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A life cycle perspective of slurry acidification strategies under different nitrogen regulations

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ABSTRACT

Livestock manure is a major contributor to ammonia and greenhouse gas emissions and treatment technologies such as slurry acidification can be used to reduce both. In this study, life cycle assessment was used to compare impact potentials of slurry acidification at either the pig housing or the field application stage with conventional slurry management. Furthermore, the effects of differences in environmental regulations concerning nitrogen application limits were analysed. The impact categories analysed were terrestrial eutrophication potential, climate change potential, marine eutrophication potential and toxicity potential. Slurry acidification reduced the terrestrial eutrophication potential by 71% for in-house acidification and by 30% for field acidification. Changes in regulatory plant-available nitrogen application limits resulted in changes in climate change potential and marine eutrophication potential, with lower limits favouring in-house acidification. Acidification can substantially reduce the environmental impacts of animal slurry, but the effect depends on the context of the regulatory regime.

1. Introduction

Global livestock production is rapidly growing as the world's population increases and becomes steadily more affluent (Sommer and Christensen, 2013). However, livestock production has a major impact on the environment. Livestock manure is responsible for approximately 40% of global ammonia (NH_3) emissions, 70% of NH_3 emissions in Europe and 80% of NH_3 emissions in Denmark (Bouwman et al., 1997; Dalgaard et al., 2014; European Centre for Ecotoxicology and Toxicology of Chemicals (1994); Van der Hoek, 1998). The largest NH_3 emissions in Denmark come from pig housing, followed by field application of pig slurry (Nielsen et al., 2014). Livestock manure is also responsible for approximately 1.8% of global greenhouse gas (GHG) emissions, 1.7% of GHG emissions in Europe and 2.8% of GHG emissions in Denmark (European Environment Agency, 2012; O'Mara, 2011).

Slurry acidification is a treatment used to reduce NH_3 emissions to allow farms to comply with national or EU legislation (*e.g.* the EU National Emission Ceiling Directive, European Commission (2001)). In 2014, approximately 12% of all animal slurry in Denmark was acidified (Kjeldal, 2015). Ammonia emissions are decreased by the reduction in pH because the proportion of ammoniacal N that is present as NH_3 is reduced (Fangueiro et al., 2015; McCrory and Hobbs, 2001; Petersen et al., 2012). When the pH is decreased from a pH of typically around 7.5 to 5.5, the gaseous acid-base compound concentration of NH_3 decreases from 1.8% to 0.02% (Fangueiro et al., 2015).

Slurry can be acidified at different stages in the manure handling chain. Acidification in the animal house involves pumping acidified slurry into the storage area beneath the slatted floors. Acidifying the slurry at the start of the manure management chain means that emissions are reduced in animal housing, in slurry storage and after field application. Ammonia emissions from pig housing 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). Another approach is to add the acid 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

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cheaper than in-house acidification as less equipment and sulphuric acid are needed for decreasing the pH of slurry. Ammonia emissions 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 the animal housing or manure storage.

In-house slurry acidification efficiently reduces GHG emissions, since the lower pH strongly reduces microbial activity (Ottosen et al., 2009; Sørensen and Eriksen, 2009). Slurry acidification reduced methane (CH_4) and nitrous oxide (N_2O) emissions during storage, and carbon dioxide (CO_2) after soil application (Berg et al., 2006; Fangueiro et al., 2010; Ottosen et al., 2009; Petersen et al., 2012). However, the reported decrease in CO_2 emissions after soil application was probably caused by the volatilisation of carbonates during the acidification process which would otherwise have been emitted after field application. Acidified slurry contained about 38% less carbon (C) than non-acidified slurry at the moment of field application (Fangueiro et al., 2010).

Improved fertiliser value of nitrogen (N) is another advantage of slurry acidification (Kai et al., 2008). 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 (MFE) value compared to untreated slurry (Sørensen and Eriksen, 2009). However, it should further be considered that N applications to crops are limited in many parts of Europe through legislation (*e.g.* the Nitrates Directive), 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.

Slurry acidification affects a number of environmental indicators during all stages of the slurry management system. A whole-farm assessment of slurry acidification, including all stages of the slurry management system, has been presented in Kai et al. (2008), but only includes NH_3 emissions. The review of slurry acidification by Fangueiro et al. (2015), mentions the need to investigate whether slurry acidification induces any burden shifting, *i.e.* whether a reduction in NH_3 losses leads to other environmental impacts at other life stages. Life cycle assessment (LCA) is a widely used approach in the analysis of environmental impacts related to slurry management (Croxatto Vega et al., 2014; De Vries et al., 2013; Hamelin et al., 2011; ten Hoeve et al., 2014), but has yet to be applied to slurry acidification. The goal of this study was therefore to use an LCA approach to investigate the environmental impacts of slurry acidification, including the potential effects of legislation. The objectives were *i)* to compare the environmental impact potentials of two different slurry acidification techniques with conventional slurry management, and *ii)* to analyse the environmental impact potentials of slurry acidification under varying N application limits.

