Interreg
Baltic Sea Region
Baltic Slurry Acidification

EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND

Animal slurry acidification: effects of slurry characteristics, use of different acids, slurry pH buffering

Maxime Joubin

Agronomy student at AGROCAMPUS OUEST, Rennes, France

Supervisors: Erik Sindhöj and Lena Rodhe, RISE

RISE Rapport 2018:15

EU STRATEGY FOR THE BALTIC SEA REGION
FLAGSHIP

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RISE Rapport 2018:15
ISBN 978-91-88695-50-5
Uppsala 2018

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Preface

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

The general aims of the project are to reduce ammonia emissions from animal production and create a more competitive and sustainable farming sector by promoting the implementation of slurry acidification techniques (SATs) throughout the Baltic Sea Region. This report falls under Work Package 2 - Technical feasibility studies which aims to identify technical issues, bottlenecks and other barriers that may hinder the implementation of slurry acidification techniques (SATs), originally developed in Denmark, to other countries in the BSR.

This report presents an initial look into how much sulfuric acid will be needed on a practical level for implementing slurry acidification in Sweden. This report also looks at the potential to use alternatives acids for acidification, particularly acids that might be allowed in organic farming.

This report and the experiments described within it are the results of an independent study by a master's student, Maxime Joubin, in Agricultural Engineering from AGROCAMPUS OUEST in Renne, France. The study was conducted during autumn 2017 at RISE in Uppsala, Sweden.

January 2018

Erik Sindhöj
Project Coordinator for Baltic Slurry Acidification

Summary

Acidification of slurry is one method to reduce ammonia emissions. Mainly implemented in Denmark, SAT use sulfuric acid to decrease the pH in in-house, in storage or in field system. Organic acids could be a good alternative to sulfuric acid to develop SATs for organic farming. Successive acidifications of slurry could be a solution to keep a stable pH and avoid ammonia emissions during all the period of storage.

In Experiment 1, sulfuric acid, nitric acid and four organic acids were tested in order to compare efficiency and the economic aspects for cattle and pig slurry acidification. In experiment 2, the buffer system of 9 different slurries (4 from cattle, 3 from pig, and 2 filtrated slurry of each) were studied after several acidifications with sulfuric acid to pH 5.5 in order to quantify the acid consumption and to determine by modelling which slurry characteristics influenced the most this consumption of acid. For both experiments, the storage temperature was 20°C.

For acid solutions with the same normality, organic acid and nitric acid were as efficient as sulfuric acid. However, results show, considering commercial concentrated acid proprieties, sulfuric acid was still the best option with a third to half of the consumption compared to other acids and acidification cost divided by 10 to compare with the use of organic acid. Acid consumption and acidification cost were highest for nitric acid. For organic acids, the acid consumption and acidification cost depended on slurry types and the target pH value. Furthermore, sulfuric acid and acetic acid had better ability to maintain the pH value below 6.4.

In experiment 2, for all slurries, the pH was not stabilized by successive acidifications, possibly due to the degradation of organic matter by acid hydrolysis and probably aerobic degradation of volatile fatty acids. The total acid consumption depended on slurry characteristics and varied between 5.97 to 8.06 liters per m^3 for cattle slurry and 6.7 to 10.7 for pig slurry.

The best model variable to explain the quantity of acid needed for the first acidification depended on the target pH. The total amount of acid needed was explained by total nitrogen, total solids, total carbon: total nitrogen ratio and volatile solids. For the total amount of acid needed for all re-acidification, total nitrogen, ammonium concentration, total carbon and volatile solids were the best sub model variables. The latter was not correlated with the acid consumption for the first titration, even though models have common variables. That supposes slurry characteristics are modified by acidification.

In conclusion, the use of organic acids was more expensive than the use of sulfuric acid. The pH can't be stabilized by successive acid additions due to the organic matter degradation and modification of slurry characteristics which influence the acid consumption.

Definitions

Titration: Common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of an identified titrand (slurry in our study). Since volume measurements play a key role in titration, it is also known as volumetric analysis. A reagent, called the titrant (acid in our study) is prepared as a standard solution. The titration permits determined from a known concentration of acid the volume needed to dercrease the pH at 6.4, 6.0 or 5.5.

Buffering capacity: It is the capacity for a solution to have of a pH evolution resistance after adding of small quantity of acid or base or after a dilution. The pH buffer components of slurries are weak acids or bases. Thus, the slurry pH is the result of several balanced chemical reactions.

Equivalent factor: Mole of acid needed to neutralize one mole of HO^-. It means, all 1N acid solutions supply one mole of hydrogen ions (H^+) in an acid–base reaction.

For example, only 0.5M of sulfuric acid solution (H_2SO_4) is needed to neutralise 1M of HO-because each molecules of H_2SO_4 gives 2 acid hydrogen (H^+) in solution. Consequently, equivalent factor of sulfuric acid is 0.5 and 0.5M of sulfuric acid = 1N of sulfuric acid. Similarly, 1M of formic acid (HCOOH) is needed to neutralise 1M of HO^-. So, the equivalent factor of formic acid is 1 and in this case 1M of formic acid = 1N of formic acid.

Normality of acid: Normality (N), also called equivalent concentration (Eq/l), express the concentration of hydronium ions (H_3O^+) or acid hydrogen (H^+) in a solution. It links with the molarity of acid solution by equivalence factor of each acid.

N = Concentration of acid solution/equivalence factor

Equivalent (Eq): The equivalent is the amount of a substance (acid) needed to supply one mole of hydrogen ions (H^+) in an acid–base reaction.

Alkalinity: amount of equivalent of protons (H^+) needed to be added to the biomass to reduce pH to 4.5. The unit is meq/l (equivalent to Eq/m^3).

1 Introduction

Acidification of slurry is one method to reduce ammonia emissions (Hjorth et al., 2015; Misselbrook et al., 2016). Slurry acidification is used 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). Slurry can be acidified at different stages of the manure handling chain: In-house, in-storage and in-field. In Sweden, legislation forbids keeping slurry in the animal house and requires frequent removal, and therefore in-house slurry acidification is not very relevant for implementation. Consequently, acidification in-storage or in-field is more suitable to control ammonia emissions in Sweden. In Denmark the in-storage technique has been developed to acidify in the storage tank or lagoon under heavy mixing just prior to spreading.

The concept of reducing slurry pH to decrease ammonia emission relies on the equilibrium between NH_4^+(aq) dissolved in slurry and NH_3(aq) (Fangueiro et al., 2015). When acidifying slurry to pH 5.5, the relative acid content is modified and 99.98% is NH_4^+ (Fangueiro et al., 2015). However, the buffering capacity of slurry permits the pH to come back at its initial pH level after acidification. Indeed, a 60 day study of pH after different slurries were acidified to pH 5.5 showed the pH increased to pH 6.4 between ten and twenty days after acidification for different acids (sulfuric acid, acetic acid, citric acid, lactic acid) (Regueiro et al., 2016). So, because of the slurry buffer system, the pH value changes in function to how long is the storage period. For in-house or in-storage system at start of 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 system. According to Peterson et al. (2012) and Hjorth et al. (2015), this rise of pH is due to: microbial activity and hydrolysis of volatile fatty acids, the 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 for pH to remain stable at 5.5 during long-term storage.

In Denmark, sulfuric acid is used to acidify slurry mainly for economic reasons, its strength and also that it acts as a sulphur fertilizer for crops. However, problems using sulfuric acid for acidification include possible toxic gas emissions like hydrogen sulphide. Moreover, sulfuric acid is not allowed in organic farming. Alternative acids have been tested to replace sulfuric acid for slurry acidification in order to improve slurry management (Regueiro et al., 2016). The acid strength, the time before pH increase, the capacity to reduce ammonia emissions and the price were arguments when choose between organic acids. The use of an organic acid to replace sulfuric acid for slurry acidification could be an opportunity for organic farms to benefit from this technology. Nevertheless, economical aspects are hardly discussed in most articles. Therefore, it is important to study the acidifying efficiency and economical aspect of using alternative acids during practical implementation of acidification techniques.

Slurry type and its components like total inorganic carbon (TAC), total ammonia nitrogen (TAN), volatile fatty acids (VFAs), other organic matters with carboxyl functional groups and some specific ions, are controlling the buffering capacity of slurry (Sommer et al., 2013; Stevens et al., 1989). The latter is composed exclusively by weak acids or bases. Thus, pH calculation at a specific time depends on several reactions which regroup different species of the same component. Early studies showed that VFAs and TAN seem to be the most important factors that influence slurry pH and the buffer system, where a high VFAs/TAN ratio was correlated with a low pH (Paul and Beauchamp, 1989, Sommer and Husted, 1995a). That explains why the buffer system is different between pig and dairy slurry but also between two different dairy cattle, or pig slurries (Sommer et al., 1995). Life conditions of animals, their feed and manure removal and management systems influence the composition of slurries and can affect their buffer system.

The aims of this study were first to compare the amount of acid needed and economical aspect of different acids to decrease slurry pH to 6.0 and determine how much time is then available to spread the slurry before the buffer system increases the pH to 6,4 again (Experiment 1). Secondly, to identify the total amount of sulfuric acid required to maintain slurry pH at 5.5 during storage for two months for different slurry types and to examine various factors affecting the buffering capacity of slurries (Experiment 2).

We hypothesized that:

i) Additives other than sulfuric acid may efficiently reduce the pH (Experiment 1).
ii) With the same normality of acid solution, strong acids (with small pKa value) should be more efficient to reduce the pH (Experiment 1).
iii) Slurry pH will be stabilized after several successive acidifications (Experiment 2).
iv) The quantity of acid needed to stabilize the pH will depend on physical and chemical properties of the slurry (Experiment 2).
v) Time to stabilize the pH may depend to slurry components (Experiment 1 and 2).

