Scientific assessment on field acidification using the SyreN acidification technology with different slurry application techniques – a theoretical approach

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The history of field acidification

Denmark has a large intensive livestock production consisting of 1.55 million cattle and 12.3 million pigs (Danmarks statistik, 2017) with an assumed yearly production of 35 million m^3 slurry. The handling of the produced slurry releases airborne ammonia (NH_3) (Sutton, Erisman, Dentener, & Moller, 2008). Deposition of NH_3 causes acidification and eutrophication of natural ecosystems (Fangmeier, Hadwiger-Fangmeier, Eerden, & Jäger, 1994). Furthermore NH_3 contributes to airborne PM2.5 and PM10 particles that can be a health hazard (Erisman & Schaap, 2004). Due to the risk of NH_3 emission, Denmark has in accordance to the Goteborg protocol, been obligated to reduce the NH_3 emission by approx. 20.000 tons (or 24% of the 2005 emission) within the year 2020 (Gothenburg protocol, 2005). As a part element to reach the goal, a new general requirement to inject slurry on grasslands and soil without growing crops was introduced in 2011 (Husdyrgødningsbekendtgørelsen, 2017). As an addition to the new legislation, technologies accepted on the Danish environmental protection agencies - environmental technology list, can replace the injection demands if the technology is equal or better at reducing NH_3 (25% reduction, compared to band hose). Based on a VERA verification, the SyreN field acidification technology, was accepted on the technology list with a reduction effect of 49% (VERA, 2012) and 40% (Environmental technology list, 2017) accordingly for cattle and pig slurry. As a general requirement acidifying to pH 6.4 or lower, was therefore accepted as supplementary technology to injection.

In 2012 approximately 10% and in 2015 20% of the Danish slurry was acidified, where 50% was acidified using the SyreN field acidification technology. It has therefore become the most widely used technology.

Introduction to acidification

So far the only commercially used chemical to acidify slurry is concentrated sulphuric acid (H_2SO_4). The acid is a waste product from the industry and therefore has a very competitive prize compared to other acids. Furthermore the sulphur content is a mineral fertilizer for crops (Marschner, 2012), which is attractive to farmers and leaves no waste. Due to practical reasons, slurry acidification only takes place in three different ways: Acid added to the slurry in the animal housing (designated “barn acidification”), acid added to the slurry in the storage tank (designated “storage acidification”) and acid added to the slurry during field application (designated “field acidification”) (Fangueiro, Hjorth, & Gioelli, 2015). Which method is the best, depends on where in the chain of slurry handling there is a need for NH_3 reduction; the earlier in the chain, the more reduction can be obtained. Barn acidification has the feature that it is the best NH_3 emission reducing technology since it reduces emission at the source. Storage acidification has the feature that it reduces NH_3 emission from the storage and reduces emission during application of slurry to the field. Field acidification only reduces NH_3 emission during field application, but does so with a much lower acid consumption. Acid consumption is much higher in barn- and storage acidification, because pH 5.5 is required to make the slurry pH storage stable. A storage stable pH is required because acidification to levels above, increases the risk that pH reestablishes at the initial level. As a general rule of thumb, 7.5 L acid/m^3 slurry is required in barn- and storage acidification (Stevens, Laughlin, & Frost, 1989) and 2.5 L/m^3 for field acidification (Seidel, Pacholski, Nyord, Vestergaard, & Kage, 2014). Fermented slurry (slurry from biogas installations) is an exception; in comparison to unfermented slurry it requires a lot of acid to reduce slurry pH. As a general rule of thumb, 5 L/m^3 with field acidification is required to reach pH 6.4, and the other technologies are far above reasonable use.