2. Materials & methods

2.1. LCA approach

This study was performed according to the LCA approach described in ISO 14040 and ISO 14044 standards (ISO 14040, 2006; ISO 14044, 2006). Whenever possible, system expansion was used to avoid allocation. LCA modelling was performed using EASETECH software (Clavreul et al., 2014). The Ecoinvent database 2010 V2.2 was used for background processes (Althaus et al., 2007; Nemecek and Kägi, 2007). The functional unit in this study was the treatment of 1000 kg of slurry excreted by fattening pigs under prevailing Danish conditions.

2.2. Scope

The geographical scope was Denmark for the slurry treatment processes (housing, storage and field application). Processes that occur outside Denmark (*e.g.* mineral fertiliser production) were also included. The technical scope for the assessment was the best available technology in Denmark. Emissions from mineral fertiliser, acidified and non-acidified slurry were analysed from the moment slurry was excreted by the pigs until 100 years after field application, including gaseous emissions, leaching to groundwater and losses to surface water from the soil and C sequestration. During these 100 years the same practice was assumed and this timeframe was chosen in order to include long-term effects of slurry application to agricultural soils. For greenhouse gases the 100-year time horizon was considered for the climate change potential.

2.3. Scenarios and system boundaries

2.3.1. System boundaries

The processes included in this study are shown in Fig. 1. The system excludes the production of the fattening pigs, and the buildings and equipment used for the storage and application of slurry. These processes were assumed to be equal for all scenarios and were assumed not to change as a result of changes in slurry management practice.

2.3.2. Scenarios

In this study, two slurry acidification scenarios were considered and compared with a reference scenario in which slurry was not acidified:

- No acidification scenario: conventional slurry management
- Field acidification scenario: identical to the no acidification scenario, apart from addition of sulphuric acid during application of the slurry to the field (Nyord et al., 2013; VERA, 2012)
- In-house acidification scenario: daily acidification of slurry during in-house storage followed by outdoor storage and land application of the acidified slurry using a trailing hose system (Danish Environmental Protection Agency, 2011; Infarm A/S, 2015)

2.4. Life cycle data inventory and assumptions

2.4.1. Chemical composition of slurry

The chemical composition of the excreted slurry had the following characteristics: dry matter 8.3%, organic matter 6.5%, total-N 0.63%, mineral-N 0.43%, total P 0.16% and total K 0.31% (Poulsen, 2013; Sommer et al., 2015). The composition after outdoor storage and at field application was derived from mass balances based on the initial slurry composition, degradation, inputs to the system and emissions from the system (Table S1, Supporting information (SI)).

2.4.2. In-house storage and acidification of slurry

Livestock management and manure treatment in all scenarios corresponded to Danish requirements and regulations. It was assumed that the fattening pigs consumed a standard Danish pig diet and were kept in pig houses with fully slatted floors. In the in-house acidification scenario, slurry in the pit below the slats was acidified with on average 9.7 kg concentrated sulphuric acid (96% H_2SO_4) per tonne of slurry to reach pH 5.5 on a daily basis (Sørensen and Eriksen, 2009). In the no acidification and field acidification scenarios, the slurry was left untreated during in-house storage. After an in-house storage time of approximately six weeks, slurry was pumped from the channels into an outdoor storage tank.

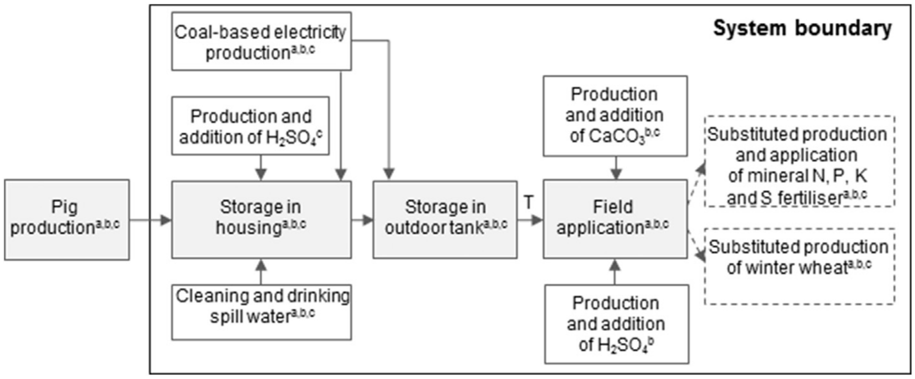

Fig. 1. System boundaries of the reference and treatment scenarios with a functional unit of 1000 kg pig slurry in Denmark. Black arrows represent mass flows; grey boxes represent the main slurry stages; dotted boxes represent substituted processes; T represents transportation; [a] is the reference scenario; [b] is the field acidification scenario; [c] is the in-house acidification scenario.

Table 1 shows the emission coefficients for the emissions analysed in the life cycle stages of the scenarios.

