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Expertise on the application of ammonia abatement techniques through "acidification of liquid manure" and its effects on soil and environment

Final Report

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Expertise on the application of ammonia abatement techniques through "acidification of liquid manure" and its effects on soil and environment

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The aim of the report is therefore to analyse the "Acidification of liquid manure" scientifically and technically more profoundly than before. The focus of the evaluation is on the effectiveness and environmental compatibility of this procedure. However, application technology and legal aspects will also be considered.

The results should flow directly into the process of the evaluation in the context of the UNECE CLRTAP. Information provided in advance was already presented to the UNECE TFRN in October 2018. In addition, the results of the project on the implementation of the European NEC Directive in Germany are to be incorporated into the development of the National Programme for Air Pollution Control. New findings from the report should also support the TA-Luft adaptation process.

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Summary

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In particular, the effectiveness and environmental compatibility of liquid manure acidification are to be assessed. In addition, a first overview of the legal classification of the procedure is given. The results can be summarised as follows:

1. The strong NH_3 emission-reducing effect of the acidification of liquid manure with H_2SO_4 has been proven beyond doubt. Acidification is one of the most effective reduction measures in the stable, during liquid manure storage and during spreading. During spreading, reductions of NH_3 outgassing are achieved which are comparable to those of liquid manure injection.
2. The changes in the manure properties induced by acidification lead to an overall improvement in the availability of the main nutrient elements N, P, Mg and Ca contained in the manure as well as to a reduced environmental impact due to nitrate leaching and nitrous oxide gas emission from the soil.
3. A quantification of the effects of manure acidification on the acid neutralisation capacity of soils shows that the effects of manure acidification on the pH buffer of soils are manageable with the available agricultural techniques.
4. Nutrient supply, growth and yield of crops are rather positively influenced by the acidification of liquid manure with H_2SO_4. Negative effects, such as oversupply of sulphur, can be avoided by farm specific adjustments.
5. According to the current state of literature, serious negative effects of acidification of liquid manure with H_2SO_4 on other environmental media are not to be expected.
6. In addition to the reduction of ammonia emissions, the acidification of liquid manure also reduces the production of the greenhouse gases methane and nitrous oxide.
7. The acidification of liquid manure in stables, liquid manure stores and during spreading is possible without danger. Technical solutions are available on the market.
8. Acidification of liquid manure is internationally and nationally recognised as BAT for reducing ammonia emissions.
9. In Germany, existing legal obstacles should be removed as a matter of priority against the background of the high environmentally benefit of liquid manure acidification.

Summary

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1 Starting position

The massive anthropogenic intervention in the global N budget has far exceeded the earth's capacity to cope with reactive nitrogen compounds. Due to its generally scarce availability in natural ecosystems, nitrogen (N), the main nutrient essential for all living organisms, is a key factor in controlling species composition and biological diversity as well as numerous processes and functions in terrestrial, limnic and marine ecosystems.

The production of reactive nitrogen compounds, which is based on the ammonia synthesis using the Haber-Bosch process patented in 1911 (*patent* 1908), today makes it possible to provide plant-available N-compounds in any quantity. This has led to an enormous increase in agricultural food production. On the other hand, by the end of the last century, this had already led to a doubling of the turnover of reactive N-binding forms in the global ecosystem (*Vitousek* et al. 1997). As N fertiliser use is below 50 % on average worldwide, more than half of the applied nitrogen remains in the environment. The resulting ecological impacts are now considered more serious than anthropogenic climate change (*Rockström* et al. 2009). According to *Steffen* et al. (2015), the earth's carrying capacity limit (62-82 Tg N a^{-1}) is exceeded by a factor of about two due to current N emissions (about 150 Tg N a^{-1}). **The reduction of N deposits into the environment must therefore be one of the most important objectives of environmental policy.**

By far the most important emitter of N is the agricultural sector. In particular, liquid manure management associated with animal husbandry makes a decisive contribution to N emissions in the form of ammonia (NH_3) into the environment.

The reason for the outgassing of NH_3 from liquid manure is the high pH value in the liquid manure, where the chemical balance between ammonium (NH_4^+) and NH_3 is on the ammonia side. By adding acid, the balance can be shifted in favour of NH_4^+. This theoretically allows the complete suppression of NH_3 outgassing from liquid manure.

In Denmark, liquid manure acidification has been considered a successful strategy to reduce NH_3 emissions for more than 10 years. It is now put into practice on more than 20% of all farms there (*Peters* 2016, zit. in *Kupper* 2017, S. 9). In other European countries, however, this technology has not yet become established. *Jacobsen* (2017) analysed the causes. These include both environmental and safety concerns. Added to this are uncertainties in the legal regulations, which have an obstructive effect.

However, against the background of the EU-wide agreed reduction targets to be achieved by 2030, other European countries such as Switzerland (*Kupper* 2017) or Poland (*Borusiewicz & Barwicki* 2017) are now also examining the effectiveness and feasibility of this technology for reducing NH_3 emissions from livestock farming under their national circumstances.

In Germany, too, the measure "Acidification of liquid manure" is discussed as one of the techniques for reducing NH_3 outgassing cited in the UNECE Ammonia Guideline and in the BAT conclusions (*Bittman* et al. 2014). This requires a comprehensive assessment of the environmental impact of this measure. However, this is not yet available. The complexity of the environmental effects of liquid manure acidification results from the fact that, in addition to the equilibrium of the ammoniacal N-species, the lowered pH value caused by acidification alters numerous other chemical equilibria, biochemical and biological reactions as well as physical properties of the liquid manure and, after spreading, the acidified liquid manure also leads to reactions in the soil, which originate from the acid itself on the one hand and from the respective conjugated base on the other. In addition, very different substances can be used to acidify liquid manure. Apart from sulphuric acid, other strong mineral acids come into question. Organic acids can also be used. In addition, there are studies on the effects of acid salts. All in all, this results in a complex system of effects which must be comprehensively investigated in order to be able to assess the potential of liquid manure acidification on the one hand and its environmental compatibility on the other.

Against this background, UBA has commissioned a compilation of the knowledge available to date on the subject and sought to address the question of whether the acidification of liquid manure can be an environmentally compatible and practicable measure to reduce NH_3 emissions from agriculture.

The objectives are, on the basis of the available findings, (1) to arrive at a comprehensive assessment of the environmental impacts of liquid manure acidification, (2) to provide information on the agronomic impacts and (3) to classify the process legally, or to identify deficits here.

2 Methods

The work is based on the evaluation of available literature, with a focus on peer-reviewed publications. Own experiments were not carried out. The literature search is carried out with "ISI Web of Knowledge" in the database "Web of Science Core Collection" under consideration of the keywords "liquid manure", "acidification" and "ammonia", according to the search rule that all three search words had to be obligatorily included in title, abstract or keyword index. For the period from 1945 up to and including 01.11.2018 a total of 141 citations were reported, taking all three keywords into account. On the basis of the summaries, 52 of these citations were excluded as not relevant to the issue, e.g. where the keyword "acidification" did not refer to the liquid manure itself but to the soil. In a second run, the result was checked using the two keywords "liquid manure" and "acidification". This resulted in 283 hits for the same period. All quotations found with the three keywords were also listed here. Nine others were considered relevant on the basis of the summaries. The oldest publication identified in this way was published in December 1989.

Only English language publications were listed. In order to check whether German-language publications were overlooked, a further search was carried out using the keywords "Gülle" and "Wirtschaftsdünger". For "Gülle" 13 citations were issued and none for farm fertiliser. In combination with the keywords "Ammonium" or "Ansäuerung", the keyword "liquid manure" also no longer provided any results. The quotations reported using the keyword "Gülle" refer to older literature as "Gülle" was translated as "liquid manure" in Anglo-Saxon countries ("Gülle as a Grassland Fertilizer" by *Herriott* et al. 1966 in the Journal of the British Grasland Society 21:85-92), or the "Zeitschrift für Pflanzenernährung und Bodenkunde" (today Journal of Plant Nutrition and Soil Science) still printed German language summaries ("Changes in phosphate concentration due to storage and shaking of liquid manure" by *Fordham & Schwertmann* 1978). The work of *Fordham & Schwertmann* (1978) is considered here because it already describes basic effects of acid addition on the chemistry of liquid manure. In addition there are three further works by these authors (*Fordham & Schwertmann* 1977a,b,c), which were published as a series under the title "Composition and Reactions of liquid manure (Gülle), with particular Reference to Phosphates: I..., II..., III) were published. This literature evaluation is thus based on a total of 102 original works.

Of particular importance are the meta-analyses by *Hou* et al. (2015) in which 126 studies published by the beginning of 2014 on the reduction of NH_3 and greenhouse gas emissions along the entire liquid manure management chain are evaluated in an integrated manner and the review by *Fangueiro* et al. (2015) in which the state of knowledge on the influence of liquid manure acidification on the liquid manure properties themselves, the soil, plant growth and other environmental impacts are evaluated until 2014. For this reason, for the present study, the publications that have appeared since *Hou* et al. (2015) and *Fangueiro* et al. (2015) are considered in this study.

In addition to the peer-reviewed original papers, reports from the recently completed Interreg Project "Baltic liquid manure Acidification" have been considered (*Foged* 2017, *Riis* 2016). In addition, there is the work of *Kupper* (2017) "Assessment of the acidification of liquid manure as a measure to reduce ammonia emissions in Switzerland - current status", which was carried out on behalf of the Swiss Federal Office for the Environment. Further ("grey") literature not available on the Web of Science could not be considered.

3 Findings and discussion

3.1 Fundamentals

3.1.1 Relevant physico-chemical properties of liquid manure

Liquid manure is a mixture of urine and faeces of farm animals, which is collected in the channels under the slatted floor of the animal houses and from there is led to storage installations or is collected and stored in a liquid manure cellar under the house. Due to the urine content as well as further dilution by rinsing / cleaning water, water for cooling purposes and water losses from the animal drinkers, the **dry matter content (DM)** in liquid manure is generally well below 10% (Table 1). The occasional discharge of waste water from the cleaning of milking parlours and installations, depending on individual farm conditions, explains the wide range of dry matter contents of cattle liquid manure. *Sommer & Husted* (1995) cite values between 2.1 and 11.4%. Pig liquid manure contains on average even less dry matter and the range of values is less than 1.5 to 2.0% (*Sommer & Husted* 1995).

Table 1: Range of properties of cattle (RG) and pig liquid manure (SG) (from Sommer & Husted 1995).

	TS [g kg $^{-1}$]	pH	EL [mS cm $^{-1}$]$^{1)}$	SNK [mmol L $^{-1}$]$^{2)}$	BNK [mmol L $^{-1}$]$^{3)}$
RG	20.8 - 114.2	7.7 - 8.1	12.6 - 18.6	18.5 - 41.1	22.7 - 31.8
SG	14.5 - 20.4	7.4 - 8.3	9.5 - 21.9	10.0 - 39.1	9.3 - 49.0

[1]Electric conductivity (EL) in mS cm^{-1}

[2]Acid neutralisation capacity (SNK). Determination by titration with 1M HCL after pH2

[3]Base neutralisation capacity (Basenneutralisationskapazität, BNK). Analysis by titration with 1M NaOH after pH 12

According to "Faustzahlen für die Landwirtschaft" (KTBL 2018), average dry matter contents of 7-10% for cattle liquid manure and 3-6% for pig liquid manure can be expected for practical purposes.

The TS influences the viscosity of the liquid manure and thus its pumping and stirring ability (*Langenegger* 1970), as well as the infiltration capacity into the soil. These properties are important with regard to the techniques used to mix acids into liquid manure and the outgassing of substances from the liquid manure. They are changed by adding acid (see chapter 3.2).

The total N content of liquid manure is between 2 and 10 kg N per m^3. The nitrogen is present in organic and ammoniacal ($NH_3 + NH_4^+$) binding form. The vast majority (> 55 - 60% for pig liquid manure, > 70% for cattle liquid manure, quoted in *Sommer & Husted* 1995) enters the liquid manure via urine in the form of urea. However, urea is hydrolysed within a short time in the liquid manure by the exoenzyme urease (urease is not present in sterile urine. If urine and faeces of the animals were collected separately, the hydrolysis of the urea could be prevented or delayed):

$$CO(NH_2)_2 + 2H_2O \rightarrow 2\ NH_4^+ + CO_3^{2-}$$

More than 50% of the nitrogen in stored liquid manure is thus present in ammoniacal form, with only less than 10% coming from the conversion of the nitrogen excreted in organic form in liquid manure (*Sommer* 1990). This is because under the anaerobic conditions in liquid manure, the release of nitrogen from organic compounds other than urea is a very slow process.

The carbonate (CO_3^{2-}) resulting from the hydrolysis of urea is in chemical equilibrium with the hydrogen carbonate (HCO_3^-):

$CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$ pKs = 10,4

At pH values below 10.4, the equilibrium is on the side of the reaction product so that protons are bound by the carbonate. This leads to increasing liquid manure pH values as a result of urea hydrolysis. In addition, with the outgassing of CO_2 from the liquid manure, the pH value continues to rise according to the following relationship:

$HCO_3^- \rightarrow OH^- + CO_2\uparrow$

The chemical balance between the ammoniacal N-species also depends on the pH-value.

