Interreg
Baltic Sea Region
Baltic Slurry Acidification

EUROPEAN REGIONAL DEVELOPMENT FUND
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Titration, buffer capacity and acid consumption of animal slurries in Baltic Sea Region countries

Report from WP2, Activity 3

EU STRATEGY FOR THE BALTIC SEA REGION
FLAGSHIP

Interreg
Baltic Sea Region
Baltic Slurry Acidification

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Titration, buffer capacity and acid consumption of animal slurries in Baltic Sea Region countries

Research results

Report from WP2, Activity 3

Leticia Pizzul, Lena Rodhe, Irena Burzynska, Marek Kierończyk, Kamila Mazur, Sebastian Neumann, Kalvi Tamm, Raimonds Jakovickis, Mateusz Sękowski

December 2018

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Preface

Baltic Slurry Acidification is a flagship project in the action plan for the EU strategy for the Baltic Sea Region (BSR). This project is being carried out between 2016-2019 with a budget of 5.2 million euro, of which 4 million euro is funded by the EU Regional Development Fund through the Interreg Baltic Sea Region Program.

Baltic Slurry Acidification aims to promote the implementation of slurry acidification techniques throughout the Baltic Sea Region. Slurry acidification techniques (SATs) will reduce ammonia emissions from livestock manure and thus reduce airborne eutrophication of the Baltic Sea.

This report refers to Work Package 2, Activity 2.3, and describes how various types of slurries from countries in the BSR respond to acidification with sulphuric acid in simulated storage, including the buffering capacity of the manure and the amounts of acid needed to maintain an appropriate pH during slurry storage. The studies have been conducted on a laboratory scale.

The experiments described contain results from Estonia, Germany, Latvia, Poland and Sweden. The research was carried out in 2017.

December 2018

Erik Sindhöj
Project Coordinator for Baltic Slurry Acidification

Summary

Slurry acidification is a method used to reduce ammonia emissions from animal manure slurries. The amount of acid needed to lower the pH to the target value and to stay at that level will depend on the buffer capacity of the slurry, which in turn is affected by the slurry composition, the acidification process and the acid used.

The main objectives of this work were to determine the amounts of concentrated sulphuric acid required to acidify pig and cattle slurries to pH 6.4, 6.0 and 5.5, and to identify the properties of the slurry that affected the buffer capacity of the samples taken in the Baltic Sea Region (BSR) countries. The pH stability of the different slurries and the total amount of acid required for maintaining the slurry pH during storage was also followed for approximately 2 months.

Additionally, the results on a laboratory scale for cattle slurry were compared with available results on a pilot scale under outdoor conditions.

The results showed that the amounts of acid required to acidify the slurries to a specific pH level varied widely between samples. For acidification to pH 6.4, the difference in acid requirement was about 40 times between the lowest and the highest acid amounts needed. For acidification to pH 6.0 the difference was 15 times, and to pH 5.5 about 9 times.

There were no strong correlations between measured slurry properties and the amounts of acid required to lower the pH to 5.5 when the samples from all the countries were analysed together. All laboratory-scale samples had to be reacidified during storage, and for most of them the amount of acid added on each occasion was quite constant, especially for pig slurries.

The average amounts of acid needed to lower the pH to 5.5 for slurry were higher on a laboratory scale compared with the amounts reported in available pilot-scale studies. These differences between the laboratory and pilot scales may be related to the smaller quantity of slurry subjected to acidification, the higher temperatures during storage and the frequent aeration (stirring) under laboratory conditions. Laboratory scale could be used to see differences in acid demand between slurry types, but the actual quantities of acid needed on the larger scale seem to be hard to estimate on a laboratory scale.

1. Introduction

Livestock manure is the main source of ammonia emissions in the Baltic Sea Region. Ammonia emissions have several negative impacts because they contribute to eutrophication and acidification through atmospheric deposition in nature and water catchment areas. For the agriculture sector, the ammonia emissions reduce the fertiliser value of animal manure, which must be compensated by costly mineral fertilisers. Ammonia is also an indirect greenhouse gas when converted to nitrous oxide (N_2O).

The influence of the pH value of the animal slurry on ammonia emissions is very significant, with lower emissions at lower slurry pH. Slurry acidification is one method used to reduce ammonia emissions (Hjorth *et al.*, 2015; Misselbrook *et al.*, 2016).

The efficiency of the acidification process depends on many parameters, such as slurry composition, the acidification process and the acid used. Sulphuric acid (H_2SO_4) is commonly used for acidification due to its relatively low price (Joubin, 2018). Using sulphuric acid for crops that need the addition of sulphur as fertilizer is economically justified.

The main objectives of this work were to:

- determine the amount of sulphuric acid required in the BSR countries to acidify different types of slurries to pH 6.4, 6.0 and 5.5,
- identify the properties of slurry that influence the amount of acid required to lower the slurry pH to 5.5,
- evaluate the pH stability of the different slurries and the total amount of acid required for maintaining the slurry pH during storage,
- compare the pH stability of acidified slurry on a laboratory scale with available results on a pilot scale under outdoor conditions.

Most of the literature review below is taken from the report “Titration and buffer capacity of slurry. Small-scale studies in Sweden” by Joubin (2018) from work conducted within WP2.3 in this project.

1.1. Slurry acidification and buffer capacity

Slurry acidification is a method used to reduce ammonia emissions (Hjorth *et al.*, 2015; Misselbrook *et al.*, 2016) that is implemented mainly in Denmark, where 20% of all animal slurry was acidified in 2016 (Karen Peters, Danish Ministry of Environment and Food, personal communication, September 28, 2016).

The concept of reducing slurry pH to reduce ammonia emission relies on the equilibrium between NH_4^+(aq) and NH_3(aq) dissolved in the slurry (Sommer *et al.*, 2013). Acidifying slurry to pH 5.5 reduces the relative concentrations of NH_3 and NH_4^+, with 99.8% present as NH_4^+ (Fangueiro *et al.*, 2015). The amount of acid required to lower the pH is determined by the buffer capacity of the slurry, which can be defined as the ability of a solution (in this case animal slurry) to resist changes in pH during the addition of strong or weak acids or bases.

The slurry type and its components such as total inorganic carbon (TIC), total ammoniacal nitrogen (TAN), volatile fatty acids (VFAs), other organic substances with carboxyl functional groups and some specific ions determine the slurry's buffering capacity (Sommer *et al.*, 2013; Stevens *et al.*, 1989).

Early studies showed that VFAs and TAN seem to be the most important factors that influence slurry pH and the buffer system, a high VFAs/TAN ratio correlating with a low pH (Paul and Beauchamp, 1989; Sommer and Husted, 1995). That explains why the buffer system is not only different between pig and dairy slurry but also between two different dairy cattle, or pig, slurries (Sommer *et al.*, 1995). The living conditions of animals, their feed and manure removal and management systems influence the composition of slurries and can affect their buffer system.

In tests conducted by Husted *et al.* (1991) using hydrochloric acid for acidification, it was concluded that the buffering system was regulated by the ammonium bicarbonate content. Furthermore, that a high buffer capacity causes an increase in the slurry pH back to the initial level. A 60-day study of pH changes after acidification of different slurries to pH 5.5 showed that pH increased to 6.4 between 10 and 20 days after acidification with different acids (sulphuric acid, acetic acid, citric acid, lactic acid) (Regueiro *et al.*, 2016).

1.2. Slurry acidification in practice

On the farm, slurry can be acidified at different stages of the manure-handling system: *in-house*, *in-storage* and *in-field*. In Denmark the *in-storage* technique has been developed to acidify in the storage tank or lagoon during mixing and is often used just before spreading. In this study, the focus is on acidification at the start of storage to investigate the effect during long-term storage. For *in-house* or *in-storage* systems, at the start of the storage period the target pH value is 5.5. For *in-storage* just before spreading the target pH value is 6.0, and 6.4 for *in-field* according to Danish regulations.

During storage the slurry pH value changes over time depending on the slurry buffer system. According to Petersen *et al.* (2012) and Hjorth *et al.* (2015), the rise in pH is due to microbial activity and the hydrolysis of VFAs, mineralization of organic nitrogen and dissolution of carbonates. Most studies measure pH changes after one acidification, but there is little information about how much acid is needed to keep the pH stable at 5.5 during long-term storage.

The most commonly used acid for slurry acidification is concentrated (95-98%) sulphuric acid (H_2SO_4). The advantages of using sulphuric acid are as follows:

- strong acid and therefore smaller volumes are needed compared with weaker acids, such as acetic acid or formic acid (Joubin, 2018);
- the S fertilizer value of the acidified slurry is increased as a result of a stable sulphate pool during storage (Eriksen *et al.* 2008);
- easily available on the market;
- inexpensive compared with alternative acids because less is needed, and the price is lower (Joubin, 2018).

On the other hand, the use of sulphuric acid can have some disadvantages:

- corrosiveness;
- hazards to animal and human health (Fangueiro *et al.*, 2015);
- the high content of inorganic S in the acidified slurry may lead to the development of odour from volatile S-containing compounds (Eriksen *et al.* 2008);
- sulphuric acid is not allowed in organic farming.

2. Material and methods

The experiments were conducted on a laboratory scale following a detailed protocol for titration and determination of the buffering capacity of the slurries, which is presented in Appendix 1. All data regarding slurry properties and pH and acid consumption from each of the participating partners were compiled in an Excel template (Appendix 2). The data were analysed by country and at regional level and presented in figures and tables.

2.1. Slurries

Pig and cattle slurries from Estonia, Germany, Latvia, Poland and Sweden were tested. Pig slurries included one sample from Estonia, three from Germany and three from Sweden (Table 1). Cattle slurries consisted of one sample from Estonia, two from Germany, one from Latvia, nine from Poland and three from Sweden (Table 2). All slurries came from conventional farms except two of the Swedish dairy cattle slurries, which were collected from organic farming.

