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

Surgörning av flytgödsel: inverkan av gödselegenskaper, användning av olika syror, pH-buffring i gödseln

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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 depends 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 cannot be 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 m³ 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.
Sammanfattning


I experiment 1 jämfördes svavelsyra, salpetersyra och fyra organiska syror med avseende på deras effektivitet samt ekonomi för surgörning av nöt- och svingödsel. I experiment 2 studerades buffersegningskaperna för nio olika flytgödseltyper (fyra från nötkreatur, tre från svin och två filtrerade gödselprover från var och en av dessa djurslag) efter flera surgörningar med svavelsyra till pH 5,5 för att kvantifiera åtgången av syra och genom modellering bestämma vilka egenskaper hos gödseln som påverkar syraåtgången mest. För båda experimenten var lagringstemperaturen 20°C.


I experiment 2 stabiliserades inte pH efter varje återkommande surgörning, kanske på grund av nedbrytning av organiskt material genom sur hydrolys och antagligen också genom aerob nedbrytning av flyktiga fettsyror. Den totala syraåtgången berodde på gödsels egenskaper och varierade mellan 5,97 och 8,06 liter per m³ för nötgödsel och 6,7 till 10,7 för svingödsel. Den bästa modellvariabeln för att förklara den mängd syra som behövs för den första surgörningen var mål-pH. Den totala mängden syra som behövs förklarades av variablerna totalkväve, torrsubstans (TS), kol/kvävekvoten och glödförlust (VS). För den totala mängden syra som efter den första surgörningen behövs för alla påföljande surgörningar var totalkväve, ammoniumkoncentration, totalkol och glödförlust de bästa delmodellvariablerna. Det senare var inte korrelerat med syraåtgången för den första titreringen, även om modellerna har gemensamma variabler. Detta tyder på att gödselns egenskaper förändras av surgörningen.

Sammanfattningsvis var användningen av organiska syror dyrare än användningen av svenska. pH-värdet kan inte stabiliseras genom återkommande surgörningar på grund av nedbrytningen av organiskt material och förändringar av gödselns egenskaper som påverkar syraåtgången.
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 decrease 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 (H₂SO₄) is needed to neutralise 1M of HO⁻-because each molecules of H₂SO₄ 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 (H₃O⁺) or acid hydrogen (H⁺) in a solution. It links with the molarity of acid solution by equivalence factor of each acid.

\[ N = \frac{\text{Concentration of acid solution}}{\text{equivalence factor}} \]

**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/m³).
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$_4^+$ 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

<table>
<thead>
<tr>
<th></th>
<th>Sulfuric acid</th>
<th>Acetic acid</th>
<th>Lactic acid</th>
<th>Oxalic acid</th>
<th>Formic acid</th>
<th>Nitric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>H2SO4</td>
<td>CH3COOH</td>
<td>CH3CH(OH)COOH</td>
<td>HOOCOOH</td>
<td>HCOOH</td>
<td>HNO3</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>98.08</td>
<td>60.05</td>
<td>90.08</td>
<td>126.065</td>
<td>46.03</td>
<td>63.01</td>
</tr>
<tr>
<td>Density</td>
<td>1.84</td>
<td>1.05</td>
<td>1.2</td>
<td>1.65</td>
<td>1.22</td>
<td>1.41</td>
</tr>
<tr>
<td>Normality for 1M solution of acid</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>pKa value</td>
<td>1.99</td>
<td>4.76</td>
<td>3.86</td>
<td>1.25 / 4.14</td>
<td>3.77</td>
<td>-1.4</td>
</tr>
<tr>
<td>% Strength of conc. acids</td>
<td>96</td>
<td>99.7</td>
<td>80</td>
<td>99.6</td>
<td>78</td>
<td>16</td>
</tr>
<tr>
<td>Price(SEK/L)²</td>
<td>1.53</td>
<td>7.14</td>
<td>4.58</td>
<td>9.39</td>
<td>7.79</td>
<td>3.9</td>
</tr>
</tbody>
</table>