With rising pH values, ammonia is increasingly emitted from liquid manure because these lead to a shift in the NH_3/NH_4^+ equilibrium in the solution towards NH_3 and the solution has only a limited absorption capacity for NH_3, so that the gas escapes into the atmosphere above the liquid manure:

$NH_4^+ + OH^- \rightarrow NH_3\uparrow + H_2O$

This process is temperature dependent. The NH_3 outgassing increases with rising temperature. *Van der Stelt* (2007) showed that at 20°C up to 5.8 times more NH_3 was emitted from liquid manure than at 4°C. However, this is not only caused by the physicochemical conditions, but it must also be taken into account that the rising temperature promotes microbiological processes that lead to the release of NH_3 from organic bonds (*Van der Stelt* et al. 2007). Rising temperature also has an effect on NH_3 outgassing when liquid manure is stored (*Misselbrook* et al. 2016). The authors recommend taking this into account when developing NH_3 emulsion reduction strategies for liquid manure storage. Cooling of liquid manure channels is therefore listed in the BAT conclusions as an effective measure to reduce NH_3 outgassing.

The quantitatively most important cause of the pH increase in liquid manure during storage is the hydrolysis of the urea excreted by the animals and the outgassing of the weak acid CO_2, which precedes NH_3 outgassing due to the more than two orders of magnitude lower solubility of CO_2 compared to NH_3:

$OC(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + 2OH^- + CO_2\uparrow$

The neutralisation of the resulting bases by acids shifts the equilibrium in favour of NH_4^+, so that the NH_3 concentration in the liquid manure and consequently the NH_3 outgassing decreases. This has been known for a long time. For example, *Jensen* (1928) and *Egner* (1932) showed already in the first decades of the last century that NH_3 outgassing from liquid farm fertilisers can be reduced by their acidification. **The pH value to be aimed at for an effective reduction of NH_3 emissions from liquid manure should be below 6. *Fangueiro* et al. (2015) recommends pH 5.5, which is also the target value in Danish practice (*Riis* 2016).**

The amount of acid required to adjust this pH value depends on the acid buffer capacity of the liquid manure, its short-term achievable alkalinity (ALK). This essentially corresponds to the particulate carbonates dissolved in liquid manure (*Husted* et al. 1991):

$$ALK\ (mmol_c\ L^{-1}) = 2(CO_3^{2-}) + HCO_3^- + OH^- - H^+ - NH^+$$

For a characteristic cattle liquid manure, *Husted* et al (1991) determined an ALK of 350 $mmol_c\ L^{-1}$ by acidimetric titration, of which only 40 $mmol_c\ L^{-1}$ could not be assigned to carbonates. These are attributed to organic anions and inorganic phosphates. For the complete neutralisation of the ALK 175 mmol sulphuric acid would be necessary. This corresponds to a sulphur concentration of 5.6 kg m^{-3} liquid manure*. Sommer and Husted* (1995) titrated 17 different liquid manure and fermentation residue samples according to pH 2. The alkalinities found were between 100 and 410 $mmol_c\ L^{-1}$. The sulphuric acid required to neutralise this alkalinity would increase the S content of the liquid manure by 1.6 to about 6.6 kg m^{-3}. *Regueiro* et al. (2016d) also come to comparable results. The authors used 203 $mmol_c$ H_2SO_4 for the titration of 1 kg pig liquid manure to pH 3.5 and 270 $mmol_c$ for 1 kg cattle liquid manure. This corresponds to S values of 3.3 or 4.3 kg t-1 liquid manure. According to *Stevens* et al. (1989), the amount of sulphuric acid required for liquid manure acidification correlates closely with the ammoniacal N (aN) content of the liquid manure. The authors required 10 mL 5 M H_2SO_4 per gram aN for the acidification of liquid manure to pH 4.

Only if the entire ALK is neutralised does the pH value in the liquid manure remain constantly low, even over long periods of storage. Otherwise, the pH value will rise due to CO_2 outgassing in advance until the NH_3 outgassing is also equivalent.

During the storage of acidified liquid manure, the pH value increases due to the decomposition of organic acids. However, if the pH value in the liquid manure is very low, so that the microbial reduction of organic acids is suppressed, the pH values may even fall further as a result of the formation of organic acids (*Misselbrook* et al. 2016).

3.1.2 Process engineering of liquid manure acidification

Liquid manure can be acidified in the barn, in storage or only when it is spread directly on the field (*Fangueiro* et al. 2015). During the acidification in the stable, which is called long-term acidification, the acid is added to the liquid manure in a mixing tank located outside the stable. Liquid manure is pumped in from the liquid manure channels of the stable, adjusted to pH 5.5 with concentrated sulphuric acid and then pumped partly into the liquid manure storage and partly back into the stable. The advantage of this treatment compared to acidification in storage and on the field is that no NH_3 escapes from the acidified liquid manure in the liquid manure channels and the H_2S outgassing is also reduced. The latter is a consequence of the reduced microbiological H_2S formation caused by sulphuric acid (see chapter 3.7). This not only leads to an improved barn climate and thus serves animal welfare, but also reduces gas emissions from the barn.

The acidification of liquid manure in storage is called short or long term acidification, depending on the time of acidification. Acidification can take place shortly before application or months before, which may require a repeat treatment due to the pH buffering caused by the degradation of organic salts.

Acidification directly during the spreading of liquid manure on the field is considered to be short-term acidification. The acid is carried along in a separate tank on the liquid manure vehicle and is mixed directly into the liquid manure stream during application. The advantage of this process over the other two is that it requires the least amount of acid.

3.1.3 Substances used for the acidification of liquid manure

Liquid manure is a complex, highly reactive biogeochemical system in which (i) electrons are transferred - biologically and protons - for energy production, (ii) elements - for body composition - are biologically assimilated from organic residues or released from them into solution, and (iii) minerals are chemically precipitated and dissolved. Substances added to liquid manure from outside are integrated into these processes, which are strongly cross-linked by interactions. Against this background, it appears useful to classify substances that can be used to lower the pH in the liquid manure solution in terms of their ability to be converted into liquid manure (Table 2).

(I) Strong mineral acids with conservative conjugated bases are acids whose conjugated bases are still present as such in the liquid manure even after a longer residence time, i.e. they are not further converted. A further distinction is made between (II) strong mineral acids with reactive conjugated bases, (III) moderately strong mineral acids, (IV) organic acids and (V) other acidifying substances that are suitable for the acidification of liquid manure.

Due to the complete dissociation, the proton equivalents of the very strong acids are fully effective in neutralising the ALK of the liquid manure. This does not apply to phosphoric acid and organic acids, which dissociate less and less as pH values fall.

In the 1990s, numerous experiments were carried out with the addition of HNO_3 to liquid manure. The strong, pH-dependent NH_3 emission-reducing effect was already apparent. For example, pH values of 4, 5.5 and 6 led to reductions in NH_3 outgassing of 85, 72 and 55 % compared to non-acidified liquid manure (*Bussink* et al. 1994). However, *Schils* et al. (1999) point out that acidification with HNO_3 leads to further, possibly unacceptable N inputs into the environment. In addition, HNO_3 is not stable during liquid manure storage. This was demonstrated by *Stevens* et al. (1995) in a laboratory incubation experiment with bovine liquid manure to which increasing amounts of HNO_3 were added. It was found that nitrate was rapidly reduced when the liquid manure pH rose above 5.5. This can lead to high N_2O emissions (*Berg* et al. 2006). Therefore HNO_3 cannot be used for liquid manure acidification in stables and liquid manure storage.

Phosphoric acid is also generally not used because this would further increase the P overhangs in liquid manure management. The BAT conclusions indicate that concentrated sulphuric acid is used, which is the practice in Denmark.

Table 2: Substances which can be used to acidify liquid manure.

Substance class	Molecular formula	pKs
Very strong mineral acids		
Sulphuric acid	H_2SO_4	-3/1.92
Hydrochloric acid	HCl	-6
Nitric acid	HNO_3	-1.32
Strong mineral acids		
Phosphoric acid	H_3PO_4	2.16/7.21/12.32
Organic acids		
Formic acid	CHOOH	3.77
Acetic acid	CH_3COOH	4.76
Citric acid	$C_6H_8O_7$	3.13/4.8/6.4
Lactic acid	$C_3H_6O_3$	3.86
Acid salts		
Aluminium sulphate	$Al_2(SO_4)_3$	
Neutral salts		
Calcium sulphate	$CaSO_4$	
Calcium chloride	$CaCl_2$	

However, the effectiveness of organic acids was also investigated in laboratory experiments. This could reduce S exposure (*Daumer* et al. 2010). The authors used formic and acetic acid to dissolve P from biologically pre-treated liquid manure with the aim of subsequently precipitating the P as struvite. Only about one third of formic acid (by mass) compared to acetic acid was needed to lower the pH to 4.5 to 5 and dissolve 80% of the P. This is due to the higher molar mass of acetic acid (60 g/mol) compared to formic acid (46 g/mol) and the higher acidity of formic acid (Table 2).

The effectiveness of acid salts was also tested in laboratory trials. The reaction of $A_2(SO_4)_3$ in the liquid manure solution leads to sulphuric acid according to the following equation:

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3\downarrow + 6H^+ + 3SO_4^{2-}$$

Besides NH_3 outgassing, aluminium sulphate also reduces pathogenic germs, binds P and reduces the nitrification rate (*Gandhapudi* et al. 2006). Sodium hydrogen sulphate ($NaHSO_4$), which is used in poultry farming for hygienic reasons, also reduced NH_3 emissions as well as emissions of methanol and ethanol from cattle liquid manure (*Sun* et al. 2008).

Vandré & Clemens (1997) tested the effectiveness of potassium chloride as well as calcium nitrate, chloride and sulphate in comparison with hydrochloric acid on cattle liquid manure. It was shown that Ca, independent of the accompanying anion, can reduce the pH-values in liquid manure or delay its re-increase. This is due to the precipitation of calcium carbonate, which converts the weak carbonic acid into the respective strong mineral acid:

$$NH_4^+ + HCO_3^- + CaCl_2 \rightarrow NH_4^+ + CaCO_3 + 2Cl^- + H^+$$

$$NH_4^+ + HCO_3^- + CaSO_4 \rightarrow NH_4^+ + CaCO_3 + SO_4^{2-} + H^+$$

Potassium, on the other hand, is not able to precipitate carbonate, which is why the K-salts did not show any effect. In the field experiment, the authors found a significant reduction in NH_3 outgassing from liquid manure treated with $CaCl_2$ or $CaSO_4$ compared to that from untreated liquid manure, but still outgassed more than 20% of the applied NH_4-N within 14 hours. Hydrochloric acid reduced the outgassing to about 20%.

In addition to the substances listed in Table 2, experiments were conducted with other substances. These include, for example, liquids produced during the carbonation of organic matter (e.g. HTC liquid). *Keskinen* et al. (2018) have shown in principle that liquid manure can be acidified with it. After the initial studies, the authors consider further research on this issue to be useful. *Gronwald* et al. (2018) also believe that HTC reduces NH_3 outgassing from cattle and poultry manure. Pyrogenic coal, on the other hand, has no effect. The effectiveness of HTC, based on low pH, is also low (19% reduction of NH_3 emissions compared to untreated control) and the authors conclude that biochar is not an effective measure to reduce NH_3 outgassing.

Acidification can also be achieved by adding sucrose, which is rapidly converted to organic acids in the anaerobic phase. *Piveteau* et al. (2017) have shown that, depending on the concentration (up to 60 g/l), pH values of about 4 can be achieved in pig liquid manure within an incubation period of about three days. However, it is also true here that the effectiveness is only of limited duration due to the mineralisation of the organic acids during the storage of the liquid manure.

Elemental sulphur (S^0) has also been used on a laboratory scale to acidify the solid press residue of liquid manure (*Gioelli* et al. 2016). Elemental sulphur (S^0) is an approved fertiliser which must first be oxidised before the sulphate can be absorbed by plants. The oxidation of ^{0} is carried out by means of thiobacilli, producing sulphuric acid. However, the availability of oxygen is decisive for the process:

$$2S^0 + 2H_2O + 3O_2 \rightarrow 2H_2SO_4$$

The conversion depends on the grain size of the sulphur, temperature, soil moisture and size of the thiobacilli population (*Yang* et al. 2010). When applied to the floor, this is completed within 4 weeks.

Gioelli et al. (2016) demonstrated a reduction of greenhouse gases by 78% and of NH_3 by 65% after 30 and 60 days of storage respectively. For acidification of the solids after separation of the liquid manure, the authors used 10 kg S^0 per t liquid manure. If 0.5% S^0 was added to the liquid manure solids, the pH reduction was too slow. When using S^0, positive phytosanitary effects can be expected as a side effect (*Haneklaus* et al. 2007). No studies have yet been carried out on the efficiency and duration of the acidification of liquid manure in liquid manure storage with S^0. Due to the lack of oxygen, however, the effects shown on the liquid manure press residue are hardly to be expected.

