

## Article

# An Incubation System for the Simulation of Ammonia Emissions from Soil Surface-Applied Slurry: Effect of pH and Acid Type

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**Abstract:** Acidification of slurry is a promising approach for reducing ammonia emissions during the application procedure. Since only a few studies have been conducted focusing on ammonia emissions during the application of liquid organic fertilizers on the soil surface, a suitable incubation system was developed to evaluate the effects of acidification under controlled conditions. This incubation system was used to measure the ammonia emissions of various liquid organic fertilizers. The substrates were acidified with sulfuric and citric acid to different pH values to determine both the influence of the pH value of the substrates and of the type of acid on the ammonia emissions. The emissions decreased with declining pH value, and the reduction in emissions compared to the initial pH of the substrate was over 86% for pH 6.5 and over 98% for pH 6.0 and below. At the same pH value, the ammonia emissions did not differ between substrates acidified with citric acid and sulfuric acid, although more than twice as much 50% citric acid was required compared to 96% sulfuric acid to achieve the same pH value. Overall, our results demonstrate that the incubation system used is suitable for measuring ammonia emissions from surface-applied liquid organic fertilizers. The system allows for the differentiation of emission levels at various pH levels and is therefore suitable for testing the effectiveness of additives for reducing ammonia emissions from liquid organic fertilizers.

**Keywords:** ammonia emission; acidification; liquid organic fertilizer; pig slurry; cattle slurry; biogas digestate



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## 1. Introduction

Ammonia emissions from agricultural activities have received increasing attention due to their environmental and public health implications. Ammonia is a major precursor of particulate matter in the atmosphere [1,2] and contributes to eutrophication [3], acidification and air quality degradation [4,5]. The development of measures to reduce ammonia emissions is therefore crucial for sustainable agriculture and environmental conservation efforts.

Agricultural practices, such as the application of liquid organic fertilizers, play a substantial role in ammonia emissions. In Germany, around 30% of total ammonia emissions from agriculture come from the spreading of liquid organic fertilizers [6]. The release of ammonia from these fertilizers is influenced by numerous factors, including temperature, pH, substrate characteristics, application methods and environmental conditions [7–9]. There are various ways to minimize ammonia emissions when spreading liquid organic fertilizers, such as spreading techniques like drag hoses or injection methods [10–12] or the use of additives [9]. In particular, the acidification of liquid organic fertilizers, in which the pH value of the fertilizer is decreased, represents a promising approach to lowering ammonia emissions during application [13,14]. Acidification shifts the chemical equilibrium between ammonium ( $\text{NH}_4^+$ ) and ammonia ( $\text{NH}_3$ ) towards  $\text{NH}_4^+$  so that less  $\text{NH}_3$  can be emitted. However, measuring ammonia emissions in the field is complicated, and the emission reductions due to acidifying liquid organic fertilizers before or during application vary greatly [15]. For example, Pedersen et al. [16] achieved emission reductions of

79 ± 18% when applying acidified cattle slurry to a loamy sand, while Wagner et al. [17] were able to reduce ammonia emissions by an average of 64% when applying acidified cattle slurry on a loamy sand. In their study with acidified slurry on grassland, Nyameasem et al. [12] found emission reductions compared to unacidified slurry of 41 ± 9%, but these reductions differed markedly between various sites with 67 ± 6%, 66 ± 12%, 30 ± 14% and 3 ± 27%. The emission reductions in the acidified substrate in relation to the non-acidified treatment in the study of ten Huf et al. [11] varied between 10 and 100% for cattle slurry and 19 and 100% for biogas digestive. In this study, significant reductions were only observed with very strong reductions of more than 83%, which shows how complicated it is to validate differences between treatments when measuring ammonia emissions in field trials. Therefore, laboratory tests based on incubation systems could be useful to evaluate the effects of different reduction methods on ammonia emissions and to test the effectiveness of additives such as acids or other products [18,19]. Incubation experiments on ammonia emissions have the advantage that a controlled environment (temperature, wind, etc.) can be established, and the results are not influenced by other factors [20].

Such incubation experiments have already been carried out focusing on many different issues related to ammonia emissions. For example, ammonia emissions have been measured during animal husbandry in feedlots [21–23] or stables [24,25] and during the storage of organic fertilizers from pig fattening [26] or cattle breeding [27,28]. Van der Stelt et al. [29] investigated the influence of additives on the volatilization of ammonia from liquid beef manure. However, in these investigations, so-called “static” chambers (i.e., without air movement) were used intending to simulate the storage of liquid manure. Reguiero et al. [30] studied several alternatives to sulfuric acid for slurry acidification, whereby these tests were also carried out in static chambers without air movement. Kavanagh et al. [31] investigated the mitigation of ammonia emissions by using acidifiers and other chemical amendments. Prado et al. [32] tested the effect of bio-acidification as an alternative to sulfuric acid in a “dynamic” chamber system by pumping air through a vessel containing the slurry. Again, these tests were performed to simulate the storage period of slurry. There have also been studies on ammonia emissions from the application of organic fertilizers [19,33]. However, these studies did not investigate the influence of additives or acidification on ammonia emissions.

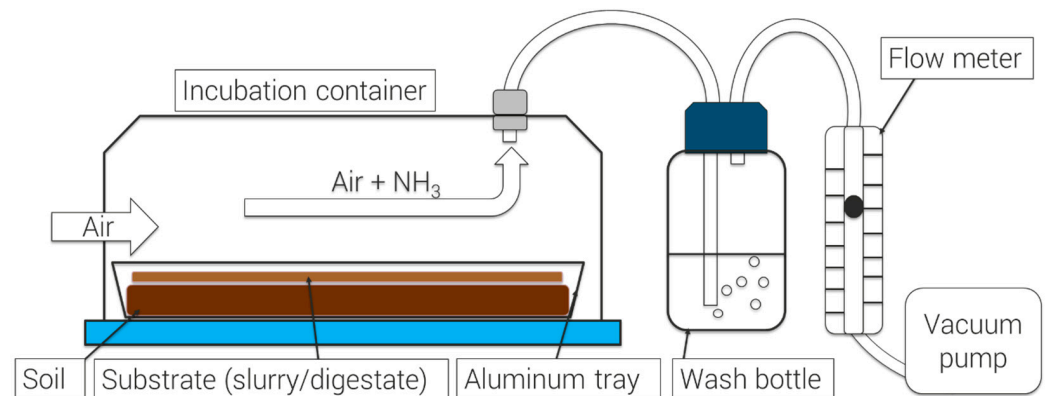
Since no studies are available that use dynamic chambers for measuring ammonia emissions from soil surface-applied liquid organic fertilizers and the effect of additives or acidification, a measurement system based on that of Kim et al. [19] was developed. This system was implemented to investigate various additives and their effect on the reduction in ammonia emissions during the application of liquid organic fertilizers. The main aim of this study was to verify the performance of the incubation system. For this purpose, we measured the ammonia emissions of acidified and soil surface-applied liquid organic fertilizers. The following hypotheses were tested: (1) the incubation system can be used to measure ammonia emissions from soil surface-applied liquid organic fertilizers, and even small differences in emission levels can be detected; (2) the lower the pH value of the liquid organic fertilizer, the lower the ammonia emissions; (3) the type of acid has no effect on ammonia emission at the same pH value in the substrate.