Slurry acidification technologies and NH_3 reduction

The NH_3 emission reduction is typically measured in percentage compared to the emission that would have been without reduction. The NH_3 reduction is measured in percentage because total NH_3 emission is highly variable and is influenced by several physical parameters such as weather, crop height, soil parameters, slurry type, slurry pH, etc. (Huijsmans, 2003). When acidifying slurry, the maximum reduction potential depends on the slurries initial pH, the higher the pH, the higher the reduction potential (Nyord, Liu, Eriksen, & Adamsen, 2015). Acidification NH_3 emission reduction potentials have been reviewed in (Fangueiro et al., 2015) and give the following reduction potentials for the individual technologies: Barn acidification (50-70%), storage acidification (50-88%) and field acidification (pig: 40-80% and cattle: 15-80%). Field acidification has a high variety of reduction potentials because of the differences in the initial pH value and the targeted pH value. But, NH_3 emission reduction percentage when acidifying slurry is expected to be comparable between slurries with the same initial pH.

Acidification effect on NH3 reduction

Based on 5 NH_3 emission trials with SyreN field acidification (Seidel, 2013) presented in (Seidel, Pacholski, Nyord, & Kage, 2012), the following NH_3 emission reduction potentials have been modeled accordingly for field acidification to pH level 6.0 and 6.4 (See figure 1).

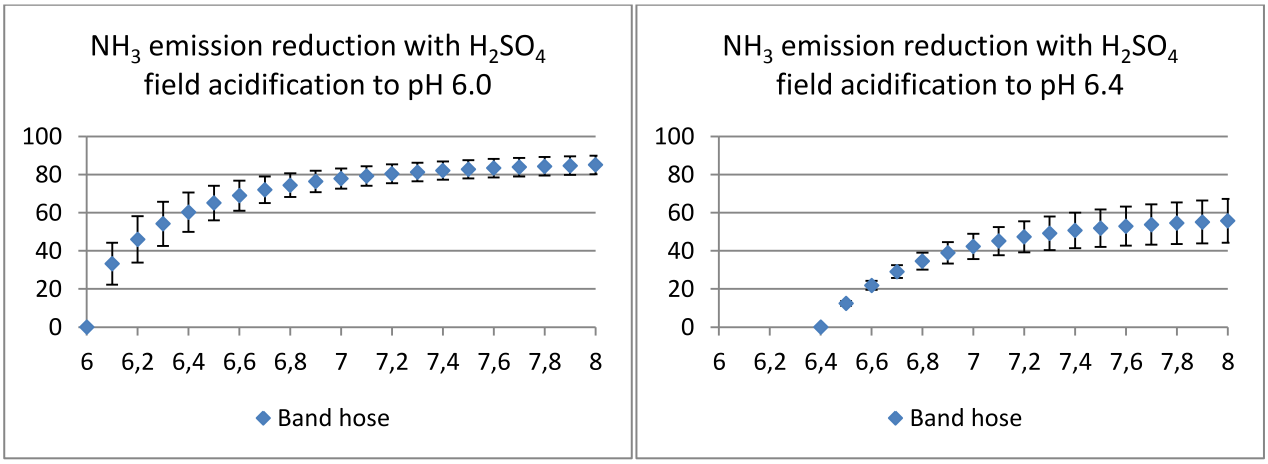

Figure 1: The graph to the left shows the NH_3 emission reduction potential for slurry pH values between 6.1 and 8, when acidifying slurry with H_2SO_4 to pH 6.0 using band hoses. And the graph to the right shows the reduction potential for slurry pH values between 6.1 and 8, when acidifying slurry with H_2SO_4 to pH 6.4 using band hoses. These are then indicated with standard error bars to show the realistic variation.

The model is a simple assessment of the 5 trials. For each trial a fitted second degree trend line was created from which pH and kg NH_3 emission could be read. The trend line was then fixed to 25 kg NH_3 emission at a certain pH (set as the initial pH), from the trend lines curve another pH (the target pH) could be read and a kg NH_3 emission identified. The percentage difference between the two NH_3 emissions is the emission reduction. All 5 emission trials showed good correlation using this method.

