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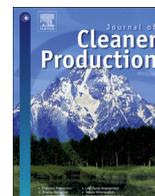


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## Alternatives to sulfuric acid for slurry acidification: impact on slurry composition and ammonia emissions during storage

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## ABSTRACT

Acidification of slurry is a treatment known to reduce ammonia emissions and it is currently applied at the farm scale in Denmark by adding concentrated sulfuric acid ( $H_2SO_4$ ). However, several risks are associated with the use of this strong acid and therefore an alternative is required to protect the health of farmers and animals. The effects of five different additives at two target pH values, 5.5 and 3.5, on the composition of two different slurries (pig and dairy) were assessed. The evolution of pH and  $NH_3$  volatilization from acidified and non-acidified slurries, kept in closed vessels at an ambient temperature of 15 °C, was followed during a storage period of 60 days. Acidification to pH 5.5 with all additives significantly reduced  $NH_3$  emissions, and the greatest decreases relative to raw slurry were obtained with  $H_2SO_4$  (75% in pig and 81% in dairy slurry) and alum (69% in pig and 87% in dairy slurry). Acidification to pH 3.5 reduced  $NH_3$  emissions in both slurries to values considered negligible during the whole storage period. However, longer storage periods should be studied to evaluate  $NH_3$  evolution and slurry composition in the longer-term. Sulfuric acid and alum were the additives which could be used in the lowest amounts to decrease the pH to 5.5 and were the most efficient in reducing  $NH_3$  emissions. Acidification promoted P solubilization, except when alum was used. Nevertheless, this initial solubilization of P when the pH was decreased to 5.5 had been reversed after two weeks of storage. In conclusion, alum can be considered as a good alternative to  $H_2SO_4$  when the pH is lowered to 5.5, as the amount of this additive used was similar to that of  $H_2SO_4$  and it was as efficient as  $H_2SO_4$  with respect to reducing  $NH_3$  volatilization during storage.

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### 1. Introduction

Ammonia ( $NH_3$ ) volatilization mainly originates from agricultural practices, which account for up to 80% of total emissions in Europe (Petersen et al., 2012). In the next few years the amount of  $NH_3$  released is expected to increase along with the intensification of livestock production, which has already been occurring over recent decades (Clarisse et al., 2009). Pig and dairy cattle slurries are an important source of  $NH_3$  volatilization in agriculture as these animals represent the largest livestock production sectors in Europe (FAOSTAT, 2014; Philippe et al., 2011). Reducing such emissions is important, to minimize the highly negative effects on the environment and the health of animals (Wang et al., 2014; Bayo et al., 2012). Furthermore, reducing the N loss increases the

fertilizer value of these slurries, leading to higher yields (Hoeve et al., 2016).

Slurry acidification decreases  $NH_3$  emissions efficiently as it modifies slurry characteristics (Figueiro et al., 2015; Hjorth et al., 2015). This treatment is currently performed at the farm scale in Denmark by addition of concentrated sulfuric acid ( $H_2SO_4$ ). The use of this additive is mainly governed by economic reasons since  $H_2SO_4$  is one of the cheaper acids available (Eriksen et al., 2008). In Denmark this practice has notably increased in recent years (Birkmose and Vestergaard, 2013) as the Danish legislation recommends this treatment to reduce  $NH_3$  emissions (Hoeve et al., 2016). However, there is a need for alternatives to  $H_2SO_4$  due to the hazards associated with this strong acid and problems related to its utilization, such as foam formation during acid addition, corrosiveness, or the possible development of volatile sulfur-containing compounds (Borst, 2001).

Acidification has been studied in the past by using different acids, mostly sulfuric and nitric (Bussink et al., 1994; Stevens et al.,

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1989). A recent study reviewed the acidification practices and mentioned the need for alternatives, for the optimization of slurry management (Fangueiro et al., 2015).

Organic acids are widely found in nature as normal plant and animal constituents. Their use may reduce NH<sub>3</sub> emissions and modify slurry characteristics without affecting the health of farmers and animals. However, the use of these additives for slurry acidification has been poorly investigated. Some additives have been tested mainly for their coagulant properties - such as aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>), referred to here as alum. Nevertheless, this additive has been mostly used in poultry litter treatment, and it proved to be efficient with regard to reducing NH<sub>3</sub> volatilization and improving the management of manure derived phosphorus (Lefcourt and Meisinger, 2001; Moore et al., 1995; Sims and Luka-McCafferty, 2002).

Until now, no systematic comparison of the additives used for acidification of slurries has been performed and there is no information about the application of different additives to different slurries, with regard to changes in the slurry composition during storage, especially for pig and dairy slurries. Indeed, it was shown that the initial chemical composition of the slurry has an important effect on the acidification process as well as on the evolution of the pH during storage. The changes in degradation pathways controlled by microorganisms observed after acidification of slurries have an effect on the slurry composition. An increase in the concentrations of soluble components in acidified slurries has been reported in previous studies (Regueiro et al., 2016) and may be pertinent during long storage periods. Therefore, it is important to understand the changes in the contents of nutrients and organic matter (OM) that occur during acidification and storage.

The influence of the initial pH during acidification and subsequent storage is significant as the pH of animal manure is usually buffered between 7.0 and 8.4 (Sommer et al., 2006). A pH of 5.5 has been chosen normally as the target value in acidification studies. However, in preliminary experiments (unpublished data) an increase (in some cases relatively fast) in pH during the storage of slurry acidified to pH 5.5 was observed, which implies new acidification of the slurry after two or three weeks. To avoid this problem, other target pH values were tested and acidification to pH 3.5 proved to be efficient at keeping the slurry pH below 6 during a long time period (>2 months).

The main objective of the present study was to find an alternative to H<sub>2</sub>SO<sub>4</sub> for slurry acidification at two target pH values, 5.5 and 3.5. The cumulative NH<sub>3</sub> emission and pH development during a 60-day storage period were followed. The effects of acidification on the slurry nutrients and OM composition were compared as well.

We hypothesized that:

- i) Acidified slurries may show a higher OM content after storage when organic additives are used.
- ii) Additives other than H<sub>2</sub>SO<sub>4</sub> may efficiently reduce NH<sub>3</sub> emissions and thus be used as alternatives to H<sub>2</sub>SO<sub>4</sub>.

## 2. Material and methods

### 2.1. Dairy and pig slurries

Fresh pig and dairy slurries, with initial pH values of 7.4 and 7.2, respectively, were collected from two farms in Lisbon, Portugal. Samples of 900 g from both slurries were acidified to pH 5.5 and pH 3.5 using five different additives. Each slurry sample was divided into three subsamples of 300 g that were then placed in airtight glass vessels of 1 L capacity. Acidified and non-acidified (control)

slurry samples were incubated for 60 days at a constant temperature of 15 °C, the mean temperature in storage tanks during winter in Portugal.

### 2.2. Acidification of slurries

Five different additives - acetic acid, citric acid, lactic acid, sulfuric acid, and alum - were used to decrease the initial pH values of the pig and dairy slurries to 5.5 and the same additives, except alum, were used to acidify slurries to pH 3.5. Thus, a total of 20 different treatments, each one with three replicates, were considered. Previous studies by Lefcourt and Meisinger (2001) demonstrated that the addition of 2.5% or 6.25% alum to dairy slurry led to the emission of similar amounts of NH<sub>3</sub> after 96 h of storage. Also, greater addition of alum may increase the soluble Al content - which would affect the subsequent use of the slurry; thus, only a target pH of 5.5 was considered with alum. The main characteristics of the additives used are shown in Table 1.

The additives were added gradually to the slurries in volumes of 0.2 mL, with continuous stirring, and pH measurement after each addition was performed using an electrode pH meter (Metrohm, Herisau, Switzerland).

The total amount of each additive was determined and titration curves in a range of pH from 7.5 to 3.5 were prepared (Fig. 1). The equivalent mass (grams of additive needed to transfer one mole of hydrogen to the slurry) for each additive was calculated, for comparison of the treatments, as follows:

$$\text{Additive Equiv.mass} = \frac{m_{\text{additive}}}{\text{Equiv.additive}} \quad (1)$$

where  $m_{\text{additive}}$  is the mass (g) of additive added to the slurry and  $\text{Equiv.additive}$  is the molecular weight of the additive (g mol<sup>-1</sup>) divided by  $\text{Equiv. } n$  (number of equivalents of the additive).