## 2. Materials and Methods

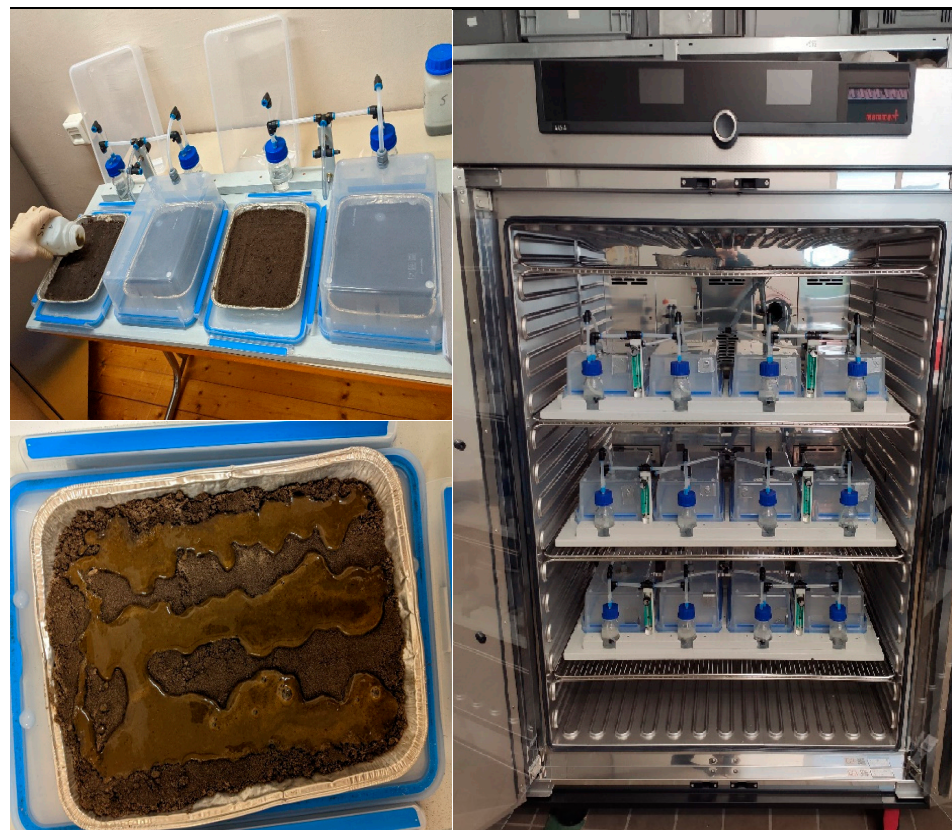
### 2.1. Design of the Incubation System

A specific measurement system was developed to investigate the effects of slurry acidification on ammonia emission during simulating slurry application on the soil surface (Figure 1). Airtight polypropylene containers (22.7 × 32.7 × 11.1 cm; V = 5.4 L) are used in which an aluminum tray filled with soil (surface area approximately 600 cm<sup>2</sup>) is placed. Various soils can be tested, and liquid organic fertilizers can be spread on the soil surface, depending on the experimental question. The containers have an air inlet and are connected to a vacuum pump (VP115, Mucola GmbH, Salzhemmendorf, Germany) via an air outlet. Wash bottles and flow meters are installed between the container and the vacuum pump.

This allows ambient air to be pumped through the containers and the corresponding wash bottle. Emitted  $\text{NH}_3$  in the container is thus collected in the acidified wash solution (50 mL 0.05 M  $\text{H}_2\text{SO}_4$ ). The air flow rate was set to  $2 \text{ L min}^{-1}$  per container via the flow meter (air exchange rate:  $0.37 \text{ min}^{-1}$ ). The entire system, which consists of twelve incubation containers with an associated wash bottle, is installed in a climate chamber (Constant Climate Chamber HPP750, Memmert GmbH & Co. KG, Schwabach, Germany) to ensure constant ambient conditions (Figure 2). The distribution of the treatments to the containers is randomized. The uniformity of the measured values from the different chambers was checked in preliminary tests by using an artificial ammonia source ( $\text{NH}_4\text{HCO}_3$ ) and by using the same slurry in all incubation containers.



**Figure 1.** Schematic design of the incubation system with incubation container, wash bottle and flow meter.



**Figure 2.** Setup of the incubation system and application of the liquid manure: liquid manure application (**top left**), the liquid manure applied to the soil in an aluminum tray (**bottom left**) and the incubation system in the climate chamber (**right**).

## 2.2. Soil Characterization

According to the United States Department of Agriculture [34], the soil used in these experiments is a sandy loam (7% clay, 19% silt, 74% sand) with a high content of soil organic carbon (SOC) of  $21.5 \text{ g kg}^{-1}$ , a total N content ( $N_t$ ) of  $1.52 \text{ g kg}^{-1}$ , a pH of 5.37, and a maximum water holding capacity ( $WHC_{\max}$ ) of  $0.23 \text{ g g}^{-1}$ . For each of the three experimental series, 500 g of the air-dried soil, sieved to 2 mm, was placed in the aluminum trays, moistened with 70 mL of distilled water to 60%  $WHC_{\max}$  and compacted to achieve a bulk density of  $1.4 \text{ g cm}^{-3}$ .

## 2.3. Substrate Characterization and Acidification

The substrates used are typical liquid farm manures selected from a survey study in north-western Germany [35]. Two pig slurries (PS), two cattle slurries (CS) and two biogas digestates (BG) were collected, each with a low (ld) and high (hd) dry matter content. The analysis results of these six substrates are shown in Table 1. The substrates were carefully homogenized for three minutes at 10,000 rpm using a stainless-steel blender (Blender CB15VXE, Waring Commercial, Torrington, CT, USA), portioned into 0.5 L plastic containers and frozen at  $-18^\circ\text{C}$ . The substrates were thawed at room temperature the day before acidification.

**Table 1.** Abbreviations (Abbr.) and characteristics (pH, dry matter [DM], total-N [ $N_t$ ], ammonium-N [ $NH_4\text{-N}$ ], phosphorus [P] and potassium [K]) of the six substrates used for the three experiments.