Average slurries have a pH level around 7.1 (Seidel et al., 2012) but with normal varieties between 6.8 and 7.8, fermented slurries normally has a pH above 7.6. The pH value 7.1 is ideal to use as a standard reference since it is the expected average pH in all unfermented slurries and as shown in figure 1, there is no significant NH_3 emission reduction above 7.1 to pH 6.0 or 6.4. From the graph above it is estimated that field acidification from pH 7.1 to pH 6.0 can reduce NH_3 emission with 79% (+/- 5), if acidifying to pH 6.4 a reduction of 45% (+/- 7) can be achieved. Fermented slurry has the potential NH_3 emission reduction of 83% (+/- 5) to pH 6.0, 53% (+/- 10) to pH 6.4, and 22% (+/- 10) to pH 7.0 (results not shown). The NH_3 emission reduction potential for fermented slurry to pH 6.4 and 7.0 has high standard errors due to lack in data acquisition in that area.

Field acidification with other application technologies than band hose

The acidification technology is generally applicable to all slurry application technologies, thus it has only been thoroughly investigated for its NH_3 emission reduction potential with band hose. The reason for this is that it's still a new technology that has been mainly used to replace the requirements of injection according to the Danish legislation. Thus, 23 experiments with nitric acid (HNO_3) slurry acidification and broadcast was made in the 90's (Bussink, Huijsmans, & Ketelaars, 1994) and showed good NH_3 reduction results similar to those shown in figure 1 above. 3 of the 23 experiments are relatable to field acidification because the acid was added just before application in the field. These have been modeled in the same way as above and the results are shown in figure 2 below.

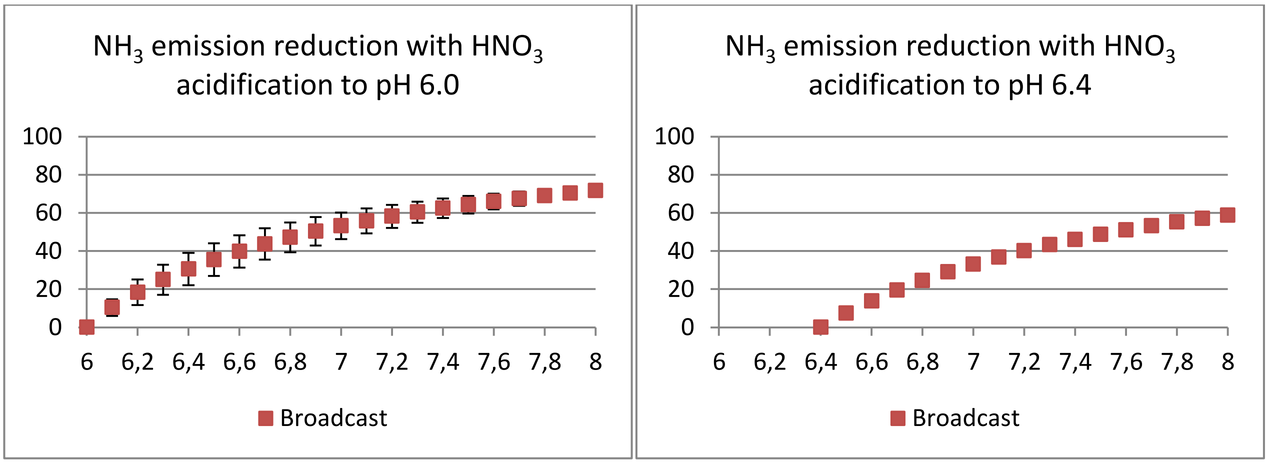

Figure 2: The graph to the left shows the NH_3 emission reduction potential for slurry pH values between 6.1 and 8, when acidifying slurry with HNO_3 to pH 6.0 using broadcast. And the graph to the right shows the NH_3 reduction potential for slurry pH values between 6.1 and 8, when acidifying slurry with HNO_3 to pH 6.4 using broadcast. These are then indicated with standard error bars to show the realistic variation.