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

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

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

<table>
<thead>
<tr>
<th>Treatment name</th>
<th>Slurry type</th>
<th>Filtered or not filtered slurry</th>
<th>Conventional or organic farm</th>
<th>Acid used</th>
<th>Target pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS_C1</td>
<td>Cattle slurry</td>
<td>Not filtered</td>
<td>Conventional</td>
<td>Sulfuric acid</td>
<td>5.5</td>
</tr>
<tr>
<td>CS_C2</td>
<td>Cattle slurry</td>
<td>Not filtered</td>
<td>Conventional</td>
<td>Sulfuric acid</td>
<td>5.5</td>
</tr>
<tr>
<td>CS_O1</td>
<td>Cattle slurry</td>
<td>Not filtered</td>
<td>Organic</td>
<td>Sulfuric acid</td>
<td>5.5</td>
</tr>
<tr>
<td>CS_O2</td>
<td>Cattle slurry</td>
<td>Not filtered</td>
<td>Organic</td>
<td>Sulfuric acid</td>
<td>5.5</td>
</tr>
<tr>
<td>PS_C1</td>
<td>Pig slurry</td>
<td>Not filtered</td>
<td>Conventional</td>
<td>Sulfuric acid</td>
<td>5.5</td>
</tr>
<tr>
<td>PS_C2</td>
<td>Pig slurry</td>
<td>Not filtered</td>
<td>Conventional</td>
<td>Sulfuric acid</td>
<td>5.5</td>
</tr>
<tr>
<td>PS_C3</td>
<td>Pig slurry</td>
<td>Not filtered</td>
<td>Conventional</td>
<td>Sulfuric acid</td>
<td>5.5</td>
</tr>
<tr>
<td>CS_C2 F</td>
<td>Cattle slurry</td>
<td>Filtered</td>
<td>Conventional</td>
<td>Sulfuric acid</td>
<td>5.5</td>
</tr>
<tr>
<td>PS_C3 F</td>
<td>Pig slurry</td>
<td>Filtered</td>
<td>Conventional</td>
<td>Sulfuric acid</td>
<td>5.5</td>
</tr>
</tbody>
</table>

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, determined 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 (NH₄-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)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Slurry types</th>
<th>TS %</th>
<th>TN Kg/T</th>
<th>NH₄-N Kg/T</th>
<th>ON Kg/T</th>
<th>TP Kg/T</th>
<th>K Kg/T</th>
<th>S Kg/T</th>
<th>Ca Kg/T</th>
<th>Mg Kg/T</th>
<th>Na Kg/T</th>
<th>TC Kg/T</th>
<th>C/N</th>
<th>VS %</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 CS</td>
<td>Cattle</td>
<td>10.4</td>
<td>4.7</td>
<td>2.1</td>
<td>2.6</td>
<td>0.78</td>
<td>4.30</td>
<td>0.59</td>
<td>1.91</td>
<td>0.65</td>
<td>0.18</td>
<td>47.3</td>
<td>10.0</td>
<td>8.4</td>
<td>7.29</td>
</tr>
<tr>
<td>1 PS</td>
<td>Pig</td>
<td>9.0</td>
<td>4.6</td>
<td>2.2</td>
<td>2.4</td>
<td>0.72</td>
<td>1.91</td>
<td>0.45</td>
<td>2.64</td>
<td>0.69</td>
<td>1.25</td>
<td>39.6</td>
<td>8.6</td>
<td>7.3</td>
<td>6.65</td>
</tr>
<tr>
<td>2 CS_C1</td>
<td>Cattle</td>
<td>8.8</td>
<td>3.8</td>
<td>1.5</td>
<td>2.4</td>
<td>0.44</td>
<td>4.34</td>
<td>0.40</td>
<td>1.47</td>
<td>0.52</td>
<td>0.69</td>
<td>39.8</td>
<td>10.3</td>
<td>7.1</td>
<td>7.37</td>
</tr>
<tr>
<td>2 CS_C2</td>
<td>Cattle</td>
<td>9.3</td>
<td>4.2</td>
<td>1.9</td>
<td>2.3</td>
<td>0.57</td>
<td>3.99</td>
<td>0.49</td>
<td>1.89</td>
<td>0.55</td>
<td>0.15</td>
<td>41.9</td>
<td>10.0</td>
<td>7.5</td>
<td>7.20</td>
</tr>
<tr>
<td>2 CS_O1</td>
<td>Cattle</td>
<td>9.4</td>
<td>4.2</td>
<td>1.8</td>
<td>2.4</td>
<td>0.51</td>
<td>3.66</td>
<td>0.32</td>
<td>1.60</td>
<td>0.57</td>
<td>0.19</td>
<td>42.7</td>
<td>10.2</td>
<td>7.7</td>
<td>6.88</td>
</tr>
<tr>
<td>2 CS_O2</td>
<td>Cattle</td>
<td>8.9</td>
<td>4.5</td>
<td>2.3</td>
<td>2.3</td>
<td>0.49</td>
<td>3.97</td>
<td>0.42</td>
<td>3.91</td>
<td>0.74</td>
<td>0.89</td>
<td>39.2</td>
<td>8.70</td>
<td>7.1</td>
<td>7.71</td>
</tr>
<tr>
<td>2 PS_C1</td>
<td>Pig</td>
<td>13.3</td>
<td>5.7</td>
<td>2.5</td>
<td>3.2</td>
<td>0.98</td>
<td>2.23</td>
<td>0.47</td>
<td>3.28</td>
<td>0.78</td>
<td>1.35</td>
<td>59.1</td>
<td>10.4</td>
<td>11.0</td>
<td>6.53</td>
</tr>
<tr>
<td>2 PS_C2</td>
<td>Pig</td>
<td>9.5</td>
<td>6.0</td>
<td>3.3</td>
<td>2.7</td>
<td>1.08</td>
<td>1.96</td>
<td>0.52</td>
<td>2.79</td>
<td>1.35</td>
<td>1.10</td>
<td>42.1</td>
<td>7.0</td>
<td>7.7</td>
<td>7.03</td>
</tr>
<tr>
<td>2 PS_C3</td>
<td>Pig</td>
<td>9.9</td>
<td>6.5</td>
<td>3.9</td>
<td>2.4</td>
<td>1.11</td>
<td>2.53</td>
<td>0.57</td>
<td>2.37</td>
<td>0.72</td>
<td>1.40</td>
<td>42.8</td>
<td>8.50</td>
<td>7.4</td>
<td>7.00</td>
</tr>
<tr>
<td>2 CS_C2 F</td>
<td>Cattle liquid fraction</td>
<td>5.82</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 PS_C3 F</td>
<td>Pig liquid fraction</td>
<td>5.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