Abbr.	Type	pH *	DM [%]	$N_t$ [ $\text{kg m}^{-3}$ ]	$NH_4\text{-N}$ [ $\text{kg m}^{-3}$ ]	P [ $\text{kg m}^{-3}$ ]	K [ $\text{kg m}^{-3}$ ]
PSld	Pig slurry (low DM)	7.54	4.69	2.82	1.44	1.21	1.22
PShd	Pig slurry (high DM)	8.10	7.39	4.90	3.04	2.08	2.32
CSld	Cattle slurry (low DM)	7.45	8.00	3.68	1.87	0.58	2.78
CShd	Cattle slurry (high DM)	7.77	11.53	3.25	1.31	0.63	4.01
BDld	Biogas digestate (low DM)	8.98	4.92	4.54	2.85	0.94	3.61
BDhd	Biogas digestate (high DM)	8.35	8.57	4.48	2.31	0.94	3.87

\* measured at  $20^\circ\text{C}$ .

Acidification took place the day before the respective start of each experiment. Amounts of 50% ( $w/w$ ) citric acid ( $M = 192.124 \text{ g mol}^{-1}$ ,  $\rho = 1.24 \text{ kg L}^{-1}$ ) and 96% ( $w/w$ ) sulfuric acid ( $M = 98.079 \text{ g mol}^{-1}$ ,  $\rho = 1.84 \text{ kg L}^{-1}$ ) were used to acidify the substrates. The acid was added to each of the substrates in small portions and stirred briefly, and then, after a short waiting period (ca 2 min), the pH value was measured using a pH electrode (WTW SenTix 41, Xylem Analytics Germany Sales GmbH & Co. KG, Weilheim, Germany) and a pH meter (WTW pH 330 m, Xylem Analytics Germany Sales GmbH & Co. KG, Weilheim, Germany). On the day of the experiment, the pH value was checked again, and additional acid was added if necessary to adjust to the intended pH value. Titration curves were generated for the substrates PSld and CSld (Figure A1) by adding a defined volume of sulfuric acid to the substrates in several steps and measuring the pH value after each step. The respective current buffer capacity (CBC) in  $\text{mmol kg}^{-1} \text{ slurry/pH}$  was calculated from these titration curves according to the method described by Overmeyer et al. [36], which represents the reciprocal slope of the titration curve (Figure A2).

## 2.4. Experiment 1

In the first experimental series (experiment 1), the general functionality of the incubation system was tested. For this purpose, one pig and one cattle slurry (PShd and CSld; see Table 1) were acidified with citric acid (50%) to different pH values (initial pH; pH 7.0; pH 6.5; pH 6.0 and pH 5.5). One hundred grams of each substrate was applied to the soil in approx. 3 cm wide strips (simulation of a field applied slurry at a rate of  $17 \text{ m}^3 \text{ ha}^{-1}$  using a drag hose application system; see Figure 2) and the aluminum trays were placed in the incubation containers at  $20^\circ\text{C}$  in the climate chamber. After two, four, six and eight



hours, the washing solutions in the wash bottles were exchanged and then analyzed in the laboratory.

### 2.5. Experiment 2

To test the repeatability of the results at low emission levels and to check if the measured values can be differentiated from the unfertilized control, a second experimental series (experiment 2) was carried out, in which two pig and two cattle slurries, as well as two biogas digestates (see Table 1), were acidified with sulfuric acid (96%) to pH 6.0. These substrates were then tested in four replicates against an unfertilized control in the incubation system, as in the previous series of experiments. Again, the washing solutions in the wash bottles were exchanged after two, four, six and eight hours and then analyzed in the laboratory.

### 2.6. Experiment 3

In a third experimental series (experiment 3), it was tested whether the reduction in ammonia emissions from slurry acidification depends only on the pH value or also on the additive used to adjust the pH value. This experiment was also designed to verify the repeatability of the results from experiment 1. For this purpose, the substrate PShd was acidified with citric acid (50%) and sulfuric acid (96%) to different pH values (initial pH, pH 7.5, pH 7.0, pH 6.5, pH 6.0 and pH 5.5), and the resulting ammonia emissions were measured in triplicate after 2, 4 and 6 h using the incubation system as described above.

### 2.7. Laboratory Analysis

In the laboratory, the ammonium content of the wash bottle solution was determined using the indophenol method according to Scheiner [37] in a spectrometer (Lambda 25, Perkin Elmer, Waltham, MA, USA). For this purpose, the solutions were diluted according to the concentration range of the calibration curve and colorized, and the absorbance was measured at a wavelength of 660 nm.

### 2.8. Mathematical Calculations and Statistical Analysis

To determine the ammonia emissions per treatment, the measured ammonium concentration per wash bottle solution was converted into a mass using the volume of the solution (50 mL) and summed up over the total duration of the respective test. The arithmetic mean per treatment was calculated from this mass of emitted  $\text{NH}_3\text{-N}$  per incubation container. The mean ammonia flux per treatment was then calculated in  $\mu\text{g NH}_3\text{-N min}^{-1}$  over the duration of the respective experiment.

For experiments 1 and 2, the proportion of the total amount of  $\text{NH}_4\text{-N}$  applied that was emitted ( $\%\text{NH}_4$ ) in *mass%* was calculated as follows:

$$\%\text{NH}_4 = \frac{m_{\text{NH}_3}}{C_{\text{NH}_4} * m_{\text{substrate}}} * 100 \quad (1)$$

where  $m_{\text{NH}_3}$  is the measured mass (mg) of emitted  $\text{NH}_3\text{-N}$  per treatment,  $C_{\text{NH}_4}$  is the  $\text{NH}_4\text{-N}$  concentration ( $\text{mg g}^{-1}$ ) of the substrate, and  $m_{\text{substrate}}$  is the actual amount (g) of substrate applied.

For experiments 1 and 3, the emission reduction ( $\%\text{red}$ ) in % was calculated as follows:

$$\%\text{red} = \frac{\text{flux}_{\text{pH}} - \text{flux}_{\text{initial}}}{\text{flux}_{\text{initial}}} * 100 \quad (2)$$

where  $\text{flux}_{\text{pH}}$  is the ammonia flux ( $\mu\text{g NH}_3\text{-N min}^{-1}$ ) at a given pH value, and  $\text{flux}_{\text{initial}}$  is the ammonia flux ( $\mu\text{g NH}_3\text{-N min}^{-1}$ ) at the initial pH value.

In experiment 3, the reduction efficiency ( $E_{\text{red}}$ ) in  $\text{mg NH}_3\text{-N m}_{\text{eq}}^{-1}$  was calculated as follows:

$$E_{\text{red}} = m_{\text{NH}_3} / m_{\text{eq}} \quad (3)$$

where  $m_{\text{NH}_3}$  is the mass (mg) of  $\text{NH}_3\text{-N}$  emitted over the entire test period, and  $m_{\text{eq}}$  is the required equivalent mass (grams of acid needed to transfer one mole of hydrogen to the substrate) added per pH level. The  $m_{\text{eq}}$  was calculated according to Reguiero et al. [30] as follows:

$$m_{\text{eq}} = \frac{m_{\text{acid}}}{M_{\text{acid}} / n_{\text{hydron}}} \quad (4)$$

where  $m_{\text{acid}}$  is the mass (g),  $M_{\text{acid}}$  is the molecular weight ( $\text{g mol}^{-1}$ ), and  $n_{\text{hydron}}$  is the number of hydrons of the acid added to the substrate.

