid separation, the addition of compounds during storage, impermeable and permeable covers and anaerobic digestion. Anaerobic digestion appears to have the greatest potential for controlling odorous emissions, but it is not economically feasible for small operations due to the high installation costs (Liu et al., 2014).

2. Environmental impacts of slurry acidification

It has been demonstrated in numerous studies that slurry acidification is an efficient technology for reducing ammonia emission (Figure 1) and thereby increasing N efficiency, while some recent studies have shown that slurry acidification might have a negative impact on N_2O emissions (Fangueiro et al., 2015b; Gómez-Muñoz et al., 2016). The net impact of soil application of acidified slurry on GHG emissions needs to be more accurately assessed since some of the available results are contradictory, and most of the previous studies were performed at laboratory scale where the soil to plant interactions were not considered. Furthermore, some studies have shown that application of acidified slurry might increase crop yields due to higher N mineralisation and dissolution of P in acidified slurries (Schils et al., 1999; Roboredo et al., 2012; Sommer et al., 2015; Gómez-Muñoz et al., 2016; Fangueiro et al., 2017).

The purpose of this report is to address several environmental aspects of acidification.

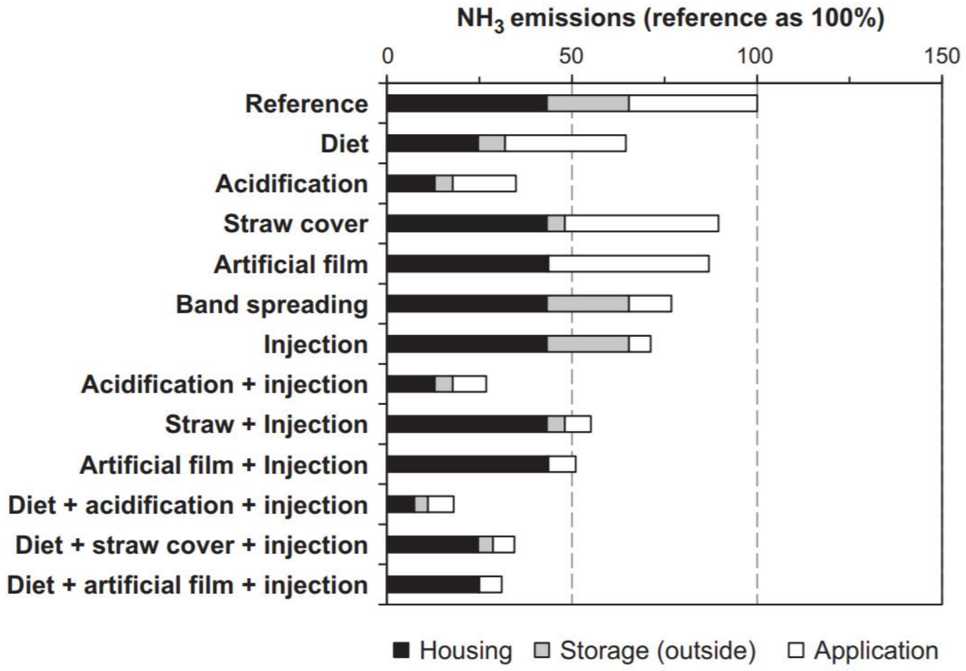

Figure 1. Impacts of mitigation measures on NH3 emissions from slurry separation-inclusive systems expressed as a percentage of the reference (i.e. slurry-based) system (Hou et al., 2015).

2.1. Impact on NH_3 emissions

Slurry pH controls the chemical equilibrium between ammonium (NH_4^+) and ammonia (NH_3) (McCrory and Hobbs, 2001). Acidification reduces losses of nitrogen by shifting this equilibrium towards a higher proportion of ammonium nitrogen, which cannot be emitted in gaseous form. Therefore, acidification of slurry is used to reduce NH_3 emissions (Stevens et al., 1989; Kai et al., 2008; Fangueiro et al., 2015a; Cocolo et al. 2016).

The efficiency of acidification with regard to reducing NH_3 emissions depends on parameters such as the additive, target pH, slurry type, and step in the slurry management chain (Table 1). Several studies have confirmed that NH_3 emissions are most directly related to the final pH of the slurry.

Table 1. Examples of reported reduction of ammonia emissions, depending on acidification type, additive, resultant pH and slurry type.

Type of acidification	Additive	Reduction, %	Source
In-house	HNO_3	37	*Bleijenberg et al. 1995, Kai et al. 2008,*
	H_2SO_4	50-70	
Storage tank	H_2SO_4	50-88	*Lefcourt and Meisinger 2001, Shi et al. 2001, Berg et al. 2006, Kai et al. 2008*
	HNO_3	29-71	
	Al_2SO_4	60-98	
	Lactic acid	65-88	
	Other acids	27-71	
At field application	Pig slurry, different acids	40-80	*Stevens et al 1989, 1992, Frost et al 1990, Bussink and Bruins 1992, Frost 1994, Kai et al 2008, Nyord et al 2013, Park et al 2018*
	Cattle slurry, different acids	15-80	

2.1.1. Effect of pH

The pH of the slurry is a key factor affecting NH_3 mitigation potential (Carozzi et al. 2013; Webb et al. 2013). The effectiveness of acidification to mitigate NH_3 emissions is significantly weakened when the pH of the acidified slurry goes up to a level of 6.0–6.5 (Dai and Blanes-Vidal, 2013; Petersen *et al*., 2014; Wang *et al*., 2014). A decrease of slurry pH value below 6.0 is generally enough to decrease NH_3 emissions between 30 and 95% after soil application (Stevens et al., 1989, 1992; Kai et al., 2008; Fangueiro et al., 2017).