2 Material and Methods

2.1 Experimental design: animal slurry, acids, pH and temperature

Experiment 1: Cattle and pig slurry samples were collected in September from the slurry storage tank of a conventional dairy and pig farm near Uppsala, Sweden. Each sample was a mixture of slurry taken from 3 different depths in the storage tank and combined to have representative sample of the stored slurry. Four organic acids, formic acid, oxalic acid, acetic acid and lactic acid, which might be easier to get approved for organic farming were studied in parallel with nitric acid and sulphur acid. Acid proprieties are summarized Table 1. Nitric acid was also tested for its capacity to provide a more balanced N:P ratio in acidified slurry. The experiment was conducted in small scale with 200ml of slurry in 400ml containers. The extra space in the containers was necessary for the foaming during acidification. Each cattle and pig slurry was titrated by 6 different acids to reach pH 6.0. Acidified and none-acidified (control) slurry samples were stored at room temperature, approx 20°C which is the average temperature in the storage tank in Sweden in August-September during fall spreading (Rodhe et al., 2009). The treatments studied are listed in Table 2. For each combination of slurry and acid, there were 3 replicates so in total, there were 42 samples. After acidification to 6.0, the pH was measured every day to determine the time until the pH buffers to above 6.4 again.

Table 1. Experiment 1: Characteristics of acids used

	Sulfuric acid	Acetic acid	Lactic acid	Oxalic acid	Formic acid	Nitric acid
Formula	H_2SO_4	CH_3COOH	$CH_3CH(OH)COOH$	HOOCCOOH	HCOOH	HNO_3
Molecular weight (g/mol)	98.08	60.05	90.08	126.065	46.03	63.01
Density	1.84	1.05	1.2	1.65	1.22	1.41
Normality for 1M solution of acid	2	1	1	2	1	1
pKa value	1.99	4.76	3.86	1.25 / 4.14	3.77	-1.4
% Strength of conc. acids [1]	96	99.7	80	99.6	78	16
Price(SEK/L) [2]	1.53	7.14	4.58	9.39	7.79	3.9

[1] *Concentrations available for purchase in bulk quantity from Brenntag Nordic AB*
[2] *Price of acid from Brenntag when purchasing an IBC, not including delivery costs.*

Table 2. Experiment 1: Treatments for slurry acidification to pH 6.0 simulating acidification at spreading time with "old" cattle slurry and pig slurry under warm condition

Name of treatment combination	Slurry types	Acids
CS	Cattle slurry	No acid (Control)
CS_S	Cattle slurry	Sulfuric acid
CS_F	Cattle slurry	Formic acid
CS_A	Cattle slurry	Acetic acid
CS_Ox	Cattle slurry	Oxalic acid
CS_L	Cattle slurry	Lactic acid
CS_N	Cattle slurry	Nitric acid
PS	Pig slurry (fatteners)	No acid (Control)
PS_S	Pig slurry (fatteners)	Sulfuric acid
PS_F	Pig slurry (fatteners)	Formic acid
PS_A	Pig slurry (fatteners)	Acetic acid
PS_Ox	Pig slurry (fatteners)	Oxalic acid
PS_L	Pig slurry (fatteners)	Lactic acid
PS_N	Pig slurry (fatteners)	Nitric acid

Experiment 2: The second experiment refers to acidification of different slurries with sulfuric acid to 5.5 simulating acidification in the beginning of the storage period. Samples of fresh slurry were fresh taken from pumping pit just outside the animal house which typically has 3-10 days storage capacity before moving the slurry to the storage tank, before it is pumped to the long-term storage. Four dairy cattle slurries and three pig slurries were tested in this experiment. In addition to this, one of the dairy and one pig slurries were filtered and their liquid fractions were also tested in this experiment. Liquid fractions were collected after filtering successively through different size screens: 6.4, 4, 2, 1.4 and 0.8 mm. Concerning cattle dairy slurries, two slurry samples came from conventional farms and two samples from organic farm. All pig slurry samples come from conventional farms. Each sample measured 200ml and was stored in 400ml containers. The storage temperature was 20°C. Slurries were titrated with sulfuric acid to pH 5.5 and the amount of acid used was recorded. After the titrations, the pH was measured every 4-5 days during two months. If the measured pH was greater than pH 5.5, slurries were re-titrated with acid again to reach pH 5.5. Titrating was repeated 9 times after the initial. There were three replicates of each treatment so in total there were 30 samples. See Table 3 for a list of all treatments.

Table 3. Experiment 2: Slurry acidification to pH 5.5 simulating acidification at start of storage period. Experiment with fresh cattle slurry and pig slurry

Treatment name	Slurry type	Filtered or not filtered slurry	Conventional or organic farm	Acid used	Target pH
CS_C1	Cattle slurry	Not filtered	Conventional	Sulfuric acid	5.5
CS_C2	Cattle slurry	Not filtered	Conventional	Sulfuric acid	5.5
CS_O1	Cattle slurry	Not filtered	Organic	Sulfuric acid	5.5
CS_O2	Cattle slurry	Not filtered	Organic	Sulfuric acid	5.5
PS_C1	Pig slurry	Not filtered	Conventional	Sulfuric acid	5.5
PS_C2	Pig slurry	Not filtered	Conventional	Sulfuric acid	5.5
PS_C3	Pig slurry	Not filtered	Conventional	Sulfuric acid	5.5
CS_C2 F	Cattle slurry	Filtered	Conventional	Sulfuric acid	5.5
PS_C3 F	Pig slurry	Filtered	Conventional	Sulfuric acid	5.5

2.2 Slurry analysis

Slurry samples for chemical and physical analysis were collected at the same time as the other samples, and were refrigerated at about 4 °C until sent to the laboratory for analysis. Only one sample of each slurry type was analysed. Slurry characteristics given by laboratory analysis are presented in table 4. Concerning the liquid fractions, only dry matter content and initial pH were measured after filtration, determine by difference of mass between before and after drying in an oven at 60 degrees during a day.

Table 4. Slurry characteristics at the start of each experiment. Total solids (TS), volatile solids (VS), total nitrogen (TN), total ammonium nitrogen (NH_4-N), total organic nitrogen (ON), total phosphorus (TP), total potassium (K), Total carbon (TC),Total sulfur (S), calcium (Ca), magnesium (Mg), natrium (Na), total carbon:total nitrogen ratio (C/N)

Experiment		Slurry types	TS %	TN Kg/T	NH4-N Kg/T	ON Kg/T	TP Kg/T	K Kg/T	S Kg/T	Ca Kg/T	Mg Kg/T	Na Kg/T	TC Kg/T	C/N	VS %	pH
1	CS	Cattle	10.4	4.7	2.1	2.6	0.78	4.30	0.59	1.91	0.65	0.18	47.3	10.0	8.4	7.29
1	PS	Pig	9.0	4.6	2.2	2.4	0.72	1.91	0.45	2.64	0.69	1.25	39.6	8.6	7.3	6.65
2	CS_C1	Cattle	8.8	3.8	1.5	2.4	0.44	4.34	0.40	1.47	0.52	0.69	39.8	10.3	7.1	7.37
2	CS_C2	Cattle	9.3	4.2	1.9	2.3	0.57	3.99	0.49	1.89	0.55	0.15	41.9	10.0	7.5	7.20
2	CS_O1	Cattle	9.4	4.2	1.8	2.4	0.51	3.66	0.32	1.60	0.57	0.19	42.7	10.2	7.7	6.88
2	CS_O2	Cattle	8.9	4.5	2.3	2.3	0.49	3.07	0.42	3.91	0.74	0.89	39.2	8.70	7.1	7,71
2	PS_C1	Pig	13.3	5.7	2.5	3.2	0.98	2.23	0.47	3.28	0.78	1.35	59.1	10.4	11.0	6.53
2	PS_C2	Pig	9.5	6	3.3	2.7	1.08	1.96	0.52	2.79	1.35	1.10	42.1	7.0	7.7	7.03
2	PS_C3	Pig	9	5	2.9	2.1	0.82	2.53	0.5	2.05	0.44	0.64	42.4	8.50	7.4	7.00
2	CS_C2 F	Cattle liquid fraction	5.82													7.57
2	PS_C3F	Pig liquid fraction	5.85													7.13

2.3 Acidification of slurries and pH evolution after acidification

In each experiment, acids were added gradually to the slurries in volumes of 1 ml with a micropipette. The pH was checked after each acid addition using an electrode pH meter (HANNA instrument edge blue uses HALO™ Bluetooth pH electrodes). Titrations were done directly in the containers. The next addition of acid was made only when the pH was stable. The slurry was constantly mixed with a magnetic mixer during the acid additions and pH measurements. At the end of each titration, the volume of acid was recorded to reach the pH 6.4 and 6. The pH value 6.4 was recorded because it is often the target value for in-field acidification systems in Denmark. It was determined by linear regression of the pH curve between two nearest successive volumes of acid around the pH 6.4. Concerning experiment 2, the initial titration was done the same day or the next day after slurry collecting. The samples which were titrated the next day were refrigerated at approximately 4 °C and then allowed to warm up to room temperature again before titrating. Acids used were diluted to 1N (Eq/L) or 0.5N for formic acid to avoid excessive foam formation, to work safety and to avoid accidentally going under our target pH. Thus, 1N acid solutions also allow for easy comparison of their efficiency. The volume of acid added/sample volume was converted to equivalent added per m^3 of slurry for easier comparison of the efficiency of different acids. Efficiency of acids was determined by the index equivalent needed/m^3 of slurry to

reduce the pH to 6.4 and 6 respectively. A small index refers to an efficient acid.

$$\frac{\text{Eq}}{\text{m3 of slurry}} = \frac{\text{Volume of acid added (l)}}{\text{Sample volume (0.2 l)} * 1000\ \text{(l/m3)}} * \text{Normality of the acid solution (Eq/l)}$$

To have an economic analysis of the slurry acidification when using of different acids, some information about concentrated acid was needed. The main characteristics of the acids used are shown in Table 1. To evaluate the slurry buffer system, acid consumption and the capacity to increase the pH after acidification were the two main parameters. The acid consumption was studied through three criteria: the amount of acid used during the first titration to reach pH 6.4, 6.0 and 5.5, the total amount of acid used after the first acidification, and the total amount of acid used. The slope of the pH curve between each re-acidification (increasing of pH level divided by number of day between 2 successive titrations) was analysed to compare the pH buffering after each re-acidification.