3.1.4 Amounts of acid used

In the reviewed studies on liquid manure acidification, the respective target pH values are always given. However, not all authors indicate the amount of acid required. Nevertheless, the large number of results now available allows a good estimate of the range of acid quantities required (Table 3).

Table 3: Amounts of sulphuric acid used

pH			Acid/Concentration	Amount	S kg/m³ kg/t	Author
Cattle liquid manure						
Start	**Goal**	**End**				
7.4	5.5	5.6	H_2SO_4/concentrated	6 ml/l	3.5	Fangueiro et al. 2018
7.6	5.5	5.6	H_2SO_4/concentrated	6 ml/l	3.5	Fangueiro et al. 2018
7.4	5.5	5.5	H_2SO_4/concentrated	7.4 ml/kg	4.3	Fangueiro et al. 2017
7.3	5.5	5.5	H_2SO_4/concentrated	5,8 ml/kg	3.3	Fangueiro et al. 2017[1)]
7.2	5.5	5.5	H_2SO_4	180 meg/kg	2.9	Regueiro et al. 2016
7.2	3.5	3.5	H_2SO_4	270 meg/kg	4.3	Regueiro et al. 2016
7.2	5.5	4.1	H_2SO_4/concentrated	5 l/880 l	3.3	Misselbrook et al. 2016
7.3	5.5	5.7	H_2SO_4/concentrated	3.5 l/880 l	2.3	Misselbrook et al. 2016
7.1	5.5	5.2	H_2SO_4	7.7 g S/l	7.7	Moset et al. 2016
Pig liquid manure						
Start	**Goal**	**End**				
7.9	5.5	5.6	H_2SO_4/18 M	18 g/l	5.9	Sigurnjak et al. 2017
8.1	5.5	5.5	H_2SO_4/18 M	18 g/l	5.9	Sigurnjak et al. 2017[2)]
7.2	5.5	5.5	H_2SO_4	135 meg/kg	2.2	Regueiro et al. 2016a
7.2	3.5	3.5	H_2SO_4	203 meg/kg	3.2	Regueiro et al. 2016a
7.0	5.5	5.3	H_2SO_4/concentrated		3.9	Cocolo et al. 2016[3)]
6.8	5.5	5.4	H_2SO_4/concentrated		3.3	Petersen et al. 2016[4)]
7.1	5.5	5.3	H_2SO_4/concentrated		3.9	Hjorth et al. 2015[5)]
7.1	5.5	5.3	H_2SO_4/concentrated		4.8	Hjorth et al. 2015[6)]
6.9	5.5	5.8	H_2SO_4/concentrated		3.7	Moset et al. 2012[7)]
6.5	5.5	5.9	H_2SO_4/concentrated		3.5	Moset et al. 2012[8)]
7.3	5.5	5.5	$Al_2(SO_4)_3$	20 g/kg	5.7	Regueiro et al. 2016b

Other substrates						
Start	**Goal**	**End**				
8.1	5.5	5.4	H_2SO_4/18 M	27 g/l	8.9	Sigurnjak et al. 2017[9)]
8.4	5.5	5.5	H_2SO_4/18 M	27 g/l	8.9	Sigurnjak et al. 2017[10)]
9.1	5.5	5.5	H_2SO_4/concentrated	17.5 ml/kg	10.1	Anthanasios et al. 2017[11)]

[1] The “liquid" phase of cattle liquid manure obtained by centrifugation

[2] "Liquid" phase of pig liquid manure obtained by centrifugation

[3] Calculated from concentration data (Cocolo et al. 2016: Tab. 1, S in Acidified liquid manure – S in Control liquid manure)

[4] Calculated from concentration data (Petersen et al. 2016: Tab. 2, S Acidified – S Reference)

[5] Calculated from concentration data (Hjorth et al. 2015: Tab. 1, S Acidified liquid manure – S Control liquid manure)

[6] Calculated from the acid consumption stated by Hjorth et al. 2015 p. 57, treatment (A)

[7] Calculated from SO_4 concentration data (Moset et al. 2012: Tab. 1, Pilot-scale Acidified liquid manure – Raw liquid manure)

[8] Calculated from SO_4 concentration data (Moset et al. 2012: Tab. 1, Full-scale Acidified liquid manure – Raw liquid manure)

[9] Fermentation residue (from co-fermentation of 20% liquid manure, 30% other agricultural residues, 50% food residues, Co-GR)

[10] Fermentation residue liquid phase (obtained from Co-GR by centrifugation)

[11] Drained fermentation residue (decanter centrifuge)

3.2 Influence of acidification on the properties of liquid manure

3.2.1 Chemistry

Besides the protonation of NH_3 other weak acids are also protonated (Table 4). This leads to increased outgassing of H_2S and volatile organic odorous substances during the treatment of liquid manure with H_2SO_4 (*Riis* 2016). Overall, however, the outgassing of these substances is little affected (*Dai & Blanes-Vidal* 2013, *Kai* et al. 2008), or they tend to be lower than those from untreated liquid manure (*Riis* 2016). This is due to the reduced microbial activity in the liquid manure caused by the addition of sulphuric acid. As the formation of H_2S is reduced after acidification of liquid manure, it is even conceivable that the amount of H_2S released when stirring untreated liquid manure, which can be hazardous to health (*Andrianmanohiarisoamanana* et al. 2015), does not occur.

Precipitates containing phosphorus such as struvite ($MgNH_4PO_4$) can be dissolved (*Hjorth* et al. 2013, 2015) or the precipitation of struvite is thus prevented, as *Fordham & Schwertmann* point out already in 1977a and 1978. As a result, all Mg and the majority of Ca and P contained in the liquid manure is transferred to the solution. The result is an improvement in the plant availability of the phosphorus contained in the liquid manure.

Table 4: Chemical reactions in the liquid manure caused by the addition of acid

Substance before acidification	Reaction	Result
Ammonia	$NH_3 + H^+ \rightarrow NH_4^+$	NH_3-Outgassing decreases
Hydrogen sulphide	$HS^- + H^+ \rightarrow H_2S$	H_2S Outgassing increases
organic acids	$RCOOM + H^+ \rightarrow R\text{-}COOH + M^+$	Outgassing of organic acids
Struvite	$MgNH_4PO_4 + 2H^+ \rightarrow Mg^{2+} + H_2PO_4^- + NH_4^+$	P solubility increases

3.2.2 Physics

Purely visually, the acidification changes the liquid manure. For example, *Fangueiro* et al. (2015) report that acidified liquid manure is less brown and more greyish in colour compared with the untreated control, which the authors explain with the hydrolysis of organic liquid manure components. Acidification of liquid manure leads to the aggregation of colloids. This can be explained by decreasing negative surface charge of the particles due to protonation (*Zhu* et al. 2012). For example, the zeta potential increased from -13.6 to -9.6 through acidification of pig liquid manure to pH 5.5 (*Hjorth* et al. 2013). This leads to lower viscosity of the liquid manure, which has consequences for the infiltration of liquid manure into the soil and for its separability (*Cocolo* et al. 2016, *Gomez-Munoz* et al. 2016).

3.2.3 Biology

Overall, the microbial metabolism in liquid manure is slowed down by acidification. This leads to lower production rates of methane and sulphides (*Ottosen* et al. 2009). Acidification of cattle liquid manure with sulphuric acid to pH 5.5 led to almost complete suppression of sulphate reduction, while sulphate addition led to strong H_2S production (*Eriksen* et al. 2012). Acidification of liquid manure can therefore lead to reduced emissions of H_2S from liquid manure. Pathogenic micro-organisms may also be suppressed by acidification of the liquid manure. *Zhang* et al (2011) conclude on the basis of studies on population dynamics of micro-organisms in the acidofil (due to the formation of fatty acids) anaeorobic phase that the acidification process reduces the number of pathogenic bacterial species in pig liquid manure.

Acidification (pH 5.5) reduced CO_2 development by 50% and delayed N-mineralisation of fermentation residue solids in a laboratory incubation experiment compared to non-acidified material (*Pantelopoulos* et al. 2016a). In contrast, the potential Nmineralisation by acidification is increased in the thin separation from liquid manure (*Regueiro* et al. 2016b).

3.3 Influence of acidification on the emission of gases from liquid manure

3.3.1 Ammonia

NH_3 emissions from livestock buildings account for a high proportion of the total NH_3 emissions from agriculture. According to *Monteny & Erisman* (1998), this represents on average about 28% of total NH_3 emissions from agriculture in the Netherlands. Depending on the barn system, between 5 and 45 g NH_3 per cow are emitted there daily. Substantial reductions (up to 50%) are possible, for example through liquid manure acidification (*Monteny & Erisman* 1998). *Kai* et al (2008) show that liquid manure acidification can reduce NH_3 emissions from pigsties by 70%. In the camp (pilot experiment in 100 l tanks) the acidification of cattle liquid manure to pH 5.5 reduced NH_3 emissions by 62% (*Sommer* et al. 2017). The pH values increased during storage, DOC was reduced to CO_2 and CH_4. *Misselbrook* et al. (2016) achieved an NH_3 emission reduction of 75% by acidification in the store, which was as effective as covering the liquid manure with an expanded clay layer (77% reduction).

During the storage of liquid manure the ammonium hydrogen carbonate concentrations increase as a result of urea hydrolysis. In addition, soluble Ca-organic complexes are slowly degraded (*Fordham & Schwertmann* 1977b, c), as a result of which the pH value of the liquid manure increases, so that the added sulphuric acid is slowly further neutralised when the Ca-organo complexes of compounds of organic acids with pKs values are below the liquid manure pH value set by acidification. The weaker acids on the other hand are already directly protonated during liquid manure acidification.

The effectiveness of acidification on NH_3 emissions is comparable to that of liquid manure injection, and can even exceed it depending on the pH in the liquid manure. *Seidel* et al. (2017) acidified cattle liquid manure to pH 6.5 and 6.0. At pH 6.0, NH_3 emissions from liquid manure applied in strips to grassland were reduced by 79% compared to untreated liquid manure, whereas at pH 6.5 they were reduced by only 42%. Injection of the liquid manure reduced NH_3 outgassing by 31 and 61% respectively (two different injection techniques). *Fangueiro* et al. (2015b) have also concluded that tape application of acidified liquid manure is a good alternative to liquid manure injection.

Kupper (2017) summarises in his report that acidification reduces NH_3 emissions from stables by 40-77% on average, from liquid manure storage by 50->90% and from field application by 40-70%.

3.3.2 Methane

During the storage of liquid manure, methane (CH_4) is produced, favoured by neutral pH values, due to the strongly reducing conditions prevailing there (*Hansen* et al. 2006). Compared with fermentation residues, considerably more CH_4 is released from unfermented liquid manure, because during fermentation the readily degradable organic compounds have already been largely reduced to CH_4 (*Regueiro* et al. 2016b). With values falling below pH 6, methanogenesis is increasingly inhibited (*Weiland* 2010). Accompanying this, the acidification of pig liquid manure and thin liquid manure separation by adding 2 to 3.5 % $Al_2(SO_4)_3$ reduced CH_4 emissions by 81 to 92% in a laboratory incubation experiment over 70 days (*Regueiro* et al. 2016d). At 81%, *Wang* et al (2014) achieved comparable reductions by acidifying the liquid manure with sulphuric acid to pH 5.5. *Petersen* et al. (2014) even demonstrated a 94% reduction in CH_4 emissions from liquid manure acidification. *Petersen* et al. also achieved a strong reduction of 67 to 87% in methane emissions from cattle liquid manure (2012). According to the authors, the cause could be inhibited methanogenesis by $_{42-}$. *Sommer* et al. (2017) also showed a significant reduction of CH_4 formation in acidified cattle liquid manure (68% reduction compared to non-acidified liquid manure). *Misselbrook* et al. (2016) also found significant reductions in CH_4 emissions from acidified liquid manure, but these were influenced by the storage temperature (82% reduction at 9.2°C and 60% reduction at 17.1°C, average air temperature during 61 to 72 days of liquid manure storage).

3.3.3 Nitrous oxide

Fangueiro et al. (2018) compared the effect of liquid manure injection and band application of acidified liquid manure with band application of untreated liquid manure. Liquid manure acidification reduced NH_3 outgassing such as injection and superficial band application of acidified liquid manure showed 65% less N_2O and 40% less CH_4 emission compared to injection. The group of authors had already shown in 2017 that CH_4 emissions are also significantly reduced by acidification of liquid manure (*Fangueiro* et al. 2017). *Park* et al. (2018) achieved about 80% reduction of N_2O emissions by acidifying the liquid manure to pH 5 compared to pH 7. *Seidel* et al. (2017) also found higher N_2O emissions after liquid manure injection on grassland in a year with overall increased denitrification compared to those after band application of acidified cattle liquid manure. However, in a test year with overall low N_2O emissions, the emission factors were not different.

Gomez-Munoz et al. (2016) report increased N_2O emissions from acidified thin swill from pig liquid manure mixed into soil in laboratory incubation. However, this is only the case in the test variant with high water contents (pF 1, near saturation).