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 blu 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 m³ of slurry for easier comparison of the efficiency of different acids. Efficiency of acids was determined by the index
equivalent needed/m³ of slurry to reduce the pH to 6.4 and 6 respectively. A small index refers to an efficient acid.

\[
\text{Eq m}^3 \text{ of slurry} = \frac{\text{Volume of acid added (l)}}{\text{Sample volume (0.2 l) \times Normality of the acid solution (Eq/l)}} \times 1000 \text{ (l/m}^3)\]

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 experiment 1, 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:

\[
Y_i = \beta_0 + \beta_1 \times TS_{ij} + \beta_2 \times Tot-N_{ij} + \beta_3 \times NH4-N_{ij} + \beta_4 \times C/N_{ij} + \beta_5 \times TotC_{ij} + \beta_6 \times VS_{ij} + \beta_7 \times InitialpH_{ij} + \varepsilon_i
\]

\[Y_i = \text{Responses variables for the slurry } i\]

\[\beta_0, \ldots, \beta_7 = \text{Unknown model parameters which were estimated}\]

\[TS_{ij}, \ldots, InitialpH_{ij} = \text{Explanatory variables for slurry } i, \text{ replicate } j\]

\[\varepsilon_i = \text{the residual}\]

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 ≥ Oxalic acid for cattle slurry. To reduce the pH to 6.0, the rank was: Lactic acid > sulfuric acid = formic acid = Nitric 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.

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Sulfuric acid</th>
<th>Acetic acid</th>
<th>Lactic acid</th>
<th>Oxalic acid</th>
<th>Formic acid</th>
<th>Nitric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of acid used</td>
<td>Pig</td>
<td>6.4</td>
<td>17.8 (a)</td>
<td>17.6 (a)</td>
<td>15.5 (a)</td>
<td>19.2 (a)</td>
<td>20.4 (a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.0</td>
<td>58.8 (b)</td>
<td>56.7 (b)</td>
<td>48.6 (a)</td>
<td>91.7 (c)</td>
<td>58.3 (b)</td>
</tr>
<tr>
<td></td>
<td>Cattle</td>
<td>6.4</td>
<td>86 (ab)</td>
<td>89.8 (b)</td>
<td>78.8 (a)</td>
<td>119.5 (c)</td>
<td>87.1 (ab)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>129.2 (a)</td>
<td>139.2 (a)</td>
<td>124 (a)</td>
<td>160.3 (c)</td>
<td>128.3 (a)</td>
</tr>
<tr>
<td>Amount of conc. acid needed</td>
<td>Pig</td>
<td>6.4</td>
<td>0.5 (a)</td>
<td>1.0 (b)</td>
<td>1.5 (c)</td>
<td>0.7 (ab)</td>
<td>1.0 (b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>1.6 (a)</td>
<td>3.3 (b)</td>
<td>4.6 (c)</td>
<td>3.5 (b)</td>
<td>2.8 (b)</td>
</tr>
<tr>
<td></td>
<td>Cattle</td>
<td>6.4</td>
<td>2.4 (a)</td>
<td>5.2 (c)</td>
<td>7.4 (d)</td>
<td>4.6 (b)</td>
<td>4.2 (b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>3.6 (a)</td>
<td>7.9 (c)</td>
<td>11.6 (d)</td>
<td>6.1 (b)</td>
<td>6.2 (b)</td>
</tr>
<tr>
<td>Acidification cost</td>
<td>Pig</td>
<td>6.4</td>
<td>0.8 (a)</td>
<td>7.2 (b)</td>
<td>6.7 (b)</td>
<td>6.9 (b)</td>
<td>7.5 (b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>2.5 (a)</td>
<td>23.2 (b)</td>
<td>20.9 (b)</td>
<td>33.0 (c)</td>
<td>22.0 (b)</td>
</tr>
<tr>
<td></td>
<td>Cattle</td>
<td>6.4</td>
<td>3.7 (a)</td>
<td>36.8 (c)</td>
<td>33.9 (bc)</td>
<td>43.1 (d)</td>
<td>32.8 (b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>5.5 (a)</td>
<td>57.0 (c)</td>
<td>53.3 (bc)</td>
<td>57.8 (c)</td>
<td>48.3 (b)</td>
</tr>
</tbody>
</table>