### 2.3. Slurry analysis

The acidified and non-acidified dairy and pig slurries were analyzed in triplicate in terms of dry matter (DM), total nitrogen (TN), and total phosphorus (TP) at the beginning and end of the storage period (Tables 2 and 3). The composition - in terms of soluble compounds (total and inorganic soluble C, soluble P (P<sub>sol</sub>), total ammonium (NH<sub>4</sub><sup>+</sup>)) as well as the microbial biomass C - was also characterized at the beginning of storage, every week during the first month of storage, and every two weeks afterwards until the end of storage.

The TN content was analyzed in fresh material by the Kjeldahl method (Horneck and Miller, 1998). The DM content was determined by drying 10 g of fresh material at 105 °C for 24 h to constant weight, and the OM content by loss on ignition after calcination at 550 °C for 4 h (APHA, 2005). The total soluble C, inorganic soluble C, NH<sub>4</sub><sup>+</sup>, and P<sub>sol</sub> were analyzed after extraction of 3-g slurry samples with 30 mL of 0.05 M CaCl<sub>2</sub> (Houba et al., 2000): after 2 h of shaking and a 10-min centrifugation, the supernatants were analyzed by segmented flow colorimetry (Autoanalyzer Skalar, Breda, The Netherlands).

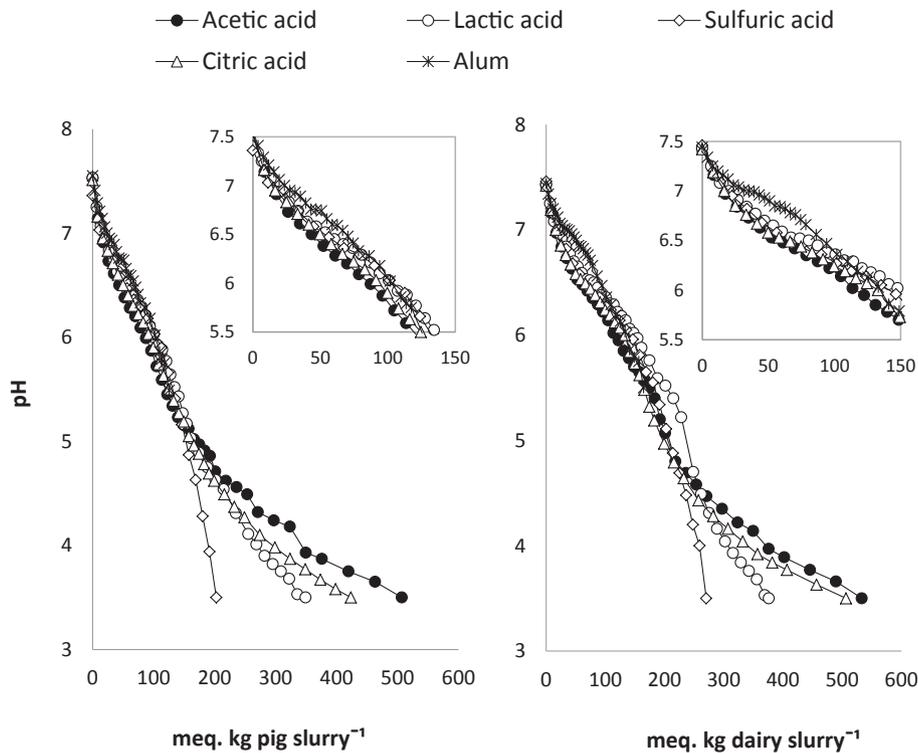
The TP concentration was quantified after digestion with hydrochloric acid, using the ammonium vanadomolybdate method with a molecular absorption spectrophotometer (Hitachi/2000).

The microbial biomass C was determined in both acidified and non-acidified pig and dairy slurries by the chloroform fumigation extraction (CFE) method (Jost et al., 2011). Slurry samples of 5 g were fumigated with ethanol-free chloroform. After 24 h, the fumigated and non-fumigated samples were extracted for 30 min,

**Table 1**  
Main characteristics of the additives and the amounts used to acidify pig and dairy slurries.

			Acetic acid	Citric acid	Lactic acid	Sulfuric acid	Aluminum sulfate
Formula			C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
Mw (g mol <sup>-1</sup> )			60.05	192.12	90.08	98.08	342.15
Equiv. n			1	3	1	2	6
pK <sub>a</sub> value			4.76	3.13/4.8/6.4	3.86	1.99	3.3/3.6
Acid amount (meq. kg slurry <sup>-1</sup> )	pH 5.5	pig dairy	122	125	134	135	125
			175	166	201	180	165
	pH 3.5	pig dairy	507	423	349	203	–
			533	507	376	270	–

Mw: Molecular weight.



**Fig. 1.** Titration curves for pig (left) and dairy (right) slurries acidified with acetic acid, lactic acid, sulfuric acid, citric acid, or aluminum sulfate in the pH range between 7.5 and 3.5. Error bars were removed for clarity.

**Table 2**

Main characteristics of non-acidified (Raw) and acidified pig slurry at the beginning (Initial) and end (Final) of the storage period, presented (on a wet weight basis) as mean values of three replicates with standard errors.

Pig slurry		DM (g kg slurry <sup>-1</sup> )		TP (g kg slurry <sup>-1</sup> )		TN (g kg slurry <sup>-1</sup> )	
		Initial	Final	Initial	Final	Initial	Final
pH 5.5	Raw	15.3 ± 0.2 <sup>h</sup>	11.7 ± 0.2 <sup>f</sup>	0.45 ± 0.02 <sup>bcde</sup>	0.45 ± 0.02 <sup>de</sup>	2.29 ± 0.06 <sup>a</sup>	2.10 ± 0.07 <sup>b</sup>
	Acetic	21.9 ± 0.1 <sup>f</sup>	18.9 ± 0.4 <sup>de</sup>	0.35 ± 0.03 <sup>e</sup>	0.35 ± 0.03 <sup>f</sup>	1.41 ± 0.03 <sup>d</sup>	1.73 ± 0.04 <sup>de</sup>
	Citric	26.2 ± 0.4 <sup>de</sup>	14.2 ± 2.7 <sup>ef</sup>	0.42 ± 0.01 <sup>de</sup>	0.42 ± 0.01 <sup>def</sup>	1.38 ± 0.14 <sup>d</sup>	1.76 ± 0.03 <sup>d</sup>
	Lactic	33.0 ± 0.5 <sup>c</sup>	20.3 ± 0.2 <sup>de</sup>	0.42 ± 0.00 <sup>de</sup>	0.42 ± 0.00 <sup>def</sup>	1.86 ± 0.10 <sup>b</sup>	2.51 ± 0.01 <sup>a</sup>
	Sulfuric	24.7 ± 0.4 <sup>e</sup>	22.9 ± 0.8 <sup>cd</sup>	0.44 ± 0.08 <sup>ab</sup>	0.40 ± 0.02 <sup>ef</sup>	1.67 ± 0.04 <sup>bc</sup>	2.18 ± 0.04 <sup>b</sup>
pH 3.5	Alum	32.1 ± 0.2 <sup>c</sup>	31.1 ± 0.6 <sup>b</sup>	0.62 ± 0.02 <sup>a</sup>	0.62 ± 0.02 <sup>a</sup>	1.51 ± 0.00 <sup>cd</sup>	1.97 ± 0.00 <sup>c</sup>
	Acetic	20.3 ± 0.2 <sup>g</sup>	18.0 ± 0.7 <sup>de</sup>	0.35 ± 0.03 <sup>e</sup>	0.48 ± 0.01 <sup>cd</sup>	1.30 ± 0.05 <sup>d</sup>	1.64 ± 0.01 <sup>e</sup>
	Citric	50.0 ± 1.1 <sup>a</sup>	49.1 ± 0.7 <sup>a</sup>	0.53 ± 0.04 <sup>abc</sup>	0.54 ± 0.02 <sup>bc</sup>	1.30 ± 0.14 <sup>d</sup>	1.94 ± 0.06 <sup>c</sup>
	Lactic	46.8 ± 0.7 <sup>b</sup>	30.6 ± 6.0 <sup>b</sup>	0.54 ± 0.00 <sup>de</sup>	0.41 ± 0.05 <sup>def</sup>	2.25 ± 0.04 <sup>a</sup>	2.44 ± 0.02 <sup>a</sup>
	Sulfuric	27.0 ± 0.5 <sup>d</sup>	27.6 ± 0.4 <sup>bc</sup>	0.58 ± 0.03 <sup>a</sup>	0.58 ± 0.03 <sup>ab</sup>	2.31 ± 0.15 <sup>a</sup>	2.46 ± 0.07 <sup>a</sup>

DM: Dry matter, TP: Total phosphorus, TN: Total nitrogen.