2.4.3. Outdoor storage of slurry

The outdoor storage tank had a PVC cover to eliminate ingress of precipitation and to reduce volatile losses. Both the acidified and non-acidified slurry remained in the outdoor storage tank for an average of six months, followed by stirring and pumping into a slurry tanker prior to land application. Pig housing and outdoor storage tanks were all assumed to be built out of concrete of such quality that it was not affected by acid (Eriksen et al., 2008; Sørensen and Eriksen, 2009).

2.4.4. Field application of slurry, field acidification and avoided fertiliser

To determine emissions associated with slurry application and soil processes, the soil-plant-atmosphere system model Daisy v. 5.20 was used (Hansen et al., 2012). In the simulations, the soil type was assumed to be a fine sandy loam soil and the climate was assumed to be that observed at a climate station in Taastrup, Denmark. Calibration of the mineralisation dynamics of the acidified and non-acidified slurry in the model was based on data from an incubation study (Gómez-Muñoz et al., 2014). It was assumed that slurry was applied to winter wheat for 100 consecutive years (see SI for more information about the set-up of the Daisy model). In the field acidification scenario, slurry was acidified with concentrated sulphuric acid (96% H_2SO_4) to pH 6.2 at the moment of application, with 5.2 kg per tonne of slurry (Nyord et al., 2013). The tractor used for slurry application was equipped with an acid tank. Acid from this tank was mixed with slurry in the hose, a few seconds before it reached the soil. In the two acidification scenarios, it was assumed that additional lime ($CaCO_3$) would have to be applied to the fields to counteract the effect of the acid on the soil pH. Petersen and Sørensen (2008) state that slurry loses its alkaline function through acidification and 300–600 kg $CaCO_3$ per hectare needs to be added to maintain soil pH. In this study, the average value of 450 kg $CaCO_3$ per hectare was applied.

Table 1
Emission coefficients during housing and storage and after field application of non-acidified, field acidified and in-house acidified slurry.

	NH_3–N kg kg N_{min}^{-1}	N_2O–N kg kg N^{-1}	NO–N kg kg N^{-1}	NO_3^-–N kg kg N^{-1}	CH_4–C kg kg OM^{-1}
Housing					
No acid, field acid	0.21[a]	0.002[b]	0.002[c]		0.005[d]
In-house acid	0.064[e]	0.002[b]	0.002[c]		0.002[d]
Storage					
No acid, field acid	0.013[f]				0.008[g]
In-house acid	0.002[f,h]				0.0004[g]
Field emissions					
No acid	0.201[i]	0.034[j]		0.111[j]	
Field acid	0.061[i]	0.036[j]		0.132[j]	
In-house acid	0.061[i]	0.036[j]		0.147[j]	
Mineral fertiliser		0.032[j]		0.133[j]	

Note: N_{min} is mineral nitrogen; OM is organic matter.
[a] 0.43 kg NH_3–N pig^{-1} (Kai et al., 2008).
[b] IPCC (2006).
[c] Dämmgen and Hutchings (2008).
[d] Based on Petersen et al. (2014a) and Sommer et al. (2007).
[e] 0.13 kg NH_3–N pig^{-1} (Kai et al., 2008).
[f] Hansen et al. (2008).
[g] Hjorth et al. (2015).
[h] 84% reduction compared to non-acidified slurry (Petersen et al., 2014b).
[i] Nyord et al. (2013).
[j] Simulation model results, NO_3^-–N is a combination of loss through drains and leaching.

Slurry was field applied in accordance with regulatory requirements (Danish Ministry of Food, Agriculture and Fishery, 2014). This directive states a yearly maximum application of 140 kg N ha^{-1} from pig slurry and a maximum of 156 kg plant-available N ha^{-1} (sum of mineral fertiliser N and plant-available manure N) for winter wheat on a sandy loam soil. The regulatory mineral N fertiliser equivalent (MFE) for pig slurry N in Denmark is 75%, regardless of the potentially higher MFE of slurry, especially in-house acidified slurry. This potentially results in higher yields when a combination of slurry and mineral fertiliser is applied instead of mineral fertiliser only. The substitution of mineral fertiliser was equal in the three scenarios. No restrictions on the application of P, K and S were assumed, but replacement was based on crop demands of 19 kg for P, 71 kg for K and 17.5 kg for S (Danish Ministry of Food, Agriculture and Fishery, 2014; SEGES, 2009). It was assumed that the marginal mineral fertilisers that were replaced were ammonium nitrate for N, ammonium sulphate for S, single super phosphate for P and potassium chloride for K. Coal was assumed to be the marginal electricity source.

Fertilisation with slurry results in higher crop yields than with mineral N fertiliser. This extra production is assumed to displace production elsewhere on the international market where it is least economically feasible. This avoided wheat production was represented by the Ecoinvent processes “wheat grains IP at farm, CH” and “wheat straw IP at farm, CH”. It should be noted that this results in relatively high GHG emissions and NO_3^- leaching compared to

Table 2
Annual per hectare fertiliser application and Daisy-simulated crop yield, crop N uptake and soil carbon sequestration for mineral fertiliser, non-acidified slurry, field-acidified slurry and in-house acidified slurry.