However, the buffering capacity of slurry permits the pH to return to its initial pH level after acidification, due to microbial activity and hydrolysis of volatile fatty acids, nitrogen mineralization and dissolution of carbonate (Peterson et al., 2012, Hjorth et al., 2015). As a result, the pH value changes relative to storage period length. Most studies measure pH changes once after the acidification, but there is little information about how much acid is needed for pH to remain steady below 6.0 during long-term storage.

2.1.2. Effect of additive

There are several possible additives to reduce manure pH. Strong acids are the additives used most commonly: sulfuric acid (H_2SO_4) is used by all the companies dealing with slurry acidification, but others, including hydrochloric acid (HCl), phosphoric acid (H_2PO_3), nitric acid (HNO_3) and alum, have been tested by various researchers. Some limitations to their use, such as their relatively high cost, corrosiveness, and hazards to animal and human health, are important issues that need to be considered. For instance, HCl is very corrosive to all materials; HNO_3 reacts with organic material and releases nitrogen to the air; H_2PO_3 contributes to more phosphorus going onto fields. This project is mainly focused on sulphuric acid since this is the most cost-effective, but also the most suitable (from multiple perspectives) acid for acidifying slurry. It also supplies sulphur, which is an important macronutrient for plants.

The efficiencies of the additives used to decrease NH_3 emissions vary significantly. The most additives are strong acids, such as H_2SO_4 or HCl. Alum has been used mainly with poultry manure and produced a decrease in NH_3 emissions similar to those obtained with strong acids.

2.1.3. Effect of acidification timing

Slurry can be acidified during each of the three major management steps: in the animal house, during storage, and at field application. In-house acidification is considered as long-term acidification and involves pumping acidified slurry into the storage area beneath the slatted floors. The additive is applied on a daily or a weekly basis. Acidifying the slurry early in the management chain leads to NH_3 emission reductions from animal housing, in slurry storage and after field application (Kai et al., 2008). Ammonia emissions from pig housing were reduced by up to 70% when slurry was acidified from pH 7.5 to pH 6 and by 67% following subsequent field application by band-spreading (Kai et al., 2008). This implies that a larger share of the N remains in the slurry that is field applied, which in turn results in an increased mineral N fertiliser equivalent compared to untreated slurry (Sørensen and Eriksen, 2009). Another effect of early acidification is that microbial activity in the slurry is greatly decreased, leading to lower CH_4 and N_2O emissions during storage (Berg et al., 2006; Ottosen et al., 2009; Sørensen and Eriksen, 2009).

Acidification during storage is typically performed shortly before the slurry is removed from the storage tank. This is a cheaper approach than in-house acidification, but problems with foaming during acid addition might occur (Fangueiro et al., 2015). Lactic acid reduced NH_3 emissions by 65–88%, with pH values between 5.7 and 4.2, whereas nitric acid reduced NH_3 emissions by only 29–71% for the same pH values. The addition of aluminium sulfate to cattle slurry gave decreases in NH_3 emissions of 60% at pH 5 and 98% at pH 4.2.

Finally, acidification during field application of slurry is considered as short-term acidification. The additive is applied in the slurry storage tank just before the slurry is applied to fields or the acid can be applied in-line on the slurry tanker during field application. This approach is cheaper than in-house acidification as less equipment and acid are needed for decreasing the pH of the slurry. Ammonia emissions were reduced by 58% during field application when the pH was decreased from 7.8 to 6.8 (Nyord et al., 2013). However, field acidification only reduces NH_3 emissions in the field and does not reduce emissions from animal housing or manure storage (ten Hoeve et al., 2015). With field application acidification, decreases of NH_3 emissions in the range of 40–80% with pig slurry and 15–80% with cattle slurry can be achieved (Stevens et al., 1989, 1992; Frost et al.,1990; Bussink and Bruins, 1992; Frost 1994; Kai et al., 2008; Nyord et al., 2013).

2.2. Impact on greenhouse gas emissions

Although acidification is considered a very effective NH_3 abatement option, its implication on GHGs is relatively poorly documented. In the next subchapters, the different GHGs, as well as their net effect, are addressed.

2.2.1. Nitrous oxide

Effects of acidification on N_2O emissions were mixed across published studies. Overall meta-analyses estimates indicate an N_2O reduction of 55 ± 45, comprising N_2O reductions of 56 ± 51% during storage of acidified manure and 52% when applied to the soils (Sajeev et al., 2017). The variations in emission reduction stem from the selection of appropriate acid and application rates, which are acknowledged in the published literature (Berg et al., 2006; Ottosen et al., 2009; Fangueiro et al., 2010; Petersen and Sommer, 2011; Petersen et al., 2012). Addition of sulfuric acid led to overall reductions in N_2O emissions by 17 ± 30% during the storage and application of acidified slurry. One of the studies, however, reported no change in N_2O emissions during storage of acidified slurry (Petersen et al., 2014). The authors suggested that they might have disturbed surface crust formation (a prime source of N_2O emissions) during acid mixing in the experiment, leading to no change in emissions. Lactic acid reduced N_2O emissions by 90% or more, while the use of nitric acid adds N to the system and also stimulates denitrification, leading to large increases in N_2O emissions (Berg et al., 2006).

The reduction in N_2O emissions happens due to the decreased activity of nitrifying bacteria with the lowering of slurry pH (Owusu-Twum et al., 2017). Furthermore, the lower N_2O emissions from acidified treatments might also be explained by the CO_2 losses that occurred during the acidification process (Fangueiro et al., 2013), which reduced the amount of soluble organic C available for denitrification and consequently reduced the N_2O emission. On the other hand, the high CO_2 emissions observed immediately after non-acidified slurry application to the soil (not observed in acidified cases) might have led to O_2 depletion, creating better conditions for denitrification and N_2O emissions.