One sample of co-digested pig slurry from Germany was also included.

Samples were characterized according to their initial pH, percentage of dry matter (DM%), total nitrogen (Tot-N), total ammoniacal nitrogen (TAN), total carbon (Tot-C) and total phosphorus (Tot-P) content. C:N ratios were calculated as Tot-C/Tot-N. The properties of slurries are described in subchapter 3.1.

2.2. Titrations

Titrations were carried out as described in Appendix 1. Briefly, small known volumes of concentrated sulphuric acid (95%) were added to the slurry sample with constant stirring at room temperature. The pH value after each addition was recorded. Swedish samples were titrated with 1N sulphuric acid, corresponding to a dilution of 19:1 (water:concentrated acid); other countries used concentrated acid.

The amount of acid added to each sample was expressed in litres (L) of concentrated acid per m^3 of slurry. The volume of acid added to lower the pH of slurry to 5.5 was plotted against the chemical properties of the slurries to find correlations.

After titration, acidified samples were stored at room temperature and used for pH stability and slurry reacidification studies.

2.3. Slurry buffer capacity during storage

The main objectives of this test were to determine the volume of acid needed to maintain the target pH value of 5.5 and to evaluate the slurry's buffering capacity. In general, the tests were carried out over a period of two months. The pH value of the acidified slurries was determined periodically after the initial addition of acid. The intervals between pH measurements were different depending on the country. The amount of acid added on each occasion was expressed as L of concentrated acid per m^3 slurry. All samples were stored at room temperature.

3. Results and discussion

3.1. Characteristics of slurry in different BSR countries

The main chemical properties of the pig and cattle slurries are shown in Tables 1 and 2, respectively. Samples differed within and between countries. These differences are often observed and can be caused by many factors such as animal species, feeding strategy and slurry management systems (Risberg *et al.*, 2017).

The dry matter content (DM%) of pig slurries varied from 0.7 to 13.3% (Table 1), whereas for cattle slurry the DM% varied less and, except for a Polish slurry (CS1_PL1) with 1.2%, were between 5 and 9.7% (Table 2). Regarding nutrient content, Tot-N, TAN and Tot-P were slightly higher in pig than in cattle slurries. However, the values varied within each type of slurry and country. The average Tot-N was 4.6 kg tonne^{-1} for pig slurry and 3.9 kg tonne^{-1} for cattle slurry. The highest value (6 kg tonne^{-1}) was found in pig slurry from a conventional farm in Sweden (PS_C2_SE) and the lowest (1.5 kg tonne^{-1}) in Polish cattle slurry (CS1_PL1). The average TAN was 2.9 kg tonne^{-1} for pig slurry and 2.0 kg tonne^{-1} for cattle slurry. The highest value (5.2 kg tonne^{-1}) was in a German pig slurry (PS F_GE) and the lowest (0.6 kg tonne^{-1}) in a Polish cattle slurry (CS1_PL1). Tot-P averaged 1.5 kg tonne^{-1} for pig slurry and 0.8 kg tonne^{-1} for cattle slurry. The highest value was 4.97 kg tonne^{-1} in a pig sample from Germany (PS F_GE) and the lowest 0.11 kg tonne^{-1} in the pig sample from Estonia. Tot-C was determined only in Estonian, Polish and Swedish samples. The average values were 42.5 and 41.0 kg tonne^{-1} for pig and cattle slurry respectively. Except for one sample that contained 20.4 kg tonne^{-1} (CS1_PL1), Tot-C values varied between 39.8 and 47.2 kg tonne^{-1} in cattle slurries. Tot-C was analysed in only four samples of pig slurry. It varied between 26.3 and 59.1 kg tonne^{-1}.

The initial pH values were in most cases around 7, ranging from 6.3 to 7.9. The highest pH (7.9) was found in pig and cattle slurry from German farms, and the lowest (pH 6.3) in a sample of cattle slurry from a Polish farm.

Table 1. Chemical properties of pig slurries before acidification. The sample code is used in figures for identification

Country	Type of slurry[a]	Code	DM	Tot-N	TAN	Tot-P	Tot-C	C/N	Initial pH
			%	kg tonne^{-1}					
Germany	Piglet slurry	PI S_GE	2.7	3.0	2.1	1.16	n.d.[b]	n.d.	6.9
Germany	Sow slurry	SS_GE	1.1	1.7	1.5	0.50	n.d.	n.d.	6.9
Germany	Pig slurry, fattener	PS F_GE	11.1	8.9	5.2	4.97	n.d.	n.d.	7.9
Germany	Co-digested pig slurry	D_GE	7.9	4.8	2.3	2.1	n.d.	n.d.	6.9
Estonia	Pig slurry	PS_EE1	0.9	2.0	2.0	0.11	26.3	13.2	7.8
Latvia	Pig slurry, fattener	PF_LV1	3.1	4.2	3.3	2.40	n.d.	n.d.	7.2
Sweden	Pig slurry	PS_C1_SE	13.3	5.7	2.5	0.98	59.1	10.4	6.5
Sweden	Pig slurry	PS_C2_SE	9.5	6.0	3.3	1.08	42.1	7.0	7.0
Sweden	Pig slurry	PS_C3_SE	9.0	5.0	2.9	0.82	42.4	8.5	7.0
Mean			**6.5**	**4.6**	**2.8**	**1.6**	**42.5**	**9.8**	**7.1**
Range			*0.9-13.3*	*1.7-8.9*	*1.5-5.2*	*0.1-4.9*	*26.3-59.1*	*7.0-13.2*	*6.5-7.9*

[a] unless stated otherwise, samples are from a conventional farm
[b] n.d.: not determined

Table 2. Chemical properties of cattle slurries before acidification. The sample code is used in figures for identification

Country	Type of slurry[a]	Code	DM	Total-N	TAN	Tot-P	Tot-C	C/N	Initial pH
			%	kg tonne^{-1}					
Estonia	Cattle slurry	CS_EE1	8.0	3.8	2.30	0.59	40.1	10.6	6.9
Germany	Cattle slurry	CS1_GE	7.0	3.5	2.00	1.50	n.d.[b]	n.d.	7.8
Germany	Cattle slurry	CS2_GE	7.0	3.5	2.00	1.50	n.d.	n.d.	7.9
Germany	Cattle slurry (separated)	CSS_GE	6.7	4.4	2.40	1.50	n.d.	n.d.	7.0
Latvia	Cattle slurry	CS_LT	6.3	3.8	2.39	0.39	n.d.	n.d.	6.8
Poland	Cattle slurry	CS1_PL1	1.2	1.5	0.60	0.30	20.4	13.6	7.3
Poland	Cattle slurry	CS2_PL1	6.7	3.1	1.40	0.46	46.2	14.9	7.1
Poland	Cattle slurry	CS_PL3	5.0	2.5	1.30	0.34	42.3	16.7	6.3
Poland	Cattle slurry	CS_PL4	9.7	4.2	2.00	1.00	43.6	10.4	6.9
Poland	Cattle slurry	CS_PL1	5.5	4.5	2.30	0.94	44.5	9.9	6.9
Poland	Cattle slurry	CS_PL2	9.5	5.1	2.70	0.74	47.2	9.3	7.6
Poland	Cattle slurry	CS_PL5	7.3	4.5	2.30	0.92	43.6	9.8	7.6
Poland	Cattle slurry	CS2_PL5	6.9	4.3	2.10	0.93	41.5	9.7	7.7
Poland	Cattle slurry	CS3_PL5	6.3	4.3	2.20	0.85	42.3	9.8	7.7
Sweden	Cattle slurry – organic farm	CS_O1_SE	9.4	4.2	1.80	0.51	42.0	10.2	6.8
Sweden	Cattle slurry – organic farm	CS_O2_SE	8.9	4.5	2.30	0.49	39.2	8.7	7.7
Sweden	Cattle slurry	CS_C1_SE	8.8	3.8	1.50	0.44	39.8	10.3	7.3
Sweden	Cattle slurry	CS_C2_SE	9.3	4.2	1.90	0.57	41.9	10.0	7.2
Mean			**7.2**	**3.9**	**2.0**	**0.8**	**41.0**	**11.0**	**7.3**
Range			*1.2-9.7*	*1.5-5.1*	*0.6-2.7*	*0.3-1.5*	*20.4-47.2*	*8.7-16.7*	*6.3-7.9*

[a] unless stated otherwise, samples are from a conventional farm
[b] n.d.: not determined

3.2. Titration results

Titrations were done on a laboratory scale in each individual country. The amounts of concentrated sulphuric acid per m^3 of slurry needed to lower the pH successively to 6.4, 6.0 and 5.5 are shown in Figure 1 (pig slurries) and Figure 2 (cattle slurries). Slurry pH is adjusted to 6.4 in "*in-field*" acidification technology when acid is applied to the slurry immediately before soil application. In "*in-storage*" acidification (just before spreading), pH 6.0 is used, while 5.5 is used for "*in-house*" and "*in-storage*" technologies when a longer period of storage in slurry tank is expected.

There was large variation across both pig and cattle samples, and the amount of acid needed in each acidification step varied between samples. For example, in some cases more than half the acid was used to reach pH 6.4 (blue bars in samples PI S_GE and PF_LV1 in Fig. 1 and CS_C1_EE1 in Fig. 2), whereas for other samples the amount was distributed more equally across the three steps (PS_C2_SE in Fig. 1 and CS2_PL5 in Fig. 2).