*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 at 5.5 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.

<table>
<thead>
<tr>
<th>Yi</th>
<th>β0</th>
<th>β1</th>
<th>β2</th>
<th>β3</th>
<th>β4</th>
<th>β5</th>
<th>β6</th>
<th>β7</th>
<th>Multiple R-square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity of acid used</td>
<td>-29.663</td>
<td>2.144</td>
<td>3.257</td>
<td>1.613</td>
<td>-0.228</td>
<td>-2.956</td>
<td>1.871</td>
<td>0.9924</td>
<td></td>
</tr>
<tr>
<td>the pH to 6.4 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quantity of acid used</td>
<td>-39.042</td>
<td>4.230</td>
<td>3.689</td>
<td>1.671</td>
<td>2.581</td>
<td>-0.580</td>
<td>-4.231</td>
<td>1.999</td>
<td>0.9955</td>
</tr>
<tr>
<td>the pH to 6.0 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quantity of acid used</td>
<td>-0.163</td>
<td>7.567</td>
<td>1.109</td>
<td></td>
<td></td>
<td>-9.431</td>
<td></td>
<td>0.9885</td>
<td></td>
</tr>
<tr>
<td>the pH to 5.5 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total amount of acid used</td>
<td>-30.031</td>
<td>8.084</td>
<td>7.042</td>
<td>2.729</td>
<td></td>
<td></td>
<td>-12.619</td>
<td>0.9887</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Total amount of acid used</td>
<td>-11.470</td>
<td>6.483</td>
<td>-5.579</td>
<td>1.604</td>
<td></td>
<td>-9.272</td>
<td></td>
<td>0.9875</td>
<td></td>
</tr>
<tr>
<td>after the first acidification 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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:
\[
\text{ACID}_{\text{Total Quantity}} = -30.031 + 8.084 \times \text{TS} + 7.042 \times \text{Tot-N} + 2.729 \times \text{C/N} + -12.619 \times \text{VS} \quad (R^2=0.9887)
\]

The best submodel for amount of acid used to decrease pH to 5.5 was:
\[
\text{ACID}_{\text{First acidification}} = -0.163 + 7.567 \times \text{TS} + 1.109 \times \text{Tot-N} + -9.431 \times \text{VS} \\
(R^2=0.9885)
\]

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.

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

<table>
<thead>
<tr>
<th>Slurry</th>
<th>CS_C1</th>
<th>CS_C2</th>
<th>CS_O1</th>
<th>CS_O2</th>
<th>PS_C1</th>
<th>PS_C2</th>
<th>PS_C3</th>
<th>CS_C1F</th>
<th>PS_C3F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>0.074</td>
<td>0.074</td>
<td>0.064</td>
<td>0.072</td>
<td>0.056</td>
<td>0.081</td>
<td>0.084</td>
<td>0.087</td>
<td>0.093</td>
</tr>
<tr>
<td>(n=3)</td>
<td>(bd)</td>
<td>(bd)</td>
<td>(ab)</td>
<td>(bc)</td>
<td>(a)</td>
<td>(cde)</td>
<td>(df)</td>
<td>(ef)</td>
<td>(f)</td>
</tr>
</tbody>
</table>
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 (Sindhøj 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 / m³ 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.

