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#### DOCTOR OF PHILOSOPHY

The impact of slurry acidification on soil and crop quality: a UK case study

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Award date: 2022

Awarding institution: Bangor University

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## The impact of slurry acidification on soil and crop quality: A United Kingdom case study



# prifysgol BANGOR university

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(2022)

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#### **Declaration**

I hereby declare that this thesis is the results of my own investigations, except where otherwise stated. All other sources are acknowledged by bibliographic references. This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree unless, as agreed by the University, for approved dual awards.

Yr wyf drwy hyn yn datgan mai canlyniad fy ymchwil fy hun yw'r thesis hwn, ac eithrio lle nodir yn wahanol. Caiff ffynonellau eraill eu cydnabod gan droednodiadau yn rhoi cyfeiriadau eglur. Nid yw sylwedd y gwaith hwn wedi cael ei dderbyn o'r blaen ar gyfer unrhyw radd, ac nid yw'n cael ei gyflwyno ar yr un pryd mewn ymgeisiaeth am unrhyw radd oni bai ei fod, fel y cytunwyd gan y Brifysgol, am gymwysterau deuol cymeradwy.

#### Acknowledgements

I would like to thank my supervisors Dave Chadwick, Davey Jones, and Tom Misselbrook for their continued support and guidance throughout my PhD, as well as the wider project team John Williams, Rachel Thorman and Dom Edwards (ADAS), and Sarah Gilhespy (Rothamsted Research). Working in such a supportive research group enabled me to continually develop throughout my studies.

Without the support from the College of Environmental Sciences and Engineering I would not have been able to continue with my experimental work throughout the Covid-19 pandemic. Working in such "unprecedented" times was a challenge, but made easier with the College's support.

Joseph Cotton provided a vast amount of technical support for the project, and endless enthusiasm when carrying out hundreds of chemical extractions each day during the fieldwork season. Llinos Hughes, Mark Hughes and Ian Harris provided a wealth of knowledge and support.

I am grateful for the help and support from the technicians at the Environment Centre for Wales, Jonathon Roberts and Sarah Chesworth. Their help and support enabled me to successfully complete all my analysis. I would like to thank all ECW colleagues who assisted with slurry application and grass harvesting.

Finally, I would like to thank my family for their support throughout the period, especially my wife Ruthie who continually supported, listened and provided all the support I could have needed throughout my studies. With Ruthie's support, everything was achievable.

#### <u>Abstract</u>

The United Kingdom has set legally binding targets to reduce ammonia (NH<sub>3</sub>) emissions by 16% in 2030, based on a 2005 baseline. The latest inventory found that agriculture is responsible for approximately 90% of total UK NH<sub>3</sub> emissions, with the manure management continuum contributing 60% of agriculture emissions. Such a loss of NH<sub>3</sub> must be targeted if the 2030 target is to be achieved, but also to improve farm sustainability as NH<sub>3</sub> emission represents a significant loss of nitrogen (N) from manures. Current Best Available Techniques (BAT) of reducing agricultural NH<sub>3</sub> emissions include slotted animal housing floors, slurry store covers, and slurry injection, all of which can be prohibitively expensive. Slurry acidification, the process of adding concentrated acid to slurry, altering the slurry pH to adjust the NH<sub>3</sub>:NH<sub>4</sub><sup>+</sup> ratio strongly in favour of NH<sub>4</sub><sup>+</sup>, is commonly used in Denmark and has been found to successfully reduce NH<sub>3</sub> emissions at all stages of the manure management continuum. However, little research has been carried out on the impact of acidified slurry on soil and crop quality from a UK perspective. This Defra funded research focused on one of five national trial sites, aimed to assess the potential of including slurry acidification in the farmer toolkit to help achieve the UK NH<sub>3</sub> reduction targets.

This study is comprised of multiple experimental chapters furthering the understanding of the impacts of slurry acidification on soil and crop quality, as well as providing policy-targeted research investigating the most efficient means to undertake acidification. The study begins with an overall introduction outlining the work undertaken (Chapter 1), as well as a literature review which explores the current literature within the research topic and establishes knowledge gaps within the current research (Chapter 2). Chapter 3 details a multi-year field experiment assessing the impact of acidified cattle slurry compared to a conventional cattle slurry, both applied by surface broadcast and band spread. This chapter also included nitrogen response plots  $(0 - 150 \text{ kg N ha}^{-1})$ , to assess fertiliser replacement values of acidified slurry. The experiment was carried out over 2 years and represented 4 single applications, spring and summer of each year, as well as plots which received repeated application of up to four applications (ranging from  $67 - 125 \text{ kg N ha}^{-1}$ ). The latter was used to assess any long term and residual impacts of applying acidified slurry. Soil chemistry - including soil pH, electrical conductivity, inorganic N and P - soil biology – including micro-, meso-, and macro-fauna, soil respiration, and greenhouse gas emissions – and soil physical characteristics were all analysed. Overall, Chapter 3 found that there were no long-term impacts of acidified slurry on either soil or crop quantity over a 2 year period. Soil pH was found to reduce by up to 0.75 units when compared to the control, directly under the band in band spread plots, but was buffered to control levels by the end of each growing period. Plots receiving acidified slurry were found to have greater soil

concentrations of  $NH_4^+$  without increasing  $NO_3^-$ . Consequently, this resulted in numerically greater N fertiliser replacement values (NFRV), and N use efficiency (NUE) by up to an additional 50%.

Alongside the field experiments, multiple bench scale experiments were carried out (Chapter 4). This included two different experiments using a Desktop Ammonia Volatilisation System (DAVoS) in combination with intact soil cores. These experiments assessed the impact of using different slurry pH levels on NH<sub>3</sub> emissions, greenhouse gas emissions, and soil inorganic N. The typical pH target for Danish in-house acidification, pH 5.5, was found to be a compromise between NH<sub>3</sub> emission reduction and the pH of slurry applied. At pH 5.5, NH<sub>3</sub>-N loss was found to be 17% of NH<sub>4</sub>-N applied, significantly lower than pH 6.5 (33%) and conventional slurry (39%), while greenhouse gases did not significantly increase. A further experiment using the DAVoS compared different application techniques in combination with acidification. Surface broadcast conventional slurry represented current UK agricultural standard practice, while shallow injection represented the BAT option for farmers. When applied in combination with acidification the results presented indicate that over a 14day period, cumulative NH3 emissions from acidified surface broadcast cattle slurry were not significantly different from conventional injection. Both methods were found to have a NH<sub>3</sub> loss of 3% of total N applied without significantly increasing short-term N<sub>2</sub>O emissions. As found in the field experiments, the DAVoS experiments showed an increase in soil solution NH<sub>4</sub><sup>+</sup> in acidified cores. The increase in soil NH4<sup>+</sup> was also found in Chapter 5. Here, repacked soil cores had acidified slurry applied and were analysed at a micro-scale using a microtome over a 42-day period. NH<sub>4</sub><sup>+</sup> was found to be contained within the top 25 mm of cores for the entire period, while a clear inhibition of nitrification occurred with conventional slurry having greater peak NO<sub>3</sub><sup>-</sup> concentrations (2861 mg NO<sub>3</sub>-N kg<sup>-1</sup>) compared to acidified slurry (2173 mg NO<sub>3</sub>-N kg<sup>-1</sup>).

The final experimental (Chapter 6) took on a policy-driven approach where slurry buffering was assessed in direct response to recommended acid quantities  $(2.2 \text{ kg t}^{-1} \text{ slurry})$  added to slurry in Danish in-field acidification. This study found that the Danish recommend quantity would on average reduce a 20 UK sample of cattle slurries by pH 0.7, and a more appropriate quantity of acid for UK slurries would be 8 kg t<sup>-1</sup> slurry. However, this represents an average value, with the key conclusion from Chapter 6 being that the unique nature of pH buffering in each slurry will require a different dose of acid.

Overall, slurry acidification was found to have limited medium- to long-term impacts on soil and crop quality in the UK. The experiments included in the study highlighted the potential of the technology to reduce  $NH_3$  emissions whilst increasing soil  $NH_4^+$  without increasing  $NO_3^-$  concentrations and  $N_2O$ 

emissions. Such evidence is supported by increased NFRV and NUE in plots receiving acidified slurry at each harvest. This research supports the inclusion of slurry acidification in a farmer's toolkit as an option to reduce NH<sub>3</sub> emissions.

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### Abbreviations

BAT - Best Available Techniques	N <sub>2</sub> O - Nitrous oxide
C - Carbon	NECR - National Emissions Ceiling
Ca - Calcium	Regulations
CH <sub>4</sub> - Methane	NFRV - Nitrogen Fertilliser Replacement Value
CO <sub>2</sub> - Carbon dioxide	NH <sub>3</sub> - Ammonia
CO <sub>2eq</sub> - Carbon dioxide equivalent	NH4 <sup>+</sup> - Ammonium
CP - Crude protein	NMVOC - Non-Methane Volatile Organic
DAVoS - Desktop Ammonia Volatilisation	Compound
System	$NO_3^-$ - Nitrate
Defra - Department for Environment, Food, and Rural Affairs	NUE - Nitrogen Use Efficiency
DiH <sub>2</sub> O - Deionized water	NVZ - Nitrate Vulnerable Zone
DM - Dry Matter	PO <sub>4</sub> <sup>3-</sup> - Phosphate
EC - Electrical Conductivity	P - Phosphorus
H <sup>+</sup> - Hydrogen ions	$PM_{2.5}$ - Fine (2.5 $\mu$ m) particulate matter
H <sub>2</sub> S - Hydrogen sulphide	Ppb - Parts per billion
H <sub>2</sub> SO <sub>4</sub> - Sulphuric acid	S - Sulphur
H <sub>3</sub> PO <sub>4</sub> - Orthophosphoric acid	TAN - Total Ammoniacal Nitrogen
IPCC - Intergovernmental Panel on Climate	TOC - Total Organic Carbon
Change	VESS - Visual Evaluation of Soil Structure
K - Potassium	VFA - Volatile Fatty Acid
Mg - Magnesium	WFPS - Water Filled Pore Space
N - Nitrogen	μS - Microsiemens

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#### Chapter 1: Introduction

#### 1.1 Background

The application of organic manures as a fertiliser has long been recognised as a mechanism to increase crop yields and productivity through the supply of key nutrients including nitrogen (N) and phosphorus (P), as well as supplying carbon (C) to the soil. However, the mismanagement of organic manures can lead to significant losses, including increased ammonia (NH<sub>3</sub>) volatilisation (Bell et al., 2016), nitrate (NO<sub>3</sub>) leaching and P losses (Zhang et al., 2017), as well as gaseous emissions such as nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>), both of which significantly contribute to global warming (IPCC, 2021; Petersen et al., 2007). Agriculture significantly contributes to greenhouse gas emissions and air pollution in the UK, and is responsible for approximately 48% of CH<sub>4</sub> emissions, 65% of N<sub>2</sub>O emissions (Defra, 2021a), and approximately 90% of total NH<sub>3</sub> emissions (Misselbrook and Gilhespy, 2021). Not only do these represent losses to the environment that can result in continued climate change, environmental degradation (Greaver et al., 2016) and impact human health (Paulot and Jacob, 2014), but the loss of  $NH_3$ ,  $NO_3^-$ , and to a lesser degree  $N_2O_3$ , also represents a loss of N available for plant uptake. Furthermore, the UK Government has legal obligations to reduce its emissions of greenhouse gases, in line with the Kyoto protocol and the UK net zero target for 2050, and air pollutants as outlined in the National Emissions Ceiling Regulations (NECR) (HM Government, 2018a). The latter legally binds the UK to reduce NH<sub>3</sub> emissions by 16% by 2030.

Given the contribution to NH<sub>3</sub> emissions from agriculture, various adaptions have been recommended through the use of Best Available Techniques (E.U., 2017) to reduce gaseous losses. Specifically for cattle management, these include the use of grooved floors in housing, covering slurry during storage, and using low emission methods at application such as band spreading and injection (Loyon et al., 2016). However, these can be prohibitively expensive and the applicability of each will vary between farms, given physical and climatic variations (Wagner et al., 2015). Slurry acidification is an additional strategy in the toolbox for some European farmers, to address NH<sub>3</sub> losses at all stages of the manure management continuum, and is becoming a subject of interest in the UK.

Adjusting the pH of slurry is not a new theory, with an early acknowledgement of the principle being noted in 1938 where the addition of acid was found to "inhibit bacteria and ammonia fixers" in organic manures (Salter and Schollenberger, 1938). The understanding surrounding the basic principle of combining acid with slurry has developed since 1938, with the addition of acid, e.g. H<sub>2</sub>SO<sub>4</sub>, now understood to shift the total ammoniacal N ratio strongly in favour of NH<sub>4</sub><sup>+</sup> rather than NH<sub>3</sub>. This results in a product with greater readily available N for plant uptake, and reduced potential

for NH<sub>3</sub> volatilisation and leaching (Berg et al., 2006b; Cocolo et al., 2016; Fangueiro et al., 2015a; Misselbrook et al., 2016; Park et al., 2017; Sommer et al., 2017). Technological advances since the latter parts of the 20<sup>th</sup> century, and the increasing demands on governments to reduce NH<sub>3</sub> emissions from agriculture has seen slurry acidification become the focus of numerous studies, featuring in recent reviews (Emmerling et al., 2020; Fangueiro et al., 2015a).

Denmark have been leaders in the development of commercial slurry acidification technologies, with recent estimations predicting that up to 20% of all slurry produced in Denmark was acidified prior to application (Toft and Madsen, 2019). Various technologies are used to acidify slurry at all stages of the cattle and pig manure management chain with the process at each stage outlined below (Birkmose and Vestergaard, 2013; Edesi et al., 2020; Fangueiro et al., 2015a; Hjorth et al., 2015; Pedersen et al., 2022; Wagner et al., 2021):

- <u>In-house</u>: slurry is removed from underneath slats daily and mixed with acid in a pre-storage tank. A quantity is pumped back into the animal building and stored under slats to minimise emissions; the remainder is removed to storage and is deemed long-term acidification with a target pH of 5.5
- <u>In-storage</u>: acid is mixed with slurry in the store until the desired pH of pH 6 is reached. The timing of in-storage acidification can vary from shortly after arrival in the tank to immediately prior to application, with greater abatement potential earlier on in storage.
- <u>In-field</u>: acid is pumped through to the slurry tanker and added to the slurry during application in order to reduce slurry to a target pH, e.g. 6.4 in Denmark. This is considered a short-term acidification.

Similar to other technologies, the use of in-house acidification can be prohibitively expensive, leading to a greater uptake in less capital intensive techniques especially contactor delivered application acidification, often using Syre-N systems which accounted for 15% of all acidified slurry (Toft and Madsen, 2019).

Extensive research has been carried out as to the effectiveness of slurry acidification on reducing NH<sub>3</sub> emissions at various stages of the manure management continuum. Authors have reported NH<sub>3</sub> emissions reductions of up to 75% in-house, 70-98% during storage and 95% at application (Eriksen et al., 2008; Fangueiro et al., 2015c; Gioelli et al., 2016; Hjorth et al., 2015; Hou et al., 2017; Petersen et al., 2016b, 2016a; Sommer et al., 2017; ten Hoeve et al., 2016). Regardless of the stage at which slurry acidification occurs and the target pH employed, there is a risk of soil pH change, N pollution

swapping and changes to microbial communities due to changes in slurry composition. However, no studies have researched the combined impact of acidified slurry on soil and crop health in UK conditions. This UK Defra funded PhD aims to address this knowledge gap to provide an understanding as to the potential to include the technology as a means to reduce NH<sub>3</sub> from UK agriculture.

#### 1.2 Aims

The broad aim of the study was to assess if there are any detrimental impacts of using slurry acidification on soil and crop quality in the UK. An important consideration is the potential role of N pollution swapping through the abatement of  $NH_3$  and consequently forms a further aspect of the study, to research the potential of increased  $N_2O$  emissions due to  $NH_3$  abatement from slurry acidification.

In order to address the overarching aim of the study, the following hypotheses will be assessed.

- a) The use of acidification will have no long-term detrimental impacts on soil and crop health. Given the underlying principle of acidification, shifting total ammoniacal N ratio in favour of NH4<sup>+</sup>, it is hypothesised that crop yields will increase following application of acidified slurry, while soils are hypothesised to buffer any changes in pH following the application of acidified slurry.
- b) The use of acidification will not result in increased N losses as a result of N pollution swapping. As acidification reduces  $NH_3$  losses by increasing  $NH_4^+$  through the addition of  $H_2SO_4$ , it is possible to expect an increase in other forms of N losses including  $NO_3^-$  and  $N_2O$ . Yet the microbial processes of nitrification and denitrification are hypothesised to be delayed due to a change in soil pH following the application of acidified slurry and allow  $NH_4^+$  to be plant-available for an extended period.
- c) Slurry application technique will not detrimentally impact the suitability of acidification as an NH<sub>3</sub> abatement technique. Given the known benefits of using alternative application techniques such as band spreading or slurry injection, it is hypothesised that combining slurry acidification and low emission techniques will not result in increased N losses (NO<sub>3</sub><sup>-</sup> and N<sub>2</sub>O) through nitrification and denitrification.
- d) A target pH of 5.5 is key to fully utilise the NH<sub>3</sub> abatement potential of slurry acidification. The use of pH 5.5 is used as the commercial target for in-house acidification systems in Denmark as a compromise between costs and NH<sub>3</sub> abatement. Therefore, it is hypothesised that the greatest abatement of NH<sub>3</sub> will be found at pH values of 5.5 or below.

#### 1.3 Thesis structure

The following thesis is formed of 8 chapters, with chapters 3-6 outlining experimental research carried out to address the above aims and objectives, and presented in the format of journal articles to be submitted. The relationship between each experimental chapter is outlined in Figure 1.1, with an overview of each chapter presented below.

#### - <u>Chapter 2 – Literature review.</u>

The chapter details the impacts of nutrient losses from the application of organic fertilisers including eutrophication, ecosystem acidification, human health implications and contributions to greenhouse gas emissions. The chapter then proceeds to outline current national and international legislation to address NH<sub>3</sub> emissions with a specific emphasis on the measures being utilised by the agriculture sector at all stages of the manure management continuum. Following this, a detailed insight into the current research surrounding slurry acidification is presented which outlines the basic principle of acid providing an additional H<sup>+</sup> ion, shifting the TAN ratio strongly in favour of NH<sub>4</sub><sup>+</sup>. A summary of the most effective acid to deliver the optimum pH is also provided, alongside the impact of acidification is then provided for current research on the impact on soil and plant health before the chapter concludes with gaps in knowledge identified through the completion of the literature review.

## - <u>Chapter 3 – Slurry acidification does not negatively impact soil and crop quality: a UK field</u> study.

The aim of the chapter was to assess the impact of slurry acidification on soil and crop quality from a UK field experiment, after single and multiple applications. Cattle slurry was applied at 40 m<sup>3</sup> ha<sup>-1</sup> by 2 application techniques, surface broadcast and band spread, to grassland plots in a randomised block design alongside various N response plots to assess fertiliser replacement value of the treatments. This experiment ran over 2 years, 2019 and 2020, where regular sampling took place to measure soil health, including pH, EC, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub>, as well as biological indicators such as micro-, meso-, and macro-fauna, and soil respiration. Greenhouse gas sampling was included for the 2020 season to assess the potential impact of N pollution swapping. Grass quality was determined at timely harvests, with dry matter content, N-offtake, nitrogen use efficiency (NUE) and nitrogen fertiliser replacement value (NFRV) measured.

 <u>Chapter 4 – Slurry acidification is as effective as slurry injection at reducing ammonia</u> emissions: a mesocosm study.

A desktop ammonia volatilisation system (DAVoS) was created to accurately measure  $NH_3$  loss from intact soil cores receiving various treatments. This chapter consists of 2 experiments with experiment 1 assessing the relationship different target pH's have on  $NH_3$  emissions, greenhouse gas emissions and soil N. The second experiment looks at the efficacy of slurry acidification compared to the BAT recommended technique of slurry injection. Regular measurements were taken during both experiments utilising acid traps for  $NH_3$  measurements, headspace sampling for greenhouse gases, and Rhizons<sup>TM</sup> for soil pore water concentrations of  $NH_4^+$  and  $NO_3^-$ .

 <u>Chapter 5 – Soil quality is most affected in the zone surrounding the nitrogen amendment: a</u> micro study.

Given the findings presented in chapters 3 and 4, this experiment was targeted at assessing the impact of acidified slurry at micro scale, over a period of time matching a summer grass growing season. The aim was to identify if there were sections of a soil core that was impacted to a greater extent following the surface application of acidified and conventional slurries and ammonium nitrate. Cattle slurry was acidified to pH 5.5 and applied at the rate of 40 m<sup>3</sup> ha<sup>-1</sup> alongside conventional slurry and ammonium nitrate, matching the total N content of the slurry treatments. A microtome was used to enable accurate micro measurements from a re-packed soil core, where slices of soil were removed at various depth intervals, from 2 mm – 10 mm, and analysed for pH, EC,  $NH_4^+$ ,  $NO_3^-$ , as well as TOC.

# - <u>Chapter 6 – Slurry acidification requires the addition of acidifying agents at an individual</u> scale to maintain the balance between soil and slurry buffering potential: a lab experiment.

The final experimental chapter was designed to address the buffering potential of individual slurries. The importance of slurry buffering has a direct consequence for policy whereby a set recommended addition of acid, as introduced in Denmark, does not take into account the individual buffering properties of each slurry. A result of this work was that each slurry has a different acid requirement to reach a target pH. To assess soil buffering, acidified slurry was added in various ratios to soil to assess the ability of the soil to buffer any pH changes as a result of the addition of acidified slurry.

#### Chapter 7 – Discussion

The discussion chapter synthesises the outcomes of the study in line with findings from the literature and the impact these have on the suitability of slurry acidification as a NH<sub>3</sub> abatement technique, as well as its limitations and recommendations for future work.

#### - Chapter 8 – Conclusions

The final chapter summarises the work completed in the thesis.



Figure 1.1: Schematic diagram of PhD thesis

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#### Chapter 2: Literature review

#### 2.1 Introduction

Access to cheap, inorganic fertilisers has increased food productivity and created increasingly industrialised, profitable and efficient agriculture units. However, a shift to synthetic fertilizer use has reduced the optimal utilisation of animal manures (Blackstock et al., 2010; Erisman et al., 2008; Gómez-Muñoz et al., 2016; Hou et al., 2018; Ottosen et al., 2009). Such an approach is problematic given inappropriate manure management results in environmental degradation, negatively impacting the sustainability of livestock production (Amon et al., 2006; Fangueiro et al., 2015c, 2016; Hou et al., 2017b; ten Hoeve et al., 2014, 2016; Yuan et al., 2018). Substitution of synthetic fertilisers with bio-based fertilisers has been identified as a way to make waste streams more sustainable, with livestock slurries used to provide nitrogen, phosphate, and potassium, to plants (Fangueiro et al., 2017; Sigurnjak et al., 2017). The application of animal waste as a N fertiliser replacement utilises the approximate 83 million tonnes of manures produced annually from housed livestock in the UK, 34 million tonnes of which are produced as undiluted slurry and 49 million tonnes as solid manures (Smith and Williams, 2016).

The management of livestock manures can have a detrimental impact to climate change, via the release of greenhouse gases, as well as air quality, especially through ammonia (NH<sub>3</sub>) volatilisation. Current NH<sub>3</sub> emissions are concentrated in the northern hemisphere but global emissions are estimated to double with increasing intensification of livestock production (Erisman et al., 2007; Philippe et al., 2011; Velthof and Mosquera, 2011). In the UK, the agriculture sector is responsible for an estimated 90% of total NH<sub>3</sub> emissions, with livestock housing and manure application the source of 60% of the agricultural sectors emissions (Figure 2.1). Huijsmans et al. (2016) identified the need to reduce NH<sub>3</sub> emissions due to the associated environmental degradation, increased N deposition and indirect N<sub>2</sub>O emissions, as well as improving N content of manures (Seidel et al., 2017). Ultimately, sustainable agriculture must aim to make optimal use of applied nutrients as current farming practises represent an environmental and economic threat due to high losses (Bhandral et al., 2009; McGechan and Wu, 1998).

#### 2.1.1 Environmental and health implications of current management

The use of livestock slurries can negatively impact environmental, human and animal health, and can contribute to the excessive build-up of soil nutrients, and the release of greenhouse gases.  $NH_3$  has been identified as indirectly increasing atmospheric  $PM_{2.5}$  concentrations and acidifying habitats when deposited (Bacenetti et al., 2016; Dai and Blanes-Vidal, 2013; Erisman et al., 2007; Goss et al., 1995; Guerci et al., 2013; McGechan and Wu, 1998; Wu et al., 2016).



#### Figure 2.1: UK NH<sub>3</sub> emissions 2019.

Panel A represents agricultures emissions within a UK perspective, while panel B separates agriculture emissions into each part of the sector data (Misselbrook and Gilhespy, 2021).

#### 2.1.2 Eutrophication

Eutrophying levels of nitrate (NO<sub>3</sub>) and phosphates (PO<sub>4</sub>) are of concern with agriculture, especially dairy, estimated to be responsible for 2 Tg of excess N entering European seas (Bouraoui and Grizzetti, 2014; Greaver et al., 2016; Havlikova et al., 2008; Zhang et al., 2017). At a UK level, agricultural run-off is thought to be responsible for 30% of Sites of Special Scientific Interest (SSSI) being in an unfavourable condition, however, the targeting of slurry application during active plant growing season could alleviate eutrophication issues (HM Government, 2018b). Yet doing so will not reduce water pollution immediately due to current ground water nutrient content (Bouraoui and Grizzetti, 2014; Zhang et al., 2017).

#### 2.1.3 Ecosystem acidification

Agricultural NH<sub>3</sub> is recognised to significantly contribute to the acidification of soils as a result of atmospheric deposition, with manure management identified as the main source of NH<sub>3</sub> losses

(Bouwman et al., 2005). Land in close proximity to a livestock production unit is found to be at greater risk from ecosystem acidification, characterised by increased acidity of soils, aluminium concentrations within the soil profile, and the leaching of base cations (Chen et al., 2015; Dai and Blanes-Vidal, 2013; Dashuan and Niu, 2015; Greaver et al., 2016; Wagner et al., 2015). However the rate at which ecosystem acidification occurs throughout a landscape can vary with climatic and topographic variations, such as rainfall and soil depth, and scale of livestock unit (Dashuan and Niu, 2015; Groot Koerkamp et al., 1998). In England, approximately 80% of Special Areas of Conservation (SAC) are estimated to receive damaging levels of atmospheric nitrogen (Defra, 2018).

#### 2.1.4 Health implications

In the atmosphere, NH<sub>3</sub> reacts with other chemicals which can then develop into fine particles (PM<sub>2.5</sub>) (Paulot and Jacob, 2014). Agriculture has been identified as indirectly contributing 5% of PM<sub>2.5</sub> emissions globally, making a reduction to NH<sub>3</sub> losses essential (Erisman et al., 2008; Webb et al., 2014b). Exposure to increased emissions is costly at the national level; Paulot and Jacob (2014) have reported that the average annual health cost for each kilogram of NH<sub>3</sub> emitted is \$3-13, while Wagner et al. (2015) suggest a saving of  $\in$ 13 for human health and a  $\in$ 9.5 saving for biodiversity for each kilogram of NH<sub>3</sub> prevented from entering the atmosphere. The effects of pollution from livestock is greatest in areas adjacent to large-scale units, with populations reporting a lower quality of life and greater levels of respiratory issues (Jensen, 2002; Wang et al., 2011).

#### 2.1.5 Climate change

Since the industrial revolution, atmospheric methane (CH<sub>4</sub>) has increased 2.5 times to approximately 1909 ppb, and nitrous oxide (N<sub>2</sub>O) concentrations have increased by 57 ppbv during the last century (IPCC, 2021). N<sub>2</sub>O is estimated to have a greenhouse gas impact of 300 CO<sub>2eq</sub> with manure management found to account for 18% of total N<sub>2</sub>O emissions. Chadwick et al. (2011) estimate that N<sub>2</sub>O emissions of manures from livestock systems equate to 30-50% of global N<sub>2</sub>O emissions from agriculture and is estimated at 2.8 Gt CO<sub>2eq</sub> per year (Pattey et al., 2005; VanderZaag et al., 2011). Eory et al. (2013) suggest that a saving of 37% of all agricultural greenhouse gas emissions annually could be found when considering fully implemented cost-effective mitigation measures in England and Wales.

#### 2.2 Current policy to address NH<sub>3</sub> emissions

Globally, agriculture is responsible for 92% of total NH<sub>3</sub> emissions, with the abatement of emissions becoming an international priority (Bell et al., 2016; Hyde et al., 2003; Webb et al., 2010). Globally, the largest emitters of NH<sub>3</sub> are China (15 Tg), USA (3.8 Tg) and EU (3.7 Tg) (Philippe et al., 2011).

Various policies have been introduced to reduce N loss globally (Gothenburg and Kyoto protocols), at a European regional level (Nitrates Directive (1991), Water Framework Directive (2000) and National Emissions Ceiling Directive (2016), and nationally.

#### 2.2.1 UK NH<sub>3</sub> emission targets

Under National Emission Ceiling Regulations (NECR) legislation (HM Government, 2018a), the UK is required to reduce NH<sub>3</sub> emissions by a minimum of 16% based on 2005 levels by 2030 (Defra, 2018; Loyon et al., 2016). During 2018, the UK government consulted on the 'Clean Air Strategy', which aims to underpin the governments approach to improving air quality. Defra have identified agriculture as key to delivering this reduction as the sector contributes approximately 90% of national NH<sub>3</sub> emissions (Defra, 2018).

Steps planned to be introduced to reduce N losses will also improve the efficiency of fertilizer use. These include the limitation of nitrogen applied, permitting large dairy farms as well as targeted NH<sub>3</sub> emission abatement regulations. The latter will include spreading urea based fertilizers alongside urease inhibitors, incorporating all spread solid manures and digestates with 12 hours on bare ground, acidification and using low emission spreading techniques (Defra, 2018).

#### 2.3 Slurry properties

Slurry is characterised as a minimally diluted anaerobic combination of excrement and bedding to create a semi-liquid solution often with an initial pH between 7.0-8.4 (Fangueiro et al., 2008; Laws et al., 2002; Ottosen et al., 2009; Owen and Silver, 2015; Regueiro et al., 2016a). Slurries are typically found to have high N, P and potassium (K) levels, but can vary as a direct response to animal diet, and growth stage (Chadwick et al., 2011; Cocolo et al., 2016; Møller et al., 2000; Perazzolo et al., 2016).

A clear use for slurry is to provide nutrients for plant growth and increasing soil organic matter, replacing significant amounts of mineral fertilisers (Fangueiro et al., 2015b; Gómez-Muñoz et al., 2016; Lewis and McGechan, 1999). Minimising  $NH_3$  losses from slurry will maximise nutrient availability and reduce the need for mineral fertilisation, but may result in N pollution swapping where N converts through microbial processes to  $NO_3^-$  and  $N_2O$  (Kai et al., 2008; Seidel et al., 2017; Sommer et al., 2017).

#### 2.4 Pathways to gaseous emissions

Pathways to gaseous emissions within the manure management system are reliant on microbial communities or enzymes being present to facilitate transformations within the relevant stages of the manure management chain and the subsequent release of gases.

#### 2.4.1 Nitrification

Nitrification is a mircobial process where nitrifying bacteria oxidise ammonia to nitrates in the presence of aerobic conditions, which can take up to 7-14 days to reach maximum nitrification (Ashman and Puri, 2009; Burns et al., 1996; Fangueiro et al., 2014; Park and Allaby, 2017; VanderZaag et al., 2011). However, the process can be limited by a reduced level of available C which acts as the energy source for bacteria (Rodhe et al., 2006).

#### 2.4.2 Denitrification

Denitrification is largely an anaerobic process found within the soil profile that converts  $NO_3^-$  to  $N_2$  in the presence of organic C with an optimum water filled pore space (WFPS) of 60% or greater (Burns et al., 1996; Philippe and Nicks, 2015; Stevens et al., 1995). The reduction of  $NO_3^-$  to  $N_2$  occurs in four stages which requires different enzymes for each however, incomplete denitrification can result in the release of  $N_2O$  and nitrogen dioxide ( $NO_2$ ) (Burns et al., 1996; Rotz, 2004).

Similar to nitrification, denitrification has been found to occur at temperatures below 8°C and creates a high emissions potential for autumn and winter applied slurry when plant requirements of N are low (Ellis et al., 1998; Thompson, 1989). Rainfall also influences the rates of denitrification especially if surface broadcast or band spreading have been employed as the application methodology. The infiltration of water and slurry particles initiates the denitrification process on contact with soil microbes (Ellis et al., 1998).

#### 2.4.3 Urea Hydrolysis

Urea hydrolysis, the biochemical decomposition of urea and water to  $CO_2$  and  $NH_3$ , is one of the most proficient enzymatic conversions known (Dai and Karring, 2014; Palanivell et al., 2015). Urease, the enzyme which initiates urea hydrolysis is abundantly found on animal housing floors when urine and faeces mix, and results in up to 90% of N compounds converted to  $NH_3$  or  $NH_4^+$  within a week (Dai and Karring, 2014; Dougherty et al., 2009; Groot Koerkamp et al., 1998; Park et al., 2017; Pereira et al., 2012; Philippe et al., 2011; Sommer and Husted, 1995a; Webb and Misselbrook, 2004).

#### 2.4.4 Methanogenesis

The microbial methanogenesis process is one that is largely found in anaerobic conditions, most likely to occur within slurry storage (Petersen et al., 2014). Methanogenesis is commonly initiated by residual populations of methanogens within the slurry store which can stimulate rapid methanogenesis, whereas slurry pits regularly emptied and washed have a delayed onset while methanogen populations increase (Haeussermann et al., 2006). Similar to urea hydrolysis, the process

of methanogenesis is temperature sensitive, with temperatures up to 25°C found to increase methanogenesis and CH<sub>4</sub> production (Pereira et al., 2012).

#### 2.5 Manure management continuum

A wide range of factors influence livestock greenhouse gas emissions, including manure characteristics, soil type and weather conditions, as well as the surface area of fresh urine or slurry exposed to air (Huijsmans et al., 2016; Pereira et al., 2011; Webb and Misselbrook, 2004). The issues surrounding greenhouse gas and NH<sub>3</sub> emissions cannot be isolated to a single step of the manure management continuum - in-house (i.), storage (ii.) and application (iii.) (Chadwick et al., 2011; Fangueiro et al., 2015a).

#### 2.5.1 In-house

Dairy cattle farming is the greatest source of  $NH_3$  emissions within the UK, with an average herd size of 148 individuals, which has risen consistently for the past 20 years (Figure 2.2). In the UK, there are two typical dairy systems:

- i) Livestock solely reared indoors with slurry collected all year round,
- ii) Livestock reared inside during winter and grazed outside during the summer with slurry only collected in the winter.



Figure 2.2: Average UK dairy herd size

The above figure shows the rise in average UK dairy herd size over the past 21 years with UK trends as well as individual nations. Data source: AHDB, 2021.

Slurry is only produced during periods of housing, all other times excreted N is directly applied to pasture but results in fewer NH<sub>3</sub> emissions as urine rapidly infiltrates before hydrolysis is complete (Webb and Misselbrook, 2004). In-house emissions depend on slurry properties, diet, age and breed, climatic conditions, building design and ventilation system, flooring and removal system, with a slatted floor found to have the lowest emissions (Baldini et al., 2016; Kai et al., 2008; Pereira et al., 2011). However, diurnal variation has been found whereby increased cattle activity throughout the day raises CH<sub>4</sub> and NH<sub>3</sub> emissions as a result of rumination and urination (Leytem et al., 2011; Wu et al., 2012).

#### 2.5.1.1 Influence of diet

Manipulating livestock diet has been identified by several authors as a means of reducing emissions throughout the entire manure management chain by altering manure characteristics (Sajeev et al., 2018). Matching the crude protein (CP) content of livestock diet to the animals requirements has been recognized as a means to reduce NH<sub>3</sub> emissions whilst not affecting the livestock's performance, by reducing urea-N (Loyon et al., 2016; Philippe et al., 2011; Rotz, 2004; Webb et al., 2014a). Loyon et al. (2016) reported that at each percentage point decrease of crude protein content of animal feed, a reduction of total NH<sub>3</sub> emissions is found by 5-15%, as well as reducing odours and VFA's (Aarnink and Verstegen, 2007; Hansen et al., 2014).

#### 2.5.2 Storage

In the UK, slurry tends to be kept in storage for a minimum of 2 months especially over autumn, winter and spring, where various greenhouse gases are emitted (Holly et al., 2017; Misselbrook et al., 2016; Owen and Silver, 2015). Disturbances during slurry storage can break the equilibrium between the slurry and the atmosphere, resulting in greater gaseous emissions (Blanes-Vidal et al., 2012).