2.4 Data analysis

To compare acids efficiency to lower the pH and their impact on pH buffering in experiment1, ANOVA (AovSum and One-way ANOVA with pairwise comparison of means) was used. Concerning the acidification of different slurries in Experiment 2, linear regression was used to bring out a potential correlation between the number of acidification and the acid efficiency or the growth of pH. ANONA (AovSum) was used to compare total acid consumption, acid efficiency and the growth of pH after successive acidifications in function to different slurries. Multiple regressions were used to find an optimal submodel to explain the acid consumption and the growth of pH. Homogeneity of variances was checked by Fisher test before ANOVA and normality of residuals was checked after the test. The R software (x64 3.4.1) with Rcmdr Package was used for ANOVA and Linear regression. RegBest function from FactoMineR package was used for the multiple regressions. RegBest function built all submodels possible and then kept only the ones with the smallest p-value of the multiple R-square test. Complete model was in the following form:

$$\mathbf{Y_i = \beta_0 + \beta_1 * TS_{ij} + \beta_2 * Tot\text{-}N_{ij} + \beta_3 * NH4\text{-}N_{ij} + \beta_4 * C/N_{ij} + \beta_5 * TotC_{ij} + \beta_6 * VS_{ij} + \beta_7 * InitialpH_{ij} + \varepsilon_{ij}}$$

Y_i = Responses variables for the slurry i
$\beta_0,\ldots,\beta_7$ = Unknown model parameters which were estimated
$TS_{i,j}, \ldots, InitialpH_{ij}$ = Explanatory variables for slurry i, replicate j
ε_i = the residual

In the complete model, all slurry characteristics given by slurry analysis were not used. This was because the number of slurries analysed was less than the number slurry characteristics measured, and there was only one slurry analysis for each of the three replicates. Consequently, it was not possible to added more than 7

variables in the complete model. The choice of which characteristics to include in the model was done based on results found in the literature (Sommer *et al.*, 2013, Paul and Beauchamp, 1989, Hjorth *et al.,* 2015), and for the purpose to easily determine the quantity of acid needed. All details on statistical results are in Appendix 1.

3 Results

3.1 Experiment 1: Comparison of different acids to lower the slurry's pH to 6.4 and 6.0

The results from the titrations with different acids showed differences in efficiency for acidification between acids (Table 5). The ANOVA test showed significant differences ($p<0.05$) (for more details see Appendix 1) in efficiency between several acids to reach the target pH, except for pig slurry to 6.4 there were no differences between acids.

To reduce the pH to 6.4, in decreasing order of acid efficiency, the rank was : Lactic acid ≥ sulfuric acid = formic acid = Nitric acid ≥ Acetic acid > Oxalic acid for cattle slurry. To reduce the pH to 6.0, the rank was: Lactic acid > sulfuric acid = formic acid = Nitric acid = Acetic acid > Oxalic acid for cattle slurry, and Lactic acid = sulfuric acid = formic acid = Nitric acid = Acetic acid > Oxalic acid for pig slurry. Thus, Oxalic acid is the least efficient acid while the other organic acids are as efficient as sulfuric acid to reduce the pH to 6.4 or 6.0 even better as for lactic acid for pig slurry acidification to pH 6.0($p<0.05$). Consequently, the quantity of acid used seems not well correlated with the strength of acids. Even if, weak organic acid like acetic acid was added in higher quantity than stronger organic acid like lactic acid and formic acid, oxalic acid which is the strongest of organic acid with a pKa of 1.2 must be added in larger quantity.

The conversion of these results with using concentrated acid gives contrasted results. Indeed, the strength differences between commercial concentrated acids influence the quantity of acid used and affect the cost of acidification (Table 5). Nitric acid is a good example to show this contrast. For equivalent normality solution, nitric acid is one of most efficient; however, this acid for toxicity reason cannot be sold with a higher strength than 16%. Consequently, taking into account strengths and prices of concentrated acids, nitric acid is the worst efficient and least economical acid. Contrary to sulfuric acid which is efficiently and economically the best acid in all points, following by organic acids which according to the criteria (slurry types and pH target) seems more or less efficient or economically interesting. Economically, lactic and formic acid are often the best organic acids for slurry acidification. However, the acidification cost is divided around by 10 with the use of sulphur acid to compare with organic acids.

Table 5. Experiment 1: Characteristics and consumption of acids used to lower slurry's pH to 6.0 and 6.4. Different letters in ( ) shows a significant difference along the row with the one-way ANOVA test with pairwise comparison of means.

		pH	Sulfuric acid	Acetic acid	Lactic acid	Oxalic acid	Formic acid	Nitric acid
Amount of acid used (Eq/m³ of slurry)	Pig	6.4	17.8 (a)	17.6 (a)	15.5 (a)	19.2 (a)	20.4 (a)	19.2 (a)
		6.0	58.8 (b)	56.7 (b)	48.6 (a)	91.7 (c)	58.3 (b)	55.7 (b)
	Cattle	6.4	86 (ab)	89.8 (b)	78.8 (a)	119.5 (c)	87.1 (ab)	85 (ab)
		6	129.2 (a)	139.2 (a)	124 (a)	160.3 (c)	128.3 (a)	127.7 (a)
Amount of conc. acid needed (L/m³ of slurry)	Pig	6.4	0.5 (a)	1.0 (b)	1.5 (c)	0.7 (ab)	1.0 (b)	5.4 (d)
		6	1.6 (a)	3.3 (b)	4.6 (c)	3.5 (b)	2.8 (b)	15.5 (d)
	Cattle	6.4	2.4 (a)	5.2 (c)	7.4 (d)	4.6 (b)	4.2 (b)	23.7 (e)
		6	3.6 (a)	7.9 (c)	11.6 (d)	6.1 (b)	6.2 (b)	35.7 (e)
Acidification cost (SEK/m³ of slurry)	Pig	6.4	0.8 (a)	7.2 (b)	6.7 (b)	6.9 (b)	7.5 (b)	20.9 (c)
		6	2.5 (a)	23.2 (b)	20.9 (b)	33.0 (c)	22.0 (b)	60.6 (d)
	Cattle	6.4	3.7 (a)	36.8 (c)	33.9 (bc)	43.1 (d)	32.8 (b)	92.6 (e)
		6	5.5 (a)	57.0 (c)	53.3 (bc)	57.8 (c)	48.3 (b)	139.1 (d)

**Price of acid according to Brenntag Nordic AB when purchasing an IBC, not including delivery costs.*

3.2 Experiment 2: Acid consumption of different slurries and characterisation of buffer system

All information concerning amount of acid used are gathered in figure 1. The quantity of acid used during the first titration to reduce the pH to 6.4, 6.0 and 5.5 and the total amount of acid used (first titration and all re-acidifications) were not significantly different between slurry type (cattle and pig slurry) ($p>0.05$). Nevertheless, differences of total acid consumption exist between different cattle slurries and different pig slurries ($p<0.05$). Filtrated slurries, by comparison with their respective initial slurries, need more acid if the target pH is 5.5 but there was no statistical difference if the target pH is 6.4 or 6.0

