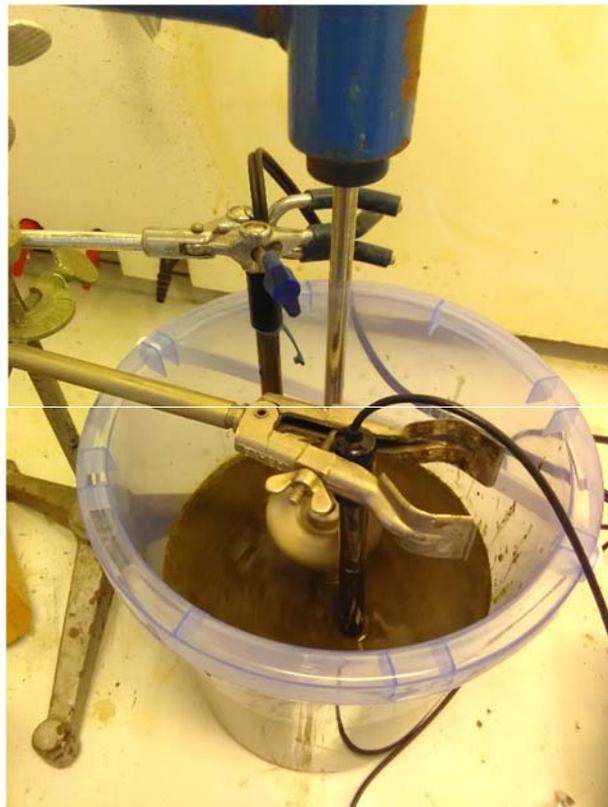


# Practical strategies for acidification of animal slurry in storage

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Master's Thesis in Soil Science  
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# Practical strategies for acidification of animal slurry in storage

Praktiska strategier för surgörning av flytgödsel i lager

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## Abstract

Animal slurry is a source of  $\text{NH}_3$  emissions which results in loss of N and decrease the nutritive value of slurry. Slurry stores in Sweden represents approximately 30% of total  $\text{NH}_3$  emissions from agricultural activities in the country. Slurry acidification is a method that effectively mitigates  $\text{NH}_3$  emissions by reducing the pH level of slurry and is done most commonly with sulphuric acid. However, slurry can negate pH reduction with its buffer capacity and increase pH after acidification. In this study, different acidification strategies were simulated in laboratory scale. Consumption of acid and foaming was compared between strategies to identify an efficient and practical method to reduce and maintain pH of slurry at 5.5 in storage. The purpose of this study was to discover a practical procedure for farmers in Sweden to implement acidification of slurry in storage to control  $\text{NH}_3$  emissions and save N during storage. The following hypotheses were tested in this study: i) Acid consumption will be greater when addition is more frequent, ii) pH will stabilize after several re-acidifications, iii) pH will stabilize faster when addition of acid is more frequent and iv) Frequent acid additions will reduce foaming and save storage capacity.

Three strategies were conducted to acidify dairy and pig slurry with sulphuric acid at 20°C. In Strategy 1, daily acidification of slurry was performed in the pump pit five days per week for two weeks, then slurry was transferred to storage where pH and temperature were measured for twelve weeks. In Strategy 2, acidification of slurry was performed after the pump pit was full, just before it was transferred to storage. These steps were repeated every week for 15 weeks and during the last week, acidification was performed in storage. In Strategy 3, acidification of slurry was performed in storage and then re-acidification was performed every week if pH had elevated back to 6.0. The results of this experiment showed that Strategy 2 required least amount of acid compared to Strategy 1 and 3, except between Strategy 1 and 2 for dairy slurry, when two weeks had passed. However, the pH in storage was higher in Strategy 2. No significant difference in acid consumption occurred between Strategy 1 and 3 during the first two weeks, even if acid was added to slurry more frequently in Strategy 1. The pH level didn't stabilize at 5.5 in any of the strategies. Foam production was much less in Strategy 1 compared to Strategy 2 and 3.

The consumption of acid was not influenced by having a more frequent acid addition to slurry and pH did not stabilize by several re-acidifications or frequent acid additions. However, frequent acid additions did minimize the foam production. This means that Strategy 1 was the most practical acidification method compared to Strategy 2 and 3.

*Keywords:* Buffer capacity, foam,  $\text{NH}_3$  emission, pH evolution, sulphuric acid

## Sammanfattning

Flytgödsel är en källa för utsläpp av  $\text{NH}_3$  som resulterar i förlust av N och reducerar näringsvärdet hos flytgödsel. Flytgödselbrunnar i Sverige representerar ungefär 30% av de totala utsläppen av  $\text{NH}_3$  från jordbruksaktiviteter i landet. Surgörning av flytgödsel är en metod som effektivt begränsar utsläpp av  $\text{NH}_3$  genom att sänka pH-värdet i flytgödsel och utförs vanligtvis med svavelsyra. Flytgödsel kan dock förhindra pH-sänkning tack vare sin buffringskapacitet och höja tillbaka pH-värdet efter surgörning. I denna studie simulerades olika surgörningsstrategier i laboratorieskala. Åtgång av syra och grad av skumning jämfördes mellan strategier för att identifiera en effektiv och praktisk metod för att reducera och bevara flytgödselns pH vid 5,5 i lagringsbrunnen. Syftet med denna studie var att hitta ett tillvägagångssätt för lantbrukare i Sverige att implementera surgörning av flytgödsel i lagringsbrunnen för att kontrollera utsläpp av  $\text{NH}_3$  och spara N under lagring. Följande hypoteser testades i denna studie: i) Åtgång av syra blir större när tillsättningen är mer frekvent. ii) pH stabiliseras efter flera upprepade surgörningar. iii) pH stabiliseras snabbare när tillsättningen av syra är mer frekvent. iv) Frekvent tillsättning av syra minskar skumning och sparar lagringskapacitet.

Tre strategier testades för att försura nöt- och svinflytgödsel med svavelsyra vid 20°C. I Strategi 1 försurades flytgödsel dagligen i pumpbrunnen fem dagar i veckan under två veckor, efteråt överfördes flytgödseln till lagringsbrunnen varpå pH och temperatur mättes under tolv veckor. I Strategi 2 försurades flytgödsel efter pumpbrunnen var fylld, precis innan det fördes till lagringsbrunnen. Dessa steg repeterades varje vecka under 15 veckor och under den sista veckan utfördes en surgörning i lagringsbrunnen. I Strategi 3 försurades flytgödsel i lagringsbrunnen och därefter utfördes upprepade surgörningar varje vecka om pH steg tillbaka till 6,0. Resultaten av experimentet visade att Strategi 2 krävde minst mängd syra jämfört med Strategi 1 och 3, förutom mellan Strategi 1 och 2 för nötflytgödsel efter två veckor passerat. Dock var pH i lagringsbrunnen högre i Strategi 2. Ingen signifikant skillnad i syraåtgång förekom mellan Strategi 1 och 3 under de två första veckorna, även om syra tillsattes flytgödseln mer frekvent i Strategi 1. pH nivån stabiliserades inte vid 5,5 i någon av strategierna. Skumproduktionen var mycket mindre i Strategi 1 jämfört med Strategi 2 och 3.

Förbrukningen av syra var inte påverkad av mer frekvent tillsats av syra till flytgödsel och pH stabiliserades inte av flera upprepade surgörningar eller frekvent tillsättning av syra. Frekvent tillsättning av syra minskade dock skumproduktionen. Detta innebär att Strategi 1 var den mest praktiska surgörningsmetoden jämfört med Strategi 2 och 3.

*Nyckelord:* Buffringskapacitet, skum,  $\text{NH}_3$  utsläpp, pH utveckling, svavelsyra

## Populärvetenskaplig sammanfattning

Flytgödsel är en växtnäringskälla som lantbrukare använder för att nyttja sin växtproduktion, men det är också en källa för ammoniakavgång som leder till förluster av flytgödselets näringsvärde. I Sverige bidrar flytgödselbrunnar med ungefär 30% av all ammoniakavgång från landets jordbruksaktiviteter. Denna ammoniakavgång begränsas genom att täcka flytgödselbrunnarna med en duk eller att en skorpa bildas vid ytan på flytgödselet. Utsläpp av ammoniak kan också begränsas genom att sänka pH i flytgödselet, som då vanligtvis utförs med starka syror som svavelsyra. Detta har visat sig vara en effektiv metod och är kommersiell i Danmark sen 2003. För närvarande finns det tre tekniker som används för att försura flytgödsel, men ingen av dem är anpassade för att förhindra ammoniakavgång under hela lagringstiden av flytgödsel i Sverige.

I denna studie simulerades tre olika surgörningsstrategier för att identifiera en effektiv och praktisk metod för att reducera flytgödselets pH till 5,5 i lagringsbrunnen. I Strategi 1 försurades flytgödsel dagligen i pumpbrunnen fem dagar i veckan under två veckor, efteråt överfördes flytgödselet till lagringsbrunnen varpå pH och temperatur mättes under tolv veckor. I Strategi 2 försurades flytgödsel efter pumpbrunnen var fylld, precis innan det fördes till lagringsbrunnen. Dessa steg repeterades varje vecka under 15 veckor och under den sista veckan utfördes en surgörning i lagringsbrunnen. I Strategi 3 försurades flytgödsel i lagringsbrunnen och därefter utfördes upprepade surgörningar varje vecka om pH steg tillbaka till 6,0.

Resultaten av experimentet visade att syraåtgång var signifikant lägst i Strategi 2. Dock var pH hos flytgödselet i lagringsbrunnen högre jämfört med de två andra strategierna och utgjorde en risk för utsläpp av ammoniak. Skumproduktionen var minst i Strategi 1 där tillsättningen av syra var mer frekvent än i Strategi 2 och 3 och var därför mest praktisk gällande reduktion av pH hos flytgödsel. Strategi 3 var inte praktisk i sig själv då det producerades mycket mer skum och pH stabiliserades inte vid 5,5 oavsett alla utförda upprepade surgörningar.

Syftet med denna studie var att upptäcka en praktisk metod för lantbrukare i Sverige att kunna försura flytgödsel i lagringsbrunnen för att kontrollera dess ammoniakavgång och spara dess näringsvärde. Strategi 1 var den mest praktiska surgörningsmetoden jämfört med Strategi 2 och 3, eftersom skumproduktionen av flytgödselet var minst på grund av den mer frekventa tillsättningen av syra.



## 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.

One technical difficulty implementing SATs in Sweden is that in-house SATs may be difficult to implement and in-storage SATs (as widely used today in Denmark) to not gain any advantage of reduced ammonia emissions during storage. Therefore, this report explores potential solutions for implementing slurry acidification during the entire storage period, which will increase the positive environmental effects of slurry acidification in Sweden. This report presents lab-scale simulations of three potential slurry acidification strategies that could be practically implemented in Sweden.

This report and the experiments described within it are the results of an independent study by a master's student, Emil Larsson, in Agronomy – Soil and Plant as well as Soil and Water Management from SLU in Uppsala, Sweden. The study was performed during autumn 2017 to spring 2018 at RISE in Uppsala, Sweden.

May 2018

Erik Sindhøj

*Project Coordinator for Baltic Slurry Acidification*



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# Table of contents

<b>List of tables</b>	<b>7</b>
<b>List of figures</b>	<b>8</b>
<b>1 Introduction</b>	<b>11</b>
1.1 Animal slurry and ammonia emissions	11
1.2 Slurry acidification	11
1.3 Buffer capacity and pH changes of slurry	14
1.4 Sulphuric acid	15
1.5 Slurry acidification during storage	16
1.6 Aim and hypotheses	17
<b>2 Material and method</b>	<b>18</b>
2.1 Animal slurry	18
2.2 Experimental plan	19
2.3 Statistics	24
<b>3 Results</b>	<b>25</b>
3.1 Evolution of acid consumption and pH with different strategies	25
3.1.1 Strategy 1	25
3.1.2 Strategy 2	28
3.1.3 Strategy 3	31
3.2 Total acid consumption between different strategies	34
3.2.1 Comparison between Strategy 1 and 2 for one week	34
3.2.2 Comparison between Strategy 1, 2 and 3 for two weeks	34
3.2.3 Comparison between Strategy 2 and 3 for 15 weeks	35
3.3 Foam production of the different strategies	37
<b>4 Discussion</b>	<b>39</b>
4.1 Acid consumption between strategies	39
4.2 Evolution of pH and ammonia emission	40
4.3 Slurry characteristics effect on acid consumption	41
4.4 Acid addition rate and foam production	42
4.5 Missing factors in lab-scale	42
4.6 Future research and recommendations	43
<b>5 Conclusion</b>	<b>45</b>

<b>References</b>	<b>46</b>
<b>Acknowledgements</b>	<b>49</b>

## List of tables

Table 1. Slurry characteristics of untreated dairy and pig slurry stored in fridge, received from analysis.	19
Table 2. Treatments of fresh dairy and pig slurry, where each treatment was replicated four times.	20