#### 2.5.2.1 <u>NH</u><sub>3</sub>

During storage, NH<sub>3</sub> is released from the surface of the slurry where equilibria develops between  $NH_4^+$  and NH<sub>3</sub> at the surface and NH<sub>3</sub> in the air above the slurry (Misselbrook et al., 2016; Stevens et al., 1989; Vaddella et al., 2013). NH<sub>3</sub> emissions from slurry has been found to range between 1.8 – 12 g NH<sub>3</sub>-N m<sup>-2</sup> d<sup>-1</sup> (Loyon et al., 2007; McGinn and Janzen, 1998). However, the addition of a store cover can reduce NH<sub>3</sub> emissions by up to 80% (Webb et al., 2014a). Keeping manure in a cool environment has been found to minimise emissions, suggesting that outdoor storage is preferred in cooler climates, although seasonal differences will occur (Haeussermann et al., 2006; Petersen et al., 1998; Webb et al., 2014a)
# 2.5.2.2 <u>CH</u><sub>4</sub>

The extent of CH<sub>4</sub> emissions will depend upon the duration of manure storage, temperature and manure composition, especially VFA's in combination with anaerobic conditions, but is estimated to equate to 12-41% of total agricultural emissions (Amon et al., 2001; Chadwick et al., 2011; Holly et al., 2017; Perälä et al., 2006; Petersen et al., 2016a; Regueiro et al., 2016a; Sommer and Husted, 1995a; Wulf et al., 2002). Similar to NH<sub>3</sub>, covering the store was found to reduce the potential of CH<sub>4</sub> loss, where a reduction of up to 90% of emissions is possible (Amon et al., 2006; Chadwick et al., 2011; Hilhorst et al., 2002; Misselbrook et al., 2016). The storage of slurry outside has been found to lower CH<sub>4</sub> emissions due to cooler environmental temperatures, however, emissions are likely to increase during summer months (Haeussermann et al., 2006; Hilhorst et al., 2002; Leytem et al., 2011; Misselbrook et al., 2016).

## 2.5.2.3 Odour

Slurry storage is a known source of malodours, which vary in extent from each livestock production unit due to variations in animal diet. The types of odours found in livestock production are often VFA's, such as butyric acid, acetic acid, and organic sulphur compounds, in addition to NH<sub>3</sub> (Neerackal et al., 2015; Webb et al., 2014a). A mitigation option proposed to minimise odour emissions during storage is the use of a cover with particular emphasis on impenetrable covers, yet these can be prohibitively expensive to install (Portejoie et al., 2003).

### 2.5.2.4 Influence of crust

Crust formation, due to gas particles moving organic matter to the surface, is directly influenced by the dry matter content of the slurry and typically stabilises 40-60 days after initiating storage (Chadwick et al., 2011; Hou et al., 2015; Misselbrook et al., 2005). A reduction in CH<sub>4</sub> emissions as a result of an extensive, sealing, crust has been estimated between 80 - 90% (Misselbrook et al., 2016; Rotz, 2004). However, Sommer et al. (2000) suggests that strongly encrusted slurries provides both aerobic and anaerobic conditions necessary to initiate nitrification and denitrification and subsequently increase N<sub>2</sub>O emissions (Berg et al., 2006a; Regueiro et al., 2016b).

# 2.5.3 Application

In general, more slurry is applied to grasslands in autumn and arable fields during spring with a greater proportion of cattle slurry being applied to grasslands (Smith and Williams, 2016). The release of  $CH_4$  and  $CO_2$  are limited at this stage with  $NH_3$  and  $N_2O$  dominating gaseous losses (Bastami et al., 2016; Sajeev et al., 2018).

### 2.5.3.1 <u>NH<sub>3</sub></u>

The NH<sub>3</sub> emitted from manure spread in UK has been estimated at 60.1 kT NH<sub>3</sub>-N yr<sup>-1</sup> which equates to approximately 22% of total UK NH<sub>3</sub> emissions (Misselbrook and Gilhespy, 2021). Once applied, slurry releases approximately 50% of its NH<sub>3</sub> emissions within the first 24 hours after application, however, the release can continue for up to 10 days following the initial application (Panetta et al., 2005). This can be reduced if abatement techniques are employed (Petersen et al., 2007).

## 2.5.3.2 <u>N<sub>2</sub>O</u>

Most emissions of N<sub>2</sub>O occur at the application stage and have been found to be greatest when applied via injection (Ellis et al., 1998; Emmerling et al., 2020; Lopez-Ridaura et al., 2009). There are various estimations as to the total N lost as N<sub>2</sub>O, ranging from 1.25% to 0.05% of total N applied to a grassland (Kroeze, 1994; Rodhe et al., 2006; Thorman et al., 2020). Ultimately, the emissions of N<sub>2</sub>O from field application of manure accounts to up to 44% of total N<sub>2</sub>O emissions from anthropogenic sources (Baral et al., 2018).

# 2.5.3.3 Odour

Application of animal slurry is the stage within manure management where odour emissions are most prevalent (Feilberg et al., 2011; Pedersen et al., 2022). 4-methyl-phenol contributes to the highest odour emissions from pig slurry, others include: reduced organic sulphur compounds, butanoic acids, 3 methylbutanoic acid, and 4-ethylphenol, while odours of sulphur compounds have been found to decline following application peaking within 20 minutes of application (Feilberg et al., 2011)

### 2.6 Influence of climate

Soil characteristics vary both spatially and temporally and are heavily impacted by weather conditions on the day of application (Bell et al., 2016).

## 2.6.1 Temperature

Soil temperature has a direct influence on greenhouse gas emissions with increased soil microbial activity in warmer soils, and promoting extensive NH<sub>3</sub> volatilisation following the application of slurry (Bourdin et al., 2014; Louro et al., 2013; Petersen et al., 1998). Bourdin et al. (2014) suggest that key factors responsible for NH<sub>3</sub> losses are air and soil temperature, and solar radiation. From a global perspective, temperature is likely to be a key variable that helps to explains regional difference of NH<sub>3</sub> emissions found (Søgaard et al., 2002).

# 2.6.2 Soil Moisture

Soil moisture is a key variable, which when altered can determine the extent of greenhouse gas emissions by altering oxygen availability and gas diffusivity (Louro et al., 2013). The highest

concentration of  $N_2O$  emissions are found in medium moisture contents, 60-80% water filled pore space, where both nitrification and denitrification occurs (Perälä et al., 2006; Regina and Alakukku, 2010; Velthof and Mosquera, 2011). Consequently, clay soils, which tend to have a higher WFPS compared to sandy soils, have an increased risk of emissions (Velthof and Mosquera, 2011).

## 2.6.3 Wind speed

Wind speed is crucial in determining emissions following application with increased wind enhancing gaseous exchange between slurry and the atmosphere, especially of NH<sub>3</sub> during the first 24 hours (Louro et al., 2013; Pain et al., 1989; Seidel et al., 2017; Søgaard et al., 2002; Thompson et al., 1990). Misselbrook et al. (2005a) found a significant relationship between NH<sub>3</sub> emissions and wind speed, with 15% greater NH<sub>3</sub> emissions per 1 m s<sup>-1</sup> increase in wind speed. This release will also be impacted by dry matter content of the applied slurry, and soil surface conditions which control infiltration potential (Bell et al., 2016; Louro et al., 2013).

### 2.7 Implications for soil quality

The use of slurries as fertilizer has considerable benefits as well as limitations. Intensive cultivation of land is often associated with decreasing soil organic matter and soil health, while the addition of manure increases soil organic matter, organic N, P and S, as well as retaining P and K ions (AHDB, 2017a; Pernes-Debuyser and Tessier, 2004; Sajeev et al., 2018). The addition of manure also increases pore space within the soil profile and creates greater water retention potential (Pernes-Debuyser and Tessier, 2004). Earthworms are vital to soil health and are responsible for the movement of nutrients within the soil profile. The addition of slurry has been found to have short-term detrimental impacts upon earthworm populations due to the addition of toxic elements but have been found to rebound to greater levels with slurry providing a nutrient source (Murchie et al., 2015).

#### 2.8 Current types of slurry treatment

Slurry treatment is becoming increasingly common as a means of reducing slurry N losses. Within the EU, 7.8% of manure was treated in 2010, although large variations occurred within countries - ranging from 0-35% - with the most common treatments including solid-liquid separation, anaerobic digestion, and acidification (Hou et al., 2017) (Table 2.1). Such treatments are largely implemented to mitigate greenhouse gas emissions, prevent malodours, reduce NH<sub>3</sub> emissions and address storage issues (Sáez et al., 2017).

Table 2.1: Current slurry treatment methods.

The below table summarises information from numerous sources.

<u>Solid – liquid separation</u>: (Chadwick et al., 2011; Cocolo et al., 2016; Fangueiro et al., 2017, 2015a, 2014, 2012; Huijsmans et al., 2016; Sigurnjak et al., 2017; Sommer et al., 2015).

Digestion: (Gioelli et al., 2016; Holly et al., 2017; Petersen et al., 2016b; Rodhe et al., 2015; Sajeev et al., 2018; Styles et al., 2016; M. Zhang et al., 2017).

Acidification: (Cocolo et al., 2016; Fangueiro et al., 2015b; Hou et al., 2017; Jacobsen, 2017; Owusu-Twum et al., 2017b; Petersen et al., 2016a; Sajeev et al., 2018; ten Hoeve et al., 2016).

Inhibitors: (De Klein and Eckard, 2008; Fangueiro et al., 2016; Owusu-Twum et al., 2017a).

Slurry treatment	Benefits	Limitations
Solid liquid	Produces 2 different fractions: solid high in P and DM, liquid high in Total Ammoniacal Nitrogen (TAN).	Can increase N <sub>2</sub> O emissions following application of liquid
separation	Well balanced N:P:K end product Reduces CH <sub>4</sub> and NH <sub>3</sub> emissions	
	Offsets carbon footprint of agriculture	Can increase NH <sub>3</sub> emissions
Digestion	Reduces CH <sub>4</sub> emissions by up to 68%	Can increase N <sub>2</sub> O emissions following application
Digestion	Increases NH4 <sup>+</sup> content of end-product	Expensive and requires high input of waste
	Widely used in EU	
Use of	Reduces N <sub>2</sub> O emission	Can increase NH <sub>3</sub> emissions
inhibitors	Commonly used on synthetic fertilisers	Effectiveness dependent on soil properties
	Efficiently reduces NH <sub>3</sub>	Expensive technology if carried out in house
Acidification	Can be performed at any part of the manure management continuum	Use of strong acid
	Improves the fertiliser value of the slurry	
	Reduces the need to use injectors at application	

# 2.9 Current types of application

The addition of slurry to the agricultural landscape presents various challenges. It is estimated that the N use efficiency of slurry is poor with only 20-50% of excreted N recovered by crops (Velthof and Mosquera, 2011). Optimising the rate, technique, and timing of manure application effectively utilises N by limiting the area and duration of contact between manure and atmosphere, thus reducing

NH<sub>3</sub> emissions (Chadwick et al., 2011; Huijsmans et al., 2016). Hou et al. (2015) reports that band spreading, broadcast then incorporation, and injection had a respective 55%, 70% and 80% reduction in NH<sub>3</sub> emissions when compared with surface broadcast. Similarly, Smith and Williams (2016) report that low emission techniques can reduce NH<sub>3</sub> emissions by 40 - 90%. Regardless of the level of abatement, there is consensus that reducing losses of N will increase the N fertiliser replacement value of slurry (Velthof and Mosquera, 2011). The current methods for slurry application have been summarised below (Table 2.2).

Table 2.2: Current slurry application methods.

The below table summarises information from a number of sources:

Surface broadcast: (Fangueiro et al., 2017; Huijsmans et al., 2016; Louro et al., 2013; Lovanh et al., 2010; Smith et al., 2000; Smith and Williams, 2016; Sørensen and Eriksen, 2009; Webb et al., 2010)

Band spreading: (AHDB, 2017b; Bourdin et al., 2014; Lovanh et al., 2010; Rodhe et al., 2006; Thompson et al., 1990; Webb et al., 2010)

Injection: (AHDB, 2017b; Bhandral et al., 2009; Chadwick et al., 2011; Fangueiro et al., 2017, 2015c; Hou et al., 2015; Perälä et al., 2006; Sajeev et al., 2018; Seidel et al., 2017; Semitela et al., 2013; Smith et al., 2000; Søgaard et al., 2002; Velthof and Mosquera, 2011; Webb et al., 2010)

Application method	Benefits	Limitations			
	Cheapest	High NH <sub>3</sub> emissions			
	Already available on most UK	Lack of precision in			
Surface broadcast	farms producing slurry	application			
		Risks sward contamination			
		Increases diffuse pollution			
	Reduces gaseous losses by	Requires maceration of slurry			
Band spread	reducing surface area of slurry	to prevent blockages			
Band spread	Improves crops yields	Requires new equipment			
	Reduces sward contamination				
	Most effective at reducing NH <sub>3</sub> emissions	High capital costs			
	Increases agronomic	Unsuitable on stony and			
Injection	performance	sloping land			
Injection	Recognised as the Best	Can damage roots of existing			
	Available Technique	crop or grass			
		Potential to increase N <sub>2</sub> O and			
		CH <sub>4</sub> emissions			

# 2.10 Importance of timing - seasonal climatic & soil variations

The application of slurry should aim to provide a balance between the period of maximum crop N requirement and the need to reduce seasonal climate effects on emissions (Bell et al., 2016). This will be beneficial to the farmer as efficient use of N by plants optimises the benefits of using slurry as a fertiliser (Bourdin et al., 2014; Perälä et al., 2006). Spring slurry application, when plants are actively growing creates a bigger N sink and meets the demands of essential nutrients for the plants (Bell et al., 2016; Chadwick et al., 2011). Autumn and winter applications have limitations as the needs of plants are reduced due to limited growth, as well as increased WFPS (Rodhe et al., 2015). The latter can increase the amount of  $N_2O$  emissions due to the presence of anaerobic conditions (Bell et al., 2016). Leaching of nitrogen is another concern with autumn and winter spreading and is restricted in areas covered by Nitrate Vulnerable Zones (NVZ) (Bell et al., 2016; Chadwick et al., 2011; Webb et al., 2010)

Ultimately, the short-term weather after application is the strongest driver in determining the total emissions. For example a combination of high temperatures, high wind velocity and low rainfall following spreading increases NH<sub>3</sub> emission with a positive correlation found between ambient temperature and NH<sub>3</sub> losses (Matsunaka et al., 2008).

# 2.11 Acidification process

As an NH<sub>3</sub> mitigation strategy, acidification can take place at any stage of the manure management continuum - animal house, manure store, during manure processing and during application. The process is explained below (Birkmose and Vestergaard, 2013; Fangueiro et al., 2015a; Hjorth et al., 2015; Pedersen et al., 2022):

- <u>In-house</u>: slurry is removed from underneath slats daily and mixed with acid in a pre-storage tank. A quantity is pumped back into the animal building and stored under slats to minimise emissions; the remainder is removed to storage and is deemed long term acidification.
- <u>In storage</u>: acid is mixed with slurry in the store until the desired pH is reached. The timing of in storage acidification can vary from shortly after arrival in the tank to immediately prior to application, with greater abatement potential earlier on in storage.
- <u>During application</u>: acid is pumped through to the slurry tanker and added to the slurry during application, this is considered a short-term acidification.

# 2.11.1 <u>Target pH</u>

The quantity of acid required to lower and maintain slurry pH to a level which significantly reduces NH<sub>3</sub> emissions depends on slurry composition, buffering capacity, and acid strength (Berg &

Pazsiczki, 2006; Fangueiro et al., 2015; Hjorth et al., 2015; Jensen, 2002; Misselbrook et al., 2016; Regueiro et al. 2016; Sommer & Hutchings, 1995). Most studies suggest a pH of between 6.0 and 5.5 provides the best compromise between cost and emission reduction, and is used commercially in Denmark (Pedersen et al., 2022). At these levels, several authors have reported NH<sub>3</sub> emission reductions of 95% from pig and 88% from cattle slurry (Hou, Velthof, & Oenema, 2015; Pain, Misselbrook, & Rees, 1994; Stevens et al., 1989; Wang, Huang, Ying, & Luo, 2014). By acidifying, the addition of an extra H<sup>+</sup> ion has been reported to shift NH<sub>3</sub>:NH<sub>4</sub><sup>+</sup> TAN ratio to a point where NH<sub>4</sub><sup>+</sup> has been found to represent >98% of TAN (Berg et al., 2006; Cocolo et al., 2016). However, when acid is added the initial pH reduction has been found to recover following degradation of organic acids, mineralisation of organic nitrogen and dissolution of carbonates (Regueiro et al., 2016). Studies have shown that additional acid is required 2-3 weeks after the initial acid application to maintain a pH below 6.0 (Misselbrook et al., 2016; Regueiro et al., 2016), but the stability of the pH will depend and vary on the individual buffer capacity of each slurry. Acidification also affects CH<sub>4</sub> emissions with reductions of 60 – 80% reported when acidifying to pH 5.5 (Berg et al., 2006; Frost et al., 1990; Misselbrook et al., 2016).

#### 2.12 Use of acids

A range of acids can be used for slurry acidification. The use of sulphuric acid ( $H_2SO_4$ ) has clear benefits over other additives (Table 2.3), features in most studies, and is the acid of choice in Denmark where slurry acidification is a commercially available NH<sub>3</sub> mitigation strategy. Recent studies (e.g. Bastami et al., 2016) have investigated the potential to include biological means of acidification which have fewer health and safety concerns, but throughout this study acidification will refer to the use of H<sub>2</sub>SO<sub>4</sub>, as commercially used in Denmark.

#### 2.12.1 Impact of using H<sub>2</sub>SO<sub>4</sub>

 $H_2SO_4$  is widely accepted as the most suitable for acidifying slurry given its relative low costs and additional benefit of increasing the fertilizer S content of slurry (Eriksen et al., 2012; Hjorth et al., 2015; Stevens et al., 1995). The recovery of sulphate during storage is an additional benefit to the acidification process that should be considered prior to application in order to maximise the acidified slurry's potential to meet the crop needs (Eriksen et al., 2012). Sommer et al. (2017) found that during the acidification process with  $H_2SO_4$ , levels of  $SO_4^{2-}$  increased from 26.5 to 232 g m<sup>-3</sup> and remain constant following acidification. However, the stimulation of sulphur reducing bacteria associated with the use of  $H_2SO_4$  has been found to increase  $H_2S$  emissions and the development of volatile sulphur-containing compounds which can have a negative impact on in-house conditions (Eriksen et al., 2012; Fangueiro et al., 2015a).

Table 2.3: <u>Summary of common a</u>	icids used for acidification.		
The above table details the positiviind indicate positives. The use of H <sub>2</sub> S	es and negatives for each acid used i O4 has clear benefits over other add	n various studies. Those in green ind litives and features in most studies.	licate negatives and those in cream
Sulphuric Acid	Nitric Acid	Lactic Acid	Alum
Greatest NH <sub>3</sub> reduction whilst using the least quantity (Regueiro et al., 2016)	Economically viable (Stevens et al., 1995)	At pH 5.73 lactic acid reduced NH <sub>3</sub> emissions by 65% (Berg et al., 2006)	Reduces amount of soluble P (Lefcourt & Meisinger, 2001)
Higher fertiliser value of slurry (Regueiro et al., 2016)	Increases rate of denitrification which lowers with lower pH (Stevens et al., 1995)	At pH 5.73 lactic acid reduced CH <sub>4</sub> emissions by 94% (Berg et al., 2006)	Successful at lowering NH <sub>3</sub> emissions (Lefcourt & Meisinger, 2001)
Microbial decomposition of organic matter during storage is inhibited (Regueiro et al., 2016)	Slurry pH increases and extra NO <sub>3</sub> added will increase denitrification and N <sub>2</sub> O emissions (Berg et al., 2006b; Fangueiro et al., 2010; Stevens et al., 1995; Vandré and Clemens, 1996)	Lactic has a relatively lower foam formation (Berg et al., 2006)	Does not react instantaneously with shurry at moderate temperatures (12-14°C) results in N losses but is (Lefcourt & Meisinger, 2001)
Combined with oxygen, secures both NH <sub>3</sub> and H.S within the manure (Jensen, 2002)	Has to added three times to maintain low pH levels (Berg et al. 2006)	Has to be added multiple times to maintain low pH (Berg et al., 2006)	Negatively impacts soil quality by increasing aluminium (T.efcourt & Meisinger, 2001)
Ammonium and plant-available nitrogen increases (Jensen, 2002)	At pH 5.2 only reduced NH <sub>3</sub> emissions by 29% (Berg et al., 2006)	Large quantity requirement to reduce pH (Berg et al., 2006)	Used to control P availability (Regueiro et al., 2016)
Reduces in-house ammonia from 8-12 ppm to 1-2 ppm (Jensen, 2002)	Not very effective at reducing CH <sub>4</sub> emissions (Berg et al., 2006)	Lowers N <sub>2</sub> O emissions by 90% (Sajeev et al., 2018)	Buffers slowly reducing CO <sub>2</sub> and NH <sub>3</sub> emissions (Regueiro et al., 2016)
pH 5.5 slurry with H <sub>2</sub> SO <sub>4</sub> has 89% efficiency relative to inorganic fertilizer (Stevens et al. 1995)	As effective as $H_2SO_4$ at lowering $NH_3$ emissions (Stevens et al., 1997)	Effective at reducing CH4 emissions when pH lowered to 4.5 (Berg and Pazsiczki, 2006)	Reduces GHG emissions from separated slurry and co-digestate (Regueiro et al., 2016)
Economically viable (Toft and Madsen, 2019)	Only has 54% N efficiency when compare with inorganic N fertilizer (Stevens et al., 1997)		
Causes excess foaming (Regueiro, et al., 2016)	Greater risk of N loss through the introduction of NO <sub>3</sub> into an anaerobic and carbon rich slurry (Stevens et al., 1997)		
Creates an excess sulphur pool which can lead to significant H <sub>2</sub> S emissions (Moset et al., 2012; Regueiro et al., 2016)	Large quantity required to lower pH increasing shury content by 2-3 fold and could meet plant requirements but will need to be spread at a very low density (Stevens et al., 1997)		
Creates a product with similar N utilization for plants as inorganic fertilizer (Stevens et al., 1997)	Less acidifying to soil than $\mathrm{H}_2\mathrm{SO}_4$ (Stevens et al., 1992)		
Effective for long term acidification (Overmeyer et al., 2021)	Can be used to create a more balance N.P.K ratio for plants requirements (Stevens et al., 1992)		

## 2.13 Emissions reduction along management chain

The effectiveness of emission abatement varies along the manure management chain, and a whole system assessment is required to ensure that any pollution swapping is accounted for (Eriksen et al., 2008; Gómez-Muñoz et al., 2016; Hou et al., 2015; Kai et al., 2008).

# 2.13.1 In-house

Several authors have reported that slurry acidification reduces in-house NH<sub>3</sub> emissions by up to 70% (Eriksen et al., 2008; Hjorth et al., 2015; Hou et al., 2017; Petersen et al., 2016b; ten Hoeve et al., 2016). However, the effectiveness of emission reduction relies on clear pathways for slurry to enter acidification channels (Petersen et al., 2016).

In-house treatment has also been found to reduce CH<sub>4</sub> emissions following acidification, however the effectiveness depends on the type of acid used with lactic acid reported to lower CH<sub>4</sub> emissions by over 90% and H<sub>2</sub>SO<sub>4</sub> reducing emissions by 67-87% (Fangueiro et al., 2015). Gioelli et al. (2016) reported that lowering slurry pH to 5.5 - 6.0 with H<sub>2</sub>SO<sub>4</sub> reduced CH<sub>4</sub> emissions by 70-90%, while Petersen et al. (2014) found that CH<sub>4</sub> emissions were reduced by 99% when pig slurry was acidified in-house.

An important consideration for slurry acidification is the potential for elevated concentrations of  $H_2S$ . Work reported by Petersen (2016) and Hutchings et al. (2016) suggested that acidifying in-house, during summer can elevate  $H_2S$  production as a result of high temperatures, stimulating sulphur reducing bacteria (Petersen et al., 2016a).

# 2.13.2 Storage

In storage, acidification has been shown to reduce  $NH_3$  emissions by up 90% compared with untreated slurry (Kai et al., 2008). Petersen et al. (2016b) reported that acidification can reduce total emissions from slurry stores by up to 98%.

# 2.13.2.1 <u>NH<sub>3</sub></u>

Throughout the literature, acidification is reported to deliver a significant reduction of  $NH_3$  emissions during storage. Petersen et al. (2012) reports the greatest finding with a reduction of 96-99% of  $NH_3$  emissions, however others report a reduction of 70 – 90% reduction (Fangueiro et al., 2015c; Gioelli et al., 2016; Hou et al., 2017; Sommer et al., 2017). Although the range is wide, there is a clear positive impact of acidification to storage  $NH_3$  emissions.

## 2.13.2.2 <u>N<sub>2</sub>O</u>

Due to the anaerobic conditions found in stored animal slurry, very little  $N_2O$  is emitted (Petersen et al., 2016a). Given the low level of emissions, acidification will not have a further abatement impact.

#### 2.13.2.3 CH<sub>4</sub>

Acidification has been found to decrease CH<sub>4</sub> emissions as a result of reduced methanogenic activity which is optimised between pH 6 - 8 (Chadwick et al., 2011; Fangueiro et al., 2015a, 2010; Petersen et al., 2016a). The range of CH<sub>4</sub> abatement when slurry is acidified to below pH 6.0 has been reported at a reduction of 63-93% and can be effective for over 100 days (Bastami et al., 2016; Eriksen et al., 2012; Hou et al., 2017, 2015; Regueiro et al., 2016b; Sajeev et al., 2018; Sommer et al., 2017; Wang et al., 2014). Petersen et al. (2014) found differences in abatement between cattle and pig slurry with a 98% CH<sub>4</sub> reduction in pig slurry and between 67-87% reduction in cattle slurry when acidified to pH 5.5 and stored for three months. The use of H<sub>2</sub>SO<sub>4</sub> has been suggested as causing toxic conditions in slurry for methanogens due to increased levels of H<sub>2</sub>S which create toxic conditions (Eriksen et al., 2012).

## 2.13.2.4 <u>CO<sub>2</sub></u>

A substantial quantity of  $CO_2$  is emitted during the acidification process through the evolution of carbonates (Fangueiro et al., 2015b; Pantelopoulos et al., 2016a). Stevens et al. (1989) reported that up to 96% of bicarbonate is converted to  $CO_2$  at pH 5 compared to just 3% at pH 8 as the additional strong acid neutralizes the alkalinity from bicarbonate, converting it to  $H_2CO_3$  and  $CO_2$ .

### 2.13.2.5 <u>H<sub>2</sub>S</u>

The majority of research has shown that the high levels of disturbance during acidification increases  $H_2S$  emissions (Dai and Blanes-Vidal, 2013; Fangueiro et al., 2017; Moset et al., 2012; Wang et al., 2014). Sommer et al. (2017) found that during acidification the final  $H_2S$  content increased from 0.33 g m<sup>-3</sup> to 0.48 g m<sup>-3</sup> and can create a substantial health risk to both livestock and humans (Dai and Blanes-Vidal, 2013; Fangueiro et al., 2015a; Frost et al., 1990).

### 2.13.3 Application

## 2.13.3.1 <u>NH</u><sub>3</sub>

Acidification has been found to reduce NH<sub>3</sub> emissions by up to 95%, as well as limiting the effect of weather conditions on NH<sub>3</sub> emissions once applied to soil. Consequently, acidification has been reported as the most effective single abatement technique to lower NH<sub>3</sub> emissions across the entire management chain (Hou et al., 2015; Petersen et al., 2016a). Petersen et al. (2016a), researched the

seasonal impact on abatement into seasons and found that autumn had the greatest reduction at 71%, with spring and summer being 66% and 44% less when compared to untreated application.

# 2.13.3.2 <u>N<sub>2</sub>O</u>

Uncertainty exists regarding the impact of acidification on  $N_2O$  emissions following slurry application. Fangueiro et al. (2015c) found that  $N_2O$  emissions reduced 59% following application, through a delay to nitrification. Such an inhibition is supported by Park et al. (2017) who noted that the amount of organic C available for denitrification is reduced as a result of CO<sub>2</sub> losses during the acidification process. However, increased readily available  $NH_4^+$  following slurry acidification may have negative impacts on  $N_2O$  emissions especially given  $N_2O$  production is favoured at low pH (Fangueiro et al., 2017; VanderZaag et al., 2011).

# 2.13.3.3 CH<sub>4</sub>

Methane emissions are typically found in-house or during storage due to the favourable anaerobic conditions found and would therefore be negligible at application (Fangueiro et al., 2017; Sommer et al., 2017).

# 2.13.3.4 <u>CO</u><sub>2</sub>

Studies report that following application of acidified slurry CO<sub>2</sub> emissions are low, reflecting the loss of carbonates during the acidification process (ten Hoeve et al., 2016).

### 2.13.3.5 <u>H<sub>2</sub>S</u>

As H<sub>2</sub>S is emitted following disturbance to the slurry, it has been observed that H<sub>2</sub>S is only emitted during the first few minutes following application with the slurry being recently disturbed (Fangueiro et al., 2015a).

#### 2.13.3.6 Odour emissions

The emissions of odours and NMVOC's have been found to increase by up to 300% following the acidification process compared to a conventional slurry (Pedersen et al., 2022). Petersen et al. (2016), states that acidification alters degradation of organic matter thus influencing emissions of odours. Furthermore, there is a possibility that a higher content of inorganic S, provided through the acidification process, can produce malodours that are especially high in butyric acid (Sørensen and Eriksen, 2009).

#### 2.14 Effects of acidification on slurry and soil properties

# 2.14.1 Biological changes of slurry post acidification

Following acidification, slurry provides an altered environment for microbes, shifting the structure of the communities present (Sørensen and Eriksen, 2009). Hjorth et al. (2015) recognised that slurry microbial communities did not adapt well to the new conditions after acidification. This has been quantified as a greater than 98% reduction in biological activity for anaerobic processes within acidified slurry, resulting in low N<sub>2</sub>O emissions (Ottosen et al., 2009; Owusu-Twum et al., 2017a). Fangueiro et al. (2015a) noted alterations to organic matter degradation during in-house and storage tank acidification with an increase of hydrolysis of organic matter when pH is lowered. While Hjorth et al. (2015) reported a reduction of microbial processes which will consequently reduce the greenhouse gas emissions at a lowered pH.

## 2.14.2 Physical and chemical changes of slurry post acidification

When acidification occurs, the increased  $H^+$  ion concentrations changes the chemical equilibrium of slurry. Fangueiro et al. (2015) found that when pH dropped from 7.5 to 5.5 the proportion of available N in the NH<sub>4</sub><sup>+</sup> form increased to over 99%, with the NH<sub>4</sub>:NH<sub>3</sub> ratio ultimately controlling the amount of NH<sub>3</sub> emitted from slurry (Berg et al., 2006a; Cocolo et al., 2016; Fangueiro et al., 2015a; Misselbrook et al., 2016; Sommer et al., 2017). Weather conditions are less likely to influence N volatilisation from acidified than non-acidified slurry as the NH<sub>4</sub><sup>+</sup> will remain in the aqueous phase unlike NH<sub>3</sub> which is likely to become mobile in the gaseous phase (Erisman et al., 2008; Pereira et al., 2011; Sommer et al., 2017; Wu et al., 2012; Zhang et al., 2005).

Several papers report that the level of dissolved phosphorous (P) increased at lower pH, with higher dissolved P concentrations reported in pig slurry than cattle slurry when H<sub>2</sub>SO<sub>4</sub> was used as the acidifying agent (Fangueiro et al., 2009; Li et al., 2020; Regueiro et al., 2016c; Roboredo et al., 2012). The difference between cattle and pig slurry may reflect higher levels of calcium (Ca) found in cattle slurry which precipitates easily, reducing the P held in smaller particles (Regueiro et al., 2016). Hjorth et al. (2015) found that levels of magnesium (Mg) and Ca were also higher in acidified slurry which can be easily released in to the soil (Fangueiro et al., 2014; Hjorth et al., 2015; Roboredo et al., 2012). The use of H<sub>2</sub>SO<sub>4</sub> will also increase the S fertilizer value of the acidified slurry, however, Petersen et al. (2016a) have warned that applications need to be managed to ensure that increased slurry S levels match crop requirements.

Acidification reduces the inorganic carbon content of slurry as a result of the neutralization of bicarbonates, which is key for the reduction of NH<sub>3</sub> volatilization (Stevens, 1992). The proportion of

bicarbonate converted to  $CO_2$  is estimated to be between 70-95% when acidification reduces slurry pH to 5-6, and has the potential to reduce inorganic soluble C content by 100% (Fangueiro, Hjorth, et al., 2015; Fangueiro et al., 2009; Pantelopoulos et al., 2016b; Regueiro et al., 2016). Petersen et al. (2016a) reported similar findings with a reduction of total inorganic carbon in acidified slurry a response to degassing of  $CO_2$ , and a reduction of microbial populations as a response to the additional acid (Sommer et al., 2017).

#### 2.15 Changes to soil properties

Following application to soil, pH of acidified slurry can increase rapidly due to high buffer potentials within carbonate-based soils which mitigate changes to soil properties induced by acidification (Fangueiro et al., 2016; Sørensen and Eriksen, 2009). An increase in slurry pH has been found immediately after contact with soil for short term acidification, but the impact of soil buffering is reduced on slurry acidified during storage (Pedersen et al., 2022). Fangueiro et al. (2018) found that soil pH levels decreased by pH 0.7 and pH 0.9 following six applications of an acidified cattle slurry (pH 5.6) to a Halpic Arenosol (initial pH 7.1) and Halpic Cambisol (initial pH 6.1), and would suggest the need for liming to commence to maintain original soil pH. However, Semitela et al. (2013) and Petersen et al. (2016a) both found that the application of acidified slurry did not impact soil solution pH, likely due to individual soil buffering capacity, and the consumption of protons by plant uptake of N and S will not increase demand on liming. In a recent UK study, soil pH was reduced by ca. 0.5 pH unit, from pH 6.4 to pH 5.9 on a free draining Eutric Cambisol and pH 5.5 to 5 on a free-draining Dystric Cambisol. This reduction in soil pH was found for the entire growing season following the application of acidified digestate (from pH 8.2 to pH 5.4) to a wheat crop (Sanchez-Rodriguez et al., 2018). Loide et al. (2020) also found that the application of acidified (pH 5) slurry, at an application rate of 45 m<sup>3</sup> ha<sup>-1</sup>, reduced soil pH but only by 0.1 pH units.

Several authors have shown that acidification delays and decreases the rate of nitrification and mineralisation within the soil (Fangueiro et al., 2015; Fangueiro et al., 2010, 2016; Pantelopoulos et al., 2016a). However, the content of easily accessible organic matter will directly affect soil microbial activity, and indirectly on crop production and nutrient removal, as most nutrients are positively correlated with carbon availability (Fangueiro et al., 2015; Fangueiro et al., 2014; Sørensen & Eriksen, 2009). The effect of applying acidified slurry on N mineralisation and immobilization has been shown according to soil type (Fangueiro et al., 2016; Pantelopoulos et al., 2016a). Fangueiro et al. (2016) found that immobilization of N was lower in a vertic cambisol for the first 8 days of the experiment and increased levels mineralization in a vertic cambisol, haplic cambisol and a haplic regosol after 92 days when comparing acidified (pH 5.5) slurry to raw slurry application. Until

nitrification resumes, the risk of nitrogen losses are reduced as the increased  $NH_4^+$  is more stable in the soil (Fangueiro et al., 2015; Fangueiro et al., 2016; Webb et al., 2014).

Application of acidified slurry increases the amount of available P when compared to non-acidified slurry, this creates a potential to increase the impact of leaching if applied in excess of plant requirements (Fangueiro et al., 2015a). When acidified with H<sub>2</sub>SO<sub>4</sub>, Fangueiro et al. (2018) noted the increase of soil extractable S. The findings showed that extractable S increased from 0.1 mg SO<sub>4</sub> kg<sup>-1</sup> in the no-treatment control to 52.2 mg SO<sub>4</sub> kg<sup>-1</sup> in acidified band spread and incorporation and 26.6 mg SO<sub>4</sub> kg<sup>-1</sup> in band spread without incorporation within a sandy soil. Within a sandy-loam soil the increase was to a lesser degree but equally present, increasing from 10.8 mg SO<sub>4</sub> kg<sup>-1</sup> in the control to 42.3 and 40.4 mg SO<sub>4</sub> kg<sup>-1</sup> for acidified band spread with incorporation and without incorporation, respectively. For both soil types, the findings were significantly different between the control and soils receiving acidified slurry (Fangueiro et al., 2018).