The situation is, however, even more complicated for soil application. It is known that N_2O emissions from agricultural soils are originated from the nitrification and denitrification processes, and denitrification is the main source of N_2O fluxes from soil amended with animal slurry (Kool et al., 2011). In controlled studies, N_2O emissions increased in the first day following slurry application (Fangueiro et al. 2008b, 2010, 2015b), no matter how the slurry was treated. For all treatments, nitrous oxide fluxes decreased during about 5 days and then peaked twice. The first peak was observed when more intense nitrification started in all treatments, while the second peak occurred when the NO_3^- concentration slowed down significantly. Nitrous oxide fluxes in acidified treatments were generally lower than in non-acidified treatments even if differences were not always statistically different (Fangueiro et al., 2015b).

2.2.2. Carbon dioxide

Carbon dioxide is a well-known greenhouse gas, but in some studies of slurry management, CO_2 emissions are not considered because they belong to the natural carbon cycle. However, when considering slurry acidification, one has to address whether such treatment does or does not induce an increase in CO_2 emissions.

The emission of CO_2 occurs mainly during the acidification process when emission rates can be 2–10-times higher than during the subsequent storage. In this way, a significant part of the carbon (about 72–96% of the bicarbonate/carbonate) initially present at the slurry is released as CO_2 during the acidification process (Stevens et al. 1989, Fangueiro et al., 2015b).

Following soil application, lower CO_2 emissions were observed in soil amended with acidified slurry relative to non-acidified slurries (Berg et al.,

2006; Fangueiro et al., 2010; Ottosen et al., 2009; Petersen et al., 2012). Such a decrease in CO_2 emissions after soil application is probably caused by the volatilisation of carbonates during the acidification process, which would otherwise have been emitted after field application. The acidified slurry contained about 38% less carbon (C) than non-acidified slurry at the moment of field application (Fangueiro et al., 2010). Also, since slurry acidification greatly reduces microbial activity and consequently O_2 consumption in soil amended with acidified slurry, it also reduces CO_2 emissions (Ottosen et al., 2009, Fangueiro et al., 2013, 2015b). The lower the CO_2 emissions, the higher the amount of carbon stored in the soil.

2.2.3. Methane

Slurry acidification acts on methanogenesis; therefore, CH_4 emissions should be lowered by long-term acidification treatments, but not by short-term acidification. Studies have reported that methanogenesis is limited by addition of acids, particularly sulfates (Petersen et al., 2012, 2014). Methanogenic activity leading to CH_4 emissions is prevalent between pH levels of 6.5 and 8.5. Acidification of manure generally reduces the pH to lower levels (below six), inhibiting methanogenesis and subsequently reducing CH_4 emissions (Wang et al., 2014).

Several studies have reported that animal slurry treatment by acidification reduces CH_4 emissions during storage by 74 ± 22% (Petersen et al., 2012, Hou et al., 2014, Fangueiro et al., 2015a, 2017, Sajeev et al., 2017). Some studies have reported that CH_4 emissions occurred for a short period (few days) after cattle-slurry application to soil. Those emissions are related to volatilisation of the CH_4 produced during storage and initially dissolved in the slurry rather than from methanogenesis from soil (Pereira et al., 2010, Chadwick et al., 2011, Fangueiro et al., 2015a).

The effect on CH_4 emissions depends strongly on the acid used. Published studies targeting different pHs reported decreases of > 90% with lactic acid against 67–87% with H_2SO_4, 40–65% with HCl, and 17–75% with nitric acid.

2.2.4. Net greenhouse gases

The general conclusion drawn from the results of several studies is that there is no net greenhouse gases emission drawback in applying acidified slurry relative to GHG emission (Figure 3) with the strong advantage of avoiding or reducing NH_3 emissions. In-house slurry acidification is especially efficient at reducing several GHG emissions since the lower pH strongly reduces microbial activity (Ottosen et al., 2009; Sørensen and Eriksen, 2009, Fangueiro et al., 2015b, Sajeev et al., 2017). Acidification of slurry to ≤ 6.0 is, therefore, a promising technique for minimizing GHG emissions from slurries.

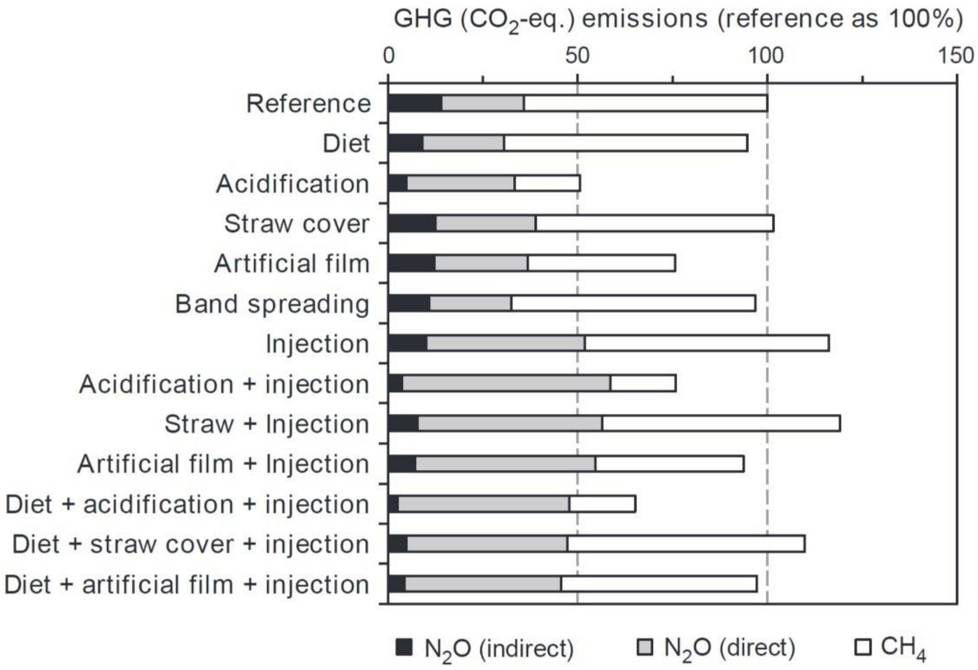

Figure 3. Impacts of mitigation measures on GHG emissions from slurry separation-inclusive systems expressed as a percentage of the reference (i.e. slurry-based) system (Hou et al., 2015).