## List of figures

- Figure 1. Equilibrium between  $\text{NH}_4^+$  and  $\text{NH}_3$ , where their concentrations are equal at pH 9 approximately (modified from Fangueiro et al., 2015). 12
- Figure 2. Three different technologies for acidification of animal slurry with target pH level of 5.5, 6.0 and 6.4 in following order. (a) In-house acidification. (b) In-storage acidification. (c) In-field acidification prior to or during field application. 13
- Figure 3. Different possible methods of slurry acidification during storage. (a) Acidification in the pump pit daily after filling with fresh slurry or once after the pump pit is full, then the acidified slurry is transferred to storage. (b) Acidification and re-acidification in storage tank, while new slurry is transferred from the pump pit. pH target is 5.5 for all methods. 17
- Figure 4. Strategy 1, where acidification of daily added dairy and pig slurry in the pump pit was performed, until pH was 5.5. Acidification was performed during five days per week for two weeks, while pH and temperature were measured. After two weeks had passed acidification stopped and slurry was transferred to storage, where pH and temperature were measured every week for twelve weeks. 21
- Figure 5. (a) Acidification performed with 200 ml pig slurry, mixed with a magnetic stirrer. (b) Measuring pH and temperature of cumulative amounts of pig slurry in storage tank, mixed with a custom-made stirrer. (c) Continuation of measuring in larger container (Photos: Larsson, 2017). 22
- Figure 6. Strategy 2, where acidification of dairy and pig slurry was performed until pH was 5.5, after the pump pit was filled, and then after slurry was transferred to storage. These steps were repeated every week for 15 weeks while pH and temperature were measured for all samples, both during acidification in the pump pit and of the accumulated amount in storage. During the 15<sup>th</sup> week, a last addition of acid in storage was performed to reduce the pH level of the total amount of slurry to 5.5. 22
- Figure 7. Strategy 3, where acidification of dairy and pig slurry was performed until pH 5.5 was reached. Afterwards, pH and temperature were measured for all samples every week. Re-acidification was performed, if the pH elevated back to a level of 6.0 in any of the acidified samples, to keep the target pH value of 5.5. Strategy 3 was performed during 15 weeks. 23

- Figure 8. Timeline of all performed acidifications with Strategy 1, 2 and 3, where each symbol represents an occasion when acidification was performed for each respective strategy. 23
- Figure 9. Acid addition in relation to cumulative amounts of dairy and pig slurry in the pump pit, to reach pH 5.5 made at ten times during two weeks in Strategy 1. Peaks of acid addition occurred during third and fifth addition, when 300 g of pig slurry and 500 g of dairy slurry were acidified respectively. Afterwards, acid consumption was steady within a range of 15-19 ml per time for both slurry types (n=4). 26
- Figure 10. Cumulative volume of acid plotted against cumulative amounts of dairy and pig slurry in the pump pit, showing a linear increase during ten times of acid addition in Strategy 1. The apparent high value for pig slurry at third addition is explained by the high acid addition shown in Figure 9 (n=4). 26
- Figure 11. Evolution of pH in relation to cumulative amounts of both acidified and non-acidified dairy and pig slurry in the pump pit during ten times of acid addition in Strategy 1. Every point represents a pH value measured before slurry was acidified. (n=4). 27
- Figure 12. Evolution of pH for both acidified and non-acidified dairy and pig slurry in storage during twelve weeks after acidification stopped in Strategy 1. (n=4). 28
- Figure 13. Cumulative volume of acid plotted against cumulative amounts of dairy and pig slurry during 15 weeks in Strategy 2, showing a linear increase at first but in time shifts to a weak exponential increase (n=4). 29
- Figure 14. Acid addition to each sample of slurry in the pump pit for each week respectively, after collection from the fridge and before transfer to storage in Strategy 2. The two trendlines with their respective functions and R<sup>2</sup>-values indicate an increasing acid consumption of both dairy and pig slurry (n=4). 29
- Figure 15. Evolution of pH in relation to cumulative amount of both acidified and non-acidified dairy and pig slurry in storage, during 15 weeks in Strategy 2. The two pH values of acidified dairy and pig slurry at 5.5 during the first week, represent recent acidified slurry from the pump pit (n=4). 30
- Figure 16. Cumulative volume of acid plotted against cumulative amounts of dairy and pig slurry during 15 weeks in Strategy 2, showing a linear increase at first but in time shifts to a weak exponential increase. The two symbols at the upper right corner show the total volume of acid, which was required to lower the pH to 5.5 for the total amount of dairy and pig slurry in storage (n=4). 31
- Figure 17. Cumulative volume of acid added to 1000 g dairy and pig slurry respectively, during 15 weeks in Strategy 3. Volume of acid during the first week represent the initial acidification and not re-acidification (n=4). 32
- Figure 18. Evolution of pH for both acidified and non-acidified dairy slurry, during 15 weeks in Strategy 3. The numbers indicate all performed re-acidifications, which were six in total (n=4). 33

- Figure 19. Evolution of pH for both acidified and non-acidified pig slurry, during 15 weeks in Strategy 3. The numbers indicate all performed re-acidifications, which were eleven in total (n=4). 33
- Figure 20. Total acid consumption by dairy and pig slurry between Strategy 1 and 2, during one week. Bold values represent pH levels obtained after the week has passed. Different letters indicate a significant difference between strategies for dairy slurry ( $p < 0.001$ ) and pig slurry ( $p < 0.001$ ) respectively (n=4). 34
- Figure 21. Total acid consumption by dairy and pig slurry between Strategy 1, 2 and 3 during two weeks. Bold values represent pH levels obtained after the two weeks have passed. Different letters indicate a significant difference between strategies for dairy slurry ( $p < 0.05$ ) and pig slurry respectively ( $p < 0.001$ ) (n=4). 35
- Figure 22. Total acid consumption by dairy and pig slurry between Strategy 2 and 3, during 15 weeks. Bold values represent pH levels obtained after the 15 weeks have passed. Different letters indicate a significant difference between strategies for dairy slurry ( $p < 0.001$ ) and pig slurry respectively ( $p < 0.001$ ) (n=4). 36
- Figure 23. Total acid consumption by dairy and pig slurry between Strategy 2 and 3, during 15 weeks. Bold values represent pH levels obtained after the 15 weeks have passed. Acid amount from the last performed acidification of slurry in storage is included and indicated by +. Different letters indicate a significant difference between strategies for dairy slurry ( $p < 0.05$ ) and pig slurry respectively ( $p < 0.001$ ) (n=4). 36
- Figure 24. Foam production for both dairy and pig slurry between Strategy 1 and 2. Acid had been added successively each day during two days of the first week with Strategy 1 and once per week with Strategy 2. Foam production was irrelevant for Strategy 1 and for Strategy 2 it was medium and minor for dairy and pig slurry respectively (n=4). 37
- Figure 25. Foam production for both dairy and pig slurry between Strategy 1 and 3. Acid had been added successively during ten times for two weeks with Strategy 1 and two times during the two weeks with Strategy 3. No foam production occurred for Strategy 1 and for Strategy 3 it was major and medium for dairy and pig slurry respectively (n=4). 38

# 1 Introduction

## 1.1 Animal slurry and ammonia emissions

Animal slurry (liquid manure) is of great interest to farmers as a source of nitrogen (N) to utilize for crop production and grassland (Fangueiro et al., 2015, 2016). However, animal slurry is also a source of emissions of greenhouse gases, such as carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O) and water (H<sub>2</sub>O) (Wang et al., 2014). Furthermore, animal slurry is the major source of ammonia (NH<sub>3</sub>) emissions to the atmosphere causing acidification of soils, eutrophication and contamination of drinking water, respiratory health disease etc. (Robinson & Robbins, 2012; Wang et al., 2014). NH<sub>3</sub> volatilization also results in loss of N in animal slurry, decreasing the nutritive value of it as a fertilizer (Wang et al., 2014). According to Gioelli et al. (2016), barn and slurry stores represent up to 80% of the total NH<sub>3</sub> emissions from agricultural activities in Europe. In Sweden, slurry stores represent approximately 30% of total NH<sub>3</sub> emissions from agricultural activities in the country (Eskilsson, 2014). More than 50% of N may be lost during and after slurry has been applied on soil due to NH<sub>3</sub> emissions, if unfavorable weather conditions occur such as high temperature, drought and wind speed. Fangueiro et al. (2015) mention several ways to reduce emissions of NH<sub>3</sub>, such as covering the storage tanks with a PVC cloth or with a natural surface crust, diet manipulation, incorporation of slurry applied on field and slurry acidification.

## 1.2 Slurry acidification

One way of mitigating NH<sub>3</sub> volatilization is to acidify the slurry to lower the pH (Fangueiro et al., 2015; Gioelli et al., 2016). By lowering the pH, the equilibrium between NH<sub>3</sub> and dissolved NH<sub>4</sub><sup>+</sup> in the slurry shifts towards a higher concentration of NH<sub>4</sub><sup>+</sup> (Figure 1) (Fangueiro et al., 2015). This is due to the addition of protons

(H<sup>+</sup>), provided by the additives according to Equation 1 (Sommer et al., 2013). Reducing the pH can be done with several natural or chemical additives, but the most common is to use strong acids such as hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>) and most commonly sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) (Fangueiro et al., 2015).

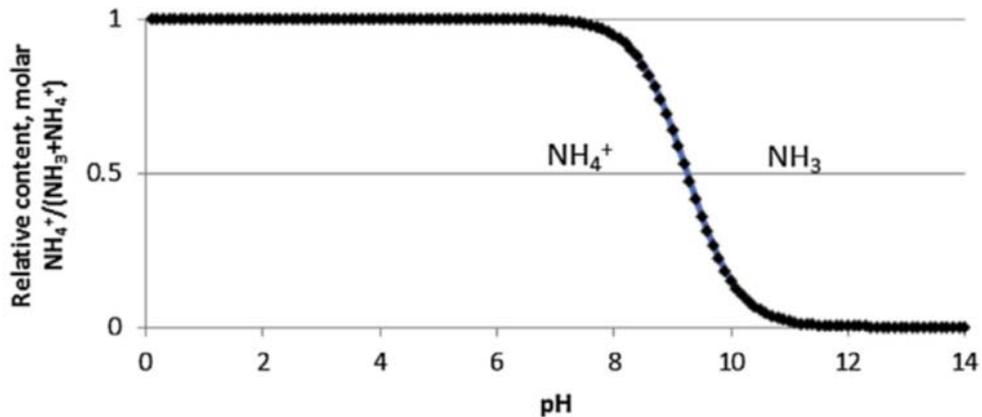
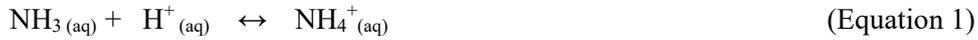


Figure 1. Equilibrium between NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub>, where their concentrations are equal at pH 9 approximately (modified from Fangueiro et al., 2015).

Slurry acidification is a recommended technique for reducing emissions of NH<sub>3</sub>, since it can cover the whole slurry management chain (Fangueiro et al., 2016). Slurry acidification can also potentially reduce cost and energy, because it can be used as an alternative to soil incorporation of slurry after application. Acidified slurry has been shown to increase crop yield as well, due to an increased contribution of N. Slurry acidification is a strategy that is widely used in Denmark at both farm and field scale and started as a full-scale commercial operation in 2003 (Fangueiro et al., 2015). In 2008, less than 2% of animal slurry was acidified but since then increased and by 2014, approximately 18% of all slurry was acidified and continued increase were to be expected (Fangueiro et al., 2015; SEGES, 2014). The pH target ranges for acidification are from between 5.5 to 6.4 depending on the type of slurry and its buffer components, the additives used to acidify, and which part of the slurry management chain acidification will be performed.

There are three technologies currently available for acidification of animal slurry (Fangueiro et al., 2015), which are:

1. In-house acidification.
2. In-storage acidification.
3. In-field acidification prior to or during field application.

Figure 2a illustrates In-house acidification, where slurry from the barn is transferred to an external tank and the additive is added to the slurry on a daily basis during stirring to reach a pH level of 5.5. Concurrently with the acidification in the tank, aeration is implemented to avoid excessive foaming, which is produced due to a release of dissolved CO<sub>2</sub> as the pH drops upon addition of acid. Afterwards, some of the slurry is returned to the barn while the rest is transferred to the storage tank.

In-storage acidification is a technology where the additive is added in the storage tank during heavy mixing (Figure 2b). Acidification is performed until pH 6.0 is met, right before the slurry will be applied on soil. Furthermore, foaming is produced during acidification and is the main practical restriction of this process.

In-field acidification prior to or during field application is illustrated in Figure 2c, where the additive is added to the slurry in a mixer on top of the tank. Acidification is performed until pH 6.4 is met, directly before fertilization will occur.