By direct comparison, acidification to pH 6.4 is identical in both models. However, acidification to pH 6.0 is modeled a bit lower than with the H_2SO_4 field acidification. It is of course impossible to directly compare the two, since there are approx. 20 years between the two measurements and both NH_3 measuring practices and computer simulations have greatly improved since then. Another experiment (Stevens, Laughlin, & Frost, 1992) measured NH_3 emission with broadcast and acidification with both NHO_3 and H_2SO_4 for comparison. This experiment showed that NH_3 could be reduced equally efficient using both acids, and reduced emission by 75% at pH 6.5 and 90% at pH 6.0. Just for a notice, the N content increased by 2 kg m^{-3} slurry using HNO_3 to acidify to pH 6.5, which is a concern to comply with the nitrate directive. The similar relations between the two acids demonstrate that acidification can reduce NH_3 emission, and that acidification can be used with different application technologies to reduce NH_3 emission up to 85%-90%. However, acidification with other application technologies, such as injection or trailing shoe is still not thoroughly investigated. But, the percentage NH_3 emission reduction is expected to be the same for all application technologies. The main difference between the slurry application technologies is the slurries surface exposure to air after application. Slurry that has been broadcasted has a high exposure to the air due to a wide spread onto the field and injection has a low exposure due to application in a drilled channel in the field (Hansen, Sommer, & Madsen, 2002). Acidification is a chemical change of the slurry and the percentage reduction should therefore not be affected by the application technique. It is expected that acidification with broad spread will have a profound effect.

Technologies that can replace incorporation 4 hours after broad spread

In Germany there is a requirement to incorporate applied slurry into the soil within 4 h. The incorporation effectively reduces total NH_3 emission. The emission reduction effect of incorporation has been presented in (Rösemann et al., 2017). Based on these results, the following NH_3 emission reductions when incorporating slurry within 4 h after application with broad spread are for accordingly cattle and pig: 48% and 64%. See table 1 below for NH_3 emission reduction results. The emission factor is an averaged value that covers a great variety. NH_3 emission is affected by e.g. weather and the realistic loss of NH_3 is from 0.21 to 0.98 kg N kg^{-1} N when using broadcast (Bussink et al., 1994).

Table 1: Results from (Rösemann et al., 2017). The table shows the NH_3 emission factor (based on the total ammonium content), from broadcast and trailing hoses with incorporation up to 48 hours after slurry application. The table also shows the NH_3 emission from trailing shoe and injection.

Application type	Emission factor (kg kg^{-1})		Reduction percentage compared to broadcast without incorporation	
	Cattle	Pig	Cattle	Pig
Broadcast, without incorporation	0,50	0,25	**0%**	**0%**
Broadcast, incorporation ≤ 1 h	0,10	0,04	80%	84%
Broadcast, incorporation ≤ 4 h	0,26	0,09	**48%**	**64%**
Broadcast, incorporation ≤ 6 h	0,35	0,11	30%	56%
Broadcast, incorporation ≤ 8 h	0,40	0,13	20%	48%
Broadcast, incorporation ≤ 12 h	0,43	0,16	14%	36%
Broadcast, incorporation ≤ 24 h	0,46	0,21	8%	16%
Broadcast, incorporation ≤ 48 h	0,50	0,25	0%	0%
Broadcast, vegetation	0,50	0,25		