For each parameter, means followed by different letters (vertical) are significantly different from each other ( $p < 0.05$ ).

by shaking with 20 mL of 0.05 M CuSO<sub>4</sub>; after a 10-min centrifugation, the supernatants were analyzed by segmented flow colorimetry (Autoanalyzer Skalar, Breda, The Netherlands). The microbial biomass C was calculated as described by Jost et al. (2011), as follows:

$$\text{Microbial biomass C} = \frac{EC}{K_{EC}} \quad (2)$$

where  $EC = (\text{Organic C extracted from fumigated slurries}) - (\text{Organic C extracted from non-fumigated slurries})$  and  $K_{EC} = 0.45$ .

**Table 3**  
Main characteristics of non-acidified (Raw) and acidified dairy slurry at the beginning (Initial) and end (Final) of the storage period, presented (on a wet weight basis) as mean values of three replicates with standard errors.

Dairy slurry		DM (g kg slurry <sup>-1</sup> )		TP (g kg slurry <sup>-1</sup> )		TN (g kg slurry <sup>-1</sup> )	
		Initial	Final	Initial	Final	Initial	Final
pH 5.5	Raw	54.8 ± 0.2 <sup>d</sup>	48.2 ± 1.3 <sup>bcd</sup>	0.62 ± 0.04 <sup>abc</sup>	0.68 ± 0.02 <sup>ab</sup>	2.26 ± 0.13 <sup>ab</sup>	2.64 ± 0.03 <sup>d</sup>
	Acetic	50.0 ± 0.3 <sup>f</sup>	45.5 ± 1.3 <sup>cdef</sup>	0.49 ± 0.07 <sup>d</sup>	0.45 ± 0.02 <sup>f</sup>	2.34 ± 0.12 <sup>a</sup>	2.10 ± 0.07 <sup>f</sup>
	Citric	54.0 ± 1.0 <sup>de</sup>	42.5 ± 1.0 <sup>f</sup>	0.56 ± 0.04 <sup>bcd</sup>	0.56 ± 0.04 <sup>cd</sup>	1.76 ± 0.00 <sup>abc</sup>	2.34 ± 0.02 <sup>e</sup>
	Lactic	62.8 ± 0.7 <sup>c</sup>	45.3 ± 1.0 <sup>def</sup>	0.64 ± 0.01 <sup>ab</sup>	0.64 ± 0.01 <sup>abc</sup>	2.45 ± 0.72 <sup>a</sup>	2.93 ± 0.02 <sup>c</sup>
	Sulfuric	47.0 ± 0.5 <sup>g</sup>	43.4 ± 0.4 <sup>ef</sup>	0.52 ± 0.05 <sup>cd</sup>	0.54 ± 0.02 <sup>def</sup>	2.28 ± 0.22 <sup>ab</sup>	3.42 ± 0.13 <sup>a</sup>
pH 3.5	Alum	50.8 ± 0.5 <sup>f</sup>	50.0 ± 3.6 <sup>bcd</sup>	0.55 ± 0.04 <sup>bcd</sup>	0.55 ± 0.04 <sup>de</sup>	1.40 ± 0.11 <sup>c</sup>	2.13 ± 0.00 <sup>f</sup>
	Acetic	50.9 ± 0.1 <sup>f</sup>	50.0 ± 0.9 <sup>bcd</sup>	0.62 ± 0.00 <sup>abc</sup>	0.60 ± 0.04 <sup>bcd</sup>	1.53 ± 0.02 <sup>bc</sup>	2.30 ± 0.03 <sup>e</sup>
	Citric	73.3 ± 0.3 <sup>b</sup>	50.9 ± 0.6 <sup>bc</sup>	0.46 ± 0.03 <sup>d</sup>	0.46 ± 0.03 <sup>ef</sup>	1.34 ± 0.19 <sup>c</sup>	2.02 ± 0.03 <sup>f</sup>
	Lactic	82.0 ± 0.2 <sup>a</sup>	66.7 ± 4.0 <sup>a</sup>	0.70 ± 0.06 <sup>a</sup>	0.70 ± 0.06 <sup>a</sup>	1.54 ± 0.02 <sup>bc</sup>	3.41 ± 0.05 <sup>ab</sup>
	Sulfuric	53.1 ± 0.5 <sup>e</sup>	53.1 ± 0.3 <sup>b</sup>	0.63 ± 0.00 <sup>abc</sup>	0.63 ± 0.00 <sup>abcd</sup>	2.24 ± 0.17 <sup>ab</sup>	3.24 ± 0.10 <sup>b</sup>

DM: Dry matter, TP: Total phosphorus, TN: Total nitrogen.

For each parameter, means followed by different letters (vertical) are significantly different from each other ( $p < 0.05$ ).

#### 2.4. NH<sub>3</sub> emissions and pH evolution during storage

Ammonia emissions were measured using acid traps with 100 mL of 0.1 M H<sub>3</sub>PO<sub>4</sub>, placed in the headspace of each glass vessel (Van der Stelt et al., 2007). The acid recipient was hanging from the airtight lid of the jar to avoid surface contact with the slurry, as shown in Fig. 2. In this method, NH<sub>3</sub> volatilization occurred in a passive way as airflow was not supplied. In contact with H<sub>3</sub>PO<sub>4</sub>, the NH<sub>3</sub> emitted from the slurry was converted into ammonium and trapped in the acid solution.

The ammonia emissions were measured simultaneously in all jars during the same time period. Short time periods of 12 h were considered at the beginning of the experiment, to avoid acid saturation, and longer ones (close to 48 h) after day 10. The concentrations of NH<sub>4</sub><sup>+</sup> in the acid traps were determined colorimetrically (Skalar ScanPlus, Breda, The Netherlands) and the cumulative NH<sub>3</sub> emission was quantified by taking into account the volume of H<sub>3</sub>PO<sub>4</sub> used and the length of time of the sampling period.

The evolution of pH was followed by measuring the pH twice per day at the beginning of the experiment and every two days after day 10 until the end of the storage period. The measurements of pH were performed at the bottom of the vessel, avoiding the slurry surface. Before the pH measurements, every jar was opened for 10 min for aeration - to liberate other gaseous emissions, such as

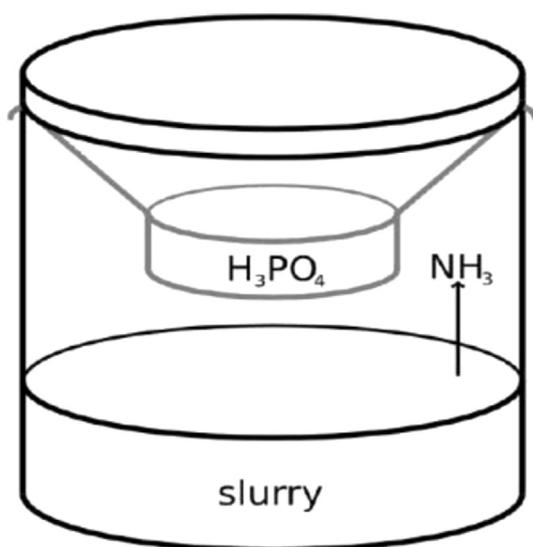


Fig. 2. Experimental setup to capture volatilized NH<sub>3</sub>.

CO<sub>2</sub>, which increase slurry pH and could interfere with slurry pH measurements (Hafner et al., 2012; Vandré and Clemens, 1997).

#### 2.5. Statistical data treatment

Each acidification treatment was replicated three times. The mean values for the main characteristics of the acidified and non-acidified slurries at the beginning and end of the storage were analyzed by one-way analysis of variance (ANOVA) and the Tukey test at the  $p < 0.05$  level. A mixed ANOVA with repeated measures was used to analyze the evolution of slurry composition during storage. The normality and homogeneity of the variances were checked by the Shapiro–Wilk and Levene test, respectively, before ANOVA. A post hoc Tukey test was used to determine the statistical significance of the differences among the specific groups within each factor. The IBM SPSS Statistics v.24 software package was used for the statistical analyses.