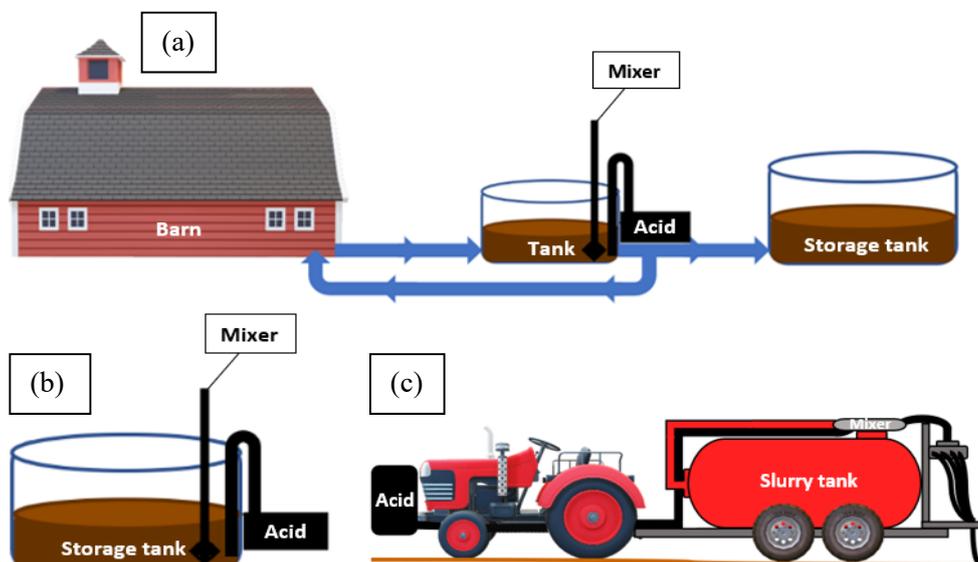


Figure 2. Three different technologies for acidification of animal slurry with target pH level of 5.5, 6.0 and 6.4 in following order. (a) In-house acidification. (b) In-storage acidification. (c) In-field acidification prior to or during field application.

In-house acidification mitigates NH<sub>3</sub> emissions during the whole slurry management chain from the barn to the field, while the other two acidification techniques only mitigate it during field application. Regulations in Sweden have led to barns being built with shallow manure channels and frequent manure removal to reduce emissions that animals and workers are exposed to inside the barn (Eskilsson, 2014). Therefore, In-house acidification is inappropriate to implement in Sweden to mitigate NH<sub>3</sub> emissions, but In-storage and In-field acidification techniques are suitable.

### 1.3 Buffer capacity and pH changes of slurry

Animal slurry has the ability to resist reduction of pH due to its strong buffer capacity (Regueiro et al., 2016). This buffer capacity consists of four processes: dissolution of carbonates, hydrolysis of carbohydrates, degradation of volatile fatty acids (VFA) and mineralization of organic N (Hjorth et al., 2015; Sommer et al., 2013). Lowering the pH results in dissolution of inorganic compounds in the slurry, such as calcium carbonate (CaCO<sub>3</sub>) which contribute with carbonate ions (CO<sub>3</sub><sup>2-</sup>). H<sup>+</sup> provided by the additives reacts with CO<sub>3</sub><sup>2-</sup> and form bicarbonate (HCO<sub>3</sub><sup>-</sup>), which negate the pH reduction. Carbohydrates are degraded by hydrolysis which is normally catalyzed by microorganism's exoenzymes, but under acidified conditions is accelerated and instead chemically catalyzed (Hjorth et al., 2015). Because of this accelerated hydrolysis, inorganic carbon like CO<sub>3</sub><sup>2-</sup> increases (Regueiro et al., 2016). VFA are degraded through methanogenesis, where methanogenic microorganisms utilize it to produce methane under anaerobic conditions (Lee et al., 2015). Under aerobic conditions VFA is instead rapidly degraded by microorganisms at a higher rate compared to anaerobic conditions (Zhang & Zhu, 2005). However, previous studies have shown that methanogenesis is decelerated under acidified conditions, because the microbial activity is inhibited (Ottosen et al., 2008; Petersen et al., 2012). Other studies indicated that mineralization of N is decreased or impeded at first, when slurry is acidified due to inhibition of microbial activity (Fangueiro et al., 2013, 2016; Regueiro et al., 2016). Therefore, the increase of pH during the first weeks after acidification is not likely because of microbial reactions, but instead chemical reactions. In this context, the dissolution of carbonates and chemical hydrolysis of carbohydrates are the main buffering process occurring when acidification is performed in storage tank or during fertilization. For in-house acidification, all buffering processes are to be considered.

The buffer components between dairy and pig slurry differs. According to Sommer et al (2013), dairy slurry contains approximately 2-3 times more base cations than pig slurry, such as calcium (Ca<sup>2+</sup>), sodium (Na<sup>+</sup>) and potassium (K<sup>+</sup>). This is due to dairy cow's intake of grass and silage. Low concentrations of Ca<sup>2+</sup> exist in solution

because it precipitates with  $\text{CO}_3^{2-}$  and form  $\text{CaCO}_3$ . Pig slurry on the other hand, contains more VFA and total N because their diet contains relatively more cereals and soybeans with easier digestibility (Kirchmann & Lundvall, 1993; Sommer et al., 2013). The organic N in pig slurry is also more easily converted to ammoniacal N ( $\text{NH}_3$  (aq) and  $\text{NH}_4^+$  (aq)), resulting in a higher concentration of these compounds than in dairy slurry (Sommer et al., 2013). The difference between the slurries buffer components may lead to a more driven buffer capacity for pig slurry than dairy slurry during the first weeks of acidification. This is due to the readily converted ammoniacal N and the dissolution of carbonates in pig slurry. On the other hand, dissolution of carbonates occurs in dairy slurry too and pig slurry contains more VFA, which reduces the pH level. Because of this, dairy slurry might require a higher acid amount during the first weeks of acidification, even if the buffer capacity is higher for pig slurry. However, during a longer acidification period, microbial reactions such as degradation of VFA and mineralization of organic N will be active. Thus, required acid amount for pig slurry might surpass dairy slurry in time.

## 1.4 Sulphuric acid

Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) is a strong acid which is colorless and odorless and is produced by a reaction between sulphur trioxide ( $\text{SO}_3$ ) and  $\text{H}_2\text{O}$  according to Equation 2 (NorFalco, 2013).



Currently, concentrated  $\text{H}_2\text{SO}_4$  is most often used in Denmark to reduce  $\text{NH}_3$  emissions, mainly because of economic reasons since it is one of the cheaper acids available (Regueiro et al., 2016). It also contributes sulphur (S) which is an essential nutrient for plants, especially oleaginous plants like rapeseed.  $\text{HNO}_3$  and  $\text{HCl}$  have been used as well and are efficient at reducing  $\text{NH}_3$  emissions, but there are also some complications with them (Fangueiro et al., 2015). Addition of  $\text{HNO}_3$  may result in higher  $\text{N}_2\text{O}$  emissions, when reacting with the slurry due to the contribution of nitrate ( $\text{NO}_3^-$ ).  $\text{HCl}$  is very corrosive compared with other acids because it has undergone fully protolysis and could damage the storage tank by degrading the concrete. However,  $\text{H}_2\text{SO}_4$  is also corrosive and should be considered when managing this acid. Furthermore, acidifying with  $\text{H}_2\text{SO}_4$  also contribute with negative effects, such as possible increase of hydrogen sulphide ( $\text{H}_2\text{S}$ ) emission. In a study performed by Moset et al. (2012),  $\text{H}_2\text{S}$  emissions increased when slurry was acidified with  $\text{H}_2\text{SO}_4$ , due to an increased activity of sulphate reducing bacteria. Nevertheless, such bacteria are pH sensitive but only part of the slurry was acidified and was increased every second week, resulting in an average pH of 8.15 due to buffering processes.

Other studies have shown a rapid increase of H<sub>2</sub>S emissions during and directly after slurry acidification to pH 5.5 with H<sub>2</sub>SO<sub>4</sub>, but not during storage (Dai & Blanes-Vidal, 2013; Hjorth et al., 2015; Wang et al., 2014). This is because sulphate reducing bacteria are inhibited by such a low pH and the emissions of H<sub>2</sub>S are mainly caused by protonation of sulphide as well as stirring of slurry. Therefore, when acidifying slurry with H<sub>2</sub>SO<sub>4</sub> to a low pH target, high levels of H<sub>2</sub>S emission should be taken into consideration since it can cause death (Wang et al., 2014).

## 1.5 Slurry acidification during storage

In-storage acidification is currently only performed shortly before the slurry is applied on soil, because the buffer capacity of the slurry initiates a pH increase which occurs after acidification (ten Hoeve et al., 2016). However, this kind of acidification technique only mitigates NH<sub>3</sub> emissions during field application and not during storage of slurry. Furthermore, excessive amounts of foam are produced when pH is dramatically decreased by addition of strong acids, such as H<sub>2</sub>SO<sub>4</sub> (Misselbrook et al., 2016). This increases the management risks and requires extra volume of the storage tank, when acidifying large amounts of slurry all at once and in turn reduces the storage capacity of slurry (Borusiewicz & Barwicki, 2017; Regueiro, et al., 2016). Foaming can be minimized through slurry aeration to make the acidification more manageable (Fangueiro et al., 2015). However, aeration of slurry causes aerobic biological degradation of VFA, which increases the pH and counteracts the mitigation of NH<sub>3</sub> emissions (Zhang & Zhu, 2005). Slurry acidification during the whole storage period might be more suitable. If slurry was continuously acidified as it is leaving the barn, then the foaming would occur before the main storage tank which would eliminate the extra need for storage capacity. This would minimize the risk of excessive foaming, save storage capacity of slurry and reduce ammonia emissions both during storage and spreading. Possible methods of acidification during storage period are as follows:

1. Daily acidification in the pump pit after filling with fresh slurry from barn until pH is 5.5 (Figure 3a). After the pump pit is full, the acidified slurry is transferred to the storage tank.
2. Acidification in the pump pit occurs once until the pH level is 5.5, after the pump pit has been filled with slurry. Afterwards, the acidified slurry is transferred to the storage tank (Figure 3a).
3. Acidification of slurry in the storage tank and then re-acidification, while new slurry is transferred from the pump pit, to keep the pH at 5.5 (Figure 3b).

A combination of acidification in the pump pit and storage tank is also possible. In that case, slurry acidification in the pump pit is performed according to one of the two mentioned methods. Afterwards, re-acidification is performed after the acidified slurry has been transferred to the storage tank to keep the pH at 5.5.

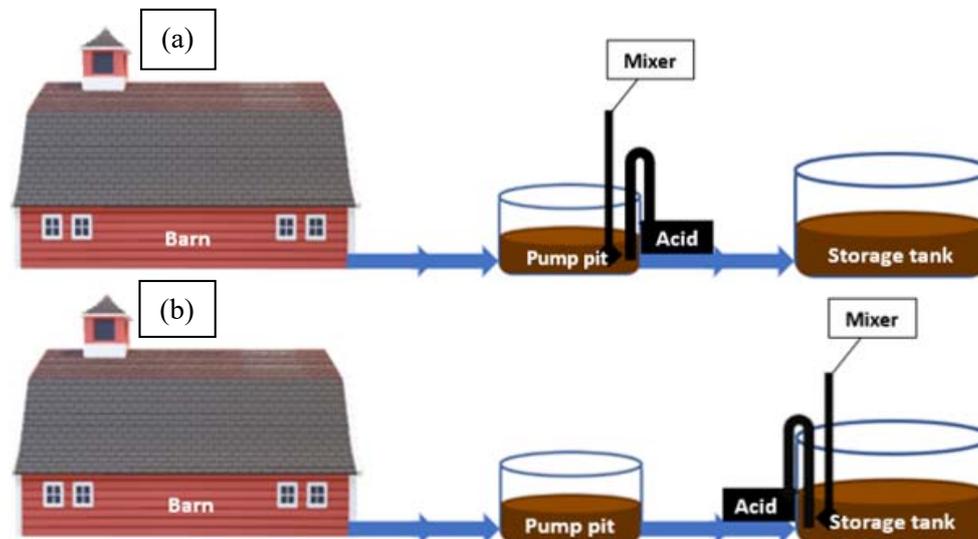


Figure 3. Different possible methods of slurry acidification during storage. (a) Acidification in the pump pit daily after filling with fresh slurry or once after the pump pit is full, then the acidified slurry is transferred to storage. (b) Acidification and re-acidification in storage tank, while new slurry is transferred from the pump pit. pH target is 5.5 for all methods.

## 1.6 Aim and hypotheses

The aim of this study was to identify an efficient and practical method for acidifying slurry during the entire storage period and thereby maximizing the mitigation of  $\text{NH}_3$  emissions. Different acidification strategies were simulated to reduce the pH of slurry to 5.5 in laboratory scale, where consumption of acid and foaming was compared between them. Purpose of this study was to discover a practical procedure for farmers in Sweden to implement acidification of slurry to control  $\text{NH}_3$  emissions and save N during storage.

Following hypotheses were tested:

- i) Acid consumption will be greater when addition is more frequent.
- ii) pH will stabilize after several re-acidifications.
- iii) pH will stabilize faster when addition of acid is more frequent.
- iv) Frequent acid additions will reduce foaming and save storage capacity.

## 2 Material and method

### 2.1 Animal slurry

Fresh dairy and pig slurry were collected from Lövsta and Fittja farms, respectively, near Uppsala Sweden.

The first and second collection of dairy slurry occurred 31<sup>st</sup> August and 12<sup>th</sup> September, respectively, from the pump pit. Both collections were performed by repeatedly lowering a 5 L bucket, tied with a rope, down into the mixed slurry to fill it and then pour it into larger containers. Lövsta farm has a dairy production of 269 cows, 238 heifers and 9 bulls, where all calves are raised. The cattle's diet consists mainly of silage complemented with concentrated fodder and to smaller amounts of hay, straw and minerals. Sanitation of the barn is performed every year but for some sections, like calving pens, it occurs more often.