Scenario	Fertiliser application			MFE N	Replaced MF	Yield		N uptake		C seq.
	Mg slurry ha^{-1}	kg slurry N ha^{-1}	kg MF N ha^{-1}	%	kg MF N	Mg grain DM ha^{-1}	Mg total DM ha^{-1}	kg grain N ha^{-1}	kg total N ha^{-1}	kg C ha^{-1}
MF	–	–	156	100	–	6.8	10.8	121	143	−76
NAS	32	140	51	75	105	7.2	11.4	130	153	−44
FAS	32	140	51	75	105	7.4	11.7	137	161	−41
IAS	32	156	51	75	105	7.7	12.0	146	170	−44

Note: All values are yearly averages based on data for 100 years; MF is mineral fertiliser; NAS is no acidification scenario; FAS is field acidification scenario; IAS is in-house acidification scenario; C seq. is carbon sequestration; DM is dry matter; total DM the sum of grain DM, stem DM, leaf DM and dead DM; total N is the sum of N in grain, in stem, in leaf and in dead crop.

values chosen for the Danish case. This was because production in Denmark was assumed to alleviate production from the least profitable site, which in turn was assumed to be one with relatively high environmental losses.

The maximum arable land area that can be fertilised by 1000 kg pig slurry is 377 m^2 in the three analysed scenarios, since Danish regulations do not adjust for the potentially higher MFE of acidified slurry. The fraction of the CO_2 emissions that represents net long-term (>1 y) changes in the soil C pool are perceived as non-biogenic emissions and hence were included in the analysis. Table 2 provides an overview of the quantities of applied slurry, slurry N, and mineral fertiliser N, modelled grain and total dry matter yields, modelled N uptake by the grain and by the whole crop and modelled soil C sequestration.

2.4.5. Impacts not included

Slurry acidification can lead to an expansion of production, as regulation of livestock production intensity may partly be focused on NH_3 emissions (Danish Ministry of the Environment, 2006). Such potential consequences in terms of increased animal production are not taken into consideration in this study. Furthermore, due to a lack of data, the effect of acidification on odorous emissions could not be analysed. For further research it might be of interest to include the odour footprint of slurry acidification in line with the method developed by Peters et al. (2014).

2.5. Impact assessment

The life cycle impact assessment was carried out in accordance with the recommendations of the ILCD (Hauschild et al., 2013). Four impact categories appeared most affected by changes in slurry management and were therefore analysed and described in the results section: terrestrial eutrophication potential (TEP) in Accumulated Exceedance (AE), climate change potential (CCP) in CO_2-equivalents (kg CO_2-eq), marine water eutrophication potential (MEP) in N-equivalents (kg N-eq) and toxicity potential (TP) in Comparative Toxic Units (CTU). Accumulated Exceedance is the sum of all areas of ecosystems multiplied by the exceedance in every ecosystem (Seppälä et al., 2006).

Furthermore, an analysis of the effect of two types of regulatory N application limits in Denmark was performed. The first type tested was the modification of the plant-available N application

Table 3
Fertiliser application and Daisy-simulated crop yield, crop N uptake and soil carbon sequestration for mineral fertiliser, non-acidified slurry, field-acidified slurry and in-house acidified slurry with varying N application limits.

Scenario	Fertiliser application			Replaced MF	Yield		N uptake		C seq.	Area for spreading 1 FU
	Mg slurry ha^{-1}	kg slurry N ha^{-1}	kg MF N ha^{-1}	kg MF N	Mg grain DM ha^{-1}	Mg total DM ha^{-1}	kg grain N ha^{-1}	kg total N ha^{-1}	kg C ha^{-1}	m^2
140 kg eff. N										
MF	–	–	140	–	6.4	10.3	112	133	−82	–
NAS	32	140	35	105	6.8	11.0	121	143	−47	377
FAS	32	140	35	105	7.1	11.3	128	151	−43	377
IAS	32	156	35	105	7.5	11.8	138	162	−45	377
170 kg eff. N										
MF	–	–	170	–	7.0	11.1	128	151	−72	–
NAS	32	140	65	105	7.4	11.6	137	161	−42	377
FAS	32	140	65	105	7.6	11.9	143	168	−40	377
IAS	32	156	65	105	7.7	12.1	151	176	−45	377
200 kg eff. N										
MF	–	–	200	–	7.4	11.6	141	165	−68	–
NAS	32	140	95	105	7.7	11.9	149	174	−41	377
FAS	32	140	95	105	7.7	12.0	154	179	−40	377
IAS	32	156	95	105	7.8	12.2	160	186	−46	377
250 kg eff. N										
MF	–	–	250	–	7.7	11.9	154	179	−67	–
NAS	32	140	145	105	7.8	12.1	162	188	−41	377
FAS	32	140	145	105	7.8	12.2	165	191	−41	377
IAS	32	156	145	105	7.9	12.3	169	196	−47	377
170 kg slurry-N										
MF	–	–	156	–	6.8	10.8	121	143	−76	–
NAS	39	170	28.5	127.5	7.3	11.5	132	155	−35	310
FAS	39	170	28.5	127.5	7.6	11.9	140	165	−32	310
IAS	39	189	28.5	127.5	7.8	12.2	151	176	−39	310