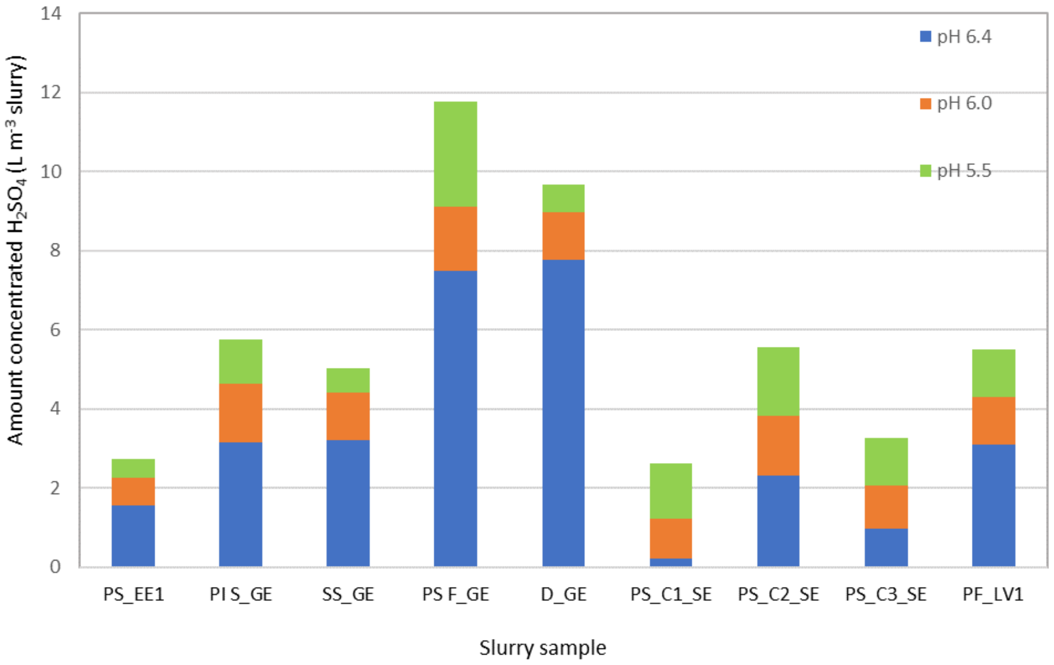

Figure 1. Amount of sulphuric acid needed to reach pH 6.4, 6.0 and 5.5 in pig slurries.

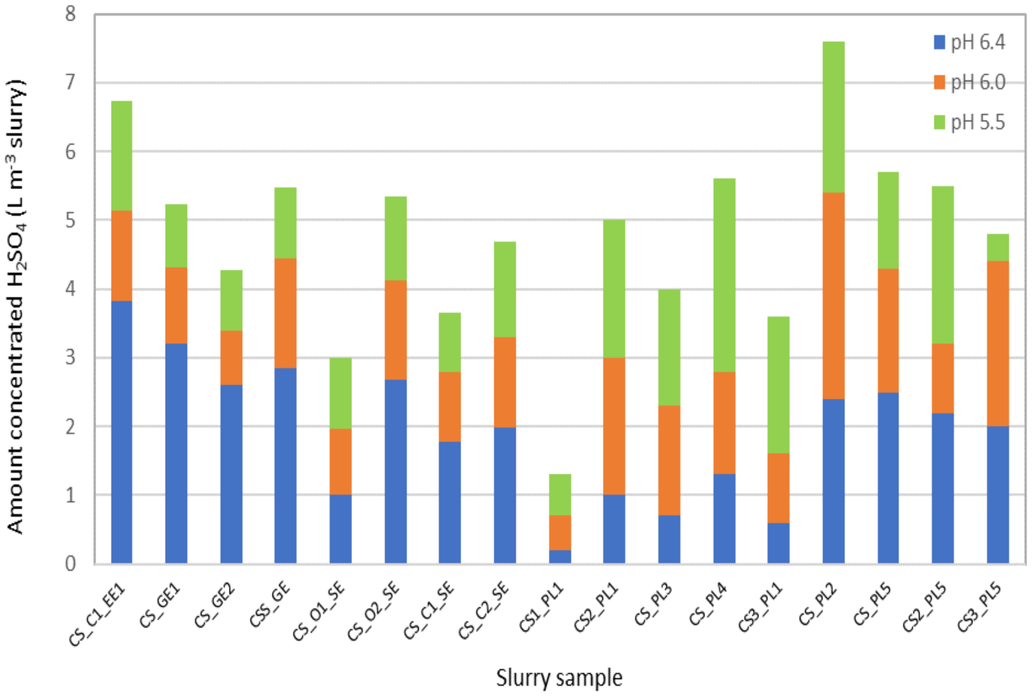

Figure 2. Amount of sulphuric acid needed to reach pH 6.4, 6.0 and 5.5 in cattle slurries.

As the main aim of this work was to study pH stability during long-term storage, the analysis of the results focused on slurry acidification to pH 5.5. The total amount of sulphuric acid needed to lower the pH to 5.5 is shown in Table 3 for pig slurries and in Table 4 for cattle slurries. The amounts varied between 1.3 and 11.8 L m^{-3} for all sampled slurries. Regarding pig slurry samples, the lowest amount was 2.6 L m^{-3} for a Swedish slurry from a conventional farm. The highest acid consumption was 11.8 L m^{-3} for a German pig slurry from fatteners. For cattle slurry, the lowest consumption of acid was 1.3 L m^{-3} and the highest 7.6 L m^{3}, both from Polish farms.

Table 3. Initial pH and volume of concentrated sulphuric acid (L m^{-3} slurry) to lower pH to 5.5 for pig slurries in BSR countries

Country	Type of slurry a	Code	Initial pH	Acid volume to reach pH 5.5 (L/m^{3})
Estonia	Pig	PS_EE1	7.8	3.2
Germany	Pig	PI S_GE	6.9	5.8
Germany	Pig	SS_GE	6.9	5.0
Germany	Pig	PS F_GE	7.9	11.8
Germany	Co-digested pig slurry	D_GE	6.9	9.7
Latvia	Pig	PF_LV1	7.2	5.4
Sweden	Pig	PS_C1_SE	6.5	2.6
Sweden	Pig	PS_C2_SE	7.0	5.6
Sweden	Pig	PS_C3_SE	7.0	3.3
Mean				*5.8*
Range				*2.6-11.8*

[a] Unless stated otherwise, sample is from a conventional farm

Table 4. Initial pH and volume of concentrated sulphuric acid (L m^{-3} slurry) to lower pH to 5.5 for cattle slurries in BSR countries

Country	Type of slurry[a]	Code	Initial pH	Acid volume to reach pH 5.5 [L m^{-3}]
Estonia	Cattle	CS_C1_EE1	6.9	6.7
Germany	Cattle	CS_GE1	7.8	5.2
Germany	Cattle	CS_GE2	7.9	4.3
Germany	Cattle	CSS_GE	7.0	5.5
Latvia	Cattle	CS_LT	6.8	2.4
Poland	Cattle	CS1_PL1	7.3	1.3
Poland	Cattle	CS2_PL1	7.1	5.0
Poland	Cattle	CS_PL3	6.3	4.0
Poland	Cattle	CS_PL4	6.9	5.6
Poland	Cattle	CS3_PL1	6.9	3.6
Poland	Cattle	CS_PL2	7.6	7.6
Poland	Cattle	CS_PL5	7.6	5.7
Poland	Cattle	CS2_PL5	7.7	5.5
Poland	Cattle	CS3_PL5	7.7	4.8
Sweden	Cattle – organic	CS_O1_SE	6.8	3.0
Sweden	Cattle – organic	CS_O2_SE	7.7	5.3
Sweden	Cattle	CS_C1_SE	7.3	3.6
Sweden	Cattle	CS_C2_SE	7.2	4.7
Mean				**4.6**
Range				*1.3-7.6*

[a] Unless stated otherwise, sample is from a conventional farm

In order to identify the factors that could predict acid consumption, the amount of acid (L) to acidify 1 m^3 slurry to pH 5.5 was plotted against several chemical parameters and a linear regression was calculated. The correlations were calculated for all samples together and individually for pig and cattle slurries as shown in Figures 3 and 4 (additional figures in Appendix 3). The coefficients of determination (R^2) are summarized in Table 5.

When both types of slurry were considered together, the coefficients were lower than when calculated alone. For both pig and cattle slurry, the correlation between the TAN and the amount of acid needed was rather pronounced with R^2 values of 0.62 for pig slurry and 0.61 for cattle slurry (Table 5 and Figs. 3 and 4). However, the exclusion of one outlier in each data set reduced the R^2 values. In general, R^2 values were low, and the number of samples was rather low to enable a conclusion to be drawn about the predicted impact of a chemical characteristic on the amount of acid needed for acidification.