### 3. Results and discussion

#### 3.1. Amounts of additives

The amount of additive used to decrease the slurry pH depends on the anions that contribute to the buffering system of the slurry. In slurry, this buffering system is very complex and mainly composed of ammonical N, carbonates, phosphates, and volatile fatty acids (Sommer and Husted, 1995). The amounts of additives required to decrease the pH in dairy slurry were notably higher than for pig slurry (Fig. 1 and Table 1), indicating that dairy slurry has a higher buffer capacity.

The acetic acid equivalent mass required to lower the pH increased significantly after reaching pH 5.5, in both slurries. This was due to the weakness of this acid, as its acid dissociation constant ( $pK_a$  4.76) is the lowest of all the additives used and only one carboxylic group was available. In contrast, this behavior was not observed with citric acid, which contains three carboxylic groups, or lactic acid, with one carboxylic and one hydroxyl group. As expected, the amount of acid required to lower the pH to a target value depended not only on the slurry composition but also on the characteristics of the additive, such as the acid strength.

The additive equivalent mass used to lower the pH to 5.5, in decreasing order, was as follows: sulfuric acid > lactic acid > citric acid = alum > acetic acid for pig slurry, and lactic acid > sulfuric acid > acetic acid > citric acid = alum for dairy slurry. In contrast, when the target pH was 3.5, the additive equivalent mass increased in the following order, for both slurries: sulfuric acid < lactic acid < citric acid < acetic acid (Fig. 1 and Table 1).

Strong acids, such as  $H_2SO_4$ , might be effective when acidifying to pH 3.5, as the amount of acid used should be low. However, as strong acids are rapidly buffered due to fast  $CO_2$  release (Vandré and Clemens, 1997), important amounts of foam are generally formed and increase the handling risk as well as the volume required in storage tanks, which quickly becomes a management problem when high volumes of slurry need to be treated. Furthermore, the use of  $H_2SO_4$  may lead to large emissions of hydrogen sulfide ( $H_2S$ ), an important odorous component which - at high levels - can cause death (Wang et al., 2014).

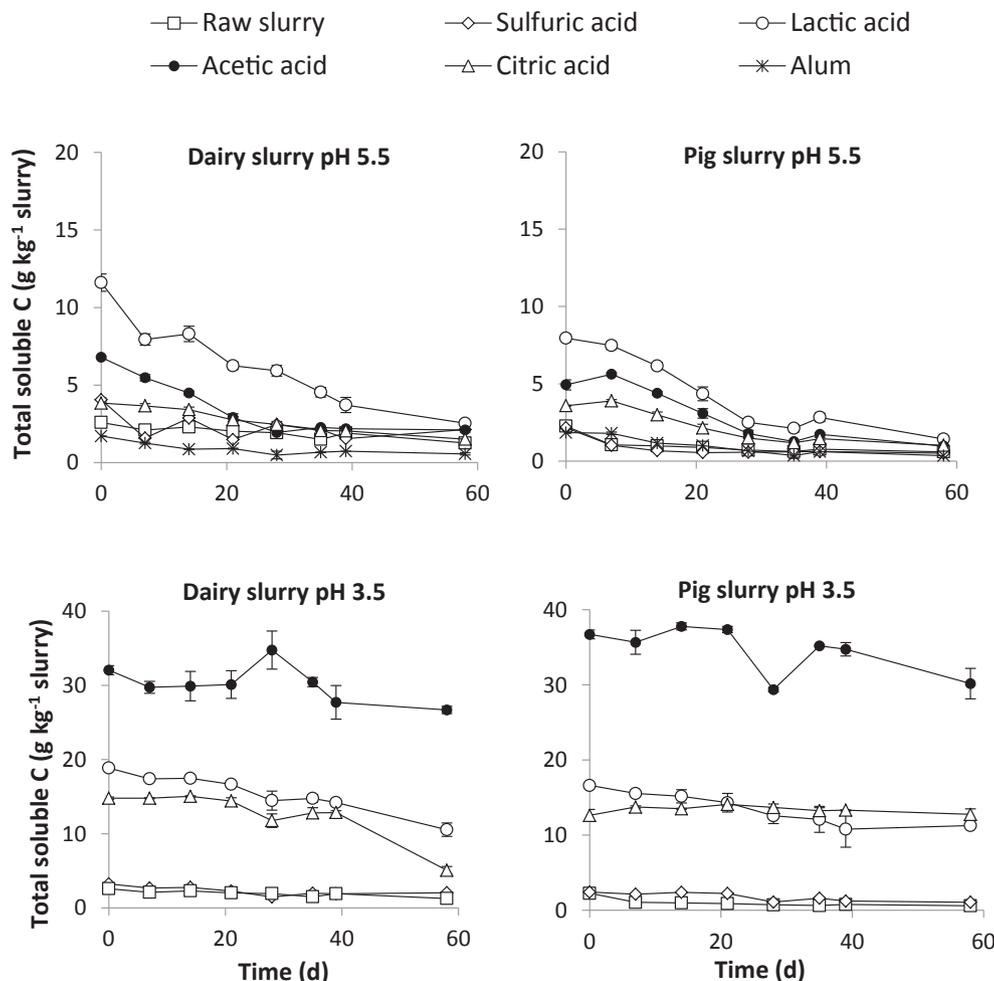
Based on the amounts ( $meq. kg\ slurry^{-1}$ ) needed to acidify pig and dairy slurry to pH 5.5, we conclude that all the additives considered here are of interest since they were all required in amounts lower than or similar to that of  $H_2SO_4$  (except lactic acid in dairy slurry).

### 3.2. Changes in slurry composition after acidification and during storage

Acidification of pig slurry with all additives significantly ( $p < 0.05$ ) increased the DM concentration (Table 2). In contrast, for dairy slurry, a significant increase was observed only when lactic acid was used (Table 3). Previous studies have shown the same findings regarding the DM increment after acidification with  $H_2SO_4$  (Fangueiro et al., 2009; Sørensen and Eriksen, 2009; Kai et al., 2008;

Eriksen et al., 2008): this was attributed to the increase in sulfate concentration corresponding to the amount added through the acid (Eriksen et al., 2008; Fangueiro et al., 2009). Nevertheless, the DM concentration decreased along the 60 days of storage and lower values were observed at the end of the incubation period, except when alum and sulfuric acid were used in both slurries to lower the pH to 5.5 and 3.5, respectively (Tables 2 and 3). However, after 60 days, raw pig slurry still had a lower DM concentration than pig slurry acidified with any of the additives. The decrease in the DM concentration may be explained by the decrease in the  $NH_4^+$  concentration, due to  $NH_3$  volatilization, and the degradation of OM during storage (Patni and Jui, 1985); both processes occurred to a lower extent when alum or sulfuric acid was used, explaining the lower decrease in the DM concentration. Indeed, the  $NH_3$  emissions were lower, and similar values of soluble C were obtained at the beginning and end of the storage, when these two additives were used (Fig. 3), suggesting inhibition or diminution of the microbial degradation of OM. Accordingly, Petersen et al. (2012) and Hjorth et al. (2015) also reported that microbial decomposition of OM during storage was inhibited when  $H_2SO_4$  was used for acidification.