The ammonia fluxes of each experiment were statistically evaluated using a one-way analysis of variance (ANOVA). In experiment 1, an ANOVA was carried out for both substrates, and the factor “pH” was fixed for each case. In experiment 2, one ANOVA was performed for each substrate, and the “treatment” factor was fixed for each case. In experiment 3, an ANOVA was carried out for each pH value level, and the factor “Acid type” was fixed for each case. In experiments 1 and 2, a single-factor ANOVA was also performed for the percentage of ammonia emissions in the applied ammonium mass. In the ANOVA of experiment 1, the factor “Treatment” was fixed, and in experiment 2, the factor “Substrate” was fixed. Following all ANOVAs with more than two test elements, significant differences between the mean ammonia fluxes per treatment were tested using Tukey’s post hoc test ( $p \leq 0.05$ ). All statistical analyses were performed with R software packages [38].

### 3. Results

#### 3.1. Experiment 1

For pig slurry, the ammonia flux at the initial pH value was  $63.79 \mu\text{g NH}_3\text{-N min}^{-1}$  and declined constantly with decreasing pH value to an ammonia flux of  $0.08 \mu\text{g NH}_3\text{-N min}^{-1}$  at pH value 5.5 (Table 2). Cattle slurry emitted  $19.16 \mu\text{g NH}_3\text{-N min}^{-1}$  at the initial pH value. Again, the ammonia flux decreased steadily with falling pH value and was finally  $0.07 \mu\text{g NH}_3\text{-N min}^{-1}$  at pH 5.5. The ammonia flux determined in the incubation containers without substrate was  $0.04 \mu\text{g NH}_3\text{-N min}^{-1}$  on average across all measurement series. The different emission levels of the treatments can be statistically confirmed for each slurry type except for the pH levels 6.0 and 5.5.

**Table 2.** Ammonia flux, standard error (SE) of the ammonia flux, percentage of total ammonia emissions of the applied ammonium mass (% $\text{NH}_4$ ) and emission reduction (% $\text{red}$ ) from pig and cattle slurry at different pH values. Different lower- or upper-case letters indicate significant differences ( $p \leq 0.05$ ) between pH value levels for the flux separately between the two substrates and for the percentage of total ammonia emissions of the applied ammonium mass together for both substrates.

Substrate	pH	Flux [ $\mu\text{g NH}_3\text{-N min}^{-1}$ ]	SE n = 4	% $\text{NH}_4$ [mass%]	% $\text{red}$ [%]
PShd Pig slurry	8.0	63.79 <sup>a</sup>	$\pm 2.01$	10.07 <sup>a</sup>	-
	7.0	19.22 <sup>b</sup>	$\pm 0.60$	3.04 <sup>c</sup>	69.9
	6.5	4.88 <sup>c</sup>	$\pm 0.08$	0.77 <sup>d</sup>	92.4
	6.0	0.19 <sup>d</sup>	$\pm 0.02$	0.03 <sup>f</sup>	99.7
	5.5	0.08 <sup>d</sup>	$\pm 0.01$	0.01 <sup>f</sup>	99.9
CSld Cattle slurry	7.3	19.16 <sup>A</sup>	$\pm 0.56$	5.29 <sup>b</sup>	-
	7.0	12.48 <sup>B</sup>	$\pm 0.18$	3.45 <sup>c</sup>	34.9
	6.5	2.53 <sup>C</sup>	$\pm 0.15$	0.70 <sup>de</sup>	86.8
	6.0	0.36 <sup>D</sup>	$\pm 0.01$	0.10 <sup>ef</sup>	98.1
	5.5	0.07 <sup>D</sup>	$\pm 0.00$	0.02 <sup>f</sup>	99.6
Soil without slurry application	-	0.04	$\pm 0.00$ *	-	-

\* n = 20 (5 measurement series with 4 replicates each).

The % $\text{NH}_4$  was 10.07% for the initial pH of PShd and thus about twice as high as for the initial pH of CSld at 5.29%. For the other pH levels, the percentages were in the same range, whereby the values for CSld were slightly higher than for PShd. The ANOVA shows no significant differences between the two substrate types per pH level. The emission reduction at pH 7.0 was about twice as high for PShd (69.9%) as for CSld (34.9%). At the lower pH levels, the emission reduction increased constantly for both substrates and approached 100%.

### 3.2. Experiment 2

The ammonia fluxes determined in experiment 2 (Table 3) at pH 6.0 were between 0.13 and 0.37  $\mu\text{g NH}_4\text{-N min}^{-1}$  and thus in the same order of magnitude as the results of the same pH value level of experiment 1 (0.19 and 0.36  $\mu\text{g NH}_4\text{-N min}^{-1}$ ). The ammonia fluxes determined in the incubation containers without substrates were lower with 0.03 to 0.13  $\mu\text{g NH}_4\text{-N min}^{-1}$ . The differences in the respective measured values of the treatments with substrate can be statistically confirmed in all cases.

**Table 3.** Ammonia flux, standard error (SE) and percentage of total ammonia emissions of the applied ammonium (% $\text{NH}_4$ ) from each two pig and cattle slurries as well as digestates with pH 6.0, each in comparison with an unfertilized control. Different lower-case letters indicate significant differences ( $p \leq 0.05$ ) between treatments or substrates.

Type of Substrate	Substrate	Flux [ $\mu\text{g NH}_3\text{-N min}^{-1}$ ]	SE n = 4	% $\text{NH}_4$ [mass%]
Pig slurry	PSld pH 6.0	0.13 <sup>a</sup>	0.003	0.044 <sup>bc</sup>
	without	0.03 <sup>b</sup>	0.002	
	PShd pH 6.0	0.23 <sup>a</sup>	0.011	0.036 <sup>c</sup>
	without	0.06 <sup>b</sup>	0.013	
Cattle slurry	CSld pH 6.0	0.30 <sup>a</sup>	0.015	0.078 <sup>ab</sup>
	without	0.13 <sup>b</sup>	0.011	
	CShd pH 6.0	0.23 <sup>a</sup>	0.008	0.083 <sup>a</sup>
	without	0.05 <sup>b</sup>	0.002	
Biogas digestate	BDld pH 6.0	0.37 <sup>a</sup>	0.010	0.062 <sup>abc</sup>
	without	0.08 <sup>b</sup>	0.020	
	BDhd pH 6.0	0.36 <sup>a</sup>	0.019	0.075 <sup>ab</sup>
	without	0.05 <sup>b</sup>	0.004	

The % $\text{NH}_4$  was between 0.04 and 0.08% and thus in the same order of magnitude as the results of the same pH value level of experiment 1 (0.03 and 0.10%). The results of the ANOVA show some significant differences between the substrates. For example, the values of the pig slurries, especially PShd, differed from the values of the cattle slurry and biogas digestates.