#### 2.16 Impacts on plant health and yield

Increased slurry NH<sub>4</sub><sup>+</sup> following acidification, and its consequential impact on crop yield and health has been subject to investigation. Loide et al. (2020) reported ryegrass yields, protein yields and P content were greatest on plots receiving 45 m<sup>3</sup> ha<sup>-1</sup> of acidified cattle slurry. Similarly Fangueiro et al. (2015a) and Eriksen et al. (2008) reported that yields have increased in winter wheat, spring barley and maize after application of acidified products.

The impact of acidification on crop yield and health has been found to vary between site and soil type. For example, Seidel et al. (2017) found significant increases in yield following the application of acidified cattle slurry, but at only one of two sites included in the study. A similar result was found for N uptake, with significant differences found but inconsistently between harvests. In a study comparing the efficiency between seasonal applications, Pain et al. (1994) found that greater dry matter yield were always present but varied in acidified plots averaging out at 2.85 t DM ha<sup>-1</sup> at 1.6 t DM ha<sup>-1</sup> at two different sites. This was attributed to the increased residual NH<sub>4</sub><sup>+</sup> following acidification, similar to Fangueiro et al. (2017) who also found treatments with the highest NH<sub>4</sub><sup>+</sup> content, returned greater oat dry matter yields.

Kai et al. (2008) found that a reduction of pH 6.1 (from pH 7.3) using  $H_2SO_4$  was sufficient to increase the nitrogen fertiliser replacement of the slurry by 16 kg N ha<sup>-1</sup>. This finding is supported by Sørensen et al. (2009) who found a 25% increase in the mineral fertilizer equivalent when comparing acidified slurry to conventional slurries based on N uptake in winter wheat and barley. Overall, it is apparent that acidification can deliver improved crop yield and quality, without being detrimental to plant health, yet the extent of the impact is site specific (Fangueiro et al., 2018, 2015c; Park et al., 2017).

# 2.17 Cost of Acidification

The implementation of acidification will add financial cost to the farm enterprise, however, costs can be offset through increasing slurry N and S fertiliser value, and improvements to the indoor environment (Petersen et al., 2012; Seidel et al., 2017; Sommer et al., 2015) (Tables 2.4 and 2.5). Birkmose and Vestergaard (2013) suggested that the cost for in house cattle acidification is only implemented from an environmental perspective due to high costs not being recovered in the final product. Yet, Jacobsen (2017) indicates that the cost of in field acidification is comparable in cost to injection of raw slurry.

The total fertiliser savings associated with reduced NH<sub>3</sub> loss is greatest at the earliest stage (see Table 2.6). However, the estimated fertilizer saving of  $\pounds 1.22$  t<sup>-1</sup> slurry does not offset the total cost associated with acidification, and the application of acidified slurry may require additional liming fields to correct soil pH (Eriksen et al., 2008; Petersen et al., 2014; Sommer et al., 2015). After three applications of acidified slurry, Frost et al. (1990) suggests that 2-3 t of liming material will be required. Ten Hoeve et al. (2016) present this as 300-600 kg/ha of CaCO<sub>3</sub> needing to be added to maintain soil pH.

#### 2.18 Health and safety considerations

The acidification process presents various health and safety risks. The use of highly corrosive and hazardous  $H_2SO_4$  can increase the release of toxic  $H_2S$  (Fangueiro et al., 2015a; Kai et al., 2008; Park et al., 2017; Regueiro et al., 2016a). Foaming presents a risk to farm workers and livestock as strong acids rapidly buffer due to fast  $CO_2$  release, and increases the amount of volume needed in storage tanks (Kai et al., 2008; Regueiro et al., 2016a). Additives can be combined with the acidified slurry to minimise foaming, such as polypropylene glycol, but this will come at an addition cost to the farmer (Pain et al., 1994). As a consequence of dealing with strong acids, specially trained workers need to handle the acid which will also add additional costs and is often carried out by contractors in Denmark (Fangueiro et al., 2015a).

Table 2.4: Costs of acidification by livestock type.

The information above indicates costs extracted from the literature. These costs have been converted to  $\pounds$  sterling based on the conversion rate from the given currency the year prior to the information being collected.

\*Includes within the cost adjustments for fertilizer requirement reduction and other operational costs.

<sup>+</sup>Calculated based on the average slurry production supplied in DEFRA (2009), and for cattle housed for 42% of the year based on Eory et al. (2016) for continuity, pigs are presumed to be housed year-round.

	Liveste	alt type	In house	(£/LSU/yr)	In Tank (	£/LSU/yr)	In field (#	E/LSU/yr)
Author	Livesto	ск туре	Min	Max	Min	Max	Min	Max
Eory et al., 2016	Cattle					£6.98		
Jacobsen &	Cattle	Small scale		$\pounds 175.08^{+}$				
Stahl, 2018*	Cattle	Large scale		$\pounds 32.88^{+}$				
Jacobsen, 2015	Cattle							£4.49+
Birkmose & Vestergaard, 2013	Pig		$\pounds 9.65^+$	£11.27+	$\pounds 3.20^{+}$	$\pounds 6.45^+$	$\pounds 3.20^{+}$	$\pounds 6.45^{+}$
Kai et al.,	Pig			£48.00				
2008*	Pig			£32.00				
Eory et al., 2016	Pig					£6.01		
Jacobsen &	Dia	Small scale		£18.22				
Stahl, 2018 *	Flg	Large scale		£5.15				
Jacobsen, 2015	Pig							£2.22+

Table 2.5: Infrastructure and maintenance costs for acidification.

The information clearly indicates the high costs related to in-house acidification but does not take into account the potential greater emission abatement through acidifying earlier in the manure management chain. All costs have been converted into £ sterling from original currency based on conversion rate in the year prior to publication.

Author	Stage of acidification	Capital cost	Maintenance (£/yr)	Acid (£/t)
Sommer, 2015	In-house	£134,146	£2,988	£0.71
Earry at al	In-house	£70,000	£5000	
Eory et al., $2016$	Storage	£9,000	£5000	£0.57
2010	In-field		£400	£1.27

Table 2.6: Nitrogen savings through acidification.

The information compiled from various studies highlights the reduction potential along the manure management chain. The reductions are found in isolation, which do not take into account the impact of previous or later management.

						Treatment		Acidified		<b>Reductions</b>	
<u>Author</u>	<u>Stage of</u> <u>Acidification</u>	Location	<u>Slurry</u> Type	Slurry	Hd	$\overline{\mathrm{NH}_3}$	Hd	<u>NH</u> 3	<u>NH<sub>3</sub> reduction</u>	pH reduction	% Reduction
			Pig	Spring	7.1	164 g N pig- <sup>1</sup>	6.1	55.5 g N pig <sup>-1</sup>	108.5 g N pig- <sup>1</sup>	1	66.16
Petersen et al., 2016	In-house	Field	Pig	Summer	7.1	284 g N pig- <sup>1</sup>	6.1	158 g N pig- <sup>1</sup>	126 g N pig- <sup>1</sup>	1	44.37
			Pig	Autumn	7.1	241.9 g N pig- <sup>1</sup>	6.1	70.9 g N pig <sup>-1</sup>	171 g N pig- <sup>1</sup>	1	70.69
Hjorth et al., 2015	In-house	Field	Pig	Raw	7.1	$21 \ \mu g \ L^{-1}$	5.3	5.6 μg L <sup>-1</sup>	15.4 μ gL <sup>-1</sup>	1.78	73.33
			Cattle	cool	7.3	$104 \text{ g } \text{NH}_3\text{-}\text{N} \text{ m}^{-3}$	5.6	$46 \text{ g } \text{NH}_3\text{-N m}^{-3}$	58 g NH <sub>3</sub> -N m <sup>-3</sup>	1.7	55.77
Misselbrook et al., 2016	Storage	Lab	Cattle	temperate	7.1	$166 \text{ g } \text{NH}_{3}\text{-N} \text{m}^{-3}$	5.5	2 g NH <sub>3</sub> -N m <sup>-3</sup>	$164 \text{ g } \text{NH}_3\text{-N} \text{m}^{-3}$	1.6	98.80
			Cattle	warm	7.3	321 g NH <sub>3</sub> -N m <sup>-3</sup>	5.1	$102 \text{ g } \text{NH}_3\text{-}\text{N} \text{m}^{-3}$	$219{ m gNH_{3}-Nm^{-3}}$	2.2	68.22
Sommer et al., 2017	Storage	Lab	Cattle	Raw	7.2	8 g N m <sup>-2</sup>	5.4	3 g N m <sup>-2</sup>	$5~{ m g~N}~{ m m}^{-2}$	1.8	62.50
Park et al., 2018	Application	Field	Pig	Raw	7.9	$4.25 \ \mathrm{kg} \ \mathrm{NH}_{3}\text{-}\mathrm{N} \ \mathrm{ha}^{-1}$	5	$1.6 \mathrm{kg}\mathrm{NH_3-N}\mathrm{ha^{-1}}$	$2.65  \mathrm{kg}  \mathrm{NH_{3}-N}  \mathrm{ha^{-1}}$	2.9	62.35
			Cattle	Raw	7.5	$41.33 \text{ kg NH}_{3}\text{-N ha}^{-1}$	5.5	$6.88  \mathrm{kg}  \mathrm{NH_3-N}  \mathrm{ha^{-1}}$	34.45 kg NH <sub>3</sub> -N ha <sup>-1</sup>	2	83.35
			Cattle	5mm sieve	7.5	33 kg NH <sub>3</sub> -N ha <sup>-1</sup>	5.5	$7.11 \ \mathrm{kg} \ \mathrm{NH}_3\text{-}\mathrm{N} \ \mathrm{ha}^{-1}$	25.89 kg NH <sub>3</sub> -N ha <sup>-1</sup>	2	78.45
Frost et al., 1990	Application	Field	Cattle	3mm sieve	7.5	30.57 kg NH <sub>3</sub> -N ha <sup>-1</sup>	5.5	7.9 kg $NH_3$ -N ha <sup>-1</sup>	22.67 kg NH <sub>3</sub> -N ha <sup>-1</sup>	2	74.16
			Cattle	0.25mm sieve	7.5	21.99 kg NH <sub>3</sub> -N ha <sup>-1</sup>	5.5	4.34 kg NH <sub>3</sub> -N ha <sup>-1</sup>	17.65 kg NH <sub>3</sub> -N ha <sup>-1</sup>	2	80.26
			Cattle	0.015 mm sieve	7.5	$16.17  \rm kg  NH_{3}$ -N ha <sup>-1</sup>	5.5	$4.53 \text{ kg } \text{NH}_{3}\text{-N} \text{ha}^{-1}$	11.64 kg NH <sub>3</sub> -N ha <sup>-1</sup>	2	71.99
Fangueiro et al., 2015	Application	Lab	Cattle	Surface applied	7.2	1.7 mg N kg <sup>-1</sup> dry soil	5.5	0.2 mg N kg <sup>-1</sup> dry soil	1.5 mg N kg <sup>-1</sup> dry soil	1.7	88.24
	4		Cattle	Surface applied LF	7.2	$0.1 \text{ mg N kg}^{-1} \text{ dry soil}$	5.5	0.1 mg N kg <sup>-1</sup> dry soil	0 mg N kg <sup>-1</sup> dry soil	1.7	0.00
Pain et al., 1994	Application	Field	Cattle	Raw	8	46.1 N kg ha <sup>-1</sup> N	5.5	14.3 N kg ha <sup>-1</sup> N	31.8 N kg ha <sup>-1</sup> N	2.5	68.98
Nirond at al 2013	Amination	Field	Pig	Field trailing hose	7.8	20.1 % TAN	6.8	6.1% TAN	14 % TAN	1	69.65
	ъррисацон	nici.r	Pig	Field soil injected	7.3	8.6 % TAN	6.2	6.9% TAN	1.7 % TAN	1.1	19.77
2100 1-1-1-F.1-B		T:11	Cattle	Band spread	7	14% TAN	6.5	8.1% TAN	5.9 % TAN	0.5	42.14
Seidel et al., 2017	Application	Field	Cattle	Band spread	7	14% TAN	9	2.9% TAN	11.1 % TAN	1	79.29

# 2.19 Conclusions and knowledge gaps

After compiling details from the literature, specific studies regarding the impact of slurry acidification on soil quality are largely absent. A number of studies include soil nutrient availability, especially N forms. Although 20 papers include pH measurements, these are mostly measurements made at the start and end of the experimental period (Figure 2.3 and 2.4).





The graph shows the number of studies including each variable, which includes experiments carried out in field and laboratory, as well as those using pig, or cattle slurry, as well as acidified digestate.



Figure 2.4: Acidified cattle slurry inclusions.

The graph shows the number of times the impact of acidified cattle slurry on soil chemical and biological, and crop quality indicators have been reported in the literature.

The duration of each experiment ranged from 30 minutes through to two years, however, the average length of experiment was 81 days, indicating a lack of insight into the repeated application of acidified slurry. Jacobsen (2017) identified the long-term impact of acidified slurry as a key knowledge gap. The following chapters will add to these knowledge gaps, including an assessment of the longer-term impact of slurry acidification on soil chemistry, and biology, as well as the impact of different application techniques on gaseous emissions.

Although impacts along the entire manure management chain have been studied, approximately 70% of research has been carried out at the application stage. Of these, 19 out of 27 reported on the impacts at storage. The remaining eight studies focused on various different stages of the management chain including separation, with limited studies assessed in-house impacts. A breakdown of studies that included emissions data are shown below (Figure 2.5) and highlight that NH<sub>3</sub> emissions have been the focus of the greatest number of studies.



Figure 2.5: Gaseous emission inclusions in acidified slurry studies.

Summary of gas emission inclusions from previous studies, NH<sub>3</sub> loss has been studied in greater detail than other emissions.

This literature review has highlighted the need for the UK agriculture sector to reduce it's NH<sub>3</sub> emissions in order to meet the 2030 NECR targets. Various techniques to abate NH<sub>3</sub> losses, including low emissions spreading techniques and slurry store covers, are currently available for farmers. However, these may not be suitable for implemention on all farms depending on farm climate, soil type and on-farm infrastructure. The use of slurry acidification is commonly used in Denmark and this review has found evidence that the technique is effective in reducing NH<sub>3</sub>, while improving the fertiliser value of slurry, but the use of slurry acidification is not widely used in the UK. This study will aim to address the knowledge gaps highlighted in Figures 2.3, 2.4 and 2.5 and provide insight into the potential for slurry acidification to be included as an option for the agriculture sector to reduce their NH<sub>3</sub> emissions through experimentation in UK conditions.

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# <u>Chapter 3:</u> <u>Slurry acidification increases NH<sub>4</sub><sup>+</sup> availability and does not lead to a long</u> <u>term reduction of soil pH: a UK field study</u>

## Abstract

The UK Government has committed to a 16% reduction in ammonia (NH<sub>3</sub>) emissions by 2030 and has identified agriculture as the main source of emissions, accounting for approximately 90% of total UK NH<sub>3</sub> emissions. Slurry acidification - the addition of concentrated acid to slurry - significantly reduces NH<sub>3</sub> volatilisation at all stages of the manure management continuum and has been reported to shift the NH<sub>3</sub>:NH<sub>4</sub> ratio strongly in favour of NH<sub>4</sub>. Additional benefits of acidification also includes the increased availability of phosphorus (P), as well as reducing methane (CH<sub>4</sub>) emissions. Before slurry acidification can be considered as a suitable NH<sub>3</sub> emissions mitigation strategy for use in the UK, the wider impacts on soil and crop quality need to be assessed.

Single and repeat application field plot-scale experiments were established on a grass ley in 2019 and 2020 to assess the immediate and legacy effect of acidified (pH 5.5) cattle slurry. Acidified and conventional slurry was applied via surface broadcast and band spreading at 40 m<sup>3</sup> ha<sup>-1</sup>, alongside inorganic fertiliser N response plots. Key soil chemical, biological and physical characteristics were sampled throughout the multi-year experiment, along with grass N use efficiency and N fertiliser replacement values at each harvest.

The data presented shows that slurry acidification has no negative impacts on soil quality when applied to a typical Welsh grassland. Short-term reductions to soil pH were found with the greatest difference between conventional and acidified treatments of 0.75 pH units under band spread applied slurry. Soil microbial respiration was inhibited over the initial 48 hours, with acidified treatments reducing soil respiration by a maximum of 1.5 g CO<sub>2</sub> m<sup>-2</sup> hr<sup>-1</sup> (75%) under band spread applied acidified slurry. The use of acidification was found to numerically increase the N fertiliser replacement value by 100% and N use efficiency by up to an additional 50%, highlighting the potential benefit of conserving NH<sub>4</sub>-N in the soil following acidified slurry application.

#### 3.1 Introduction

Ammonia (NH<sub>3</sub>) volatilisation from slurry decreases its fertilizer value, damages sensitive ecosystems when deposited, and acts as a precursor to PM<sub>10</sub> and PM<sub>2.5</sub> air pollution (Chen et al., 2015; Greaver et al., 2016; Paulot and Jacob, 2014; Sommer et al., 1991; Velthof and Mosquera, 2011). Commercial slurry acidification - the addition of concentrate H<sub>2</sub>SO<sub>4</sub> to slurry - is an NH<sub>3</sub> abatement tool used to minimise NH<sub>3</sub> loss from the all stages of the manure management continuum (housing and storage: Owusu-Twum et al., 2017b; Petersen et al., 2016a, spreading: Nyord et al., 2013). The addition of H<sub>2</sub>SO<sub>4</sub> shifts the NH<sub>3</sub>:NH<sub>4</sub><sup>+</sup> ratio to a point where NH<sub>4</sub><sup>+</sup> represents up to 98% of total ammoniacal N (TAN), a form of N that is plant available, and less prone to leaching and volatilizing (Berg et al., 2006b; Cocolo et al., 2016; Fangueiro et al., 2015a; Misselbrook et al., 2016; Park et al., 2017; Sommer et al., 2017). In addition, slurry acidification can bring benefits beyond those involved with lower NH<sub>3</sub> volatilisation, such as the reduction of methane (CH<sub>4</sub>) emissions during slurry storage (Bastami et al., 2016; Misselbrook et al., 2016).

The target pH for commercial in-house slurry acidification is pH 5.5 (Fangueiro et al., 2015a), which has the potential to influence soil pH once applied, and has been the subject of various studies. A UK based experiment (Sánchez-Rodríguez et al., 2018) found a reduction of soil pH on a Dystric Cambisol with a maximum difference (1 pH unit) from the unamended control found after 1 month, following a single application of acidified digestate. The same experiment found conventional digestate initially reduced soil pH before returning to the control value by the end of the first month after application (Sánchez-Rodríguez et al., 2018). However, D'Annibale et al. (2019) noted that there was little change to soil pH after 28 days when digestate was applied via surface broadcasting. Following band spread application, Pedersen et al. (2017) reported a reduction of up to pH 1.1 (initial soil pH 6.5) beneath slurry bands following application of acidified (pH 5.5) cattle slurry as well as diffusing into the soil between the bands, yet conventional slurry either retained or increased the soil pH when compared to the soil pH pre-application (pH 6.5). Given that some other authors have reported no significant differences found between acidified and conventional applications (Christel et al., 2016; Fangueiro et al., 2018, 2015b; Sigurnjak et al., 2017), the impact of acidified slurry on soil pH is ultimately dependent on factors including soil type, initial soil pH, soil organic matter, and number of slurry applications.

The chemical process of slurry acidification shifts slurry TAN to be dominated by  $NH_{4^+}$  and consequently impact soil inorganic N concentrations. As with any slurry application, soil  $NH_{4^+}$  concentrations have been found to increase immediately following application of acidified slurry, yet the increase is often greater in scale and persists for longer periods when compared to conventional

slurry. D'Annibale et al. (2019) reported greater  $NH_4^+$  concentrations are found in acidified treatments up to 28 days after application. Similar findings are outlined in Sánchez-Rodríguez et al. (2018) where soil  $NH_4^+$  concentrations remained greater in acidified plot for up to 6 weeks compared to conventional digestate plots which returned to control (no amendment) concentrations at 4 weeks.

Following the application of acidified slurry, it is paramount for N to remain in plant available forms in the soil profile (i.e. not leached as  $NO_3^-$  or denitrified) if acidification is to improve the fertilizer equivalent of the slurry. Microbial processes such as nitrification have been found to be delayed in plots receiving acidified digestate. Fangueiro et al. (2015a) reviewed data which highlighted a delay in nitrification in acidified treatments by between 20 and 60 days, compared to conventional slurry. A more recent study (Park et al., 2017) provided further evidence of such a delay with acidified pig slurry plots reaching peak  $NO_3^-$  concentrations 40 days after that of conventional slurry. Such a delay in nitrification has been described as a direct response of nitrifying bacteria being inhibited in a soil below pH 6.0.

Denitrification has also been subject to study to assess if greater concentrations of soil NH<sub>4</sub><sup>+</sup> results in potential N pollution swapping, most notably increased N<sub>2</sub>O emissions, a greenhouse gas approximately 300 times more potent than CO<sub>2</sub> (IPCC, 2021). N<sub>2</sub>O-N emissions have been found to be lower for acidified pig slurry until day 50 when compared to conventional slurry, after which cumulative N<sub>2</sub>O-N emissions remained greater until the end of the experiment (Fangueiro et al., 2010). Contrary to this study, others have found that N<sub>2</sub>O emissions decreased by up to 72% when pig slurry was applied at pH 5, likely a response of denitrifying populations and activity levels reacting to changes in soil pH (Park et al., 2017; Sánchez-Rodríguez et al., 2018). A reduction in microbial consumption of C, i.e. reduced CO<sub>2</sub> emissions as well as increased soil organic matter content, has been measured in acidified plots compared to conventional slurry or digestate (Fangueiro et al., 2018; Pantelopoulos et al., 2016a).

Crop yields and N offtake have been found to increase as a result of prolonged increases in soil NH<sub>4</sub><sup>+</sup> concentrations in response to reduced NH<sub>3</sub> emissions and delayed microbial processes following the application of acidified slurry (Frost et al., 1990; Pantelopoulos et al., 2017). However, the conditions during and immediately after application are vital for available N to reach the root zone of plants. Dry conditions have been shown to promote the crusting of slurry before it is able to percolate into the soil, thus reducing N availability, whereas rainfall immediately after application can limit NH<sub>3</sub> volatilisation and reduce the gains in yield expected from acidifying when compared to a conventional slurry (Fangueiro et al., 2018; Frost et al., 1990). Dry matter yield and N offtake are also highly

dependent on soil type with factors such as soil texture and organic matter content having a significant impact, as well as the timing of application in relation to plant growth stages (Fangueiro et al., 2018; Seidel et al., 2017). A number of authors have reported an increase of both arable and grass dry matter (DM) yields following acidified treatments being applied (Fangueiro et al., 2018, 2017; Pedersen et al., 2017; Sánchez-Rodríguez et al., 2018) while others found that DM yields were not significantly different to conventional slurry (Fangueiro et al., 2015; Seidel et al., 2017). Studies reporting N fertilizer replacement values (NFRV) comparing conventional and acidified slurry or digestates have found NFRV increased from 25 - 43% when acidified treatments have been applied to winter wheat and up to 40% for ryegrass (Birkmose and Vestergaard, 2013; Kai et al., 2008; Pantelopoulos et al., 2017; Sánchez-Rodríguez et al., 2018; Seidel et al., 2017).

Acidification has also been found to impact phosphorus availability within slurry. Fangueiro et al. (2018) stated that acidified slurry solubilized and increased P availability, yet warns of increased leaching and immobilization within soil. This is furthered by Pedersen et al. (2017) and Li et al. (2020) who state that acidification significantly increased water extractable P in slurry acidified to pH 5.5 compared to untreated slurry, but is at risk of being lost due to immobility within the soil. Acidification has been reported not to impact organic forms of P and mineralization of P, but could inhibit P immobilization as a possible consequence on enzyme shifts reflecting the change in soil pH as well as increases dissolved inorganic-P and P content in the smallest particulate fractions (Li et al., 2020, 2019; Roboredo et al., 2012). Soil type is found to influence P availability, with Fangueiro et al. (2018) reporting that in sandy soil more P was solubilized after acidified slurry was incorporated, whereas in a sandy loam large amounts of P was immobilized.

Following application of acidified slurry, key soil quality parameters have been found to increase, including electrical conductivity (EC) in soil amended with acidified slurry and sulphur (S) availability when compared to conventional slurry (Fangueiro et al., 2018; Sánchez-Rodríguez et al., 2018; Sigurnjak et al., 2017). Pedersen et al. (2017) reported that as a consequence of struvite dissolution and P bound to calcium phosphate minerals, acidification has increased magnesium (Mg) and calcium (Ca) levels found in the acidified slurry (Li et al., 2019; Roboredo et al., 2012). Similarly, potassium (K) has also been found to significantly increase when acidified slurry was surface spread (Fangueiro et al., 2018).

Given that the UK government has committed to a 16% reduction in NH<sub>3</sub> emissions by 2030, acidification could be included as a mitigation strategy for the agricultural sector (HM Government, 2018a), alongside other NH<sub>3</sub> mitigation strategies, e.g. slurry injection, band spreading, and rapid

incorporation of slurry on arable land (Defra, 2018). This research will address the knowledge gaps surrounding the impact of slurry acidification on soil and crop quality, especially soil pH and alterations to microbial processes, which could be problematic for land managers. This requires greater research from a UK perspective as to the suitability of the abatement technology, especially given the impact of climatic variables underpinning the importance of multi-season and multi-year experimentation.

#### 3.2 <u>Aim</u>

The main aim of the study was to understand the impact of slurry acidification on soil and crop productivity. Biological, chemical, and physical characteristics were assessed to comprehensively understand the impact in a UK setting.

# 3.3 Hypothesis

- a) Based on the results found by others, there will be no negative impact of slurry acidification and application technique on soil pH
- b) The availability of NH<sub>4</sub>-N will increase in acidified plots, without resulting in increased  $N_2O$  emissions or  $NO_3^-$  leaching
- c) Fertilizer value of slurry will improve with the addition of acidified slurry compared to conventional slurry
- d) There will be no long-term impact on soil fauna communities following the application of acidified slurry compared to conventional slurry or ammonium nitrate application.

# 3.4 Methods

#### 3.4.1 Experimental Design and Establishment

A 1 ha plot (Henfaes Research Station, Abergwyngregyn, North Wales - 53°14′21 N, 4°0′50 W; 10 m above sea level), was ploughed and reseeded with an Italian ryegrass mix (Sabre mix) (Oliver Seeds, Worcestershire, UK) in Autumn 2018, before initiating experimentation in spring 2019. Four separate experiments were carried out in this grassland area; Spring 2019, Summer 2019, Spring 2020 and Summer 2020. The site is characterised as a free draining Eutric Cambisol with a sandy clay loam texture and crumb structure (Table 3.1).

For each experiment, plots (10 m x 2.5 m) were established in a randomised block design with 3 replicates (Appendix 1.1). The treatments used at each application included acidified and conventional cattle slurry, applied via surface broadcasting and band spreading, with additional N (ammonium nitrate) response plots comprising control (0 kg N ha<sup>-1</sup>), 25 kg N ha<sup>-1</sup>, 50 kg N ha<sup>-1</sup>, 100 kg N ha<sup>-1</sup> and 150 kg N ha<sup>-1</sup> included to calculate N fertiliser replacement rates.

A further experiment was established alongside the four single applications to investigation the impacts of repeated applications of acidified slurry on soil quality indicators. Conventional slurry and acidified slurry were surface broadcast to replicate plots in a randomised block design with plots receiving up to four repeated treatments. Throughout the experiment all plots received two applications, six plots for each treatment then received an additional application (three applications), with a final three plots receiving four applications.

#### 3.4.2 <u>Slurry properties</u>

Cattle slurry was sourced from 3 different dairy cattle farms in North Wales across the 4 applications (Table 3.2). Once delivered to the field site, the slurry was mixed within the tanker before being pumped into two identical storage tanks ( $1.75 \text{ m}^3$ ). One tank stored conventional (as delivered) slurry, the other tank was acidified to pH 5.5 with 98% H<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich, UK). The slurry tanks were covered prior to slurry application.

#### 3.4.3 Acidification

Acidification was performed in tank, replicating storage acidification. A 1 l aliquot was sampled from the slurry tank to be acidified and a titration was performed to indicate the quantity of  $H_2SO_4$  required for the tank quantity. For tank acidification,  $H_2SO_4$  was added gradually, stirred, and pH measured with a mobile Hanna Instruments pH meter. Acidification took place up to 5 days (range 1-5 days) before application. In spring and summer 2020 slurry pH increased as a result of buffering and additional  $H_2SO_4$  was added on the day of application (Appendix 1.2).

#### 3.4.4 Slurry application

At application, each slurry storage tank was homogenised, with large pieces of dry matter removed to ensure a representative sample was applied to each plot. Both slurry application methods were applied at a rate of 40 m<sup>3</sup> ha<sup>-1</sup>, typical of moderate output grazing livestock farming systems (Defra, 2021), using watering cans with (surface broadcasting) or without (band spreading) spoon attachments. Surface broadcast treatment resulted in 100% coverage of each plot whereas plot coverage for band spreading ranged from 20 - 37% for conventional slurry band spread and 23 - 33% for acidified band spread (Appendix 1.3).

#### 3.4.5 Soil sampling

Topsoil (0-7.5 cm) was randomly sampled (10 per plot) in each plot and bulked to provide one composite sample per plot after vegetation and stones were removed. During 2019, all slurry treatments and control (no-amendment) were included in regular soil sampling. Soil samples were collected from the band itself (0 cm) and midway between the bands (15 cm) to assess any diffusion

effects. Ammonium nitrate (100 kg N ha<sup>-1</sup>) was included in regular soil sampling in 2020, alongside the control and slurry treatments to understand the relative impacts of slurry treatments in comparison with a typical rate of ammonium nitrate fertiliser application in a grazing livestock system (Defra, 2021b).

In 2019, soil samples were collected three times in the first week after application, bi-weekly for the following two weeks and weekly thereafter until harvest, with a final sample being collected the day before harvest, in 2019. In spring 2020, the Covid-19 pandemic restricted sampling frequency to 4 sample points in the first week after application, and then weekly thereafter until the end of the growing season. For the Summer 2020 experiment, soil sampling returned to greater frequency. In week 1, samples were collected on 4 occasions, 3 in week 2, 2 in week 3 and 4, then weekly until harvest.

# 3.4.6 Soil Measurements

#### 3.4.6.1 Soil chemical analysis

At each application, soil pH was measured in 1:2.5 (w/v) (soil: DiH<sub>2</sub>O) using a using a Hanna Instruments Model 210 pH meter (Hanna Instruments Ltd., Leighton Buzzard, UK). Soil EC was measured with a Jenway conductivity probe in conjunction with a Jenway 4520 conductivity meter (Cole-Palmer Ltd., Stone, UK). Extractable NH<sub>4</sub>-N and NO<sub>3</sub>-N was measured using a 0.5 M K<sub>2</sub>SO<sub>4</sub> extraction (1:5 w/v). Acetic acid extractable phosphorus was measured using 1:5 (w/v) soil to 0.5 M acetic acid solution. Soil NH<sub>4</sub>-N, NO<sub>3</sub>-N and PO<sub>4</sub>-P concentrations were analysed using the Mulvaney (1996), Miranda et al. (2001), and Murphy and Riley (1962) colorimetric methodologies for analysis on an Epoch<sup>®</sup> microplate spectrophotometer (Bio Tek Instruments Inc., Winooski, USA).

Remaining soil samples were oven dried at 105°C for 24 hours to calculate gravimetric moisture content.

# 3.4.6.2 Soil biology analysis

# 3.4.6.2.1 Greenhouse gas sampling and analysis

Nitrous oxide ( $N_2O$ ) sampling was included in 2020 to help understand the wider impacts of slurry acidification. However due to Covid-19 restrictions sampling was limited to one application - spring 2020. Gas sampling matched the soil sampling over the period.

Replication for greenhouse gas sampling was increased (n=5) by the introduction of specific greenhouse gas sampling plots (6 m<sup>2</sup>) (Appendix 1.1). Three static chambers (40 cm x 40 cm x 25 cm) were randomly positioned and inserted to a depth of 5 cm within each plot. The sampling method

outlined in Cardenas et al. (2016), was employed. At each sample point, 10 ambient air samples were collected (T0) as the lids were placed on the chambers, with all static chambers sampled after 60 minutes closure (T60), as previous research has demonstrated that linear increases of headspace N<sub>2</sub>O concentrations occur within 1 hour for this headspace volume when N is applied to the soil (Chadwick et al., 2014). Linearity checks were made on headspace N<sub>2</sub>O concentrations by randomly selecting one chamber from each experimental block and collecting headspace samples at T10, T20, T30, T40, and T50, in addition to T60 minutes. A 20 ml syringe was used to collect headspace gas samples from each chamber, which were then stored in 20 ml pre-evacuated glass vials before analysis. N<sub>2</sub>O analysis was performed on a Varian 450 Gas Chromatograph (Agilent Technologies, Santa Clara, CA) fitted with an ECD, with cumulative greenhouse gas totals calculated using the trapezoidal rule (Marsden et al., 2016).

#### 3.4.6.2.2 CO<sub>2</sub> Respiration

An EGM-5 portable  $CO_2$  gas analyser (PP Systems, Amesbury, USA) was used to detect  $CO_2$  fluxes on each slurry and control plot. The analyser detected  $CO_2$  levels over a 2-minute period after placement on the soil surface. The linear increase in headspace  $CO_2$  concentration was used to determine the flux. Samples were taken over the initial 18 days following application mirroring the time points of the soil and greenhouse gas sampling regime.

#### 3.4.6.2.3 Earthworm Counts

Earthworm sampling occurred following harvest in summer 2020, with all repeat plots, control and a single application of ammonium nitrate (100 kg N ha<sup>-1</sup>) included in sampling. A block of soil was removed from the field (20 cm x 20 cm x 25 cm) and destructively sampled, based on the methods outlined in Fusaro et al. (2018). Earthworms were collected, with all soil removed, before being counted and weighed. The earthworm numbers were then extrapolated to give values of earthworm density (number) m<sup>-2</sup> and earthworm biomass (weight) m<sup>-2</sup>.

# 3.4.6.2.4 Mesofauna

Soil mesofauna samples were collected using a core (10 cm diameter and 7.5 cm deep) from plots receiving four repeated slurry broadcast applications of both acidified and conventional slurry, control (no amendment), and ammonium nitrate. A Tullgren funnel was used over a 7-day period with samples being collected in 70% ethanol. Identification was carried out at ADAS Gleadthorpe to order or suborder level for mites, and order or superfamily for collembola, as detailed in George et al. (2017).

#### 3.4.6.2.5 Soil microbial 16S sequencing

Samples were taken from the topsoil (0-7.5 cm) of plots receiving 4 applications of surface broadcast acidified and conventional slurry immediately after application, at day 21 - the day where soil pH was greatest from 2019 applications - and at harvest, day 49. Following sampling, soil was stored at -80°C. Microbial genomic DNA was extracted from the sampled soils as per protocol set out in the DNeasy PowerSoil Pro Kit (Qiagen,UK). The quality and concentration of extracted DNA was evaluated using gel electrophoresis and by Qubit 4.0 Fluorometer dsDNA BR Assay Kit (Life Technologies, Carlsbad, CA). Libraries of 16S rRNA gene amplicons were prepared by single PCR with double-indexed fusion primers as outlined in Fadrosh et al. (2014). The PCR was performed on an Illumina MiSeq platform (Illumina, San Diego, CA) using 500-cycle v2 chemistry ( $2 \times 250$  bp paired-end reads) at the Centre for Environmental Biotechnology, Bangor. Outputs were analysed using the "vegan" (Oksanen et al. 2020) and "phyloseq" (McMurdie and Holmes, 2013) packages, with results graphed using "ggplot2" (Wickham, 2016).

#### 3.4.6.3 Soil physical analysis

#### 3.4.6.3.1 Visual Evaluation of Soil Structure (VESS).

At the conclusion of the multi-year experiment a visual evaluation of soil structure (VESS) was undertaken on all repeat plots. An intact sod of soil (20 cm x 20 cm x 25 cm) was removed from each plot and separated at each visible horizontal change in soil texture. These were then evaluated in terms of their structure in line with the methods outlined in Guimarães et al. (2011).

# 3.4.6.4 Plant analyses

# 3.4.6.4.1 Grass quantity

Grass harvests were carried out a minimum of 8 weeks after slurry and fertiliser application, and once (at least) 60% of the grass had gone to seed. A 12 m<sup>2</sup> area was cut and weighed (fresh weight) from each plot with a sub-sample weighed (fresh weight) in the laboratory and dried at 80°C for a minimum of 48 hours to determine DM yield. A sub-sample was then ground and analysed for total N using a TruSpec analyser (Leco Corp., St Joseph, MI) to determine N offtake.

## 3.4.6.4.2 Nitrogen use efficiency (NUE)

Nitrogen use efficiency was calculated by using total N analysis and DM yield to determine N offtake and was calculated based on the equations outlined in Sánchez-Rodríguez et al. (2018).