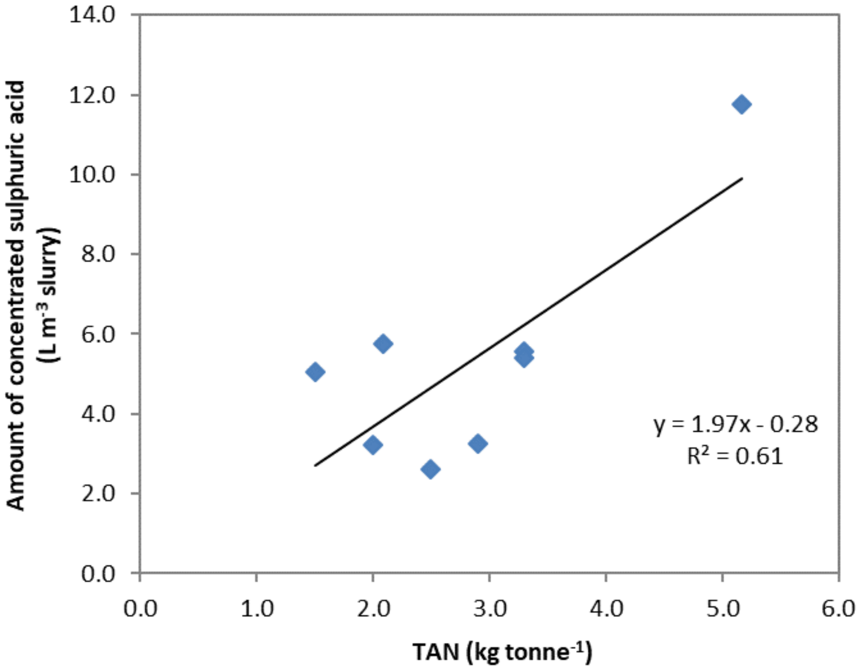

Figure 3. Amount of sulphuric acid needed to lower pig slurry pH to 5.5 as a function of slurry TAN. The co-digested slurry sample was not included in the calculations.

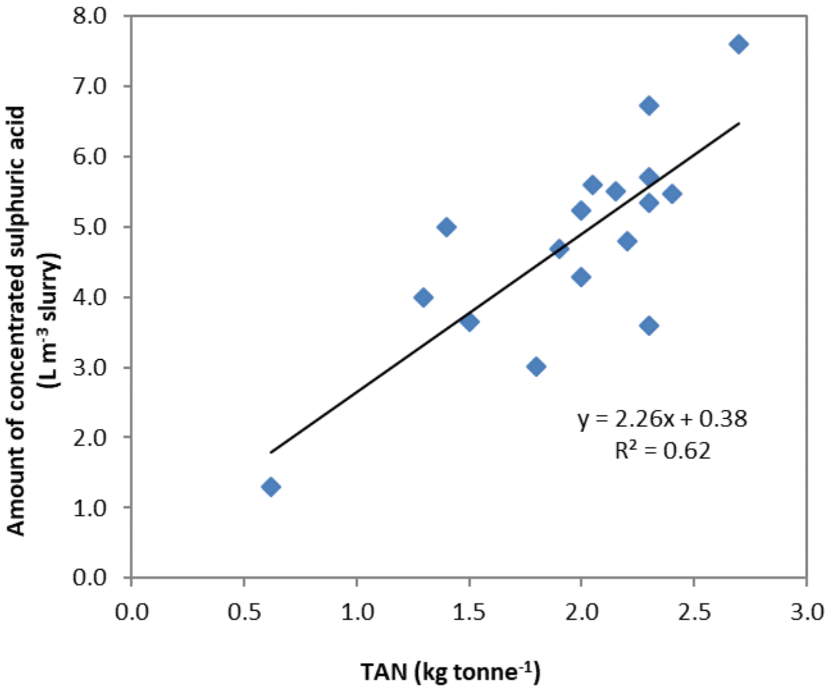

Figure 4. Amount of sulphuric acid needed to lower cattle slurry pH to 5.5 as a function of slurry TAN.

Table 5. Coefficient of determination for chemical parameters vs. amount of sulphuric acid used in titration to pH 5.5. The co-digested slurry sample was not included in the calculations

Type of slurry	Chemical parameter	R^2	Number of samples
Pig	Dry matter	0.03	8
Pig	Tot-N	0.39	8
Pig	TAN	0.61	8
Pig	Tot-P	0.82	8
Pig	Tot-C	0.04	4
Pig	C/N	0.45	4
Pig	Initial pH	0.43	8
Cattle	Dry matter	0.35	17
Cattle	Tot-N	0.42	17
Cattle	TAN	0.62	17
Cattle	Tot-P	0.10	17
Cattle	Tot-C	0.42	14
Cattle	C/N	0.15	14
Cattle	Initial pH	0.16	17
All	Dry matter	0.09	25
All	Tot-N	0.40	25
All	TAN	0.54	25
All	Tot-P	0.53	25
All	Tot-C	0.11	18
All	C/N	0.12	18
All	Initial pH	0.19	25

3.3. Slurry buffer capacity and acid consumption during storage

After initial acidification to pH 5.5, samples were stored at room temperature. The pH value of the slurry was measured periodically and readjusted to 5.5 as necessary. Because the time intervals between pH determination and storage were not the same for all the countries (Figs. 5a, b, c and d), it is difficult to compare all the results together. In general, all the samples had to be reacidified within a period of 30 days.

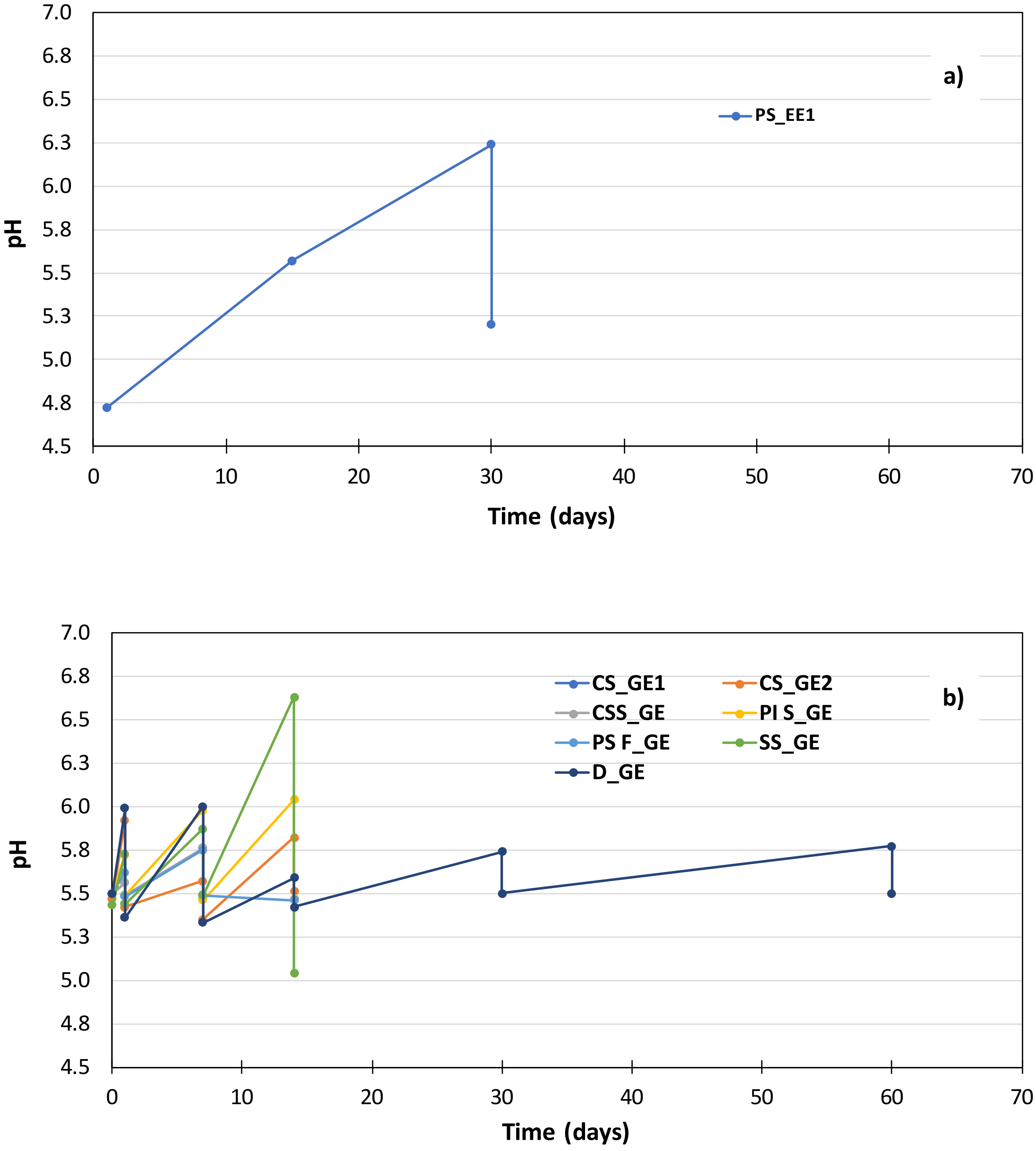

Figure 5 a-b. pH variation in slurry samples after initial acidification (time 0) and with successive adjustments by country a) Estonia; and b) Germany.