Broadcast, grassland	0,60	0,30		
Trailing hose, without incorporation	0,46	0,175	8%	30%
Trailing hose, incorporation ≤ 1 h	0,04	0,02	92%	92%
Trailing hose, incorporation ≤ 4 h	0,15	0,06	70%	76%
Trailing hose, incorporation ≤ 6 h	0,20	0,08	60%	68%
Trailing hose, incorporation ≤ 8 h	0,24	0,0925	**52%**	**63%**
Trailing hose, incorporation ≤ 12 h	0,30	0,11	40%	56%
Trailing hose, incorporation ≤ 24 h	0,39	0,14	22%	44%
Trailing hose, incorporation ≤ 48 h	0,46	0,17	8%	32%
Trailing hose, short vegetation	0,50	0,25		
Trailing hose, beneath vegetation	0,35	0,125		
Trailing hose, grassland	0,54	0,21		
Trailing shoe	0,36	0,12	**28%**	**52%**
Injection technique	0,24	0,06	**52%**	**76%**

Based on these results; the technologies that can replace broadcast with incorporation after 4 h is: trailing hoses with incorporation within 8 h, which have a reduction percentage of 52% and 63% for cattle and pig accordingly, and injection that has a reduction percentage of 52% and 76% for cattle and pig accordingly.

Acidification levels that could replace the incorporation requirement

Based on the technologies that would require incorporation (broadcast, trailing hose and trailing shoe) different pH requirement can be calculated, so that applying slurry can be just as effective at reducing NH_3 emission as broadcast with incorporation after 4 h. Since acidification works as a percentage reduction, the percentage reduction from the application types to broadcast with incorporation within 4 h must be calculated. The difference in percentage is listed in table 2 below.

Table 2: Additional reduction requirement for the application types to reach the same NH_3 emission reduction as broadcast with incorporation within 4 h.

Application type	Additional reduction percentage required to replace incorporation within 4 h requirement	
	Cattle	Pig
Broadcast	48%	64%
Trailing hose	43%	49%
Trailing shoe	28%	25%

Cattle

Based on results from (Rösemann et al., 2017), broadcast with cattle slurry and incorporation within 4 h, has an NH_3 emission reduction of 48%. Field acidification to pH 6.4 with cattle slurry has already been verified with VERA, and shown a reducing effect of 49% with trailing hoses. Since broadcast and trailing hose application with cattle slurry has similar NH_3 emissions (0.5 kg kg^{-1} and 0.46 kg kg^{-1} accordingly) table 1, means that field acidification to pH 6.4 has the potential to replace the incorporation requirement.

Trailing shoe is more effective at reducing NH_3 emission than trailing hoses (0.36 kg kg^{-1} and 0.46 kg kg^{-1} accordingly), see table 1. The reduction requirement to be as good as the incorporation requirement is 28%. With an acidification from 7.1 to 6.6, an NH_3 reduction of average 30% (+/- 7) is achieved. This should be the minimum pH requirement for acidification with cattle slurry and trailing shoe.

Pig

Based on results from (Rösemann et al., 2017), broadcast with pig slurry and incorporation within 4 h, has an NH_3 emission reduction of 64%. The VERA verification on pig slurry with acidification to pH 6.4 has a reduction of 40%. This pH level is therefore not good enough to replace the incorporation requirement after broadcast, or replace incorporation after trailing hose. However, it is more than sufficiently for trailing shoe. To reach at least 64% reduction with broadcast, field acidification needs to be reduced from pH 7.1 to 6.1, which will give a 70% (+/- 5) reduction, alternatively reduction to pH 6.2 gives 61% (+/- 6). To reach the 48% reduction requirement with trailing hose, field acidification needs to be reduced from pH 7.1 to 6.3, which will give a 53% (+/- 7). To reach the 25% reduction requirement with trailing shoe, field acidification needs to be reduced from pH 7.1 to 6.6, which will give a reduction of 30% (+/- 7).