2.3. Life cycle assessment

In a life cycle assessment (LCA) of acidified slurry, Hoeve et al. (2016a, b) investigated several environmental effects of pig slurry acidification and separation in Danish conditions. The LCA included resource use and environmental impact potentials associated with indoor and outdoor storage and field application of slurry, as well as its treatment fractions, field processes, transportation between the different life cycle stages, production and use of electricity, sulphuric acid, and agricultural lime, and the production, transportation and application of mineral fertiliser. We rely on these authors' findings about climate change, terrestrial, marine and freshwater eutrophication, fossil resource depletion and toxicity potential.

2.3.1. Climate change potential

A life cycle assessment (Hoeve et al., 2016a,b) resulted in net positive climate change potential (CCP) compared to mineral fertilizer, regardless of how the slurry was treated (Figure 4). Emissions associated with the use of mineral fertiliser were subtracted from emissions associated with the use of slurry. This led to positive N_2O field emissions (higher for slurry than for mineral fertiliser) and C sequestration (higher for slurry than for mineral fertiliser, meaning a negative net non-biogenic CO_2-emission).

Slurry acidification showed a CCP that was slightly lower than the scenario without acidification for the in-house acidification scenario, and 60% higher for the field acidification scenario. The main positive contributors to CCP were the net emissions from the field (N_2O), emissions from slurry storage in animal housing (N_2O and CH_4) and emissions from the slurry in outdoor storage (CH_4). In both acidification scenarios, extra GHG emissions were associated with the production and use of H_2SO_4 and $CaCO_3$. Negative emissions mean GHG savings by the avoided production of mineral fertiliser and avoided production of wheat on the international market due to higher yields when non-acidified or acidified slurry was used, compared to the use of mineral fertiliser.

The field acidification scenario showed the highest net CCP, partly caused by emissions from the production and addition of sulphuric acid and lime. In the in-house acidification scenario, these emissions were offset by a reduction in GHG emissions during slurry storage in animal housing and outdoors. Net field emissions are the increases in emissions resulting from the replacement of mineral N fertiliser by the slurry.

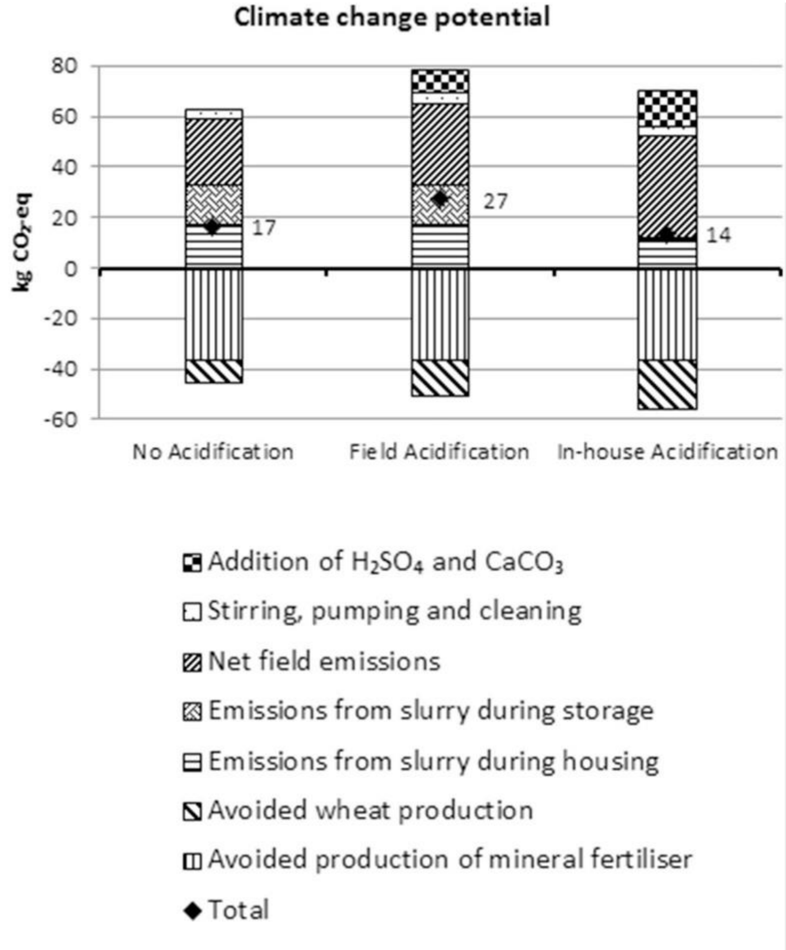

Figure 4. Impact assessment of the no acidification, field acidification and in-house acidification scenarios for pig slurry, divided into stages compared to the application of mineral fertiliser alone in Danish conditions (Hoeve et al., 2016a).

In total, global warming potential (GWP) are about the same for bandspreading and injection considering also the additional mineral N to add when bandspreading. The mineral N causes GHG release when produced and also in itself after spread on farm land. Still the benefits from injection are that you reduce eutrophication and acidification with lower ammonia emissions.