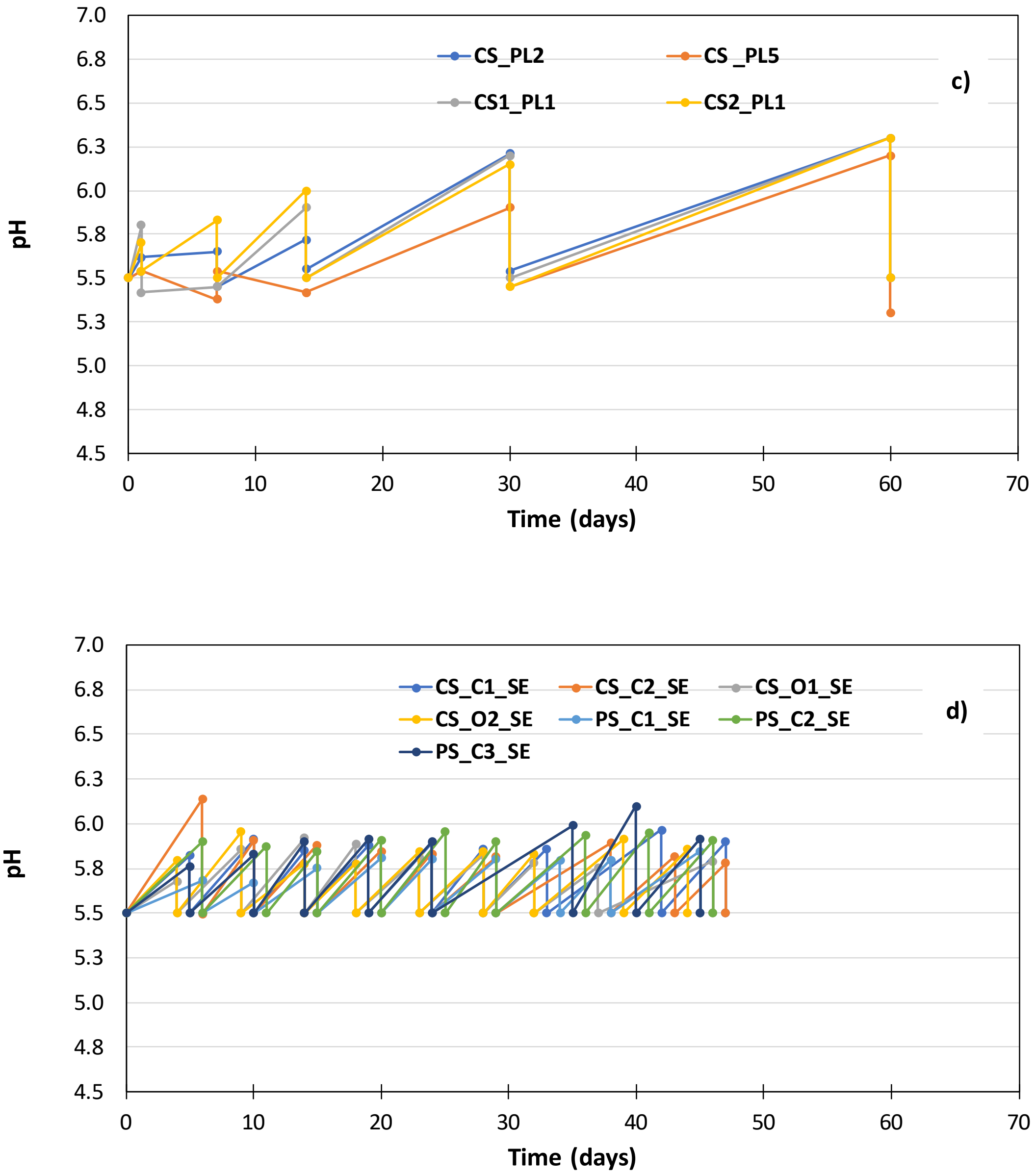

Figure 5 c-d. pH variation in slurry samples after initial acidification (time 0) and with successive adjustments by country c) Poland and d) Sweden.

For most of them the amount of acid added on each occasion was quite constant, especially for pig slurries (Fig. 6). In some cases, for example Swedish cattle slurries (Fig. 7), the acid consumption fell over time. Overall pH stability was not achieved in any of the samples. Similar results were obtained by Joubin (2018), who compared the effect of several acids on pH stability after acidification. The inability to maintain a pH of 5.5 may be due to a combination of biological, chemical and experimental factors, such as aerobic degradation of VFAs, degradation of organic matter by acid hydrolysis and the storage temperature (Joubin 2018 and references therein).

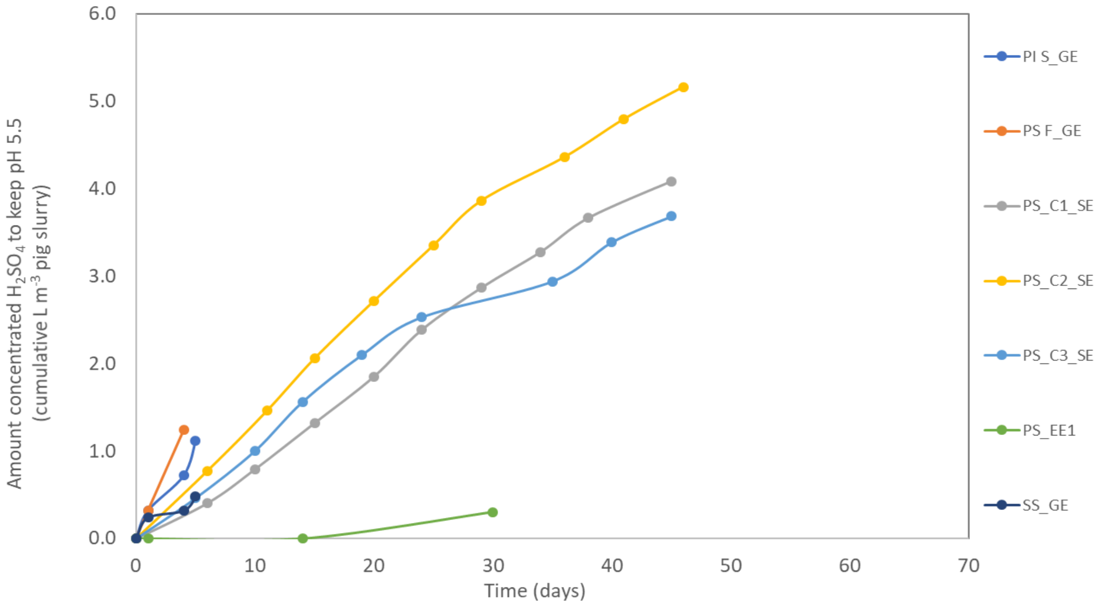

Figure 6. Cumulative amount of sulphuric acid used during storage to maintain the pig slurry pH at 5.5. The samples are from different BSR countries. Slurry codes are presented in Table 3. The amount of concentrated acid added for the initial acidification is not included in the calculations.

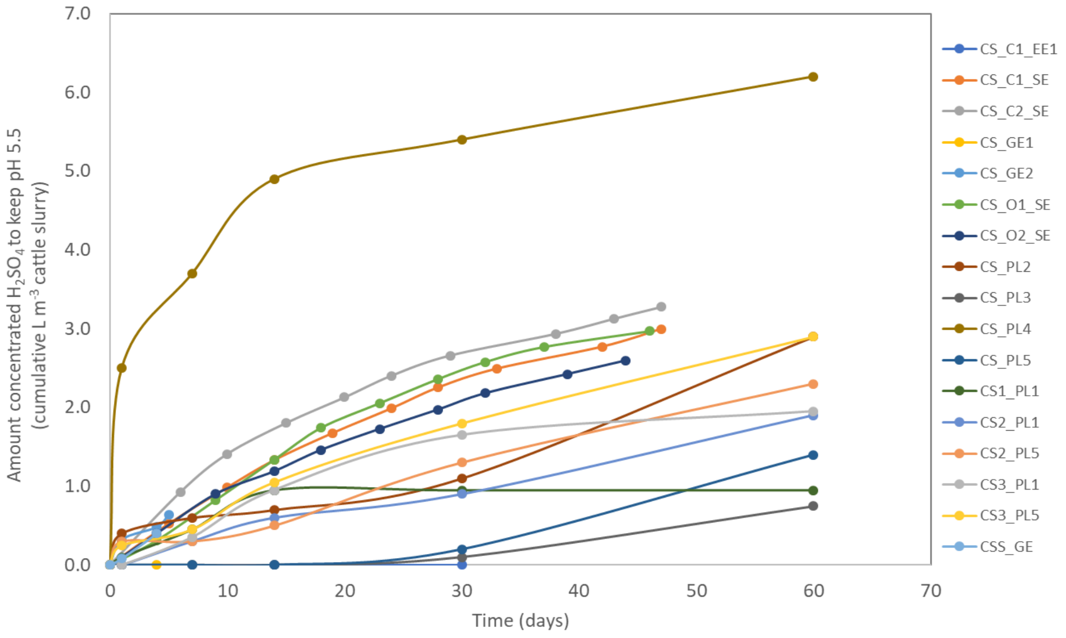

Figure 7. Cumulative amount of sulphuric acid used during storage to lower the cattle slurry pH to 5.5 and maintain that value. The samples are from different BSR countries. Slurry codes are presented in Table 4. The amount of concentrated acid added for the initial acidification is not included in the calculations.

3.4. Acid consumption – laboratory- vs. pilot-scale studies

The results obtained on a laboratory scale were compared with the data available from pilot-scale studies that also include gas emission measurements (Misselbrook *et al.*, 2016; Petersen *et al.*, 2014; Rodhe *et al.*, manuscript).

For cattle slurry stored in volumes of about 0.9 m^3 for approx. 70 days at mean air temperatures of 7.3, 11.0 and 17.2 °C, Misselbrook *et al.* (2016) used 2.25, 4.5 and 3.1 L m^{-3} respectively to reach pH 5.5 at the start of storage. This is less than the mean value of 4.65 L m^{-3} for acid consumption to reach pH 5.5 on a laboratory scale (see Table 4). Furthermore, in our pilot study with stored cattle slurry (digested and non-digested, acidified and non-acidified), the acid consumption for lowering the cattle slurry pH from 6.9 to 5.5 was only 1.1 L m^{-3} (Rodhe *et al.*, manuscript). This value is lower than the lowest value registered in this laboratory study (Polish cattle slurry, 1.3 L m^{-3}), Table 5. In addition, no significant pH changes were observed during the 4-month storage period (Rodhe *et al.*, manuscript). For pig slurry, Petersen *et al.* (2014) used 3.3 L m^{-3} to reach pH 5.5 on a pilot scale with volume 6.5 m^3 and 83 days' storage. This is also less than the mean amount of acid used on a laboratory scale (5.2 L m^{-3}) (see Table 3).