# 3.4.6.4.3 <u>N fertiliser replacement value (NFRV)</u>

To calculate the NFRV, the values for control and N response treatments (25, 50, 75, 100, and 150 kg N ha<sup>-1</sup>) DM yield and N offtake were modelled in a regression creating N response curves. The

regression equation was used to calculate the NFRV for DM yield and N offtake for each treatment and application similar to that used in Frost et al. (1990).

# 3.4.7 Weather conditions

Weather data was collected throughout the experimental period on a Campbell Scientific (Loughborough, UK) weather station situated at Henfaes Research Station. Daily mean temperatures and rainfall were calculated from the raw data provided. Water filled pore space was calculated using the provided volumetric moisture content.

## 3.4.8 Statistical analysis

Throughout the experiment, statistical analysis was performed using R v. 4.1717 (R Core Team, 2019) where a *p* value of p<0.05 was accepted as significant. Where data met normality assumptions, a linear mixed model was used to assess variables against slurry treatment and time following application. These were then subjected to an ANOVA (stats package, R Core Team, 2019) and if significant differences were found "lsmeans" (emmeans, Lenth, 2021) was used to carry out Tukey post-hoc tests. For single time point data analysis, an ANOVA (stats package, R Core Team, 2019) was performed. Where data failed to meet normality assumptions, a non-parametric Kruskal-Wallis test (stats package, R Core Team, 2019) was performed. All repeated application statistical analysis was performed using the same techniques as that outlined for single applications, but was carried out for each growing period. All results were graphical illustrated with "ggplot2" (Wickham, 2016).

## 3.5 <u>Results</u>

# 3.5.1 Soil properties

Throughout the experimental period pre-application soil properties remained similar with the exception of PO<sub>4</sub>-P in summer 2020. The greater levels of PO<sub>4</sub>-P found here is a result of sampling occurring following phosphate fertiliser application to the field.

#### 3.5.2 Slurry Properties

Applied slurry properties varied at each application (Table 3.2). Organic matter ranged from 2.1% (Application 1) to 5.7% (Application 3), and ammonium N applied ranging from 586 mg kg<sup>-1</sup> ( $\pm$  29.57 Application 1) to 1240.3 mg kg<sup>-1</sup> ( $\pm$ 14.4 Application 4).

# Table 3.1: Pre-application soil properties (0-10 cm).

Values shown represent means  $\pm$  standard error (n=3). All values are expressed on a dry matter basis with the exception of pH and EC. Organic matter was only measured at the beginning of the experiment and represents values for all areas of the 1 ha plot.

		20	10			20	20	
		20	19			20	20	
	Spring	±	Summer	±	Spring	±	Summer	±
Organic matter (%)	5.7	0.10						
pH	6.1	0.13	6.9	0.05	6.4	0.05	6.3	0.09
EC ( $\mu$ S cm <sup>-1</sup> )	79.1	54.10	24.6	1.66	63.6	5.48	60.1	2.42
Extractable NH4 <sup>+</sup> (mg N kg <sup>-1</sup> )	1.1	0.07	1.0	0.06	0.8	0.04	3.2	0.63
Extractable NO3 <sup>-</sup> (mg N kg <sup>-1</sup> )	0.9	0.03	0.5	0.03	0.4	0.14	3.7	0.24
Extractable PO <sub>4</sub> (mg P kg <sup>-1</sup> )	5.6	0.76	6.0	0.47	10.0	1.51	53.0	26.7
Bulk density (g cm <sup>-3</sup> )	1.1	0.07	1.1	0.03	1.1	0.07	1.1	0.06

3.5.3 Soil Chemistry

# 3.5.3.1 <u>pH</u>

Over four separate applications, soil pH followed a general trend, albeit non-significant with the exception of summer 2020 (Figure 3.1). Acidified slurry was found to reduce soil pH following each application method when compared to conventional slurry. The inclusion of ammonium nitrate gives a clear indication as to the change in pH compared to common agricultural practises and shows the soil pH change within plots receiving acidified slurry resembling a similar reduction to that of plots receiving ammonium nitrate.

Significant reductions in soil pH following application in summer 2020 were consistently found between samples taken on the acidified band of slurry (0 cm) and all conventional slurry treatments. Such a difference was observed from 1 day after application through to harvest (day 48), with soil pH from the acidified band spread treatment having a minimum pH of 5.75 ( $\pm$  0.13, day 14) while the lowest pH for the conventional band spread treatment being pH 6.17 ( $\pm$  0.02, day 6 on band) and pH 6.23 ( $\pm$  0.03, day 31 between bands). The soil pH between the bands of the conventional slurry treatment was similar to the control, which had a minimum of pH 6.19 ( $\pm$  0.03, day 10).

Slurry analysis carried c application in the Bangor	out by <b>N</b> r Univer	NRM (0 sity lab	Cawood oratory	l Scient . Value	ific Ltd s shown	l., Brac	knell, U ent mea	JK) wit ns, and	th the e error ba	xceptic ars repr	on of pl esent Sl	H, which $EM$ ( $n=$	ch meas ₌3).	ured at	the tin	le of
Slurry origin: application application 4 – a large da	ns 1 and uiry herd	2 – a lɛ l, Gwyn	rge dai edd, No	ry herd orth Wa	in Conv les.	wy, No	rth Wale	ss; appl	ication	3 – a si	nall dai	ry herd	in Gwy	medd, 1	Vorth W	ales;
_		Andica	tion 1			Andica	tion 3			Annlica	tion 2			Andres	tion 4	
	Raw	randdy +	Acid	+	Raw	+	Acid	+	Raw		Acid	+	Mean		Mean	+
Oven dry solids (%)	4.2	0.20	4.0	0.31	4.1	0.17	3.7	0.51	7.7	0.41	8.0	0.14	4.2	0.25	4.5	0.10
Organic Matter (%)	2.4	0.15	2.1	0.16	2.6	0.11	2.3	0.36	5.3	0.28	5.7	0.20	2.6	0.17	2.6	0.08
Total N (mg/kg)	1666.7	33.33	1700.0	100.00	1866.7	33.33	1833.3	66.67	2966.7	33.33	3133.3	233.33	2300.0	57.74	2200.0	0.00
Ammonium Nitrogen (mg/kg)	586.0	29.57	587.3	9.56	695.0	7.37	0.669	5.51	1206.3	14.71	1198.3	8.88	1120.3	19.17	1240.3	14.38
Total N: NH4-N (%)	35.1	1.39	34.7	1.53	37.3	1.01	38.2	1.63	40.7	0.85	38.7	2.84	48.8	1.97	56.4	0.65
Total P (mg/kg)	282.3	2.60	280.3	4.33	303.0	4.93	300.3	1.20	525.3	6.12	517.0	4.62	402.7	4.84	423.0	4.58
Total Potassium (mg/kg)	2050.7	27.14	2062.7	11.46	2552.7	54.72	2568.0	2.52	1972.0	16.56	1941.3	21.34	1883.0	4.58	1999.3	19.88
Total Magnesium (mg/kg)	290.7	2.85	292.7	3.84	489.3	10.40	492.0	3.06	425.0	4.51	424.0	5.29	470.7	5.84	497.3	4.18
Total Copper (mg/kg)	3.7	0.04	3.6	0.11	2.5	0.03	2.5	0.03	3.8	0.13	3.6	0.09	2.8	0.08	2.9	0.04
Total Zinc (mg/kg)	7.7	0.08	7.6	0.20	9.6	0.31	9.0	0.12	14.3	0.97	14.0	1.00	6.6	0.13	7.0	0.02
Total Sulphur (mg/kg)	258.0	3.06	1084.7	18.26	256.0	3.21	723.7	10.27	324.7	8.69	761.7	39.28	248.0	9.07	1815.7	16.27
Total Calcium (mg/kg)	809.3	9.21	805.0	11.93	915.7	14.95	910.0	4.16	1488.0	34.53	1512.3	53.32	804.0	17.56	856.7	9.33
РН	6.7		5.4		6.8		5.7		6.7		5.2		6.9		5.2	
Acid requirement (I 98% $H_2SO_4 m^3$ )			2.4				2.8				2.7				4.3	



Figure 3.1: Soil pH change from application to harvest over four separate applications spanning 2 years.

Each application is separated into comparable application type. Points show mean values and error bars represent  $\pm$  SEM (*n*=3).

Following 4 repeated applications of slurry, similar trends were found to that of individual applications, i.e. with no significant legacy impact of slurry acidification on soil pH. By the end of each growing period, there were no statistical difference found between the soil pH of control and acidified broadcast treatments, regardless of the number of applications (Figure 3.2).



Figure 3.2: pH change following up to 4 applications of acidified and conventional slurry.

All plots received slurry at application 1 and 2 (n=9). Six of these plots then received a third application, with three then receiving a fourth application. Points show mean values and error bars represent SEM.

# 3.5.3.2 Soil Electrical Conductivity

The application of both slurry treatments and ammonium nitrate fertiliser (100 kg N ha<sup>-1</sup>) increased soil EC (Figure 3.3). Data collected in spring 2019 failed to meet normality assumptions, with a Kruskal-Wallis test being carried out. The test highlighted differences between soil EC and treatment, and time. All subsequent application data met normality when log transformed with significant differences found.



Figure 3.3: Soil EC change from application to harvest over four separate applications spanning 2 years.

Each application is separated into comparable application type. Points show mean values and error bars represent  $\pm$  SEM (*n*=3)

During summer 2019, soil EC in the slurry treatments were significantly greater than the control immediately after application until day 52, after which a significant difference was only found between acidified broadcast and the control. Immediately following application, soil EC was found to be the greatest for acidified treatments and conventional broadcast (band spread –  $184 \pm 5 \,\mu\text{S cm}^{-1}$ ; broadcast –  $162 \pm 18 \,\mu\text{S cm}^{-1}$ ; conventional broadcast -  $96 \pm 9 \,\mu\text{S cm}^{-1}$ ). However, conventional broadcast slurry reached a maximum at day 4 ( $162 \pm 20 \,\mu\text{S cm}^{-1}$ ). For each treatment the lowest

soil EC following application was found at harvest. The soil EC in the acidified band spread (0 cm) plots was found to be significantly greater than inter-row (15 cm) conventional slurry for the first 31 days.

The period of statistical difference for spring 2020 was shorter than summer 2019 and confined to the initial 23 days following application with band spread (0 cm) treatments reaching the greatest conductivity (acidified band spread 0 cm –  $492 \pm 125 \,\mu\text{S cm}^{-1}$ , day 1). Other treatments peaked in the second half of the experiment, where soil EC was impacted by the drought conditions during the period. Once more significant differences in soil EC were found between the control and all treatments, yet it was only the band spread application of both conventional and acidified slurry, and acidified broadcast that persisted as significant beyond the initial 4 days from application.

Following application in summer 2020, significant differences in soil EC were found between all treatments and the control. Differences were consistently found within the 14 days following application for conventional slurry and ammonium nitrate, the differences between acidified slurry and the control persisted for longer (to day 17 - acidified broadcast, to day 21 - acidified band spread (15 cm), and to day 48 - acidified band spread (0 cm)). The greatest soil EC was again found on the band following acidified band spread (418  $\pm$  49  $\mu$ S cm<sup>-1</sup>, day 1), and was significantly greater than all other treatments for the summer 2020 season.

Trends found after repeated applications of slurry follow that of the single applications where significant differences between treatment soil EC and the control became non-significant by the end of the experiment. There was no evidence of a legacy effect of repeated applications on soil EC (Appendix 1.4).

## 3.5.3.3 Ammonium & Nitrate

A general trend can be seen (Figure 3.4) where slurry and ammonium nitrate application immediately increased NH<sub>4</sub>-N concentrations, and a delayed increase in NO<sub>3</sub>-N occurred for slurry treatments when compared to ammonium nitrate fertiliser application. The slurry used during both 2020 applications had greater concentrations of NH<sub>4</sub>-N, explaining the disparities in raw values between 2020 and 2019.





#### 3.5.3.3.1 Spring 2019

The data presented for spring 2019 failed to meet normality assumptions for both NH<sub>4</sub>-N and NO<sub>3</sub>-N concentrations; therefore, a Kruskal-Wallis test was carried out and found that significant differences were only present between soil NH<sub>4</sub>-N concentrations and treatment, and NO<sub>3</sub>-N concentrations and treatment. The greatest levels of NH<sub>4</sub>-N and NO<sub>3</sub>-N found during the spring 2019 application were detected in acidified band spread (0 cm) plots (16.3  $\pm$  10.04 mg NH<sub>4</sub>-N kg<sup>-1</sup>, day 1; 8.8  $\pm$  3.47 mg NO<sub>3</sub>-N kg<sup>-1</sup>, day 8). Plots receiving conventional band spread (0 cm) slurry had comparable peak concentrations of NO<sub>3</sub>-N at the same time point as the acidified counterpart (7.4  $\pm$  4.22 mg NO<sub>3</sub>-N kg<sup>-1</sup>) indicating that there was no inhibition of nitrification.

## 3.5.3.3.2 Summer 2019

Significant differences were found following summer 2019 application with NH<sub>4</sub>-N concentrations found to differ between treatments in the initial 8 days. The addition of a slurry treatment significantly increased concentrations of soil NH<sub>4</sub>-N when compared to the control. Acidification led to significantly greater concentrations  $(12.1 \pm 2.33 \text{ mg NH}_4\text{-N kg}^{-1})$  of soil NH<sub>4</sub>-N in acidified broadcast plots compared to conventional broadcast  $(3.9 \pm 1.01 \text{ mg NH}_4\text{-N kg}^{-1})$  between day 2 and 4. No significant differences were found between acidified (maximum:  $9.4 \pm 1.41 \text{ mg NH}_4\text{-N kg}^{-1}$ , day 2) and conventional broad spread (maximum:  $8.9 \pm 3.73 \text{ mf NH}_4\text{-N kg}^{-1}$ , day 4) soil NH<sub>4</sub>-N concentrations.

Low concentrations of NO<sub>3</sub>-N were found following slurry application in summer 2019 application with values consistent with that of the control. A Kruskal-Wallis test highlighted that significant differences occurred for NO<sub>3</sub>-N concentrations and treatment. Both slurry treatments initially peaked on day 8 for surface broadcast and band spread (0 cm) applications before reaching a maximum on day 31. Similar to the results following the spring 2019 application, there was no evidence that at field scale, acidification inhibited nitrification.

#### 3.5.3.3.3 Spring 2020

With the exception of differences between the ammonium nitrate treatment and control, and inter row (15 cm) band spread treatments, all significant soil concentration NH<sub>4</sub>-N differences were found within the initial 16 days following spring 2020 application. Peak concentrations occurred for all treatments immediately after application. The greatest values for band spread (0 cm) application was found in conventional slurry plots ( $108.1 \pm 7.36 \text{ mg NH}_4$ -N kg<sup>-1</sup>, day 4) compared to acidified band spread (0 cm) ( $71.2 \pm 6.68 \text{ mg NH}_4$ -N kg<sup>-1</sup>, day 2), although significant difference were only found on day 4 for the band spread treatments. No significant differences were found throughout spring

2020 between each of the broadcast applications, although numerically greater values were found in acidified plots.

Given the use of ammonium nitrate fertilizer, it was unsurprising that the greatest values of NO<sub>3</sub>-N concentrations were found in ammonium nitrate plots reaching a maximum of 70.9 ( $\pm$  16.94) mg NO<sub>3</sub>-N kg<sup>-1</sup> on day 3. Little difference was found between soil NO<sub>3</sub>-N concentrations of surface broadcast treatments and control. Plots receiving band spread slurry (0 cm) peaked on day 16, with acidified slurry peaking at 10.8 ( $\pm$  2.12) mg NO<sub>3</sub>-N kg<sup>-1</sup> and conventional peaking at 7.6 ( $\pm$  0.28) mg NO<sub>3</sub>-N kg<sup>-1</sup>. A Kruskal-Wallis test was performed with significant differences found between soil NO<sub>3</sub>-N concentrations and treatment, and time following application.

#### 3.5.3.3.4 <u>Summer 2020</u>

During the final application, summer 2020, significant differences for soil NH<sub>4</sub>-N concentrations were found during the initial period following application. Similar to spring 2020, plots receiving ammonium nitrate had remained significantly greater than inter row band spread and control plots until day 14, whereas differences between other treatments lasted until day 10. From day 2 until day 10 acidified band spread (0 cm) was found to have significantly greater soil NH<sub>4</sub>-N concentrations when compared to conventional band spread (0 cm) (acidified band spread peak: 78.4  $\pm$  6.61 mg NH<sub>4</sub>-N kg<sup>-1</sup>, day 2; convention band spread 70.2  $\pm$  15.56 mg NH<sub>4</sub>-N kg<sup>-1</sup>, day 3). In contrast, no significant difference was found between the acidified equivalent application methods.

Up until day 24, ammonium nitrate plots were found to have significantly greater soil NO<sub>3</sub>-N concentrations than all treatments. In keeping with previous applications, soil NO<sub>3</sub>-N concentrations for band spread (0 cm) reached a maximum in week 2 (conventional slurry -  $23.7 \pm 1.32$  mg NO<sub>3</sub>-N kg<sup>-1</sup>, day 8; acidified slurry –  $21.2 \pm 2.78$  mg NO<sub>3</sub>-N kg<sup>-1</sup>, day 10). However, the delay in acidified band spread plots reaching maximum NO<sub>3</sub>-N concentrations indicates a short-lived inhibition of nitrification. This was not the case for broadcast application where both treatments reached a maximum at day 8, although concentrations of NO<sub>3</sub>-N remained higher in acidified plots for a greater period than conventional slurry.

The transient nature of soil concentrations of NH<sub>4</sub>-N and NO<sub>3</sub>-N following multiple applications resulted in no significant differences being found between the control and acidified slurry at the conclusion of each growing period. There was no evidence of a legacy effect following multiple applications of either slurry treatment (Appendix 1.5).

## 3.5.3.4 Phosphate

The acetic acid extractable phosphorus was found to have little difference across all four applications (Appendix 1.6). Significant differences were only found in spring 2019 after a Kruskal-Wallis test was performed which indicated that PO<sub>4</sub>-P concentration was significantly affected by treatment, as well as over time following application. All subsequent applications met normality assumptions but no significant differences were present. There was no significant effect of repeated slurry applications (conventional or acidified) on soil PO<sub>4</sub>-P concentrations, with values being the same as the control at the conclusion of the experimental period (Appendix 1.7).

# 3.5.4 Soil Biology

## 3.5.4.1 Greenhouse Gas Emissions

The initial plan was to measure greenhouse gas emissions for the slurry applications in Spring 2020 and Summer 2020, however Covid-19 restrictions meant that it was only possible to sample throughout the spring 2020 season. The results show that no significant differences occurred for any of the three greenhouse gases sampled (N<sub>2</sub>O, CH<sub>4</sub>, CO<sub>2</sub>) (Figure 3.5).

 $N_2O$  emissions had a single clear peak lasting between 2 and 4 days after application, accounting for 56% of total  $N_2O$  from the ammonium nitrate treatment, 49% for acidified band spread, and 31% for conventional band spread slurry. Following this period, a decline in soil moisture was observed due to unusually dry weather conditions, resulting in few additional emissions of  $N_2O$ -N. A general trend was detected where band spreading resulted in greater  $N_2O$ -N emissions than surface broadcast, while acidified surface broadcast resulted in greater  $N_2O$ -N loss than conventional broadcast slurry. This indicates that  $NH_3$  abatement results in numerical increases in  $N_2O$ -N emissions, although the results presented here are not significantly different (Table 3.3).

The emission of CH<sub>4</sub> followed the expected trend with all emissions found in the three days following application (Figure 3.5). Band spread applied slurry emitted the greatest concentration of CH<sub>4</sub>-C (acidified –  $39.0 \pm 5.81$  g CH<sub>4</sub>-C ha<sup>-1</sup> d<sup>-1</sup>; conventional  $53.6 \pm 7.65$  g CH<sub>4</sub>-C ha<sup>-1</sup> d<sup>-1</sup>) with emissions of surface broadcast found to be less, but not significantly so (acidified –  $17.7 \pm 2.21$  g CH<sub>4</sub>-C ha<sup>-1</sup> d<sup>-1</sup>; conventional  $34.2 \pm 4.63$  g CH<sub>4</sub>-C ha<sup>-1</sup> d<sup>-1</sup>). Beyond day 2, CH<sub>4</sub> emissions declined with plots becoming a sink for CH<sub>4</sub> emissions by day 4.

No significant differences were found between treatments and CO<sub>2</sub> emissions. However, by the end of the experiment, acidified treatments were found to have a greater cumulative loss of CO<sub>2</sub>-C than

the conventional slurry equivalents (Table 3.3) indicating that there was no long-term inhibition of soil microbial activity.



Figure 3.5 Cumulative soil greenhouse gas emissions following application of treatment, spring 2020.

Points show mean values and error bars represent  $\pm$  SEM (n=5).

Mean values are presented for total cumulative emissions at the end of the 79-day sampling period (n=5),  $\pm$ Table 3.3: Cumulative greenhouse gas emissions at the end of the experimental period. represent SEM.

Treatment	Cum. N <sub>2</sub> O emissions (g N <sub>2</sub> O-N ha d <sup>-1</sup> )	+	Emission factor	+	Cum.CH <sub>4</sub> emissions (g CH <sub>4</sub> -C ha d <sup>-1</sup> )	+	Cum. CO <sub>2</sub> emissions (kg CO <sub>2</sub> -C ha d <sup>-1</sup> )	+
Ammonium Nitrate	557.1	168.99	0.36	0.17	-811.4	66.27	277.1	135.96
Acidified Band Spread	367.9	156.78	0.14	60.0	-608.4	111.65	384.2	57.74
Acidified Broadcast	307.4	68.34	0.03	0.03	-664.2	113.04	375.8	99.44
Control	198.6	58.25			-697.2	101.75	422.4	226.24
Conventional Band Spread	405.8	128.44	0.12	0.13	-726.0	120.87	264.3	92.98
Conventional Broadcast	238.3	72.42	0.03	0.05	-669.1	105.04	359.2	91.68

3.5.4.2 Soil Respiration

Figure 3.6 shows the  $CO_2$  soil respiration for both 2019 application and summer 2020. Spring 2020 was omitted from sampling given its inclusion in greenhouse gas sampling alongside N<sub>2</sub>O, and CH<sub>4</sub> using the chamber methodology (Figure 3.5). A general trend can be seen in Figure 3.6 where acidification reduces soil respiration immediately following application for up to 72 hours. However, for both applications in 2019 slurry treatments increase soil respiration following application,



whereas summer 2020 shows an inhibitory impact on CO<sub>2</sub> respiration with all treatments respiring less than the control.

Figure 3.6: Soil CO<sub>2</sub> respiration following application of treatment over three separate applications spanning 2 years.

Spring 2020 was excluded from sampling, as  $CO_2$  was included in greenhouse gas sampling. Each application is separated into comparable application type. Points show mean values and error bars represent SEM ± (*n*=3).

In the three applications included on Figure 3.6, significant differences were only observed in summer 2019. All significant differences were confined to the initial 48 hours following application, with conventional slurry treatments increasing soil respiration with conventional band spread (0 cm) having the greatest soil respiration 24 hours after application ( $2.0 \pm 0.08$  g CO<sub>2</sub> m<sup>-2</sup> hr<sup>-1</sup>) when compared to acidified equivalents. After 48 hours, no further significant differences were found.

## 3.5.4.3 Earthworm abundance

There were no significant differences between the treatments for earthworm density and biomass following repeated slurry applications (Figure 3.7). A general trend can be seen where earthworm biomass increases following greater numbers of applications but was not significant given the variability in biomass within each treatment and number of applications. As expected, the addition of either conventional or acidified slurry increased earthworm biomass when compared to the control, but surprisingly little difference was found between all sampled plots and earthworm density.



Figure 3.7: Earthworm density and biomass.

Samples were taken from plots receiving up to four repeated applications of acidified and conventional slurry. Control was included to provide a baseline, ammonium nitrate plots were included to provide insight into the impact of the agricultural norm. Each application is separated into number of slurry applications received. Bars show mean values and error bars represent  $\pm$  SEM (*n*=3).

# 3.5.4.4 Meso-Fauna

No significant differences were found in meso-fauna groups between plots receiving four applications of conventional or acidified broadcast, ammonium nitrate and the control (Figure 3.8). This was the case in all instances where it was possible to carry out statistical analysis, for all groups of soil mesofauna.



# 3.5.4.5 Soil microbial 16S sequencing

Clear changes to the soil microbial community were found immediately following the fourth application of acidified slurry (Figure 3.9). By day 21, both slurry amendments were clustered but separate from the control, while at the time of harvest all samples are similar.



Figure 3.9: NMDS of soil microbial communities following four repeated applications of acidified and conventional slurry.

The 10 most abundant microbial order were analysed (Figure 3.10) and show a consistent reduction in relative abundance of *Nitrosomonadaceae* throughout the 49-day period, with relative reductions greatest immediately following application. The treatment impact on other orders relative abundance fluctuate throughout the period.





# 3.5.5 Soil Physical properties

# 3.5.5.1 Visual Evaluation of Soil Structure (VESS)

At the conclusion of the experiment, no significant differences were found in the VESS score between slurry type and number of applications received (Figure 3.11). Given that the field was ploughed and reseeded prior to establishing the experiment in 2018, the results were as expected with a very friable base to each soil sample.



Figure 3.11: Visual evaluation of soil structure.

Soil was from plots receiving up to four repeated applications of acidified and conventional slurry. Control was included to provide a baseline. Each treatment is separated into number of slurry applications received. Bars show mean values and error bars represent  $\pm$  SEM (*n*=3).

# 3.5.6 Plant Quantity

# 3.5.6.1 Dry Matter Yield

No significant differences were found between slurry type and application method for single application plots, and application method and number of applications received for dry matter yield (Figure 3.12). Across the majority of four applications, acidified treatments yielded a numerically greater DM yield then the conventional counterparts, which was also found in repeat application plots (Appendix 1.8).



Figure 3.12: Dry matter yield from 4 single applications of acidified and conventional slurry. N response plots are included for relative comparison. Bars show mean values and error bars represent  $\pm$  SEM (*n*=3).

# 3.5.6.2 N Use Efficiency (NUE)

There was no significant effect of slurry treatment on NUE at each harvest (Table 3.4), or following repeated application (Table 3.5), with low overall NUE found across all treatments and applications. However, a general trend can be seen where plots receiving acidified treatments have a numerically greater NUE than those receiving the equivalent application method of conventional slurry, with the exception of broadcast spring 2020.

Table 3.4: Nitrogen Use Efficiency (NUE) of slurry treatments applied in the 4 seasons. Mean values are presented as a percentage of the total N applied,  $\pm$  represent SEM (*n*=3).

	Spring 2019 (% N applied)	±	Summer 2019 (% N applied)	±	Spring 2020 (% N applied)	±	Summer 2020 (% N applied)	±
Acidified Band spread	34.3	8.65	10.0	2.97	21.3	2.94	25.6	4.00
Acidified Broadcast	31.3	15.61	13.4	5.03	10.9	2.34	18.1	1.82
Band spread	19.9	2.53	7.7	1.48	19.2	4.27	16.2	3.13
Broadcast	20.2	9.47	5.3	2.50	16.5	3.77	10.4	3.41

At each harvest, band spreading was frequently found to have greater NUE than surface broadcast slurry, with the combination of acidification and band spreading giving the greatest NUE, except for summer 2019. Similar trends are also present for repeated applications (Table 3.5) where no legacy impact can be seen between the two slurry treatments regardless of application number.

Table 3.5: Nitrogen Use Efficiency (NUE) of four repeat applications of slurry.

Mean values are presented as a percentage of the total N applied,  $\pm$  represent SEM.

2 repeat applications – n=9 (2019) & n=3 (2020), 3 repeat applications – n=6 (Spring 2020) & n=3 (Summer 2020), 4 repeat applications – n=3

	Spring		Summer		Spring		Summer	
	2019	±	2019	$\pm$	2020	$\pm$	2020	±
	(% N applied)		(% N applied)		(% N applied)		(% N applied)	
2 repeat acidified broadcast applications	27.8	6.80	39.7	4.76				
2 repeat broadcast applications	24.0	7.79	36.6	5.48				
3 repeat acidified broadcast applications					27.7	4.95		
3 repeat broadcast applications					22.5	0.81		
4 repeat acidified broadcast applications							34.1	22.35
4 repeat broadcast Applications							31.4	2.29

### 3.5.6.3 Nitrogen Fertilizer Replacement Value (NFRV)

Similar trends can be found for NFRV as presented in the above section for NUE. Here nonsignificant differences can be found with acidification resulting in numerically greater NFRV for equivalent conventional treatments (Table 3.6), while band spreading increased NFRV when compared with broadcast. In general, the combination of acidification and band spreading was found to give the greatest NFRV, with the exception of summer 2019.

When assessing the impact of repeated applications, no legacy effect was apparent with both slurry treatment being non-significant at each harvest point (Table 3.7). Larger NFRV was found in the summer 2020 application compared with previous applications, likely a response to greater  $NH_4^+$  applied from the slurry (Table 3.6 and Table 3.7).

Table 3.6: Nitrogen fertilizer replacement value of four single applications of slurry.

Mean values are presented based on a regression equation based on the known nitrogen response plots,  $\pm$  represent SEM (*n*=3).

\*Quadratic regression r<sup>2</sup>=0.99, <sup>#</sup>Quadratic regression r<sup>2</sup>=0.64, ~Quadratic regression r<sup>2</sup>=0.82  $^+$ Quadratic regression r<sup>2</sup>=0.98

	Spring 2019 (kg N ha <sup>-1</sup> )*	±	Summer 2019 (kg N ha <sup>-1</sup> )#	±	Spring 2020 (kg N ha <sup>-1</sup> )~	±	Summer 2020 (kg N ha <sup>-1</sup> ) <sup>+</sup>	±
Acidified Band spread	25.59	7.12	15.8	2.29	39.8	8.78	77.3	10.96
Acidified Broadcast	24.6	15.46	18.8	4.22	19.8	3.43	56.8	5.00
Band spread	13.0	1.82	14.2	1.33	33.1	7.29	54.2	10.21
Broadcast	13.1	5.91	12.1	2.25	28.6	6.82	37.4	10.19

Table 3.7: Nitrogen fertilizer replacement value following repeated applications of slurry.

Mean values are presented based on a regression equation based on the known nitrogen response plots, ± represent SEM.

2 repeat applications – n=9 (2019) & n=3 (2020), 3 repeat applications – n=6 (Spring 2020) & n=3 (Summer 2020), 4 repeat applications – n=3

\*Quadratic regression r<sup>2</sup>=0.99 <sup>#</sup>Quadratic regression r<sup>2</sup>=0.6.4 ~Quadratic regression r<sup>2</sup>=0.82 <sup>+</sup>Quadratic regression r<sup>2</sup>=0.98

	Spring 2019 (kg N ha <sup>-1</sup> )*	±	Summer 2019 (kg N ha <sup>-1</sup> ) <sup>#</sup>	±	Spring 2020 (kg N ha <sup>-1</sup> )~	±	Summer 2020 (kg N ha <sup>-1</sup> ) <sup>+</sup>	±
2 repeat acidified broadcast applications	15.5	2.83	8.0	1.94				
2 repeat broadcast applications	16.1	6.13	7.6	1.56				
3 repeat acidified broadcast applications					50.4	7.40		
3 repeat broadcast applications					38.5	1.62		
4 repeat Acidified Broadcast Applications							100.7	6.37
4 repeat broadcast Applications							97.42	8.74

# 3.5.7 Weather data

Figure 3.13 shows the weather and ground conditions throughout the 2 years of field experimentation. A drought period followed spring application 2020 giving unusually dry soil moisture levels throughout the period.


#### 3.6 Discussion

The following discussion will directly address the hypotheses established in section 3 above.

## a) There will be no negative impact of slurry acidification and application technique on soil pH

The application techniques employed throughout the experiment assesses the most widely used method of application in the UK, surface broadcast, and a low emissions alternative, band spread. Soil pH is a key soil health indicator which is regularly managed to maintain optimum conditions for crop growth (Goulding, 2016). Previous work identified how under bands of acidified cattle slurry, soil pH was found to reduce to a greater extent than surface broadcast (Fangueiro et al., 2018; Pedersen et al., 2017), which was in agreement with results from these experiments. However, unlike Fangueiro et al. (2018), the differences found in soil pH following acidified band spread, when compared to the non-amendment control, were non-significant at the conclusion of this experiment with the exception of the short growing season in summer 2020. Given the longer previous growing seasons, it would be reasonable to expect the trend in soil pH from the shorter summer 2020 application to mirror that of previous applications and continue to buffer to match the pH of the control. Acidified broadcast slurry was found to reduce soil pH at each application, yet was found to buffer back to the control over a period of 20-84 days, which was also found to also be the case after 4 repeated applications. The evidence provided here of soil pH reductions following application of acidified slurry by both application methods and its consequential soil buffering to that of the control (no-amendment), suggests that liming may be required to adjust soil pH following several years of application. But the soil acidification following N addition by the acidified slurry was no worse than from the ammonium nitrate fertiliser applications suggesting there would be no additional need to lime in order to adjust soil pH if already applying ammonium nitrate.

# b) The availability of NH4-N will increase in acidified plots, without resulting in N pollution swapping

Acidification has clear benefits to soil NH<sub>4</sub>-N concentrations while maintaining greater concentrations for extended periods when compared to conventional slurry and has previously been reported by various authors (D'Annibale et al., 2019; Fangueiro et al., 2016, 2010; Sánchez-Rodríguez et al., 2018). The results presented here add further support to previous evidence, where elevated concentrations of soil NH<sub>4</sub>-N clearly persists for longer in acidified plots compared to conventional slurry for both application methods in 2020.

There is a potential for N swapping to occur given the associated increases of soil  $NH_4^+$  following application of acidified slurry, e.g. with greater N<sub>2</sub>O emissions following slurry injection to reduce NH<sub>3</sub> emissions and increasing soil  $NH_4^+$  concentrations compared with surface broadcasting (Chadwick et al., 2011; Petersen and Sommer, 2011). However, there were no significant differences in N<sub>2</sub>O emissions from the acidified slurry treatments compared with conventional slurry, and at the end of the experiment cumulative N<sub>2</sub>O fluxes were numerically greater from the conventional broadcast slurry compared with the acidified slurry. This has been found to be the case in other studies (Malique et al. 2021), who also reported lower than expected N<sub>2</sub>O fluxes presented in Thorman et al. (2020) when rainfall was low.

Delays to nitrification and denitrification where not observed here to the same extent as previous findings of up to 60 days, possibly a consequence of lesser reductions in soil pH (Fangueiro et al., 2010; Park et al., 2017; Sánchez-Rodríguez et al., 2018). An inhibitory effect of nitrification was only observed over a 48-hour period in both 2020 applications, while rates of denitrification and consequential N<sub>2</sub>O emissions have been dominated by application method, as opposed to slurry type. It is therefore possible to conclude that greater concentrations of soil NH<sub>4</sub>-N following application of acidified slurry does not lead N pollution swapping and will instead result in greater crop NUE and NFRV.

#### c) Fertilizer value of slurry will improve with the addition of acidified slurry

The benefits of reducing NH<sub>3</sub> volatilisation and increasing soil NH<sub>4</sub>-N concentrations following the application of acidified slurry has direct consequences on crop NUE and NFRV. Although the NUE was found to be lower than expected, the general trend of acidification increasing NUE shows the benefits that can be gained from applying acidified slurry (acidified band spread 11-72% > conventional, acidified broadcast -34-153% > conventional). The comparable levels of soil NH<sub>4</sub>-N found in conventional slurry band spread plots (0 cm) in spring 2020 also resulted in higher NUE and NFRV, similar to that of the equivalent acidified treatment. This was likely a result of the weather conditions directly following application, with a dry period leading to crusting and reduced volatilisation, thus nullifying the benefits of acidification.

The percentage increases found in this experiment for NFRV show a range of 11-97% increase for acidified band spread plots and a -31-88% increase for acidified broadcast plots when compared to the conventional equivalents. This was notably greater than the results presented by Birkmose et al. (2013) and Pantelopoulos et al. (2017) after acidified slurry or digestate was applied to a ryegrass

sward. The greater percentage increase in NFRV from acidified plots presented here was likely a result of low NFRV for conventional plots, making the increase from acidification greater in scale.

The data presented for plots receiving multiple applications of slurry show similar trends for increases of both NUE and NFRV, yet the magnitude was reduced. NFRV ranges from -4-31% change following receiving acidified slurry, while NUE increases by 8 - 23%. Nevertheless, the data presented will have direct implications on when assessing the benefits of acidification by increasing the fertiliser value of the slurry, and offsetting costs associated to the process.