2.3.2. Eutrophication potential

According to Hoeve et al. (2016a,b), slurry acidification is the preferred technology for reducing terrestrial eutrophication potential, with potential impact decreases of 31% for field acidification and 72% for in-house acidification compared to the reference scenario (Figure 5a). This result was expected since the terrestrial eutrophication potential is mainly caused by NH_3 emissions. The in-house acidification facilitated large decreases in NH_3 emissions, starting from slurry storage in animal housing all the way to field application. Field acidification only decreased NH_3 emissions during and shortly after field application. The housing stage was the main contributor to the terrestrial eutrophication potential for all scenarios, followed by the field application stage. The net impact potential for field-acidified slurry was approximately 30% lower than for non-acidified slurry, while for in-house acidified slurry, it was approximately 71% lower. This is because field acidification only affects field emissions, whereas in-house acidification affects emissions from all stages of slurry management.

For marine eutrophication potential (Figure 5b), contributing and saving processes largely cancelled each other out, resulting in a small total impact potential. The positive and negative contributions were especially large for the in-house acidification scenario. Net field emissions and replacement of winter wheat production elsewhere in the world were the main factors influencing marine eutrophication potential.

For freshwater eutrophication potential, slurry acidification only had a minor effect due to savings from avoided wheat production.

In the same study (Hoeve et al., 2016a), in all three scenarios, the net marine water eutrophication potential (MEP) was close to zero, due to both eutrophication-enhancing and hampering processes that to a large extent cancel one another out (Figure 2 for Danish conditions). Increased yields caused by non-acidified or acidified slurry applications saved the production of wheat on the international market, which was represented by a negative eutrophication potential. The main processes contributing to the MEP were the emissions from the field (mainly NO_3^- leaching) and from the slurry storage in pig housing (mainly NH_3 volatilisation). The in-house acidification scenario showed both the highest positive, but also largest avoided MEP. The higher positive potential was caused by a slurry N input to the field of 156 kg N ha^{-1} in the in-house acidification scenario compared to 140 kg N ha^{-1} in the other two scenarios, leading to increased NO_3^- leaching. The main avoided contributor to MEP was the avoided production of the extra winter wheat yield through the use of non-acidified or acidified slurry.

2.3.3. Fossil resource depletion potential

For fossil resource depletion potential, Hoeve et al. (2016b) showed a negative impact potential for all slurry related scenarios, since resource savings from avoided production of mineral fertiliser and avoided wheat production elsewhere in the world were greater than resource use for manure management, acidification and tractor use. Savings were smaller for acidification scenarios, due to fossil resource consumption for acidification. For the two acidification scenarios, however, this was partly (in-house acidification) or completely (field acidification) counteracted by the greatest savings coming from avoided wheat production elsewhere in the world.

2.3.4. Toxicity potential

Two categories of toxicity potential were influenced by slurry treatment, namely non-carcinogenic human toxicity and total ecotoxicity (Hoeve et al., 2016b). Treatment by acidification showed minor improvements for ecotoxicity potential, but not for human toxicity potential.