First collection of pig slurry occurred 4<sup>th</sup> September from the main cross-channel that empties slurry from the barn to the pumping pit. The second collection occurred 3<sup>rd</sup> October from the pump pit. Both collections were performed the same way as for the dairy slurry. Fittja farm has a production of 3240 fattening pigs, which is divided into 9 sections with 360 pigs in each and 360 piglets are bought every second week. The pig's diet consisted mainly of barley mixed with approximately 20% of peas and to smaller amounts of wheat and soybean, which was wetted with water. Their diet was also complemented with premix, which is a mixture containing amino acids and minerals with changing proportions depending on the nutritive status of the diet. Sanitation of the barn was performed after every second batch.

All collected slurry was stored in covered plastic barrels and buckets in a refrigerator at 5°C until it was used. After the slurry was collected, samples were sent for chemical analysis. (Table 1).

Table 1. Slurry characteristics of untreated dairy and pig slurry stored in fridge, received from analysis.

<b>Properties</b>	<b>Dairy slurry</b>	<b>Pig slurry</b>
DM (%)	9.3	9.0
Tot-N (kg/ton)	4.2	4.6
Org-N (kg/ton)	2.3	2.4
NH <sub>4</sub> <sup>+</sup> -N (kg/ton)	1.9	2.2
Tot-C (kg/ton)	41.9	39.6
C/N-ratio	10.0	8.6
Tot-P (kg/ton)	0.57	0.72
Tot-K (kg/ton)	3.99	1.91
Tot-Mg (kg/ton)	0.55	0.69
Tot-Ca (kg/ton)	1.89	2.64
Tot-Na (kg/ton)	0.15	1.25
Tot-S (kg/ton)	0.49	0.45

## 2.2 Experimental plan

Three different strategies of adding acid to the animal slurry were simulated in laboratory scale:

1. Daily acidification in the pump pit Monday-Friday (2 weeks), pumping to storage (12 weeks).
2. One-time batch acidification in the pump pit, pumping every week to storage (15 weeks) and acidification in storage (15<sup>th</sup> week).
3. Acidification and re-acidification in storage (15 weeks).

An experiment with twelve treatments was conducted to simulate the three strategies for dairy and pig slurry, with both acidified and non-acidified slurry according to Table 2. Each treatment was replicated four times, so there was a total of 48 samples.

Table 2. Treatments of fresh dairy and pig slurry, where each treatment was replicated four times.

<b>Treatment</b>	<b>Strategy</b>	<b>Type of slurry</b>	<b>Acid</b>
1. CS_1_S	1. Daily, pumping pit	Dairy	Sulfuric acid
2. CS_1	1. Daily, pumping pit	Dairy	No acid (control)
3. PS_1_S	1. Daily, pumping pit	Pig	Sulfuric acid
4. PS_1	1. Daily, pumping pit	Pig	No acid (control)
5. CS_2_S	2. Weekly, pumping pit	Dairy	Sulfuric acid
6. CS_2	2. Weekly, pumping pit	Dairy	No acid (control)
7. PS_2_S	2. Weekly, pumping pit	Pig	Sulfuric acid
8. PS_2	2. Weekly, pumping pit	Pig	No acid (control)
9. CS_3_S	3. Re-acidification, storage	Dairy	Sulfuric acid
10. CS_3	3. Re-acidification, storage	Dairy	No acid (control)
11. PS_3_S	3. Re-acidification, storage	Pig	Sulfuric acid
12. PS_3	3. Re-acidification, storage	Pig	No acid (control)

One hour prior to every performed acidification, slurry was collected from the refrigerator in 500 ml containers and put in the lab at room temperature (20°C). In all strategies, half of the samples for each slurry type were acidified with 0.5 M sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) to lower the pH to 5.5, and non-acidified samples acted as control. Acid was added within the range of 1-10 ml successively, depending on the amount of slurry, with a micropipette and pH and temperature were measured with an Orion 920A+ instrument (SCANDONIVATA AB, Sweden). Samples were weighed with a PB1502-S/FACT (Mettler Toledo, Switzerland) and volume was measured visually by checking a ml scale on the containers. Before and during all acidifications and measuring, samples were stirred with either a magnetic or custom-made stirrer to make them homogenous. Control samples were stirred as well during measuring, but for a shorter amount of time. A timeline of all acidifications performed in all strategies is presented in Figure 8. In all strategies, height of the foam produced was measured with a ruler and by multiplying the foam height with the containers area the volume of the foam was calculated. The volume of the produced foam was then calculated as percent of the slurry's volume. All samples were stored in room temperature, covered with aluminum foil as a lid, when no acidification or measuring was performed.

During the 1<sup>st</sup> day of the experiment with Strategy 1, eight samples of 100 ml dairy and pig slurry each were weighed. Acidification of slurry was performed while measuring pH and temperature (Figure 4). Afterwards, the control samples were

measured. On the 2<sup>nd</sup> day, additional eight 100 ml samples of dairy and pig slurry each were weighed and added to the earlier samples resulting in 200 ml samples of slurry. Acidification and measuring was then performed as earlier described. These steps were repeated for five days per week for two weeks and at the 5<sup>th</sup> day, the accumulated amount of slurry was transferred to larger containers to avoid overflow. After two weeks the total amount of slurry for each sample reached 1 L, which represented the capacity of the pump pit. All samples were then transferred to containers representing the storage tank, where pH and temperature were measured every week during twelve weeks (Figure 4). After twelve weeks had passed, Strategy 1 was completed.

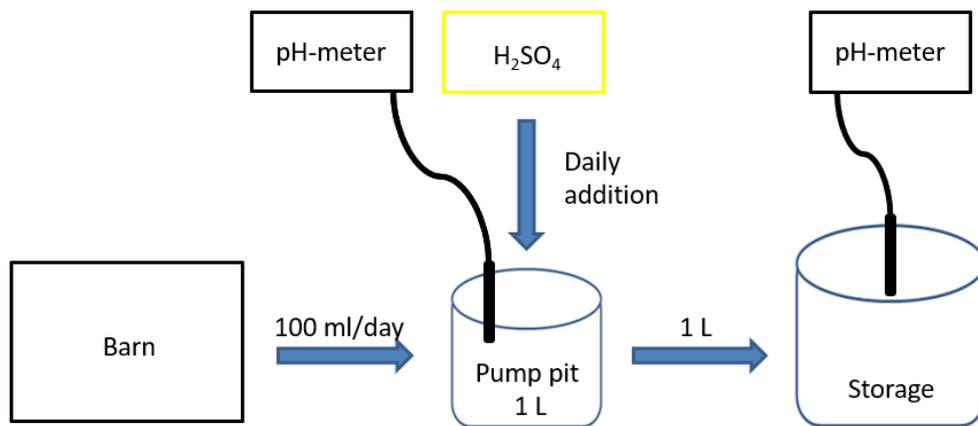


Figure 4. Strategy 1, where acidification of daily added dairy and pig slurry in the pump pit was performed, until pH was 5.5. Acidification was performed during five days per week for two weeks, while pH and temperature were measured. After two weeks had passed acidification stopped and slurry was transferred to storage, where pH and temperature were measured every week for twelve weeks.

The experiment simulating Strategy 2, started with weighing eight 200 ml samples of dairy and pig slurry each, representing the capacity of the pump pit (Figure 5a and 6). Acidification was performed for each slurry type, while measuring their pH and temperature, control samples were then measured. Directly after acidification and measuring, each sample was transferred into larger containers that represented the storage tank (Figure 5b and 6). Next week, additional eight 200 ml samples of dairy and pig slurry each were weighed. Acidification and measuring were performed as earlier described, then these samples were transferred to the same respective storage tanks as earlier samples. Afterwards, the pH and temperature were measured for the accumulated amount of slurry in the storage tanks, but no re-acidification was performed. These steps were repeated every week during 15 weeks

and at the 9<sup>th</sup> week, the accumulated amount of slurry was transferred to larger containers to avoid overflow (Figure 5c). During the 15<sup>th</sup> week, a last acidification was performed for the total amount of slurry in the storage tanks to reduce the pH to 5.5 (Figure 6), since the slurry had buffered for 15 weeks. Strategy 2 was completed after the last acidification was performed.

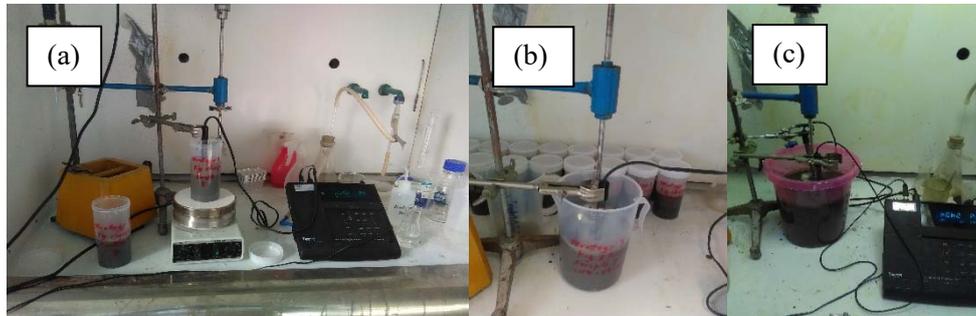


Figure 5. (a) Acidification performed with 200 ml pig slurry, mixed with a magnetic stirrer. (b) Measuring pH and temperature of cumulative amounts of pig slurry in storage tank, mixed with a custom-made stirrer. (c) Continuation of measuring in larger container (Photos: Larsson, 2017).

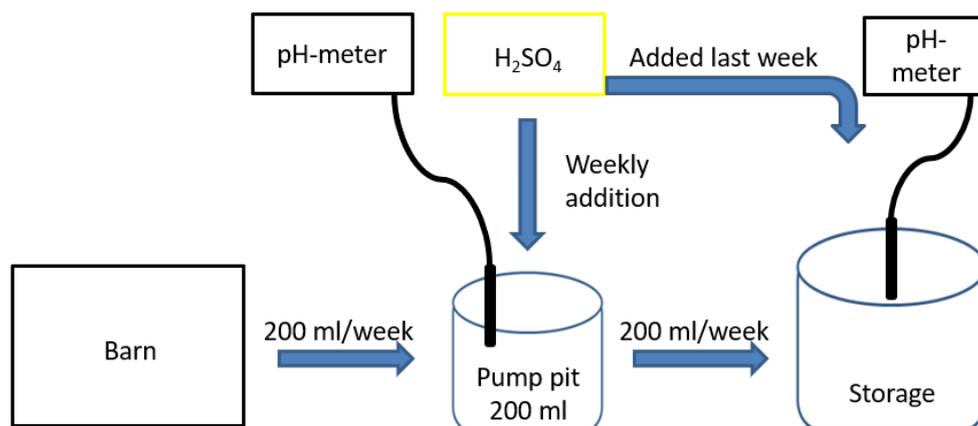


Figure 6. Strategy 2, where acidification of dairy and pig slurry was performed until pH was 5.5, after the pump pit was filled, and then after slurry was transferred to storage. These steps were repeated every week for 15 weeks while pH and temperature were measured for all samples, both during acidification in the pump pit and of the accumulated amount in storage. During the 15<sup>th</sup> week, a last addition of acid in storage was performed to reduce the pH level of the total amount of slurry to 5.5.

The experiment simulating Strategy 3, started with weighing eight 1 L samples of dairy and pig slurry each, representing the storage tank (Figure 7). Acidification was



## 2.3 Statistics

One-way ANOVA was used to compare the total consumption of acid between the different strategies. Following comparisons between strategies were: Strategy 1 and 2 during one week, Strategy 1, 2 and 3 during two weeks and Strategy 2 and 3 for the whole laboratory study of 15 weeks. For multiple comparisons, the posthoc test Tukey's honestly significant difference (HSD) was used to identify which comparisons were significantly different. Rstudio was the software operated for ANOVA analysis and the posthoc test Tukey HSD.

## 3 Results

In this chapter, data of temperature changes is not included, because values were within a small range of 19-21°C in all strategies. Thus, it is not regarded as an influencing factor on acid consumption, pH evolution or foam production between strategies.

### 3.1 Evolution of acid consumption and pH with different strategies

#### 3.1.1 Strategy 1

In this section, the ten days of performed acidification during two weeks are referred to as acid addition times instead.

Results from the performance of Strategy 1, showed no noticeable difference in acid consumption between dairy and pig slurry to reach pH 5.5, except for the third and fifth acid addition (Figure 9). After the fifth addition, the acid consumption was steady at the range of 15-19 ml for both slurry types, which was slightly higher than during the first two additions. Figure 10 presents the cumulative volume of acid added in relation to cumulative amounts of slurry. A linear increase of the cumulative amount of acid is observed for both dairy and pig slurry, with similar values between them, during the ten times of acid addition performed for two weeks. However, a deviating value can also be observed at the third addition for pig slurry which is explained by the high acid addition shown in Figure 9.