### 3.3. Experiment 3

Ammonia fluxes determined in experiment 3 were 56.69  $\mu\text{g NH}_4\text{-N min}^{-1}$  at an initial pH of 8.1 and declined with decreasing pH (Table 4). The fluxes for the two different acid types showed only very small differences at the same pH value. These differences are only significant at pH 6.0.

**Table 4.** Ammonia flux, standard error (SE) of ammonia flux, emission reduction (%<sub>red</sub>), amount of added acid and reduction efficiency (E<sub>red</sub>) from pig slurry acidified with citric or sulfuric acid at different pH values. Different lower-case letters indicate significant differences ( $p \leq 0.05$ ) between acid types.

pH	Acid	Flux [ $\mu\text{g NH}_3\text{-N min}^{-1}$ ]	SE n = 3	% <sub>red</sub> [%]	Amount of Acid Added [mg kg <sup>-1</sup> Slurry]	E <sub>red</sub> [mg NH <sub>3</sub> -N m <sub>eq</sub> <sup>-1</sup> ]
8.1	-	56.69	±2.75	-	-	-
7.5	Citric	46.07	±0.79	18.7	9.3	8.8
	Sulfuric	46.26	±3.11	18.4	4.2	7.6
7.0	Citric	17.55	±0.81	69.0	26.9	12.5
	Sulfuric	18.92	±0.94	66.6	10.3	13.7
6.5	Citric	3.89	±0.16	93.1	37.7	9.7
	Sulfuric	2.50	±0.37	95.6	15.1	10.6
6.0	Citric	0.28 <sup>b</sup>	±0.01	99.5	45.8	3.4
	Sulfuric	0.51 <sup>a</sup>	±0.01	99.1	20.5	1.1
5.5	Citric	0.07	±0.00	99.9	47.8	0.8
	Sulfuric	0.13	±0.02	99.8	21.9	0.8

n.s. = not significant.

The %<sub>red</sub> for both acid types was just over 18% at pH 7.5, around 68% at pH 7.0, around 94% at pH 6.5, and over 99% at pH 6.0 and pH 5.5. These values correspond almost exactly to the emission reductions at the same pH levels that were determined with the same substrate in experiment 1.

The weight-related amount of citric acid required to reach the pH levels was 9.3 mg kg<sup>-1</sup> slurry at pH 7.5 and increased with decreasing pH up to an addition of 47.8 mg kg<sup>-1</sup> slurry at pH 5.5. In the case of sulfuric acid, 4.2 mg kg<sup>-1</sup> slurry was required to achieve a pH value of 7.5. The required addition quantities increased with decreasing pH value up to 21.9 mg kg<sup>-1</sup> slurry to reach pH 5.5. On average, more than twice as much citric acid was required to achieve the same pH value as with sulfuric acid.

The E<sub>red</sub> of citric acid was 8.8 mg NH<sub>3</sub>-N m<sub>eq</sub><sup>-1</sup> at pH 7.5, increased to 12.5 mg NH<sub>3</sub>-N m<sub>eq</sub><sup>-1</sup> at pH 7.0 and then decreased constantly with decreasing pH to a value of 0.8 mg NH<sub>3</sub>-N m<sub>eq</sub><sup>-1</sup> at pH 5.5. For sulfuric acid, the reduction efficiency at pH 7.5 was 7.6 mg NH<sub>3</sub>-N m<sub>eq</sub><sup>-1</sup>, then increased to 13.7 mg NH<sub>3</sub>-N m<sub>eq</sub><sup>-1</sup> at pH 7.0 and then also decreased constantly to 0.8 mg NH<sub>3</sub>-N m<sub>eq</sub><sup>-1</sup> at pH 5.5.

#### 4. Discussion

As expected, and in agreement with several other studies [13,14,39], the results from experiment 1 revealed that the lower the pH value of the slurry, the lower the ammonia emissions from the applied slurry. This occurs regardless of the type of substrate. Despite the variability associated with the application of organic fertilizers, the values fluctuate only slightly, allowing for statistical validation of the different emission levels across pH levels of the substrates with the methodology used, except for the differences between pH 5.5 and pH 6.0. The emission reductions achieved at different pH levels are somewhat comparable to those reported in other studies but even higher in all cases. So, the emission reduction due to the acidification of cattle slurry to pH 6.0 by Andersson et al. [40] was about 83%, while the emission reductions in the studies conducted by Fanguiero et al. [41,42] and Frost et al. [43] by acidifying cattle slurry to pH 5.5 were 81%, 88% and 83%, respectively. In another study, Fanguiero et al. [44] were able to reduce ammonia emissions by 96% on sandy soil and 92% on sandy loam soil by acidifying cattle manure to pH 5.6. The considerably higher reduction values observed are presumably due to the controlled environment in our experiments, while many other studies were conducted under field conditions, where additional environmental factors (wind, temperature, etc.) and larger measurement uncertainties can significantly influence NH<sub>3</sub> emissions. Pedersen et al. [45]



demonstrated in their study that, among other factors, temperature and sunlight need to be considered when analyzing ammonia emissions.

As is common practice on many farms, the same amount of liquid organic fertilizer was applied for each substrate type in our experiments. However, as the substrates had different ammonium concentrations, the % $\text{NH}_4$  should be considered for a reasonable comparison. These percentages differed significantly at the initial pH, primarily because the initial pH values of the two substrates under investigation were markedly different (pH 8.0 for PS and pH 7.3 for the cattle slurry). At the other tested pH levels, the % $\text{NH}_4$  of the two substrate types was within the same range. This suggests that pH value and ammonium content are the two key factors influencing ammonia emissions from liquid manures, a finding supported by several studies [7,46,47].

Overall, experiment 1 demonstrates that the incubation system that has been developed is suitable for measuring ammonia emissions from liquid organic fertilizers applied to the soil surface. The system allows for a clear differentiation of emission levels at various pH levels, and differences between treatments can be statistically verified (with the exception of the very low pH values of 6.0 and 5.5 in the substrates). To check the reliability of the incubation system at low ammonia emission, a repeatability test (experiment 2) was carried out in which two substrates (low and high DM) of each of the three different substrate types were acidified to pH 6.0 and then tested against an unfertilized control. The results obtained with a comparable ammonia emission level for all substrates at pH 6.0 but a statistically significant difference to the control values show that ammonia emissions in the very-low-value range can also be reliably measured with the incubation system. The fact that there is no statistically significant difference between the pH 6.0 and 5.5 treatments in the first experiment can be attributed to the broad emission range tested. The high ammonia emission values at the high pH levels lead to relatively larger variances. This makes it much more difficult to statistically validate the differences between the pH value levels in the low emission level when comparing all pH treatments.