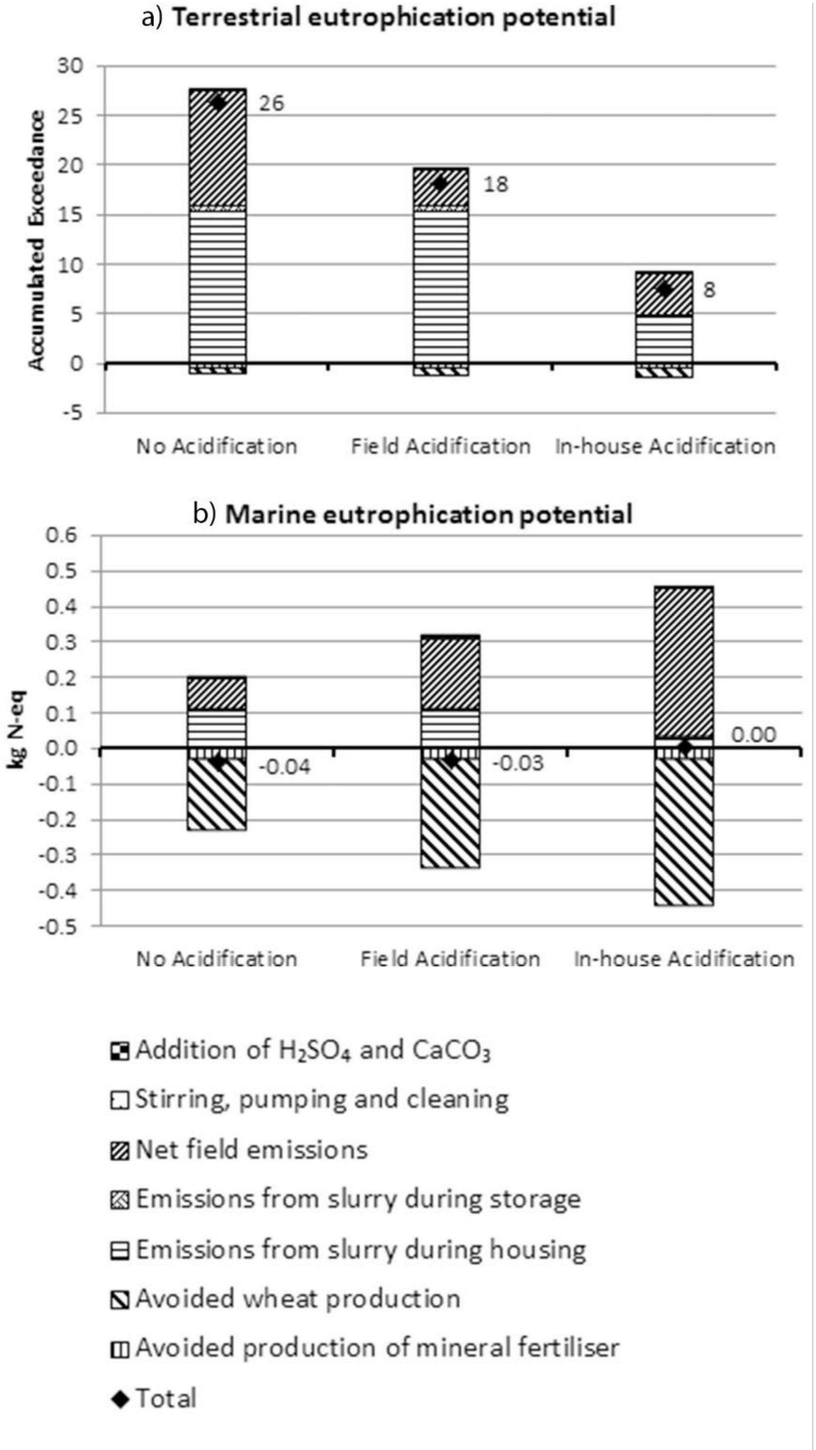

Figure 5. Eutrophication impact assessment of the no acidification, field acidification and in-house acidification scenarios in Danish conditions, divided into stages compared to the application of mineral fertiliser alone (adjusted from Hoeve et al., 2016a).

2.4. Mineral fertiliser value

Improved fertiliser value of nitrogen (N) is an advantage of slurry acidification (Kai et al., 2008, Fangueiro et al., 2015a, Figure 6). The effect of slurry acidification on the mineral fertilizer equivalent (MFE) has been estimated in several studies, but the results varied significantly. Sorensen and Eriksen (2009) observed no significant effects of slurry acidification on the MFE when slurry was incorporated before sowing a barley crop. However, the same authors reported an increase of the MFE in a range of 39–63% for cattle slurry and 74–100% with pig slurry, when acidified slurry was band applied. Kai et al. (2008) reported a 43% increase of the MFE with the application of acidified slurry, relative to the raw slurry, in a 3-year experiment with winter wheat and spring barley rotation. These authors also reported that N fertilization is easier to manage with acidified slurry since its NH_4^+ content is more constant relative to non-acidified slurry due to minimal NH_3 losses. This point is essential to increasing the farmer's confidence in using slurry as a substitute for mineral fertilizer.

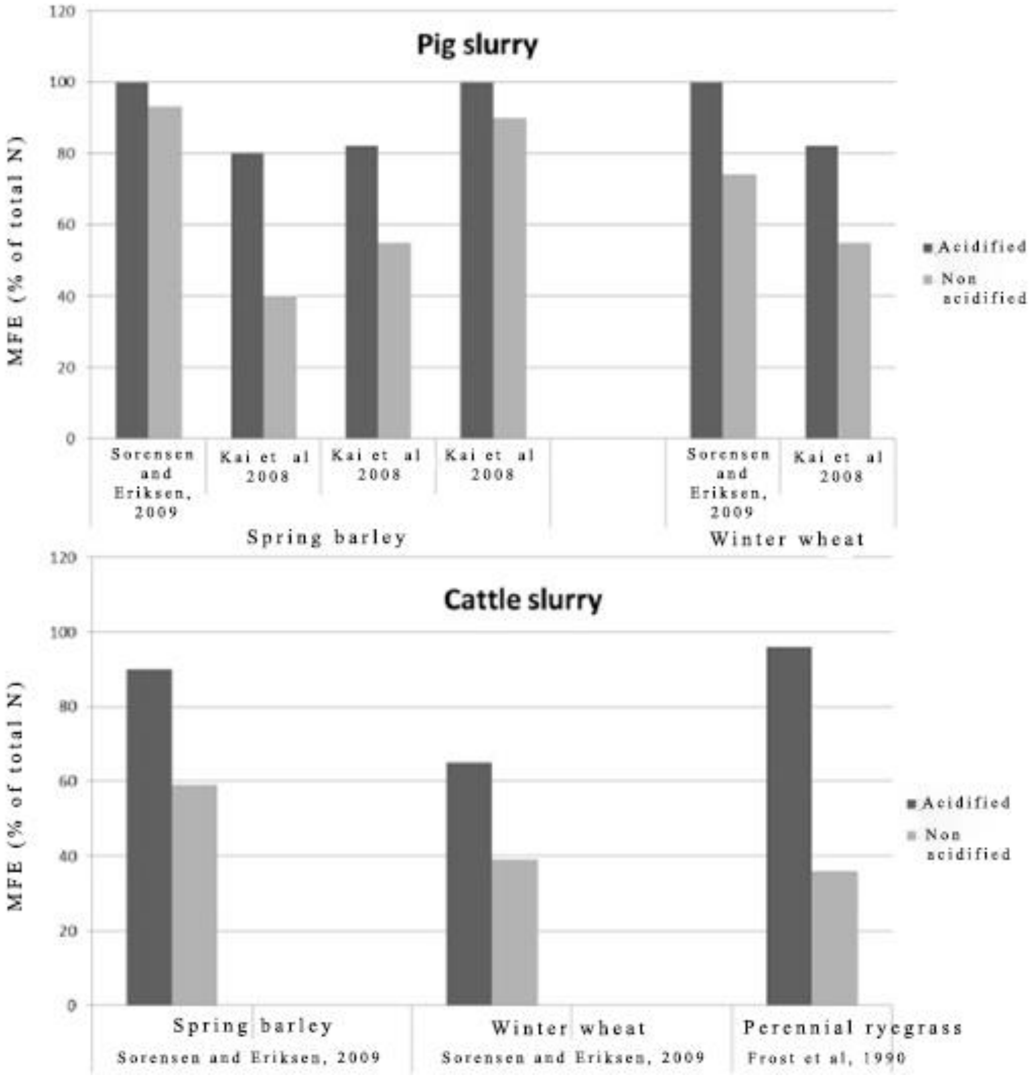

Figure 6. The effect of slurry acidification on the mineral fertilizer equivalent (MFE) (Fangueiro et al., 2015a).