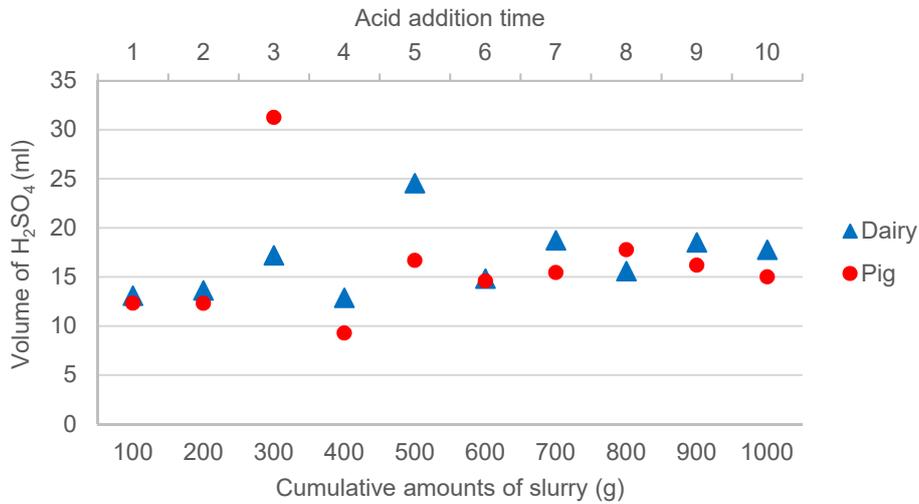


Figure 9. Acid addition in relation to cumulative amounts of dairy and pig slurry in the pump pit, to reach pH 5.5 made at ten times during two weeks in Strategy 1. Peaks of acid addition occurred during third and fifth addition, when 300 g of pig slurry and 500 g of dairy slurry were acidified respectively. Afterwards, acid consumption was steady within a range of 15-19 ml per time for both slurry types (n=4).

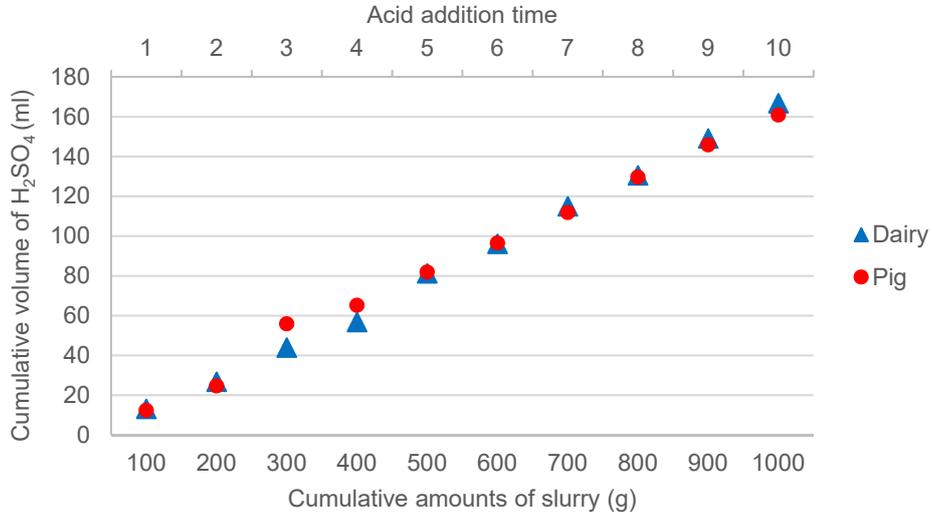


Figure 10. Cumulative volume of acid plotted against cumulative amounts of dairy and pig slurry in the pump pit, showing a linear increase during ten times of acid addition in Strategy 1. The apparent high value for pig slurry at third addition is explained by the high acid addition shown in Figure 9 (n=4).

In Figure 11, pH level is plotted against both acidified and non-acidified cumulative slurry amount together with times of acid additions. Each point is a pH value measured before every performed daily acid addition. The level of pH fluctuated during the first four times, but then steadily decreased every time, for both acidified slurry types. The pH level was not greatly differing between dairy and pig slurry, but dairy slurry had a slightly higher pH level than pig slurry during the steady decrease from fifth addition and forward. Non-acidified slurries had a stable pH level during the whole period, except between the third and fifth addition, and it was also higher for dairy slurry compared to pig slurry.

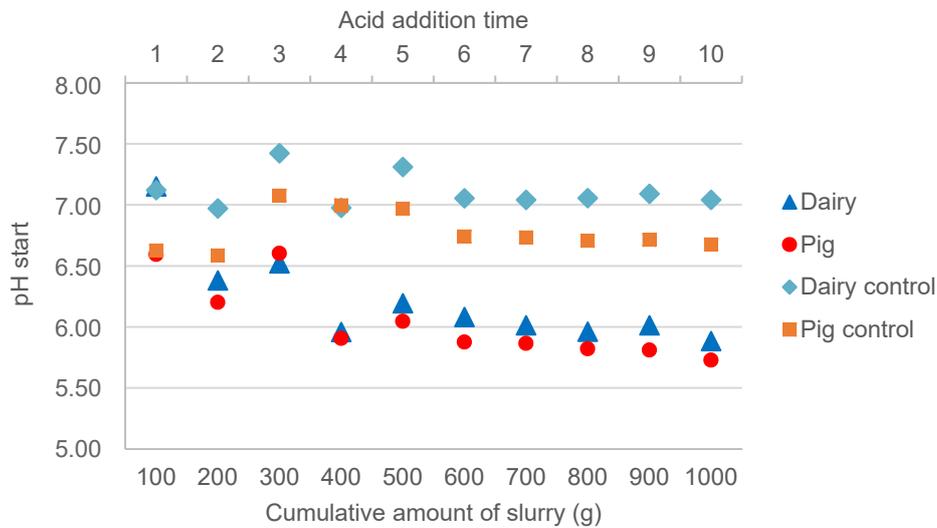


Figure 11. Evolution of pH in relation to cumulative amounts of both acidified and non-acidified dairy and pig slurry in the pump pit during ten times of acid addition in Strategy 1. Every point represents a pH value measured before slurry was acidified. (n=4).

Evolution of pH for both acidified and non-acidified slurries during twelve weeks, after acidification stopped, is presented in Figure 12. A pH increase is observed for all slurries, but acidified slurries had a more rapid increase during the first three weeks than non-acidified slurries. Afterwards, evolution of pH was similar for all slurries until the 9<sup>th</sup> week, where it leveled off and became stable for non-acidified slurries. During all twelve weeks, acidified pig slurry had a higher pH level than acidified dairy slurry and for non-acidified slurries it was the opposite until the 9<sup>th</sup> week. During the last week, the pH level of acidified pig slurry was almost as high as the non-acidified slurries.

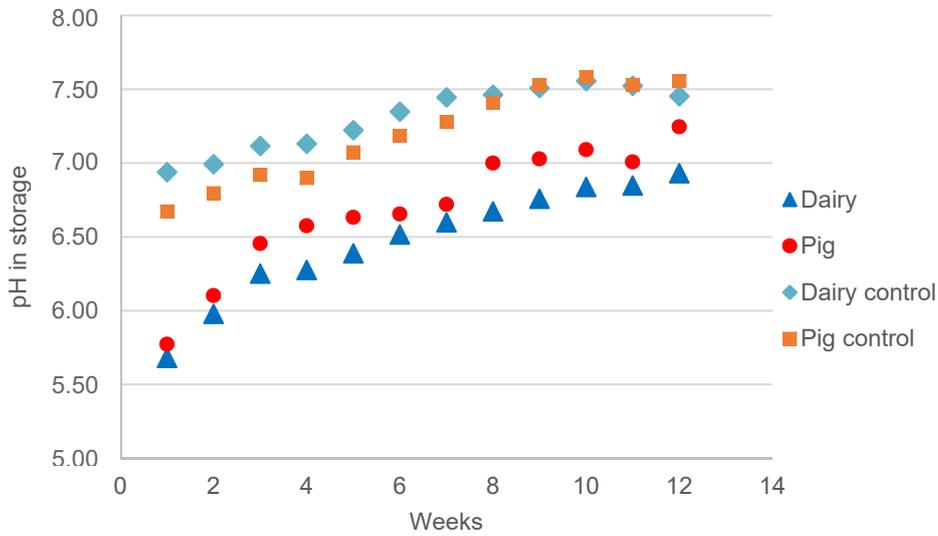


Figure 12. Evolution of pH for both acidified and non-acidified dairy and pig slurry in storage during twelve weeks after acidification stopped in Strategy 1. (n=4).

### 3.1.2 Strategy 2

Results from the performance of Strategy 2 showed a difference in consumption of acid between the two types of slurry to reach pH 5.5, where dairy slurry surpassed pig slurry during all weeks (Figure 13-14). Figure 13 shows the cumulative volume of acid in relation to cumulative amounts of slurry for 15 weeks. A linear increase of the cumulative acid volume occurred at first, but in time shifted to a weak exponential increase for both dairy and pig slurry. This is explained by Figure 14, which presents the acid addition to each sample of slurry in the pump pit for each respective week, after they were collected from the fridge and before being transferred to storage. The required volume of acid, to lower pH to 5.5 for both dairy and pig slurry, increased linearly with approximately 1 ml per each week. This is indicated by the two trendlines and their respective functions and  $R^2$ -values (Figure 14). According to Figure 13, the difference of cumulative volume of acid between dairy and pig slurry is increasing with each week. This is also explained by Figure 14, where dairy samples of slurry always require more acid than samples of pig slurry.

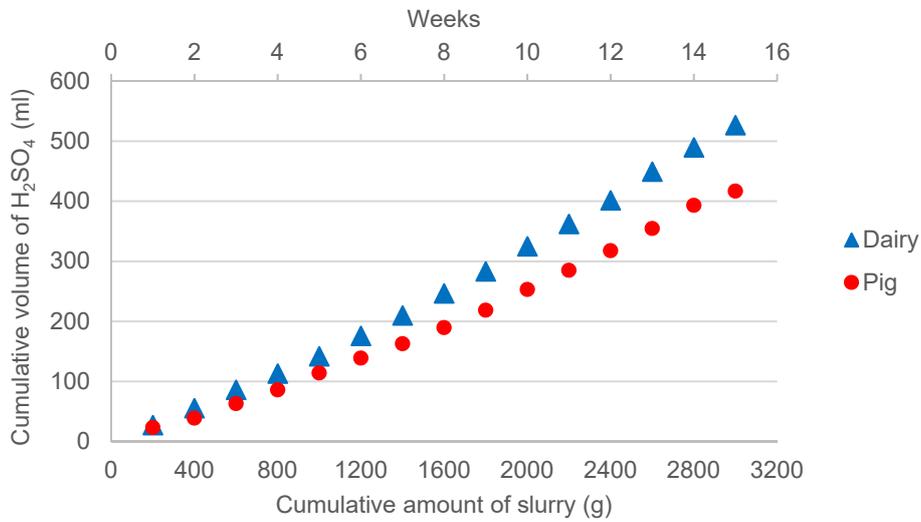


Figure 13. Cumulative volume of acid plotted against cumulative amounts of dairy and pig slurry during 15 weeks in Strategy 2, showing a linear increase at first but in time shifts to a weak exponential increase (n=4).

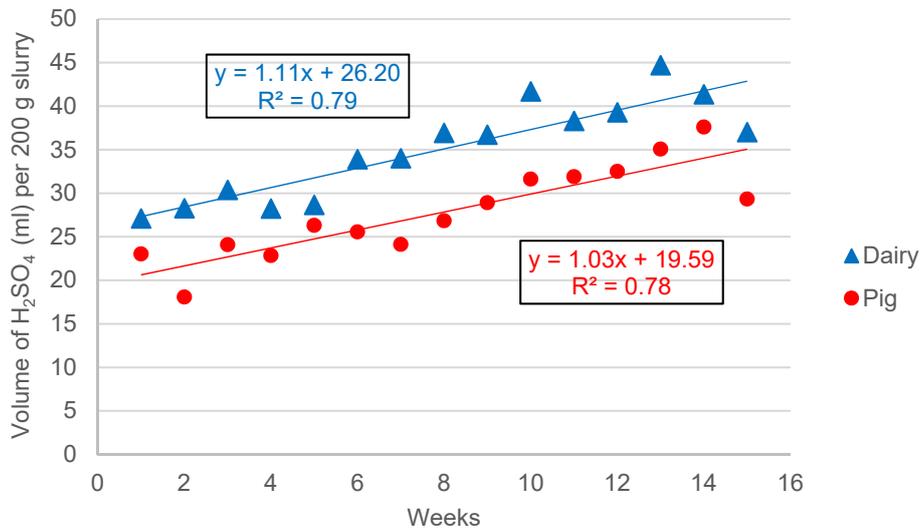


Figure 14. Acid addition to each sample of slurry in the pump pit for each week respectively, after collection from the fridge and before transfer to storage in Strategy 2. The two trend-lines with their respective functions and R<sup>2</sup>-values indicate an increasing acid consumption of both dairy and pig slurry (n=4).

In Figure 15, pH level is plotted against both acidified and non-acidified cumulative slurry amount in storage, for 15 weeks. Each point is a pH value measured after slurry samples have been transferred to storage. The level of pH for 200 g acidified slurries was at 5.5 in the beginning of the first week, as expected since slurry had been acidified recently in the pump pit and then transferred to storage. After one week, the same amount of acidified dairy and pig slurry had their pH level increased to 6.3 and 6.6 respectively. After additional 200 g acidified slurries in storage the total amount of 400 g slurries had a pH level of 6.0 and 6.4 for dairy and pig slurry respectively, even though half of their amounts had been acidified to pH 5.5 recently. During week 3-9, the pH level was stable for acidified dairy and pig slurry at approximately 6.1 and 6.5 respectively. Afterwards, the pH level increased until week 13 and was stable again at approximately 6.4 and 6.8 for dairy and pig slurry respectively. During all weeks after the first acidification, pig slurry had a higher pH level than dairy slurry with an average difference of 0.4 pH units. Non-acidified slurries had a pH increase with increasing amounts during the first three weeks. Afterwards, the pH level of pig slurry was stable until the very last week, while dairy slurry had a pH decrease before becoming stable. During the first four weeks, non-acidified dairy slurry had a higher pH level than non-acidified pig slurry, but afterwards they had a similar pH level at approximately 7.0. During the last week, the pH level of acidified pig slurry was almost as high as the non-acidified slurries.