The total soluble C concentration was significantly ( $p < 0.05$ ) increased with the addition of organic acids, a change that was not observed when sulfuric acid or alum was used (Fig. 3). With the addition of a strong acid, such as sulfuric acid, carbonates react with



**Fig. 3.** Evolution of soluble C in non-acidified (raw) slurry and in acidified pig and dairy slurries during the 60-day storage period, presented as mean values of three replicates. Bars indicate standard errors.

the protons, releasing  $\text{CO}_2$ ; thus, soluble inorganic C was not present in the slurry either (Fig. 4). By adding alum, the carbonates should precipitate as aluminum carbonate, hence avoiding  $\text{CO}_2$  release (Lameijer and Vervoort, 1995). The storage time as well as the interaction between the time and treatments had a highly significant ( $P < 0.05$ ) effect on the total soluble C concentration. Thus, the total soluble C concentration in both acidified slurries at pH 5.5 was significantly ( $P < 0.05$ ) higher than in raw slurries, except when alum was used (a decrease was observed) and when  $\text{H}_2\text{SO}_4$  was used (no significant difference) (Fig. 3). The increase in the total soluble C concentration at the beginning of the storage due to the addition of organic acids rapidly diminished in slurries acidified to pH 5.5 during the first 30 days of storage, followed by a slower loss after day 30 until the end of storage (Fig. 3). However, the soluble C in acidified slurries at pH 3.5 remained constant until day 40 and slightly decreased afterwards until the end of storage (Fig. 3). Acidification has been shown to promote hydrolysis (Hjorth et al., 2015); thus, easily degradable monomers such as low-molecular-weight carbohydrates were available for conversion. The initial fast decrease in total soluble C when organic acids were used for acidification to pH 5.5 may have been due to the degradation of these free carbohydrates and dissociated organic acids,

with the corresponding increase in inorganic C (Fig. 4) - which increased pH (Fig. 8) and promoted growth of the microbial biomass (Fig. 5).

Inorganic soluble C was not detectable after acidification with all additives, in both slurries (Fig. 4). This was due to the release of most of the inorganic C as  $\text{CO}_2$  during acidification, which induces the conversion of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  to  $\text{H}_2\text{CO}_3$  and  $\text{CO}_2$  (Stevens et al., 1995). The storage time as well as the interaction between the time and treatments had a highly significant ( $P < 0.05$ ) effect on the inorganic soluble C concentration in the slurries. In acidified slurries at pH 3.5, inorganic C was below the detection limit along the whole storage period, except when lactic acid was used in both slurries and citric acid in dairy slurry (which gave a significant increase in inorganic C from day 40 of the storage). The inorganic C concentration in acidified slurries at pH 5.5 showed a continuous increase from the beginning until the end of the storage, with values in all acidified pig and dairy slurries that were significantly ( $P < 0.05$ ) lower than in raw slurries, except when acetic or lactic acid was used in dairy slurry and acetic or citric acid was used in pig slurry (Fig. 4).

The microbial biomass C concentration in raw slurries decreased from the beginning until the end of the storage. However, the

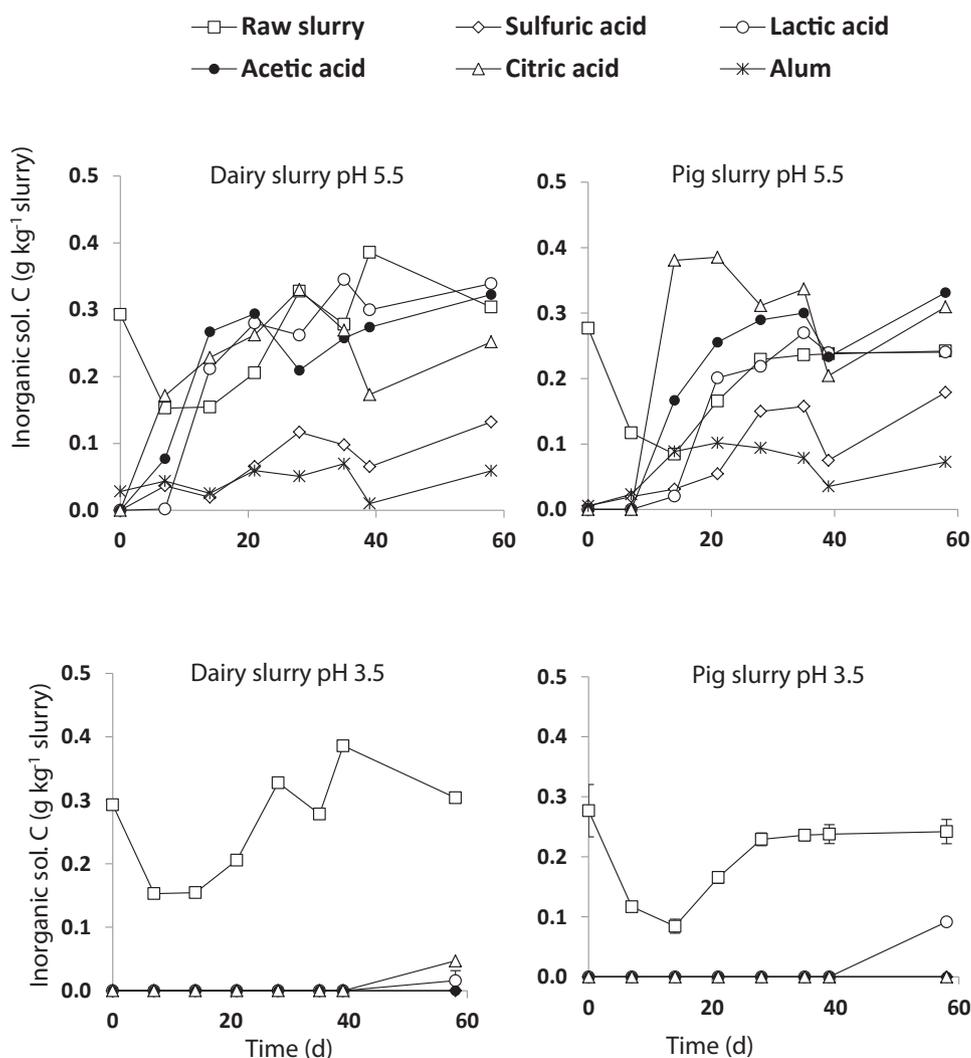
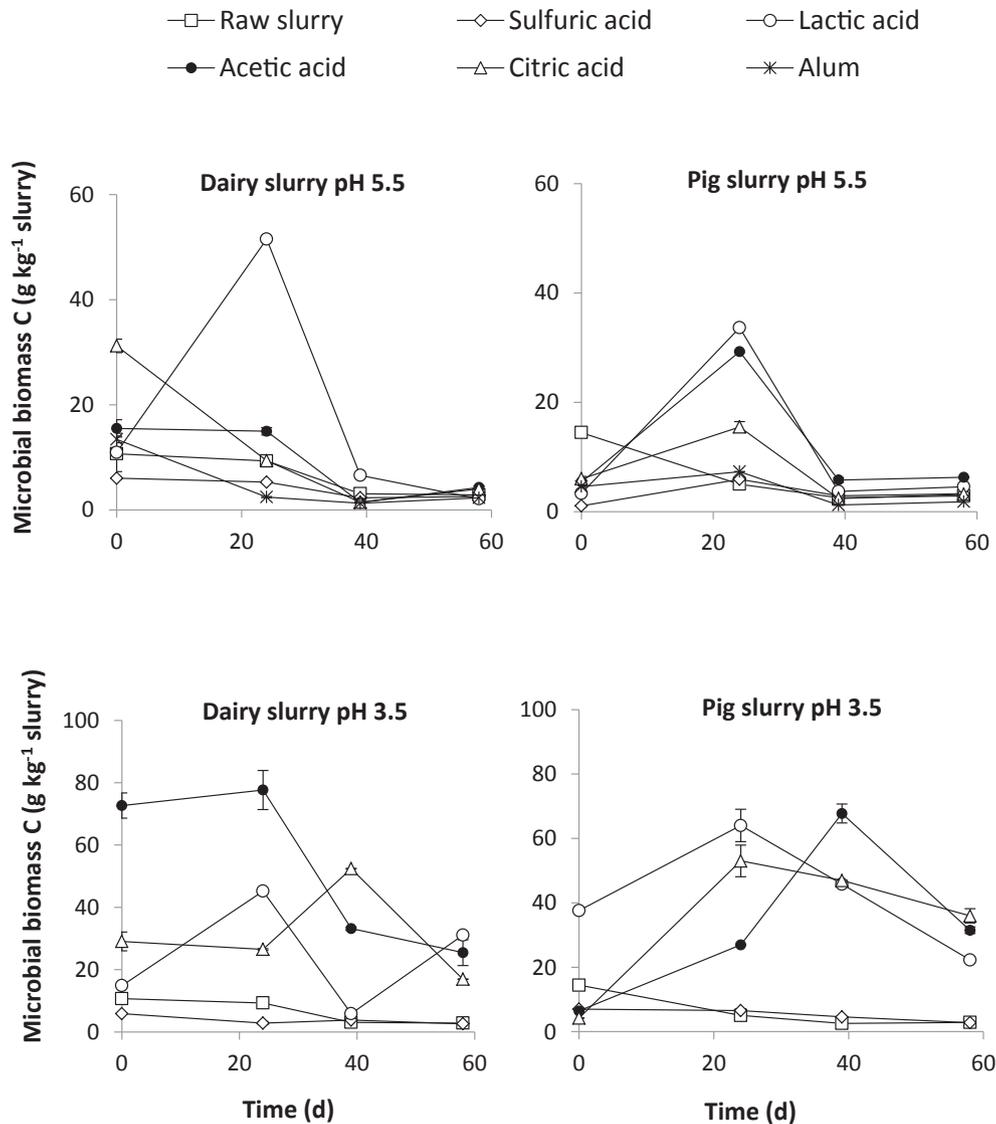


Fig. 4. Evolution of inorganic soluble C in non-acidified (raw) slurry and in acidified pig and dairy slurries during the 60-day storage period, presented as mean values of three replicates. Error bars were removed for clarity.