The results compiled here are consistent with the analysis by *Hou* et al. (2015), who evaluated a total of 126 studies on the environmental impacts of liquid manure management in terms of reduction potential**. Central results of this meta-analysis are: liquid manure acidification reduces NH_3 and CH_4 emissions, while liquid manure injection promotes N_2O emissions.**

3.4 Effect of liquid manure acidification on the soil

Acidification of liquid manure with sulphuric acid changes the liquid manure properties compared to those of untreated liquid manure. The acid neutralisation capacity (SNK) decreases, the S-content increases, the P-solubility increases, the flowability is changed, the microbial composition/activity is altered. The following shows how these changes affect soil properties that are crucial for soil fertility.

3.4.1 Soil acidity

When acidified liquid manure is applied, acid is added to the soil in comparison with non-acidified liquid manure. If strong mineral acids are used to acidify the liquid manure, the total amount of acid contributes to the reduction of the SNK of the soil. This is not the case when organic acids are used, as these are completely broken down in the soil to CO_2 and H_2O.

By adding four kg of sulphur per m^{-3} in the form of H_2SO_4, 250 mol H^+ are added to the liquid manure. At an annual liquid manure application of 30 m^3 per ha, this leads to an additional acid load rate of 7.5 kmol ha^{-1} a^{-1}, in addition to the soil acidification caused by agricultural land use in any case (leaching, acid-effect fertilisation, plant removal, etc.). This exposure rate exceeds the silicate buffer rate of soils by far, so that the soils cannot compensate for the acidity without liming measures.

Mathematically, this additional amount of acid can be neutralised by 375 kg $CaCO_3$. This is equivalent to about one third of the average annual lime requirement of arable soils in Germany (500 to 1,600 kg $CaCO_3$ ha^{-1} a^{-1}). If compensatory liming is not carried out, the pH and base saturation of the soil will decrease as a result of decreasing SNK of the soil. For example, the pH values of various soils to which a total of about 720 kg S ha^{-1} with acidified cattle liquid manure was added over a period of three years fell by 0.9 to 1.4 units (*Fangueiro* et al. 2018).

The added sulphur remains largely in oxidic form, even if the acidified liquid manure is stored for a long time; it can therefore be absorbed by the soil into the plants and its availability is comparable to that of mineral S fertilisers (*Eriksen* et al. 2008).

3.4.2 Nutrient availability

From studies with acidified cattle liquid manure in laboratory experiments, *Fangureiro* et al. (2015c) conclude that N availability is improved by acidification. *Seidel* et al. (2017) also found significantly increased N-use efficiency of cattle liquid manure acidified to pH 6.0 (88% based on N-mineral fertiliser utilisation), while the mineral N of the liquid manure after acidification to pH 6.5 and injection was only utilised to 39 to 44%. The authors also attribute this to a possible pH effect on the soil (pH 7.3), as a result of which the mobility of N and other nutrients may have increased.

Sigurnjak et al. (2017) found a slightly reduced N-effect of acidified liquid manure in a short-term pot experiment with lettuce, which could be due to delayed nitrification. However, the authors expect this to be a short-term effect that should not play a role in plants with a longer vegetation period. In accordance with this interpretation, *Pantelopoulos* et al. (2017) showed that acidified fermentation residues in a pot test with ryegrass showed similar N-fertilising effects as mineral N-fertiliser.

Acidification of the liquid phase of cattle liquid manure (sulphuric acid, pH 5.5) reduced N_2O emissions by a factor of 2 compared to those after application of non-acidified reference liquid manure in a laboratory incubation experiment and had a comparable effect to a synthetic nitrification inhibitor (3,4-dimethylpyrazole phosphate, DMPP) (*Owusu-Twum* et al. 2017). The solid phase of previously acidified pig liquid manure showed higher N availability compared to untreated solid phase (*Regueiro* et al. 2016a). The improvement in N-use efficiency, which is equivalent to that of KAS, has also been demonstrated (*Schils* et al. 1999). *Frost* et al. (1990) showed that the utilisation efficiency of ammoniacal nitrogen in liquid manure in relation to mineral N-fertiliser by ryegrass could be increased from 39% to 96% by acidification.

Acidification with sulphuric acid to pH 5.5 significantly increased the P availability (ion exchange resin extractable fraction) in a laboratory incubation experiment with a sandy (88% S), humus-poor soil (4.6 g C/kg) soil (pH_{H2O} 5.4) (*Roboredo* et al. 2012). In contrast, Christel et al. (2016) found no significant effect of acidification of pig liquid manure (pH 5.5, sulphuric acid) on P availability, also in a laboratory incubation experiment. However, the authors used the solid phase of the liquid manure previously acidified under practical conditions, obtained by pressing or centrifugation, for their experiments. It can therefore be assumed that the proportion of organically bound phosphorus, which is only available after mineralisation, is higher in the acidified variants than in the non-acidified variants.

The improved P availability demonstrated in incubation experiments through acidification is also accompanied by an increased P uptake by plants. For example, *Pedersen* et al. (2017) demonstrated significantly increased P uptake of maize plants from acidified liquid manure in a pot experiment. The P uptake and also the dry matter yield increased with falling pH values of the liquid manure adjusted with sulphuric acid to pH 6.5, 5.5 and 3.5. The authors conclude from their results that if acidified liquid manure is injected, it may be possible to dispense with underfoot fertilisation of maize with mineral P.

Acidified liquid manure increased the Zn uptake of lettuce (*Lactuca sativa* L.) in a pot experiment (*Sigurnjak* et al. 2017).

3.4.3 Soil biology

According to *Fangueiro* et al. (2016), the acidification of pig liquid manure (pH 5) after application leads to a delay in nitrification (see also *Ottensen* et al. 2009), which may be comparable to the effect of a synthetic nitrification inhibitor (*Park* et al. 2018). This was accompanied by a reduction in nitrate leaching (-18%) and nitrous oxide emissions (-79%). *Fangueiro* et al. (2016) also showed that N mineralisation can be increased by acidification of liquid manure. No negative effects on enzyme activities in the soil by acidified liquid manure were found (*Fangueiro* et al. 2105b). *Park* et al. (2018) show that the nitrification of ammonium from liquid manure is delayed by acidification to pH 5. This resulted in lower NO_3 leaching losses compared to those after application of liquid manure whose pH was adjusted to 7.

Mahran et al. (2009) have found strong effects of the application of pig liquid manure on the population dynamics of different nematodes in a mesocosm experiment, but no clear differences between acidified (sulphuric acid, to pH 5.5) and untreated liquid manure were found. However, the authors point out that plant pathogenic nematodes (*Pratylenchus* spp.) are selectively and permanently damaged, which should be the subject of further investigations.

On the basis of current knowledge, it can be assumed that no negative impacts on soil biology are to be feared if the rules of good soil management practice are observed.

3.4.4 Pollution

Based on literature references, *Kupper* (2017, p. 29) calculated potential heavy metal inputs into the soil that could be caused by heavy metal contamination of sulphuric acid. The author's analysis leads to the conclusion that the heavy metal load of the soil would increase by a few per mille to a maximum of 1.33% (Cd) when liquid manure is acidified.

The use of $Al_2(SO_4)_3$ for the acidification of liquid manure introduces Al as well as S into the soil. Assuming the quantity by *Regueiro* et al. (2016d) of 20 g $Al_2(SO_4)_3$ per kg of liquid manure, this means that at an annual liquid manure application of 30 m^3 per ha, about 95 kg Al is added to the soil. In relation to the natural Al content of soils, this is a negligible amount. This is because aluminium is the third most common element in soil-forming rocks, after oxygen and silicon, with an average mass fraction of around 7%. In soils it is mainly contained in the silicates and pedogenic Al-Hydroxo compounds. Comparable to the latter are the Al-hydroxides $Al(OH)_3$ formed during the reaction of $Al_2(SO_4)_3$ in liquid manure according to the following reaction, which precipitate as a solid phase in the liquid manure and reach the soil during the spreading of the liquid manure:

$$Al_2(SO_4)_3 + H_2O \rightarrow 2Al(OH)_3\downarrow + 6H^+ + 3SO_4^{2-}$$

Due to their large and at the same time reactive surface, the Al hydroxides in soils are of great importance for the buffering of nutrients and pollutants. They also sorb organic molecules and protect them from microbial degradation (*Zieger* et al. 2018).

3.5 Effect of liquid manure acidification on plant growth

From the point of view of plant nutrition, the facts described in detail below must be observed when acidifying liquid manure in order to avoid possible health hazards for humans and animals as well as yield and quality reductions.

In the case of liquid manure acidified with sulphuric acid, sulphur (S) may be applied in quantities that exceed the requirements of crops, as the following calculations show. Acidification to pH 5.5 is necessary to successfully reduce gas emissions (CH_4 and NH_3) from liquid manure and fermentation residues (*Wang* et al. 2014). Acidification in Denmark is done with concentrated sulphuric acid (H_2SO_4).

The quantities required depend, among other things, on the animal species and the dry matter content of the liquid manure. In the case of cattle and pig liquid manure, approximately 5.5 kg of H_2SO_4 per m^3 is required, whereas in the case of pig liquid manure, a consumption of up to 15 kg of H_2SO_4 per m^3 is reported in order to lower the pH to 5.5 (*Kupper* 2017). *Andersen* (2013) attributed this disproportionately high sulphuric acid consumption to higher temperatures and therefore also higher mineralisation rates and the higher proportion of ammonia and ammonium in the total N content, so that this value must be regarded as an exceptional value that has little relevance in practice.

Decisive for an estimation of the S-loads are the legally prescribed maximum quantities for N and P. As an example, Table 5 shows the S-loads spread with cattle and pig liquid manure as a function of dry matter content, which result from the application of 170 kg N/ha a (91/676/EEC, Nitrates Directive) and 22 kg P/ha a (*Jacobsen* 2012) with cattle and pig liquid manure. In addition, the quantities of liquid manure that add 50 and 100 kg S/ha to the soil are indicated. In the case of pig liquid manure, a quantity of 5.5 kg H_2SO_4 on the one hand and 15 kg H_2SO_4 on the other hand was assumed, which corresponds approximately to the maximum value given by *Hjorth* et al. (2015) for pig liquid manure with high dry matter content (cf. Table 2).

Table 5: S loads (kg/ha) spread with cattle and pig liquid manure depending on dry matter content and upper limits for N and P application.

	Cattle			Pig		
H_2SO_4 (kg/m³)		5.5			5.5	15
S_{H2SO4} (kg/m³)	1.8	1.8	1.8	1.8	1.8	4.9
TM[1),2)]	5%	8%	10%	3%	5%	7%
N (kg/m³)[1),2)]	2.9	3.9	4.5	4.3	5.5	6.5
P (kg/m³)[1),2)]	0.52	0.74	0.92	0.74	1.22	1.7
Kg S/170 kg N m³ liquid manure	106 59	79 44	68 38	71 40	56 31	128 26
Kg S/22 kg P m³ liquid manure	76 42	54 30	43 24	54 30	32 18	63 13
m³ liquid manure/50 kg S	28	28	28	28	28	10
m³ liquid manure/80 kg S	44	44	44	44	44	16

[1,2] (LWK-SH2018, LWK-NRW 2014); liquid manure itself delivers an additional 0.07 kg S per kg N (Haneklaus et al. 2006a); red numbers= S- loads >80 kg/ha S, yellow numbers= S- loads 50-79 kg/ha S

Based on these figures, for example, in the case of acidified (15 kg H_2SO_4) pig liquid manure (7% DM), at a current maximum permitted application of 170 kg N/ha a, an average of 128 kg S/ha would be applied. If the maximum amount of liquid manure to be applied was based on the P requirement, 63 kg S/ha would be added to the soil (Table 5). In comparison, acidified (5.5 kg H_2SO_4) cattle liquid manure (8% DM) with 170 kg/ha*a N, an average of 79 kg/ha S would be applied and 54 kg/ha S if the application rate corresponds to the P requirement of 22 kg/ha*a P on average.

This means that in the case of pig liquid manure with acidification quantities of 15.0 kg H_2SO_4, the S-loads can significantly exceed the S-demand of the crops. **In accordance with Kupper (2017), it should therefore be required that the quantity of acidified liquid manure applied should be adapted to the S requirement of the crops.**

This would in some cases significantly reduce the quantities of liquid manure applied (Table 5). With a demand-oriented application rate of maximum 50 kg/ha S to cereals and 80 kg/ha to rape seed via acidified pig liquid manure (15 kg H_2SO_4), this would correspond to a reduction of the maximum amount of liquid manure to be applied from 26 to 10 m3. For cattle liquid manure with a high N content, on the other hand, the legally permitted amount of N fertiliser can be supplied with acidified liquid manure when cultivating rapeseed without an oversupply of S.

An oversupply of S is particularly critical on grassland. The trials by *Birkmose* (2016) quoted in *Kupper* 2017 have shown that up to 130 kg S/ha are spread over acidified liquid manure, which far exceeds the requirement of the clover/grass mixture of 30 kg/ha*a. Only with a number of 3 liquid manure applications and a consumption of 1 L H_2SO_4/t of liquid manure or 1 application and 3 L H_2SO_4 /t of liquid manure would the supply and withdrawal of S be balanced (Table 6).

Table 6: Comparison of supply of S via acidified liquid manure as a function of the amount of H_2SO_4 applied (96%) and the number of liquid manure applications and S withdrawal by clover grass (Birkmose 2016).