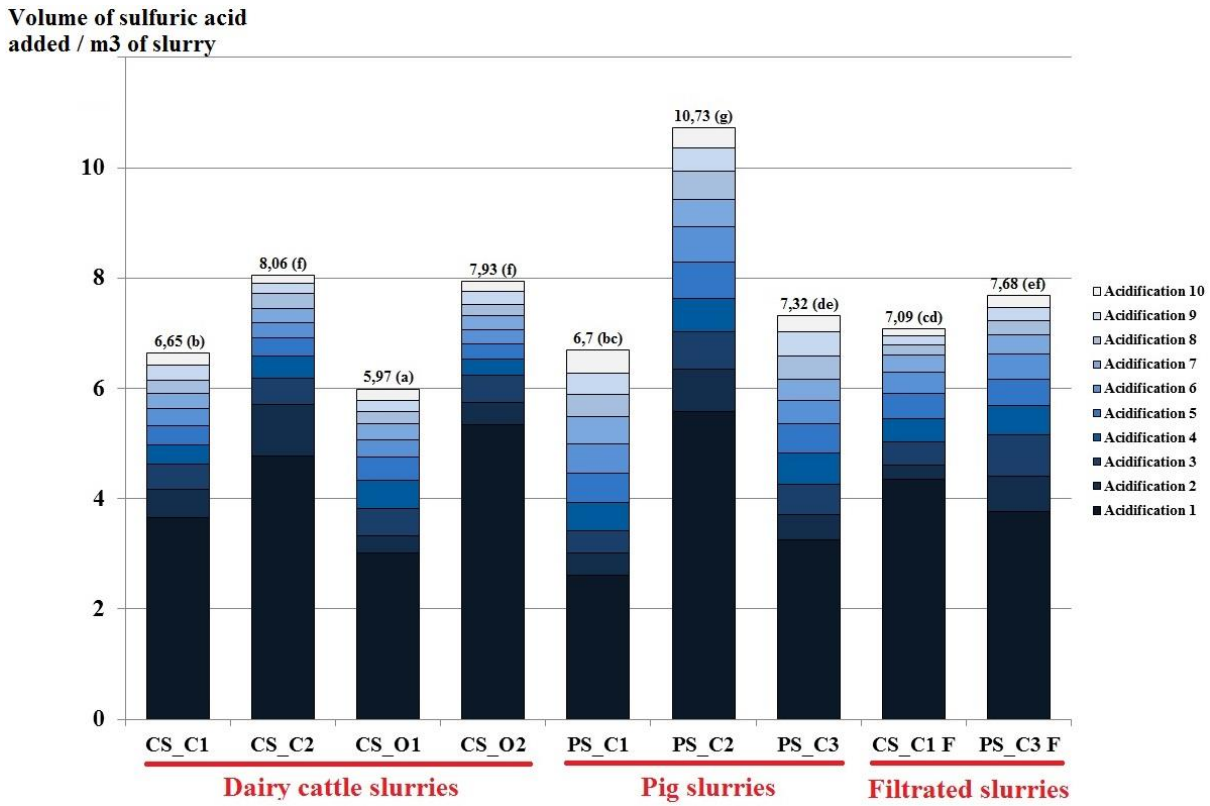

Figure 1. Experiment 2: Volume of sulfuric acid added / m3 of slurry at each acidification to maintain pH at5.5 during two months. Total amount of acid used is listed at the top of each column. Different letters show significant differences.

Results from the multiple regressions by RegBest function are presented in Table 4. For the initial acidification, results show that the best model variables depend on the target pH. For example, initial pH, total carbon and C:N ratio were in the best submodels for target pH 6.4 and 6.0 but total solids (TS), total nitrogen (Tot-N) and volatile solids (VS) were a better fit for target pH 5.5. Nitrogen content seems to more clearly influence the buffer system when acidifying down to 5.5 than when only to 6.0.

Table 6. Experiment 2: Result of RegBest function with all parameters values of the best submodel.

Yi	β0	β1 TS	β2 Tot-N	β3 NH4+	β4 C/N	β5 Tot-C	β6 VS	β7 Initial pH	Multiple R-square
Quantity of acid used to decrease the pH to 6.4 [1]	-29.663	2.144	3.257		1.613	-0.228	-2.956	1.871	0.9924
Quantity of acid used to decrease the pH to 6.0 [1]	-39.042	4.230	3.689	1.671	2.581	-0.580	-4.231	1.999	0.9955
Quantity of acid used to decrease the pH to 5.5 [2]	-0.163	7.567	1.109				-9.431		0.9885
Total amount of acid used [2]	-30.031	8.084	7.042		2.729		-12.619		0.9887
Total amount of acid used after the first acidification [2]	-11.470		6.483	-5.579		1.604	-9.272		0.9875

[1] *These submodels was gotten with results of titration of experiment 1 and 2*
[2] *These submodels was gotten with results of experiment 2 without results on filtrated slurries (no analyses)*

The total amount of acid used, which is the sum of all successive acid additions, is best explained by essentially the same variables: total solids, total nitrogen, total carbon:total nitrogen ratio and volatile solid. Volatile solids support the idea of a possible organic carbon and VFA conversion into inorganic carbon which generates an increase of pH. Concerning the amount of acid used after the first acidification, the best sub-model takes into account the following variables: total nitrogen, ammonium concentration, total carbon and volatile acid. The quantity of acid used to decrease the pH to 5.5 is not linearly correlated the total amount of acid used after the first acidification (all re-acidification) ($p>0.05$).

The best submodel for total amount of acid used was:
$ACID_{Total\ Quantity}$= -30.031 + 8.084 * TS + 7.042 * Tot-N + 2.729 * C/N + -12.619 * VS (R^2=0,9887)

The best submodel for amount of acid used to decrease pH to 5.5 was:

$ACID_{First\ acidification}$ = -0.163 + 7.567 * TS + 1.109 * Tot-N + -9.431 * VS (R^2=0,9885)

3.3 Experiment 1 and 2: Evolution of slurry pH after acidification

Concerning experiment 1, the slurry acidification experiment with different acids, the pH began to increase the day after acidification for all slurries (figure 2). Time, acid type and interaction between them influence significantly the pH evolution ($p<0.05$) for cattle slurry and pig slurry. So, the time to come back to a pH value of 6.4 was different between treatments. For both slurry types, acetic acid and sulfuric acid where the best acids to keep the pH value under 6.4. Indeed with acetic and

sulfuric acid for cattle slurry, pH 6.4 is overtaken three days after acidification against two for other acids. For pig slurry, with acetic and sulfuric acid, pH 6.4 is overtaken four days after acidification against three or two with other acids.

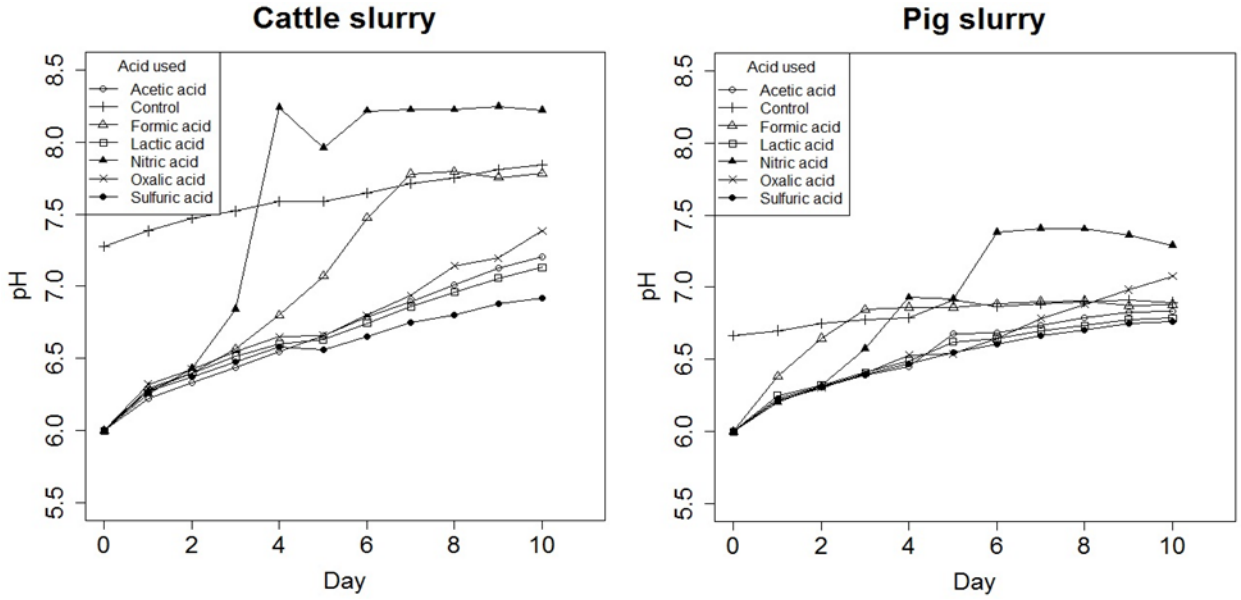

Figure 2. Experiment 1: Evolution of slurry pH after acidification with different acids. Error bars (n=3) were removed for clarity.

For experiment 2, even after nine acidifications, the pH had not stabilized and continued to increase after each acidification (Figure 3). The increase in pH after each acidification can be described by the slope of the change in pH over time. However, while we expected the slope to decrease with successive re-acidification, there was no correlation between the slope values and the number of re-acidifications ($p>0.05$). Thus, it seems to be difficult to predict the increase in pH of slurry after acidification. However, average slope values (Table 7) are different between different cattle slurries and different pig slurries ($p<0.05$) which indicates that this buffer system component is linked with initial characteristics of slurries.

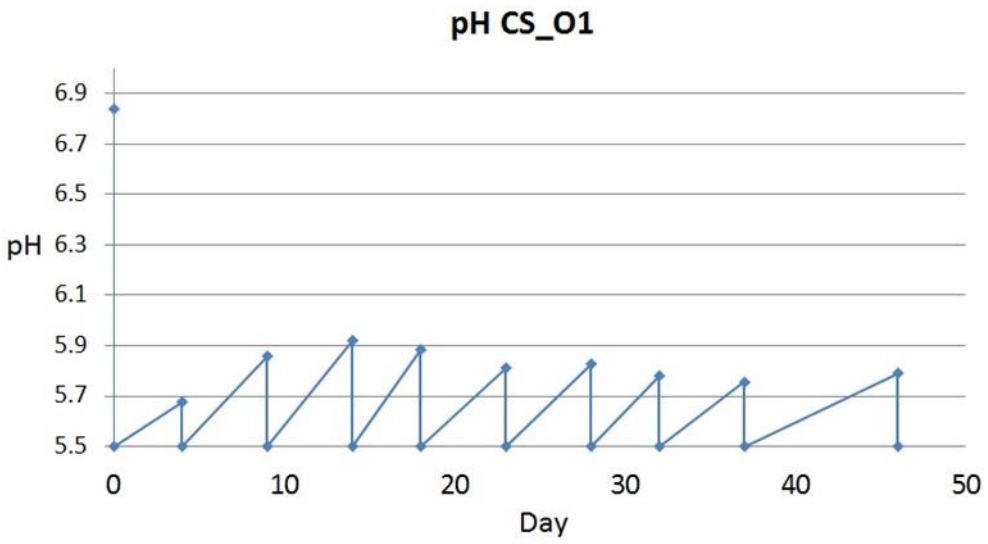

Figure 3. Experiment 2: Example of evolution of cattle slurry pH after several additions of sulphuric acid. (n=3).