#### d) There will be no long-term impact on soil fauna communities

Little evidence was provided in the literature of the impact of slurry acidification on soil faunal communities, especially following multiple applications. This experiment has addressed that knowledge gap by providing evidence of non-significant long-term changes in soil micro-, meso- and macro fauna.

Evidence of short-term changes to soil respiration were clear in the initial 48 hour following application of acidified slurry when compared to conventional slurry. However, these short-term changes had no long-term impact on soil respiration and microbial activity, exemplified by the lack of significant differences found in all cumulative greenhouse gas emissions over the single growing period. As expected, multiple applications of slurry increased earthworm biomass, albeit nonsignificantly, from other treatments. As earthworms are considered bio-indicators of soil health due to the chemical, physical and biological benefits they bring to the soil (Fusaro et al., 2018), the lack of differences between slurry treatments and numbers of applications provides evidence of no negative impacts from multiple applications of acidified slurry. Similarly, where statistical analysis could be performed, any differences in meso-fauna abundance was found to be non-significant between treatments and importantly with number of applications. Clear evidence was provided of a short-term microbial community shift following the fourth repeated application of acidified slurry, however, at the time of harvest no differences were observed between treatment and the control suggesting similar short-term impacts to soil fauna communities. Such a finding was supported by the reduction in soil respiration rates. However, the reduction in Nitrosomonadaceae relative abundance, while providing evidence of a reduction to nitrogen cycling microbes, suggests that certain soil microbes are affected to a greater degree than others following the repeat application of acidification. The findings presented contradicts those of Edesi et al. (2020) who found that the only microbe impacted were Actinobacteria after the application of acidified (pH 6) pig slurry, and Malique et al. (2021) who reported tendencies of greater activity of nitrogen cycling after the

application of acidified cattle slurry. Consequently, the reduction in *Nitrosomonadaceae* would require future research to determine the mechanisms reducing the relative abundance over an extended period, especially given soil pH had returned to control levels. However, the overall impact on soil fauna provides evidence of the long-term sustainability of repeated applications of acidified slurry when applied to a grass ley. Yet, the duration of this experiment restricted application numbers to four, and the true "long-term" effects remain uncertain, and would require further applications to definitively assess the long-term impact.

#### 3.7 Conclusions

The overall aim of these experiments were to comprehensively assess the impact of acidified slurry on soil chemical, biological, and physical characteristics, as well as crop yield and quality in a UK setting, and in doing so address the key knowledge gaps identified in the literature. The clear conclusion from all aspects of the experimentation was that there are no long-term impacts of slurry acidification on soil quality. Microbial processes of nitrification and denitrification, underpinning the potential for N pollution swapping, were not impacted by the application of acidified slurry. Such evidence furthers the understanding of the long-term sustainability of slurry acidification application to a typical Welsh grassland. Grass NUE and NFRV were found to numerically increase, albeit not significantly so, but highlights the role acidification can have in improving the fertiliser quality of slurry.

To truly understand the long-term impact of slurry acidification more repeated applications will be required yet the data provided highlights the potential slurry acidification has in reducing NH<sub>3</sub> emissions, without impeding soil or crop health. Ultimately, the data presented shows that slurry acidification has no negative impacts on soil quality when applied to a typical Welsh grassland and can increase crop quality.

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## <u>Chapter 4:</u> <u>Slurry acidification is as effective as slurry injection at reducing ammonia</u> <u>emissions: a mesocosm study</u>

#### Abstract

Agriculture is the greatest source (90%) of ammonia (NH<sub>3</sub>) emissions in the UK, and if reductions of 16% by 2030 are to be achieved, the largest emitters will need to take action. The addition of concentrated acid to slurry - slurry acidification - has been found to reduce NH<sub>3</sub> loss. The technique of slurry acidification is widely used in Denmark, and a number of studies into the impact of slurry acidification on NH<sub>3</sub> emissions have been carried out on soils typically found in continental Europe. To assess the potential of slurry acidification to reduce UK NH<sub>3</sub> emissions, it is important that data are generated from UK soils, and compares the technique to the current Best Available Technique, slurry injection, and that the wider impacts of slurry acidification are evaluated, e.g. impacts on nitrous oxide (N<sub>2</sub>O) emissions.

In this study, two experiments were performed using a 12-chamber desktop ammonia volatilisation system (DAVoS) to assess the impacts of slurry acidification on NH<sub>3</sub> loss, N<sub>2</sub>O emissions, soil water mineral N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) dynamics and soil NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> content at the end of the experiments. Experiment 1 assessed the impacts of slurry acidification to different target pH values of 4.5, 5.5 and 6.5, and a conventional (non-acidified) slurry for reference. Experiment 2 assessed the impact of application method with conventional slurry and acidified slurry (pH 5.5) applied using surface broadcast and injection. In both experiments, cattle slurry was applied at a rate of 40 m<sup>3</sup> ha<sup>-1</sup>.

The results highlighted the potential slurry acidification can have in reducing NH<sub>3</sub> emissions and the role technology has in reaching the 2030 emissions reduction target. Acidification to pH 5.5 and below was found to significantly reduce NH<sub>3</sub> loss (% of total N applied) from 9.4% for conventional slurry to 4.6% at pH 5.5 and 0.4% at pH 4.8 over a two-week period. When acidified, surface broadcast slurry was found to reduce NH<sub>3</sub> emissions to the same extent as conventional slurry injection, while acidified slurry was found to potentially delay nitrification, and not significantly alter N<sub>2</sub>O emissions from comparable conventional slurry. Partial N<sub>2</sub>O emission factors were found to range from 0.02 % for broadcast conventional acidified slurry to 0.04% for acidified broadcast slurry, while N loss as NH<sub>3</sub> was significantly reduced from 4.2% of N applied in surface broadcast to 2.1% in acidified injection.

#### 4.1 Introduction

Slurry acidification, the process of adding concentrated acid, e.g. sulphuric acid ( $H_2SO_4$ ) to slurry, as an ammonia ( $NH_3$ ) emissions abatement technique, has been widely used in Denmark as a Best Available Technique to limit  $NH_3$  losses (Fangueiro et al., 2015a). The process of acidification shifts the total ammoniacal N (TAN) content of slurry from being dominated by easily volatilizable  $NH_3$  to the stable and plant available  $NH_4^+$ , which following acidification has been found to represent up to 98% of TAN (Berg et al., 2006; Cocolo et al., 2016; Husted et al., 1991).

The reduction of NH<sub>3</sub> emissions following acidification has been the subject of many studies to validate the principle of shifting TAN dominance to NH<sub>4</sub><sup>+</sup> with very clear outcomes, as well as additional benefits including the reduction of methane emissions (Bastami et al., 2016; Misselbrook et al., 2016). However, variations have been found between slurry types, target pH and soil types. For example, Stevens et al. (1989) reported that at pH 7.0, 23% of applied NH<sub>4</sub>-N for cattle slurry was lost through volatilisation over the first three days following application, which was reduced to 95% when acidified to pH 5.5. Seidel et al. (2017) highlights the role acidification can play in NH<sub>3</sub> abatement strategies by comparing acidification to band spread slurry at a field-plot scale. When acidified band spread slurry, and a 77% reduction at pH 6.0, highlighting the importance of the final slurry pH in controlling NH<sub>3</sub> volatilization. The latter equated to 6.6% of applied TAN, whereas at pH 6.5 up to 20% of TAN was volatilised over the first four days (Seidel et al., 2017).

Considering acidification is available as an NH<sub>3</sub> abatement technology, Fangueiro et al. (2018) compared NH<sub>3</sub> emissions of acidified treatments to alternative low NH<sub>3</sub> emission application methods at the field-plot scale. This study showed that acidification abated similar amounts of NH<sub>3</sub> to slurry injection of the conventional (non-acidified) treatment, similarly acidified band spread slurry showed similar NH<sub>3</sub> losses to a conventional application. Nyord et al. (2013) found that the combination of trailing hose and acidification delivered a reduction in NH<sub>3</sub> emissions similar to injected non-acidified slurry.

The impact of acidification on NH<sub>3</sub> emissions is found immediately after application, Stevens et al. (1989) found that when cattle slurry was applied at pH 5.5, <0.1% of total NH<sub>4</sub>-N applied was lost compared to 3.0% at pH 7.5 over the first 2 hours of application. Ammonia abatement duration has also been studied over a longer time period; Park et al. (2017) found that the use of acidification significantly reduced these cumulative emissions by 61% at pH 5 over the initial 2 week period. The findings of Frost et al. (1990) show a 85% reduction of NH<sub>3</sub> emissions from acidified slurry in the initial 101 hours following application. Likewise, Fangueiro

et al. (2017) reported that NH<sub>3</sub> emissions from an acidified liquid fraction of separated slurry was similar to a soil only control for 2.5 days following application, equating to 79% lower emissions than a untreated liquid fraction.

The increased risk of N pollution swapping from NH<sub>3</sub> abatement, and especially the release of nitrous oxide (N<sub>2</sub>O), a greenhouse gas approximately 300 times more potent than CO<sub>2</sub> (IPCC, 2021), has resulted in GHG measurements being included in various studies. The main factors controlling N<sub>2</sub>O emissions are the amount of NO<sub>3</sub>-N (that arises following nitrification of the slurry NH<sub>4</sub>-N) and soluble organic C for nitrification and denitrification, both of which are impacted by acidification (Park et al., 2017). In the majority of studies, acidification was found to reduce N<sub>2</sub>O emission, or have little impact when compared to the conventional equivalent (Fangueiro et al., 2017, 2015b; Seidel et al., 2017).

The timing of N<sub>2</sub>O peaks from soil have been found to vary as a result of slurry acidification, yet the majority of emissions still occur during the initial two weeks after application (Gómez-Muñoz et al., 2016). An initial peak was found by Fangueiro et al. (2015b) to be more intense than the second peak, with the latter often coinciding with a plateauing of soil  $NO_3^-$  concentration and indicating the resulting ceasing of nitrification. A delay in N<sub>2</sub>O peaks have been found in a number of papers whereby treatments have delayed or reduced the initial release of N<sub>2</sub>O indicating an inhibitory effect of acidification on nitrification and denitrification (Fangueiro et al., 2018, 2017, 2015b). When applied to perennial ryegrass, Park et al. (2017) found that during the length of a growing season the daily N<sub>2</sub>O emissions reported from a cattle slurry acidified to pH 5 remained lower than emissions from the unacidified slurry (pH 7).

Application technique has been found to impact the N<sub>2</sub>O emissions as a result of creating anaerobic hotspots within the soil profile, favouring denitrification (Chadwick et al., 2011; Fangueiro et al., 2015b; Petersen and Sommer, 2011). Fangueiro et al. (2017) found that both injection and slurry acidification combined with incorporation immediately increased N<sub>2</sub>O emissions, yet surface broadcast slurry emitted the lowest levels N<sub>2</sub>O (Fangueiro et al., 2015b). However, in terms of total N losses, injection has been found to be most effective means of application to retain slurry N within the soil, with acidified slurry found to be more effective than conventional slurry (Fangueiro et al., 2017). This was confirmed in a later publication where acidified band spread slurry was been found to have similar N losses (NH<sub>3</sub> and N<sub>2</sub>O combined) to slurry injection and was 92% lower than non-acidified band spread slurry followed by incorporation (Fangueiro et al., 2018).

#### 4.2 Aims

Given the majority of previous work has been carried out in Mediterranean soils and climate, this study, comprising of two small-scale, short-term experiments, aimed to assess the impact of both slurry pH and the impact of application technique on NH<sub>3</sub> and N<sub>2</sub>O emissions in a typical UK grassland soil. Soil mineral N dynamics were also measured to understand patterns of gaseous emissions. The results would provide an indication of the feasibility for the use of acidification with surface broadcast slurry as a mitigation approach, compared to expensive low trajectory slurry spreading methods (e.g. shallow injection), whilst exploring any potential co-benefits or trade-offs of NH<sub>3</sub> mitigation on N<sub>2</sub>O losses, as well as exploring the impact on emissions by combining low emissions techniques and acidification.

#### 4.3 Hypotheses

Two experiments were established to address the following hypotheses:

- a. A reduction in NH<sub>3</sub> loss will be greatest in slurries with the lowest pH
- b. The greatest concentration of slurry NH<sub>4</sub>-N will be found in soil water receiving the lowest slurry pH
- c. NH<sub>3</sub> emissions from acidified broadcast slurry will be comparable to shallow injection of conventional slurry
- d. The use of slurry injection will out-perform surface broadcast in terms of retaining greater levels of slurry-N
- e. Application of acidified slurry will result in lower N<sub>2</sub>O emissions compared to conventional slurry regardless of application method.

Hypotheses a. is addressed in experiment one, while hypotheses b., c., d., and e. are addressed in experiment two.

#### 4.4 Methods

#### 4.4.1 Experimental design

Two experiments were carried out to address the aims and hypotheses, using a desktop ammonia volatilisation system (DAVoS) consisting of 12 chambers (Appendix 2.1), as described in Misselbrook et al. (2005) (Figure 4.1).

Intact soil cores (0-15 cm) were collected in plastic drainpipe (83 mm inside diameter), from three discrete areas of grassland at Henfaes Research Station, North Wales (53°14′21.3 N, 4°0′50.3 W; 10 m above sea level). The soil is described as a free-draining Eutric Cambisol characterised with a sandy clay loam texture. Cores from these three sites were then used as replicates for each slurry

treatment (*n*=3). The collection sites had been used as a multi-year grass lay sown with Oliver seeds "Sabre" mix (an Italian and Perennial Rye Grass mix with Festulolium), which had received 50 kg N ha<sup>-1</sup> of ammonium nitrate six months prior to sampling. Each intact core had a diameter that allowed it to be inserted into the bench-top system tightly. Each core had a single Rhizon<sup>TM</sup> sampler (Rhizosphere Research Products, Wageningen, Netherlands) inserted vertical to enable sampling of soil solution. The soil cores were kept inside for a week to acclimatise at 60% water filled pore space prior to starting the experiment, with multiple additional soil samples collected at each site for analysis prior to starting the experiment.

## 4.4.1.1 Ammonia volatilization measurements

A vacuum pump drew air through an acid trap containing 200 ml of 0.0125 M orthophosphoric acid ( $H_3PO_4$ ) to remove any  $NH_3$  from the ambient air, before passing through the sealed chamber with any  $NH_3$  emitted from the chamber deposited in a following acid trap. The system operated with a flow rate of 3 l min<sup>-1</sup> through each chamber.

Before experiments were carried out, NH<sub>3</sub> recovery tests were performed on the DAVoS system using the method outline in Misselbrook et al. (2005). 20 ml of 2 g l<sup>-1</sup> N of ammonium sulphate was mixed with 1 ml of sodium bicarbonate in a Petri dish at 13 cm from the base of the chamber, and was allowed to volatilise for 4 hours before 1 ml of 2 M H<sub>2</sub>SO<sub>4</sub> was added to end volatilisation. The recovery tests resulted in an average 94 % ( $\pm$  1.8 %) recovery following 1 trap change at 4 hours across all chambers.



## Figure 4.1: Schematic of DAVoS

Each acid trap was filled with 200 ml 0.125 M  $H_3PO_4$  with the pump drawing air through each chamber at 3 1 min<sup>-1</sup>. The contents of "acid trap 1" was retained for chemical analysis at each sampling point.

#### 4.4.1.2 Greenhouse Gas measurements

Greenhouse gases were sampled by closing valves either side of the chamber when the pump had been switched off (at the time when acid traps were being changed) and sampling the headspace above the soil via a silicone suba-seal permanently inserted into the lid of the chamber.

#### 4.4.2 Experiment 1 – Effect of slurry pH on NH<sub>3</sub> and N<sub>2</sub>O emissions

This experiment was established to assess the impact of different slurry pH alongside a conventional unamended slurry on subsequent NH<sub>3</sub> and N<sub>2</sub>O emissions after application to soil. This will further the research of others into the impact of slurry acidification on NH<sub>3</sub> emissions, but importantly this experiment was carried out on a UK soil and also determined the impact of slurry pH level on greenhouse gas emissions and soil water mineral N dynamics.

Slurry used in the experiment was collected from an aboveground slurry store located on a dairy farm in Abergwyngregyn (North Wales, 53°23'52.0 N, 4°02'18.5 W). 20 litres of slurry was thoroughly mixed and divided into 4 separate 5 L containers, prior to acidification to the target pH's, 4.5, 5.5, and 6.5, using 96% H<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich, UK). The fourth treatment was non-acidified slurry (pH 7.5). A subsample of each slurry treatment was retained and analysed for dry matter content, total Kjeldahl N, NO<sub>3</sub>-N, NH<sub>4</sub>-N, phosphorus (P), potassium (K), total magnesium (Mg), metals (total copper, zinc), sulphur (S), calcium (Ca), and sodium (Na), using conventional accredited methods (NRM, Cawood Scientific Ltd., Bracknell, UK) (Table 4.2). Slurry pH was also determined on these slurry treatments in the Bangor University laboratory immediately after application to the cores.

Each slurry treatment was applied to the surface of the sward of the soil cores (n=3) to simulate surface broadcasting at an equivalent application rate of 40 m<sup>3</sup> ha<sup>-1</sup>, typical of moderate output grazing livestock farming systems (Defra, 2021), and immediately inserted into the DAVoS. The DAVoS was situated in a temperature control laboratory for the duration of the experiment with an average temperature of 18.4°C (±0.12°C). Sampling of greenhouse gas, NH<sub>3</sub> loss, and soil solution was carried out intensively during the first fortnight (0 hour, 1 hour, 24 hour, 27 hour, and then daily on day 2, 3, 4, 5, 7, 8, 9, 11, 14) after which analysis of the acid traps had shown that NH<sub>3</sub> emission had ceased. Greenhouse gas sampling continued, and measurements were made until there were no significant differences between the treatment and control values (Charteris et al., 2020). The greenhouse gas sampling continued at regular intervals throughout the rest of the experiment (day 15, 18, 23, 27, 32, 34, 41, 77, 83, 94, and 109). At the conclusion of the experiment, each core was destructively sampled and analysed for extractable NH<sub>4</sub>-N and NO<sub>3</sub>-N, using 1:5 (w/v) K<sub>2</sub>SO<sub>4</sub> extractions for colorimetric analysis (Miranda et al. 2001); Mulvaney, 1996) on an Epoch<sup>®</sup> microplate spectrophotometer (Bio Tek Instruments Inc., Winooski, USA).

## 4.4.3 Experiment 2 – the effect of application methods and slurry pH on $NH_3$ and $N_2O$ emissions

Experiment 2 was established to directly address the three hypotheses assessing how different slurry application methods in combination with slurry acidification performed in terms of NH<sub>3</sub> emission abatement when compared to conventional slurry. This will have direct implications on policy and practice, and the role slurry acidification can play alongside existing technologies to abate NH<sub>3</sub> emissions. This experiment aimed to assess if expensive low emission application equipment was required compared to surface broadcast, a method commonly used in the UK, in combination with slurry acidification. The inclusion of slurry acidification and injection in the study aimed to assess if benefits are compounded by combining low emission methods, and if so will indicate the maximum possible NH<sub>3</sub> reduction.

Slurry was provided by the same farm as described for Experiment 1. 10 L of slurry was mixed thoroughly and divided into two 5-litre containers. One portion was acidified to pH 5.5, using 96% H<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich, UK), with the other portion remaining as conventional slurry. There were 4 slurry treatments in this experiment: acidified surface broadcast (AB), acidified injection (AI), conventional surface broadcast (CB), conventional injection (CI). Each treatment was replicated 3 times using intact grassland soil cores sampled from the same field and in the same way as in Experiment 1. Rhizon samplers were inserted into the soil cores as in Experiment 1 to facilitate collection of soil solution, and soil moisture content held at 60% WFPS. The DAVoS was situated in a temperature controlled laboratory for the duration of the experiment with an average temperature of 18.1°C (±0.09°C). Slurry was applied at the equivalent rate of 40 m<sup>3</sup> ha<sup>-1</sup> representing typical application rates of moderate output grazing livestock farming systems (Defra, 2021). Both acidified and conventional slurry injection treatments were applied to simulate shallow injection with slots in the soil 50 mm deep. Following application, both slurries (acidified and conventional) were chemically analysed by NRM Laboratories (Cawood Scientific Ltd., Bracknell, UK) for the same parameters described for Experiment 1, and slurry pH was measured in the Bangor University laboratory just after application.

Ammonia emission, greenhouse gas emission and soil solution (Rhizon samplers) sampling was carried out over a 2 week period occurring at: 0 hour, 1 hour, 6 hour, 24 hour, 30 hour, and then daily on days 2, 3, 4, 5, 9, 10, 11, 14. This experiment ran for 14 days, to assess the short-term impact of

slurry acidification gaseous emissions but still capturing the main 'envelope' of gaseous N losses as outlined in Gómez-Muñoz et al. (2016)

#### 4.4.4 Analytical methods

#### 4.4.4.1 Acid trap analysis

At each sample point, the acid trap between the chamber and pump containing emitted  $NH_3$  from the chamber was decanted into a 20 ml plastic labelled vial. Each sample was later analysed using the Mulvaney (1996) method for colorimetric determination of  $NH_4$ -N concentration. The quantity of  $NH_3$ -N emitted from the chamber was then calculated by multiplying the  $NH_4$ -N concentration by the volume of  $H_3PO_4$  in each acid trap.

#### 4.4.4.2 Soil Solution Analysis

Samples were collected in 9 ml Vacutest<sup>®</sup> (Padua, Italy) vials attached to the Rhizon samplers after each greenhouse gas sampling, and analysed for NH<sub>4</sub>-N and NO<sub>3</sub>-N, using colorimetric methods (Miranda et al. 2001; Mulvaney, 1996) on an Epoch<sup>®</sup> microplate spectrophotometer (Bio Tek Instruments Inc., Winooski, USA).

#### 4.4.4.3 Gas Analysis

Samples were collected after the vacuum pump had been turned off for acid trap changes and the ball valves on each chamber had been closed. Gas samples were taken from the headspace (0.5 litres) via a silicone septum in the lid of each chamber using a needle and 20 ml syringe and injected into a preevacuated 20 ml glass vial. A headspace gas sample was taken at 0 minutes and 40 minutes, with three chambers randomly selected at each sample point for additional sampling to check the linearity of greenhouse gas concentration accumulation in the headspace (with samples taken at T0, T10, T20, T30 and T40). Greenhouse gas analysis (CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O) was carried out on a Perkin Elmer 580 Gas Chromatograph (GC), with a Turbo Matrix 110 auto sampler (Perkin Elmer Inc., Beverly, CT, USA). Cumulative emission fluxes were calculated based on the trapezoidal integration method outlined in Cardenas et al. (2016). Linearity samples were analysed, with emissions found to be linear on 56% of occasions when accepted at R<sup>2</sup>>0.95, and 70% of occasions at R<sup>2</sup>>0.9 in experiment 2. The majority of occasions were linearity was not met was during periods of low flux such, similar to the findings of others (Chadwick et al., 2014; Marsden et al., 2016).

#### 4.4.5 Soil Analysis

At the conclusion of the experiment, each core was destructively sampled in two depth (0-7.5 cm and 7.5-15 cm). Soil pH was measured using a Hanna instruments Model 210 pH meter (Hanna Instruments Ltd., Leighton Buzzard, UK). Soil EC was measured using a Jenway conductivity probe alongside a Jenway 4520 conductivity meter (Cole-Palmer Ltd., Stone, UK). Both soil pH and EC was measured using a 1:2.5 soil to DiH<sub>2</sub>O (w:v) solution. Extractable NH<sub>4</sub>-N and NO<sub>3</sub>-N concentration was measured using a 0.5 M K<sub>2</sub>SO<sub>4</sub> extraction (5 g fresh soil : 25 ml extractant) and employing the Mulvaney (1996) and Miranda et al. (2001) methodologies as outlined above.

#### 4.4.6 Data Processing

#### 4.4.6.1 Method for calculating percentage water filled pore space (WFPS)

To ensure that all cores were kept at 60% WFPS, a moisture content suitable for both nitrification and denitrification to occur, replicate cores taken from the same sites as experimental cores were dried at 105°C, with bulk density subsequently calculated from the volume of the core. The calculations to convert bulk density into WFPS as outlined in Louro et al. (2013) was used, where particle density was assumed to be 2.65 g cm<sup>-3</sup>. Water was then added on a weekly basis to adjust for moisture loss over the period to maintain the target WFPS.

#### 4.4.6.2 Method for calculating NH<sub>3</sub> fluxes and cumulative

NH<sub>3</sub> fluxes were calculated on the colorimetric output outlined above based on NH<sub>4</sub>-N values. This then allowed for percentages to be calculated for the quantity of N lost in terms of total N applied, as well as a percentage of total NH<sub>4</sub>-N applied. Fluxes were calculated based on the methods outlined in Misselbrook et al. (2005) by using the trapezoidal rule.

#### 4.4.7 Statistical analysis

Throughout both experiments, statistical analysis was performed using R v. 4.1717 (R Core Team, 2019) where a significance level of p < 0.05 was accepted as significant. Where data was deemed normal, linear models were used to assess variable against slurry treatment/application technique and time following application. These were then subjected to an ANOVA (stats package, R Core Team, 2019) and if significant differences were found "lsmeans" (emmeans, Lenth, 2021) was used to carry out Tukey post-hoc tests. Where data failed to meet normality assumption a non-parametric Kruskal-Wallis test (stats package, R Core Team, 2019) was performed. One-way ANOVA's (stats package, R Core Team, 2019) were carried out on single time point data including cumulative totals at the end of the experimental period. All results were graphical illustrated with "ggplot2" (Wickham, 2016).

## 4.5 <u>Results</u>

### 4.5.1 Soil properties

Soil analysis was carried out for soil used in both experiments (Table 4.1) with the results showing little variation between sites. Extractable  $NH_4^+$  was found be greater at site 2 than the other sites, but still represented low levels of extractable  $NH_4^+$ .

Table 4.1: Pre-application soil properties.

Multiple cores (n=3) were taken at each sampling point and averaged with  $\pm$  representing

	Site 1	Site 2	Site 3
Bulk Density (g cm <sup>-3</sup> )	1.0 ±0.03	1.0±0.06	1.0±0.01
Organic Matter (%)	5.3±0.1	5.8±0.03	5.6±0.14
рН	6.4±0.08	6.4±0.1	6.7±0.06
EC (μS cm <sup>-1</sup> )	41.3±12	32.1±7	29.7±10
Total N (mg N kg <sup>-1</sup> )	3.8±0.2	3.5±0.5	3.6±0.3
Total C (mg C kg <sup>-1</sup> )	32.2±6.5	28.9±4.2	30.6.±5.7
C:N ratio	8.5±0.4	8.3±0.3	8.5±0.5
Extractable NO3 <sup>-</sup> (mg N kg <sup>-1</sup> )	0.9±0.2	1.2±0.4	2.4±0.7
Extractable NH4 <sup>+</sup> (mg N kg <sup>-1</sup> )	2.4±0.6	12.0±2.1	3.5±1.1

## 4.5.2 Experiment 1 - Effect of slurry pH on NH<sub>3</sub> and N<sub>2</sub>O emissions

## 4.5.2.1 Slurry properties

Applied slurry properties varied at each application (Table 4.2). Organic matter ranged from 10.3% when acidified to pH 4.5 to 8.92% as conventional slurry. All other properties remained similar for all treatments with the exception of sulphur, which increased at lower pH due to the addition of  $H_2SO_4$ .

Table 4.2: Slurry characteristics of each treatment applied to cores.

Analysis was performed by NRM laboratories (Bracknell, UK) with the exception of pH which was measured in the Bangor University laboratory just after slurry treatment applications. Data are expressed on a fresh weight basis.

	Unit	pH 4.5	рН 5.5	pH 6.5	pH 7.5
<b>Oven Dry Solids</b>	%	10.3	9.25	9.07	8.92
Total Kjeldahl N	% w/w	0.40	0.37	0.41	0.41
NO3-N	mg kg <sup>-1</sup>	<10	<10	<10	<10
NH4 <sup>+</sup> -N	mg kg <sup>-1</sup>	1616	1654	1638	1626
Total Phosphorus (P)	mg kg <sup>-1</sup>	625	621	609	629
Total Potassium (K)	mg kg <sup>-1</sup>	2164	2185	2160	2245
Total Magnesium (Mg)	mg kg <sup>-1</sup>	470	463	460	472
Total Copper (Cu)	mg kg <sup>-1</sup>	2.91	2.84	2.72	2.78
Total Zinc (Zn)	mg kg <sup>-1</sup>	15.6	13.6	14.1	16.1
Total Sulphur (S)	mg kg <sup>-1</sup>	3638	1343	824	453
Total Calcium (Ca)	mg kg <sup>-1</sup>	1173	1127	1146	1204
Total Sodium (Na)	mg kg <sup>-1</sup>	599	600	588	610
pH (Neat)		4.47	5.43	6.60	7.69
Acid requirement (ml 1M H <sub>2</sub> S04 100 ml <sup>-1</sup> )		8	5.5	2	

## $4.5.2.2 \ \underline{NH_3 \ loss}$

Figure 4.2 shows the impact of slurry pH on  $NH_3$  loss, with slurry receiving the greatest levels of acidification retaining the greatest level of N. A Kruskal-Wallis test was performed and showed significant (*p*<0.05) differences between total N loss and different slurry pH, and total N loss and days following application.



Figure 4.2: Cumulative NH<sub>3</sub> loss after acidification to varying pH values. Points show mean values and error bars represent  $\pm$  SEM (*n*=3)

At the conclusion of sampling, slurry pH was found to have significant differences on both cumulative NH<sub>3</sub>-N loss as a percentage of total N applied and as a percentage of total NH<sub>4</sub>-N applied. These differences were found following log transformation and analysis via a one-way ANOVA (Table 4.3).

Table 4.3: Cumulative percentage N loss after acidification to varying pH

Cumulative N loss (percentage N loss of total N applied, and percentage N loss of total NH<sub>4</sub>-N applied) 14 days after application for four different slurry pH (n=3). Significant differences (p<0.05) are represented by different letters. Values represent means and ± SEM (n=3).

рН	Mean % NH3-N loss of TN applied	+	Mean % NH3-N loss of NH4-N applied	±
4.5	0.4 <sup>c</sup>	0.03	1.58 <sup>c</sup>	0.13
5.5	4.6 <sup>b</sup>	1.22	16.9 <sup>b</sup>	4.6
6.5	7.9 <sup>ab</sup>	0.61	32.8 <sup>a</sup>	2.6
7.38	9.4 <sup>a</sup>	0.33	39.2 <sup>a</sup>	1.3

#### 4.5.2.3 N2O emissions

Figure 4.3 indicates that the greatest reduction in slurry pH reduces N<sub>2</sub>O emissions over the initial 24 days following application. However, once the delay in emissions has elapsed, the pH 4.5 treatment became the greatest emitter of N<sub>2</sub>O by the end of the experiment. A Kruskal-Wallis test was carried out, with a significant difference (p<0.05) found when analysing cumulative N<sub>2</sub>O loss against time following application.



Figure 4.3: Cumulative N<sub>2</sub>O loss after acidification slurry to varying pH.

Cumulative N<sub>2</sub>O loss over the 109-day experiment following application of slurry applied at four different pH with emissions displayed as mean for each treatment. Points show mean values and error bars represent SEM  $\pm$  (*n*=3). Fluxes expressed on a soil dry weight basis.

Emissions factors for each treatment are shown in Table 4.4, where slurry acidified to pH 4.5 was found to have a greater emission factor than all other treatments, although there were no significant differences found between all treatments. This was reflective of the findings shown in Figure 4.3 with pH 4.5 having the greatest loss of  $N_2O$ .

Table 4.4: Cumulative N<sub>2</sub>O emissions displayed as an emissions factor.

Cumulative N<sub>2</sub>O loss (percentage N loss of total N applied at the conclusion of the experiment for four different slurry pH (n=3). No significant differences (p<0.05) were found. Values represent means and ± SEM (n=3).

pH	N2O EF (% total N applied)	±
4.5	0.13	0.07
5.5	0.06	0.01
6.5	0.09	0.03
7.4	0.11	0.04

#### 4.5.2.4 Soil Extractable NH<sub>4</sub>-N and NO<sub>3</sub>-N

At the conclusion of the 109-day experiment, no significant differences were found between treatments for both soil extractable NH<sub>4</sub>-N and NO<sub>3</sub>-N. Greater numerical values of both extractable NH<sub>4</sub>-N and NO<sub>3</sub>-N were found in the upper layer of cores receiving slurry acidified to pH 4.5 (Figure 4.4).



Figure 4.4: Extractable NH<sub>4</sub>-N and NO<sub>3</sub>-N at the end of the experiment after application of slurry at four different pH.

Quantity of extractable NH<sub>4</sub>-N (panel A) and NO<sub>3</sub>-N (Panel B) found after 109 days. Each core was separated into "Top" (0 - 7.5 cm) (Panels A and B) and "Base" (7.5 – 15 cm). Bars show mean values and error bars represent  $\pm$  SEM (*n*=3). Data expressed on a soil dry weight basis.

## 4.5.1 Experiment 2 – The effect of application method and slurry pH on NH<sub>3</sub> and N<sub>2</sub>O emissions

#### 4.5.1.1 Slurry properties

The slurry analysis showed a reduction in dry matter following acidification from 9 % to 7.68 following acidification as well as an increase in sulphur as a result of  $H_2SO_4$  addition (Table 4.5).

Table 4.5: Slurry characteristics of acidified and conventional slurry.

Analyses was performed by NRM laboratories (Bracknell, UK) with the exception of pH which was measured immediately after application at Bangor University. Data are expressed on a dry weight basis.

	Unit	Conventional	Acidified
<b>Oven Dry Solids</b>	%	9.01	7.68
Total Kjeldahl N	% w/w	0.17	0.15
NO3-N	mg kg <sup>-1</sup>	<10	<10
NH4 <sup>+</sup> -N	mg kg <sup>-1</sup>	490	498
Total Phosphorus (P)	mg kg <sup>-1</sup>	381	384
Total Potassium (K)	mg kg <sup>-1</sup>	1535	1516
Total Magnesium (Mg)	mg kg <sup>-1</sup>	478	462
Total Copper (Cu)	mg kg <sup>-1</sup>	2.57	2.52
Total Zinc (Zn)	mg kg <sup>-1</sup>	13.2	12.5
Total Sulphur (S)	mg kg <sup>-1</sup>	259	1126
Total Calcium (Ca)	mg kg <sup>-1</sup>	1291	1221
Total Sodium (Na)	mg kg <sup>-1</sup>	296	291
рН		7.62	5.39

## 4.5.1.2 <u>NH<sub>3</sub> loss</u>

After log transformation, both acidified application techniques (AB  $26.1 \pm 1.63 \text{ mg NH}_3 \text{ m}^{-2}$  and AI  $23.9 \pm 2.90 \text{ mg NH}_3 \text{ m}^{-2}$ ) were found to have significantly lower (p < 0.05) NH<sub>3</sub>-N loss than CB (86.8  $\pm 14.32 \text{ mg NH}_3 \text{ m}^{-2}$ ) one hour after slurry application (Figure 4.6). CI ( $35.0 \pm 3.08 \text{ mg NH}_3 \text{ m}^{-2}$ ) also resulted in significantly lower NH<sub>3</sub>-N losses than CB after 1 hour. No significant differences were found between AB and CB, and CB and CI after day 11 (p>0.05). Additionally, NH<sub>3</sub>-N loss following application by AI was found to be significantly lower than CI from hour 6 until the end of the experiment.

Final cumulative NH<sub>3</sub>-N loss expressed as a % total N applied (Table 4.5) showed a significant difference between AI and CB and CI, as well as CI and AB and CB when log transformed (p<0.05). Similar trends are also seen when losses are expressed as a % of total NH<sub>4</sub>-N applied. Significant differences were identified in Table 4.6 where injection of acidified slurry resulted in significantly lower NH<sub>3</sub>-N loss, and conventional surface broadcast lost significantly more NH<sub>3</sub>-N than all other treatments.



Figure 4.5: Cumulative ammonia loss after slurry acidification and different slurry application techniques.

Points show mean values and error bars represent  $\pm$  SEM (*n*=3).

Table 4.6: Final cumulative percentage ammonia loss after slurry acidification and different slurry application techniques.

Cumulative NH<sub>3</sub>-N loss (percentage NH<sub>3</sub>-N loss of total N applied, and percentage NH<sub>3</sub>-N loss of total NH<sub>4</sub>-N applied) 14 days after application for acidified (pH 5.5) and conventional slurry applied via surface broadcast or shallow injection pH. Significant differences (p<0.05) are represented by different letters. Values represent means and ± SEM (n=3).