These differences between the laboratory and pilot scales may be related to the smaller quantity of slurry subjected to acidification, the higher temperatures during storage and the frequent aeration (stirring) under laboratory conditions. Laboratory scale could be used to see differences in acid demand between slurry types, but the quantities of acid needed seem to be different, as they were higher compared with pilot scale.

4. Conclusions

- The amount of concentrated sulphuric acid required in the BSR countries to acidify different types of slurries to pH 6.4 varied widely by about 40 times between the lowest and the highest requirement. For acidification to pH 6.0, the amount varied by 15 times, and for pH 5.5 about 9 times.
- There was no strong correlation between measured slurry properties and the amounts of acid required to lower pH to 5.5 when the samples from all the countries were analysed together.
- The pH had to be adjusted in all samples during storage to maintain it at 5.5. For most of the samples, the amount of acid added on each occasion during storage was quite constant, especially for pig slurries.
- The mean amounts of acid needed to lower the pH to 5.5 for slurry were higher on a laboratory scale compared with the amounts reported in available pilot-scale studies. Another difference between scales was that during the laboratory studies, pH increased quickly and had to be adjusted frequently, while on a pilot scale the pH was maintained with just a minor increase during the 4-month outdoor storage period.

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Appendix 1. Methodology for slurry titrations

The titration techniques are based on the sequential addition of small volumes of concentrated sulphuric acid to the sample of slurry, and measurement of the pH value.

During the addition of sulphuric acid, ammonium ions contained in the slurry react with the acid, forming ammonium sulphate.

1) Set up the ring stand, burette clamp and burette or pipette.

2) Fill the container with an exact volume of slurry to be tested, for example 500 or 1000 mL. Larger amounts may be needed for thick slurry with bedding material. The container should be not more than half full to allow for mixing and foaming during acidification.

3) Fill the burette with concentrated sulphuric acid to the zero marking. If using a pipette or some other instrument to deliver the acid, make a note of the starting volume.

4) Turn on the mixer and adjust the intensity to an adequate level.

5) Measure and record the temperature of the slurry.

6) Insert the pH meter into the slurry, securing it in place with the clamp if necessary, and calibrate the pH meter.

7) Record the pH of the slurry.

8) Add small amounts of acid step-wise to the slurry.

Attention: The reaction between acid and slurry can be vigorous, causing considerable foaming and increasing the temperature. Consequently, add acid step-wise in small amounts in the range 0.01-0.1 mL. Note that the amount of acid required to lower the pH is likely to be 1-5 mL per 1000 mL slurry. The maximum step-wise volume to use is 0.1 mL if the volume of slurry is 1000 mL, and 0.05 mL if the volume of slurry is 500 mL. This degree of sensitivity is needed for scaling up the results for farm applications.

9) Mix thoroughly and allow time for the chemical reaction to occur.

10) Measure the pH of the slurry.

11) Repeat steps 7-9 until the target pH 6.4 is achieved.

12) Record the amount of acid used, the pH and temperature.

13) Repeat steps 8-12 with the target pH 6.0. If the buffer capacity is to be tested (Part II of the manual), repeat steps 8-12 again with target pH 5.5.

14) If possible, store the acidified slurry (at ambient temperature) for 24 hours and then repeating steps 10-13. If you have several samples, ensure they are marked so they are identifiable.

15) Dispose of the slurry sample appropriately, clean the workplace and store the acid safely.

16) Record all data in the Excel file (see Appendix 2 for an example).

Appendix 2. Example of data to be entered into the Excel file for the titration and buffer capacity tests, and chemical analysis data

1. Sampling description. Example of data.

Sample No.	Sampling date	Type of slurry and production (dairy/ beef/fatteners/sows/etc.), housing	Additives in barn? (straw, sawdust, etc.)	Sampling point (pumping pit/ storage/spreader tanker/etc.)	Approx. age of slurry at sampling	Approx. storage temp between sampling and titration, °C
1.	29.06.2016	Dairy slurry, cubicle houses	Straw, some water	Pumping pit	4 days	4
2.						

In Excel file, in Sheet "Sampling data, titrating, buffering capacity":

Information about the sample						
Sample No.	Sampling date	Type of slurry and production (dairy/ beef/fatteners/sows/etc.), housing system	Additives in barn? (straw, sawdust, etc.)	Sampling point (in-house storage/pumping pit/ storage/spreader tanker/etc.)	Approx. age of slurry at sampling	Approx. storage temp between sampling and titration, °C

2. Titrations and buffering within 1 day. Examples of data.

Sample No.	Date of titration	Volume of slurry sample, mL	Initial pH	Initial slurry temp ºC	Volume of acid (mL) to lower pH to 6.4	Volume of acid (mL) to lower pH to 6.0	(OPTIONAL) Volume of acid (mL) to lower pH to 5.5	1. Final pH	Acid addition rate (acid volume/slurry volume), L m^{-3}	Slurry temp ºC	pH	Volume of acid (mL) to lower pH to 6.0 (or 5.5 if that was the target)	Final pH
1.	1.07.2016	500	7.27	19.5	1.21	1.62	2.37	5.5		15	5.9	0.38	5.5
2.													

In Excel file, in Sheet “Sampling data, titrating, buffering capacity”: Titrating including buffering 1 day.

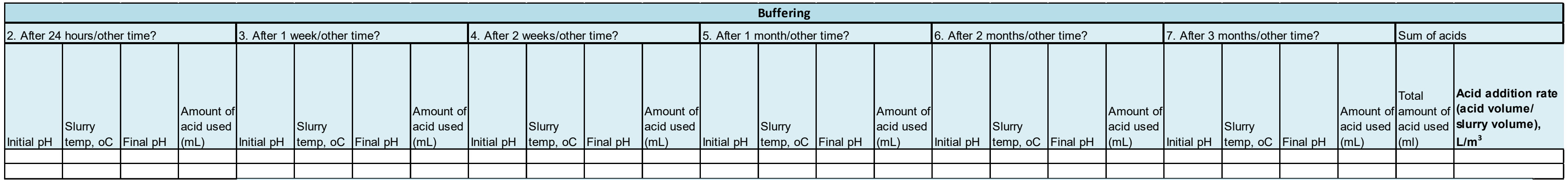
Titration										**Buffering**			
										2. After 24 hours/other time?			
Date of titration	Volume of slurry sample, mL	Initial pH	Initial slurry temp, °C	Volume of acid (mL) to lower pH to 6.4	Volume of acid (mL) to lower pH to 6.0	Volume of acid (mL) to lower pH to 5.5	Final pH	Total amounts of acid used (mL) pH 5.5	**Acid addition rate (acid volume/ slurry volume),** L m^{-3} **(pH 5.5)**	Initial pH	Slurry temp, ◦ C	Final pH	Amount of acid used (mL)

3. Buffer capacity, up to three months. Examples of data.

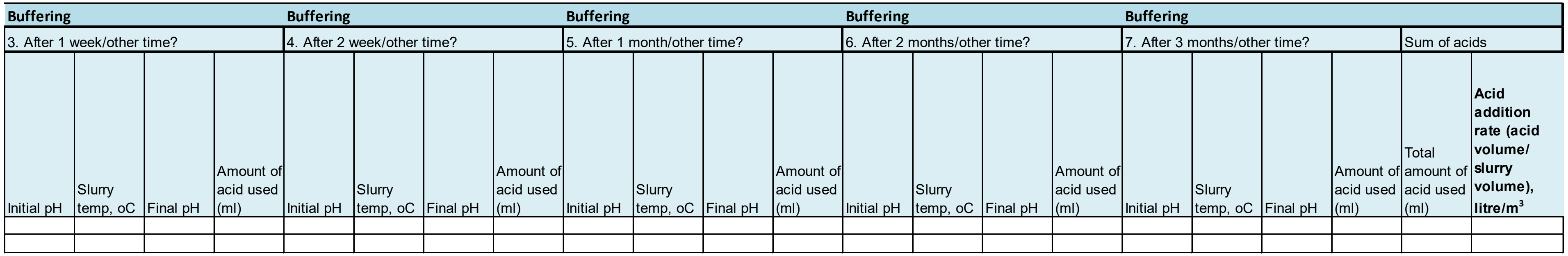
Sample No.	Date of re-acidification	Target pH	Storage temp °C	pH	Volume of acid (mL) to lower pH to target	Final pH	Date of re-acidification	pH	Volume of acid (mL) to lower pH to target	Final pH
1.	1.09.2016	5.5	15	5.6	0.1	5.5				
2.										

In the Excel file, the continued data for re-acidification will be entered on the same line.

In Excel file, in Sheet "Sampling data, titrating, buffering capacity": buffering capacity.



Buffering																									
2. After 24 hours/other time?				3. After 1 week/other time?				4. After 2 weeks/other time?				5. After 1 month/other time?				6. After 2 months/other time?				7. After 3 months/other time?				Sum of acids	
Initial pH	Slurry temp, oC	Final pH	Amount of acid used (mL)	Initial pH	Slurry temp, oC	Final pH	Amount of acid used (mL)	Initial pH	Slurry temp, oC	Final pH	Amount of acid used (mL)	Initial pH	Slurry temp, oC	Final pH	Amount of acid used (mL)	Initial pH	Slurry temp, oC	Final pH	Amount of acid used (mL)	Initial pH	Slurry temp, oC	Final pH	Amount of acid used (mL)	Total amount of acid used (ml)	**Acid addition rate (acid volume/ slurry volume), L/m^3**



Buffering				**Buffering**				**Buffering**				**Buffering**				**Buffering**					
3. After 1 week/other time?				4. After 2 week/other time?				5. After 1 month/other time?				6. After 2 months/other time?				7. After 3 months/other time?				Sum of acids	
Initial pH	Slurry temp, oC	Final pH	Amount of acid used (ml)	Initial pH	Slurry temp, oC	Final pH	Amount of acid used (ml)	Initial pH	Slurry temp, oC	Final pH	Amount of acid used (ml)	Initial pH	Slurry temp, oC	Final pH	Amount of acid used (ml)	Initial pH	Slurry temp, oC	Final pH	Amount of acid used (ml)	Total amount of acid used (ml)	**Acid addition rate (acid volume/ slurry volume), litre/m^3**

4. Manure analysis, units based on wet weight.

Example of data.