Table 7. Experiment 2: Average slope of the change in pH over time after each acidification. Different letters in ( ) shows a significant difference with the one-way ANOVA test with pairwise comparison of means.

Slurry	CS_C1	CS_C2	CS_O1	CS_O2	PS_C1	PS_C2	PS_C3	CS_C1F	PS_C3F
Slope	0.074	0.074	0.064	0.072	0.056	0.081	0.084	0.087	0.093
(n=3)	(bd)	(bd)	(ab)	(bc)	(a)	(cde)	(df)	(ef)	(f)

4 Discussion

4.1 Experiment 1: Comparison of different acids to lower the slurry's pH to 6.4 and 6.0

This experiment in small scale simulates the acidification of cattle and pig slurry by different acids just before spreading. The target pH chosen for this experiment was 6.0 because is currently used in slurry acidification in the storage before spreading (Sindhöj and Rodhe, 2013, SEGES, 2014). Moreover, it seems to be the pH of interest in this case because to lower the pH to 5.5 is more expensive. The amount of acid needed to decrease a slurry type's pH depends on characteristics of the slurry but also characteristics of the acid like pKa value, number of equivalence. Previous study made by Regueiro *et al.* (2016) tested efficiency of different additives including organic acid like acetic acid, citric acid and lactic acid to reduce the slurry pH to 5.5 and 3.5 in order to find alternatives to sulphuric acid. The efficiency was determined by the index milliequivalent needed / litre of slurry but it is equal of equivalent needed / m^3 of slurry. Similarly in this study, organic acids (excepted lactic acid for dairy cattle slurry) were as efficient as sulfuric acid to decrease the slurry pH to 5.5. Regueiro et al. (2016) went further to show the organic acids are less efficient than sulfuric acid to reach the pH 3.5. Thus, the weakness of organic acids seems affected their efficiency for titration under the pH 5.5.

4.2 Experiment 2: Acid consumption and modelling

The slurry buffer system can be evaluated by the quantity of acid used to reduce the pH of slurries and its capacity to increase the pH after acidification. Contrary to the study of Regueiro *et al.* (2016), these results do not show that cattle slurries have a higher buffering capacity than pig slurries, which translates to a higher acid consumption during the first titration. Moreover, Sommer et al. (1995) indicated that the residual alkalinity, probably due to high-molecular-weight organic matter with carboxyl functional groups, was correlated with dry matter content. Thus, the total of acid needed should be lower for filtrated slurries which have less dry matter content than infiltrated slurry. Our result contrasted this result. The filtration may impact other factors than only reduce the dry matter content and could modify other slurry characteristics which influence the buffer system. For this test, the dairy and pig slurry with highest acid use in the initial titration to 5.5 was chosen for the separation test. The study of all filtrated slurry characteristics could offer better explanations.

Concerning modelling, previous selection of variables could have influenced results of submodels. Moreover, modelling takes into account only the initial slurry

characteristics and not the evolution of the characteristics after acidification. Indeed Regueiro et al. (2016) and Hjorth et al. (2015) detected after acidification, in addition to a degradation of carbohydrates, a mineral dissolution of components such as phosphor, magnesium or calcium which can affect the pH and the decrease of inorganic carbon (carbonates) which react with the protons, realising carbon dioxide. Thus, re-acidified slurries likely did not have the same characteristics as initially. This can explain why there is no correlation between the quantity of acid used for the first titration and the total amount of acid used for all re-acidifications. However, with present models, multiple R-square value were always higher than 0.98 which translate that each response variable (quantity of acid used to decrease the pH to 6.4, 6.0, 5.5, the total amount of acid used and the total amount of acid used after the first acidification (all re-acidifications)) is explained at least 98% by the model. Cattle and pig slurries were not separated to build the models because the separation would generate a decreased number of variables in the complete model. Thus, these models can be used for all slurry type. Consequently, slurries were taken like entities characterise by its chemical, physical and biological characteristics.

The difference in best model variables according to the pH target confirms that the buffer system is different in function of the pH and components of slurries have a more or less impact on it (Sommer *et al.*, 1995b). Total nitrogen, total solids, total carbon:total nitrogen ratio and volatile solids were the best sub model variables to explain the total amount of acid used. More precisely, ammonium concentration impacts the buffer system (Sommer *et al.*, 2013, Paul and Beauchamp, 1989). Total solids (or dry matter) and volatile solids, which represents the amount of organic solids in slurry, can after time with microbial degradation be a source of inorganic carbon and volatile fatty acids (VFA) which are well described components of the buffer system (Sommer *et al.*, 2013). The study of VFA and total inorganic carbon (TIC) could offer better fitting models. However, according to Sommer and Husted (1995), high-molecular-weight organic matter with carboxyl functional groups, which is part of VS, contributes also to the pH buffering capacity. Moreover, total nitrogen, total ammonium, total carbon and volatile solids which were best model variables for the total amount of acid used for re-acidifications suggest the idea of a degradation of organic matter after the slurry acidification.

4.3 Experiment 1 and 2: Increase of pH after acidification

For experiment 1, the increase of slurry pH after acidification with different acids and the incapacity, in experiment 2, to stabilise the pH after several acidification suggest a multiple chemical, physical and biological processes which influence the pH. A recent study (Hjorth *et al.,* 2015) indicates that acidification alters slurry composition by degradation of carbohydrates (cellulose and hemicellulose) by acid hydrolysis. Indeed, this degradation seems not due to microbial activity which is reduced by acidification (Ottosen *et al.*, 2008; Regueiro *et al.*, 2016), but by conditions in favour to the activation of exoenzymes which catalyse the hydrolysis.

Yen *et al.* (2007) confirms the action of cellulase enzymes in the anaerobic digestion of cellulose. Outputs of this hydrolysis are small sugars and inorganic soluble C (Regueiro *et al.*, 2016) which increase the pH. Thus, the activation of enzymatic hydrolysis could take place after each acidification and thus add to the rise of pH. However, in the experiment 1, the pH increasing in the control suggests that the mixing before each measure of pH promote the aerobic degradation by microbial activity of organic material and VFA which would reduce the quantity of acid and by consequence increases the pH (Sommer *et al.*, 2013, Paul and Beauchamp, 1989, Sørensen *et al.*, 2009).

Concerning the difference of time to reach the pH 6.4 in function to acid type (experiment 1), acetic acid could keep the pH more long-time under the pH 6.4 to compare other organic acids because it is a VFA and a high concentration of VFA causes inhibition of cellulolytic activity (Siegert and Banks, 2005). Thus, with acetic acid, the acid hydrolysis seems lower than with the use of other organic acids. Nevertheless, the good efficiency of sulfuric acid on this effect to compare with other acids and the soar of pH three days after acidification for nitric acid treatment are not clear.

The temperature influence also the pH increases (Misselbrook *et al.*, 2016). The pH increase after acidification seems very fast to compare with other studies (Regueiro *et al.*, 2016, Misselbrook *et al.*, 2016). That may due to the storage temperature, which was higher (20°C) than in the other studies (15 and 17°C). This relatively high value of temperature does not represent the average temperature during all the slurry storage period in Sweden (Rodhe *et al.*, 2009) but it was chosen to accelerate the process and to simulate in 2 months a long period of storage.

5 Conclusion

These results show that in terms of equivalent normality solutions the organic acids were mostly as efficient as sulfuric acid to reduce the pH to 6.0 or 6.4. However, taking into account the properties of the studied acids in commercially available concentrations, sulfuric acid outperforms other acids with the lowest quantity of concentrated acid needed and an acidification cost only about one tenth of the cost for acidification with organic acids.

Our study shows, with experiment 2 concerning the buffer system, the incapacity to stabilize the pH at 5.5 by several successive acidifications. After each acidification, an increase of pH was detected. This pH increasing does not decrease after several acidifications and it is not correlated with the number of acidification. Nevertheless, the average increase of pH after acidifications is different between slurries and it depends on a combination of different characteristics of slurry.

Acknowledgments

The authors thank all farmers who have given slurry samples, Agrilab for the slurry analysis, Brenntag Nordic AB company to give all information about commercial concentrated acids and Marianne Tersmeden for the collect of slurries. This study was supported and funded by the Interreg BSR project Baltic Slurry Acidification.

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Appendix

Is acid efficiency different in function to acid type?

ANOVA test with using function **AovSum** from **FactoMineR** package + One-way ANOVA with Pairwise test: Multiple comparisons of means.

Cattle slurry

To reach pH 6.4

```
Ftest
             SS df     MS F value       Pr(>F)
Slurry    3113.91  5 622.78  47.945 0.0000001617 ***
Residuals  155.87 12  12.99
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Ttest
             Estimate Std. Error  t value Pr(>|t|)
(Intercept)     91.0417     0.8495 107.1714  < 2e-16 ***
Slurry - CS_A   -1.2083     1.8995  -0.6361  0.53664
Slurry - CS_F   -3.9583     1.8995  -2.0838  0.05922 .
Slurry - CS_L  -12.2083     1.8995  -6.4270  0.00003 ***
Slurry - CS_N   -6.0417     1.8995  -3.1806  0.00791 **
Slurry - CS_Ox  28.4583     1.8995  14.9818  < 2e-16 ***
Slurry - CS_S   -5.0417     1.8995  -2.6542  0.02102 *
```

```
CS_A  CS_F  CS_L  CS_N CS_Ox  CS_S
 "b"  "ab"   "a"  "ab"   "c"  "ab"
```

F-test result shows one of acids has a significantly different efficiency. T-test and pairwise test classifys acids according efficiency (letters give the increasing order of Eq/$m^3$of slurry.)