The comparison of the % $\text{NH}_4$  shows, on the one hand, that the values measured with the incubation container system are repeatable compared to the first experiment. For the substrates PShd and CSld tested again, the values are very similar (PShd: 0.03% versus 0.04%; CSld: 0.10% versus 0.08%). On the other hand, although the values of the different substrates are again in the same value range despite the very low emission level at pH 6.0, they differ in some cases by a factor of up to 2. This confirms once again that the pH value and the ammonium content are the two most important factors for ammonia emissions from liquid organic fertilizers. On the other hand, it shows that other factors also influence the level of ammonia emissions.

It is worthwhile to note that the two pig slurries showed comparatively low  $\text{NH}_3$  emissions in relation to the amount of ammonium applied at pH 6.0. This could be due to the fluidity or the ability of the pig slurry to infiltrate into the soil, as the exposed surface of the emitting substrate is an important factor for the level of ammonia emissions. The larger the surface area, the more ammonia can be released into the surrounding air [8,48,49]. This means that less ammonia can be emitted from a substrate that infiltrates into the soil more rapidly [50,51]. The ability to infiltrate into the soil depends mostly on the dry matter content of a substrate. The pig slurry used in the trial had a rather high dry matter content (see Table 1). Other aspects that contribute to the level of ammonia emissions must also be considered. For example, the fluidity and ability to infiltrate into the soil are not only determined by the dry matter content of a substrate but also by its viscosity [50,52]. The viscosity of liquid organic fertilizers can vary considerably [53] and may have been additionally affected by homogenization of the substrates in a high-performance mixer in our experiments. However, as our experiments did not focus on clarifying these relationships, the viscosity of the substrates used was not analyzed.

The comparison of slurry acidified with citric acid and sulfuric acid in experiment 3 shows that ammonia emissions were in the same value range at each pH value level. Ammonia fluxes differed in each case and, in some cases, even statistically significantly. As the

values within a treatment show relatively small variances and the differences between the two acid types at pH 6.0 were statistically significant, these differences cannot be explained by uncertainties in the experimental setup and procedure or in the laboratory analysis. The differences observed also do not indicate a clear tendency in favor of a particular type of acid, so this result can be attributed to the heterogeneity of the liquid organic fertilizer and the uncertainties regarding the acidification of these liquid organic fertilizers. Acidification and measurement of the pH value are complicated because these liquid organic fertilizers are not homogeneous and monophasic substances. They consist of both liquid and solid components and can have very different textures and consistencies [54,55]. Furthermore, there are different buffer systems in liquid organic fertilizers, which act in different pH ranges, can vary in strength and, to some extent, influence each other [56]. For example, the PShd used for this experiment has a buffer system in the pH 7 to pH 6 range (see Figure A2). The buffer that is effective in this pH range is the hydrogen carbonate ( $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ ) buffer [36], which is the most important buffer in liquid organic fertilizers [57]. This buffer ensures that the pH value of the substrate changes little to not at all when an acid from the corresponding buffer range is added.

During slurry acidification, both the buffer effect and the heterogeneity of the liquid organic fertilizer have an effect. When an acid dose is added, it must react with the chemical substances in the substrate. Due to the heterogeneity of the substrate, the acid and the reactants do not immediately come into direct contact with each other. When the acid is added, the measured pH value initially drops. It then reacts with the buffer so that the pH value rises again. It should be noted that the buffer that mainly acts in this range is the hydrogen carbonate buffer. The resulting  $\text{CO}_2$  leads to foam formation on the surface of the substrate [58]. However, the foaming makes it difficult to measure the pH value. It is, therefore, complicated to adjust such substrates to an exact pH value; thus, uncertainties can be assumed here. To avoid these problems, in our experiments, the pH value of the substrate was initially adjusted the day before the actual experiment and checked again the next day. In almost all cases, acid had to be added to the substrate again, as the pH value had risen again. In addition, the exact measurement of the pH value was also difficult due to the previously mentioned heterogeneity of the liquid organic fertilizers. Overall, it can, therefore, be said that the type of acid has no influence on ammonia emissions when the pH value of the substrate is the same.

A comparison of the %<sub>red</sub> achieved at the various pH levels in experiment 3 with those of experiment 1, in which the same substrates were used, shows that they were in the same range in each case. This once again confirms the repeatability of the results achieved with the developed incubation system.

To assess the efficiency of acidification with the two types of acid and to check whether other effects besides the change in pH value contribute to the reduction in emissions, the amount of acid required to achieve a certain pH level with citric and sulfuric acid was compared. This comparison shows considerable differences between the sulfuric and citric acids. On average, 2.3 times more citric acid is required by mass than sulfuric acid to achieve the same pH value. However, this could be expected, as the used citric acid (50%) has only half the mass fraction of the sulfuric acid (96%). This means that 1.92 times more acid was added per mass of “acid product” with the sulfuric acid than with the citric acid. In addition, sulfuric acid has only about half the molar mass ( $98.1 \text{ g mol}^{-1}$ ) compared to citric acid ( $192.1 \text{ g mol}^{-1}$ ). This means that almost twice as much of the substance per mass of acid is added to the substrate with sulfuric acid than with citric acid. In contrast, citric acid, as a three-proton acid, has a higher valency than the two-proton sulfuric acid, i.e., three protons are added to the substrate per mol of citric acid, whereas only two protons are added per mol of divalent sulfuric acid, which corresponds to a factor of two thirds. If all three factors are taken together, acidification with 96% sulfuric acid is, therefore, theoretically, about 2.5 times more effective by mass than with 50% citric acid. For this reason, sulfuric acid is used almost exclusively in agricultural practice for the acidification of liquid farm fertilizers [13,30,58].

To identify the pH range in which the acidification of liquid organic fertilizers is most efficient, the  $E_{red}$  was calculated for the different pH levels. This indicates how much less mass of ammonia was emitted per added  $m_{eq}$ . The  $E_{red}$  for almost all pH levels are in the same value range for both types of acid. This result is confirmed by the study conducted by Regueiro et al. [30], in which the same  $m_{eq}$  was required for acidification when titrating pig and cattle slurry to pH 5.0 with citric and sulfuric acid. The distinct differences at pH level 6.0 can be attributed to the already described variations in the acidification of liquid organic fertilizers and their adjustment to a specific pH value. These variances play an even greater role here, as differences in the values between the individual pH levels are considered. Thus, large deviations in the  $E_{red}$  of the two acid types at pH 6.0 can be explained by the different ammonia fluxes measured at pH 6.5 and 6.0. The reduction from pH 6.5 to pH 6.0 is considerably higher for citric acid compared to sulfuric acid, as a noticeably higher ammonia flux was measured at pH 6.5 and a significantly lower one at pH 6.0. Thus, the  $\%_{red}$  in citric acid at pH 6.0 is significantly higher, and, therefore, the  $E_{red}$  is also high.