References

Misselbrook, T., Hunt, J., Perazzolo, F., Provolo, G., 2016. Greenhouse Gas and Ammonia Emissions from Slurry Storage: Impacts of Temperature and Potential Mitigation through Covering (Pig Slurry) or Acidification (Cattle Slurry)


SEGES, 2014. Status, economy and consideration by acidification of slurry. Danish Farmers Advisory Service. Translate by Erik Sindhöj


## 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.

<table>
<thead>
<tr>
<th></th>
<th>Cattle slurry</th>
<th>Pig slurry</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>To reach pH 6.4</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-test</td>
<td>25 df</td>
<td>MS F value</td>
</tr>
<tr>
<td>Residuals</td>
<td>150.77</td>
<td>12</td>
</tr>
<tr>
<td>Sig. codes:</td>
<td>0.001</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>To reach pH 6.0</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-test</td>
<td>55 df</td>
<td>MS F value</td>
</tr>
<tr>
<td>Residuals</td>
<td>462.53</td>
<td>12</td>
</tr>
<tr>
<td>Sig. codes:</td>
<td>0.001</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>To reach pH 6.4</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-test</td>
<td>25 df</td>
<td>MS F value</td>
</tr>
<tr>
<td>Residuals</td>
<td>150.77</td>
<td>12</td>
</tr>
<tr>
<td>Sig. codes:</td>
<td>0.001</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>To reach pH 6.0</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-test</td>
<td>55 df</td>
<td>MS F value</td>
</tr>
<tr>
<td>Residuals</td>
<td>462.53</td>
<td>12</td>
</tr>
<tr>
<td>Sig. codes:</td>
<td>0.001</td>
<td>0.01</td>
</tr>
</tbody>
</table>

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

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

*F*-test result shows one of acids has a significantly different efficiency. T-test and pairwise test classifies 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

<table>
<thead>
<tr>
<th></th>
<th>To reach pH 6.4</th>
<th>To reach pH 6.0</th>
<th>Pig slurry</th>
<th>To reach pH 6.4</th>
<th>To reach pH 6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Test</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SS df</td>
<td>MS F value</td>
<td>Pr(&gt;F)</td>
<td>SS df</td>
<td>MS F value</td>
</tr>
<tr>
<td>Slurry</td>
<td>-10.00</td>
<td>314.00</td>
<td>0.0000</td>
<td>-12.00</td>
<td>314.00</td>
</tr>
<tr>
<td>Residuals</td>
<td>3.30</td>
<td>0.0010</td>
<td>0.30</td>
<td>3.30</td>
<td>0.0010</td>
</tr>
<tr>
<td>Sig. codes:</td>
<td>0 ****</td>
<td>0.001 ***</td>
<td>0.01 **</td>
<td>0.05 *</td>
<td>0.1</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Cattle slurry</th>
<th>To reach pH 6.4</th>
<th>To reach pH 6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>SS df</td>
<td>MS F value</td>
</tr>
<tr>
<td>Slurry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residuals</td>
<td>23.3  12.1  1.95</td>
<td></td>
</tr>
<tr>
<td>Signif. codes</td>
<td>0.0001 0.001 0.01 0.05 '0.1 0.1</td>
<td></td>
</tr>
<tr>
<td>Test</td>
<td>Estimate Std. Error t value Pr(&gt;</td>
<td>t</td>
</tr>
<tr>
<td>(Intercept)</td>
<td>42.38132 0.26741 122.5020 &lt; 2e-16 ***</td>
<td>63.72466 0.84502 72.1421 &lt; 2e-16 ***</td>
</tr>
<tr>
<td>Slurry - CA</td>
<td>3.50971 0.78506 4.77484 0.02948</td>
<td>Slurry - CL</td>
</tr>
<tr>
<td>Slurry - CS</td>
<td>-7.29357 0.73506 -9.9302 &lt; 2e-16 ***</td>
<td>Slurry - CE</td>
</tr>
<tr>
<td>Slurry - CL</td>
<td>-8.45802 0.75506 -11.5542 &lt; 2e-16 ***</td>
<td>Slurry - CR</td>
</tr>
<tr>
<td>Slurry - CS</td>
<td>50.24285 0.75506 66.5552 &lt; 2e-16 ***</td>
<td>Slurry - CS</td>
</tr>
<tr>
<td>Slurry - CS</td>
<td>0.49430 0.73506 0.65484 0.36340</td>
<td>Slurry - CE</td>
</tr>
<tr>
<td>Slurry - CS</td>
<td>-36.69940 0.73506 -46.5256 &lt; 2e-16 ***</td>
<td>Slurry - CS</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pig slurry</th>
<th>To reach pH 6.4</th>
<th>To reach pH 6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>SS df</td>
<td>MS F value</td>
</tr>
<tr>
<td>Slurry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residuals</td>
<td>31.4  12.1  2.42</td>
<td></td>
</tr>
<tr>
<td>Signif. codes</td>
<td>0.0001 0.001 0.01 0.05 '0.1 0.1</td>
<td></td>
</tr>
<tr>
<td>Test</td>
<td>Estimate Std. Error t value Pr(&gt;</td>
<td>t</td>
</tr>
<tr>
<td>(Intercept)</td>
<td>30.74971 0.36156 84.6543 &lt; 2e-16 ***</td>
<td>30.74971 0.36156 84.6543 &lt; 2e-16 ***</td>
</tr>
<tr>
<td>Slurry - PA</td>
<td>0.47808 0.36156 0.78319 0.46154</td>
<td>Slurry - PA</td>
</tr>
<tr>
<td>Slurry - PS</td>
<td>-1.76984 0.36156 -5.0124 0.00012 ***</td>
<td>Slurry - PS</td>
</tr>
<tr>
<td>Slurry - PL</td>
<td>-7.30435 0.36156 -19.7372 0.00003 ***</td>
<td>Slurry - PL</td>
</tr>
<tr>
<td>Slurry - PO</td>
<td>4.73218 0.36156 13.1932 0.00002 ***</td>
<td>Slurry - PO</td>
</tr>
</tbody>
</table>