Note: All values are per year; eff. N is crop specific effective N application limit; MF is mineral fertiliser; FU is functional unit (1000 kg slurry); NAS is no acidification scenario; FAS is field acidification scenario; IAS is in-house acidification scenario; C seq. is carbon sequestration; DM is dry matter; total DM the sum of grain DM, stem DM, leaf DM and dead DM; total N is the sum of N in grain, in stem, in leaf and in dead crop.

limits, which for winter wheat has a current value of 156 kg N ha^{-1}. This value was altered to 140, 170, 200 and 250 kg N ha^{-1}. In all cases the maximum of 140 kg total-N from slurry was applied, with the amount of mineral fertiliser applied adjusted to balance the difference between effective slurry total-N and the plant-available N limit. The second type of modification of the regulatory N application limits was an alteration of the maximum allowed slurry total-N application. The value of 140 kg total-N ha^{-1} from pig slurry, as specified in Danish regulations, was changed to 170 kg total-N ha^{-1} from pig slurry (as specified by the EU Nitrates Directive of the European Commission (1991)). In this second type of modification, 156 kg N ha^{-1} for winter wheat was kept constant as the plant-available N application limit in both cases. Table 3 provides an overview of the quantities of applied slurry, slurry N and mineral fertiliser N, modelled grain and total dry matter yields, modelled N uptake by the grain and by the whole crop, modelled soil C sequestration and modelled area for the application of 1000 kg slurry. All values are expressed on a per hectare basis, apart from the modelled area for application of 1000 kg slurry.

2.6. Sensitivity analysis

A sensitivity analysis was performed to examine the influence of changes in selected agricultural management choices and model parameters. Main parameters affecting impact potentials were found to be the emission coefficients for NH_3 emissions. The lowest and highest possible values for NH_3 emission coefficients from housing, storage, and field application of acidified and non-acidified slurry were estimated based on the literature (Table 4). A scenario analysis was performed in which all the low values were used at the same time to see the result of low NH_3 emissions and all the high estimates were used to test the effect of high emissions. Furthermore, the effect of altering the process used to model avoided wheat production was analysed. This was done by using another Ecoinvent process with lower nitrate leaching values, “wheat grains conventional, Saxony-Anhalt, at farm, DE”.

3. Results

3.1. Terrestrial eutrophication potential

Environmental savings due to the avoided production of mineral fertiliser and avoided crop production are represented by negative values in Fig. 2. Net field emissions are the increases in emissions resulting from the replacement of mineral N fertiliser by slurry. The housing stage was the main contributor to the terrestrial eutrophication potential (TEP) 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. Results are shown for TEP, but the pattern shown is similar to that of terrestrial acidification potential since emissions of NH_3 were the main contributor to these two impact categories.

Table 4
Lowest and highest reasonable emission coefficients from literature for NH_3.

	NH_3 housing kg pig^{-1}	NH_3 storage kg kg N^{-1}	NH_3 field kg kg N_{min}^{-1}
No acidification			
Low	0.38[a]	0.013[b]	0.182[d]
High	0.49[a]	–	0.22[d]
Field acidification			
Low	0.38[a]	0.013[b]	0.039[d]
High	0.49[a]	–	0.083[d]
In-house acidification			
Low	0.07[a]	0.001[a]	0.039[d]
High	0.19[a]	0.002[c]	0.083[d]
Mineral fertiliser			
Low	–	–	–
High	–	–	–

Note: N_{min} is mineral nitrogen.
[a] Kai et al. (2008).
[b] Hansen et al. (2008).
[c] Dai and Blanes-Vidal (2013).
[d] Nyord et al. (2013).

3.2. Climate change potential

All scenarios showed a net positive climate change potential (CCP), no matter how slurry was treated (Fig. 2). The “net emissions from the field” process contains modelled emissions from the Daisy model. 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).

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 slurry in outdoor storage (CH_4). Negative emissions showed 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. These emissions were only 36% of those for the no acidification and field acidification scenarios.

3.3. Marine water eutrophication potential

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 (Fig. 2). 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.

3.4. Toxicity potential

Human non-carcinogenic toxicity potential and total ecotoxicity potential showed similar patterns for the three scenarios analysed (see Table S2, SI). Field application of the slurry fractions, and especially zinc accumulation in agricultural soil, contributed most to TP, but in all scenarios the same amount of slurry was handled and applied to the field. Zinc and copper concentrations in pig