Sample No.	pH	TS (%)	Tot-N (kg/t)	NH_4-N (kg/t)	Tot-P (kg/t)	Tot-K (kg/t)	S (kg/t)	Ca (kg/t)	Mg (kg/t)			
1.	7.2	7.8	4.3	2.1	0.65	2.00	0.4	1.33	0.57			
2.												

Excel file layout: In Sheet “Chemical and physical properties”.

Sample No.	Sampling date	Type of slurry and production (dairy/beef/fatteners/sows/etc)	TS	Tot-N	NH4-N	Tot-P	Tot-K	S	Ca	Mg	Na	Tot-C	C/N	pH
			%	kg/tonne	kg/tonne	kg/tonne	kg/tonne	kg/tonne	kg/tonne	kg/tonne	kg/tonne	kg/tonne		

Appendix 3. Main correlations for slurry titrations with sulphuric acid

In order to identify the factors that might predict acid consumption, the amount of acid (L) to acidify 1 m^3 to pH 5.5 was plotted against several chemical parameters and a linear regression was calculated. The correlations were calculated for all samples together and individually for pig and cattle slurries.

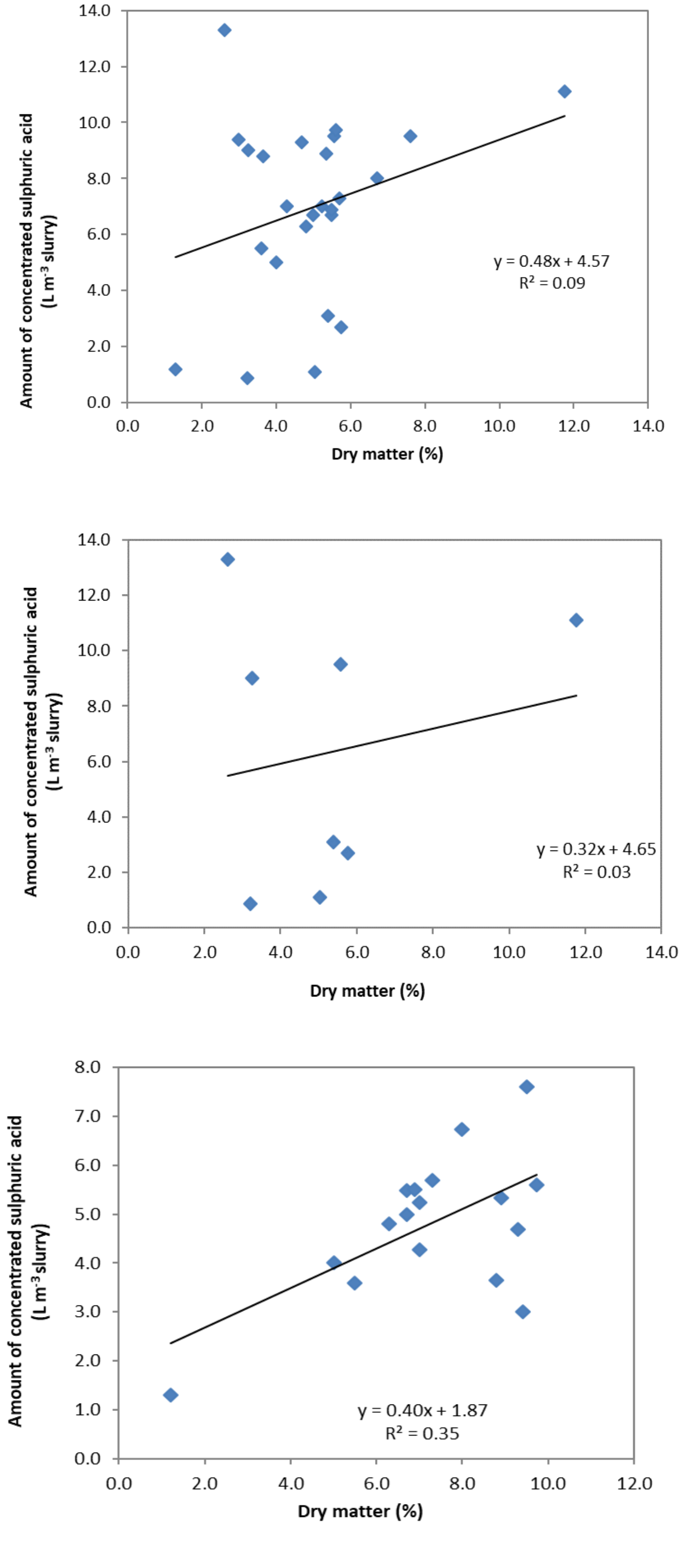


Figure 8. Amount of sulphuric acid needed to lower (a) all, (b) pig and (c) cattle slurry pH to 5.5 as a function of dry matter content (%). Samples for all participating countries are included.

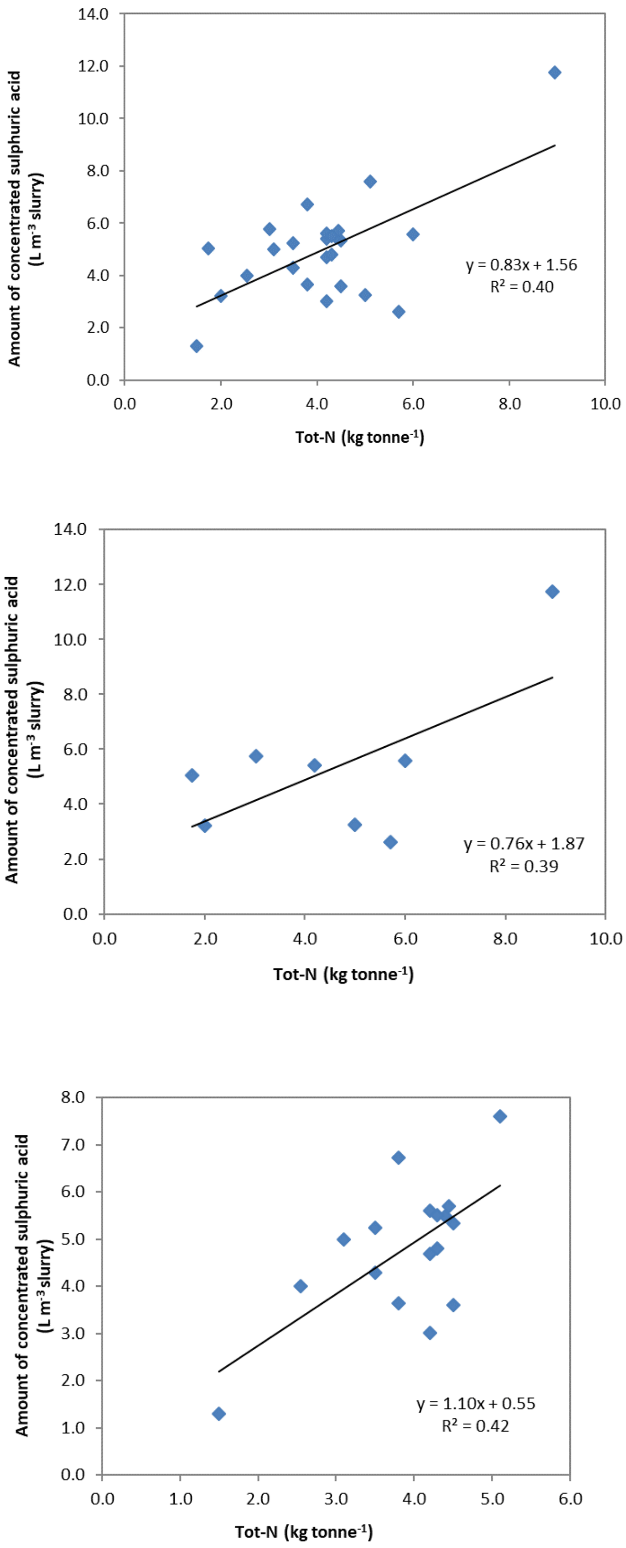


Figure 9. Amount of sulphuric acid needed to lower (a) all, (b) pig and (c) cattle slurry pH to 5.5 as a function of total nitrogen content (Tot-N). Samples for all participating countries are included.