Treatment	Mean % NH <sub>3</sub> -N loss of TN applied	±	Mean % NH3-N loss of NH4-N applied	±
Acidified Broadcast	3.0 <sup>b</sup>	0.17	15 <sup>bc</sup>	0.81
Acidified Injection	2.1 °	0.18	10.3 <sup>c</sup>	0.91
Broadcast	4.2 <sup>a</sup>	0.31	24.2 <sup>a</sup>	1.82
Injection	3.0 <sup>b</sup>	0.21	17.3 <sup>b</sup>	1.19

## 4.5.1.3 N2O emissions

No significant differences were found when comparing log-transformed N<sub>2</sub>O flux data of acidified and conventional slurry applied via surface broadcast and shallow injection over the 14-day period experiment. Figure 4.6 shows AB emitted the greatest cumulative quantity of N<sub>2</sub>O ( $10.3 \pm 5.02 \ \mu g \ N \ kg^{-1} \ hr^{-1}$ ) whilst CB emitted the least ( $3.7 \pm 2.23 \ \mu g \ N \ kg^{-1} \ hr^{-1}$ ). Both AI ( $5.4 \pm 2.06 \ \mu g \ N \ kg^{-1} \ hr^{-1}$ ) and CI ( $5.8 \pm 2.43 \ \mu g \ N \ kg^{-1} \ hr^{-1}$ ) emitted similar quantities.



Figure 4.6: Cumulative  $N_2O$  loss after slurry acidification and different slurry application techniques.

Cumulative N<sub>2</sub>O loss over the 14-day experiment following application of acidified (pH 5.5) and conventional slurry applied via surface broadcast and injection. Points show mean values and error bars represent  $\pm$  SEM (*n*=3). Fluxes expressed on a soil dry weight basis.

Given the short-term nature of the experiment, only partial emissions factor (EF) could be calculated given the potential for the longer-term nature of  $N_2O$  emissions. The partial EF for each treatment are shown in Table 4.7 where the greatest numerical EF was found following the application of acidified slurry which was surface broadcast. However, all differences between treatments were found to be non-significant.

Table 4.7: Cumulative N<sub>2</sub>O emissions displayed as a partial emissions factor.

Cumulative N<sub>2</sub>O loss (percentage N loss of total N applied) for four different treatments (n=3) after 14 days. Significant differences (p<0.05) are represented by different letters. Values represent means and ± SEM (n=3).

Application method	N2O EF (% N applied)	±
Acidified broadcast	0.04	0.02
Acidified injection	0.02	0.01
Broadcast	0.02	0.01
Injection	0.02	0.01

#### 4.5.1.4 Soil solution NH<sub>4</sub>-N and NO<sub>3</sub>-N

The results shown (Figure 4.7 – panel A) clearly indicate the greatest concentrations of soil solution NH<sub>4</sub>-N were detected in soil receiving AI, peaking at a mean of 19.9 mg NH<sub>4</sub>-N l<sup>-1</sup> ( $\pm$  12.4). Soil solution NH<sub>4</sub>-N concentrations in the AI treatment were found to be significantly greater (*p*<0.05) than both conventional treatments (CB and CI) until day eight, after which no significant differences were found between treatments. Although greater concentrations of NH<sub>4</sub>-N were found to be present in soil receiving AB (peaking at 3.1 mg NH<sub>4</sub>-N l<sup>-1</sup>  $\pm$  1.7) compared to conventional slurry (CB 2.6 mg NH<sub>4</sub>-N l<sup>-1</sup>  $\pm$  0.9, CI 1.7 mg NH<sub>4</sub>-N l<sup>-1</sup>  $\pm$  1.4), no significant differences were found. All statistical analyses were performed on log-transformed data.



Figure 4.7: Soil solution NH<sub>4</sub>-N and NO<sub>3</sub>-N after slurry acidification and different slurry application techniques.

Concentrations of NH<sub>4</sub>-N (panel A) and NO<sub>3</sub>-N (Panel B) in soil solution following application of acidified slurry (pH 5.5) and conventional slurry via surface broadcast and shallow injection. Points show mean values and error bars represent  $\pm$  SEM (*n*=3)

Throughout the 14-day experimental period there were no clear differences between treatments for soil solution concentrations of NO<sub>3</sub>-N (Figure 4.8 – panel B) given the large standard error at each time point. However, at a broad level NO<sub>3</sub>-N concentrations in CB were generally lower than all other treatments, and there was an overall significant trend of increasing soil solution NO<sub>3</sub>-N concentrations following application of the slurry treatments (p<0.05).

#### 4.5.1.5 Soil extractable NH<sub>4</sub>-N and NO<sub>3</sub>-N

Acidified broadcast slurry was found to have numerically greater levels of both extractable  $NH_4$ -N and  $NO_3$ -N at the conclusion of the experiment in the top 7.5 of the soil core (Figure 4.8). However, at the conclusion of the experiment no significant differences were found between treatments.



Figure 4.8: Extractable NH<sub>4</sub>-N and NO<sub>3</sub>-N at the end of the experiment after slurry application using acidified or conventional and surface broadcast or shallow injection.

Concentrations of extractable NH<sub>4</sub>-N (panel A) and NO<sub>3</sub>-N (Panel B) found at the conclusion of the experiment. Each core was separated into "Top" (0 - 7.5 cm) and "Base" (7.5 – 15 cm). Bars show mean values and error bars represent  $\pm$  SEM (*n*=3). Data expressed on a soil dry weight basis.

### 4.6 Discussion

The following discussion will directly address the hypotheses outlined in sections 3 after a brief overview of the slurry used in a typical UK context.

The slurry used in both experiments were higher in dry matter than the typical 6-8% dry matter outlined in RB209 (AHDB, 2017). A strong relationship has been found between dry matter content and available nutrients, therefore it was appropriate to use the linear regressions presented in Williams et al. (2016) to assess the nutrient content of slurries used in a UK context. Table 4.8 shows similarities with RB209 expected values based on the linear regressions with the exception of total Kjeldahl N, which was an order of magnitude lower than expected. This explains the lower overall NH<sub>3</sub> loss found in experiment 2 compared to those found in experiment 1 where a slurry with a comparable dry matter content was applied to similar environmental conditions.

Table 4.8: Comparison of slurry used in this chapter compared to the data outlined in "RB209".

	Experiment 1	RB209	Experiment 2	RB209
Oven Dry Solids	8.92		9.01	
Total Kjeldahl Nitrogen	4.10	3.32	0.17	3.34
Ammonium Nitrogen	1.63	1.20	0.98	1.20
Total Phosphorus	1.44	1.41	1.74	1.42
Total Potassium	2.69	3.21	3.69	3.23
Total Sulphur	1.13	0.95	1.30	0.96

Units are presented as kg m<sup>-3</sup>.

#### a) A reduction in NH<sub>3</sub> loss will be greatest in slurries with the lowest pH

The results presented in experiment 1 support the findings of other authors who report that acidification reduced NH<sub>3</sub> emissions following application. When considering the quantities of N loss reported in the literature, the impact of emissions reduction in this experiment was less but still significantly different to surface broadcast conventional slurry. Stevens et al. (1989) reported that when cattle slurry was acidified to pH 5.5, NH<sub>3</sub> loss was reduced by 95% compared to slurry at pH 7 in the three days after application. However, in this experiment a similar scale of reduction was only found between slurry at pH 7.4 and pH 4.5 at the same time point. Over a greater time period, Park et al. (2017) found that the majority of pig slurry NH<sub>3</sub> emissions occurred over the initial 2 weeks after application which were reduced by 60.9% following acidification to pH 5. In terms of NH<sub>3</sub> emissions, acidifying to pH 5.5 reduced total N loss by 52%, and total NH<sub>4</sub>-N applied by 59% during the initial 14 days following application (Figure 4.1, Table 4.3 & 4.4). Although not measured, the slurry used in this experiment was thought to have a rapid buffering capacity, with NH<sub>3</sub> emissions

found from pH 5.5 slurry from day 1 in both experiments (Figure 4.2 and Figure 4.6). Such a finding indicates the importance of initially acidifying to pH 5.5 to allow for immediate buffering while maintaining a reduced NH<sub>3</sub> loss. Overall, the results highlight the important contribution acidification could deliver in terms of UK agriculture delivering significant reductions in NH<sub>3</sub> emissions in order for the UK to reach a reduction in total NH<sub>3</sub> emissions set out in the NECR (HM Government, 2018).

## b) The greatest concentration of slurry NH<sub>4</sub>-N will be found in soil receiving the lowest slurry pH

The reduction in NH<sub>3</sub> emissions was found to have a direct positive impact on soil solution NH<sub>4</sub>-N quantities, where the treatments with reduced N loss can be seen to influence greater retention of slurry NH<sub>4</sub>-N in the soil (Figure 4.7). The findings presented in various papers (Fangueiro et al., 2018, 2017, 2015b) suggests that acidification inhibits and delays nitrification. The influence of acidification on delaying nitrification can be seen to have the same affect regardless of acidity with all acidified slurry treatments resulting in a similar delay to peak soil solution NO<sub>3</sub>-N concentration at both pH 6.5, 5.5, and 4.5. By the end of the experiment soil extractable NH<sub>4</sub>-N and NO<sub>3</sub>-N concentrations were not significantly different between treatments (Figure 4.5), which further supports the short-term nature of any delays to nitrification. This initial increase in slurry NH<sub>4</sub>-N retention in the soil, without increasing soil solution or extractable soil NO<sub>3</sub>-N concentrations, indicates the potential slurry acidification has in terms of increasing the fertiliser value of slurry without evidence of pollution swapping, but highlights and the importance of applying slurry at an appropriate time for maximum plant uptake.

## c) NH<sub>3</sub> emissions from acidified broadcast application will be comparable to shallow injection of conventional slurry

Experiment 2 clearly shows the potential acidification has in reducing NH<sub>3</sub> emissions regardless of application technique (Figure 4.6). The inclusion of combining both abatement methods, acidification and injections, provided an insight and potential maximum reduction in NH<sub>3</sub> abatement. The use of acidification, and acidification in combination with injection, will increase the economic impact on the agricultural sector but were found to be the most effective at reducing emissions. The reduction in NH<sub>3</sub>-N loss was found to range between 55-70% when comparing both acidified (pH 5.5) treatments to conventional surface broadcast. It was apparent that acidified broadcast was as effective at reducing NH<sub>3</sub> emissions as the current BAT, slurry injection in this experiment. When assessing the impact acidification has on NH<sub>3</sub> emissions in terms of loss as a percentage of total N and NH<sub>4</sub>-N applied, experiment 2 found a smaller reduction than measured in experiment 1. Acidification in

combination with surface broadcast and injection showed a reduction in total N loss of 29 and 50%, and total NH<sub>4</sub>-N loss of 39 and 58% respectively, shown in experiment 2. This emphasises how the amount of slurry-N retained following acidification varies between slurry types. The importance of this research clearly demonstrates how slurry acidification is comparable to the current BAT for NH<sub>3</sub> emission reductions. This experiment used one slurry type at a mesocosm scale, yet if similar results were to be found with more slurry types and at a greater scale, the results would suggest that acidification in combination with surface broadcast would be as effective as conventional shallow slurry injection. Therefore, when considering options available to farmers for NH<sub>3</sub> abatement, surface broadcasting of acidified slurry could be offered as an alternative to shallow injection. This would benefit farms where land is unsuitable for slurry injection and may provide a more cost-effective means of reducing NH<sub>3</sub> emissions.

## d) The use of slurry injection will out-perform surface broadcast in terms of retaining greater levels of slurry NH4-N

The use of acidification in combination with shallow injection has been found to result in greater concentrations of soil solution NH<sub>4</sub>-N when compared to the surface broadcast acidified slurry and was also the case for conventional slurry. However, acidified surface broadcast had numerically greater concentrations of NH<sub>4</sub>-N when compared to conventional slurry applied via shallow injection. The results presented here support the findings of Fangueiro et al. (2017) who found injection was most effective at retaining slurry N. However, purely in terms of NH<sub>3</sub> abatement the combination of injection and acidification would be costly to the farmer when compared to each technique individually. Therefore, in terms of policy, acidification is more effective as a NH<sub>3</sub> abatement technique than shallow injection with greater NH<sub>4</sub>-N concentrations remaining in soil solution. The results presented highlight the potential of acidification to increase the fertiliser value of slurry as shown by the greater concentrations of soil solution NH<sub>4</sub><sup>+</sup> (Figure 4.7). Similar findings are also presented in the literature (D'Annibale et al., 2019; Fangueiro et al., 2016; Sánchez-Rodríguez et al., 2018) where greater concentrations of soil NH4<sup>+</sup> were also found following the application of acidified slurry. However, given the short-term nature of said increases (7-21 days) it is vital that acidified slurry is applied during periods of active plant growth to maximise benefits of greater concentrations of NH<sub>4</sub><sup>+</sup>, and prevent N pollution swapping (Bell et al., 2016; Chadwick et al., 2011). In a practical sense, this underlines the potential value of slurry acidification for farmers in areas unsuitable for shallow injection, if similar results are found on different soil types.

## e) Application of acidified slurry will result in lower N<sub>2</sub>O emissions when compared to conventional slurry regardless of application method.

Given the potential of increased N<sub>2</sub>O emissions, as a result of greater NH<sub>4</sub>-N concentrations available for nitrification and denitrification following the application of acidified slurry and injection of slurry, it was important to ensure that N pollution swapping does not occur. Both Figures 4.3 and 4.6 show a result similar to that published by others whereby acidification had little impact on N<sub>2</sub>O emissions when compared to conventional slurry (Fangueiro et al., 2017, 2015b; Seidel et al., 2017). When slurry pH was reduced to pH 4.5 nitrification and denitrification rates are potentially inhibited (as shown in Figure 4.3), but total cumulative N<sub>2</sub>O loss from the acidified treatment was not significantly different from that of conventional slurry. Petersen and Sommer (2011) found that injection can lead to localised hotspots of anaerobic conditions in the soil profile resulting in greater N<sub>2</sub>O emissions. This was not the case during this experiment (Figure 4.6) where no significant differences were found between both acidified and conventional slurry injection and the surface broadcast equivalents. The N<sub>2</sub>O emissions factor reported in Table 4.4 were low but comparable to slurry emission factors found by others (Thorman et al., 2020), whereas the short-term nature of experiment 2 meant that only a partial emission factors could be produced. However, the emissions factors shown in both experiments (Table 4.4 and 4.6) find that acidified treatments are numerically greater than nonacidified suggesting there was a marginal increase on N pollution swapping, albeit non-significant which was also found by Malique et al. (2021). This is of importance in terms of N pollution swapping and the sustainable use of slurry acidification across the UK as a NH<sub>3</sub> abatement strategy. However, further experimentation would be required on multiple soil types to fully understand the potential of N emissions following acidification.

#### 4.7 Conclusions

The results of these two short-term bench-scale experiments show the potential of slurry acidification to reduce N loss through NH<sub>3</sub> emissions from a UK soil, and provide a percentage reduction similar to those found in European studies. The reduction of NH<sub>3</sub> loss through combining slurry acidification and different slurry application techniques clearly shows that acidification of cattle slurry applied through surface broadcast was comparable to conventional slurry injection. This has strong policy implications by providing clear evidence of the performance of traditional surface broadcasting and low emission slurry spreading practises compared with a new technology for UK agriculture, slurry acidification. Importantly, the results presented, combining slurry acidification with shallow injection, demonstrates reduced NH<sub>3</sub> loss and increased NH<sub>4</sub>-N availability without significantly increasing concentrations of NO<sub>3</sub>-N and N<sub>2</sub>O emissions. This was the same for slurry acidified to pH
4.5 but also for all acidified slurries, showing the potential fertilizer benefits of acidification without increasing pollution. Ultimately, the use of slurry acidification has beneficial impacts on retaining N within a UK soil without leading to increased NO<sub>3</sub>-N and N<sub>2</sub>O.

#### 4.8 References

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### <u>Chapter 5: Soil quality is most affected in the zone surrounding the nitrogen</u> <u>amendment: a micro study.</u>

#### Abstract

Agriculture is responsible for an approximate 90% of UK total ammonia (NH<sub>3</sub>) emissions, which are legally required to be reduced by 16% by 2030. Slurry acidification, the adjustment of slurry pH through the addition of  $H_2SO_4$ , is effective as an NH<sub>3</sub> abatement technique commercially used in Denmark, and is of increasing interest by policy makers in the UK. The process of adding a concentrate acid shifts the total ammoniacal nitrogen strongly in favour of  $NH_4^+$ .

Previous studies have been carried out into the effect of acidified slurry on topsoil, yet no research has been carried out on the micro-scale identifying changes in the topsoil profile. This experiment measures the impact of acidified (pH 5.5) cattle slurry compared to conventional slurry applied via surface broadcast at a rate of 40 m<sup>3</sup> ha<sup>-1</sup> and ammonium nitrate, matching the total N content of the slurry treatments. A microtome was used to enable accurate micro measurements from a re-packed soil core, where slices of soil were removed at various depth intervals, from 2 mm – 10 mm, and analysed for pH, EC,  $NH_4^+$ ,  $NO_3^-$ , as well as TOC and microbial respiration using <sup>14</sup>C labelled glucose.

The results indicated that a clear inhibition of nitrification occurred with concentrations of NO<sub>3</sub>peaking on day 21, the same time as conventional slurry but to a lesser degree (conventional slurry:  $2861 \pm 340 \text{ mg NO}_3\text{-N kg}^{-1}$ , acidified slurry:  $2173 \pm 658 \text{ mg NO}_3\text{-N kg}^{-1}$ ) while NH<sub>4</sub><sup>+</sup> concentrations were slower to decrease following application of acidified slurry. This was further supported by a short-term delay in microbial respiration. Concentrations of NH<sub>4</sub><sup>+</sup> were confined to the top 25 mm of soil cores, supporting previous research on NH<sub>4</sub><sup>+</sup> sorption to organic matter, whereas NO<sub>3</sub><sup>-</sup> was found throughout the entire core by the end of the experiment. Other indicators such as soil electrical conductivity (EC), total organic carbon (TOC), and to a lesser extent pH, saw changes to soil quality decreasing down the soil profile.

This was the first study researching the impact of acidified slurry on soil quality at the micro-scale and clearly demonstrates that the area directly surrounding the application of a N amendment was most impacted.

#### 5.1 Introduction

Slurry acidification, the addition of sulphuric acid ( $H_2SO_4$ ) to conventional slurry, has been used in Europe, especially Denmark, as an ammonia ( $NH_3$ ) emissions abatement technique (Fangueiro et al., 2015a). The principle behind acidification is the additional  $H^+$  ion added via  $H_2SO_4$  shifts the  $NH_3:NH_4^+$  ratio strongly in favour of the  $NH_4^+$  form, which unlike  $NH_3$  is stable in a liquid form (Husted et al., 1991). Such a shift has been found to generate a slurry product where over 98% of total ammoniacal (TAN) is  $NH_4^+$ ; thus reducing N losses through volatilisation (Berg et al., 2006; Cocolo et al., 2016; Petersen and Sommer, 2011).

Following the application of acidified slurry, various authors have found that the adjusted pH of acidified slurry alters soil pH with the majority of authors reporting an acidifying effect as a result. D'annibale (2019) found that soil pH reduced by approximately 1 unit during the first month after the application of acidified slurry, at pH 5.3 from an original 7.5, and remaining stable thereafter. Likewise, Sánchez-Rodríguez (2018) found a decrease of soil pH of up to 1 pH unit, with the change in pH reaching a maximum approximately 90 days after application of an acidified digestate at pH 5.4, reduced from pH 8.24. This mirrors an earlier study (Frost et al., 1990) which reported a reduction in soil pH from 6.2 to 5.8 after receiving three applications of slurry in a single year when slurry was acidified to pH 5.5 from an original source of between pH 7.2 – 7.8. Pedersen et al. (2017) reported that beneath the unacidified treatments no change or an increase in soil pH was found, yet below the bands of band spread pH 5.5 acidified slurry, soil pH decreased. This is further corroborated by Fangueiro et al. (2018) who found a decrease in soil pH of 0.9 and 1.4 in sandy and sandy-loam soil, respectively, when acidified (pH 5.6) cattle slurry was compared to an conventional slurry control (pH 7.4 – 7.6) and incorporated band applied conventional slurry.

However, a number of studies have found a lesser effect on soil pH, or no impact following the addition of acidified slurry. Fangueiro et al. (2015c) found that there was no significant difference between an unfertilised control and plots receiving acidified cattle slurry (pH 5.0), a result of the soil buffering capacity. Sigurnjak et al. (2017) reported that there was no difference to the soil pH when comparing acidified (pH 5.6) and unacidified (pH 7.9) pig slurry at harvest, 54 days after application, while Loide et al. (2020) found a decrease in soil acidity of 0.1 pH unit following an high application rate (45 m<sup>3</sup> ha<sup>-1</sup>) of acidified (pH 5.0) cattle slurry.

The application of acidified slurry has previously been found to increase soil EC immediately after application. Fangueiro et al. (2015c) found that during the 20 day period following application, band spread acidified slurry and liquid fraction had a higher soil EC, yet by the end of the experiment these

values had returned to the control values, likely as a result of plant uptake and leaching of ions. Similar findings were presented in both Sigurnjak et al. (2017) and Sánchez-Rodríguez et al. (2018) where soil EC was found to be greatest following the application of acidified products.

The fundamental principle behind acidification being a NH<sub>3</sub> abatement technique would infer that the quantity of NH<sub>4</sub>-N found in the soil following acidified treatments would be greater than that following untreated slurry application. This was found to be the case in D'annibale et al. (2019), who reported concentrations of soil NH<sub>4</sub>-N peaked immediately following application to a greater extent than conventional and remained greater for the first 28 days, but then decreased to the level of the conventional slurry equivalent. Similar findings were presented in Fangueiro et al. (2010) who found that after 10 days of remaining at a constant level, NH<sub>4</sub>-N decreased at a slower rate than the nonacidified treatments. This is an important consideration when assessing the potential slurry acidification has to increase the NUE of the crop where greater concentrations of NH<sub>4</sub>-N is taken up by plants (Fangueiro et al., 2018). If plants are not able to take up the additional NH<sub>4</sub>-N, N pollution swapping may occur through the microbial processes of nitrification and denitrification leading to increased N losses through NO<sub>3</sub><sup>-</sup> and N<sub>2</sub>O (Cameira et al., 2019; Malique et al., 2021). The impact of soil type can also alter the concentration of NH<sub>4</sub><sup>+</sup> following acidified slurry and digestate being applied. At 2 sites, Sánchez-Rodríguez (2018) found soil NH4<sup>+</sup> concentrations increased following the application of acidified digestate, but declined at a greater rate on a Eutric Cambisol compared with a free draining Dystric Cambisol. Similar conclusions have been found in other papers as well as the impact of pre-treatments of slurry before acidification (Fangueiro et al., 2016). The same study suggested that differences in NH<sub>4</sub><sup>+</sup> was due to a combination of effects, including the period of time nitrification was inhibited, as well as soil type with sandy soils allowing gaseous exchange and have low cation exchange capacity and adsorption sites.

Various pre-treatments prior to acidification have formed the basis of studies with separation commonly used. Low dry matter slurries, although at lower risk of high NH<sub>3</sub> emissions due to rapid infiltration (Bhandral et al., 2009), have been the subject to research. Fangueiro et al. (2015b) found that both the application of solid and liquid fractions of acidified slurry to soil resulted in greater concentration of soil  $NH_4^+$  when compared to unacidified slurry fractions after day 7, and remained significantly greater throughout the duration of the experiment. This was echoed in Fangueiro et al. (2013) as well as Owusu-Twum et al. (2017), although the findings in the latter study were not significantly different.

Potential N pollution swapping, as a result of increased nitrification from greater NH<sub>4</sub>-N availability,

has previously been included in studies. D'annibale et al. (2019) reported that differences between soil NO<sub>3</sub>-N values were found throughout an incubation experiment. After 28 days, the author reported that NO<sub>3</sub>-N concentrations were significantly greater in untreated slurry at a high application rate, yet by day 56, the only significant differences were found between acidified and unacidified low application rates, with acidified slurry being significantly greater. Such an inhibitory effect of acidified slurry on nitrifiers has been hypothesized in a number of papers. Fangueiro et al. (2013) reported that acidified slurries were found to result in lower concentrations of soil NO<sub>3</sub>-N than unacidified slurries and was the case for both acidified slurries with low and high dry matter contents. Nitrification, in the same paper, was found to be lower or similar to the conventional slurry control for the low dry matter content acidified slurry, while Fangueiro et al. (2010) reported a delay of up to 8 days for the initiation of nitrification in acidified treated slurries. Sigurnjak et al. (2017) also found that the concentration of NO<sub>3</sub>-N in soils receiving untreated slurry remained significantly greater when compared to those receiving acidified slurry and digestate. A further experiment using whole and liquid fractions of slurry found that there was no significant difference between NO<sub>3</sub><sup>-</sup> concentrations between acidified and non-acidified treatments throughout the 92 days of the experiment, but mean values were lower for acidified liquid fractions when compared to untreated liquid fractions (Fangueiro et al., 2015b). In a UK setting, the application of acidified digestate to soil was found to result in soil NO<sub>3</sub><sup>-</sup> concentrations that were 25-33% lower when compared to untreated digestate at two field sites (Sánchez-Rodríguez et al., 2018). In this study, peak soil NO3<sup>-</sup> concentrations were found earlier than others have reported, at day 1 (Sánchez-Rodríguez et al., 2018).

Fangueiro et al. (2016) found that the length of the inhibitory effect of acidification on nitrification is dependent on soil type whereby  $NO_3^-$  concentrations in a vertic cambisol remained low for 3 days, yet a haplic arenosol remained low for 15 days after receiving acidified treatments. Such a soil type variation was also presented in Cameira et al. (2019) where high levels of soil NO<sub>3</sub>-N concentration were found in soil receiving acidified band spread and unacidified dairy cattle slurry but no trend was found on a sandy loam soil.

A healthy functioning soil fauna community is key to nutrient cycling, and has been found to be sensitive to changes in soil conditions. Some have found that microbial sulfate cycling has been limited following the surface application of acidified (pH 5.5) pig slurry due to alterations to pH (Eriksen et al., 2008), which has also been suggested as causing a delay to microbial nitrogen processing (Fangueiro et al., 2013). Such an impact has been found to reduce microbial C biomass over the entire three-week experimental period. However, Edesi et al. (2020) have found that the

application of acidified (pH 5.9) pig slurry did not impact microbial structure. The measurement of microbial activity is vital to understand the potential impact on soil health following the application of acidified slurry.

#### 5.2 <u>Aims</u>

Although the impact of slurry acidification on soil quality and nutrient dynamics has been studied, little work has been carried out at the micro-scale to assess the localised impact of slurry acidification on chemical and biological indicators of soil health.

The aim of the experiment was to understand the impact of slurry acidification on soil chemical and biological properties in the top (7.5 cm) soil below the slurry. This will support field-scale research and provide further insight for the zone of the soil profile most affected by the surface application of slurry. This will have practical implications as to the application of slurry and positive or negative consequences for the surrounding soil.

#### 5.3 Hypotheses

The following hypotheses were addressed in this experiment:

- a. Change in soil pH and EC will be greatest in the soil immediately below the applied slurry and decrease down the soil profile but buffer back to the levels found in the control over time.
- b. Acidified slurry will result in greater soil NH<sub>4</sub><sup>+</sup> concentration in the upper layers, with reduced transformation to NO<sub>3</sub><sup>-</sup>.
- c. Microbiological respiration will be initially impacted by the application of acidified slurry, over a 24 48 hour period, before recovering to the respiration rates found in conventional slurry.

#### 5.4 Methods

#### 5.4.1 Experimental design

The experiment was established using topsoil from Henfaes Research Station ( $53^{\circ}14'N$ ,  $4^{\circ}01'W$ ), characterised as a free draining Eutric Cambisol with a sandy loam texture. The soil was collected from three discrete areas of a grassland field sown with Oliver seeds "Sabre mix" 2 years previously, which have not received N fertilizer for at least 12 months (Table 5.1). The vegetation layer was removed in-field before being sieved to 2mm and packed into open ended 68 cm<sup>3</sup> plastic cylinders (3.4 cm diameter and 7.5 cm length) by tapping the cylinder on a hard surface as it was being filled. This procedure resulted in a bulk density of 1.2 g cm<sup>-3</sup>, similar to that of the intact soil in the field (1.13 g cm<sup>-3</sup>). The soil moisture content was then adjusted to 50% water filled pore space (WFPS). Each core was covered at the top and bottom with parafilm to allow gas diffusion but prevent drying

until destructive sampling.

Slurry was collected from a slurry tank located on a dairy farm in Abergwyngregyn (North Wales, 53°23' N, 4°02'W), subsampled and acidified to the target pH 5.5 using 98% H<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich, UK). A subsample was retained, representing conventional unacidified slurry. NRM Laboratories (Bracknell, UK) carried out chemical analysis of each slurry following application (Table 5.2).

Each soil type (n=3) received the following treatments: Control (no amendment), acidified cattle slurry, conventional cattle slurry, or ammonium nitrate fertiliser to match the total N applied in the slurry treatments - 80 kg N ha<sup>-1</sup>. Each treatment was replicated 6 times to allow for destructive sampling at each time point, day 1, 3, 7, 14, 21 and 42. Both slurry treatments were applied at the equivalent rate of 40 m<sup>3</sup> ha<sup>-1</sup>, typical of moderate output grazing livestock farming systems (Defra, 2021) (Table 5.2). An identical set of cores were established for measuring soil microbial respiration on days 1, 3 and 7, following previous indications that differences in soil respiration was restricted to the first week following application.

#### 5.4.2 Soil sampling

A Brunel bench microtome (Brunel Microscopes, UK) was used to destructively sample each core into 12 segments (Figure 5.1). The microtome pushed the soil up the cylinder by the desired depth and a sharp bladed knife was used to scrape the soil into a weighing boat (2 mm soil depths resulted in ca. 1.5g fresh weight of soil). From this, soil was subsampled for the chemical and biological properties described below.



Figure 5.1: A schematic diagram of a microtome.

The microtome exposed the desired amount of soil core by pushing the soil from the base of an open-ended cylinder. Once above the top of the cylinder, a sharp blade sliced the soil into a weighing boat. The soil was sampled in 2 mm depths for the top 10 mm, 5 mm for between 10-15 mm, and then every 10 mm from 15 mm to 75 mm.

#### 5.4.2.1 Chemical indicators

For each soil depth segment the soil sample was mixed before 0.3 g was added to a 1.5 ml Eppendorf tube for a 0.5 M K<sub>2</sub>SO<sub>4</sub> extraction at 1:5 soil:extractant (w:v) for N (NH<sub>4</sub>-N, NO<sub>3</sub>-N) analysis. Samples were shaken at 250 rpm for 30 mins, centrifuged at 14,000 rpm for 5 minutes, before 1 ml of supernatant was removed into a clean 1.5 ml Eppendorf and frozen at -20°C prior to analysis. A further 0.3 g of soil was added to a separate 1.5 ml Eppendorf tube with diH<sub>2</sub>O at 1:5 soil: diH<sub>2</sub>O (w:v) to measure pH and EC, with the remaining sample weighed and oven dried at 105°C for 24 hours to calculate gravimetric moisture content.

Soil pH was measured using a Hanna instruments micro-pH electrode (HI-1330B) in conjunction with a Hanna instruments Model 210 pH meter (Hanna Instruments Ltd., Leighton Buzzard, and UK). Soil EC was measured using a Jenway micro-volume conductivity probe alongside a Jenway 4520 conductivity meter (Cole-Palmer Ltd., Stone, UK).

 $NH_4^+$  and  $NO_3^-$  concentrations in the K<sub>2</sub>SO<sub>4</sub> extractions were analysed colorimetrically following the methods of Mulvaney (1996) and Miranda et al. (2001), respectively. The concentrations were determined using an Epoch<sup>®</sup> microplate spectrophotometer (Bio Tek Instruments Inc., Winooski, USA). Total dissolved organic carbon (TOC) concentrations were measured in the K<sub>2</sub>SO<sub>4</sub> extractions using a Multi N/C 2100/2100 analyser (AnalytikJena AG, Jena, Germany).

#### 5.4.2.2 Biological indicators

A second set of cores were established in an identical manner to those described in section 5.4.1. with the same treatments applied. As outlined in Jones et al. (2019), 0.6 g of soil from each soil depth was placed in a 50 ml sterile centrifuge tube and 40  $\mu$ l of 10 mM <sup>14</sup>C-labelled glucose (0.7 kBq per 40  $\mu$ l) added. A scintillation vial containing 1 ml of 1 M NaOH was placed inside the 50 ml centrifuge tube which was then sealed, so any <sup>14</sup>CO<sub>2</sub> emitted during microbial respiration was trapped in the NaOH. After 1 hour, each scintillation vial was removed from the sample and the contents analysed on a Wallac 1404 liquid scintillation counter (Perkin Elmer, UK) to determine the percentage recovery of <sup>14</sup>C-glucose that was respired in each sample based on <sup>14</sup>C concentrations found in the scintillation fluid.

#### 5.4.3 Statistical analysis

Throughout the experiment statistical analysis was performed using R v. 4.1717 (R Core Team, 2019) where a significance level of p < 0.05 was accepted as significant. Where data was deemed normal, a linear mixed model was used to assess variables against slurry treatment, segment depth, and time following application. These were then subjected to an ANOVA (stats package, R Core Team, 2019) and if significant differences were found "lsmeans" (emmeans, Lenth, 2021) was used to carry out Tukey post-hoc tests. Where data failed to meet normality assumption a non-parametric Kruskal-Wallis test (stats package, R Core Team, 2019) was performed. All results were graphical illustrated with "ggplot2" (Wickham, 2016).

#### 5.5 <u>Results</u>

#### 5.5.1 Soil analysis

Table 5.1 outlines the soil analysis at the start of the experiment, with higher than expected extractable  $NO_3^-$  concentrations, likely a result of sieving stimulating nitrification.

Table 5.1: Pre-application soil properties.

Values shown represent means with  $\pm$  indicating standard error (*n*=12). All values are expressed on a dry matter basis with the exception of pH and EC.

	Site 1	±	Site 2	±	Site 3	±
<b>Organic Matter (%)</b>	5.3	0.10	5.8	0.03	5.6	0.14
рН	6.5	0.08	6.5	0.07	6.4	0.06
EC (μS cm <sup>-1</sup> )	38.2	4.52	23.0	1.29	24.6	1.52
Total N (mg N kg <sup>-1</sup> )	3.8	0.2	3.5	0.5	3.6	0.3
Total C (mg C kg <sup>-1</sup> )	325.2	0.65	28.9	4.2	30.6	5.7
C:N ratio	8.5	0.4	8.3	0.3	8.5	0.5
Extractable NO3 <sup>-</sup> (mg N kg <sup>-1</sup> )	175.7	15.53	103.2	6.05	132.9	7.31
Extractable NH4 <sup>+</sup> (mg N kg <sup>-1</sup> )	21.8	4.69	28.9	2.80	69.7	2.88

#### 5.5.2 Slurry analysis

Slurry analysis presented in Table 5.2 details the characteristics found in the acidified and conventional slurry. Low extractable NH<sub>4</sub>-N was found in both slurries likely a result of the low dry matter content of the slurry, where dry matter has been found to be a controlling factor of slurry nutrients (AHDB, 2017).

Table 5.2: Slurry characteristics of each treatment applied to cores.

Analysis was carried out at Bangor University\* and NRM laboratories.

		рН 5.5	Raw
Oven Dry Solids	%	2.75	2.75
Kjeldahl N	% w/w	0.20	0.20
K2SO4 extractable NO3-N	mg/l	8.01	7.38
K2SO4 extractable NH4-N	mg/l	184.84	177.73
Acetic Acid extractable PO <sub>4</sub> -P	mg/l	18.64	13.47
Total Potassium	% w/w	0.17	0.17
Total Magnesium	% w/w	0.02	0.02
Total Copper	mg/kg	1.34	1.34
Total Zinc	mg/kg	5.79	5.79
Total Sodium	% w/w	0.05	0.05
Total Calcium	mg/kg	727.00	727.00
*pH 1:5 H2O		5.5	7.34

#### 5.5.3 <u>pH</u>

The acidifying impact following application of acidified slurry (pH 5.5) was limited to the final day of experiment where a significant difference to the control was observed in the top 10-15 mm (Figure 5.2). Prior to this, all significant differences (day 1 and 2: 4-6 mm, 6-8 mm, 35-45 mm, 45-55 mm; day 7 and 14: 4-6 mm, 45-55 mm; day 21: 45-55 mm) showed that the control had a more acidic pH when compared to acidified slurry. Synthetic fertilizer, significantly lowered soil pH compared to other treatments yet the impact between depths varied between each treatment. Synthetic fertilizer had a significantly lower pH than acidified slurry, with a minimum pH of pH 4.5 ± 0.16 (at 8-10 mm on day 21) and a maximum of pH 6.0 ± 0.09 (at 65 – 75 mm on day 42). In comparison, acidified slurry reached a minimum pH of 5.5 ± 0.15 (at 8 – 10 mm on day 42) and a maximum of pH 7.5 ± 0.08 (at 6 – 8 mm on day 1). Similarly, cores receiving acidified slurry were found to have a significantly greater soil pH than those receiving conventional slurry until day 42, after which soil pH decreased for treatments receiving acidified slurry.