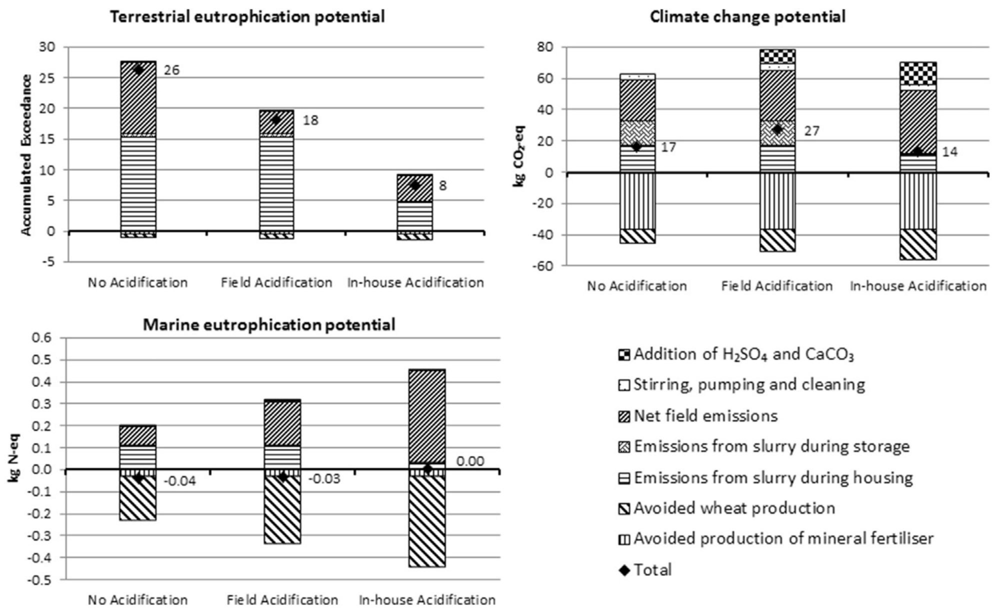

Fig. 2. Impact assessment of the no acidification, field acidification and in-house acidification scenarios, divided into stages compared to application of mineral fertiliser alone.

slurry were high compared to other slurry types, due to the addition of these elements to the pig feed, but copper did not have the same impact potential on toxicity as zinc. Furthermore, it was assumed that the same amount of mineral fertiliser was replaced in the three scenarios, and therefore the TPs from the mineral fertiliser were equal in all scenarios.

3.5. Role of regulation

Changes in regulatory crop-specific plant-available N application limits resulted in changes in CCP and MEP (Fig. 3), while for TEP and TP this variation had no effect. The insensitivity of the latter impact category resulted from the fact that the substances contributing to toxicity were not affected by plant-available N application limits. The amount of NH_3 emitted, which results in terrestrial eutrophication, was also unaffected by increased plant-available N application limits because only the amount of mineral fertiliser applied increased. When the crop-specific N application limits for winter wheat were reduced from 156 kg ha^{-1} to 140 kg ha^{-1}, the in-house acidification scenario in particular showed a reduction in CCP and MEP. This scenario showed the largest yield response (Table 3) and became the most favourable scenario for all the impact categories analysed, as it already showed the lowest TEP (see Fig. 2). When plant-available N application limits were increased, CCP increased for all scenarios, and the in-house acidification scenario showed a small but consistently higher impact potential than the no acidification scenario. With all plant-available N application limits, the field acidification scenario showed the highest CCP, mainly caused by emissions from the production and addition of sulphuric acid and lime. MEP increased for all scenarios when higher plant-available N application limits were allowed. The in-house acidification scenario in particular showed a large increase compared to the current value of 156 kg effective N ha^{-1}. When the regulations regarding the amount of slurry total-N application per hectare were altered from the current Danish level of 140 kg to the EU Nitrates Directive level of 170 kg (see the right-hand part of Fig. 3), the effect on CCP, MEP and terrestrial acidification potential remained almost the same. As Table 3 shows, the greatest effect of increasing the slurry total-N application limit from 140 to 170 kg ha^{-1} is the area that is needed for the application of 1000 kg slurry: this area decreased from 377 m^2 to 310 m^2.

3.6. Sensitivity analysis

High NH_3 emission coefficients led to a higher TEP, as NH_3 is the main contributor to this impact category (Fig. 4). In contrast, high NH_3 emission coefficients led to lower CCP and MEP, because more N was emitted as NH_3 and less N was left to be emitted as N_2O or leached as NO_3^-. The results showed that NH_3 emission coefficients did have an influence on all impact categories analysed, but the scenarios showed equal trends. The sensitivity analysis on the choice of avoided wheat production process showed that MEP was the main impact category influenced by the change. The impact potentials for TEP increased by 0.5% for the scenario without acidification to 4.0% for the in-house acidification scenario, while CCP decreased by 0.9% for the field acidification scenario to 1.8% for the in-house acidification scenario. The MEP increased for all scenarios, with 0.11 kg N-eq for the scenario without acidification, 0.17 kg N-eq for the scenario with field acidification and 0.23 kg N-eq for the in-house acidification scenario (Fig. 5). The ranking of scenarios was not altered by the choice of process describing avoided wheat production, but the impact potentials of the acidification scenarios increased more than in the scenario without acidification, making acidification less favourable than no treatment.