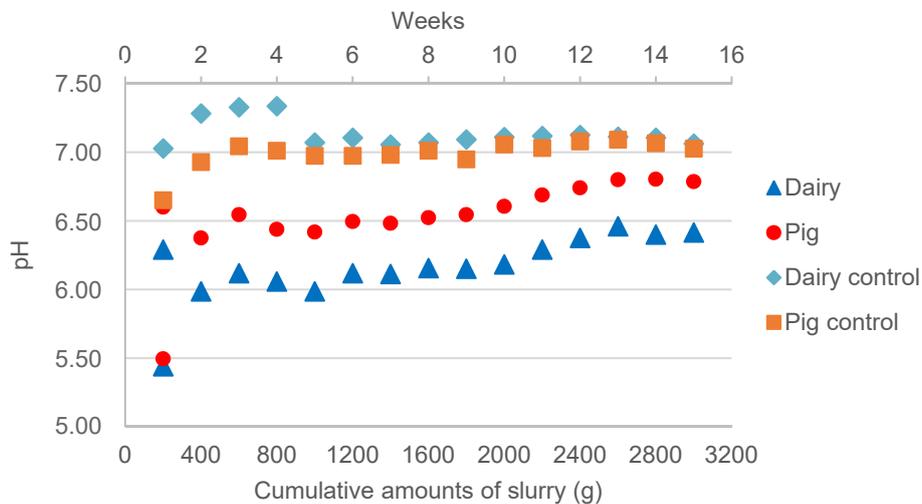


Figure 15. Evolution of pH in relation to cumulative amount of both acidified and non-acidified dairy and pig slurry in storage, during 15 weeks in Strategy 2. The two pH values of acidified dairy and pig slurry at 5.5 during the first week, represent recent acidified slurry from the pump pit (n=4).

Figure 16 presents the same information as Figure 13, but also include results from the last performed acidification of the total amount of slurry in storage and the y-axis has been extended from 600 ml to 1000 ml. The two symbols at the upper right corner of the figure show the total volume of acid that was required to lower the pH to 5.5 for 3000 g dairy and pig slurry respectively. As mentioned earlier, dairy slurry surpassed pig slurry in consumption of acid during all weeks to reach pH 5.5. However, the pH level of the total amount of acidified slurry in storage increased during the storage period, where dairy and pig slurry ended up with a pH level of approximately 6.4 and 6.8 respectively (Figure 15). After the last acidification, pig slurry surpassed dairy slurry in consumption of acid with 173 ml (Figure 16).

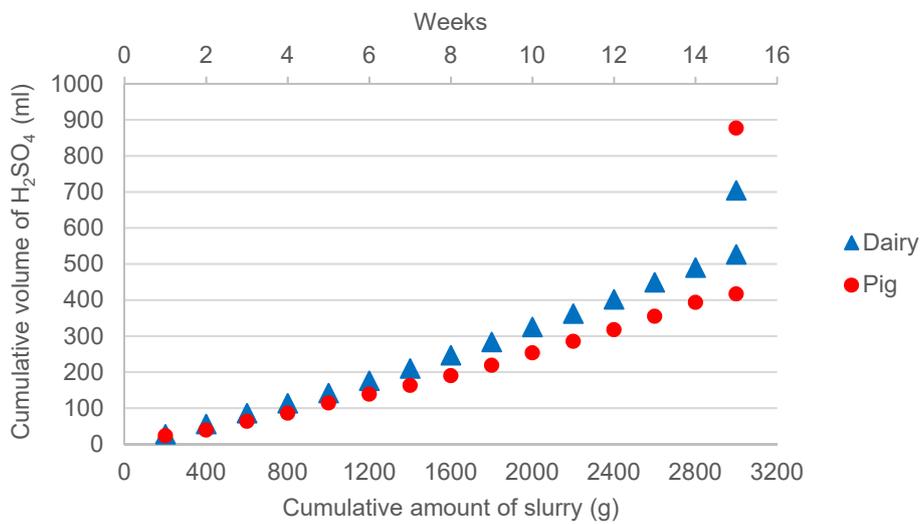


Figure 16. Cumulative volume of acid plotted against cumulative amounts of dairy and pig slurry during 15 weeks in Strategy 2, showing a linear increase at first but in time shifts to a weak exponential increase. The two symbols at the upper right corner show the total volume of acid, which was required to lower the pH to 5.5 for the total amount of dairy and pig slurry in storage (n=4).

### 3.1.3 Strategy 3

Results from the performance of Strategy 3 showed a difference in acid consumption between dairy and pig slurry to reach pH 5.5, as well as in number of re-acidifications needed to keep the target pH level (Figure 17-19). The cumulative volume of acid for dairy slurry was slightly higher than for pig slurry, during the first three weeks (Figure 17). After three weeks had passed, pig slurry surpassed dairy slurry in acid consumption and the difference between them increased with every week. This can be explained by the more frequent re-acidifications that were needed for

pig slurry to keep the pH level down at 5.5 compared to dairy slurry (Figure 18-19). Dairy slurry needed only six re-acidifications (Figure 18), while pig slurry needed eleven re-acidifications (Figure 19) which are indicated by the blue and red numbers respectively. The required volume of acid needed to keep the pH level at 5.5, decreased for every performed re-acidification of both dairy and pig slurry and is observed by the two curves which levels off with time in Figure 17. After acidification was performed during the last week, pig slurry had required approximately 91 ml more acid than dairy slurry in total. The pH level of non-acidified slurries increased until week 13, where dairy and pig slurry ended up with a pH level of 7.8 (Figure 18) and 8.3 (Figure 19) respectively.

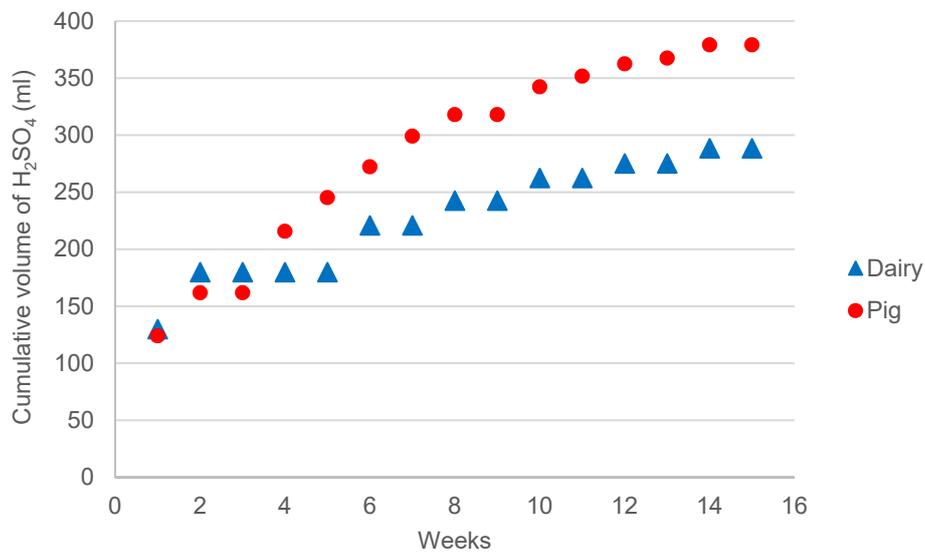


Figure 17. Cumulative volume of acid added to 1000 g dairy and pig slurry respectively, during 15 weeks in Strategy 3. Volume of acid during the first week represent the initial acidification and not re-acidification (n=4).

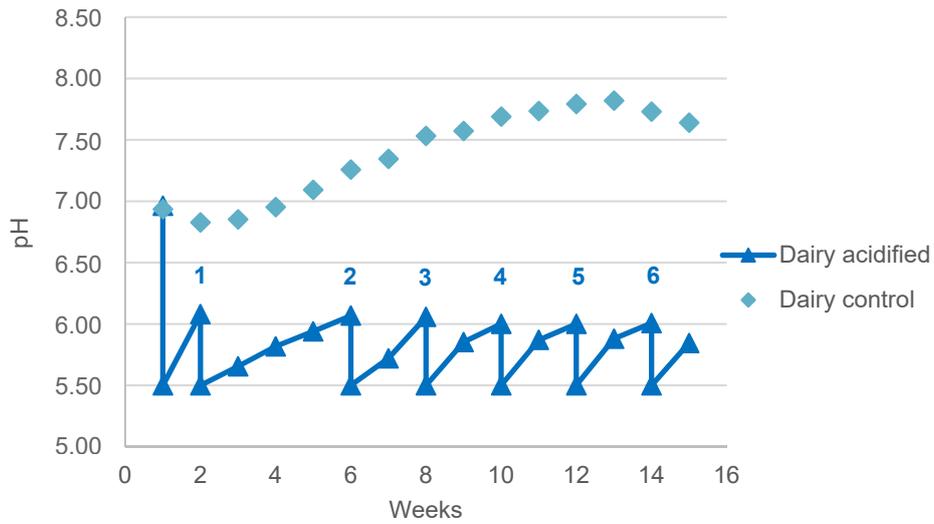


Figure 18. Evolution of pH for both acidified and non-acidified dairy slurry, during 15 weeks in Strategy 3. The numbers indicate all performed re-acidifications, which were six in total (n=4).

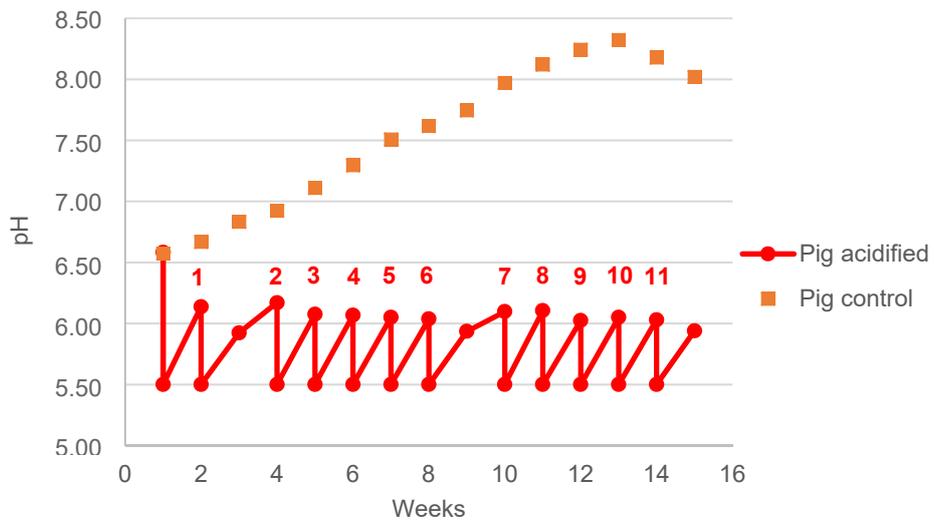


Figure 19. Evolution of pH for both acidified and non-acidified pig slurry, during 15 weeks in Strategy 3. The numbers indicate all performed re-acidifications, which were eleven in total (n=4).

## 3.2 Total acid consumption between different strategies

In this section, Figure 20-23 presents the total consumption of concentrated acid (18.2 M) in liter per ton between different strategies, during different time periods. Furthermore, no comparison is made between dairy and pig slurry.

### 3.2.1 Comparison between Strategy 1 and 2 for one week

Figure 20 presents the total amount of acid consumed by dairy and pig slurry, to reach a pH level of 5.5, during the performance of Strategy 1 and 2 for one week. Values in bold represent pH levels obtained after the week has passed. Total acid consumption was significantly lower for both dairy and pig slurry with 16.6% and 29.8% respectively, when Strategy 2 was performed compared to Strategy 1. However, during the 1<sup>st</sup> week of Strategy 2, the pH level of dairy and pig slurry in storage had elevated back to 6.3 and 6.6 respectively.

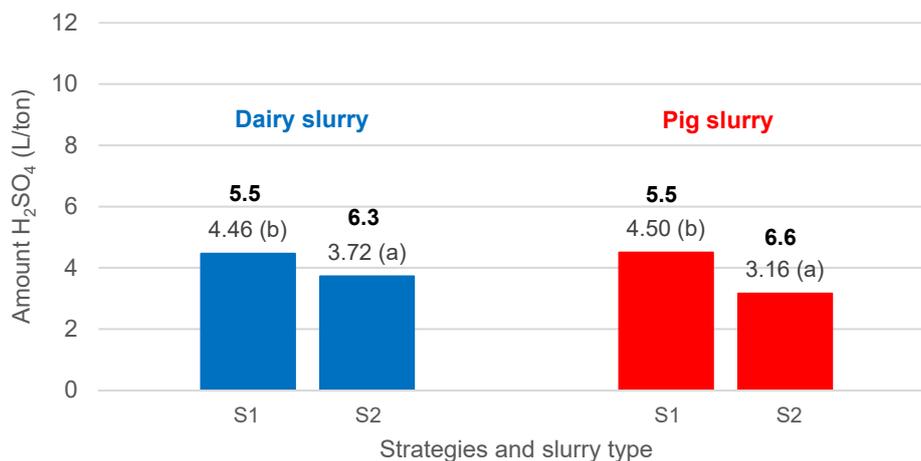


Figure 20. Total acid consumption by dairy and pig slurry between Strategy 1 and 2, during one week. Bold values represent pH levels obtained after the week has passed. Different letters indicate a significant difference between strategies for dairy slurry ( $p < 0.001$ ) and pig slurry ( $p < 0.001$ ) respectively ( $n=4$ ).