To reach pH 6.0

```
Ftest
             SS df     MS F value    Pr(>F)
Slurry    2736.28  5 547.26  11.668 0.0002853 ***
Residuals  562.83 12  46.90
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Ttest
             Estimate Std. Error t value Pr(>|t|)
(Intercept)    134.7778     1.6142 83.4940  < 2e-16 ***
Slurry - CS_A    4.3889     3.6095  1.2159  0.24739
Slurry - CS_F   -6.4444     3.6095 -1.7854  0.09947 .
Slurry - CS_L  -10.7778     3.6095 -2.9859  0.01136 *
Slurry - CS_N   -7.1111     3.6095 -1.9701  0.07234 .
Slurry - CS_Ox  25.5556     3.6095  7.0801  0.00001 ***
Slurry - CS_S   -5.6111     3.6095 -1.5545  0.14602
```

```
CS_A  CS_F  CS_L  CS_N CS_Ox  CS_S
 "a"  "a"   "a"  "a"   "b"  "a"
```

F-test result shows one of acids has a significantly different efficiency. T-test and pairwise test classifys acids according efficiency (letters give the increasing order of Eq/m^3 of slurry.)

Pig slurry

To reach pH 6.4

```
Ftest
             SS df    MS F value Pr(>F)
Slurry    39.685  5 7.937  2.0589 0.1417
Residuals 46.260 12 3.855

Ttest
             Estimate Std. Error t value Pr(>|t|)
(Intercept)    18.22917    0.46278 39.3903  < 2e-16 ***
Slurry - PS_A  -0.64583    1.03482 -0.6241  0.54424
Slurry - PS_F   1.81250    1.03482  1.7515  0.10535
Slurry - PS_L  -2.72917    1.03482 -2.6373  0.02168 *
Slurry - PS_N   0.93750    1.03482  0.9060  0.38279
Slurry - PS_Ox  1.02083    1.03482  0.9865  0.34337
Slurry - PS_S  -0.39583    1.03482 -0.3825  0.70877
```

```
PS_A  PS_F  PS_L  PS_N PS_Ox  PS_S
 "a"  "a"   "a"  "a"   "a"  "a"
```

No significant difference on efficiency of acid to reduce the pH to 6.4 ($p>0.05$).

To reach pH 6.0

```
Ftest
             SS df     MS F value    Pr(>F)
Slurry    3447.4  5 689.48  120.13 8.074e-10 ***
Residuals   68.9 12   5.74
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Ttest
             Estimate Std. Error  t value Pr(>|t|)
(Intercept)     61.63889    0.56468 109.1568  < 2e-16 ***
Slurry - PS_A   -4.97222    1.26267  -3.9379  0.00197 **
Slurry - PS_F   -3.30556    1.26267  -2.6179  0.02247 *
Slurry - PS_L  -12.97222    1.26267 -10.2737  < 2e-16 ***
Slurry - PS_N   -5.97222    1.26267  -4.7298  0.00049 ***
Slurry - PS_Ox  30.02778    1.26267  23.7812  < 2e-16 ***
Slurry - PS_S   -2.80556    1.26267  -2.2219  0.04628 *
```

```
PS_A  PS_F  PS_L  PS_N PS_Ox  PS_S
 "b"  "b"   "a"  "b"   "c"  "b"
```

F-test result shows one of acids has a significantly different efficiency. T-test and pairwise test classifys acids according efficiency (letters give the increasing order of Eq/m^3 of slurry.)

Is concentrated acid consumption different in function to acid type?

ANOVA test with using function **AovSum** from **FactoMineR** package + One-way ANOVA with Pairwise test

Cattle slurry

To reach pH 6.4

```
Ftest
            SS df      MS F value    Pr(>F)
Slurry    920.83  5 184.165  4983.5 < 2.2e-16 ***
Residuals   0.44 12   0.037
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Ttest
               Estimate Std. Error  t value Pr(>|t|)
(Intercept)     8.147633   0.045311 179.8175  < 2e-16 ***
Slurry - CS_A  -1.725619   0.101317 -17.0318  < 2e-16 ***
Slurry - CS_F  -3.792520   0.101317 -37.4320  < 2e-16 ***
Slurry - CS_L  -0.750438   0.101317  -7.4068  0.00001 ***
Slurry - CS_N  15.592837   0.101317 153.9008  < 2e-16 ***
Slurry - CS_Ox -3.564218   0.101317 -35.1787  < 2e-16 ***
Slurry - CS_S  -5.760042   0.101317 -56.8514  < 2e-16 ***
```

```
CS_A  CS_F  CS_L  CS_N CS_Ox  CS_S
 "c"   "b"   "d"   "e"   "b"   "a"
```

To reach pH 6.0

```
Ftest
            SS df      MS F value    Pr(>F)
Slurry    2099.59  5 419.92  1271.5 6.541e-16 ***
Residuals    3.96 12   0.33
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Ttest
               Estimate Std. Error  t value Pr(>|t|)
(Intercept)     12.23250    0.13545  90.3079  < 2e-16 ***
Slurry - CS_A   -2.28374    0.30288  -7.5400  0.00001 ***
Slurry - CS_F   -5.81444    0.30288 -19.1970  < 2e-16 ***
Slurry - CS_L   -0.59717    0.30288  -1.9716  0.07215 .
Slurry - CS_N   23.42476    0.30288  77.3393  < 2e-16 ***
Slurry - CS_Ox  -6.08292    0.30288 -20.0834  < 2e-16 ***
Slurry - CS_S   -8.64649    0.30288 -28.5473  < 2e-16 ***
```

```
CS_A  CS_F  CS_L  CS_N CS_Ox  CS_S
 "c"   "b"   "d"   "e"   "b"   "a"
```

Pig slurry

To reach pH 6.4

```
Ftest
            SS df     MS F value    Pr(>F)
Slurry    49.393  5 9.8787  482.24 2.149e-13 ***
Residuals 0.246 12 0.0205
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Ttest
               Estimate Std. Error  t value Pr(>|t|)
(Intercept)     1.716732   0.033735  50.8888  < 2e-16 ***
Slurry - PS_A  -0.459733   0.075434  -6.0945  0.00005 ***
Slurry - PS_F  -0.714431   0.075434  -9.4710  < 2e-16 ***
Slurry - PS_L  -0.262316   0.075434  -3.4774  0.00457 **
Slurry - PS_N   3.636511   0.075434  48.2081  < 2e-16 ***
Slurry - PS_Ox -0.978400   0.075434 -12.9703  < 2e-16 ***
Slurry - PS_S  -1.221631   0.075434 -16.1948  < 2e-16 ***
```

```
PS_A  PS_F  PS_L  PS_N PS_Ox  PS_S
"cd"  "bc"   "d"   "e"  "ab"   "a"
```

To reach pH 6.0

```
Ftest
            SS df     MS F value    Pr(>F)
Slurry    388.16  5 77.632  572.32 7.734e-14 ***
Residuals   1.63 12  0.136
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Ttest
               Estimate Std. Error  t value Pr(>|t|)
(Intercept)     5.371961   0.086809  61.8826  < 2e-16 ***
Slurry - PS_A  -1.320969   0.194110  -6.8052  0.00002 ***
Slurry - PS_F  -2.454661   0.194110 -12.6457  < 2e-16 ***
Slurry - PS_L  -0.805406   0.194110  -4.1492  0.00135 **
Slurry - PS_N  10.175719   0.194110  52.4223  < 2e-16 ***
Slurry - PS_Ox -1.856092   0.194110  -9.5620  < 2e-16 ***
Slurry - PS_S  -3.738590   0.194110 -19.2601  < 2e-16 ***
```

```
PS_A  PS_F  PS_L  PS_N PS_Ox  PS_S
"cd"   "b"   "d"   "e"  "bc"   "a"
```

For each case, at least one of these treatments is significantly different($p<0.05$). Pairwise test shows that the quantity of concentrated acid is the less important when sulfuric acid is used following by formic and oxalic acid then acetic acid, lactic acid and the acid which must be added in the most quantity is nitric acid.

Is acidification cost different in function to acid type?

ANOVA test with using function **AovSum** from **FactoMineR** package + One-way ANOVA with Pairwise test: Multiple comparisons of means.