4. Discussion

The decreased environmental burdens of slurry acidification, particularly in-house acidification, were mainly due to large reductions in NH_3 emissions. A considerable advantage of in-house acidification compared to acidification in the field is that NH_3 emissions are reduced throughout the manure management chain. With respect to CCP, the reduction in GHG emissions during storage of acidified slurry in animal housing and in an outdoor storage tank counterbalance additional GHG emissions due to the addition of

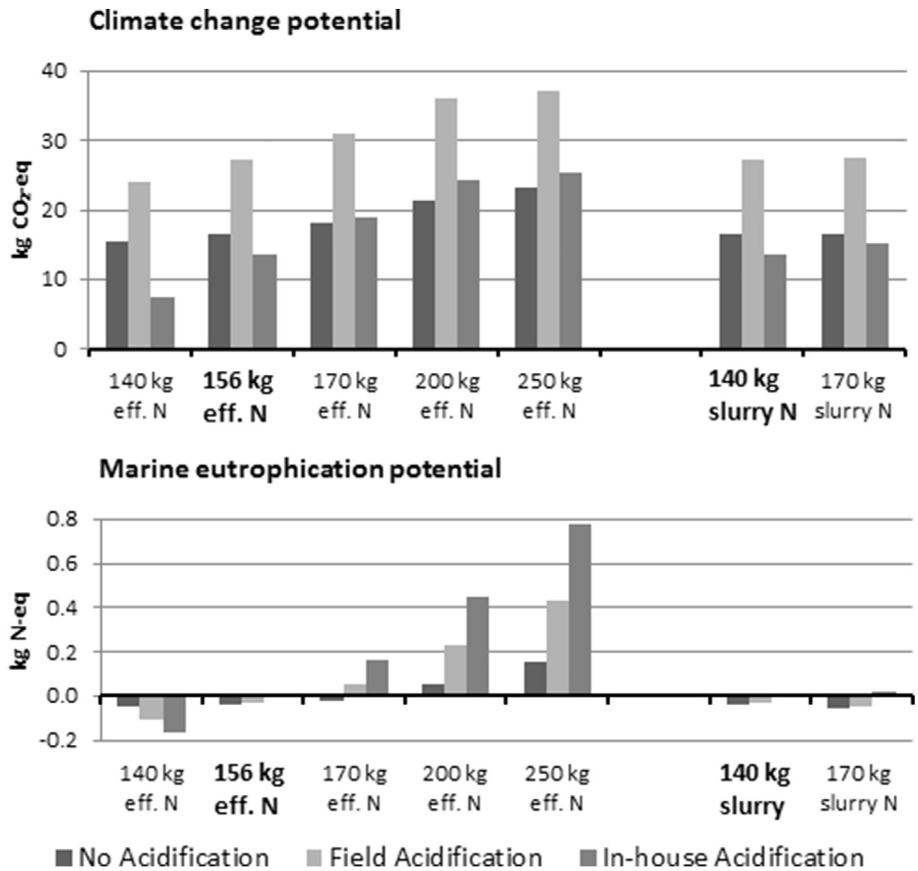

Fig. 3. The variation in climate change potential and marine eutrophication potential with increasing crop-specific effective N application limits (columns 1 to 5, all comply with the slurry total-N application limit of 140 kg N $(ha \cdot yr)^{-1}$) and the Danish and EU slurry total-N application limits (columns 6 and 7, all comply with the crop specific effective N application limit of 156 kg $(ha \cdot yr)^{-1}$). Columns 2 and 6 repeat values from Fig. 2, current N regulatory values in Denmark, and are presented in bold.

sulphuric acid and lime. However, this is not the case for field acidification, the scenario with the highest CCP.

Slurry acidification is so far only common practice in Denmark and the dissemination of slurry acidification technology to other countries will depend on legislation in the country of interest (Fangueiro et al., 2015). Denmark is an example of a country with an intensive agricultural production system and with stringent environmental regulations (Van Grinsven et al., 2012). In order to reduce losses of N, economically sub-optimal N fertilisation limits were introduced in 1998. This regulatory regime has a considerable