Figure 5.2: Changes to soil pH over time and depth following the application of conventional slurry, acidified slurry and ammonium nitrate.

Bars show mean values and error bars represent  $\pm$  SEM (*n*=3).

#### 5.5.4 <u>EC</u>

The findings presented in Figure 5.3 show that changes to soil EC where most pronounced during the first week following application, after which no significant differences were found between treatments although they remained greater than the control. Soil EC was greater for acidified slurry throughout the experiment at all dates and depths, and had not returned to the control level by the end of the experiment, as was ammonium nitrate. All treatments peaked on day 3, before reducing to day 7 and remaining stable until day 42 (acidified slurry:  $2283 \pm 88 \ \mu\text{S cm}^{-1}$  at 0-2 mm, conventional slurry:  $1080 \pm 151 \ \mu\text{S cm}^{-1}$  at 0-2 mm, ammonium nitrate:  $2103 \pm 842 \ \mu\text{S cm}^{-1}$  at 0-2 mm). Differences occurred between acidified slurry and ammonium nitrate, and conventional slurry where the soil EC increased immediately following application and was approximately twice as great that found in cores receiving conventional slurry.

At 10-15 mm, acidified slurry had a significantly greater soil EC ( $488 \pm 27 \ \mu S \ cm^{-1}$ ) than cores receiving ammonium nitrate ( $329 \pm 44 \ \mu S \ cm^{-1}$ ); however, at depths below 45 mm significantly greater soil EC was found for ammonium nitrate. At these greater depths, a maximum EC was found at  $1838 \pm 245 \ \mu S \ cm^{-1}$  for acidified slurry (10 -15 mm) while the same depth for core receiving synthetic cores measured  $857 \pm 314 \ \mu S \ cm^{-1}$ .



Figure 5.3: Changes to soil EC over time and depth following the application of conventional slurry, acidified slurry and ammonium nitrate.

Bars show mean values and error bars represent  $\pm$  SEM (*n*=3)

#### 5.5.5 Soil inorganic N

Figure 5.4 highlights initial increases of NH<sub>4</sub>-N levels in soil cores receiving any of the three treatments compared to the control, while there was a clear delay in NO<sub>3</sub>-N formation for cores receiving slurry treatments. A Kruskal-Wallis test was performed on NH<sub>4</sub>-N concentrations, which found significant differences (p<0.05) between: treatment type, depth of soil, and time following application. A linear mixed model combined with a Tukey post-hoc test was performed on NO<sub>3</sub>-N with significant differences found between variables.



Figure 5.4: Changes to soil NH<sub>4</sub>-N and NO<sub>3</sub>-N availability over time and depth following the application of conventional slurry, acidified slurry and ammonium nitrate.

Bars show mean values and error bars represent  $\pm$  SEM (*n*=3)

Each of the treatments had the greatest levels of  $NH_4^+$  at the top of the core immediately following application (Synthetic fertilizer: day 1, depth 2-4 mm, 9016 mg ± 912 mg NH<sub>4</sub>-N kg<sup>-1</sup>; conventional slurry: day 3, depth 0-2 mm, 5901 ± 429 mg NH<sub>4</sub>-N kg<sup>-1</sup>; acidified slurry: day 1, depth 0-2 mm, 5394 ± 302 mg NH<sub>4</sub>-N kg<sup>-1</sup>). A clear decrease in NH<sub>4</sub><sup>+</sup> concentration was observed over time, with lowest levels of NH<sub>4</sub><sup>+</sup> found at each depth at day 42.

Although the greatest levels of NH4<sup>+</sup> were confined to top 35 mm throughout the experiment, NO3<sup>-</sup>

levels increased through the entire core from day 7 onwards. The timing of peak NO<sub>3</sub><sup>-</sup>varied for each treatment but was consistently found at surface (0-2 mm) level. Ammonium nitrate peaked at day 1 ( $6950 \pm 1129 \text{ mg NO}_3\text{-N kg}^{-1}$ ) whereas both slurry treatments peaked at day 21 (conventional slurry:  $2861 \pm 340 \text{ mg NO}_3\text{-N kg}^{-1}$ , acidified slurry:  $2173 \pm 658 \text{ mg NO}_3\text{-N kg}^{-1}$ ).

#### 5.5.6 <u>TOC</u>

Figure 5.5 shows the greatest levels of total organic carbon (TOC) were present in the cores receiving acidified slurry, with conventional slurry also increasing TOC but to a lesser extent. A Kruskal-Wallis test was carried out which indicated that there are significant differences between TOC concentration and treatment, soil depth, and days following application. Each treatment peaked at different times throughout the experiment, with peaks being recorded at the soil surface. Peak values for each treatment were: Acidified slurry 36.5  $\pm$  12.04 mg TOC 1<sup>-1</sup> (day 3, 0-2 mm), conventional slurry 11.5  $\pm$  2.04 mg TOC 1<sup>-1</sup> (day 14, 0-2 mm), ammonium nitrate 9.4  $\pm$  8.50 mg TOC 1<sup>-1</sup> (day1, 0-2 mm) and control 6.1  $\pm$  5.34 mg TOC 1<sup>-1</sup> (day 7, 15 – 25mm).

The declining levels of TOC found in acidified soil cores at day 7 support the results above, which show an inhibitory impact of acidified slurry on microbial activity up until this point. By day 21, levels of TOC were close to the control and remained low until the end of the experimental period coinciding with a stabilisation of NO<sub>3</sub>-N levels found within the soil core for all treatments.



Figure 5.5: Changes to soil TOC over time and depth following the application of conventional slurry, acidified slurry and ammonium nitrate.

Bars show mean values and error bars represent  $\pm$  SEM (*n*=3)

#### 5.5.7 Microbial respiration

Although few significant differences were found between treatments (Figure 5.6), a clear inhibitory effect was apparent on day 1 to a depth of 6-8 mm for all treatments compared to the control. By day 7, the end of this measurement period, microbial activity from cores receiving a treatment had returned to, or exceeded, the level of the control. This aligns with the delay in nitrification and increasing  $NO_3^-$  from day 7. Throughout the experiment, significant differences were only found between the control and treatments, and restricted to the top 25 mm (Day 1, depth 10-15 mm control 4.4 ± 0.46 % recovery CO<sub>2</sub> applied, acidified slurry 3.7 ± 0.35 %; depth 15-25 mm, control 3.7 ± 0.39 %, conventional slurry 4.0 ± 0.29 %, acidified 3.18 ± 0.79%; Day 3, depth 0-2 mm, control 4.5 ± 0.39 %, conventional slurry 2.1 ± 0.99 %; Day 7, depth 4-6 mm, control 2.8 ± 0.77 %, ammonium nitrate 2.4 ± 0.47%).



Figure 5.6: Changes to soil microbial respiration over time and depth following the application of conventional slurry, acidified slurry and ammonium nitrate.

Bars show mean values and error bars represent  $\pm$  SEM (*n*=3)

#### 5.6 Discussion

The following discussion is going to directly address the hypotheses established above:

a) Change in soil pH and EC will be greatest in the soil immediately below the applied slurry and decrease down the soil profile but buffer back to the levels found in the control over time.

The results presented in Figure 5.2 and 5.3 clearly show that changes to soil pH and EC were greatest at the point of application, with changes occurring immediately after application (day 1) at the surface layer of the core. The impact was greatest for soil pH following the application of ammonium nitrate which was a consequence of the acidifying process of nitrification (Goulding, 2016). The release of volatile fatty acids, a known control of pH (Paul and Beauchamp, 1989; Sommer and Husted, 1995), could explain the initial increase of alkalinity in soil pH following the application of acidified slurry. Also rapid slurry buffering, as found in Chapter 4 of this thesis, could explain the increased alkalinity found immediately after application which has the potential to reduce after multiple applications. However, the findings presented here contradict many others who reported that the application of acidified reduced soil pH by up to pH 1.1 (D'Annibale et al., 2019; Fangueiro et al., 2018; Frost et al., 1990; Pedersen et al., 2017; Sánchez-Rodríguez et al., 2018). Such reductions in soil pH were

found on soils that had an initial soil pH (pH 7.1 - 6.1) greater than the target slurry pH (pH 5.6 - 5.3) and receiving up to 6 applications of slurry. Others (Fangueiro et al., 2015b; Loide et al., 2020; Sigurnjak et al., 2017) found that the impact of acidification was limited on soil pH given that initial soil pH (pH 4.8 - 5.5) was similar to that of acidified slurry (pH 5 - 5.6), but no authors reported an increase in soil pH. The low dry matter content of the slurry used in this experiment (2.7%) would have increased infiltration rates immediately altering the soil chemistry and biology, when compared to the dry matter content of slurry used in experiments found to reduce soil pH (5-15%). With the exception of acidified slurry, which became significantly different to the control at day 42, a clear buffer effect can be seen where soil pH was resembling the control by the conclusion of the experiment.

An immediate increase in soil EC was presented in Figure 5.3 following the application of all fertiliser treatments, peaking at day 3, and becoming non-significant from the control after the first week, with the greatest increase found in the top 10 mm of soil. Peak soil EC has been found to be short in duration with Fangueiro et al. (2015c) reporting greater soil EC in the 20 days following the application of band spread acidified slurry. Similar to the impact on pH, the varying nature of individual slurries can be seen when assessing the duration of other reported increases in soil EC. Sigurnjak et al. (2017), for example, found significant differences between treatments at the end of a 120 day experiment involving acidified pig slurry, but concluded at a lower soil EC than the results presented here after 42 days. This therefore suggests the decrease of soil EC would continue over time, but as neither of these studies analysed the samples at a micro scale, determining the impact of sampling depth was difficult to separate from the entire topsoil profile EC. An example of this can be seen when comparing acidified and conventional slurry in this experiment, with acidified slurry significantly different but only within the top 25 mm.

The movement of ions through the soil profile and the consequential impact on soil chemical properties was evident here, with significant differences found between ammonium nitrate cores and those receiving acidified slurry on day 1. At 10-15 mm, acidified slurry had a significantly greater soil EC ( $488 \pm 27 \ \mu\text{S cm}^{-1}$ ) than cores receiving ammonium nitrate ( $329 \pm 44 \ \mu\text{S cm}^{-1}$ ); however, at depths below 45 mm significantly greater soil EC was found for ammonium nitrate. This suggests that the immediate movement of ions, e.g.  $NO_3^-$ , from ammonium nitrate, was more rapid than that of the acidified slurry (which contained little  $NO_3^-$ , Figure 5.3). This was further supported by the results from day 3, where acidified slurry was found to have a greater soil EC than that found in ammonium nitrate cores.

# b) Acidified slurry will result in greater soil NH4<sup>+</sup> concentration in the upper layers, with reduced transformation to NO3<sup>-</sup>.

Throughout the experiment acidified slurry was found to have increased concentrations of NH4<sup>+</sup> which decreased at a slower rate than conventional slurry and ammonium nitrate. This reflects the findings of many other studies including D'annibale et al. (2019) who reported that NH<sub>4</sub>-N was greatest immediately following application and decreased over time. The greatest changes to soil NH4<sup>+</sup> concentrations were confined to the top 35mm throughout the experiment whereas NO3-N levels increased through the entire core (75mm) from day 7 onwards. Various authors have reported the impact of NH<sub>4</sub><sup>+</sup> sorption to organic matter and clay particles, with Fernando et al. (2005) also stating that NH4<sup>+</sup> sorption was greater with increased TOC. Such a finding was supported with the results outlined in Figures 5.4 and 5.5 where TOC was greatest for acidified slurry in the top 25 mm, matching that of increased NH<sub>4</sub><sup>+</sup> concentrations. The diffusion of nitrate from slurry through the soil core aligned with the theoretical rate of 2 mm a day (Molénat and Gascuel-Odoux, 2002) when assessing both slurry applications, whereas increased nitrate levels were found within the top 15mm from day 1. The latter was likely a response to the immediate availability of NO<sub>3</sub><sup>-</sup> from the application of ammonium nitrate, whereas nitrification has to occur before NO<sub>3</sub><sup>-</sup> will be present in cores receiving slurry treatments. Unlike the sorption of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> was found throughout the entire soil core for all treatments by the end of the experiment.

A clear delay of nitrification was found to persist until day 7 for acidified slurry, compared to day 3 for conventional slurry. This reflects the findings of Fangueiro et al. (2016) and Cameira et al. (2019) who found that the inhibitory impact of nitrification was found to last between 3 and 15 days following application, but was soil-type dependent. Such a delay in nitrification was also clear when assessing NH<sub>4</sub>-N concentrations, especially at the conclusion of the experiment. Fangueiro et al. (2015b, 2013, 2010) and Owusu-Twum (2017) reported similar findings to those presented in Figure 5.3 where soil receiving acidified slurry retained greater levels of NH<sub>4</sub>-N than the conventional equivalent. Throughout the experiment, the availability of NO<sub>3</sub>-N in cores receiving acidified slurry was found to be lower than conventional slurry at all depths. This corroborates with the results of D'annibale(2019), Fangueiro et al. (2013) and Sigurnjak et al. (2017) who all reported greater levels of NO<sub>3</sub>-N consistently found following conventional slurry application.

# c) Microbiological respiration will be initially impacted by the application of acidified slurry, over a 24 - 48 hour period, before recovering to the respiration rates found in conventional slurry.

Previous work carried out (Chapter 3) found a reduced rate of microbial respiration during the initial 48-hour period after application of acidified slurry before returning and exceeding microbial respiration from an unfertilised control on field plots. Such an inhibitory impact was also found during this experiment at day one, further supporting earlier work and provides an insight into the delay in nitrification provided in Figure 5.4. However, the rapid increase in CO<sub>2</sub> respiration at day 3 suggests that any impact was short in extent while microbes respond to altered conditions. Similar links between microbial processing and the inhibition on nitrification and nutrient cycling has been reported by others (Eriksen et al., 2008; Fangueiro et al., 2016, 2013; Malique et al., 2021; Semitela et al., 2013). However, the impact reported here was to a lesser degree in duration with this study supporting the work of Edesi et al. (2020) who found there were no long term impact on soil microbes.

#### 5.7 Conclusions

The experiment clearly demonstrates that the area directly receiving a treatment, be it slurry or ammonium nitrate sees the greatest change immediately after application. This was found to be the case for soil EC, pH, NH<sub>4</sub>-N, and TOC. These characteristics all began to return to control levels by the end of the experiment, mirroring the findings of others. However, an increase in soil pH following the application of acidified slurry has not previously been reported before and will require further investigation as to the causation, likely a result of rapid slurry buffering as found in Chapter 4. Comparison of the results from this microtome experiment with the literature was limited because of the coarser resolution of soil depth sampled and analysed in the majority of published studies compared to those sampled in this experiment but total top-soil analysis from others has been included in the discussion.

A clear inhibition of nitrification occurred during the first 7 days leading to a delayed peak of NO<sub>3</sub>-N N for acidified slurry, with a quicker rate of nitrification found for conventional slurry (with NO<sub>3</sub>-N appearing by day 3), while high levels of NO<sub>3</sub>-N were found immediately after application of ammonium nitrate (ammonium nitrate). Regardless of the treatment, NO<sub>3</sub>-N was still found to be greatest at the surface layer. Diffusion of soil chemical changes down the soil profile varied with characteristic analysed, for example NH<sub>4</sub>-N was largely constrained to the top 35 mm whereas NO<sub>3</sub>-N was found throughout the profile over the 42-day experiment, reflecting the differences in the charges of these two ions. The reduced microbial respiration of the <sup>14</sup>C-glucose following the addition

acidified slurry aligned with the simultaneous reduction in nitrification in the same treatment (compared to the conventional slurry), suggesting that slurry acidification affected this key microbial process in the short-term. Indeed, the evidence provided in this experiment shows there was no medium- to long-term negative impacts of applying acidified slurry to this soil. The delay in nitrification observed here following the application of acidified slurry has the potential to positively influence crop yields given the extended period slurry NH<sub>4</sub>-N was available in the soil, but would require further experimentation to include yield as a measurement.

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## <u>Chapter 6: Slurry acidification requires the addition of acidifying agents at an</u> <u>individual scale to maintain the balance between soil and slurry buffering potential:</u> <u>a lab experiment</u>

#### Abstract

Slurry pH is widely acknowledged as having a complex buffering system, which alters when concentrated acid, commonly H<sub>2</sub>SO<sub>4</sub>, is added. The accurate reduction of slurry pH is key to utilising the potential 90% reduction in NH<sub>3</sub> emissions when slurry is acidified to pH 5.5. A policy shift in Denmark to introduce a pre-determined quantity of acid for acidification of all slurries will be assessed during this experiment in relation to the impact this would have if the UK government were to follow similar advice. One study included in this Chapter assessed the quantity of acid required to meet a target pH for 20 UK cattle slurries and 1 food-waste based digestate, with a further experiment to determine the impact of various ratios of soil and acidified slurry in combination to understand tipping points in soil buffering potential. The overall findings of the research highlighted how the use of a pre-determined quantity of acid to acidify slurry, 2.2 kg H<sub>2</sub>SO<sub>4</sub> per tonne of slurry, would limit the emission abatement potential of the technique. The average reduction in pH associated with the equivalent use of Danish recommendation was found to reduce slurry pH by pH 0.7, with only two slurries found to be below pH 6, while none of the sampled slurries reached the commercial target of pH 5.5 for in-house acidification. Soil buffering of slurry pH became dominant when slurry acidified to pH 5.5 made up over 40% of the soil:slurry combination, and highlights the requirement of accurate application to limit pooling of slurry, and maximise the contact between slurry and soil.

#### 6.1 Introduction

The benefits of amending slurry with acids to minimize N loss, thus increasing the N fertilizer value of the product, has been recognised for nearly a century (Husted et al., 1991; Salter and Schollenberger, 1938). The addition of acid to slurry is now a commercial option for farming operations across Europe, particularly Denmark, with sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) widely used as the acidifying agent. Many authors have researched the mechanisms controlling slurry pH (Regueiro et al., 2016a; Sommer et al., 2017, 1991; Sørensen and Eriksen, 2009; Stevens et al., 1989; Vandré and Clemens, 1996). Common throughout these past studies is the understanding that slurry has a complex buffering system, able to resist pH change, consisting of various compounds including ammoniacal N (TAN), carbonates, phosphates, volatile fatty acids (VFA) and the importance of pH on NH<sub>3</sub> volatilisation (Husted et al., 1991; Paul and Beauchamp, 1989; Sommer and Husted, 1995a; Vandré and Clemens, 1996; Wang et al., 2015). Paul and Beauchamp (1989) found that when present in high concentrations, VFA's and TAN are dominant controlling factors of slurry pH, whereby VFA's decrease slurry pH, and increased TAN increases slurry pH. In addition to the chemical processes impacting the amount of acid required, Sigurnjak et al. (2017) reports that manure type, animal source and duration of storage all influence the slurry's buffering capacity. When compared to pig slurry, cattle slurry has been found to require greater quantities of acid to reach a target pH, likely a result of typically greater dry matter content. This suggests the buffering potential is greater in cattle slurry (Regueiro et al., 2016a) although this has been disputed by others (Joubin, 2018) indicating the variation in individual slurries.

Stevens et al. (1989) state that pH 5.5 is the optimum to reduce NH<sub>3</sub> losses. This is due to the shift of the equilibrium of NH<sub>4</sub><sup>+</sup>: NH<sub>3</sub> towards greater quantities of NH<sub>4</sub><sup>+</sup> within the liquid fraction of slurry, with NH<sub>3</sub> volatilisation being greater in pH neutral or alkaline conditions (Stevens et al., 1989; Vandré and Clemens, 1996). Therefore, loss of NH<sub>3</sub> from slurry will correlate with the loss of alkalinity once acidified, and has been found to reach an 88% reduction in NH<sub>3</sub> emissions from pig slurry and 95% reduction in NH<sub>3</sub> emissions from and cattle slurry (Husted et al., 1991; Stevens et al., 1989). The dynamics of slurry's buffering capacity remains after initial acidification, with increases to pH observed after the addition of acidifying agents (Petersen et al., 2012; Regueiro et al., 2016a; Vandré and Clemens, 1996). Joubin (2018) found that slurry buffering was initiated the day after acidification occurred (to a target slurry pH of 6.0) and pH still increased between 10 consecutive acid additions. Regueiro et al. (2016) reported similar findings, where slurry pH was found to buffer rapidly after the addition of strong acid and had returned to a similar pH to the initial slurry after 20 days. Likewise,

Pedersen et al. (2017) found that further acidification was required after storage when using 18 M  $H_2SO_4$  to acidify cattle slurry to pH 5.5 and 3.8.

Various factors have been proposed for the mechanism of pH buffering following acidification. Hjorth et al. (2015) suggest that microbial activity was responsible for a rise in pH. Similarly, Petersen et al. (2012) indicate that catabolic activity induces increased pH, the accumulation and release of CO<sub>2</sub>, mineralisation of N or dissolution of carbonates. The underlying process resulting in the increase of slurry pH is the consumption of H<sup>+</sup>, at a near neutral pH this was found to be a result of VFA production (Paul and Beauchamp, 1989; Vandré and Clemens, 1996).

The soil and fertilizer interface also controls pH buffering, with slurry pH found to increase once applied, especially if contact between soil and slurry was limited (Vandré and Clemens, 1996). Paul and Beauchamp (1989) indicated that the oxidation of VFA's when exposed to air, such as when surface spreading slurry, increases slurry pH, CO<sub>2</sub> and NH<sub>3</sub> volatilization (Vandré and Clemens, 1996).

Previous studies have found various components of the slurry that have a direct correlation with slurry pH, Stevens et al. (1989) reported that the quantity of NH<sub>4</sub>–N within a slurry influenced the amount of H<sub>2</sub>SO<sub>4</sub> required to acidify. Likewise, a more recent study indicated that total N content of slurry samples had a greater impact when acidifying beyond pH 6 (Joubin, 2018). However, slurry properties have been found to differ at a local level highlighted by Hjorth et al. (2015) who found an 11% difference in H<sub>2</sub>SO<sub>4</sub> requirements between two pig housing units.

An accurate measure of acid required will reduce health and safety risks associated with excess foaming and the extra head space required in slurry tanks to compensate for this, as well as limit  $H_2S$ emissions (Regueiro et al., 2016a). The work carried out in this Chapter assessed the impact of pH using a pre-determined quantity of acid, similar to the Danish governments policy to reduce NH<sub>3</sub> by 25%, in line with the national target (Nyord et al., 2021). Furthermore, little work has been carried out researching the impact acidified slurry has upon the potential for soil to buffer pH. This is important in a policy context to assess if there is a tipping point at which soil would not buffer additional acidity and consequently require more frequent external management to re-adjust soil pH.

#### 6.2 <u>Aims</u>

The main aims of the research were to assess if the 'constant' recommendation put forward by Denmark for  $H_2SO_4$  quantity required to meet targets would be suitable for the UK to adopt. To complement this policy-focussed aim, a further aspect of the research aimed to establish if there was a tipping point following the application of acidified dairy slurry, and the impact of different slurry

pH, has on soil pH. In order to address these aims, two experiments were carried out, one to assess the acid requirements for a range of slurry and digestate samples to reach a pre-determined pH, and one to determine soil-buffering potential.

#### 6.3 Hypothesis

The experiments were deigned to test the following hypotheses:

- a. The Danish recommendation of 2.2 kg H<sub>2</sub>SO<sub>4</sub> per tonne of (any) slurry will be sufficient to reach a pH of 5.5 for a range of typical UK slurries and a digestate.
- b. The reduction of dairy slurry pH will not be linear with the quantity of acid added, and will vary between slurry types.
- c. A point exists at which soil will not be able to buffer dairy slurry pH.

#### 6.4 Methods

Two experiments have been established to address the aims and hypotheses.

#### 6.4.1 Experiment 1 - Slurry buffering

#### 6.4.1.1 Slurry sampling

Samples of dairy slurry and digestate were provided by North Wyke (Rothamsted Research, UK), NRM (Cawood Scientific Ltd., Bracknell, UK), ADAS (Boxworth, UK) and Bangor University. Detailed chemical composition of the slurries and digestate were analysed by NRM (Cawood Scientific Ltd., Bracknell, UK) (Appendix 3.1) prior to acidification and samples were kept in cold storage, 4°C, until analysis could be carried out.

#### 6.4.1.2 Acidification

To replicate commercial acidification in Denmark, sulphuric acid ( $H_2SO_4$ ) was used as the acidifying agent. For all slurries aliquots of 500 µl of 1 M  $H_2SO_4$  were added in succession to 100 ml of slurry, mixed thoroughly with its pH measured using a Hanna instruments Model 210 pH meter (Hanna Instruments Ltd., Leighton Buzzard, UK). The addition of  $H_2SO_4$  continued at 500 µl until pH 3.5 was reached, with a titration curve created. Quantities of acid added was converted into milliequivalents (mEq) required for a litre of slurry for comparison with previous studies carried out.

#### 6.4.2 Experiment 2 - Soil buffering

#### 6.4.2.1 Experimental design

Soil described as a free-draining Eutric Cambisol, with a sandy clay loam texture, was collected from three discrete areas at Henfaes Research Station (Abergwyngregyn, North Wales; 53°14′21 N, 4°0′50 W; 10 m above sea level) and sieved to 5 mm to remove large stones.

Analysis of each soil sample was carried out at Bangor University. Organic matter content was calculated using loss on ignition with a muffle furnace set at a temperature of 450°C for 16 hours. Soil pH was measured in 1:2.5 (w/v) (soil: DiH<sub>2</sub>O) using a using a Hanna instruments Model 210 pH meter (Hanna Instruments Ltd., Leighton Buzzard, UK). Soil EC was measured with a Jenway conductivity probe in conjunction with a Jenway 4520 conductivity meter (Cole-Palmer Ltd., Stone, UK). Extractable NH<sub>4</sub>-N and NO<sub>3</sub>-N was measured using a 0.5 M K<sub>2</sub>SO<sub>4</sub> extraction (1:5 w/v).

NH<sub>4</sub>-N and NO<sub>3</sub>-N concentrations in the K<sub>2</sub>SO<sub>4</sub> extractions were analysed colorimetrically following the methods of Mulvaney (1996) and Miranda et al. (2001), respectively. The concentrations were determined using an Epoch® microplate spectrophotometer (Bio Tek Instruments Inc., Winooski, USA). A sample of soil was dried and analysed for total N and C using a TruSpec analyser (Leco Corp., St Joseph, MI).

Slurry used in the experiment was collected from an above-ground slurry store located on a dairy farm in Abergwyngregyn (North Wales,  $53^{\circ}23'52.0$  N,  $4^{\circ}02'18.5$  W). 15 litres of slurry was thoroughly mixed and divided into 3 separate 5 L containers, prior to acidification to the target pH's, 4.5, and 5.5, using 98% H<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich, UK). The final treatment was non-acidified slurry (pH 7.5). A subsample of each slurry treatment was retained and analysed using conventional accredited methods (NRM, Cawood Scientific Ltd., Bracknell, UK).

Slurry was applied to the soil at a range of proportions (by weight), from 100% slurry (0% soil) to 100% soil (0% slurry), in 10% increments. The soil and slurry were mixed thoroughly and incubated in covered trays for 128 days. The treatments are summarised in Table 6.1 below:

#### 6.4.2.2 Sampling

Following initial homogenisation of soil and slurry, pH was measured at regular points (day 3, 7, 14, 21, 28, 35, 42, 70, 77, 84, 128). Each tray was homogenised at point of sampling, after which 10 g of soil:slurry mix was added to 25 ml DiH<sub>2</sub>O (1:2.5 w:v) with pH measured using a Hanna Instruments Model 210 pH meter (Hanna Instruments Ltd., Leighton Buzzard, UK).

#### 6.4.3 <u>Statistical analysis</u>

Throughout the soil buffering experiment, statistical analyses was performed using R v. 4.1717 (R Core Team, 2019) where a significance level of p < 0.05 was accepted as significant. Where data were deemed normal, mixed linear models were used to assess soil pH against slurry treatment and slurry percentage content. These were then subjected to an ANOVA (stats package, R Core Team, 2019) and if significant differences were found "lsmeans" (emmeans, Lenth, 2021) was used to carry out Tukey post-hoc tests. Where data failed to meet normality assumption a non-parametric Kruskal-Wallis test (stats package, R Core Team, 2019) was performed. All results were graphical illustrated with "ggplot2" (Wickham, 2016).

Treatment ID	g soil per tray	g slurry per tray
0%	200	0
10%	180	20
20%	160	40
30%	140	60
40%	120	80
50%	100	100
60%	80	120
70%	60	140
80%	40	160
90%	20	180
100%	0	200

Table 6.1: The proportions of soil and slurry in the soil buffering experimental treatment	nents.
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#### 6.5 Results

#### 6.5.1 Experiment 1 - Slurry buffering

The results presented in Figure 6.1 highlight the difference between the recommendations for future Danish commercial acidification of 2.2 kg  $H_2SO_4$  for each tonne of slurry acidified and the amount of acid required to reduce 20 typical UK dairy cattle slurries and 1 digestate. The titration curves presented in this research highlight how the addition of acid at the rate of Danish recommendations would result in an average slurry pH reduction to approximately pH 6.8. This was greater than the commercial in-house target pH of 5.5, with only two slurries being below pH 6 at the Danish

recommendation. However Figure 6.2 indicates the role initial slurry pH has on the quantity of acid required to reach pH 5.5. Three clear groups are found in the 21 samples included in the slurry, with similarities found between slurries received with an initial pH greater than pH 7.5, those between 7.0-7.5, and those below pH 7.0. The slurries with an initial pH above pH 7.5 required approximately twice the quantity of acid as those below pH 7.0 to reach a target pH of pH 5.5, highlighting the importance of initial pH in determining acid requirement.



Figure 6.1: Titration curves of 20 different UK dairy slurries and 1 digestate.

The red dashed line indicates the current recommended acid requirement for Denmark; the blue dashed line represents the recommended target pH of 5.5. Data represents mean pH with  $\pm$  indicating standard error (n=21).



#### 6.5.2 Experiment 2 - Soil buffering

#### 6.5.2.1 Soil analysis

Table 6.2 outlines the soil chemistry from samples used in the experiment with little difference found between the sites, except site 2 NH<sub>4</sub>-N concentrations which were an order of magnitude greater than the other sites, but still represented a low NH<sub>4</sub>-N concentration.

#### Table 6.2: Pre-application soil properties.

Values shown represent means with  $\pm$  indicating standard error (*n*=3). All values are expressed on a dry matter basis with the exception of pH and EC.

	Site 1	Site 2	Site 3
Organic Matter (%)	5.3±0.1	5.8±0.03	5.6±0.14
pН	6.4±0.08	6.4±0.1	6.7±0.06
EC (μS cm <sup>-1</sup> )	41.3±12	32.1±7	29.7±10
Total N (mg N kg <sup>-1</sup> )	3.8±0.2	3.5±0.5	3.6±0.3
Total C (mg C kg <sup>-1</sup> )	32.2±6.5	28.9±4.2	30.6.±5.7
C:N ratio	8.5±0.4	8.3±0.3	8.5±0.5
Extractable NO3 <sup>-</sup> (mg N kg <sup>-1</sup> )	0.9±0.2	1.2±0.4	2.4±0.7
Extractable NH4 <sup>+</sup> (mg N kg <sup>-1</sup> )	2.4±0.6	12.0±2.1	3.5±1.1

#### 6.5.2.2 Slurry analysis

Slurry analysis (Table 6.3) showed little difference following acidification with the exception to total S content which increased as a result of the  $H_2SO_4$  addition.
Table 6.3: Slurry characteristics of each treatment applied to various quantities of soil.

All analyses were carried out at NRM with the exception of pH which was carried out at Bangor University to ensure pH presented here represented the pH at application. Data are expressed on a fresh weight basis.

	Unit	pH 4.5	рН 5.5	pH 7.5
<b>Oven Dry Solids</b>	%	10.3	9.25	8.92
Total Kjeldahl N	% w/w	0.40	0.37	0.41
NO3-N	mg kg <sup>-1</sup>	<10	<10	<10
NH4 <sup>+</sup> -N	mg kg <sup>-1</sup>	1616	1654	1626
Total Phosphorus (P)	mg kg <sup>-1</sup>	625	621	629
Total Potassium (K)	mg kg <sup>-1</sup>	2164	2185	2245
Total Magnesium (Mg)	mg kg <sup>-1</sup>	470	463	472
Total Copper (Cu)	mg kg <sup>-1</sup>	2.91	2.84	2.78
Total Zinc (Zn)	mg kg <sup>-1</sup>	15.6	13.6	16.1
Total Sulphur (S)	mg kg <sup>-1</sup>	3638	1343	453
Total Calcium (Ca)	mg kg <sup>-1</sup>	1173	1127	1204
Total Sodium (Na)	mg kg <sup>-1</sup>	599	600	610
рН		4.47	5.64	7.69

#### 6.5.2.3 Soil buffering

Statistical differences were found when analysing the soil:slurry combinations at all percentages and slurry pH (Figure 6.3), with the exception of 100 % soil where no differences were found, as expected. Significant difference were consistently found between pH 7.5 and all other slurry pH, while differences were non-significant at all soil:slurry combinations for pH 4.5 and 5.5 slurries. The inclusion of "days following application" in the mixed linear model resulted in non-normal data, consequently the time element was analysed separately. A Kruskal-Wallis test was carried out, showing differences between pH and time following application.



Figure 6.3: pH change over time for each slurry-soil treatment at different percentage increase of slurry.

Values shown represent means with error bars indicating  $\pm$  SEM (n=3)

#### 6.6 Discussion

The following discussion addresses each hypothesis in turn.

# a) The recommendation of 2.2 kg H<sub>2</sub>SO<sub>4</sub> per tonne of slurry will be sufficient to reach pH 5.5 on UK slurries.

As outlined in Fangueiro et al. (2015a), pH 5.5 is the commercially used target pH of in-house acidification systems in Denmark. Previous research has shown that when cattle slurry was acidified to pH 5.5 the reduction in NH<sub>3</sub> emissions can reach a maximum of 95 % (Frost et al., 1990; Pain et al., 1990; Stevens et al., 1989). Given the UK legislated target to reduce NH<sub>3</sub> emissions by 16 % in 2030 (HM Government, 2018a) it is essential that if the NH<sub>3</sub> target is to be reached agriculture, and manure management in particular, adopts practices that deliver greatest reductions were possible. The results shown in Figure 6.1 clearly indicate that the recommendations used in Denmark of adding 2.2 kg of 96% H<sub>2</sub>SO<sub>4</sub> would not be suitable for reducing UK slurry sufficiently to maximise the potential

for acidification. If the UK were to pursue a policy similar to Denmark and prescribe a set amount of acid per tonne of slurry, a more appropriate quantity would be closer to 8 kg 96% H<sub>2</sub>SO<sub>4</sub> per tonne slurry, or 174 mEq. However, given the range in titration curves presented, the use of a set quantity of acid, based on an average, would acidify some slurries beyond the pH 5.5 target, while others would not be acidified to the target pH 5.5. It is also important to consider the type of slurry used in this experiment, given Denmark is dominated by pig slurry, while cattle slurry was used in this experiment reflecting the typical slurry management in the western parts of the UK. The 20 slurries sampled in experiment 1 indicated that the greatest determinant of total acid requirement to reach pH 5.5 was the initial pH of the slurry. Slurries over pH 7.5 have been found to have a greater acid requirement to overcome buffering potential as outlined in Fangueiro et al. 2015, and Sommer and Husted 1995b. The results presented support this previous finding, however there was no other controlling mechanism found (Appendix 3) in the samples presented in this experiment. Regardless of the slurry used and based on these results, a recommendation for future UK policy would be to acidify each slurry individually to a target pH of 5.5 rather than applying a prescribed quantity of acid per tonne of slurry.

# b) The reduction of slurry pH will not be linear with the quantity of acid added, and will vary between slurry types.

The slurries included in Figure 6.1 show a non-linear relationship between the quantity of acid added and the pH of the slurry, most notable in slurries over pH 7.5. Slurries that start with a more alkaline pH have a greater acid requirement to achieve the pH 5.5 target used in commercial in-house acidification. This research was in line with the findings of others (Sommer et al., 1991; Sommer and Husted, 1995b; Stevens et al., 1989) who all report a greater acid requirement per pH unit reduction between pH 7 and pH 6, followed by a rapid reduction in slurry pH. However, the reduction of pH for the slurries starting at a more neutral pH have a reduced buffering capacity to acidification and a more linear relationship between pH and acid requirement, similar to the findings of Regueiro et al. (2016a) when using H<sub>2</sub>SO<sub>4</sub> as the acidifying agent.