Cattle slurry

To reach pH 6.4

```
Ftest
             SS df      MS F value    Pr(>F)
Slurry    12476.5  5 2495.31  1282.8 6.204e-16 ***
Residuals    23.3 12    1.95
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Ttest
             Estimate Std. Error  t value Pr(>|t|)
(Intercept)     42.36182    0.32874 128.8620  < 2e-16 ***
Slurry - CS_A    3.50971    0.73508   4.7746  0.00045 ***
Slurry - CS_F   -7.29947    0.73508  -9.9302  < 2e-16 ***
Slurry - CS_L   -8.45801    0.73508 -11.5062  < 2e-16 ***
Slurry - CS_N   50.24285    0.73508  68.3502  < 2e-16 ***
Slurry - CS_Ox   0.69450    0.73508   0.9448  0.36340
Slurry - CS_S  -38.68960    0.73508 -52.6332  < 2e-16 ***
```

```
CS_A  CS_F  CS_L  CS_N CS_Ox  CS_S
 "c"   "b"   "b"   "d"   "c"   "a"
```

To reach pH 6.0

```
Ftest
             SS df     MS F value    Pr(>F)
Slurry    28224.5  5 5644.9   669.3 3.037e-14 ***
Residuals   101.2 12    8.4
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Ttest
             Estimate Std. Error  t value Pr(>|t|)
(Intercept)     63.07246    0.68451  92.1421  < 2e-16 ***
Slurry - CS_A    7.99011    1.53062   5.2202  0.00021 ***
Slurry - CS_F  -11.40163    1.53062  -7.4490  0.00001 ***
Slurry - CS_L   -9.74385    1.53062  -6.3660  0.00004 ***
Slurry - CS_N   76.01612    1.53062  49.6637  < 2e-16 ***
Slurry - CS_Ox  -5.30373    1.53062  -3.4651  0.00467 **
Slurry - CS_S  -57.55702    1.53062 -37.6038  < 2e-16 ***
```

```
CS_A  CS_F  CS_L  CS_N CS_Ox  CS_S
 "c"   "b"   "b"   "d"   "b"   "a"
```

Pig slurry

To reach pH 6.4

```
Ftest
             SS df      MS F value    Pr(>F)
Slurry    657.39  5 131.478  201.98 3.787e-11 ***
Residuals   7.81 12   0.651
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Ttest
             Estimate Std. Error  t value Pr(>|t|)
(Intercept)     8.71547    0.19017  45.8300  < 2e-16 ***
Slurry - PS_A   0.26310    0.42523   0.6187  0.54767
Slurry - PS_F  -0.64609    0.42523  -1.5194  0.15456
Slurry - PS_L  -2.04939    0.42523  -4.8195  0.00042 ***
Slurry - PS_N  12.16598    0.42523  28.6102  < 2e-16 ***
Slurry - PS_Ox -1.77962    0.42523  -4.1850  0.00127 **
Slurry - PS_S  -7.95398    0.42523 -18.7050  < 2e-16 ***
```

```
PS_A  PS_F  PS_L  PS_N PS_Ox  PS_S
 "c"  "bc"   "b"   "d"  "bc"   "a"
```

To reach pH 6.0

```
Ftest
             SS df      MS F value    Pr(>F)
Slurry    5434.7  5 1086.94  414.77 5.277e-13 ***
Residuals   31.4 12    2.62
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Ttest
             Estimate Std. Error  t value Pr(>|t|)
(Intercept)     28.25658    0.38156  74.0557  < 2e-16 ***
Slurry - PS_A    0.67908    0.85319   0.7959  0.44154
Slurry - PS_F   -4.76984    0.85319  -5.5906  0.00012 ***
Slurry - PS_L   -7.32653    0.85319  -8.5872  < 2e-16 ***
Slurry - PS_N   32.39040    0.85319  37.9638  < 2e-16 ***
Slurry - PS_Ox   4.77128    0.85319   5.5923  0.00012 ***
Slurry - PS_S  -25.74438    0.85319 -30.1742  < 2e-16 ***
```

```
PS_A  PS_F  PS_L  PS_N PS_Ox  PS_S
 "c"   "b"   "b"   "d"   "c"   "a"
```

Yes, signicantly different. $p<0.05$ for each case. At least one of these treatments is significantly different. Pairwise test shows that acididcation is cheapest with sulfuric acid in each case. Rank of other acids depends on slurry type and target pH value. Nevertheless, lactic acid and formic acid seem the best alternatives to sulfuric acid. Nitric acid is the worst option.

Is acid consumption during the first titration different between slurry type?

ANOVA test with using function **AovSum** from **FactoMineR** package

To reach pH 6.4

```
Ftest
                    SS df     MS F value  Pr(>F)
Type.of.slurry  2.4643  1 2.4643  4.2445 0.05334 .
Residuals      11.0313 19 0.5806
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Ttest
                                  Estimate Std. Error t value Pr(>|t|)
(Intercept)                        1.51122    0.16800  8.9955  < 2e-16 ***
Type.of.slurry - dairy cattle slurry  0.34611    0.16800  2.0602  0.05334 .
Type.of.slurry - pig slurry         -0.34611    0.16800 -2.0602  0.05334 .
```

To reach pH 6.0

```
Ftest
                    SS df      MS F value Pr(>F)
Type.of.slurry  2.1874  1 2.18737  2.2426 0.1507
Residuals      18.5324 19 0.97539

Ttest
                                  Estimate Std. Error t value Pr(>|t|)
(Intercept)                        2.69675    0.21775 12.3847   <2e-16 ***
Type.of.slurry - dairy cattle slurry  0.32608    0.21775  1.4975   0.1507
Type.of.slurry - pig slurry         -0.32608    0.21775 -1.4975   0.1507
```

To reach pH 5.5

```
Ftest
                    SS df      MS F value Pr(>F)
Type.of.slurry  0.7366  1 0.73656  0.5657 0.4612
Residuals      24.7391 19 1.30206

Ttest
                                  Estimate Std. Error t value Pr(>|t|)
(Intercept)                        4.00478    0.25158 15.9182   <2e-16 ***
Type.of.slurry - dairy cattle slurry  0.18922    0.25158  0.7521   0.4612
Type.of.slurry - pig slurry         -0.18922    0.25158 -0.7521   0.4612
```

There is not significant difference of concentrated acid consumption to reach pH 6.4, 6.0 or 5.5 between pig and cattle slurries($p>0.05$).

Is the total amount of acid used (all acidifications) different in function to slurry type?

ANOVA test with using function **AovSum** from **FactoMineR** package

```
> AovSum(Total.amount.of.acid.used ~ Type.of.slurry, data=Dataset)
Ftest
                   SS df     MS F value  Pr(>F)
Type.of.slurry  6.215  1 6.2153  3.1175 0.09352 .
Residuals      37.880 19 1.9937
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Ttest
                                      Estimate Std. Error t value Pr(>|t|)
(Intercept)                            7.70233    0.31131 24.7416  < 2e-16 ***
Type.of.slurry - dairy cattle slurry -0.54967    0.31131 -1.7656  0.09352 .
Type.of.slurry - pig slurry           0.54967    0.31131  1.7656  0.09352 .
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

There is not significant difference of total acid consumption between pig and cattle slurries($p>0.05$).

Is the total amount of acid used (all acidifications) different in function to slurries?

ANOVA test with using function **AovSum** from **FactoMineR** package + One-way ANOVA with Pairwise test

```
Ftest
             SS df     MS F value    Pr(>F)
Slurry    44.545  8 5.5681  284.36 < 2.2e-16 ***
Residuals  0.352 18 0.0196
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Ttest
               Estimate Std. Error  t value Pr(>|t|)
(Intercept)     7.57007    0.02693 281.1011  < 2e-16 ***
Slurry - CS_C1  -0.92407    0.07617 -12.1318  < 2e-16 ***
Slurry - CS_C1F -0.48274    0.07617  -6.3377  0.00001 ***
Slurry - CS_C2   0.48593    0.07617   6.3795  0.00001 ***
Slurry - CS_O1  -1.59607    0.07617 -20.9542  < 2e-16 ***
Slurry - CS_O2   0.36459    0.07617   4.7866  0.00015 ***
Slurry - PS_C1  -0.87007    0.07617 -11.4228  < 2e-16 ***
Slurry - PS_C2   3.16459    0.07617  41.5466  < 2e-16 ***
Slurry - PS_C3  -0.24874    0.07617  -3.2656  0.00430 **
Slurry - PS_C3F  0.10659    0.07617   1.3994  0.17869
```

```
CS_C1 CS_C1F  CS_C2  CS_O1  CS_O2  PS_C1  PS_C2  PS_C3 PS_C3F
  "b"   "cd"    "f"    "a"    "f"   "bc"    "g"   "de"   "ef"
```

F-test result shows at least one of slurry has a consumption of sulfuric acid significantly different. T-test and pairwise test classifys the total amount of acid used in function to slurries (letters give the increasing order)

Is acid consumption during the first titration different if slurries are filtrated?

ANOVA test with using function **AovSum** from **FactoMineR** package

To reach pH 6.4	To reach pH 6.0	To reach pH 5.5
Ftest SS df MS F value Pr(>F) Filtration 0.39494 1 0.39494 2.0617 0.1816 Residuals 1.91565 10 0.19156 Ttest Estimate Std. Error t value Pr(>|t|) (Intercept) 1.56508 0.12635 12.3871 <2e-16 *** Filtration - Filtration 0.18142 0.12635 1.4359 0.1816 Filtration - No Filtration -0.18142 0.12635 -1.4359 0.1816 --- Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1	Ftest SS df MS F value Pr(>F) Filtration 0.81224 1 0.81224 4.5579 0.05853 . Residuals 1.78206 10 0.17821 --- Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1 Ttest Estimate Std. Error t value Pr(>|t|) (Intercept) 2.67750 0.12186 21.9714 < 2e-16 *** Filtration - Filtration 0.26017 0.12186 2.1349 0.05853 . Filtration - No Filtration -0.26017 0.12186 -2.1349 0.05853 . --- Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1	Ftest SS df MS F value Pr(>F) Filtration 0.81224 1 0.81224 4.5579 0.05853 . Residuals 1.78206 10 0.17821 --- Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1 Ttest Estimate Std. Error t value Pr(>|t|) (Intercept) 2.67750 0.12186 21.9714 < 2e-16 *** Filtration - Filtration 0.26017 0.12186 2.1349 0.05853 . Filtration - No Filtration -0.26017 0.12186 -2.1349 0.05853 . --- Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
There is not significant difference of concentrated acid consumption to reach pH 6.4 or 6.0 between filtrated and no filtrated slurries ($p>0.05$).This test was done without seperation of slurry types (pig and cattle slurry).		There is a significant difference of concentrated acid consumption to reach pH 5.5 between filtrated and no filtrated slurries ($p<0.05$). According to the T-test, the amount of acid used to reach the pH 5.5 is higher for filtrated slurry (around +0,6 Litter of acid/m^3 of slurry).This test was done without seperation of slurry types (pig and cattle slurry).

Models – **RegBest** function from **FactoMineR** package

Quantity of acid to reduce the pH to 6.4