Yes, significantly different. p<0.05 for each case. At least one of these treatments is significantly different. Pairwise test shows that acidification 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

<table>
<thead>
<tr>
<th></th>
<th>To reach pH 6.4</th>
<th>To reach pH 6.0</th>
<th>To reach pH 5.5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Test</strong></td>
<td><strong>SS df MS F value Pr(&gt;F)</strong></td>
<td><strong>SS df MS F value Pr(&gt;F)</strong></td>
<td><strong>SS df MS F value Pr(&gt;F)</strong></td>
</tr>
<tr>
<td>Type.of.slurry</td>
<td>2.0563 1 2.0563 1.9420 0.09094</td>
<td>2.1876 1 2.1876 1.2068 0.18077</td>
<td>0.7366 1 0.7366 0.18077 0.4642</td>
</tr>
<tr>
<td>Residuals</td>
<td>18.5924 19 0.87599</td>
<td>18.5924 19 0.87599</td>
<td>24.7331 19 1.30204</td>
</tr>
<tr>
<td><strong>Signif. codes:</strong></td>
<td>0 '<em><strong>' 0.001 '</strong></em>' 0.01 '**' 0.05 '*' 0.1 ' ' 1</td>
<td>0 '<em><strong>' 0.001 '</strong></em>' 0.01 '**' 0.05 '*' 0.1 ' ' 1</td>
<td>0 '<em><strong>' 0.001 '</strong></em>' 0.01 '**' 0.05 '*' 0.1 ' ' 1</td>
</tr>
</tbody>
</table>

| **Test**               | **Estimate Std. Error t value Pr(>|t|)** | **Estimate Std. Error t value Pr(>|t|)** | **Estimate Std. Error t value Pr(>|t|)** |
|------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| (Intercept)            | 1.80122 0.18400 9.7955 < 2e-16 ***     | 1.80122 0.18400 9.7955 < 2e-16 ***     | 1.80122 0.18400 9.7955 < 2e-16 ***     |
| Type.of.slurry - dairy cattle slurry | -0.36611 0.16000 2.3002 0.09353 . | -0.36611 0.16000 2.3002 0.09353 . | -0.36611 0.16000 2.3002 0.09353 . |
| Type.of.slurry - pig slurry     | -0.34561 0.16000 -0.0002 0.00088 . | -0.34561 0.16000 -0.0002 0.00088 . | -0.34561 0.16000 -0.0002 0.00088 . |