Summary

Application type	Can replace the incorporation requirement		pH level required to replace the incorporation requirement	
	Cattle	Pig	Cattle	Pig
Broadcast, without incorporation	No	No	6.4	6.1
Broadcast, with incorporation within 4 h	Yes	Yes	-	-
Trailing hose, without incorporation	No	No	6.4	6.3
Trailing hose, with incorporation within 8 h	Yes	Yes	-	-
Trailing shoe	No	No	6.6	6.6
Injection technique	Yes	Yes	-	-

References

Bussink, D. W., Huijsmans, J. F. M., & Ketelaars, J. J. M. H. (1994). Ammonia volatilization from nitric-acid-treated cattle slurry surface applied to grassland. *Netherlands Journal of Agricultural Science, 42*(2), 293-309.

Danmarks statistik. (2017). Husdyr (http://www.dst.dk/da/Statistik/emner/erhvervslivets-sektorer/landbrug-gartneri-og-skovbrug/husdyr) Retrieved 5 june, 2017

Environmental technology list. (2017). http://eng.mst.dk/topics/agriculture/environmental-technologies-for-livestock-holdings/land-applied-manure/ Retrieved 5 june, 2017

Erisman, J. W., & Schaap, M. (2004). The need for ammonia abatement with respect to secondary PM reductions in Europe. *Environ Pollut, 129*(1), 159-163.

Fangmeier, A., Hadwiger-Fangmeier, A., Eerden, L. V. d., & Jäger, H. J. (1994). Effects of atmospheric ammonia on vegetation - a review. *Environ Pollut, 86*, 43-82.

Fangueiro, D., Hjorth, M., & Gioelli, F. (2015). Acidification of animal slurry--a review. *J Environ Manage, 149*, 46-56. doi: 10.1016/j.jenvman.2014.10.001

1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone to the Convention on Long-range Transboundary Pollution (2005).
Hansen, M. N., Sommer, S. G., & Madsen, N. P. (2002). Reduction of ammonia emission by shallow slurry injection. *Journal of Environmental Quality, 32*(3), 1099-1104.
Huijsmans, J. F. M. (2003). Manure application and ammonia volatilization *PHD thesis, Wageningen University*.
Husdyrgødningsbekendtgørelsen, BEK nr 374 af 19/04/2017 (2017).
Marschner, P. (2012). *Mineral nutrition of higher plants* (Vol. 3): Acedemic press.
Nyord, T., Liu, D., Eriksen, J., & Adamsen, A. P. S. (2015). Effect of acidification and soil injection of animal slurry on ammonia and odour emission. *Ramiran article*.
Rösemann, C., Haenel, H.-D., Dämmgen, U., Freibauer, A., Döring, U., Wulf, S., . . . Osterburg, B. (2017). Calculations of gaseous and particulate emissions from German agriculture 1990 – 2015 : Report on methods and data (RMD) Submission 2017. *Thünen Report 46*.
Seidel, A. (2013). [Personal communication: Results from field acidification NH3 emission trials at marsch and jyndevad].
Seidel, A., Pacholski, A., Nyord, T., & Kage, H. (2012). Erhöhung der N-Effizienz aus Gülle und Gärresten durch Ansäuern Güstow.
Seidel, A., Pacholski, A., Nyord, T., Vestergaard, A., & Kage, H. (2014). Reduction of ammonia losses after spreading of cattle slurry to grassland by acidification and injection. *Summary of two years experiments*.
Stevens, R. J., Laughlin, R. J., & Frost, J. P. (1989). Effect of acidification with sulphuric acid on the volatilization of ammonia from cow and pig slurries. *Journal of Agricultural Science, 113*, 389-395.
Stevens, R. J., Laughlin, R. J., & Frost, J. P. (1992). Effect of separation, dillution, washing and acidification on ammonia volatilization from surface-applied cattle slurry. *Journal of Agricultural Science, 119*, 383-389.
Sutton, M. A., Erisman, J. W., Dentener, F., & Moller, D. (2008). Ammonia in the environment: from ancient times to the present. *Environ Pollut, 156*(3), 583-604. doi: 10.1016/j.envpol.2008.03.013
VERA. (2012). *VERA verification statement (SyreN)*.