```
Residuals:
      Min        1Q    Median        3Q       Max
-0.177326 -0.024050  0.008524  0.031119  0.195521

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept) -29.66299    1.32308 -22.420 1.21e-15 ***
TS            2.14447    0.19485  11.006 6.17e-10 ***
Tot.N         3.25656    0.21840  14.911 2.68e-12 ***
Tot.C        -0.22822    0.03774  -6.046 6.54e-06 ***
C.N           1.61337    0.12536  12.869 3.91e-11 ***
VS           -2.95563    0.31225  -9.466 7.90e-09 ***
Initial.pH    1.87139    0.07574  24.708  < 2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Residual standard error: 0.085 on 20 degrees of freedom
Multiple R-squared:  0.9924, Adjusted R-squared:  0.9901
F-statistic:   433 on 6 and 20 DF,  p-value: < 2.2e-16
```

Best submodel variables: TS, Tot-N, Tot-C, C/N, VS, Initial pH

Quantity of acid to reduce the pH to 6.0

```
Residuals:
      Min        1Q    Median        3Q       Max
-0.179223 -0.035806 -0.007311  0.028415  0.142541

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept) -39.04217    2.13681 -18.271 1.64e-13 ***
TS            4.22983    0.35220  12.010 2.56e-10 ***
Tot.N         3.68923    0.20455  18.036 2.07e-13 ***
NH4.N         1.67077    0.41282   4.047 0.000688 ***
Tot.C        -0.57952    0.07904  -7.332 5.97e-07 ***
C.N           2.58084    0.24361  10.594 2.06e-09 ***
VS           -4.23086    0.31070 -13.617 2.98e-11 ***
Initial.pH    1.99883    0.07490  26.685  < 2e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 '

Residual standard error: 0.07961 on 19 degrees of freedom
Multiple R-squared:  0.9955, Adjusted R-squared:  0.9938
F-statistic: 596.1 on 7 and 19 DF,  p-value: < 2.2e-16
```

Best submodel variables: TS, Tot-N, NH4-N, Tot-C, C/N, VS, Initial pH

Quantity of acid to reduce the pH to 5.5

```
Residuals:
     Min       1Q   Median       3Q      Max
-0.18793 -0.08971  0.01847  0.05847  0.25029

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept) -0.16297    0.30212  -0.539    0.597
TS           7.56710    0.28596  26.462 2.96e-15 ***
Tot.N        1.10935    0.04702  23.591 1.98e-14 ***
VS          -9.43052    0.32954 -28.617 8.03e-16 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Residual standard error: 0.1313 on 17 degrees of freedom
Multiple R-squared:  0.9885, Adjusted R-squared:  0.9865
F-statistic: 486.6 on 3 and 17 DF,  p-value: < 2.2e-16
```

Best submodel variables: TS, Tot-N, VS

Total amount of acid used

```
Residuals:
     Min       1Q   Median       3Q      Max
-0.24573 -0.12157 -0.01757  0.06619  0.33022

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept) -30.0307     3.6895  -8.140 4.43e-07 ***
TS            8.0843     0.4340  18.629 2.85e-12 ***
Tot.N         7.0421     0.5937  11.862 2.43e-09 ***
C.N           2.7294     0.3301   8.268 3.61e-07 ***
VS          -12.6186     0.6897 -18.296 3.76e-12 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Residual standard error: 0.1761 on 16 degrees of freedom
Multiple R-squared:  0.9887, Adjusted R-squared:  0.9859
F-statistic: 351.4 on 4 and 16 DF,  p-value: 2.294e-15
```

Best sub-model variables: TS, Tot-N, C/N, VS

Total amount of acid used after the first acidification

```
Residuals:
     Min       1Q   Median       3Q      Max
-0.14684 -0.06580 -0.01127  0.03798  0.18466

Coefficients:
             Estimate Std. Error t value Pr(>|t|)
(Intercept) -11.4697     0.7036  -16.30 2.18e-11 ***
Tot.N         6.4829     0.3603   17.99 4.85e-12 ***
NH4.N        -5.5789     0.3753  -14.87 8.73e-11 ***
Tot.C         1.6036     0.1001   16.01 2.86e-11 ***
VS           -9.2716     0.5678  -16.33 2.13e-11 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

Residual standard error: 0.1063 on 16 degrees of freedom
Multiple R-squared:  0.9875, Adjusted R-squared:  0.9844
F-statistic: 315.8 on 4 and 16 DF,  p-value: 5.329e-15
```

Best sub-model variables: Tot-N, NH4-N, Tot-C, VS

Relation between the amount of acid used for the first acidification and the amount of acid used after the first acidification (all re-acidifications)?

Linear regression

```
Residuals:
    Min      1Q  Median      3Q     Max
-1.5015 -0.8423 -0.3207  0.8399  1.5103

Coefficients:
                                                    Estimate Std. Error t value Pr(>|t|)
(Intercept)                                          3.83084    0.89788   4.267 0.000249 ***
Total.amount.of.acid.used.after.the.first.acidification  0.05801    0.24791   0.234 0.816907
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 1.019 on 25 degrees of freedom
Multiple R-squared:  0.002185, Adjusted R-squared:  -0.03773
F-statistic: 0.05475 on 1 and 25 DF,  p-value: 0.8169
```

There is no linear correlation between the amount of acid used for the first acidification and the amount of acid used after the first acidification (all re-acidifications) (p=0.8169).

Is pH evolution after acidification different in function to acid type used?

ANOVA test with interaction with using function **AovSum** from **FactoMineR** package

Cattle slurry

Ftest

	SS	df	MS	F value	Pr(>F)	
acid	25.021	6	4.1702	1616.737	< 2.2e-16	***
day	38.960	10	3.8960	1510.435	< 2.2e-16	***
acid:day	12.309	60	0.2052	79.536	< 2.2e-16	***
Residuals	0.273	106	0.0026			

F-test result shows time, acid type and interaction between them influence significantly the pH evolution ($p<0.05$). T-test is not represented here.

Pig slurry

Ftest

	SS	df	MS	F value	Pr(>F)	
acid	3.3485	6	0.55808	265.812	< 2.2e-16	***
day	15.5440	10	1.55440	740.357	< 2.2e-16	***
acid:day	3.7436	60	0.06239	29.718	< 2.2e-16	***
Residuals	0.2226	106	0.00210			

F-test result shows time, acid type and interaction between them influence significantly the pH evolution ($p<0.05$). T-test is not represented here.

Relation between slope and number of acidification?

Linear regression

```
lm(formula = Slope.pH.curve ~ number.of.acidification, data = slope)

Residuals:
      Min        1Q    Median        3Q       Max
-0.053504 -0.011164 -0.000824  0.012176  0.052877

Coefficients:
                           Estimate Std. Error t value Pr(>|t|)
(Intercept)               0.0738441  0.0029647  24.908   <2e-16 ***
number.of.acidification -0.0003401  0.0005268  -0.646    0.519
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.0187 on 187 degrees of freedom
Multiple R-squared:  0.002224, Adjusted R-squared:  -0.003112
F-statistic: 0.4167 on 1 and 187 DF,  p-value: 0.5194
```

There is no linear correlation between slope of pH curve after acidification and the number of acidifiction (p=0.519). Thus, it seems to be not possible to forecast the daily pH increasing after acidification.

Is slope different in function to slurries?

ANOVA test with using function **AovSum** from **FactoMineR** package + One-way ANOVA with Pairwise test

```
Ftest
                SS df         MS F value        Pr(>F)
Slurry    0.0032598  8 0.00040748  25.455 0.00000002693 ***
Residuals 0.0002881 18 0.00001601
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 

Ttest
                  Estimate  Std. Error t value Pr(>|t|)
(Intercept)      0.07615220  0.00076999 98.9003  < 2e-16 ***
Slurry - CS_C1  -0.00192792  0.00217786 -0.8852  0.38770
Slurry - CS_C1F  0.01129430  0.00217786  5.1860  0.00006 ***
Slurry - CS_C2  -0.00254726  0.00217786 -1.1696  0.25741
Slurry - CS_O1  -0.01212751  0.00217786 -5.5685  0.00003 ***
Slurry - CS_O2  -0.00425802  0.00217786 -1.9551  0.06628 .
Slurry - PS_C1  -0.02032856  0.00217786 -9.3342  < 2e-16 ***
Slurry - PS_C2   0.00531870  0.00217786  2.4422  0.02515 *
Slurry - PS_C3   0.00781076  0.00217786  3.5864  0.00211 **
Slurry - PS_C3F  0.01676550  0.00217786  7.6982  < 2e-16 ***
```

```
CS_C1 CS_C1F  CS_C2  CS_O1  CS_O2  PS_C1  PS_C2  PS_C3 PS_C3F
 "bd"    "e"   "bd"   "ab"   "bc"    "a"  "cde"   "de"    "e"
```

F-test result shows one of average slope of pH increases has a significantly different. T-test and pairwise test classifys average slope (letters give the increasing order)

Interreg Baltic Sea Region

EUROPEAN UNION
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Baltic Slurry Acidification

www.balticslurry.eu

Summary of the project

Baltic Slurry Acidification is an agro-environmental project funded by the Interreg Baltic Sea Region program in the priority area Natural Resources Focusing on Clear Waters. The aim of the project is to reduce nitrogen loss from animal production by testing, demonstrating and promoting the use of slurry acidification techniques in countries around the Baltic Sea.

Summary of the report

This study looked at the potential to use different acids for slurry acidification and to identify the amount of sulfuric acid required to maintain a slurry pH at 5.5 during storage time.

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Contributing partner

RI. SE