**Fig. 5.** Evolution of microbial biomass C in non-acidified (raw) slurry and in acidified pig and dairy slurries during the 60-day storage period, presented as mean values of three replicates. Bars indicate standard errors.

microbial biomass evolved differently in acidified slurries depending on the additive used (Fig. 5). Thus, when sulfuric acid or alum was used, the microbial biomass followed the same trend as in non-acidified slurries but with significantly ( $P < 0.05$ ) lower values along the storage. The interaction storage time-treatment (acid used) had a significant ( $P < 0.05$ ) effect on the biomass evolution. The use of acetic or lactic acid significantly ( $P < 0.05$ ) increased the microbial biomass until day 30, relative to raw slurries, decreasing afterwards until the end of the storage (Fig. 5). This initial increase was probably related to the degradation of dissociated organic acids explained previously. After day 30 of the storage the easily degradable OM was probably depleted; thus, the microbial biomass C decreased until the end of the storage due to a lack of C for the maintenance of the microorganisms (Fig. 5). In accordance with this, the values of soluble C in raw slurries in the last stage of the storage were similar to the initial values (Fig. 3).

The total N concentration in the pig and dairy slurries was not affected by acidification (Tables 2 and 3). However, after 60 days of storage, lower N concentrations were observed in non-acidified

slurries due to  $\text{NH}_3$  volatilization. As expected, the initial concentrations of ammonium ( $\text{NH}_4^+$ ) in both slurries acidified with any of the additives were significantly higher than in raw slurries (Fig. 6). Overall, the dairy and pig slurries acidified to pH 5.5 had significantly ( $P < 0.05$ ) higher  $\text{NH}_4^+$  concentrations during the whole storage period when  $\text{H}_2\text{SO}_4$  or alum was used. However, the slurries acidified to pH 3.5 with any of the additives used had significantly ( $P < 0.05$ ) higher  $\text{NH}_4^+$  concentrations during the whole storage period, relative to raw slurries. The time and the time-treatment interaction had a significant ( $P < 0.05$ ) effect on the total  $\text{NH}_4^+$  concentration. During the first 20 days of incubation, the concentration of  $\text{NH}_4^+$  significantly decreased, probably due to its consumption by microorganisms as the microbial biomass C increased during this initial storage time (Fig. 5). However, a significant increase in the  $\text{NH}_4^+$  concentration was observed between days 20 and 30 of the storage, in both slurries, as well as a slight increase from day 40 to the end of the storage. The greatest decrease in the  $\text{NH}_4^+$  concentration at the end of the experiment in both slurries acidified to pH 5.5 was observed when alum was used. The reason

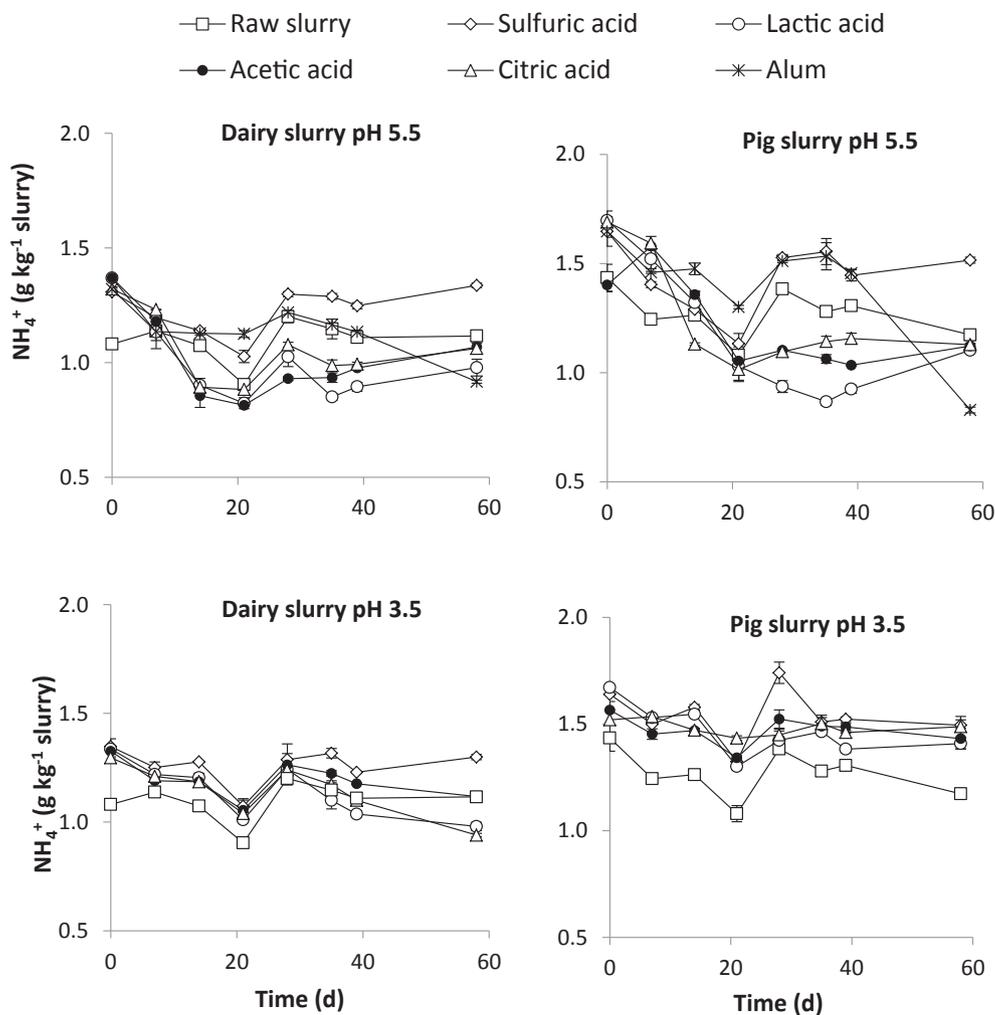


Fig. 6. Evolution of the ammonium ( $\text{NH}_4^+$ ) concentration in non-acidified (raw) slurry and in acidified pig and dairy slurries during the 60-day storage period, presented as mean values of three replicates. Bars indicate standard errors.