2.4.1. Nitrogen

Lower NH_3 losses following acidification mean more slurry total-N and plant-available N remains in the slurry applied to fields, resulting in an increased mineral N fertiliser equivalent value compared to untreated slurry (Kai et al., 2008; Sørensen and Eriksen, 2009). However, it should further be considered that N applications to crops are limited in many parts of Europe through legislation since the yield response to N decreases with increasing application levels and NO_3^- leaching increases. For this reason, the production and environmental impacts of slurry acidification technologies will be affected by how regulatory limits frame N application levels.

2.4.2. Phosphorus

Several studies (Fangueiro et al., 2009; Daumer et al., 2010; Roboredo et al., 2012) observed almost complete dissolution of slurry P when lowering the pH, thus the acidified slurry has higher concentrations of dissolved inorganic compounds – relative to untreated slurry – with positive impacts on its phosphorus fertilizer value. Roboredo et al. (2012) followed the dynamics of P in soil amended with acidified or non-acidified pig slurry and observed a significant effect of acidification on the P availability in the soil, as well as its evolution over time. Slurry acidification can induce the dissolution of some inorganic phosphates, leading to higher inorganic P concentrations in the most labile fraction. Also, Petersen et al. (2013) reported an increase of P availability in soils amended with acidified slurry, relative to the non-acidified slurry.

The decrease of slurry pH is generally accompanied by an increase in its conductivity, due mainly to the dissolution of minerals (Hjorth et al., 2013). Because the chemical reactions are rapid, the dissolution of the inorganic minerals might occur for both the short- and long-term acidification technologies.

2.5. Nutrients and pathogens leaching and run-off

Fangueiro et al. (2014) showed that both acidification and separation had significant effects on the composition of the leachates. None of the strategies proposed decreased the potential leaching of slurry nutrients and pathogens relative to the surface application of the whole slurry, except for the acidified whole slurry that decreased the potential leaching of total carbon (Table 2). Nevertheless, surface application of acidified cattle slurry increased the leaching risk for NH_4^+, salts, and pathogens. The injection was equivalent to surface application regarding several parameters but led to a worsening of NO_3^-, total P, and pathogens leaching. However, surface application of the liquid fraction (both acidified and non-acidified) had a negative impact on the potential leaching and, therefore, should be recommended only in cases where the leaching potential is low. Nevertheless, one should bear in mind that efficient slurry management should minimize environmental impacts as well as human community impacts, namely in terms of odours and landscape, what give a strong advantage to slurry injection relative to other options.

The main problem associated with N_{org} leaching is the subsequent potential for bacterial growth, phytoplankton growth, photochemical decomposition, and abiotic adsorption (Berman and Bronk, 2003). The effect of acidification on N_{org} leaching is not, however, clear, but the effect of solid-liquid separation is significant. N_{org} leaching should also be considered in future experiments dealing with acidified slurries at the field scale.

A strong effect of acidification on P leaching has been shown in some studies (Daumer et al., 2010; Fangueiro et al., 2009). A strong dissolution of slurry P occurred when the pH was lowered. However, P leaching in soil amended with animal slurry relies mainly on the soil properties (Glaesner et al., 2011). Liu et al. (2012) compared P leaching from two soils (loamy sand and clay loam) following pig slurry application and observed significant effects of the slurry application on P leaching only in the clay loam soil; in the loamy sand soil the leaching was similar in amended and non-amended soils.

A strong increase of the electric conductivity (EC) has observed in the leachates from the acidified treatments, relative to the non-acidified treatments (Amin et al. 2013, Fangueiro et al., 2014). Acidification induces the dissolution of some metal complexes that can be easily released into the soil water.

Higher fecal coliform and *E. coli* populations were observed in acidified materials (Fangueiro et al., 2014), in agreement with previous studies that indicated higher survival of *E. coli* and fecal coliforms at low pH (close to 6) than at high pH (close to 8) (Franz et al., 2005). According to Semenov et al. (2009), the highest risk of pathogen leaching is immediately after slurry application. Since weather forecasts have a significant confidence interval of almost 3 days, slurry application should be prevented when rainfall is expected.

Three aspects have to be considered here: the survival (or even multiplication) of the pathogens after acidification or separation, then after soil application, and finally the movement of the pathogens in the soil column. The effect of acidification on the potential leaching of faecal coliforms is unclear, but it clearly increased the potential leaching of *E. coli*. By maintaining more mineral N in the slurry, acidification might prolong *E. coli* activity. Semenov et al. (2009) indicated that the leaching potential of *E. coli* in soil is affected by the type of manure (solid manure or slurry) and the method of its application (e.g., spreading on the soil surface or injection into the soil). To minimize the risk of water contamination, these authors recommended the surface application of slurry.

2.6. Impact on hydrogen sulfide

Hydrogen sulphide is a dangerous/hazardous gas that (like methane) is produced by bacteria in the slurry. This means that the production of the gas is a continuous process. Some gas slips away, but the main part is captured in the slurry structures as small bubbles, that are released when the slurry is agitated. This means that the longer the slurry has been stored before agitation, the higher is the hydrogen gas release when agitated. This has great importance for how the slurry system is designed, and if the slurry is floating out of the stable by gravity forces to a pumping pit outside the barn, then the main hydrogen sulphide part is released in the pumping pit. This is the reason why many countries, including Denmark, do not allow pumping of slurry inside stables and have requirements to the maximal size of slurry channels under the stables; the bigger they are, the greater the amount of hydrogen sulphide that can potentially be released inside the stable.

In-house acidification reduces the risks associated with hydrogen sulphide in two ways:

- The low pH is in itself reducing the activity of the hydrogen sulphide bacteria, which have a growing range of pH 5.5 to 8.5 (Filtronics, 2018).
- The frequent recirculation of the slurry in case of in-house acidification would lead to smaller amounts of hydrogen sulphate to be accumulated in the slurry, compared to similar slurry systems without in-house acidification, and in-house acidification systems are designed with pumping/agitation happening outside the stable in a pumping pit.