This research was key to the practical understanding of slurry acidification, and the potential for inclusion in UK policy to reduce NH<sub>3</sub> emissions. It was clear that slurries and the single digestate from around the UK vary in how they respond to acidification, with Hjorth et al. (2015) reporting similar results for swine manure with an 11% difference between two local pig housing units. The addition of a pre-determined quantity of acid to slurry runs the risk of exceeding a buffering tipping point, resulting in a sudden reduction of pH and requiring further intervention to rectify the slurry

pH. Consequently, if slurry acidification was to be included in future government schemes there was a real need for acidification to be carried out at an individual basis rather than a recommended amount, unlike the future acidification policy in Denmark.

#### c) A point exists at which soil will not be able to buffer slurry pH.

Given the results presented in Figure 6.3, the addition of acidified slurry determines the overall pH of the soil:slurry combination regardless of the ratio. Significant differences found between treatments indicates that the addition of H<sub>2</sub>SO<sub>4</sub> reduces pH of both soil and slurry when combined. However, the acidification to pH 4.5 was found to not be significantly different from pH 5.5, likely a result of the complex buffering systems previously outlined (Paul and Beauchamp, 1989; Petersen et al., 2012; Regueiro et al., 2016a; Vandré and Clemens, 1996).

This research shows that beyond 40% slurry content, the pH of the soil:slurry combination resembles that of 100% slurry, which corroborates with Vandré et al. (1996) who recognised that when contact between soil and slurry was limited, pH change was driven by change in slurry pH. From a policy perspective this may alter the land management requirements given soil pH is a key indicator to soil health and crop growth (Goulding, 2016) and is likely to change depending on slurry application type. Research carried out by Pedersen et al. (2017), Fangueiro et al. (2018), and in other chapters of this thesis show that soil pH under acidified bands following band spreading changes to a greater extent than surface broadcast. This was once more indicative of a reduced interaction between soil and slurry where soil has become dominated by slurry pH change.

#### 6.7 Conclusions

The two experiments outlined show the complex nature of slurry and soil buffering of pH and the variation found between slurry types. Proposals set out in Denmark to introduce a pre-determined quantity for acidification would underutilise the potential slurry acidification has in reducing NH<sub>3</sub> emissions and therefore requires acidification to be performed at an individual basis. Furthermore, when the quantity of slurry in contact with soil increases, the buffering within the applied slurry, opposed to the soil, become dominant in controlling pH, highlighting the need to ensure accurate and even application of slurry. This would minimise the pooling of acidified slurry and subsequent intervention by land managers. However, given the experiment on soil buffering only includes one cattle slurry, broad conclusions cannot be widely applied before further research is carried out especially given the acknowledgement of variation in slurry composition.

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## Chapter 7: Discussion

The following discussion directly addresses the aims and hypotheses outlined in the introduction of the thesis, all under the overarching aim "to assess if there are any detrimental impacts of using acidified slurry on soil and crop quality in the UK". Table 7.1 summarises the thesis results, which is proceeded with an overview of how experimental slurries compare to typical UK values.

Table 7.1: Summary of thesis results. ~ Short term response \*Results from multiple applications

Soil and cro	p quality indicator	Conventional slurry	Acidified slurry (pH 5.5)	Ammonium nitrate fertiliser
	Microbial respiration~			
G . 11 k . 1	Microbial communities*			
Soli biology	Meso-fauna*			
	Earthworms*			
			-	
	pН			
	EC			
G - 11 - 1	$\mathrm{NH_{4}^{+}}$			
Soll chemistry	NO <sub>3</sub> -			
	PO <sub>4</sub>			
	TOC			
Soil physical	VESS			
Cogoong amiggiong	N <sub>2</sub> O			
Gaseous emissions	NH <sub>3</sub>			
	DM yield			
Сгор	NFRV			
	NUE			

#### Legend

Long term positive	Whole growing season
Medium term positive	Between 1 week - 1 month
Short term positive	<1 week
No impact	
Short term negative	<1 week
Medium term negative	Between 1 week - 1 month
Long term negative	Whole growing season
Not determined	

The work presented throughout this thesis is part of a wider Defra funded project with sites undertaking similar experimentation across different soil types and climatic zones in the UK, with crop and manure or digestate application reflecting the typical agricultural norm in the locality. Across the project results broadly show similarity to those presented in Chapter 3, where no negative changes to soil quality where found at the harvest immediately following application, while increases in NUE and NFRV where found following the application of acidified slurry or digestate. At the conclusion of the Defra funded project a report will be submitted, which will collate site data from all UK sites and will include the results presented in this thesis.

#### **Overview of slurry properties**

Throughout the experiment, slurry was used from various dairy farms across the North Wales region and consequently represent different herd management. Dry matter is a key indicator for nutrient content of slurries and is used within the guide for farmers to estimate nutrient contents (AHDB, 2017). The slurry used in the experiments have been compared to the typical values expected based on the linear regressions included in the "RB209" database (Williams et al., 2016) and were found to show a level of similarity to the expected nutrient values (Appendix 4.1). Exceptions to the typical values for UK slurry was the nutrient content of slurry used in Chapter 4 (experiment 2), which had a lower than expect N content, and Chapter 5, where the DM content was greater. However, given these were samples provided from commercial farms it was deemed suitable to include all samples in studies as they represent "real" slurry that could be subjected to commercial acidification in the future.

#### The use of acidification will have no long-term detrimental impacts on soil and crop health.

The overall purpose of the study was to provide information to inform UK government as to the impact of slurry acidification on soil and crop quality at one of 5 experimental sites as part of the Defra project "Investigating the feasibility of slurry acidification in the United Kingdom through field trials" (SCF0215). The outcome will underpin the potential for slurry acidification to be recommended to farmers as a means of reducing total UK NH<sub>3</sub> emissions by 16% for the 2030 target (HM Government, 2018). The findings presented in the study show over a two-year period that there are no long-term negative impacts on soil and crop health.

Given the specific aims of the study, the direct measurement of soil health was measured in various forms in each of the experimental chapters (3-6), while the impact on crop health was solely included in Chapter 3, summarised in Table 7.1. Figure 3.1 provides evidence of changes to soil pH, which

has been highlighted as a concern to farmers at various industry and policy events attended throughout the study. The results show that a reduced pH was found immediately following the application of acidified slurry, and reached a maximum difference from the control between 14 and 21 days from application across the 4 growing seasons (experiments). A similar experiment on the same soil type, this time using acidified (pH 5.4) digestate, found that the impact on soil pH continued to decrease until 90 days following application (Sánchez-Rodríguez et al., 2018). The addition of ammonium nitrate fertiliser (100 kg N ha<sup>-1</sup>) in 2020, as part of the fertiliser response plots, also resulted in reduced soil pH, and there was no significant difference between soil pH between the acidified slurry and ammonium nitrate treatments. This supports the findings of Semitela et al. (2013) and Edesi et al. (2020) who both found that at the conclusion of the experiment there was no difference in soil pH and consequently no need to increase liming frequency to maintain soil pH. Such a finding was significant to the overall sustainability of acidification within the agricultural landscape as the addition of liming materials would risk increased stimulation of nitrification and denitrification (VanderZaag et al., 2011), as well as adding economic burden to the farming enterprise (Goulding, 2016).

Chapter 6, experiment 2 assessed the impact of slurry and soil pH buffering capacity, whereby the buffering capacity of the soil to acidified slurry was overcome once the percentage of slurry exceed 40% (w:w) in combination with soil. The importance of this finding will be realised when considering the potential changes to soil pH after acidified slurry was spread via band spreading, as found in this study, limiting the contact between soil and slurry for pH buffering to occur (Fangueiro et al., 2018; Pedersen et al., 2017; Vandré and Clemens, 1996). The inclusion of repeated slurry application plots in this study highlighted that there were no long-term residual effects of repeated applications of acidified slurry on pH of the particular soil type used throughout the experiment.

Increased concentrations of NH<sub>4</sub><sup>+</sup> were found following the application of acidified slurry (compared with non-acidified slurry) at both large (field), mesocosm and at a micro scale, as described in Chapters 3, 4 and 5. A result of process driven changes to the chemical characteristics of slurry where the NH<sub>3</sub>:NH<sub>4</sub><sup>+</sup> ratio is represented by up to 98% NH<sub>4</sub><sup>+</sup> following acidification (Cocolo et al., 2016; Petersen and Sommer, 2011) and the potential delays to microbial process of nitrification (Fangueiro et al., 2016). Such an increase in soil NH<sub>4</sub><sup>+</sup> concentrations were found to be numerically greater in acidified slurry treatments than conventional slurry treatments in these experiments, supporting the results of others (D'Annibale et al., 2019; Fangueiro et al., 2016, 2010; Sánchez-Rodríguez et al., 2018). Figure 3.5 indicated that soil NH<sub>4</sub><sup>+</sup> concentrations were consistently greater for surface

broadcast plots receiving acidified slurry in comparison to conventional slurry. This was further corroborated by the research carried out in Chapter 5 where concentrations of soil NH4<sup>+</sup> were found to be significantly greater in the top 35 mm of the soil profile due to sorption (Fernando et al., 2005). Soil biology is a key indicator of soil health but was found to be largely absent from previous studies involving slurry acidification application. Those studies that have included soil biology found that soil microbial communities were not different following 1 annual application of acidified pig slurry (pH 6.0) over 2 years (Edesi et al., 2020), and that mesofauna (collembola) was not negatively impacted by acidified slurry application rates of 30 and 90 m<sup>3</sup> ha<sup>-1</sup>. The study presented here assessed micro-, meso-, and macro-fauna from plots receiving 4 repeated applications of acidified slurry over 2 years, and showed no long-term significant differences found compared with conventional slurry, similar to the previous studies. However, the use of 16S sequencing found that the relative abundance of Nitrosomonadaceae was reduced for an entire growing season. This provides insight into the fact some soil microorganisms will be impacted to a greater extent than others, and supports the findings of reduced N cycling following the application acidified slurry (Fangueiro et al., 2010; Park et al., 2017; Sánchez-Rodríguez et al., 2018). Short-term impacts of applying acidified slurry on soil microbial activity were explored throughout the study via the measurement of soil respiration (Figure 3.7) and the use of <sup>14</sup>C labelled glucose (Figure 5.6) to measure microbial activity. Both of these types of measurement indicate that activity was reduced immediately following application, but returns to and exceeds control levels of activity by day 3, supporting the understanding of limited long-term impact of acidified slurry on soil biology. No significant differences were found between treatments on meso- and macro-fauna.

In summary, results indicate there was no long-term impact of slurry acidification found on soil chemical and biological indicators of soil quality. Increased soil  $NH_4^+$  concentrations (the result of reduce  $NH_3$  volatilisation) were linked to improved crop performance compared to conventional slurry (Fangueiro et al., 2018, 2017, 2015b; Pedersen et al., 2017; Sánchez-Rodríguez et al., 2018; Seidel et al., 2017). The results presented in Chapter 5.5 indicated similar findings where acidification numerically increased  $NH_4^+$  which is likely to increase NUE, NFRV and dry matter yields, however theincrease in  $NH_4^+$  were not significantly different. Given the current increase in prices of mineral N fertiliser, reaching up to £1000 t for ammonium nitrate in spring 2022 (Horne, 2022), the increased utilisation of crop available N following slurry acidification will bring additional benefits in reducing the reliance on manufactured fertiliser.

The use of acidification will not result in increased N losses as a result of N pollution swapping. Retaining greater quantities of available N in acidified slurry in the form of  $NH_4^+$  increases the potential risk of N pollution swapping whereby the microbial processes of nitrification and denitrification can convert excess  $NH_4^+$  to  $NO_3^-$  and  $N_2O$  (Chadwick et al., 2011: Thorman et al, 2020), amongst other forms of N. These are of particular concern due to the risk of  $NO_3^-$  leaching given the recently published "Reduction and Prevention of Agricultural Diffuse Pollution (England) Regulations" (Defra, 2018a), and the global warming impact of  $N_2O$  (Fangueiro et al., 2017; VanderZaag et al., 2011).

Field experimentation, presented in Chapter 3 highlighted that although the acidification process increased soil  $NH_4^+$  concentrations following acidified surface broadcast applications, there was no significant increase in soil  $NO_3^-$  concentrations. This corroborates the findings of others including Fangueiro et al. (2015a), who indicated that the delay to nitrification can be last between 20 - 60 days. This study found a much shorter delay than that reported elsewhere, sometimes with no delay, but consistently with lower peak  $NO_3^-$  concentrations (Figure 3.5). A reduction in nitrification was supported by the reduction in relative abundance of the nitrogen cycling bacteria, *Nitrosomonadaceae*, found after 4 repeated applications of acidified slurry (Figure 3.11). Figure 5.4 indicates that there are no hot spots of increased  $NO_3^-$  concentrations for acidified slurry are consistently lower than conventional slurry at all depths.

The evidence for reduced denitrification and the consequential release of  $N_2O$ , was less clear. Table 3.3 outlines the cumulative  $N_2O$  emissions from field-scale plots, highlighting acidified band spread slurry had numerically lower  $N_2O$  emissions than conventional band spread slurry, but  $N_2O$  emissions from the acidified surface broadcast slurry treatment was numerically greater than the conventional equivalent. This application season was particularly dry, which was likely to have hindered denitrifier microbial activity, but may also represent future climatic conditions. In this instance, application method had a greater impact on emissions than slurry pH, contrasting with the interpretation of Sánchez-Rodríguez et al. (2018) who attributed the reduction in  $N_2O$  was a result of soil pH change. In experiment 2 of Chapter 4, acidified broadcast slurry numerically increased short-term cumulative  $N_2O$  emissions compared to all other treatments, similar to the results presented in Malique et al. (2021).

Consequently, the evidence provided in this study supports the idea that the use of acidified slurry will not increase soil  $NO_3^-$ . However, the evidence regarding the potential of acidification to limit N<sub>2</sub>O emissions was less clear. Although no significant differences were found, acidified treatments were found to numerically increase N<sub>2</sub>O loss. Such findings reiterate the importance of applying manures at appropriate times of active plant growth, which will limit longer term losses if plants are not able to utilise additional  $NH_4^+$  concentrations (Cameira et al., 2019; Malique et al., 2021).

# Slurry application technique used will not detrimentally impact the suitability of acidification as an NH<sub>3</sub> abatement technique.

The study included a number of different application techniques at various scales, from replicating band spreading at field plot size, to simulated slurry injection in a mesocosm, both of which were compared to the current standard UK application technique, surface broadcasting. The comparison of band spread and surface broadcast slurry application, in Chapter 3, highlighted that a greater reduction in soil pH (Figure 3.1) and EC (Figure 3.2) was found under slurry bands, similar to that reported by Fangueiro et al. (2018) and Pedersen et al. (2017). However, in both of these instances pH and EC values had returned to those of the control by the end of each growing period, as found previously (Fangueiro et al., 2015b). Little evidence was found to indicate the benefit of using acidified band spread application to increase soil NH<sub>4</sub><sup>+</sup> concentrations when compared to conventional band spread application, as a direct consequence of limiting NH<sub>3</sub> emissions. This was found in three of the four applications. However, in contrast to Cameira et al. (2019), soil NO<sub>3</sub><sup>-</sup> concentrations in acidified plots did not exceed concentrations found in conventional slurry plots, and the delay to nitrification found in acidified plots resulted in greater concentrations of NH4<sup>+</sup> remaining for plant uptake. This extended the period of time for plant growth to benefit from the greater NH<sub>4</sub><sup>+</sup> availability, improving crop responses and underlines the importance of applying fertiliser products at times of maximum plant uptake.

Experiment 2 in Chapter 4 directly compared the impact of the Best Available Techniques (BAT) recommended, i.e. slurry injection, with surface broadcasting, slurry acidification and conventional slurry. Clear evidence was provided, where cumulative NH<sub>3</sub> loss was found to be significantly lower for acidified surface broadcast than conventional slurry injection, whilst not resulting in significantly greater N<sub>2</sub>O losses. The lack of significantly increased N<sub>2</sub>O emissions supports the findings of Malique et al. (2021) who also found numerically, but not significantly, greater N<sub>2</sub>O emissions following application of acidified slurry.

This research, if proved to be consistent on different soils and at more credible scale, has potential major consequences in terms of the agricultural sector leading the reduction of national NH<sub>3</sub> emissions. Currently the 'Clean Air Strategy' indicates that all manure spreading will need to be carried out via low emission methods (Defra, 2018b), with associated costs to farmers (and Government via grant aid). However, the potential of acidification applied via surface broadcast was as effective as slurry injection in terms of NH<sub>3</sub> abatement. This, therefore raises the potential for slurry acidification to be used instead of low emissions techniques without the need to immediately replace farm equipment if using systems similar to Syre-N in Denmark (Toft and Madsen, 2019). The acidification of slurry at application has been previously comparable in costs to injection of raw slurry (Jacobsen, 2017), and provides an alternative option to reduce NH<sub>3</sub> emissions especially in areas not suitable for injection. The suitability of slurry acidification to be included as an option for the agricultural sector to reduce NH<sub>3</sub> emissions was apparent given the results presented throughout this study. Therefore the use of the technology is suitable for promotion alongside covering slurry stores through the delivery of grant-aid for farmers. In addition, some farmers opt for contractor delivered low emission slurry application, therefore the potential for farmers to use a contractor delivered acidification, similar to Syre-N would ease the introduction of the technology into the UK agricultural landscape.

#### A target pH of 5.5 is key to fully utilise the NH<sub>3</sub> abatement potential of slurry acidification.

The pH reduction target for in-house slurry acidification for commercial use in Denmark was set at pH 5.5 to account for any buffering of slurry between acidification and application (Pedersen et al., 2022). The shorter-term acidification targets for Danish acidification where long-term buffering is less of a concern have been set at pH 6 for storage and pH 6.4 at application (Edesi et al., 2020). Throughout this study, the aim has been to assess the impact of slurry acidification at pH 5.5 on soil and crop quality based on the Danish in-house acidification guidance for pH reductions, and represents the lowest likely (most extreme) value for applied slurry following commercial acidification. Experiences from the field experiments (Chapter 3) indicated that the buffering of slurry pH was almost immediate, with acid being added to the slurry twice before application in a short time period (1-3 days) following the initial acidification (Appendix 1.2). pH buffering by slurry has been reported previously but over a longer period of time, e.g. Misselbrook et al. (2016) and Regueiro et al. (2016). Such a buffering potential for the slurries used in Chapter 3 vary, and indicate the importance of individual acid requirements for each slurry type, with 50% of slurries used requiring a single addition of acid when acidified up to 5 days prior to application. Considering this in the context of current Danish recommendations, albeit for a pig dominated agriculture sector, the use of

a target pH of 6 during acidification in storage seems to potentially reduce the effectiveness of  $NH_3$  abatement from acidification due to the immediate buffering outlined in the field experiments. The largely positive impact on soil and crop quality outlined in Chapter 3 with no long-term reduction to soil pH (Figure 3.1), increased soil concentrations of  $NH_4^+$  without increasing  $NO_3^-$  (Figure 3.5), and numerical increases of NUE (Table 3.8), suggest that acidification is sustainable when applied at pH 5.5.

Further to the findings presented in Chapter 3 outlining the benefits to soil and crop quality, the inclusion of experiment 1 in Chapter 4 clearly shows the benefit of acidifying to pH 5.5 on NH<sub>3</sub> abatement. Significant differences were presented in Table 4.8 when comparing NH<sub>3</sub> loss as a percentage of total NH<sub>4</sub> applied in slurry at pH 6.5 and conventional (pH 7.38), corroborating results presented by Seidel et al. (2017) and Stevens et al. (1989). Based on the results outlined in this paper (Stevens et al., 1989), the use of acidifying slurry to pH 5.5 would reduce NH<sub>3</sub> emissions by an approximately 50% when compared to pH 6.5, and 57% compared to conventional slurry as a percentage of total NH<sub>4</sub>-N applied. Although slurry acidified to pH 4.5 was included in this experiment as an example of the potential reduction to NH<sub>3</sub> emissions if more extreme slurry acidification was implemented (or accidentally achieved due to overcoming the slurry buffering capacity (Sánchez-Rodríguez et al., 2018)), previous studies suggest that a target pH of 5.5 – 6 should be used. This has been highlighted as a compromise between cost of acidification and emissions reduction, as well as avoiding additional logistical and health and safety considerations of using a lower target pH, as well as the potential of corrosion to machinery (Dai and Blanes-Vidal, 2013; Fangueiro et al., 2015a; Misselbrook et al., 2016). By opting for a compromising pH and reducting the quantity of acid added, the potential risk to increase H<sub>2</sub>S emissions is limited. Such a limit to potentially deadly releases of H<sub>2</sub>S is essential to maintain safe conditions for livestock and agricultural workers (Eriksen et al., 2012; Fangueiro et al., 2015a). Therefore, the optimum pH for acidified slurry in terms of NH<sub>3</sub> abatement has been reaffirmed as pH 5.5 when considering UK slurry and soil types.

In terms of policy options available to the UK government in recommending suitable measures to achieve a target pH, Chapter 6, experiment 1 demonstrates through the use of titrations that the quantity of acid required to lower slurry pH varies between samples (Figure 6.2). The recent change in Danish policy to using a pre-determined quantity of acid to achieve a pH reduction to reduce NH<sub>3</sub> emissions by 25% (Pedersen et al., 2022), would not fully utilise the technology in relation to NH<sub>3</sub> abatement in the UK. Therefore to maximise the benefits of NH<sub>3</sub> abatement from slurry acidification

with the overall aim of achieving a 16% reduction of total  $NH_3$  emissions by 2030 (HM Government, 2018), the most effective and efficient pH should be used as a target, which this study has shown to be pH 5.5.

#### 7.1 Limitations of current work

This wider project that this PhD study was aligned to, was funded by Defra as part of a multi-site experiment replicating the same fieldwork at ADAS research farms and North Wyke (Rothamsted Research). However, the study presented here only represents the impact of slurry acidification one soil, crop and climatic type. The synthesis of data across all project sites will strengthen the evidence base surrounding the impact of slurry acidification in a wider UK context.

The scale of research was also a limitation within this study. For example NH<sub>3</sub>, emissions data was determined in a controlled bench-scale mesocosm study. This mesocosm study is useful in a theoretical level for comparing treatments, but is limited in scaling up to representative field conditions. Similarly, in the smaller laboratory-based experiments, the study was limited in the number of different slurry types used. However, the slurry composition used in most experiments resembled that of typical UK slurries based on RB209 values. This suggests that the slurries included would perform in a similar manner to other typical UK slurries. Regardless, the inclusion of greater numbers of slurry types, as well as anaerobic digestate, would provide greater insight into the effect of acidification.

The onset of the Covid-19 pandemic limited greenhouse gas (GHG) sampling at the field plot level, and the season when GHG emissions were measured was atypical, being unseasonably dry, limiting the applicability to scale the results up to a national level.

#### 7.2 Recommendations for future work

Future work that is still outstanding for slurry acidification from a UK perspective is the long-term impact. This study included 4 repeated applications to the same plots over a 2-year period, with the experimental plots receiving a further 2 applications after the completion of my PhD measurements. However, it would be beneficial to assess longer-term impacts of applying acidified slurry to soil, and determine the impacts on microbial and chemical indicators of soil quality. Therefore, I would recommend the establishment of long-term experimental plots to assess an extended period of repeated applications. Similarly, the number of annual applications could be increased to represent a more intensive farming system. Importantly, any long-term experiments should include several inorganic fertiliser application rate treatments, so direct comparisons can be made with the reference situation.

Other areas of future work that would be essential would be to clarify  $N_2O$  emissions. The literature and this study have shown inconsistent results of the impact of slurry acidification on denitrification. Given the large  $CO_2$  equivalence (global warming potential) of  $N_2O$ , it is essential that the controlling mechanisms is found. This would provide an insight to the N pollution swapping potential of slurry acidification to be established, and would require multiple sites from numerous climatic, soil, slurry types. Timing of application is an important consideration that has not been fully explored during this study, especially autumn applications which potentially could result in greater leaching. This would be a timely consideration given the recent publication of the "Reduction and Prevention of Agricultural Diffuse Pollution (England) Regulations" (Defra, 2018a). Given the increased  $NH_4^+$ concentrations following application of acidified slurry it is reasonable to hypothesis that increased nitrate leaching would occur during periods of limited plant uptake.

The management of slurry identified by the Health and Safety Executive as a source of potentially toxic gases, with the addition of  $H_2SO_4$  recognised by several authors to increased the potential of  $H_2S$  emissions (Eriksen et al., 2012; Fangueiro et al., 2015a). Therefore to minimise exposure of farm workers and livestock to harmful gaseous emissions further work is required to ensure the addition of  $H_2SO_4$  does not increase the release of  $H_2S$  to harmful levels.

Evidence has been provided through this study that acidification is effective at reducing NH<sub>3</sub> emissions. The next steps would be to conduct similar experiments comparing method of application and slurry acidification on NH<sub>3</sub> emissions at a greater spatial scale, and then engage farming groups and livestock industry sectors to establish the feasibility to use slurry acidification at a farm level, as well as any common concerns held in farming networks that could limit the uptake of the technology, and limit the reduction of NH<sub>3</sub> emissions.

From a technical perspective future work should include the increased replication of the DAVoS to strengthen results, as well as improving the potential to maintain healthy plant growth. This experiment was the first carried out using the system, and provided quality results on soil and gaseous emissions. However, the limited plant growth meant that an overall N balance was not possible as plant N offtake could not be calculated.

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#### Chapter 8: Conclusions

Clear and apparent conclusions can be ascertained following the completion of the study, where slurry acidification has been found to impact soil health in the short-term, identified by reductions in soil pH and soil CO<sub>2</sub> respiration. Yet by the end of each harvest period indicators of soil health had returned to control levels. The exception of this was the continued difference to relative abundance of individual soil microorganisms, which were impacted for an entire growing season after 4 repeated applications. Following the application of acidified cattle slurry, soil NH<sub>4</sub><sup>+</sup> concentration was found to be greater than for the non-acidified slurry treatment, leading to increases in crop yields, NUE and NFRV. Although the potential for acidification to increase N<sub>2</sub>O emissions was outlined, any increases were found to be non-significant, and consequently there is supporting evidence that slurry acidification does not lead to increased N pollution swapping.

The study also provided evidence of perhaps a more cost-effective way in which slurry acidification could be utilised to meet the UK's impending ammonia emission mitigation target of 16% by 2030 (based on 2005 levels). In terms of NH<sub>3</sub> abatement, the use of surface broadcast acidified slurry was found to be as effective as slurry injection, which would allow slurry acidification to be used in more circumstances, as injection is limited by soil type and topography of the farm. Results also demonstrate the importance of achieving a target slurry pH (of 5.5), accounting for the range of buffering capacities of different slurries (and digestates).

Overall, the data provided in this thesis highlights that slurry acidification could be implemented sustainably within the UK agricultural sector to reduce NH<sub>3</sub> emissions to help achieve the 16% reduction in total NH<sub>3</sub> emissions by 2030, although these data only represent the effects of acidification on one soil type in one geographical area. However, the results presented represent the expected impact on soil and crop health when applied at appropriate times and rates to growing crops. Therefore these conclusions are only valid where best farm practises are adhered to, and rely on farmers to ensure that manures are applied to meet crop demands.

## Chapter 9: Appendix

## Appendix 1 – Chapter 3

## Appendix 1.1 - Field experiment lay out

Control 0	Slurry BS	A Slurry BC		N 50 kg/ha	Control 0	A	Slurry BC
N 25 kg/ha	A slurry BS	Slurry BC		N 25 kg/ha	N 75 kg/ha	N	I 25 kg∕ha
Slurry BC	N 100kg/ha	N 25 kg/ha		A Slurry BC	N 50 kg/ha	S	lurry BS
Slurry BS	N 150 kg/ha	N 50 kg/ha		Slurry BC	Slurry BS	N	l 150 kg/ha
A slurry BS	N 75 kg/ha	Control 0		N 75 kg/ha	N 150 kg/ha	N	I 50 kg∕ha
N 150 kg/ha	Slurry BC	N 75 kg/ha		Control 0	N 100kg/ha	S	lurry BC
N 75 kg/ha	N 25 kg/ha	Slurry BS		Slurry BS	A slurry BS	N	l 100kg/ha
N 50 kg/ha	N 50 kg/ha	N 150 kg/ha		N 150 kg/ha	Slurry BC	C	Control 0
N 100kg/ha	A Slurry BC	N 100kg/ha		N 100kg/ha	A Slurry BC	A	slurry BS
A Slurry BC	Control 0	A slurry BS		A slurry BS	N 25 kg/ha	N	N 75 kg/ha
BC App 1+2	ABC App 1+2+3	BC App 1+2		N 100kg/ha	N 150 kg/ha	A	Slurry BC
BC App 1+2+3+4	BC App 1+2	BC App 1+2+3+4		N 50 kg/ha	Slurry BC	S	lurry BC
ABC App 1+2	ABC App 1+2+3+4	ABC App 1+2+3		Slurry BC	A Slurry BC	C	Control 0
ABC App 1+2+3	BC App 1+2+3	ABC App 1+2+3+4		A Slurry BC	Control 0	N	l 150 kg/ha
ABC App 1+2+3+4	BC App 1+2+3+4	BC App 1+2+3		Control 0	A slurry BS	N	V 25 kg/ha
BC App 1+2+3	ABC App 1+2	ABC App 1+2		N 150 kg/ha	N 100kg/ha	S	lurry BS
N 75 kg/ha	N 150 kg/ha	N 25 kg/ha		N 75 kg/ha	N 25 kg/ha	N	100kg/ha
N 150 kg/ha	N 100kg/ha	Slurry BS		A slurry BS	N 50 kg/ha	N	I 50 kg∕ha
A Slurry BC	A Slurry BC	Slurry BC		Slurry BS	Slurry BS	N	I 75 kg∕ha
Slurry BC	Slurry BC	A Slurry BC		N 25 kg/ha	N 75 kg/ha	A	slurry BS
Control 0	Control 0	Control 0		N 25 kg/ha	Slurry BS	N	I 50 kg/ha
N 50 kg/ha	N 50 kg/ha	A slurry BS		A slurry BS	N 75 kg/ha	N	l 150 kg/ha
Slurry BS	N 25 kg/ha	N 100kg/ha		N 100kg/ha	A slurry BS	N	1 75 kg/ha
BC, ABC, N100, BS	C0, ABC [] C0, N100	ABC, BC, ABS, BS		ABS,CO, BC, ABC	BS, N100 [] ABS, N100	B	C, ABC,CO, BS
	Application 1						
	Application 2		BC	Broadcast			
	Application 3		BS	Bandspread			
	Application 4		А	Acidified			
	Repeat Applications		CO	Control			
	Gas sampling App 3		N1	l 100 kg N ha-1			
	Gas sampling App 4						

## Appendix 1.2 – Acid requirements for slurry acidification

Acidification requirements for four different slurry types. Both applications in 2020 were acidified twice due to pH buffering between initial acidification and application.

Application	Initial pH	Acidification date	Acid required for tank (l)	Application date	Application pH
Spring 2019	6.7	12.4.19	2.4	15.4.19	5.4
Summer 2019	6.78	12.6.19	2.75	17.6.19	5.67
Spring 2020	6.7	13.3.20 & 16.3.20	2.7 (1.7 + 1)	16.3.20	5.2
Summer 2020	6.87	6.7.20&7.7.20	4.3 (3.5 + 0.8)	7.7.20	5.22

Appendix 1.3 – plot coverage of band spread plots

Band spread plot coverage (% Total plot). Percentage coverage was estimated from a quadrat placed of images take at application. Values represent means (n=3), ± indicates SEM.

	Band spread		Acidified band sp	oread
	Plot coverage (%)	±	Plot coverage (%)	±
Application 1	20	0.58	23	1.45
Application 2	37	1.67	33	2.50
Application 3	25	2.67	27	0.67
Application 4	23	1.00	22	1.67



## Appendix 1.4 – Soil EC – repeat application plots



Appendix 1.5 - Soil NH<sub>4</sub>-N and NO<sub>3</sub>-N - repeat application plots





Appendix 1.6 - Soil PO<sub>4</sub>-P – single application plots



## Appendix 1.7 - Soil PO<sub>4</sub>-P - repeat application plots



## Appendix 1.8 – DM yield - Repeat application plot

## Appendix 2 – Chapter 4



Appendix 2.1 – Photograph of Davos in operation

## Appendix 3 – Chapter 6

## Appendix 3.1 – Slurry metadata

Organisation	Type	Acid	Oven Dry Solids	Total Kjeldahl Nitrogen	Nitrate Nitrogen	Ammonium Nitrogen	Total Phosphorus (P)	Total Potassium (K)	Total Magnesium (Mg)	Total Copper (Cu)	Total Zinc (Zn)	Total Sulphur (S)	Total Calcium (Ca)
NRM	SLURRY	8.25	8.99	0.43	<10	2189	570	3289	588	Э	14	479	1022
NRM	SLURRY	6.14	7.42	0.3	<10	1018	432	2267	329	2	8	457	619
NRM	SLURRY	9	4.28	0.2	<10	964	315	2259	257	4	5	250	525
NRM	SLURRY	5.5	9.52	0.41	<10	1871	584	2823	479	4	13	398	920
NRM	SLURRY	5	9.19	0.36	<10	1002	847	2647	650	4	18	427	1751
NRM	SLURRY	8	11.6	0.42	<10	1192	1073	2791	921	43	52	631	2797
NRM	SLURRY	5	12.5	0.46	<10	1338	1017	3251	828	14	34	540	2494
Rothamsted Research	SLURRY	10.5	5.74	0.31	<10	1677	414	2300	571	Э	14	349	1292
Rothamsted Research	SLURRY	10	5.07	0.31	<10	1689	384	2283	565	£	13	336	1255
Rothamsted Research	SLURRY	10	4.52	0.31	<10	1778	375	2702	544	3	14	301	1146
Rothamsted Research	SLURRY	10	5.61	0.31	<10	1691	402	2647	580	3	15	312	1252
Rothamsted Research	SLURRY	6	5.44	0.32	<10	1692	412	2597	572	3	14	325	1235
Bangor University	SLURRY	5.5	8.92	0.41	<10	1626	629	2245	472	3	16	453	1204
Bangor University	SLURRY	7.88	9.01	0.17	<10	490	381	1535	478	3	13	259	1291
Bangor University	SLURRY	2.5	3.82	0.17	<10	644	278	2004	285	4	8	252	791
Bangor University	SLURRY	5	3.7	0.22	<10	1139	393	1874	459	3	6	230	769
Bangor University	SLURRY	4	2.75	0.2	<10	1140	269	1699	237	1	6	216	727
ADAS	Digestate	3.5	4.51	0.64	<10	4612	781	1613	167	7	52	810	2288
ADAS	SLURRY	10.5	5.28	0.46	<10	2935	1084	2667	660	12	66	749	1381
ADAS	SLURRY	10	1.66	0.24	<10	2016	95	2193	58	3	34	2687	200
ADAS	SLURRY	11	1.63	0.23	<10	2051	98	2227	59	3	34	2753	205
ADAS	SLURRY	11	1.64	0.24	<10	2005	97	2199	58	3	34	27	202
Average		7.47	6.04	0.32		1671	497	2369	446.20	5.89	21.92	601.87	1153
SEM		0.58	0.68	0.02		184.19	63.70	100.20	51.04	1.89	3.62	151.06	148.51

## Appendix 4 – Discussion

Appendix 4.1 – Slurry	comparison to RB209	expected values
$\pi \mu \mu \nu \mu \mu \mu \pi $	COMParison to RD207	capecieu values.
	*	-

				Chap	ter 3					Chap	ter 4		Chap	ter 5	Chap	ter 6
	App 1	<b>RB209</b>	App 2	<b>RB209</b>	App 3	<b>RB209</b>	App 4	<b>RB209</b>	Exp 1	RB209	Exp 2	<b>RB209</b>		<b>RB209</b>	Exp 2	<b>RB209</b>
Oven Dry Solids	4.20		4.22		7.69		4.19		8.92		9.01		2.75		8.9	
Total Kjeldahl Nitrogen	1.67	2.09	1.80	2.10	2.97	3.00	2.30	2.09	4.10	3.32	0.17	3.34	4	1.715	4.1	3.314
Ammonium Nitrogen	0.59	0.96	0.71	0.96	1.21	1.13	1.12	0.96	1.63	1.20	0.98	1.20	2.28	0.8875	1.63	1.195
Total Phosphorus	0.65	0.80	0.69	0.80	1.21	1.25	0.92	0.80	1.44	1.41	1.74	1.42	1.24	0.6075	1.44	1.407
Total Potassium	2.46	2.17	3.06	2.18	2.37	2.94	2.26	2.17	2.69	3.21	3.69	3.23	4.02	1.855	2.69	3.208
Total Sulphur	0.64	0.53	0.64	0.53	0.81	0.84	0.62	0.53	1.13	0.95	1.30	0.96	1.1	0.3975	1.13	0.951