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

```r
> AovSum(Total.amount.of.acid.used ~ Type.of.slurry, data=Dataset)
F-test
                      SS  df     MS      F value    Pr(>F)
Type.of.slurry        6.215  1   6.2153   3.1175  0.09352 .
Residuals              87.880 19  4.6737
---
Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

T-test
                   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

<table>
<thead>
<tr>
<th>F-test</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F value</th>
<th>Pr(&gt;F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry</td>
<td>44.545</td>
<td>8</td>
<td>5.681</td>
<td>284.36</td>
<td>&lt; 2.2e-16 ***</td>
</tr>
<tr>
<td>Residuals</td>
<td>0.352</td>
<td>18</td>
<td>0.0196</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1

| T-test       | 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 | 0.40593  | 0.07617    | 6.3795   | 0.00001 ***|
| Slurry - CS.O1 | -1.59607 | 0.07617    | -20.9542 | < 2e-16 ***|
| Slurry - CS.C2 | 0.36459  | 0.07617    | 4.7866   | 0.00015 ***|
| Slurry - CS.C1 | -0.87007 | 0.07617    | -11.4228 | < 2e-16 ***|
| Slurry - CS.C2 | 3.16459  | 0.07617    | 41.5466  | < 2e-16 ***|
| Slurry - CS.C3 | -0.24874 | 0.07617    | -3.2656  | 0.00430 **  |
| Slurry - PS.C3 | 0.10659  | 0.07617    | 1.3994   | 0.17869    |

F-test result shows at least one of slurry has a consumption of sulfuric acid significantly different. T-test and pairwise test classify 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

| Test   | SS df | MS F value | Pr(>|F|) |
|--------|-------|-------------|---------|
| Filtration | 0.39694 | 1 | 0.39694 | 2.0821 0.1016 |
| Residuals  | 1.78660 | 10 | 0.17866 |

To reach pH 6.4

- Signif. codes: 0 **** 0.001 *** 0.01 ** 0.05 * 0.1 ' 1

To reach pH 6.0

- Signif. codes: 0 **** 0.001 *** 0.01 ** 0.05 * 0.1 ' 1

To reach pH 5.5

- 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 separation 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/m³ of slurry). This test was done without separation of slurry types (pig and cattle slurry).
### Models – RegBest function from FactoMineR package

<table>
<thead>
<tr>
<th>Models</th>
<th>Quantity of acid to reduce the pH to 6.4</th>
<th>Quantity of acid to reduce the pH to 6.0</th>
<th>Quantity of acid to reduce the pH to 5.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residuals:</td>
<td>Min</td>
<td>IQ</td>
<td>Median</td>
</tr>
<tr>
<td></td>
<td>-0.179223</td>
<td>-0.035806</td>
<td>-0.007311</td>
</tr>
<tr>
<td>Coefficients:</td>
<td>Estimate</td>
<td>Std. Error</td>
<td>t value</td>
</tr>
<tr>
<td>(Intercept)</td>
<td>-39.04217</td>
<td>2.15881</td>
<td>-18.271</td>
</tr>
<tr>
<td>TS</td>
<td>4.22583</td>
<td>0.35520</td>
<td>12.010</td>
</tr>
<tr>
<td>Tot-N</td>
<td>3.99923</td>
<td>0.20655</td>
<td>19.036</td>
</tr>
<tr>
<td>H4-N</td>
<td>1.67377</td>
<td>0.21202</td>
<td>7.807</td>
</tr>
<tr>
<td>Tot-C</td>
<td>-3.57952</td>
<td>0.07904</td>
<td>-4.532</td>
</tr>
<tr>
<td>C-N</td>
<td>2.58084</td>
<td>0.24956</td>
<td>10.469</td>
</tr>
<tr>
<td>VS</td>
<td>-4.23858</td>
<td>0.16070</td>
<td>-26.317</td>
</tr>
<tr>
<td>Initial pH</td>
<td>1.99885</td>
<td>0.07690</td>
<td>26.885</td>
</tr>
<tr>
<td>Signif. codes:</td>
<td>0 '**<em><em>' 0.001 '</em>' 0.01 '</em>' 0.05 '.' 0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Residual standard error: | 0.07961 on 19 degrees of freedom Multiple R-squared: 0.9986, Adjusted R-squared: 0.9985 F-statistic: 49.1 on 8 and 10 DF, p-value: <2e-16

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

<table>
<thead>
<tr>
<th>Models</th>
<th>Total amount of acid used</th>
<th>Total amount of acid used after the first acidification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residuals:</td>
<td>Min</td>
<td>IQ</td>
</tr>
<tr>
<td></td>
<td>-0.1484</td>
<td>-0.06550</td>
</tr>
<tr>