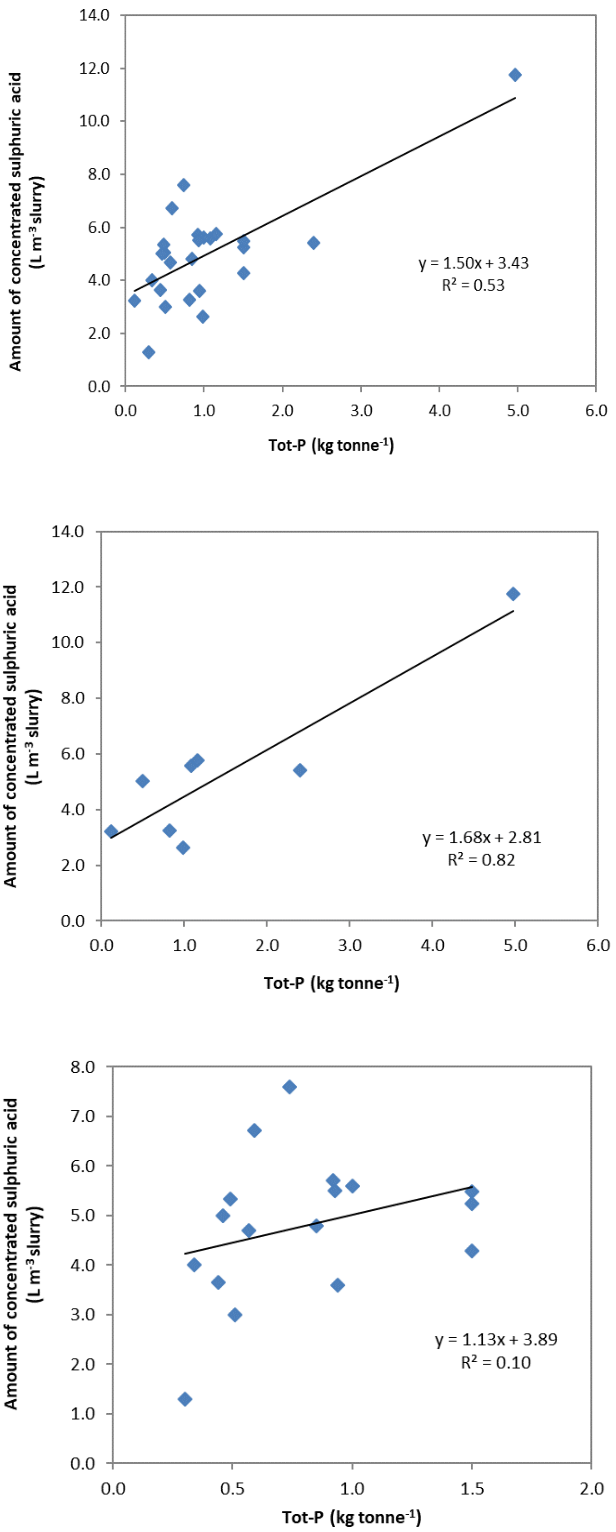


Figure 10. Amount of sulphuric acid needed to lower (a) all, (b) pig and (c) cattle slurry pH to 5.5 as a function of total phosphorus content (Tot-P). Samples for all participating countries are included.

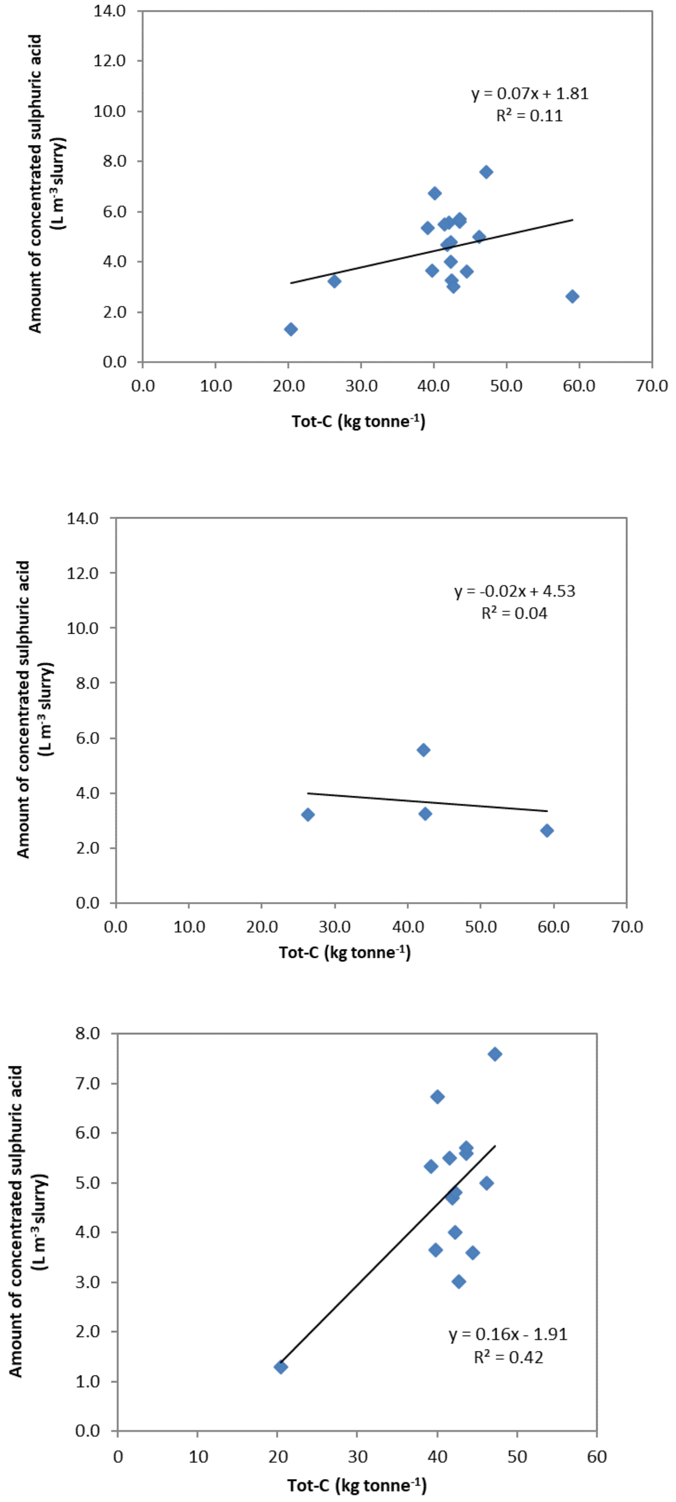


Figure 11. Amount of sulphuric acid needed to lower (a) all, (b) pig and (c) cattle slurry pH to 5.5 as a function of total carbon content (Tot-C). Samples for all participating countries are included.

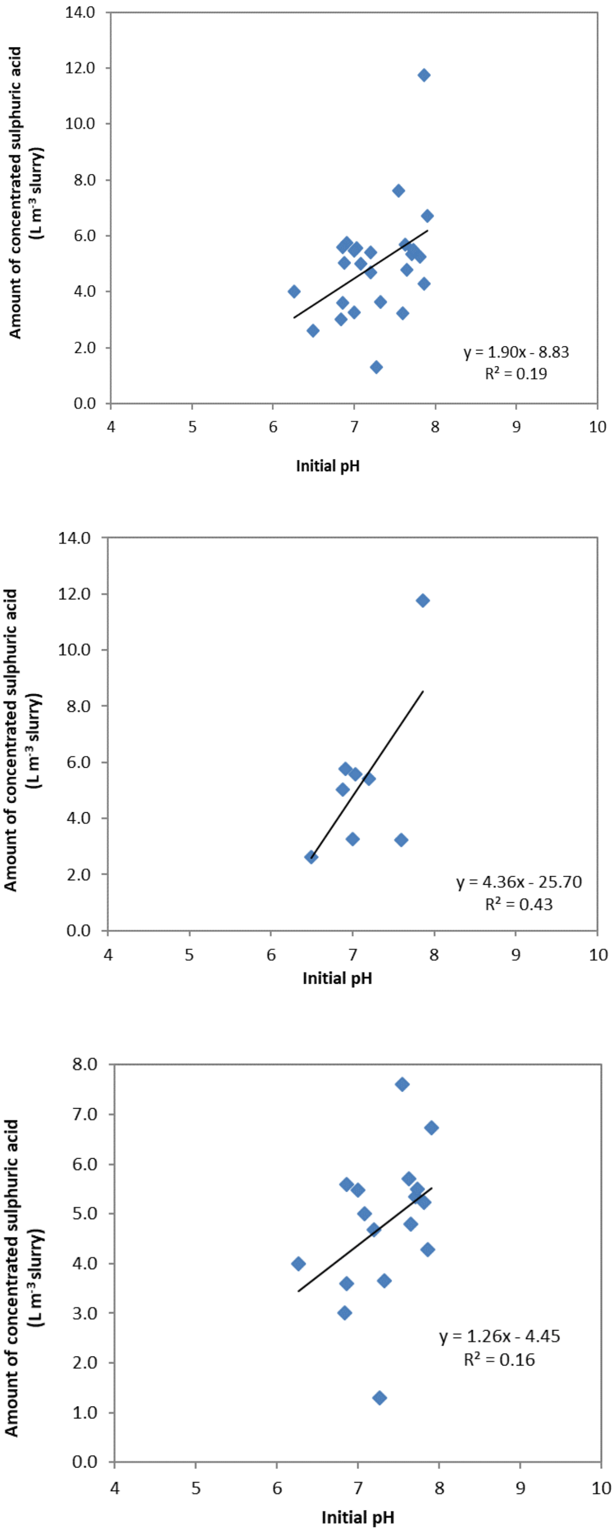


Figure 12. Amount of sulphuric acid needed to lower (a) all, (b) pig and (c) cattle slurry pH to 5.5 as a function initial pH. Samples for all participating countries are included.

Baltic Slurry Acidification

EUROPEAN REGIONAL DEVELOPMENT FUND

EUROPEAN UNION

www.balticslurry.eu

Summary of the project

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

Summary of the report

This report describes how various types of animal slurry from BSR countries respond to acidification with sulphuric acid in simulated storage conditions. It includes the buffering capacity of the manure and the amounts of acid needed to maintain pH during storage. The studies have been conducted on a laboratory scale in Work Package 2.3.

Contributing partners:

- RISE – Agrifood and Bioscience, Sweden
- ECRI – Estonian Crop Research Institute, Estonia
- ITP – Institute of Technology and Life Sciences, Poland
- Union Farmers Parliament, Latvia
- State Agency for Agriculture, Environment and Rural Areas of German Federal State Schleswig-Holstein, Germany
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