S Requirement (kg/ha)	Number of Application	Spreading of 20 t liquid manure/application		
		1 L H_2SO_4/t	2 L H_2SO_4/t	3 L H_2SO_4/t
30 kg/ha S	1	11	22	32
30 kg/ha S	2	22	43	65
30 kg/ha S	3	32	65	97
30 kg/ha S	4	43	86	130

The S fertilisation recommendations for rapeseed are between 40-80 kg/ha S, for cereals 25-50 kg/ha S at the start of vegetation (*Haneklaus* et al. 2006a). With a maximum application rate of ≤80 kg/ha S, no negative effects on plant growth and subsequent crops are expected (*Haneklaus* et al. 2006a). In autumn, application rates of 10-15 kg/ha for cereals and 15-30 kg/ha for oilseed rape are sufficient to meet demand and promote natural resistance to pathogens (*Haneklaus* et al. 2006a). In general, yield losses of ~10% must be expected at application rates of >100 kg/ha S; brassicaceae are less sensitive to high S doses due to their secondary sulphur metabolism (*Haneklaus* et al. 2006a and b).

According to *Kupper* (2017), the acidification of various types of liquid manure resulted in an average yield increase of 0.17 t/ha at an average yield level of 7 t/ha of winter wheat. The positive impact on earnings can therefore be classified as negligible and not statistically certain. It is possible to save 15-30 kg/ha N in mineral form through acidification (*Kupper* 2017), which must be taken into account accordingly for the maximum amount of 170 kg/ha N in organic form!

S is generally considered to be highly compatible with plants (*Haneklaus* et al. 2006b). Too high a supply of S manifests itself in early leaf fall (*Motavalli* et al. 2006). Physiologically, high S concentrations seem to induce Ca deficiency in such a way that no S homeostasis takes place in the plants (*Haneklaus* et al. 2006b). Nutrient enhancement trials usually focus on the effect relationships between S-supply and yield, quality and plant health in terms of acute and latent deficiency, while a surplus of S receives little attention. *Haneklaus* et al. (2006) have compiled available experimental results on the effect of increased S doses on plant growth and, based on a metadata analysis, derived upper critical S contents associated with a 10% decrease in yield (Table 7).

Table 7: Critical total sulphur concentrations (mg/g S, T.M.) in young leaves of rapeseed and sugar beet as well as the total above-ground leaf mass of cereals during initial budding or early closing of rows (Haneklaus et al. 2006b).

	Deficiency	Optimal supply		Surplus
Crop	Symptom threshold value	Lower critical S content (- 5% yield)	Yield threshold value	Upper critical S content (- 10% yield)
Grain	< 1.2	3.2	4.0	> 7.5
Rapeseed	< 2.8[2] and <3.5[3]	5.5	6.5	> 14.0
Sugar beet	< 1.7	3.0	3.5	> 4.5

[1]Rapeseed, grain and sugar beet yields
[2]Single and [3]double zero rapeseed variety characters

Too high a supply of S is particularly critical on grassland, where animal health can be at risk. In ruminants, S levels of >0.38% S (T.M.) in growth cause polioencephalomalacia, neurological damage and haemolytic anaemia (*Stoewsand* 1995, *Gould* et al. 2002). *Kamphues* et al. (2016) consider the S requirement in the feed to be covered at 0.15-0.2% (T.M.). At contents of >0.25%, Cu and Se deficiency can be induced and at concentrations of >0.3% there is a risk of induction of PEM.

3.6 Effects of acidification on the mechanical separability of liquid manure

As acidification alters the chemical, physical and biological properties of liquid manure, effects on liquid manure separation can also be expected. *Cocolo* et al. (2016) showed that acidification with H_2SO_4 leads to larger particles, lower viscosity and lower surface charge of the particles in the liquid manure. The reason for the formation of larger particles is the aggregation of previously dispersed particles due to the decrease in surface charges.

The physico-chemical changes in the liquid manure properties cause increasing flow rates in the screw press, centrifuge and flocculation with subsequent drainage (screw press, decanter centrifuge, flocculation + drainage). This accelerates the separation of liquid manure with all three separation techniques tested by *Cocolo* et al. (2016). In line with this, *Gomez-Munoz* et al. (2016) also found lower separation efficiency of acidified liquid manure compared to that of untreated liquid manure. However, this is at the expense of the quality of the separated solid phase, whose dry matter, P:N ratio, fertiliser value and energy content decreased in favour of the liquid fraction (*Cocolo* et al. 2016). Acidification leads to dissolution of phosphates such as struvite and carbonates, so that P, Ca and Mg deposition in the solid phase is reduced (*Fangueiro* et al. 2009). *Regueiro* et al. (2016c) also found higher levels of phosphorus in the liquid phase of mechanically separated liquid manure due to acidification. This also explains the lower P:N ratios in the solid phase of liquid manure acidified before separation.

In contrast to the effect of H_2SO_4 by *Regueiro* et al. (2016c), the $Al_2(SO_4)_3$ used for liquid manure acidification improved the effectiveness of liquid manure separation. Aluminium sulphate led to larger particles and almost complete separation of the phosphorus in the solid phase.

Acidification before mechanical separation also reduced NH_3 outgassing during pressing with the screw press (*Regueiro* et al. 2016a). The authors conclude that liquid manure separation is environmentally sound if acidification is employed using the cheaper pressing method compared to centrifugation.

3.7 Biogas from acidified liquid manure

The use of liquid manure as a co-substrate in biogas production replaces fossil fuels and thus makes a positive contribution to climate protection in agriculture. The fermentation process and biogas yield are crucially dependent on the quality of the fermentation substrates and the physio-chemical conditions in the fermentation reactor. Of the chemical factors, the pH value and sulphur content in particular play a decisive role. Since both variables are strongly changed by liquid manure acidification with sulphuric acid, effects of liquid manure acidification on biogas production can be expected when using liquid manure from co-substrate. This assumption is supported by numerous studies which have provided reliable evidence that CH_4 emissions from animal stables and liquid manure stores are significantly reduced by acidification of the liquid manure (e.g. *Petersen* et al. 2012, *Regueiro* et al. 2016b, *Wang* et al. 2014).

Overall, the microbial substance turnover in liquid manure is slowed down by acidification, and methanogenesis is also increasingly inhibited when values fall below pH 6 (*Weiland* 2010). This leads to lower production rates of CH_4 and sulphides (*Ottosen* et al. 2009), which can causally explain the above-mentioned finding of a tendency towards reduced emission of H_2S from acidified liquid manure. However, the literature is ambiguous here. For example, *Dai & Blanes-Vidal* (2013) found no significant effect of acidification of pig liquid manure with H_2SO_4 on H_2S emissions. A specific inhibition of methane production due to SO_4^{2-} was demonstrated by *Moset* et al. (2012). The authors found a more than 40% decrease in CH_4 production when 2.5 kg SO_4^{-2} per m3 (0.83 kg S m^3) was added to pig liquid manure and 2.0 kg SO_4^{2-} (0.67 kg S m^3) to cattle liquid manure.

Moset et al. (2016) investigated the influence of increasing amounts of acidified cattle liquid manure as a co-substrate on biogas formation. With the addition of small quantities, the CH_4 yield was increased by 10%, but with a proportion of 20% acidified cattle liquid manure in the fermentation reactor, the CH_4 yield already decreased significantly by 30%.

It follows from these results that the sulphuric acid used for liquid manure acidification in the barn is not suitable for farms with co-fermentation of liquid manure. The fermentation residues can then only be acidified with H_2SO_4 during application, which significantly reduces ammonia emissions in the field, but leads to high S inputs into the soil due to the relatively high acid neutralisation capacity of fermentation residues.

However, a combination of the processes "liquid manure acidification with H_2SO_4 in the stable" and "liquid manure separation" with subsequent exclusive use of the thick separation as co-substrate in biogas production is conceivable. This combination would exploit the advantages of each method while avoiding disadvantages: (1) Acidification in the barn leads to a maximum reduction of NH_3 outgassing along the entire liquid manure chain from the barn to the storage and spreading. (2) At the same time, CH_4 emissions are greatly reduced. (3) Acidification in the stable improves the climate in the stable and therefore has a positive effect on animal welfare. (4) Acidification transfers the phosphorus into the liquid phase and thus reduces the P-load in the fermentation residue. (5) Phosphorus can be recovered from the liquid phase in the form of struvite and used specifically as a mineral fertiliser. (6) Also the SO_4^{2-} remains predominantly in the liquid phase and therefore does not burden the fermentation process. (7) With the solid phase, only the energy-rich part of the liquid manure enters the fermentation reactor, there is no unnecessary dilution of the energy sources in the fermentation reactor. If the transfer of phosphorus into the liquid phase does not seem sensible from the point of view of individual nutrient management, acidification in the barn can be carried out with $Al_3(SO_4)_3$. As a result, P is bound to the Al hydroxides formed during the reaction of $Al_3(SO_4)_2$ and separated with the solid phase during liquid manure separation.

For the acidification of l liquid manure in the stable, organic acids could possibly also be of interest, as they would on the one hand reduce the NH_3 emission from the stable and also improve the stable climate, and on the other hand reduce to methane in the fermentation reactor and thus increase the biogas yield. If acetic acid is used, which is also formed in the biogas reactor during acetogenesis from the products of acidogenesis as substrate of methanogenesis, about 0.4 kg biogas (CH_4) would be produced per kg acetic acid (80%). Under normal conditions, this corresponds to a biogas volume of about 740 litres. The additional biogas yield can cover part of the costs of acidification. According to *Daumer* et al. (2010), one kg of acetic acid costs about 1 €. *Daumer* et al. (2010) added 20 g acetic acid (80%) to 1 kg pig liquid manure and achieved pH values between 4.5 and 5. Taking this dosage as reference, the additional biogas yield would be about 15 m^3 per tonne of liquid manure, which corresponds to an increase in biogas production from liquid manure of more than 50% (biogas yield from pig liquid manure = 22 m^3 per tonne of fresh matter, biogas yield from cattle liquid manure = 26 m^3 per tonne of fresh matter, *Linke* et al. 2006). Regueiro et al. (2016d) titrated pig liquid manure with 122 and beef liquid manure with 175 mmol acetic acid per kg to pH 5.5. In order to reduce the pH values in the two liquid manure samples to 3.5, 507 for
pig liquid manure and 533 mmol acetic acid per kg for cattle liquid manure were required.

Table 8: Possible additional methane yields by acidifying the liquid manure with acetic acid.

Author	Animal species	pH	Amount of acetic acid mmol kg^{-1} 1)	kg t^{-1}_{FM} 2)	Methane Nm
Daumer et al. (2010)	Pig	4.5 – 5		20	12.0
Regueiro et al. (2016d)	Pig	5.5	122	2.7	
	Pig	3.5	423		9.5
	Cattle	5.5	175		3.9
	Cattle	3.5	533		11.9

Compared to the use of H_2SO_4 , however, it is to be expected that a similar reduction of CH_4 formation in the barn will not be achieved; it is even conceivable that CH_4 emission from the barn will be promoted.

3.8 influence of acidification on the concrete

During liquid manure acidification in the barn and in the store, it must be checked whether the measure can lead to damage to the structures. As the mixing of the acid into the liquid manure takes place in specially designed reactors, the structures do not come into direct contact with the concentrated sulphuric acid which strongly attacks the concrete. The pH values after the reaction of the sulphuric acid with the liquid manure are between 5.5 and 6.5. Liquid manure tanks are classified in exposure class XA1 with regard to chemical attack. The pH value may lie between 5.5 and 6.5. Accordingly, the lowering of the original pH value of the liquid manure through acidification should not yet require a change in the exposure class.

However, it is uncertain whether the additional input of sulphate by the sulphuric acid leads to a classification of the concrete in exposure class XA2. This is the case when the sulphate concentration is above 600 g m^{-3}, which will regularly be the case when acidifying with sulphuric acid. A classification from XA1 to XA2 would mean that a higher concrete quality is required for container construction, which is possible for new buildings without any problems, but would be a problem for existing buildings. However, it should be noted that liquid manure tanks in outdoor areas are classified in XF3 because of frost attack, which covers XA2. Only liquid manure channels and liquid manure cellars would then still be affected, because they do not have to be designed for XF3. However, there is a need for further research and legal uncertainty.

4 Legal aspects

Within the framework of this chapter, an overview of the legal provisions relevant to licensing practice shall be presented, the consequences of acidification according to the applicable legal situation shall be identified and the resulting need for modification shall be outlined. However, an exhaustive legal treatment of the subject is not provided for in this expert opinion.

4.1 International agreements and regulations relating to the reduction of emissions

4.1.1 Convention on Long-Range Transboundary Air Pollution and EU Directive "National Emission Ceilings" (NEC Directive)

Emissions of air pollutants must be reduced in order to prevent and avoid negative effects on human health and ecosystems. Action at national level is often not sufficient because air pollutants can be transported over long distances.