<td>Coefficients:</td>
<td>Estimate</td>
<td>Std. Error</td>
</tr>
<tr>
<td>(Intercept)</td>
<td>-11.4697</td>
<td>0.7036</td>
</tr>
<tr>
<td>Tot-N</td>
<td>6.4229</td>
<td>0.3603</td>
</tr>
<tr>
<td>NH4-N</td>
<td>-5.5789</td>
<td>0.5753</td>
</tr>
<tr>
<td>Tot-C</td>
<td>1.6036</td>
<td>0.1001</td>
</tr>
<tr>
<td>VS</td>
<td>-9.2716</td>
<td>0.5678</td>
</tr>
<tr>
<td>Signif. codes:</td>
<td>0 '**<em><em>' 0.001 '</em>' 0.01 '</em>' 0.05 '.' 0.1</td>
<td></td>
</tr>
</tbody>
</table>
| Residual standard error: | 0.1063 on 18 degrees of freedom Multiple R-squared: 0.9975, Adjusted R-squared: 0.9944 F-statistic: 315.1 on 4 and 16 DF, p-value: 5.329e-15

**Best submodel variables:** TS, Tot-N, NH4-N, Tot-C, C-N, VS
### Linear regression

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

**Coefficients:**

|                          | Estimate | Std. Error | t value | Pr(>|t|) |
|--------------------------|----------|------------|---------|---------|
| (Intercept)              | 3.8308   | 0.8978     | 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: 0.002185 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

<table>
<thead>
<tr>
<th></th>
<th>Cattle slurry</th>
<th>Pig slurry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ftest</td>
<td>Ftest</td>
</tr>
<tr>
<td>acid</td>
<td>SS 25.021, df 6, MS 4.1702, F value 1616.737, Pr(&gt;F) &lt; 2.2e-16 ***</td>
<td>acid SS 3.3485, df 6, MS 0.55808, F value 265.812, Pr(&gt;F) &lt; 2.2e-16 ***</td>
</tr>
<tr>
<td>day</td>
<td>SS 38.960, df 10, MS 3.8960, F value 1510.435, Pr(&gt;F) &lt; 2.2e-16 ***</td>
<td>day SS 15.5440, df 10, MS 1.55440, F value 740.357, Pr(&gt;F) &lt; 2.2e-16 ***</td>
</tr>
<tr>
<td>acid:day</td>
<td>SS 12.309, df 60, MS 0.2052, F value 79.536, Pr(&gt;F) &lt; 2.2e-16 ***</td>
<td>acid:day SS 3.7436, df 60, MS 0.06239, F value 29.718, Pr(&gt;F) &lt; 2.2e-16 ***</td>
</tr>
<tr>
<td>Residuals</td>
<td>SS 0.273, df 106, MS 0.0026</td>
<td>Residuals SS 0.2226, df 106, MS 0.00210</td>
</tr>
</tbody>
</table>

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

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

Residuals:

<table>
<thead>
<tr>
<th>Min</th>
<th>1Q</th>
<th>Median</th>
<th>3Q</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.053504</td>
<td>-0.011164</td>
<td>-0.000824</td>
<td>0.012176</td>
<td>0.052877</td>
</tr>
</tbody>
</table>

Coefficients:

| Estimate | Std. Error | t value | Pr(>|t|) |
|----------|------------|---------|---------|
| (Intercept) | 0.0733441 | 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 acidification (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

<table>
<thead>
<tr>
<th>Test</th>
<th>SS df</th>
<th>MS F value</th>
<th>Pr(&gt;F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slurry</td>
<td>0.0032699</td>
<td>8 0.00040798</td>
<td>29.666 0.0000002683 ***</td>
</tr>
<tr>
<td>Residuals</td>
<td>0.0002381</td>
<td>18 0.0001601</td>
<td></td>
</tr>
</tbody>
</table>

Signif. codes:  0 '****' 0.001 ***' 0.01 **' 0.05 '*' 0.1 '

T-test

| Test        | Estimate | Std. Error | t value | Pr(>|t|) |
|-------------|----------|------------|---------|---------|
| (Intercept) | 0.0761522 | 0.00766998 | 98.9065 < 2e-16 *** |
| Slurry - CS_C1 | -0.00129792 | 0.00217766 | -0.6006 0.553583 *** |
| Slurry - CS_C2 | -0.00129490 | 0.00217766 | -0.6006 0.553583 *** |
| Slurry - CS_C2F | -0.00264726 | 0.00217766 | -1.1666 0.25761 |
| Slurry - CS_C3 | -0.01212751 | 0.00217766 | -5.6505 0.000003 *** |
| Slurry - CS_C5 | -0.00026866 | 0.00217766 | -0.4886 0.62767 |
| Slurry - PS_C1 | -0.02022866 | 0.00217766 | -9.3342 < 2e-16 *** |
| Slurry - PS_C2 | 0.00810874 | 0.00217766 | 3.7844 0.000011 ** |
| Slurry - PS_C3 | 0.00781076 | 0.00217766 | 3.8644 0.000029 ** |
| Slurry - PS_C3F | 0.01676500 | 0.00217766 | 7.6662 < 2e-16 *** |

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

Contributing partner

RISE