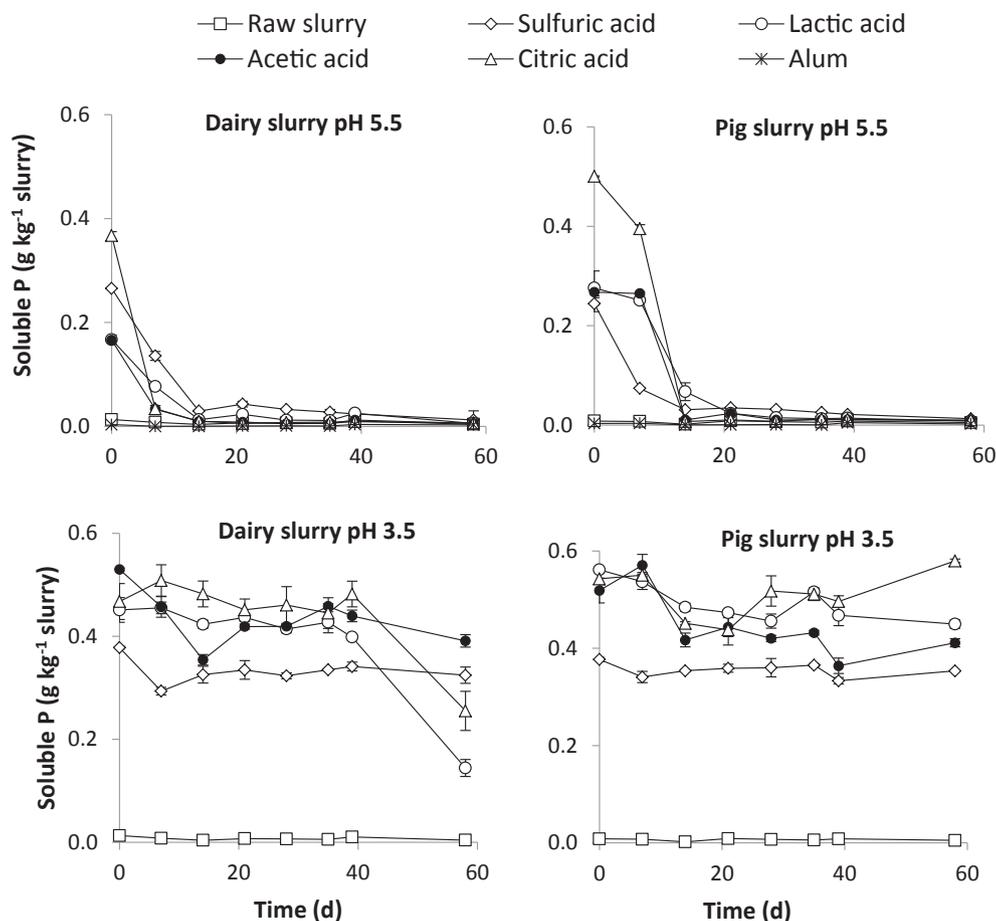
for this decrease is not clear. Indeed, no significant  $\text{NH}_3$  volatilization occurred when this additive was used and this loss of  $\text{NH}_4^+$  cannot be associated with nitrification since acidification diminished this process.

The total P concentration of the slurries was not affected by acidification (Tables 2 and 3) and the concentrations of P at the end of the storage remained similar to the initial values, meaning that microorganisms did not consume P during storage. However, acidification significantly ( $P < 0.05$ ) increased the soluble P (Psol) concentration in both slurries, except in the case of alum - when no significant difference was observed (Fig. 7). This is in agreement with results obtained by Lefcourt and Meisinger (2001) and might be explained by the reactions between alum and water, leading to the formation of an insoluble Al phosphate compound. These authors observed also significant increments in soluble Al, but only when alum concentrations of 2.5% or higher were used. The dose of alum used in our study was 1% (w/w); therefore, no significant effect was expected. The storage time had a significant effect ( $P < 0.05$ ) on the Psol concentration. The increment in Psol in slurries acidified to pH 5.5 was drastically dissipated during the storage until day 15, when the concentrations had reached values close to the initial values in raw slurries (Fig. 7). In contrast, the Psol concentration in slurries acidified to pH 3.5 decreased slightly over time - probably due to the very low pH values, which promote

solubilization of P - except when citric or lactic acid was used to acidify dairy slurry; in these cases, Psol drastically decreased after day 40 (Fig. 7). The most important parameter concerning eutrophication is phosphorus, but there is no strict regulation in most European countries regarding the limits for slurry disposal, to avoid P pollution. Approximately 90% of the P in runoff is dissolved P, the form most readily available for algal uptake (Nahm, 2005). Therefore, on farms where the application of slurry could be performed after acidification, the use of alum may be beneficial to minimize the impact of slurry on water eutrophication and consequently to minimize the global impact of animal production on the environment (González-García et al., 2015). Previous studies have shown that alum is efficient in the treatment of poultry litter and its subsequent land application. Moore et al. (2000) used alum to avoid P runoff without increasing the Al availability in soils or for plant uptake. Therefore, a similar behavior in pig and dairy slurries treated with alum and then applied to soil might be expected. On the other hand, acidified slurry might also be used for anaerobic codigestion, in which case the issue of P should not be a problem.

### 3.3. Evolution of pH during storage

The storage time as well as the interaction between the time and treatments had a significant ( $P < 0.05$ ) effect on slurry pH. The pH



**Fig. 7.** Evolution of soluble P in non-acidified (raw) slurry and in acidified pig and dairy slurries during the 60-day storage period, presented as mean values of three replicates. Bars indicate standard errors.

values of the pig and dairy slurries acidified to pH 5.5 rapidly increased from the beginning of the storage, to values between 6.8 and 7.3 in both slurries at day 20 (Fig. 8). In this initial phase, the pH values tended to increase more in dairy than in pig slurry, and in both slurries the values were slightly higher when acetic or citric acid was used. The main difference between the acidified slurries was related to the pH evolution from day 20 to the end of the storage period, when pig slurries always had higher values than dairy slurries. The pH values of the pig and dairy slurries initially acidified to pH 5.5 had surpassed the initial pH values of the raw slurries by day 40 of the storage, except when  $H_2SO_4$  and alum were used to acidify pig and dairy slurry, respectively (Fig. 8).

Decreasing the pH to 3.5 resulted in a constant evolution of pH during the 60 days of storage (Fig. 8). The highest pH increase was observed between days 15 and 20, with a maximum value of 4.5 in both slurries when  $H_2SO_4$  was used. The pH values for all treatments were constant from day 20 until the end of the storage period, except when lactic or citric acid was used in dairy slurry – where a significantly ( $P < 0.05$ ) higher value of pH (5.6) was reached at the end of the storage (Fig. 8).

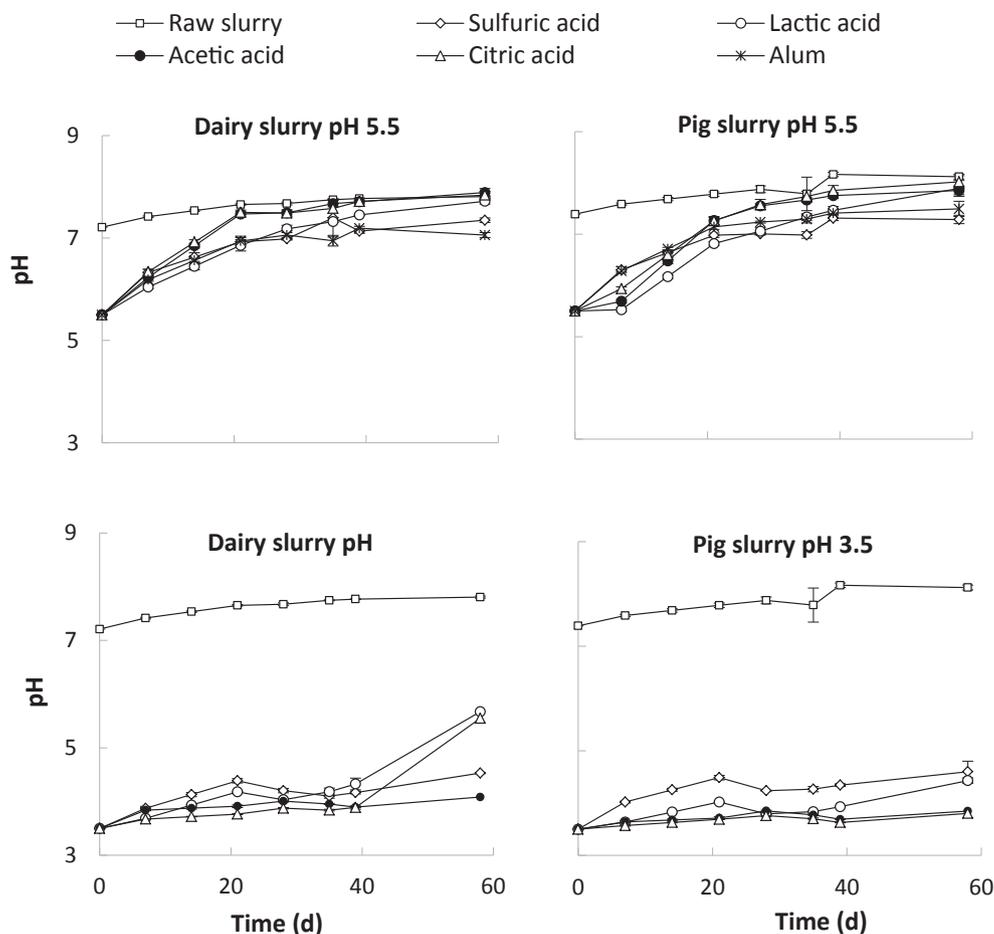
The same tendency in pH evolution was observed by Eriksen et al. (2008), with even higher pH values being reached over a longer storage period, and they attributed this pH increase to microbial activity in the slurry. Kai et al. (2008) and Petersen et al. (2012) explained this gradual pH increase after acidification by the degradation of dissociated organic acids as well as the mineralization of organic N and dissolution of carbonates. The decrease in

the  $NH_4^+$  concentration explained before (Fig. 6) during the initial stage of the storage suggests that mineralization did not take place and, thus, cannot be the reason for the pH increase during the first two weeks of storage. Therefore, we assume that the pH increase during this initial phase was mostly due to degradation of dissociated organic acids.