Therefore, the EU and the other parties to the Convention on Long-Range Transboundary Air Pollution have set national emission reduction commitments for the air pollutants sulphur dioxide (SO_2), nitrogen oxides (NOx), ammonia (NH_3) and non-methane volatile organic compounds (NMVOC) in the Gothenburg Protocol (= Multilateral Protocol) for 2005. In May 2012, the Parties agreed to amend the Gothenburg Protocol. It lays down percentage emission reduction commitments for 2020 and all subsequent years for the above pollutants. The reduction targets are based on 2005 emissions. Germany has ratified the amendments to the Protocol 2017 by means of a law amending the Multicomponent Protocol. At the end of 2013, the EU Commission proposed a follow-up directive to the NEC Directive to implement the amended Gothenburg Protocol.
At the end of June 2016, the EU Commission, the European Council and the European Parliament agreed on reduction commitments, which are also stated as relative changes compared to 2005 emissions. This new NEC Directive (EU) 2016/2284 entered into force on 14/12/2016. The reduction commitments for the period 2020 - 2029 are identical to those of the amended Gothenburg Protocol, and significantly larger reductions are envisaged for emissions from 2030 onwards. According to this, German ammonia emissions must be reduced by 29% by 2030 compared to 2005.

The new NEC Directive includes extensive reporting obligations. In addition to annual emission reporting, emission forecasts for the above air pollutants must be submitted every two years. In addition, a national clean air programme must be drawn up and updated at least every four years. In addition to emission forecasts, this programme must also contain strategies and measures to reduce emissions, including an assessment of reduction potentials. The first national clean air programme was submitted to the EU Commission in May 2019.

As an important measure to reduce emissions of ammonia, the Clean Air Programme includes the acidification of liquid manure and fermentation residues (referred to there, among other things, as "liquid manure neutralisation in stables and stores"). On the basis of current knowledge it can be assumed that the reduction commitments in Germany cannot be met without acidification of liquid manure and fermentation residues.

4.1.2 EU Directive "Industrial Emissions" (IE Directive)

In addition to compliance with the national emission ceilings, which refer to emissions throughout Germany (area-related immission control), sector-specific regulations also lay down emission limit values for pollutants according to the state of the technology for facilities (installation-related immission control) as well as other emission-limiting regulations.

Directive 2010/75/EU on industrial emissions (IE Directive) replaces the Directive on integrated pollution prevention and control (IPPC Directive). The Directive entered into force on 6 January 2011 and is the main European regulatory basis for the approval and operation of industrial installations. Its main objective is to harmonise environmental standards in Europe and thereby create fairer conditions of competition. One of the main developments compared to the IPPC Directive is the strengthening of the "BREF documents", which contain regulations on "Best Available Techniques" in the areas of industrial installations of particular environmental relevance. Emissions from livestock farming are covered by the BREF "Intensive livestock farming of pigs and poultry". The factsheet describes the best available techniques for reducing emissions, thus setting out the state of the art at EU level.

The main objective of the Directive is to identify new techniques and processes for industrial activities that protect the environment as Best Available Techniques (BAT) and then to bring them to fruition as quickly as possible and in a uniform manner throughout the EU.

The BAT conclusions, which are the main outcome of the preparation of each BREF document, are adopted at European level under the IE Directive and published in the EU's Official Journal. In Germany, new requirements from the conclusions of the BREF documents are implemented in a General Administrative Regulation or taken into account in the preparation of the update of the TA-Luft and by revising the relevant Federal Immission Control Ordinances or, if necessary, other ordinances.

For the acidification of liquid manure, the implementing decision (EU) 2017/302 of the EU Commission of 15 February 2017 on conclusions on the best available techniques (BAT) pursuant to Directive 2010/75/EU of the European Parliament and of the Council with regard to the intensive rearing of poultry or pigs is relevant. It lists the acidification of liquid manure to reduce ammonia emissions from liquid manure storage (BAT 16), liquid manure spreading (BAT 21) and pig housing (BAT 30).

This means that the acidification of liquid manure in the barn, in storage and during spreading as a measure to reduce NH3 emissions from livestock farming is not only legitimised at EU level, but within the scope of the Directive as a possible measure must be compulsorily transposed into the national law of the EU Member States.

The provisions of the IE Directive are explicitly limited to so-called "intensive livestock farming". This only covers large livestock holdings with more than 40,000 places for poultry, more than 2,000 places for fattening pigs and more than 750 places for sows. The largest emission-relevant livestock sector, cattle farming, is not covered by the IE Directive, nor is pig and poultry farming below the thresholds of the IE Directive.

4.1.3 Implementation assistance

In accordance with the agreements reached in the 1999 Gothenburg Protocol, various documents have been drawn up by the UN/ECE technical groups to help Member States implement emission reduction measures in agriculture. Firstly, the "Guideline for the Prevention and Reduction of Ammonia Emissions from Agricultural Sources" was revised and published in 2014. The guideline describes the various measures, identifies their reduction potentials and gives advice on which measures are the most suitable for the respective site conditions. With the "Guidelines for Good Practice in Emission Reduction", a basic framework was drawn up in 2015 on the basis of the findings of the Guideline for Emission Reduction, which the Member States can use to implement the "Rules of Good Practice in Ammonia Emission Reduction". These national rules must be published by the ratifying Member States. In Germany, these are currently being developed in an interministerial working group of BMU and BMEL.

Both UN/ECE documents mention the acidification of liquid manure in the barn, during storage and during spreading as an effective measure to reduce NH_3 outgassing. Bittman et al. (2014) pointed out that the acidification of liquid manure in pigsties leads to NH_3 emission reductions of 70%. With regard to the acidification of liquid manure in storage and during spreading (60% reduction of NH_3 emissions), the authors already point out in paragraph 175 that not only sulphuric acid, but in principle also other mineral acids and also organic acids should be considered as effective liquid manure additives. Salts are also mentioned as possible additives.

4.2 Relevant national legal provisions for the licensing practice

The liquid manure acidification can be carried out as described in chapter 3.1.2 in the barn, in the store or when spreading liquid manure on the fields. This initially requires the set-up of the respective technical equipment required for this purpose, e.g. acid storage tanks and mixing reactors. In many cases this will take place on existing agricultural enterprises, i.e. it will involve possible changes to the installations and/or their use. In this respect, liquid manure acidification requires structural additions to existing stables, liquid manure stores and tractors. The acidification of liquid manure also leads to changes in the way farms operate. In some cases, acidified liquid manure is produced and stored on farms. The acid to be used must be stored on farms. Acidified liquid manure or acid is also transported to a farm, usually on public roads. Acidified liquid manure is spread on farmland.

4.2.1 Formal approval requirements for structural measures

For structural alterations of stables or storage installations, in particular, permits according to the Federal Immission Control Act (BImSchG) or building permits may be required.

4.2.1.1 BImSchG approval

A distinction must first be made as to whether the already constructed barn or the already constructed storage installation has itself already been approved as an installation within the meaning of the BImSchG due to a certain size, e.g. according to No. 7.1 of Annex 1 of the 4th Federal Immission Control Act. BImSchV as an animal husbandry plant or according to No. 9.36 of Annex 1 of the 4. BImSchV as liquid manure storage. If this is the case, the modification of these installations may be subject to a permit pursuant to Article 16 of the Federal Immission Control Act if it is substantial because the harmful environmental impacts or other hazards may increase. This must be assessed on a case-by-case basis.

Even the "working" tractor in the field is basically an installation within the meaning of article 3 para. 5 of the BImSchG. In annex 1 of the 4. BImSchV, however, no approval requirements are standardised for this purpose. The installation of acid tanks on the tractor should therefore not require approval under the BImSchG.

4.2.1.2 Building permit

If no permit under the BImSchG was required for the existing plant, a building permit may be necessary. This depends on the respective national regulations. However, if tanks and reactors are installed in an existing building or liquid manure storage installation, a building permit should not be required because the building is already constructed and a change of use in the sense of building law is unlikely to occur.
If these are "free-standing" outside of livestock buildings, it will depend on the details of the building regulations of the respective state law concerned and their size in each individual case whether they require a building permit.

If concrete from liquid manure channels and liquid manure cellars approved under building law is replaced, there could possibly be a modification of a structural installation requiring a permit. It will probably depend on whether this is regarded as a significant change in the building fabric according to the traffic perception, which will depend on the individual case and can be assessed differently from region to region (cf. Spannowsky/Otto/Kemper, BeckOK Federal State Building Order Niedersachsen, 12. Edition, Stand: 30.11.2018, § 63 NBauO Rn. 19, beck-online; Simon/Busse/Decker, 133. EL April 2019, BayBO Art. 55, 122. EL, Mai 2013, Rn. 26, 27, beck-online).

4.2.2 Material requirements according to the WHG

4.2.2.1 Requirements of Section 62 (1) WHG

Pursuant to Article 62 para. 1 sentence 1 of the Federal Water Act (WHG), installations for storing, filling, producing and treating substances hazardous to water must be designed, constructed, maintained, operated and decommissioned in such a way that no adverse change in the properties of water bodies is to be expected (so-called principle of concern). For facilities handling substances hazardous to water and for storing and filling liquid manure, liquid manure and silage effluent (JGS) and comparable substances produced in agriculture, Article 62 paragraph 1, sub-paragraph 3 of WHG gives privileges to the extent that only the best possible protection of water bodies against adverse changes in their properties can be achieved. This means that protective measures may have to be taken (cf. Berendes/Janssen-Overath, in: Berendes/Frenz/Müggenborg, WHG, 2nd edition 2017, § 62 marginal note 26 a.E.). For the provision of Section 62 of WHG, there are specific requirements in the Ordinance on Installations for Handling Substances Hazardous to Water (AwSV). According to Section 13 (3) AwSV, special rules apply to the so-called JGS plants (liquid manure, liquid manure and silage effluent plants) within the meaning of Section 2 (13) AwSV. The special regulations for JGS installations concretise the privileges under Section 62, paragraph 1, sub-paragraph 3 of WHG.

The classic liquid manure stores for non-acidified liquid manure are therefore privileged. It would therefore be fundamentally disadvantageous in terms of licensing law if liquid manure storage installations in which acidified liquid manure is stored could no longer be classified as JGS installation. This must be investigated immediately.

Mixed reactors may not even be privileged, but would have to be classified as installations for the treatment of substances hazardous to water.

4.2.2.2 JGS installations pursuant to Article 2 para 13 of AwSV

JGS installations are defined in Section 2 paragraph 13 of AwSV as installations for the storage or filling exclusively of

- farm fertilisers, in particular liquid manure or solid liquid manure within the meaning of section 2, paragraph 1 of the German Fertiliser Act (No 2-4) (DüngG)
- Liquid manure

According to article 2, paragraph 1 of Fertilizer Act 4, liquid manure is farm manure made from all animal excrements, even with small quantities of litter or fodder residues or the addition of water, the dry matter content of which does not exceed 15 percent. Acid is neither an animal excrement nor litter, nor feed residue nor water. Accordingly, acidified liquid manure is no longer liquid manure within the meaning of article 2 of Fertilizer Act 4.

Acidified liquid manure should not fall within the definition of farm fertiliser under Article 2 of Fertilizer Act 2 either, because it does not result from the mere aerobic or anaerobic (without oxygen) treatment of an animal excrement or plant substance. Acidified liquid manure is also unlikely to fall under any of the other provisions of Article 2 (13) of AwSV.

Consequently, according to the current legal situation, plants for the storage of acidified liquid manure should no longer be JGS installations within the meaning of the AwSV according to the legal definitions.

4.2.2.3 Possible influence of a broader interpretation of the AwSV by the BLAK working group

However, taking into account a reference paper of the BLAK working group, it must be examined whether a deviating and expanding interpretation would be legally justifiable. In the "Notes agreed between the Federal Government and the States on the interpretation and implementation of the Ordinance on Installations for Handling Substances Hazardous to Water (AwSV)", the working group takes a more generous line at any rate for washing water from milk production (so-called milking house water) and for washing water produced in certain exhaust air purification plants. According to this agreement, they are to be allowed to be fed into the privileged JGS installations without losing their privileged status. However, milking house water contains small amounts of detergents and disinfectants. In exhaust air purification systems with biofilters with nitrogen separation or bioscrubbers, the filter material is kept at a constant pH value between 6 and 7.5 with a mineral acid (usually sulphuric acid) and a lye. The washing water from these plants therefore contains an acid and a lye. According to the guidance document, the discharge of the washing water was in line with normal practice before the AwSV was issued. It had not been addressed in the legislative procedure and should therefore probably not be prohibited. Only a small and necessary amount of washing water was used in agricultural practices. The requirements for the storage of such water should not be higher than those for liquid manure, liquid manure and silage effluent. Its initiation was therefore also appropriate from the point of view of proportionality. Washing water from chemical washers, which are intended to keep the filter material at a pH value of 1.5 to 5, may not be fed into JGS installations. (cf. https://www.bmu.de/fileadmin/Daten_BMU/Download_PDF/Binnengewaesser (inland waters)/awsv_hinweise_interpretation_bf.pdf (interpretation of awsw references). Chemical washers are therefore likely to be more acidic than biofilters and washers and therefore contain more acid. They can also be replaced by biofilters and scrubbers that use less acid (proportionality).

According to this approach, certain amounts of acid should therefore be permissible after all, irrespective of the wording of the law and the prevailing opinion on it.