More interesting is the comparison of the  $E_{red}$  at the different pH levels independent of the type of acid. Here, it can be seen that the  $E_{red}$  increases from pH 7.5 to pH 7.0 and then decreases steadily with decreasing pH value. Given the theoretical background of the effect of pH on the level of ammonia emissions, the fact that the  $E_{red}$  is lower between pH 8.1 and 7.5 than between pH 7.5 and 7.0 is not plausible. Acidification of the liquid organic fertilizer shifts the balance between  $NH_4^+$  and  $NH_3$  towards  $NH_4^+$  so that less ammonia is emitted. This equilibrium is also a buffer system and is mainly effective in the pH range of 10.0 to 8.0 [36,58]. Acidification below pH 8.0 to pH 7.5 should, therefore, significantly reduce ammonia emissions. When looking at the titration curve and the CBC of substrate 1 (Figures A1 and A2), no pronounced buffer is effective for this substrate above pH 7.5. Here, the addition of acid is efficient in terms of reducing the pH value. Between pH 7.5 and 7.0, on the other hand, there is already a pronounced buffer effect, which is mainly caused by the hydrogen carbonate buffer, which acts in the pH range of 7.5 to 5.5 [36,56,59]. Acidification should, therefore, be markedly less efficient here.

The question arises as to why the  $E_{red}$  is higher in this pH range. One explanation might be that the incubation system can no longer completely capture the very high ammonia emissions at higher pH values of the substrates. The air exchange rate that we used for our incubation system is comparatively low at  $0.37 \text{ min}^{-1}$ . There are some studies that have worked with similar exchange rates [23,25,27,60]. However, these studies mostly simulated the storage of organic fertilizers so that the emitting surface area in relation to the amount of slurry used for the experiment was also substantially lower. Other studies have worked with higher exchange rates [19,28,61]. In their incubation experiments, Kim and Kim [33] have shown that the ammonia flux is in a linear relationship to the air flow through the incubation chamber. It must be kept in mind that if the exchange rate is too low, the ammonia accumulates in the incubation chambers, causing a relatively high concentration in the air above the emitting surface. As this reduces the concentration gradient between the surface of the substrate and the air in the chamber, the emission rate also decreases. This effect is also referred to as the “oasis effect” when measuring ammonia emissions in the field [62–64]. As a result, the ammonia emissions at very high ammonia fluxes, and thus, the reduction efficiency is underestimated with the method used. To be able to measure and differentiate the emissions at very high ammonia fluxes with our incubation system, either the exchange rate needs to be increased by a higher air flow or the emissions reduced by smaller amounts of surface-applied substrate.

In the incubation system of Kim et al. [19], the exchange rate of around  $1.09 \text{ min}^{-1}$  is markedly higher than in the system presented here at  $0.37 \text{ min}^{-1}$ , while the usable surface area for spreading the fertilizer is slightly larger in the system of Kim et al. at  $0.1 \text{ m}^2$  compared to  $0.06 \text{ m}^2$  in our system. The higher air exchange rate is possible because in the system of Kim et al., only one container is used at a time, while twelve containers can be used simultaneously in our system. This has the advantage that it is possible to measure

several repetitions of one treatment as well as several treatments, e.g., several application rates of an additive, at the same time. Both systems, therefore, have their advantages and disadvantages, although they follow the same approach. A combination of both systems with several containers and a sufficiently high exchange rate would be the best option.

However, apart from the very high emission rates, acidification is hardly efficient below pH 6.5 for the pig slurry with a high DM (PShd). This can be explained by the relationship between the ammonia emissions and the equilibrium between  $\text{NH}_4^+$  and  $\text{NH}_3$ . Below pH 7.0, there is hardly any ammonia left, so it cannot be emitted. A further pH reduction, therefore, has no effect. On the other hand, the pH value of the liquid organic fertilizer may rise again after application to the soil [65]. The application of the liquid organic fertilizer results in an extreme increase in exposed surface area, so that  $\text{CO}_2$  is emitted from the fertilizer, and thus its pH value increases [59,66]. After the pH value has increased again, ammonia is also present in the solution again, which then might be emitted. However, if the hydrogen carbonate buffer has been completely depleted during acidification, no more  $\text{CO}_2$  can evolve so that the pH value of the substrate remains stable. It could, therefore, be effective in completely depleting the hydrogen carbonate buffer during acidification so that the pH value remains stable even after application on the soil surface. Pedersen et al. [16] were able to show that the pH value of slurry that had already been acidified in a storage tank increased less after application than that of slurry acidified directly during the application process in the field and untreated slurry. They attributed this to the hydrogen carbonate buffer that had already been depleted, the microbial inhibition and the resulting lower  $\text{CO}_2$  emission after application of the slurry acidified in storage.

This effect is mainly relevant for substrates with a pronounced hydrogen carbonate buffer. However, it must be kept in mind that every substrate is different and that the buffer systems can change over time during the storage of liquid organic fertilizer [36]. Furthermore, since the buffering effect of a substrate cannot be estimated from the generally available analytical values [59,66,67], it is not possible to predict how large the buffering effect of a substrate is and how much acid is finally required to achieve a certain pH value.

## 5. Conclusions

According to the first hypothesis, our results demonstrate that the developed incubation system is suitable for measuring ammonia emissions of soil surface-applied liquid organic fertilizers and to differentiate between different emission levels, even in the very low emission range. Such an experimental setup is, therefore, suitable for testing various slurry additives and their effectiveness in reducing ammonia emissions from liquid organic fertilizers spread on the soil surface and for demonstrating general relationships. This system can be used to test the numerous slurry additives on the market and determine their effectiveness in reducing ammonia emissions. However, it was found that the air exchange rate tended to be too low for the chosen amount of fertilizer in the incubation containers. For future work, either the exchange rate should be increased, or the amount of applied liquid organic fertilizer should be reduced. According to the second hypothesis, we were able to show that the lower the pH value of the liquid organic fertilizer, the lower the ammonia emissions. The reduction in emissions compared to the initial pH of the substrate was over 86% for pH 6.5 and over 98% for pH 6.0 and below. According to the third hypothesis, the results show that ammonia emissions do not differ between substrates acidified with citric acid and sulfuric acid at the same pH. The type of acid, therefore, has no effect on ammonia emission at the same pH value in the substrate. As the emission reductions achieved in our experiments by acidification of the liquid organic fertilizers are substantially higher than in most field studies, the transferability of the results to field conditions should be verified in future experiments. It could be useful to simulate other environmental factors in the incubation containers, such as solar radiation. Furthermore, the air flow in the containers could be set so high that a wind effect can be simulated. In addition, effects such as the increase in pH value of the liquid organic fertilizer after application to the soil surface and the resulting increase in ammonia emissions could be

investigated. This might also lead to a better recommendation for a target pH value for slurry acidification.