Thus, there will be the higher release of hydrogen sulphide when the slurry is moved or agitated, whether acidified or not. In line with this, the VERA Verification Statement behind the approval of JH Agros in-house acidification system for pigs (VERA, 2016) states: "An increased hydrogen sulphide concentration was observed when the daily flushing of the manure took place during treatment of the manure. The higher H_2S levels lasted less than 1 hour per day. To prevent any risks for the user, the stirring of the slurry is done outside the animal house in the process tank which is equipped with decals warning against H_2S”.

The concentrations of hydrogen sulphide during recirculation of slurry in case of in-house acidification was measured by the Danish Pig Research Centre. The trial report (Leegard Riis, 2016) shows that in-house acidification significantly lower hydrogen sulphide concentration in the stables (by 67%, $P < 0.001$), despite the expectation that the higher S-content in the slurry would give a better basis for the hydrogen sulphide formation. However, the measurements were only pointed measurements, and more research is needed to fully clarify the impact of slurry acidification on hydrogen sulphide concentrations in stables.

Hydrogen sulfide emissions were unaffected by acidification in some studies, but in others showed a decrease. An increase of H_2S emissions has been observed immediately after acidification; this can happen because existing sulfide is protonated and also due to the initiation of mixing. When acidification is performed with H_2SO_4, an increase of H_2S might occur since the activity of sulfate-reducing bacteria can be stimulated by the addition of inorganic sulfur. Nevertheless, such bacteria are also sensitive to pH; consequently, acidification to low pH might limit their activity and hence H_2S emissions. Furthermore, H_2S emissions can be avoided by oxygenation of acidified slurry (Jensen, 2002). Additionally, the lower rate of organic matter degradation might decrease the production of sulphate and, thus, sulfide.

Conclusions and discussion

A summary of the impacts of surry acidification on several environmental parameters is given in Table 2. Based on this, we concluded that slurry acidification leads to decreased environmental burdens, largely due to reductions in NH_3 emissions. In-house acidification especially leads to reduced NH_3 emissions throughout the whole manure management chain.

There is no net greenhouse gases emission drawback in applying acidified slurry relative to GHG emission. In-house slurry acidification efficiently reduces several GHG emissions.

With respect to climate change potential from the life cycle analyses, the reduction in ammonia and GHG emissions during storage of acidified slurry in animal housing and in an outdoor storage tank counterbalance additional GHG emissions due to the production of sulphuric acid and lime. However, this is not the case for field acidification, which results in slightly higher CCP compared to the non-acidified scenario. Slurry acidification is the preferred technology for reducing terrestrial eutrophication potential; the effect is smaller for the marine and freshwater eutrophication potential. Fossil depletion potential decreases slightly due to avoidance of mineral fertilizer production; toxicity potential is only slightly affected, since positive and negative impacts weight each other out.

The main problem associated with slurry acidification is nutrient and pathogen leaching and higher survival of some pathogens. Since the highest risk of pathogen leaching is immediately after slurry application, slurry application should be avoided when rainfall is expected. Also, to minimize the risk of water contamination, surface application of slurry is recommended.

Table 2. Effect of slurry acidification relative to using non-acidified slurry on some environmental parameters.

Parameter	Effect
N_2O emission	↘
CH_4 emission	↘
NH_3 emission	↘
CO_2 emission	↘
Net GHG	↘
LCA climate change potential	↘ in-house ↗ field
LCA terrestrial eutrophication potential	↘
LCA freshwater and marine eutrophication potential	↔
LCA fossil depletion potential	↘
LCA toxicity potential	↔
Mineral fertilizer value (N, P)	↗
NO_3^- leaching	↔
NH_4^+ leaching	↗
N_{org} leaching	↔

C_{total} leaching	↘
P_{total} leaching	↔
Pathogens leaching	↗
EC	↗

When looking at environmental impacts, it is important to consider the extent of interactions between the emissions along the manure management chain for different stages and for various abatement options. We, thus, should not limit research to a single pollutant to abate either air pollution from increased NH_3 emissions or climate change impacts due to GHGs. Given the extent of interactions between multiple pollutants, any one-dimensional policy initiatives might prove to be suboptimal. From a broader point of view, acidification of manure is a promising abatement option, reducing not only NH_3 emissions but also CH_4 N_2O when averaged over housing, storage and application stages relative to the untreated raw slurry. To avoid as much leaching as possible, more research needs to be done, and awareness needs to be proliferated about suitable application methods.

Interreg
Baltic Sea Region
Baltic Slurry Acidification

EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND

www.balticslurry.eu

Summary of the project

Baltic Slurry Acidification is an agro-environmental project financed by Interreg Baltic Sea Region under the priority area Natural resources and specific objective Clear Waters. The aim of the project is to reduce nitrogen losses from livestock production by promoting the use of slurry acidification techniques in the Baltic Sea Region and, thus, to mitigate eutrophication of the Baltic Sea. The Baltic Slurry Acidification project started on March 2016 and will continue until February 2019.

Summary of the report

The aim of this report is to provide a literature-based understanding of the environmental effects of slurry acidification. This report will be the main output since target groups such as farmers, advisors and authorities at various levels will utilise the results when assessing the environmental impact of their livestock operations.

Contributing partners

RISE – Agrifood and Bioscience, Sweden

Association of ProAgria Center, Finland

ECRI – Estonian Crop Research Institute, Estonia

ITP – Institute of Technology and Life Sciences, Poland

Latvian Rural Advisory and Training Centre, Latvia

Lithuanian Agricultural Advisory Service, Lithuania

State Agency for Agriculture, Environment and Rural Areas of German Federal State Schleswig-Holstein, Germany

Union Framers Parliament, Latvia

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