The jury is still out on whether the references can still be classified as legally justifiable. Acidified liquid manure should be brought to a pH value of less than 6, 5.5 is recommended. In terms of pH value, the acidified liquid manure is thus located exactly between the biofilters and biowashers and the chemical washers. However, it has to be considered that the total washing water is likely to represent only a very small proportion of the quantities fed into the JGS installations, while all liquid manure is expected to be acidified. Consequently, according to the considerations of the BLAK working group on biofilters/washers and chemical washers, acidified liquid manure should no longer be fed into JGS installations.

4.2.2.4 Acidified liquid manure as a “comparable substance produced in agriculture”

However, it may also be possible to subsume acidified liquid manure directly under the privilege of Article 62, paragraph 1, sub-paragraph of 3 of WHG, namely as a "comparable substance produced in agriculture". This addition was inserted into the new WHG 2010 in order to achieve objectively justified equal treatment of comparable substances produced in agriculture. For example, biomass for or fermentation residues from biogas plants now also fall under the privilege. Contrary to the Federal Council's original proposal to create an extension for comparable substances produced in agriculture, the regulation for comparable accumulating substances was made to also cover substances that accumulate as waste. (cf. BT-Drs. 16/13306, pp. 14, 30; Berendes/Janssen-Overath, in: Berendes/Frenz/Müggenborg, WHG, 2nd edition 2017, § 62 marginal note 25). From the point of view of equal treatment alone, acidified liquid manure could possibly also be classified under a "comparable substance produced in agriculture". However, only substances of animal or plant origin that have not been mixed with other substances, such as chemicals, are to be subsumed under this category because the hazard potential then changes (cf. Landmann/Rohmer UmweltR/Meyer, 78. EL December 2015, WHG, § 62 marginal note 24, beck-online). As a result, the subsumption of acidified liquid manure under Section 62 (1) sentence 3 WHG is thus excluded.

4.2.2.5 Interim result for 4.2.2

According to the above explanations, there is a clear predominant water law argument in favour of the assumption that acidified liquid manure loses its legal privileges and is therefore formally subject to additional requirements under licensing law. Thus, if acidified liquid manure cannot be given preferential treatment, a suitability test pursuant to Article 63(1) WHG will be required.

This raises the question as to whether this is objectively justified in view of the hazard potential of acidified liquid manure and the reduction in environmental impact which acidification is intended to achieve. There are doubts about this. Rather, the technical results of this expert opinion speak in favour of a - at least clarifying - amendment of the WHG or the AwSV. As far as can be seen, no other higher-ranking provisions of environmental law should stand in its way.

For example, the AwSV makes a fundamental distinction, even for substances and mixtures pursuant to Article 3 (1), between substances that are not hazardous to water and substances hazardous to water in water hazard classes (WGK) 1 to 3. However, according to article 3 paragraph 2 of AwSV, there are also generally water-polluting substances that are not classified in WGKs. According to Article 3, paragraph 2 of AwSV, these include in particular liquid manure, liquid manure and silage effluent. According to Article 3, paragraph 2 of AwSV, the substances which may be discharged into the privileged JGS installations within the meaning of Article 2, paragraph 13 of AwSV are likely to be generally hazardous to water.

Sulphuric acid is probably a WGK 1 substance. A mixture containing sulphuric acid as a substance of WGK 1 would be classified as not hazardous to water according to No. 2.2 of Annex 1 to the AwSV, if the requirements of letters a) to i) are met. According to letter a), the content of substances in WGK 1 must be less than three percent by mass.

It is questionable whether this regulation can also be applied to substances generally hazardous to water. This means that a mixture that is generally hazardous to water and contains a substance of WGK 1 is still generally hazardous to water if the substance of WGK 1 in the mixture is below 3%. The AwSV expressly does not regulate this. However, the conclusion in terms of content is nevertheless obvious. According to the quantities given in Table 3 in Chapter 3.1.4, the proportion of acid in the acidified liquid manure should be below 2%. The other conditions of point 2.2. of Annex 1 to the AwSV should be fulfilled. This means that a mixture with so little sulphuric acid should still be classified as generally hazardous to water.

This could lead to the conclusion that acidified liquid manure does not have a significantly higher hazard potential for the aquatic environment than non-acidified liquid manure, even beyond the environmental benefits of acidification in the other quality requirements.

According to the technical findings of this expert opinion, there would therefore be nothing to prevent the legislator from clarifying the law in such a way as to favour acidification.

4.2.3 Requirements for the application of acidified liquid manure according to fertilizer law

4.2.3.1 Acidified liquid manure as fertilizer according to DüngG

As already stated above, acidified liquid manure should no longer be covered by the definition of liquid manure in article 2 of Fertiliser Act 4 or the definition of farm fertiliser in 2 article of Fertiliser Act 2. According to article 2 of Fertiliser Act 1 fertilisers are substances which are intended to

- supply nutrients to crops in order to promote their growth, increase their yield or improve their quality, or
- to maintain or improve soil fertility.

This general concept of fertiliser, which also covers conventional liquid manure used as farm fertiliser, should also cover acidified liquid manure. According to article 3, paragraph 1, sub-paragraph 1 of Fertiliser Act, substances, pursuant to Article 2 of Fertiliser Act 1, may only be used if they comply either with a type approved by a directly applicable EU legal act on the marketing or use of fertilisers or with the requirements of a regulation on the marketing of fertilisers. Under Section 3, paragraph 1, sub-paragraph 2 of the Fertiliser Act, an exception to this rule applies to farmyard liquid manure produced on the farm. This exception no longer applies to acidified liquid manure.

4.2.3.2 Acidified liquid manure as fertilizer according to DüMV

One regulation that is relevant for the investigation is the Fertiliser Ordinance (DüMV) with requirements for the marketing of fertilisers. According to its Section 4(1), conventional liquid manure may be marketed as farm fertiliser if certain conditions are met. In particular, additives of other substances may only be added in accordance with the requirements of Annex 2 of the DüMV. Table 8 of Annex 2 of the DüMV regulates secondary components. Inorganic acids like sulphuric acid do not appear there. In No. 8.3.8 of Table 8 of Annex 2 of the DüMV, detergents and disinfectants (which may contain acids) without perfluorinated tensides and only in unavoidable proportions are permissible as foreign constituents within the scope of the necessary cleaning and disinfection of stables and facilities. According to the Preliminary Remarks No. 1 for Table 8 Annex 2 to DüMV, the substances listed in Table 1 also belong to the minor constituents. No. 1.2.9 and No. 1.2.10 of Table 1 list sulphur as an element, with the restriction that this only applies to soil additives, plant additives and culture media. As a consequence, acidified liquid manure may no longer be used as farm fertiliser without amending the DüMV (or EU legislation).

However, it is possible that acidified liquid manure may be marketed and used as other fertilisers. According to section 3 paragraph 1 of DüMV, fertilisers must correspond to a fertiliser type approved by DüMV. These are regulated in Annex 1. According to the preliminary remarks and instructions for fertiliser types in Appendix 1 to DüMV in No. 1.1, fertilisers must be in the solid state of aggregation, unless the type description permits a different state of aggregation. Acidified liquid manure should not have a solid but a liquid aggregate state. In Section 3, Appendix 1, in the case of the organic and organic-mineral fertilisers listed in column 5, substances in liquid form as listed in Table 7 of Appendix 2 are also permissible. However, acid-enriched liquid manure should not fall under Table 7, Annex 2 of DüMV.

Consequently, acidified liquid manure cannot be used as other fertiliser at present.

4.2.3.3 Requirements of the fertiliser ordinance

If an amendment to the DüMV permits the spreading of acidified liquid manure, the requirements of the Fertiliser Ordinance (DüV) must be met for the then permissible spreading. This regulates good professional practice. This means that requirements under the Federal Soil Protection Act (BBodSchG) and the Federal Nature Conservation Act (BNatSchG) are then also met. According to article 7 of BBodSchG, a duty of precaution must be fulfilled. According to article 17 of BBodSchG, this is fulfilled by good professional practice in agricultural land use. Under article 5, paragraph 2, sub-paragraph 6 of the Federal Nature Conservation Act, fertilisers must be applied in accordance with the provisions of specialist agricultural legislation.

According to article 6, para. 3, sub-paragraph 1 of DüV, from 01.02.2020 on arable land and from 01.02.2025 on grassland, liquid fertilisers with a substantial content of available nitrogen or ammonium nitrogen may only be applied to the soil in strips or directly into the soil. Exemptions may be granted under article 6, paragraph 3, sub-paragraph 3 of DüV for other processes if these lead to comparably low ammonia emissions. This means that such a derogation would be necessary for acidified liquid manure. A clear legal regulation would also be more practicable in this respect.

4.2.4 Requirements according to the Recycling Management Act

If necessary, additional requirements may result from the Closed Substance Cycle and Waste Management Act (KrWG) for acidified liquid manure. Under article 2, paragraph 2, sub-paragraph 4 of the KrWG, only faeces and other natural non-hazardous agricultural materials used in agriculture which do not harm the environment or endanger human health are excluded from the scope of the Act. Conventional liquid manure is included. This could be assessed differently for acidified liquid manure. However, if clarifications and adjustments are made in the above-mentioned laws for acidified liquid manure, the KrWG is unlikely to assess it differently in terms of its potential for damage and danger.

4.2.5 Requirements for the transport of acid and acidified liquid manure by road

The Carriage of Hazardous Goods by Road is subject to the Hazardous Goods Transport Act (GGBefG). On the basis of article 3 of the GGBefG, the Regulation on the national and international transport of hazardous goods by road, rail and inland waterways (GGVSEB) was adopted (cf. I, No. 33 of 24.06.2009, p. 1389). According to article 1, paragraph 3, no. 1, sub-section a of GGVSEB, the provisions of parts 1 to 9 of Annexes A and B to the European Convention of 30 September 1957 on the carriage of hazardous goods by road and the provisions of Annex 2 No 1 to 3 and Annex 3
apply to national transport by road. Part 3 of the ADR in Chapter 3.2 contains a list of hazardous goods. In Table A, for example, sulphuric acid with more than 51% acid as a Class 8 hazardous material is listed as a corrosive substance under UN number 1830. Part 1 in Chapter 1.4 sets out the safety obligations of the parties involved. Part 8 of Chapter 8.2 stipulates that drivers of vehicles transporting hazardous goods require a training certificate, which according to 8.2.2.8.2 is only valid for five years.

Chapter 3.2 in no. 3.1.3 specifies when mixtures are subject to ADR. Mixtures must be subject to the classification criteria of the ADR. Acidified liquid manure should therefore be treated according to chapter 2.2. No. 2.2.8 are subject to the ADR if it is itself classified as a corrosive substance. To do so, it should be able to cause irreversible damage to the skin according to no. 2.2.8.1.1, which is probably not the case.

Parts 1 to 9 of the ADR also apply to cross-border and intra-Community transport by road in accordance with § 1 (3) No. 1 (b) GGVSEB.

International transport is also subject to ADR, which Germany adopted by the Consent Act of 18.08.1969.

There are also the directives implementing the Regulation on the transport of hazardous goods by road and rail (RSE). These contain application instructions for GGVSE and ADR, forms, samples as well as the catalogue of fines and warnings. The countries transpose the RSE into general administrative provisions. This may result in additions to the explanations.

Another potentially relevant regulation is the Regulation for Commissioners for Hazardous Goods (GvV), according to which every company involved in the transport of hazardous substances, including road transport, which is not exempted under Section 2 of the German Civil Code (GbV), must appoint a hazardous goods officer. An exemption depends, inter alia, on the quantities transported.

4.2.6 Requirements for the handling of acid and acidified liquid manure on farms

The handling of hazardous substances is governed by the Ordinance on Hazardous Substances (GefStoffV) based on the Chemicals Act and the Occupational Safety and Health Act. This regulates in particular requirements for the handling of hazardous substances. According to article 2 paragraph 1, no. 1 of GefStoffV, hazardous substances are dangerous substances and mixtures according to section 3. According to Section 3 (1) of the Ordinance on Hazardous Substances, hazardous are those substances and mixtures that meet the criteria of Annex I of Regulation (EC) No. 1272/2008. Point 3.2 of the Regulation lists substances with corrosive and irritant effects on the skin, which may include sulphuric acid. Acidified liquid manure could also be included because of its sulphuric acid content. There are specific regulations on when even small proportions will suffice. Acidified liquid manure may also be a hazardous substance due to the possibility that flammable gases according to No. 2.2 may be produced.

On the basis of section 20 of GefStoffVO a committee for hazardous substances is formed which decides on Technical Rules for Hazardous Substances (TRGS). TRGS 500 (protective measures), TRGS 509 (storage of liquid and solid hazardous substances in fixed containers and filling and emptying points for mobile containers) and TRGS 510 (storage of hazardous substances in mobile containers) are likely to be decisive in this respect.

5 Summary and Conclusion

The ecological impacts of anthropogenic intervention in the global nitrogen (N) balance are now considered to be more serious than those resulting from climate change caused by anthropogenic trace gas emissions (*Steffen* et al. 2015, *Rockström* et al. 2009). The reduction of N inputs into the environment is therefore one of the most important objectives of environmental policy.