### 3.4. Cumulative $NH_3$ emissions during storage

Acidification to pH 5.5 significantly ( $P < 0.05$ ) reduced the  $NH_3$  emissions from both slurries, with  $H_2SO_4$  and alum leading to the greatest reductions (Fig. 9).

Acidification to pH 5.5 reduced the cumulative  $NH_3$  volatilization by 75% when  $H_2SO_4$  was used in pig slurry and by 81% when alum was used in dairy slurry, relative to the non-acidified slurries. Similar trends regarding the decrease in  $NH_3$  volatilization were observed in the dairy and pig slurries, depending on the additive used (Fig. 9). The interaction storage time-treatment (acid used) had a significant ( $P < 0.05$ ) effect on the cumulative  $NH_3$  emissions. At the end of the storage, all the treatments showed significantly ( $P < 0.05$ ) lower cumulative  $NH_3$  emissions than the raw slurries, with  $H_2SO_4$  and alum showing the lowest emissions and no significant ( $P > 0.05$ ) difference between them. The reductions in  $NH_3$  volatilization led to higher fertilization values of the slurries, as N losses were reduced. The use of alum or  $H_2SO_4$  resulted in the lowest percentage losses of TN and  $NH_4^+$  in both slurries (with no significant ( $P > 0.05$ ) differences between



**Fig. 8.** Evolution of pH in non-acidified (raw) slurry and in acidified pig and dairy slurries during the 60-day storage period, presented as mean values of three replicates. Bars indicate standard errors.

them) followed by acetic and lactic acid (which did not differ significantly) and then citric acid, with the highest N loss. The highest cumulative  $\text{NH}_3$  emissions in both slurries when citric acid was used were probably due to higher catabolic activity, as this additive gave the greatest decreases in DM concentration during storage (Tables 2 and 3) with the corresponding highest OM degradation. High OM degradation, as referred to previously, led to the release of  $\text{CO}_2$  - which raised the pH and promoted  $\text{NH}_3$  volatilization.

Acidification of the pig and dairy slurries to pH 3.5 resulted in values of  $\text{NH}_3$  volatilization which can be considered negligible. The accumulated volatilization of  $\text{NH}_3$  at the end of the experimental period did not exceed  $2 \text{ mg NH}_3 \text{ kg}^{-1}$  slurry in pig slurry and  $9 \text{ mg NH}_3 \text{ kg}^{-1}$  slurry in dairy slurry. Therefore, the reduction in the cumulative  $\text{NH}_3$  volatilization achieved by using the additives was as great as 100% during the 60 days of storage.

Some crust formation was observed in the dairy slurry acidified to pH 5.5, 15 days after the start of the experiment. However, no crust was formed in pig slurry, or in dairy slurry acidified to pH 3.5. Previous studies have shown no relationship between crust formation and  $\text{NH}_3$  volatilization (Petersen et al., 2014); thus, the lesser  $\text{NH}_3$  volatilization in dairy slurry relative to pig slurry cannot be attributed to crust formation.

Previous studies by Sørensen and Eriksen (2009) proved that slurries acidified in laboratory conditions behaved similarly to slurries acidified on-farm, and that the differences could be considered negligible. However, the validation in larger-scale

scenarios of our results obtained in laboratory conditions should be considered in future studies.

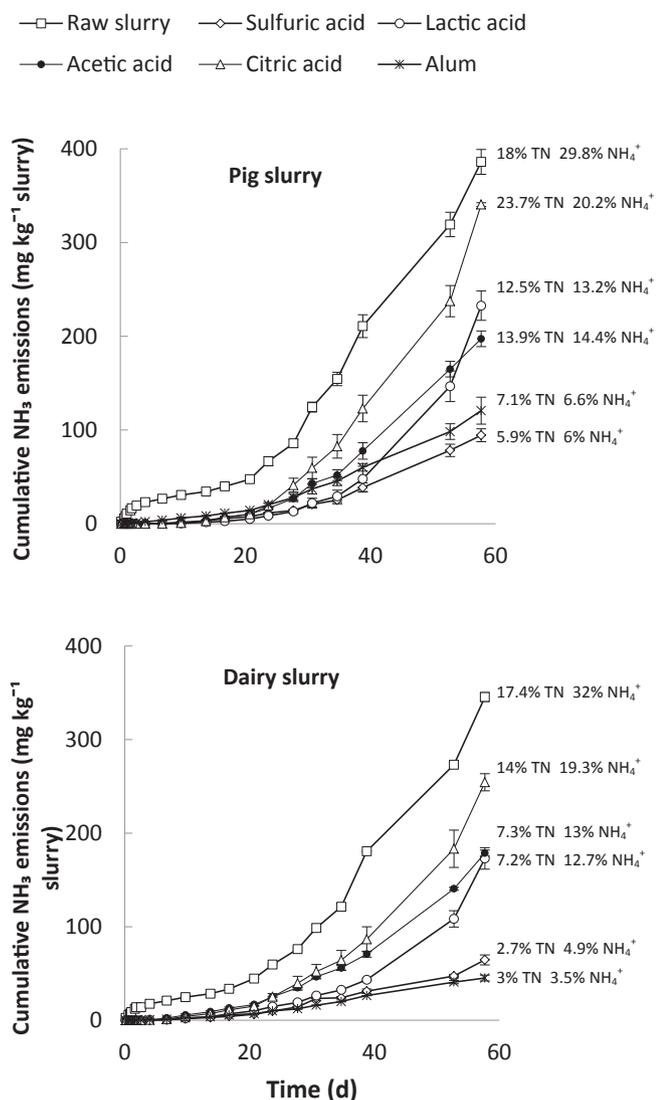
#### 4. Conclusions

Acidification of pig and dairy slurries with all the additives tested efficiently reduced  $\text{NH}_3$  emissions during storage. Acidification affected differently the slurry composition - especially the DM,  $\text{NH}_4^+$ , and soluble P concentrations - depending on the additive used and the type of slurry treated (pig or dairy).

Our results show that acidification promoted P solubilization, except when alum was used. A high alum concentration should be avoided if slurry is intended to be used as fertilizer, as the availability of P may be reduced. Nevertheless, the use of slurries acidified with alum for soil application as organic fertilizers still requires further study. Additionally, the initial solubilization of P when the pH was decreased to 5.5 had been reversed after two weeks of storage, which could be beneficial on farms surrounded by areas facing problems with P disposal.

Pig and dairy slurries acidified to pH 3.5 showed negligible  $\text{NH}_3$  volatilization. However, studies on  $\text{NH}_3$  emissions over longer storage periods would be required to assess the advantages of acidifying to pH 3.5. This target pH of 3.5 could avoid the re-acidification of slurry to pH 5.5 once the pH has increased, which is normally required.

Sulfuric acid and alum were the additives required in the lowest amounts to decrease the pH to 5.5 and were the most efficient at



**Fig. 9.** Evolution of the cumulative NH<sub>3</sub> emissions for non-acidified (raw) slurry and for pig and dairy slurries acidified to pH 5.5 during the 60-day storage period, presented as mean values of three replicates. Bars indicate standard errors. Values represent the cumulative NH<sub>3</sub> as a percentage of the initial total nitrogen content and initial ammonium content.

reducing NH<sub>3</sub> emissions. Therefore, alum can be considered a good alternative to H<sub>2</sub>SO<sub>4</sub> when lowering the pH to 5.5.

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