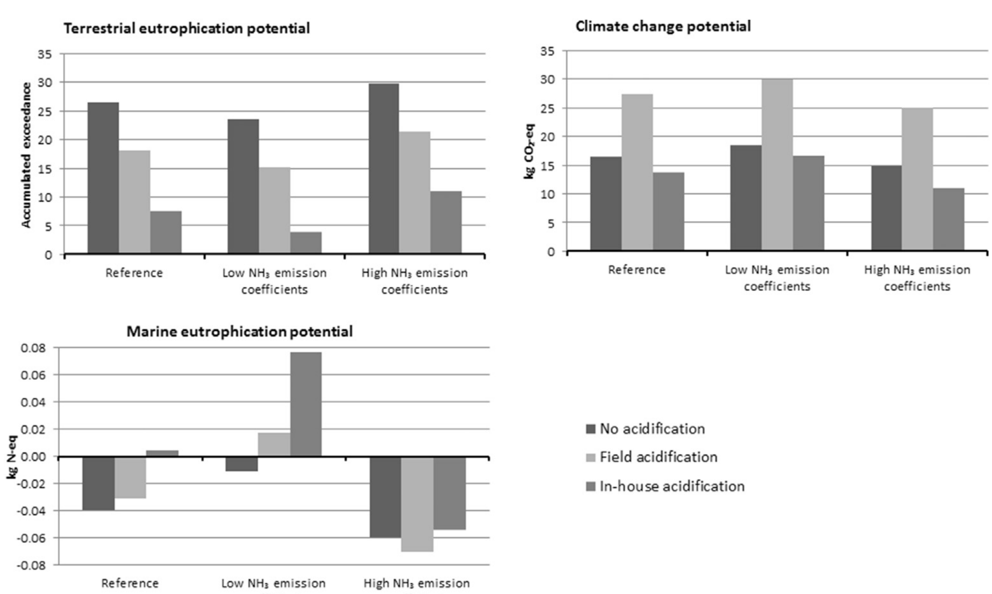

Fig. 4. Sensitivity analysis for NH_3 emission coefficients from slurry in housing, in storage and on the field. Terrestrial eutrophication potential (TEP, in Accumulated Exceedance), climate change potential (CCP, in kg CO_2-eq) and marine eutrophication potential (MEP, in kg N-eq) for reference, low and high NH_3 emission coefficients.

influence on the environmental impacts of slurry acidification. Farmers applying acidification technology are not required to adjust N application to account for the higher N content in acidified slurry, *i.e.* the regulatory MFE value is the same as for non-acidified slurry. The higher amounts of available N applied mean that crop yields increase when acidified slurry is applied. These higher yields provide a strong economic incentive for farmers to invest in acidification technology that at the same time will reduce NH_3 emissions. If in the future the regulatory MFE of acidified slurry were increased to take the increased retention of N into account, these yield advantages could be lost and the farmers would be much less inclined to apply acidification technology. In contrast, farmers in other countries with different regulatory policies may not have the same economic incentive for applying the acidification technology.

The underlying mechanism for the higher N_2O emission from the acidified slurry (see Table 1) is mainly that ammonium is retained in the system as a consequence of the acidification. This leaves more ammonium in the system to be nitrified and denitrified, which are the processes in Daisy leading to the formation of N_2O.

Although the in-house acidified slurry has a lower C content at the moment of field application due to high emissions of CO_2 during acidification (mainly biogenic, since it is derived from the degradation of organic matter in slurry), the simulations in this study showed that the net soil C sequestration is similar to that of non-acidified and field-acidified slurry. This is because the C in carbonates is the first C source to be emitted after field application. Acidification of slurry only shifts the emission of CO_2 from carbonates from the soil to the manure management chain, and the net effect after 100 years is equal for the three scenarios.

In life cycle assessments of agricultural systems, dealing with natural, dynamic processes remains a challenge, as LCA models are based on a linear approach. Field processes and accompanying emissions are particularly difficult to capture in a simplified linear model. By using a process-based simulation model to assess losses to the environment from field-applied slurry, the nonlinearity of the processes was embraced, but in doing so it should be made plain that these results are context-specific. This dependence on context is likely to be a feature of any LCA dealing with complex biological systems and is a matter that deserves greater attention.

If the reduction of NH_3 emissions is the only focus, acidification appears to be a favourable slurry treatment option as NH_3 emissions were reduced by up to 71% compared to no acidification. However, as discussed above, slurry application regulations had a major influence on whether acidification was favourable for other emission potentials. Furthermore, slurry acidification in combination with other treatment technologies such as anaerobic digestion and solid–liquid separation might show favourable synergies (Fangueiro et al., 2015).

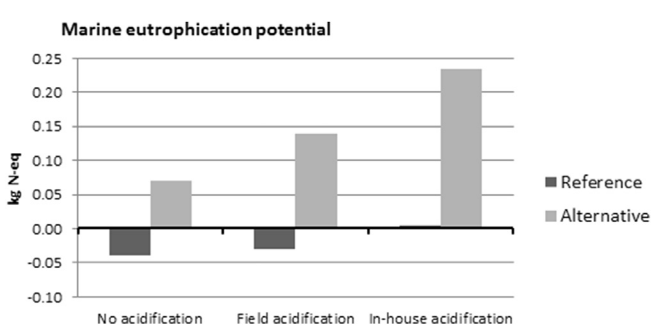

Fig. 5. Marine eutrophication potential (MEP, in kg N-eq) in the sensitivity analysis for reference Ecoinvent process ("wheat grains IP at farm, CH") used for avoided wheat production process and the alternative Ecoinvent process ("wheat grains conventional, Saxony-Anhalt, at farm, DE").

5. Conclusions

Acidification has the potential to reduce the environmental impacts of animal slurry, but it will only be widely implemented when it is economically advantageous for the farmer as well as advantageous for the environment. The mechanisms of environmental regulations need to provide a strong economic incentive for the farmers, in the form of subsidies or possibilities to increase profits, if the technology is to become more widely applied.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jclepro.2016.04.014.

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