By far the most important emitter of N is the agricultural sector. In particular, liquid manure-based livestock farming is a major contributor to ammonia (NH_3) emissions to the environment.

The reason for the outgassing of NH_3 from liquid manure is the high pH value in the manure, where the chemical equilibrium between NH_4^+ and NH_3 is on the ammonia side. By adding acid, the balance can be shifted in favour of NH_4^+. This theoretically allows the complete suppression of NH_3 outgassing from liquid manure.

In addition to the equilibrium of the ammoniacal N-species, the pH value in liquid manure also influences other chemical equilibria, biochemical and biological reactions and physical properties of the liquid manure. After spreading, acidified liquid manure also leads to reactions in the soil, which are caused by the acid on the one hand and the conjugated base on the other. In addition, very different substances can be used to acidify liquid manure. In addition to sulphuric acid, other strong mineral acids are possible, organic acids can also be used, and there are also studies on the effects of acid salts. All in all, this results in a complex structure of effects which must be comprehensively investigated in order to be able to assess the environmental compatibility of manure acidification. Against this background, UBA has commissioned UBA to compile the knowledge available to date on the subject and to address the question of whether the acidification of liquid manure can be an environmentally sound, practicable measure to reduce NH_3 emissions from agriculture.

With regard to the use of sulphuric acid for manure acidification, numerous studies are now available which, in addition to the emission-reducing effect, were aimed at the effects on the manure properties themselves as well as on the soil and plant growth.

5.1 How much is the NH_3 emission from liquid manure reduced by acidification with H_2SO_4?

Acidification can take place in the barn, in the store or principally during spreading. Acidification in the barn reduces NH_3 outgassing in the barn and store as well as during application, while the addition of H_2SO_4 directly during application can only reduce NH_3 outgassing in the field. In their literature review, *Fangueiro* et al. (2015) have cited reduction rates ranging from 15 to 98% across all methods. The effectiveness of acidification is strongly dependent on the pH value set in the liquid manure. For example, pH values of 6.0, 5.8 and 5.5 reduced NH_3 outgassing from acidified liquid manure by 50, 62 and 77% compared to that from untreated liquid manure in a laboratory experiment (*Dai & Blanes-Vidal* 2013). Under practical conditions in pig houses in Denmark, the acidification of liquid manure in the house by means of the "JH Forsuring NH_{4+} system" (daily acidification in the reaction tank to pH 5.5 with 5.8 to 7.1 kg 96% H_2SO_4 per porker and return of part of the acidified liquid manure to the house, transfer of the rest of the acidified liquid manure to the manure store) resulted in a reduction of 63 - 66% in house emissions compared to those from control houses (*Riis*, 2016).

Conclusion: The strong NH_3 emission-reducing effect of the acidification of liquid manure with H_2SO_4 has been proven beyond doubt. Acidification is one of the most effective reduction measures in the stable, during liquid manure storage and during spreading. During spreading, reductions of NH_3 outgassing are achieved which are comparable to those of liquid manure injection.

5.2 What other properties of liquid manure are changed by acidification with H_2SO_4?

Chemical properties: This leads to protonation of other weak acids (e.g.

$HS^- + H^+ = H_2S$, $RCOO- + H^+ = R\text{-}COOH$). During the treatment of liquid manure with H_2SO_4, this can lead to increased outgassing of H_2S and volatile organic odorous substances (*Riis* 2016). Overall, however, the outgassing of these substances is little affected (*Dai & BlanesVidal* 2013, *Kai* et al. 2008) or they tend to be even lower than those from untreated liquid manure (*Riis* 2016). Phosphorus-containing precipitates can be dissolved (*Hjorth* et al. 2015, z.B. $MgNH_4PO_4 + 2H^+ = Mg^{2+} + H_2PO^- + NH^+$). The result is an improvement in the plant availability of the main nutritional elements contained in the liquid manure.

Biological properties: Overall, the microbial metabolism in liquid manure is slowed down by acidification. This leads to lower production rates of methane and sulphides (*Ottosen* et al. 2009), which can causally explain the above-mentioned finding of usually reduced emissions of H_2S from acidified liquid manure. In accordance with *Fangueiro* et al. (2016), the acidification of liquid pig manure (pH 5) after application resulted in a delay of nitrification in the soil comparable to the effect of a synthetic nitrification inhibitor (*Park* et al. 2018). This was accompanied by a reduction in nitrate leaching (-18%) and nitrous oxide emissions (-79%). *Fangueiro* et al. (2016) also showed that N mineralisation can be increased by acidification of liquid manure.

Conclusion: The changes in the manure properties induced by acidification lead to an overall improvement in the availability of the main nutrient elements N, P, Mg and Ca contained in the manure as well as to a reduced environmental impact due to nitrate leaching and nitrous oxide gas emission from the soil.

5.3 What effects on the soil can be expected?

The acid introduced into the soil by acidification of liquid manure is buffered in the soil, which may, but does not necessarily have to, lead to a decrease in the acid neutralisation capacity (SNK) of the soil. This is because the SNK is influenced by the overall fertilisation strategy. If, for example, the use of liquid manure acidified with H_2SO_4 results in the use of an S-free mineral N fertiliser instead of ammonium sulphate due to the resulting lower S requirement from other fertilisers, the SNK balance can even become positive. Ultimately, the extent of the influence of the acidification of liquid manure on the SNK of the soil depends decisively on the sulphur balance of the soil. If the additional sulphur entering the soil with the acidified liquid manure is completely absorbed by the crop and removed again with the harvest, there is no decrease in SNK due to manure treatment. For every 10 kg S that remain in the soil (or are washed out with the leachate), the SNK decreases by 0.625 kmol. This SNK loss can be compensated by 31.25 kg $CaCO_3$.

Whether the application of acidified liquid manure directly leads to a decrease in soil reaction depends not only on the amount of fertilised manure and the amount of acid it contains, but also on the pH buffering capacity of the soil. Fangueiro et al. (2018) found significant decreases in soil pH values after three years in a field trial. It must be taken into account that the investigated soils were extremely low in buffers (sands, humus content below 1%) and the given amounts of liquid manure and S were very high. However, for average well buffered arable soils, it is not expected that the liming regime based on good agricultural practice will need to be changed. However, depending on the S-balance of the soils, an average increase in lime requirements is to be expected.

Conclusion: A quantification of the effects of acidification of liquid manure on the acid neutralisation capacity of soils shows that the effects of manure acidification on the pH buffer of soils can be controlled with the available agricultural techniques.

5.4 What are the effects on plant nutrition and yield?

Negative effects on plant nutrition and yield have not yet been reported in the literature. Positive effects are more likely to be seen, which may be due to better availability of the main nutritional elements in the liquid manure and the often described increased mineral fertiliser equivalence of manure nitrogen after acidification (Kai et al. 2008).

Sulphuric acid provides the nutrient element S, so that the S supply of the plants is directly influenced by the acidification of the liquid manure with H_2SO_4. The use of liquid manure acidified by H_2SO_4 could in future lead to a reduction in the use of S-containing fertilisers, e.g. ammonium sulphate, which have been used up to now.

Conclusion: Nutrient supply, growth and yield of crops are rather positively influenced by the acidification of liquid manure with H_2SO_4.

5.5 Are negative effects on other environmental matrices to be expected?

Due to the lower N outgassing losses during acidification of liquid manure, the N contained in the liquid manure can be more reliably included in N fertilisation planning. This leads to a reduction of the "risk surcharges" for N fertilisation and ultimately to lower N pollution of air and groundwater. Increased leaching of sulphate (SO_4^{2-}) into the groundwater must be expected. Compared to the SO_4^{2-} concentrations naturally present in groundwater, however, the input is insignificant.

Conclusion: According to the current status of the literature evaluation, serious negative effects of acidification of liquid manure with H_2SO_4 on other environmental matrices are not to be expected.

5.6 Is the acidification of liquid manure with H_2SO_4 technically feasible?

In Denmark, the acidification of liquid manure with H_2SO_4 has been practised for years. Established techniques are available for the acidification of liquid manure in barns and liquid manure stores as well as for manure spreading. The technical feasibility of acidification of liquid manure has thus been demonstrated in principle (*Foged* 2017). According to *Toft* (2018, oral communication), since 2010, > 5 million m^3 of liquid manure has been acidified during application without problems using the SyreN system, of which 87 units are in use.

Conclusion: The acidification of liquid manure in stables, liquid manure stores and during spreading is possible without danger. Technical solutions are available on the market.

5.7 What is the legal situation?

There is no legal regulation prohibiting the use of acids to reduce emissions from liquid manure. Acidification of liquid manure is identified as state of the art in the BAT reference document for pigs and poultry for facilities covered by the Industrial Plant Directive. The cross-territory provisions of the NEC_RL and the Gothenburg Protocol set high ambitions, and the United Nations guidelines also list the acidification of liquid manure as an important option for reducing emissions. The Federal Government's Clean Air Plan includes acidification as an integral part of achieving the reduction targets within the framework of cross-area immission control.

Many years of practical experience with the acidification of liquid manure in Denmark have shown that, if the acid is handled correctly and properly, there is no reason to fear dangers for man and the environment, but that significant benefits for environmental and climate protection can be expected.

A first precedent for the use of sulphuric acid in livestock housing to reduce emissions has also been set in Germany with the approval of a dairy plant for the acidification of liquid manure by JH Agro A/S (DK) in Lower Saxony. The acidification of liquid manure during the application of liquid fertilisers is also already common practice in Germany. It is offered and practised, for example, by the companies Blunk GmbH in Schleswig-Holstein and Dettmer Agrar-Service GmbH in Lower Saxony as a service to agriculture.

Conclusion: The use of acids to reduce harmful gas emissions from liquid manure is already possible in Germany under the existing legal conditions. Further adaptation of the legal framework should further facilitate the use of acid in agricultural enterprises. There is an immediate need for action with regard to the provisions of the WHG and the DüG with regard to the status of acid-treated liquid manure as farm fertiliser. Further laws have to be adapted with regard to acidification to ensure legal certainty for the operator and user. In addition, the technical questions regarding the exposure class of the concrete for liquid manure channels and storage facilities have to be clarified.

6 Overall assessment

The current state of knowledge shows a high potential of acidification of liquid manure to improve the environmental compatibility of manure management, which can be exploited if the technique is flexibly combined with other techniques to avoid environmental pollution, depending on operational possibilities. The considerations are mainly based on the results of process studies, which were mainly carried out at laboratories and also technology centres. There are no studies on the effectiveness of these process combinations under practical conditions. In view of the high environmental potential of these process combinations, corresponding investigations are considered urgently necessary.

The conclusions drawn here regarding the environmental effectiveness of acidification of liquid manure are fully supported by the results of the recently completed Interreg research project "Baltic liquid manure Acidification". In addition, the interdisciplinary research project also demonstrated positive economic effects. The overall conclusions formulated as a policy recommendation at the final seminar are (*Lyngso* 2019):

"liquid manure acidification technologies (SATs) have the potential to give a major lift to the economy and the environment in the Baltic Sea Region, and in the same time give substantial greenhouse gas emission reductions:

Implementing the potential for use of SATs in the Baltic Sea Region countries would have a positive net economic effect of in total € 2.2 billion per year, to which come an estimated N abatement value of M€ 147 per year related to the aquatic environment, and positive healthcare sector effects in Russia and Belarus.

For the entire region, the implementation of liquid manure acidification in accordance with the estimated, weighed potential of 245 million tonnes of liquid manure, would annually mean a reduced ammonia emission of 167.1 Kt, and as a result of this a reduced atmospheric N deposition of 56,000 – 91,000 tonnes. In addition, the greenhouse gas emission would be reduced with 1.5 Mt CO_2*."*

7 Ten theses in conclusion

1. Acidification of liquid manure is one of the most effective measures to reduce ammonia losses in livestock farming and farm fertiliser processing.
2. It will not be possible to comply with the Federal Government's Clean Air Plan without acidification of liquid manure.
3. The acidification of liquid manure and fermentation residues can compensate for previous failures in emission reduction policy. It is therefore an important transitional technology for agri-environmental policy. More extensive avoidance and reduction technologies must be developed simultaneously.
4. Acidification of liquid manure has considerable positive deadweight effects for climate protection. These bring benefits for farmers and the society.
5. (Unnecessary) regulatory hurdles are to be removed with BMU-BMEL committees (e.g. AwSV).
6. Protective measures for the concrete must be provided for the implementation of the measure in the barn and in the storage. Research should verify the harmlessness of the concrete attack.
7. The sulphur of sulphuric acid is a valuable plant nutrient. Clear recommendations must be developed to avoid sulphur over-fertilisation.
8. Not all farms (animal husbandry and biogas) are suitable for the application of acids. These must be described transparently.
9. Safety regulations for storage, transport and use of acid must be "translated" into appropriate agricultural regulations and advisory brochures.
10. Training of farmers in the use of acid must become as natural as for the use of other chemicals and plant protection products.

Finally, we would like to point out that the measure "Acidification of liquid manure" is an effective and largely environmentally compatible technique for reducing N deposits into the environment. However, the measure does not address the causes of the nitrogen problem.

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