### 3.2.2 Comparison between Strategy 1, 2 and 3 for two weeks

Figure 21 presents the total amount of acid consumed by dairy and pig slurry, to reach a pH level of 5.5, during the two first weeks with Strategy 1, 2 and 3. The bold values represent pH levels obtained after the two weeks have passed. Total acid consumption was significantly lower for dairy slurry with 23%, when Strategy 2

was performed compared to Strategy 3. Total acid consumption was also significantly lower for pig slurry with 40%, when Strategy 2 was performed compared to both Strategy 1 and 3. It can be noted that during the 2<sup>nd</sup> week of Strategy 2, the pH level of dairy and pig slurry in storage was 6.0 and 6.4 respectively. No significant difference in acid consumption could be observed between Strategy 1 and 3 for pig slurry or between Strategy 1 and the other strategies for dairy slurry.

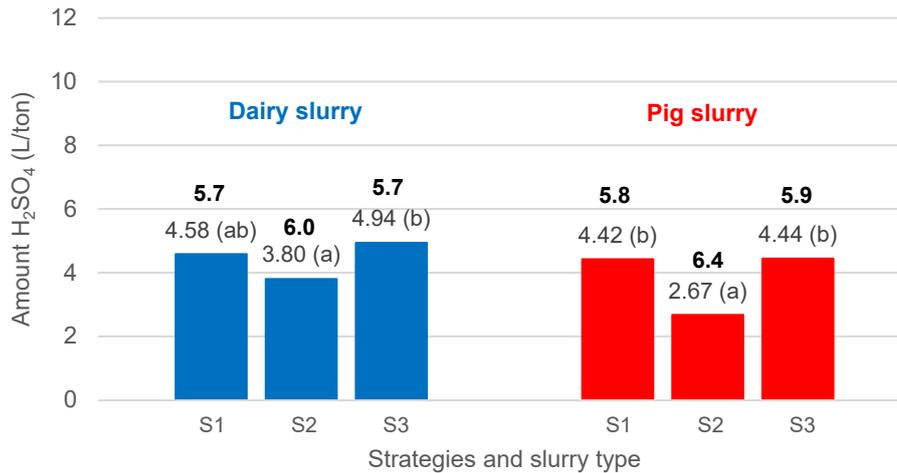


Figure 21. Total acid consumption by dairy and pig slurry between Strategy 1, 2 and 3 during two weeks. Bold values represent pH levels obtained after the two weeks have passed. Different letters indicate a significant difference between strategies for dairy slurry ( $p < 0.05$ ) and pig slurry respectively ( $p < 0.001$ ) ( $n=4$ ).

### 3.2.3 Comparison between Strategy 2 and 3 for 15 weeks

Figure 22 presents the total amount of acid consumed by dairy and pig slurry, to reach a pH level of 5.5 in end of storage period, during the performance of Strategy 2 and 3 for 15 weeks. The bold values represent pH levels obtained after the 15 weeks have passed. Total acid consumption was significantly lower for both dairy and pig slurry with 39.1% and 63.3% respectively, when Strategy 2 was performed compared to Strategy 3. It can be noted that during the 15<sup>th</sup> week of Strategy 2, the pH level of dairy and pig slurry in storage was 6.4 and 6.8 respectively. Figure 23 has the same information as Figure 22, but also include results from the last performed acidification of the total amount of dairy and pig slurry in storage. Total acid consumption was still significantly lower for both dairy and pig slurry with 18.6% and 22.9% respectively, even with the extra acid addition.

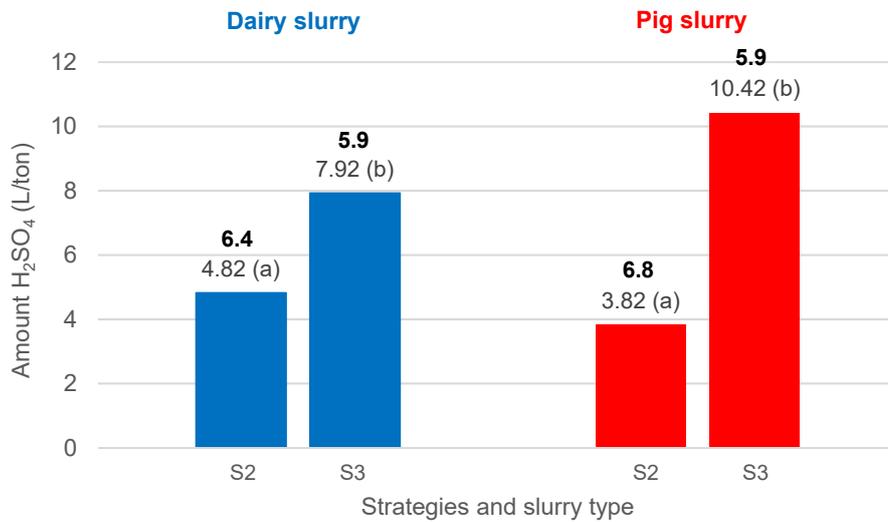


Figure 22. Total acid consumption by dairy and pig slurry between Strategy 2 and 3, during 15 weeks. Bold values represent pH levels obtained after the 15 weeks have passed. Different letters indicate a significant difference between strategies for dairy slurry ( $p < 0.001$ ) and pig slurry respectively ( $p < 0.001$ ) ( $n=4$ ).

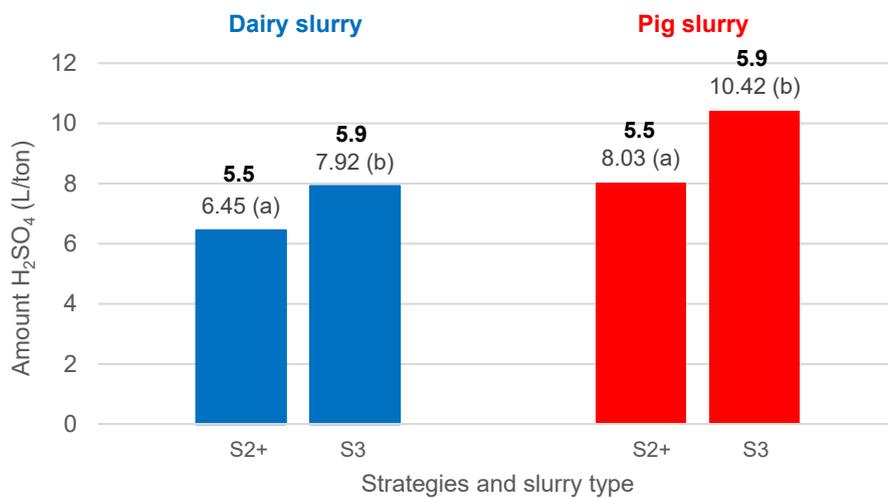


Figure 23. Total acid consumption by dairy and pig slurry between Strategy 2 and 3, during 15 weeks. Bold values represent pH levels obtained after the 15 weeks have passed. Acid amount from the last performed acidification of slurry in storage is included and indicated by +. Different letters indicate a significant difference between strategies for dairy slurry ( $p < 0.05$ ) and pig slurry respectively ( $p < 0.001$ ) ( $n=4$ ).

### 3.3 Foam production of the different strategies

In this section, results only show foam production between Strategy 1 and 2 during the first two days of the first week and between Strategy 1 and 3 during the first two weeks. Furthermore, level of foaming is categorized in five different conditions based on how much volume of foam is produced relative to the slurry's volume:

Irrelevant	< 10%
Minor	10-20%
Medium	20-40%
Major	40-60%
Extreme	> 60%

Figure 24 shows the foam production from 200 ml dairy and pig slurry during acidification between Strategy 1 and 2. Foam production from both dairy and pig slurry were less for Strategy 1, where acid had been added successively each day during two days of the first week, compared to Strategy 2 where acidification occurred all at once. Level of foaming was irrelevant for both dairy and pig slurry with Strategy 1. With Strategy 2, the level of foaming was medium for dairy slurry and minor for pig slurry.

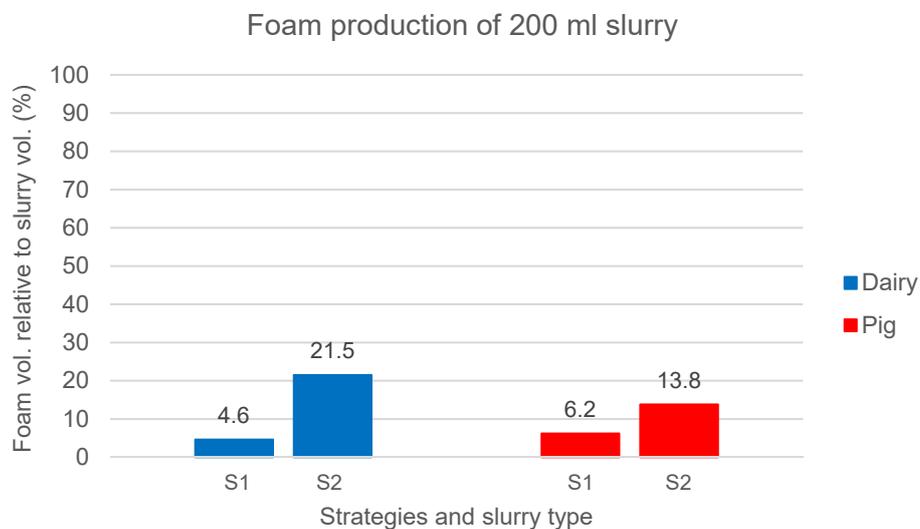


Figure 24. Foam production for both dairy and pig slurry between Strategy 1 and 2. Acid had been added successively each day during two days of the first week with Strategy 1 and once per week with Strategy 2. Foam production was irrelevant for Strategy 1 and for Strategy 2 it was medium and minor for dairy and pig slurry respectively (n=4).

Figure 25 shows the foam production of 1000 ml dairy and pig slurry during acidification between Strategy 1 and 3. Foam production of both dairy and pig slurry did not occur for Strategy 1, where acid had been added successively during ten times for two weeks. With Strategy 3, the level of foaming was major for dairy slurry and medium for pig slurry, where one acidification and one re-acidification had been performed during the two weeks.

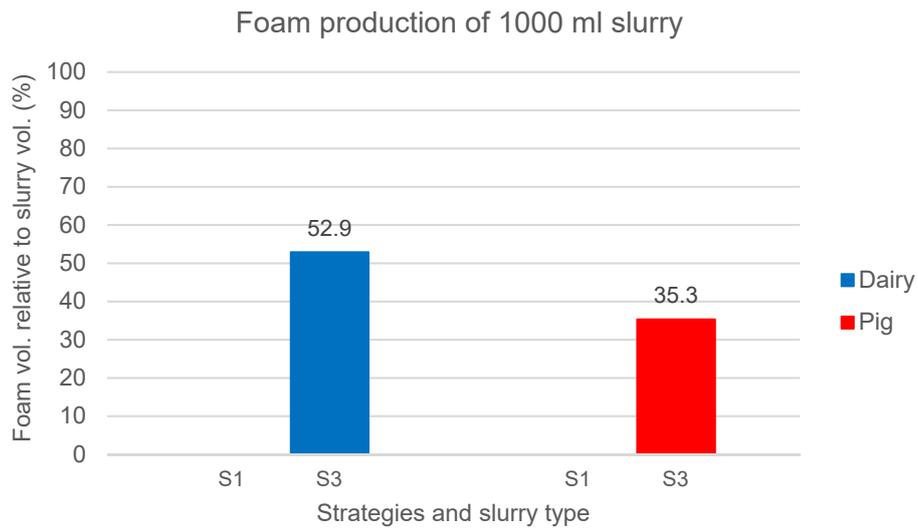


Figure 25. Foam production for both dairy and pig slurry between Strategy 1 and 3. Acid had been added successively during ten times for two weeks with Strategy 1 and two times during the two weeks with Strategy 3. No foam production occurred for Strategy 1 and for Strategy 3 it was major and medium for dairy and pig slurry respectively (n=4).