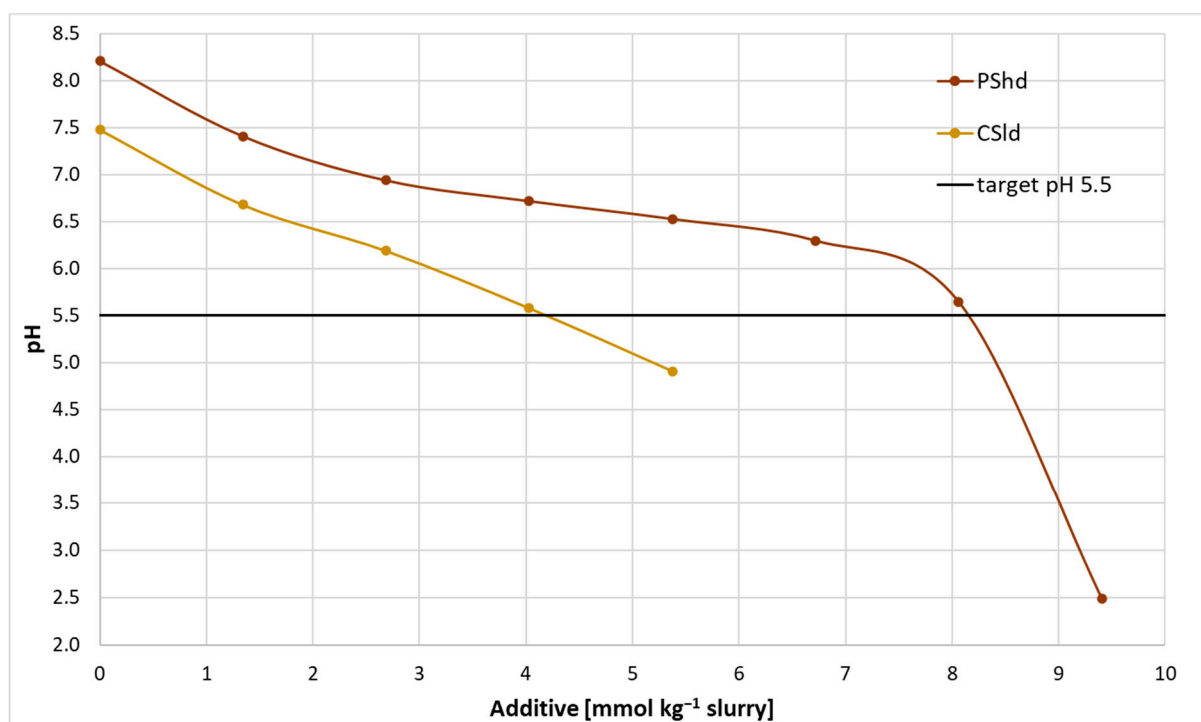
**Author Contributions:** Conceptualization, N.C.T.E. and H.-W.O.; methodology, N.C.T.E. and H.-W.O.; software, N.C.T.E.; validation, N.C.T.E. and H.-W.O.; formal analysis, N.C.T.E.; investigation, N.C.T.E.; resources, N.C.T.E. and H.-W.O.; data curation, N.C.T.E.; writing—original draft preparation, N.C.T.E.; writing—review and editing, H.-W.O.; visualization, N.C.T.E.; supervision, H.-W.O.; project administration, H.-W.O.; funding acquisition, H.-W.O. All authors have read and agreed to the published version of the manuscript.

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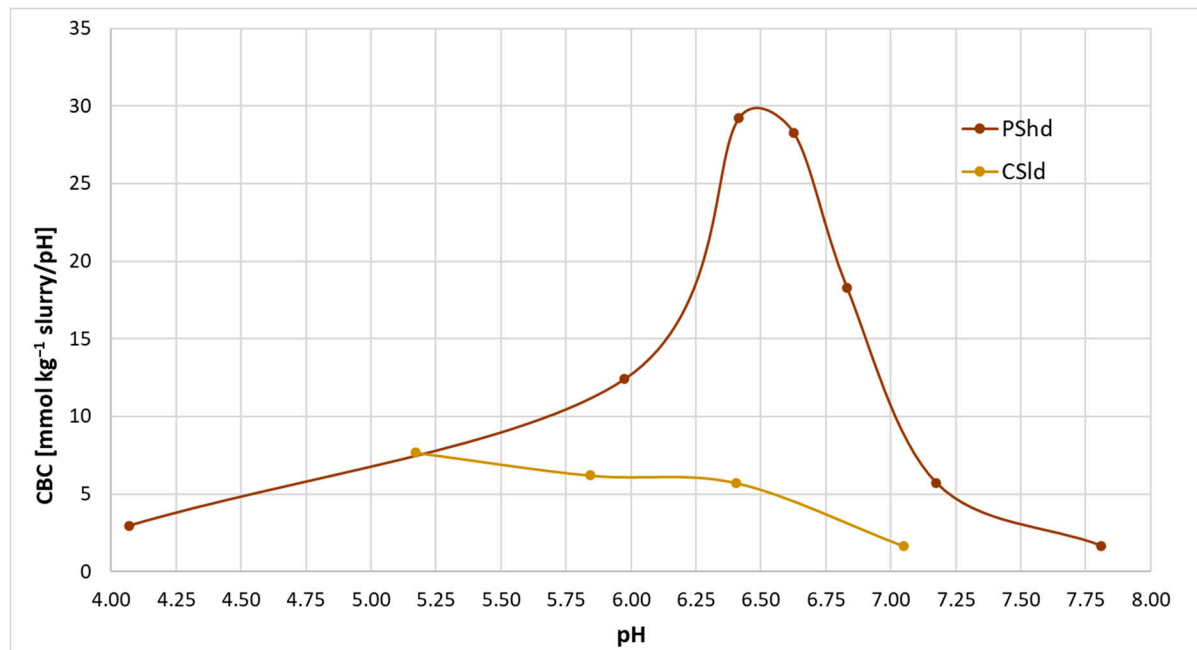
## Appendix A



**Figure A1.** Titration curve of the substrates PShd (pig slurry high dry matter) and CSld (cattle slurry low dry matter), as well as the target pH 5.5.



## Appendix B



**Figure A2.** Current buffer capacity (CBC) of the substrates PShd (pig slurry high dry matter) and CSld (cattle slurry low dry matter).

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