## 4 Discussion

### 4.1 Acid consumption between strategies

The results showed significant differences between strategies in sulfuric acid ( $\text{H}_2\text{SO}_4$ ) consumption, that was required to lower the pH level of dairy and pig slurry to 5.5 (Figure 20-23). Strategy 2 required least amount of acid in all comparisons except when two weeks had passed for dairy slurry, then no significant difference occurred between Strategy 1 and 2. However, the pH level of the total amount of dairy and pig slurry in storage was not reduced after addition of newly acidified slurry to the previously acidified slurry, during the performance of Strategy 2 (Figure 15). If pH would have been kept at 5.5 in storage as well, the acid consumption by dairy and pig slurry might have been higher during the first two weeks, when performing Strategy 2 compared to Strategy 1 and 3. Nevertheless, the acid consumption of Strategy 2 was significantly lower than Strategy 3 during 15 weeks, even including the last performed acidification in storage to lower the pH level to 5.5 (Figure 22-23). This is probably because the total amount of slurry in storage was in a less acidified condition since the pH level was not repeatedly reduced to 5.5 in Strategy 2 compared to Strategy 3. Under acidified conditions, hydrolysis of carbohydrates is accelerated and shifts from being microbially catalyzed to chemically catalyzed (Hjorth et al., 2015). However, the pH level was already over 6.0 for both slurries during the third week and continued to increase (Figure 15). Therefore, hydrolysis of carbohydrates probably decelerated and shifted back to being microbially catalyzed. This is most certainly the case for pig slurry which had a higher pH level than dairy slurry. In Strategy 3 both slurries were re-acidified as soon as the pH elevated back to 6.0 and were kept at an acidified state. Therefore, hydrolysis of carbohydrates was most likely always chemically catalyzed and more rapid in Strategy 3, where acid was more frequently added in storage compared to Strategy 2. There was no significant difference in acid consumption between Strategy 1 and 3 during the first two weeks. This indicate that acid consumption was not increased

because of a more frequent acid addition to the slurry, but rather because pH of the slurry was repeatedly reduced enough for the hydrolysis to be accelerated.

## 4.2 Evolution of pH and ammonia emission

The frequent acid additions in the pump pit in Strategy 1 seems to have a stabilizing effect on pH level of the cumulative amounts of dairy and pig slurry. This is seen in Figure 11, where the pH level before each performed acid addition of both slurries was steadily decreasing from the fifth addition and approaching the target value of 5.5. One week after acidification stopped, the pH of both slurries in storage was still at a similar level very close to 5.5, but after that it started to rapidly increase (Figure 12). After four weeks, the pH level of pig slurry was more than 6.5 and continued to increase resulting in a risk for increasing ammonia ( $\text{NH}_3$ ) emissions. In Strategy 2, where acid was added to slurry only once per week in the pump pit just before transferring it to storage, the pH level never stabilized at the target value of 5.5 in storage. It did however stabilize at 6.1 and 6.5 for dairy and pig slurry, respectively, during six weeks from the third to ninth week in Strategy 2 (Figure 15). The increase of pH in storage is unfavorable since it increases the risk for increasing  $\text{NH}_3$  emissions. On the other hand, the maximum pH of acidified dairy and pig slurry was 6.4 and 6.8 respectively and was obtained first after 13 weeks (Figure 15). Theoretically this shouldn't pose a risk for a rapid increase of  $\text{NH}_3$  emissions, according to the equilibrium state between  $\text{NH}_4$  and  $\text{NH}_3$  (Figure 1). This is supported by previous studies performed by Petersen et al (2012), where  $\text{NH}_3$  emissions of acidified dairy slurry increased from 8% to only 12% relative to non-acidified slurries when pH increased from 5.5 to 6.5 during 13 weeks. In another study performed by Regueiro et al (2016), the increase in  $\text{NH}_3$  emissions were negligible when the pH level increased from 5.5 to 6.8 for both dairy and pig slurry.

Also, in Strategy 3, the pH level didn't stabilize no matter how many re-acidifications were performed. It increased from 5.5 to 6.0 at approximately the same rate for dairy and pig slurry, respectively, during all 15 weeks (Figure 18-19). The only exception was after the first re-acidification for dairy slurry, where the pH increase took twice as long (Figure 18). The slower pH increase could be due to a deceleration of the dissolution of  $\text{CO}_3^{2-}$ , caused by the depletion of precipitated  $\text{CaCO}_3$ , and that degradation of VFA and mineralization of N were still impeded by the acidification. However, why the pH never stabilized is probably due to the accelerated hydrolysis of carbohydrates occurring after every re-acidification. Degradation of VFA and mineralization of N may have occurred between re-acidifications as well when the pH level was closer to 6.0. This would also explain how the pH increased

at the same rate, even though the buffer capacity of both slurries decreased with every week and consequently decreased the required amount of acid (Figure 17-19).

### 4.3 Slurry characteristics effect on acid consumption

Pig slurry had a stronger buffer capacity than dairy slurry during the first week in all strategies, since the required volume of acid per each pH unit decrease was higher for pig slurry. Nevertheless, no difference in acid consumption was observed between dairy and pig slurry in any of the strategies when the first week passed. After two weeks, dairy slurry had consumed more acid than pig slurry in all strategies which is shown in Figure 10, 13 and 17. This is probably because of the lower initial pH level in samples of pig slurry, due to a higher content of VFA. Furthermore, the buffer capacity was at a similar level between dairy and pig slurry after the first week. However, the acid consumption by pig slurry exceeded dairy slurry during the fourth week with the performance of Strategy 3 and the difference between them increased with every passing week (Figure 17). Pig slurry also exceeded dairy slurry in acid consumption when the last acidification was performed in Strategy 2 (Figure 16). The stronger buffer capacity of pig slurry during the first week can be explained by the pig's diet and the characteristics total N and  $\text{Ca}^{2+}$  of both slurries, shown in Table 1. As mentioned earlier, pig slurry is expected to contain more VFA than dairy slurry, but also more total N since their diet mainly consisted of cereals with 20% peas and to smaller amounts of soybean. This is indeed verified by Table 1 where the total N for pig slurry is 25% higher than for dairy slurry. Pig slurry also contains more  $\text{Ca}^{2+}$  than dairy slurry with approximately 36%, which is contradictory to the statement made by Sommer et al. (2013) that dairy slurry contains 2-3 times more base cations. However, the pig's diet was complemented with premix, which is a mixture of amino acids and minerals and could be the reason for the higher content of  $\text{Ca}^{2+}$  resulting in a higher content of precipitated  $\text{CaCO}_3$ . With these characteristics it's reasonable that dissolution of carbonates would be more driven in pig slurry than dairy slurry during the first week. They also explain the higher consumption of acid by pig slurry in Strategy 2 and 3, since they would contribute with more rapid pH increases after acidification resulting in a higher pH level.

An important issue that should be considered is that dairy and pig slurry in this study were collected from only one farm each. Thus, even if pig slurry required more acid than dairy slurry in this experiment, it is not an absolute fact and will of course depend on what kind of diet the animals receive. A similar experiment to Strategy 3 was performed by Joubin (2018), where dairy and pig slurry was acidified with  $\text{H}_2\text{SO}_4$  to lower and keep the pH level to 5.5 during two months. In this experiment

there were no significant difference in acid consumption between dairy and pig slurry.

#### 4.4 Acid addition rate and foam production

Foam production was much less when acid was added daily to dairy and pig slurry in Strategy 1 compared to when acid was added once a week in Strategy 2 and 3 (Figure 24-25). Level of foaming was already irrelevant during the second acid addition in Strategy 1, since only 5.6% and 6.2% volume of foam was produced for 200 ml dairy and pig slurry respectively. The foam production in Strategy 2 was not at any extreme level, but it was high enough to reduce the capacity of the pump pit with 13-18%. However, the following 200 ml samples collected from the refrigerator each week during 15 weeks had an increasing level of foaming, because of the increasing required amount of acid (Figure 14). After five weeks, the level of foaming was major for both dairy and pig slurry and after 10 weeks it was extreme. After ten successive acid additions in the pump pit, no production of foam occurred for 1000 ml dairy and pig slurry in Strategy 1. In Strategy 3, the same volume of dairy and pig slurry in storage had a foam production of 52.9% and 35.3% of the slurry volume, respectively, after two acid additions. The major level of foaming that occurred for dairy slurry in Strategy 3 implies that only 60% of the storage capacity could be used, otherwise the foaming would be unmanageable. These results indicate that when acid is frequently added to smaller amounts of slurry while filling the pump pit or storage, the risk of excessive foaming is greatly reduced compared to when acidifying in the pump pit or storage once their filled.

#### 4.5 Missing factors in lab-scale

The simulation of Strategy 3 in the lab scale was differing a little from the suggested method of acidification during storage of slurry. In Strategy 3, the same batch of slurry was re-acidified every week if pH elevated back to 6.0, but there was never any transfer of new slurry from the pump pit to the storage. However, even if fresh slurry were transferred to the storage every week, the results regarding acid consumption would probably be the same. This is because accelerated hydrolysis would still be initiated by all re-acidifications to keep the pH level under 6.0. This is also supported by Strategy 1 which resembles a similar simulation, since slurry is re-acidified in the pump pit when acid is added to a mixture of fresh and previously acidified slurry. The only difference is that the re-acidification occurred each day in the pump pit instead, but there was no significant difference in acid consumption after two weeks between Strategy 1 and 3 (Figure 21). The performance of Strategy

3 also showed clear results that the pH level didn't stabilize at 5.5 for the same batch of slurry, no matter how many re-acidifications were performed.

There are also other factors that are not accounted for when performing the strategies in lab-scale compared to if they would have been performed in full-scale, such as temperature changes, wind speed etc. The temperature for instance in the lab room was constant at approximately 20°C, which resulted in a temperature range of 19-21°C for all samples of slurry during the whole experiment for 15 weeks. Such a high temperature does not represent an average temperature in Sweden which normally is under 10°C during storage of slurry (Rodhe et al., 2009, 2012). A higher temperature will result in a more rapid pH increase, which causes an increase in NH<sub>3</sub> emissions as well (Misselbrook et al., 2016). This is probably because chemical and microbial activity are increasing with increasing temperature, which means that buffer capacity and pH increase will be faster. Therefore, the acid consumption by all strategies would most likely be lower if they would be performed in full-scale. This is supported by a study performed by Rodhe et al., (2018) where the pH level of fresh slurry was lowered with H<sub>2</sub>SO<sub>4</sub> to 5.0 in a pilot-scale with an air temperature of 13°C and to 5.5 in lab-scale at 20°C. The required amount of concentrated sulphuric acid (96%) was 1.15 L/m<sup>3</sup> of slurry in the pilot-scale and 2.5 L/m<sup>3</sup> in the lab-scale. Furthermore, the pH level of slurry in the pilot-scale, after acidification, remained within a range of 5.3-5.7 during storage between 1 May and 29 August with an average temperature of 13°C. Therefore, re-acidification in storage will most likely not be necessary during the winter season and acidification in the pump pit once per week performed in Strategy 2 will suffice to mitigate NH<sub>3</sub> emissions. On the other hand, the acid consumption between Strategy 1 and 2 may be similar as well if there is no pH increase. Strategy 1 would then be more suitable regarding less excessive foam production. However, when spring approaches and the temperature increases, the rise of pH and NH<sub>3</sub> emissions need to be accounted for.

## 4.6 Future research and recommendations

H<sub>2</sub>SO<sub>4</sub> is an effective additive to utilize for slurry acidification, but it's not allowed in organic farming (Joubin, 2018). However, organic acids such as acetic acid and citric acid are allowed and could be a good alternative to H<sub>2</sub>SO<sub>4</sub>. Previous studies performed by Regueiro et al. (2016) have shown that acetic acid and citric acid, are as efficient as sulfuric acid to lower the pH level of slurry to 5.5. Simulations on how to efficiently implement slurry acidification with these organic acids should be performed to identify a practical method for organic farmers to mitigate NH<sub>3</sub> emissions. Furthermore, stirring slurry increases the NH<sub>3</sub> emissions according to Dai and Blanes-Vidal (2013). This might be because of a promoted aerobic degradation of

VFA suggested by Joubin (2018) and would explain the pH increase of non-acidified slurries in all strategies (Figure 12, 15, 18 and 19). Future simulations of slurry acidification should consider excluding stirring of slurry and pH measurement should be performed at different depths at several locations in the container to receive a representative pH value.

## 5 Conclusion

The results of this experiment showed that Strategy 2 required least amount of acid compared to Strategy 1 and 3 in all comparisons except when two weeks had passed for dairy slurry, then no significant difference occurred between Strategy 1 and 2. No significant difference in acid consumption occurred between Strategy 1 and 3 during the first two weeks, even if acid was added to slurry more frequently in Strategy 1. The frequent acid additions in the pump pit in Strategy 1 was only able to keep the pH level of slurry in storage close to 5.5 one week after acidification stopped, but after that the pH increased rapidly. The pH level didn't stabilize at 5.5 in storage during the performance of Strategy 2 or 3. No matter how many re-acidifications were performed in Strategy 3, the pH level didn't stabilize. Instead it increased from 5.5. to 6.0 at approximately the same rate during all 15 weeks. Foam production was much less when acid was added daily to slurry in Strategy 1 compared to when acid was added once a week in Strategy 2 and 3. These results contribute with following answers to the hypotheses:

- i) Acid consumption was not greater because of a more frequent addition to slurry, but rather because pH was repeatedly reduced low enough to keep an accelerated hydrolysis of carbohydrates.
- ii) pH did not stabilize after several re-acidifications and kept increasing with the same rate.
- iii) pH did not stabilize faster when addition of acid was more frequent.
- iv) Frequent acid addition minimized the foam production and saved the storage capacity.

The most recommended strategy to use regarding lowest amount of acid to control  $\text{NH}_3$  emissions is Strategy 2, but the increasing pH in storage would need to be checked regularly. Re-acidification might be needed depending on the ambient temperature affecting the pH evolution of slurry. Strategy 1 was most practical regarding minimized risk of excessive foam production, but it does require a greater amount of acid compared to Strategy 2. Strategy 3 is not really a practical procedure to be implemented on its own, instead it should be combined with Strategy 1 or 2.

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